Charles University in Prague
Faculty of Science

Ph. D. study program: Macromolecular Chemistry

IONIC POLYACETYLENE TYPE POLYMERS AND POLYMER NETWORKS BY CATALYST-FREE QUATERNIZATION POLYMERIZATION

Iontové polymery a polymerní sítě polyacetylenického typu připravené metodou kvaternizační polymerizace

Doctoral Thesis

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Prague, 2016

STATEMENT

I hereby declare that this thesis is my own work and that all the sources are accurately mentioned in the References section. To the best of my knowledge and belief, it contains neither material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the University or other Institute of higher education, except for the already published results, which are included in the list of attachments.

Prague, July 27, 2016

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Tomáš Faukner

ACKNOWLEDGEMENT

At this place I would like to thank to my supervisor dr. Jiří Zedník for his assistance and comments. He is also greatly acknowledged for some advanced NMR and photoluminescence measurements.

I would like to give special thanks to Doc. Jan Sedláček for his immense enthusiasm, willingness, his great ability to impart knowledge and for his bright suggestions and useful advices.

Ing. A. Zukal, CSc. (ÚFCH JH AV ČR) is greatly acknowledged for measurements of adsorption isotherms and theirs interpretation.

Ing. J. Brus, Ph.D. (ÚMCH AV ČR) is greatly acknowledged for measurements of solid state NMR.

RNDr. Ivana Šloufová Ph.D. is greatly acknowledged for SERS measurements.

Ing. Zuzana Walterová (ÚMCH AV ČR) is greatly acknowledged for MALDI spectra measurements.

Zuzana Kálalová (ÚMCH AV ČR) is greatly acknowledged for the elemental analysis measurements.

The Grant Agency of the Charles University (project no. 626512) and the Czech Science Foundation (project no. 15–09637S and P108/12/1143) are greatly acknowledged for financial support.

Many thanks belong to the colleagues of the Department of Physical and Macromolecular Chemistry for pleasant atmosphere and fruitful discussions.

Special thank belongs to my family, especially to my wife Anna for her unlimited patience.

ABSTRACT

The composition and structure of a series of ionic π-conjugated poly(monosubstituted acetylene)s prepared via catalyst-free quaternization polymerization (QP) of 2-ethynylpyridine (2EP) activated with equimolar amount of alkyl halide [RX = ethyl bromide, ethyl iodide, nonyl bromide and haxadecyl (cetyl) bromide] as a quaternizing agent (QA) have been studied in detail. The performed QPs gave ionic polymers well soluble in polar solvents, with approximately half of pyridine rings quaternized, which implies that also non-quaternized monomers were involved in the process of QP. The configurational structure of polyacetylene main chains was suggested based on ^{1}H NMR, IR as well as Raman (SERS) spectral methods. The QPs in bulk gave more expected irregular *cis*/*trans* polymers while the QPs in acetonitrile solution gave high-*cis* polymers.

A series of prepared symmetrical bi-pyridylacetylene based monomers has been polymerized via QP approach resulting into a series of new ionic π-conjugated poly(disubstituted acetylene) type materials. It is therefore obvious that the mechanism of quaternization activation frequently applied on monosubstituted pyridylacetylenes is efficient also for the polymerization of disubstituted bi-pyridylacetylenes. The structure of resulting materials can be easily tuned via the selection of QA. When monofunctional benzyl bromide was applied the linear ionic π-conjugated polyacetylene type polymers were obtained. When bifunctional 1,4-bis(bromomethyl)benzene was applied, the ionic polymer networks were obtained. The network structure is formed by interconnected π-conjugated polyacetylene type chains and the ionic alternating chains. The degrees of quaternization of prepared materials ranging from 0.27 to 1.20, which implies that (i) also non-quaternized bi-pyridylacetylene monomers are involved in the QP process and (ii) the structure of monomer (mainly the positional isomerism of N atom of pyridyl groups) as well as structure of QA affect the resulting degree of quaternization. Owing to the ionic nature, all linear polymers were well soluble in common polar solvents. Both linear polymers and polymer networks exhibit photoluminescence, furthermore, polymer networks prepared from *para*-pyridyl based monomers strongly emit in visible region. Due to the highly cross-linked structure, polymer networks also shown moderate CO_2 adsorption capacity up to 13.6 cm^3 g^{-1} (STP) and exceptionally high ethanol vapor capture capacity up to 24.5 wt% (293 K).

ABSTRAKT

Byla provedena detailní studie složení a konfigurační struktury série iontových π-konjugovaných poly(monosubstituovaných acetylenů) připravených kvaternizační polymerizací (QP) 2-ethynylpyridinu (2EP) s equimolárním množstvím alkyl halogenidu (RX = ethyl bromid, ethyl jodid, nonyl bromid, hexadecyl (cetyl) bromid) jako kvaternizačního činidla (QA). Všechny produkty, dobře rozpustné v polárních rozpouštědlech, vykazovaly stupeň kvaternizace cca. 0.5, což naznačuje, že i nekvaternizované monomery byly zapojeny do polymerního řetězce. Na základě výsledků ^{1}H NMR, IR a Raman (SERS) spektrálních metod byla určena konfigurační struktura polyacetylenických řetězců připravených polymerů: polymery připravené bez přídavku rozpouštědla vykazovaly více očekávanou nepravidelnou *cis*/*trans* konfiguraci, kdežto polymery připravené v roztoku acetonitrilu vykazovaly vysoký podíl *cis* jednotek.

Symetrické bi-pyridylacetylenické monomery, které byly v rámci této studie nasyntetizovány, byly polymerizovány metodou QP za vzniku série nových iontový disubstituovaných polyacetylenických materiálů. Mechanismus, který je používán zejména k polymerizaci monosubstituovaných pyridylacetylenických monomerů je tedy efektivní i v případě symetrických disubstituovaných pyridylacetylenických monomerů. Výběrem QA lze také snadno ovlivnit strukturu výsledných materiálů. Pokud byl využit monofunkční benzyl bromid jako QA, byly získány iontové lineární π-konjugované polymery dobře rozpustné v polárních rozpouštědlech. Pokud však byl použit bifunkční 1,4-bis(bromomethyl)benzen jako QA, produktem QP byly nerozpustné polyacetylenické polymerní sítě. Vysoce zesíťovaná struktura, je v tomto případě výsledkem vzájemného propojení dvou typů řetězců: polyacetylenického a alternačního iontového řetězce. Stupeň kvaternizace připravených materiálů se pohyboval od 0.27 do 1.20, což naznačuje, že také nekvaternizované bi-pyridylacetylenické monomery byly zapojeny do polymerizačního procesu a stupeň kvaternizace závisí jak na struktuře monomeru, (a to zejména pozici N atomu pyridylu – *ortho* nebo *para*) tak i funkcionalitě zvoleného QA. Jak lineární polymery, tak i polymerní sítě vykazovaly fotoluminiscenci. Polymerní sítě připravené z *para*-pyridylických monomerů dokonce silně emitovaly ve viditelné oblasti. U polymerních sítí byla také prokázána mírná adsorpční kapacita záchytu CO_2 [13.6 cm^3 g^{-1} (STP)] a vysoká adsorpční kapacita záchytu par etanolu, která dosahovala až 24.5 wt% (293 K).

KEYWORDS

Quaternization polymerization, catalyst-free polymerization, spontaneous polymerization, ethynylpyridines, pyridylacetylenes, bi-pyridylacetylenes, disubstituted acetylenes, conjugated polymers, polyacetylenes, conjugated polyelectrolytes, CPE, polymer networks, ionic polymers, cross-linked structure, degree of quaternization, configurational structure, photoluminescence, charge-transfer complex, intersystem crossing, gas sorption, vapor sorption, ethanol vapor, TGA, S_{BET}, MALDI-TOF MS, SERS

KLÍČOVÁ SLOVA

Kvaternizační polymerizace, polymerizace bez přídavku katalyzátoru, spontánní polymerizace, ethynylpyridiny, pyridylacetyleny, bi-pyridylacetyleny, disubstituované acetyleny, konjugované polymery, polyacetyleny, konjugované polyelektrolyty, CPE, iontové polymerní sítě, iontové polymery, zesíťovaná struktura, stupeň kvaternizace, konfigurační struktura, fotoluminiscence, komplex přenosu náboje, mezistémový přechod, adsorpce plynů, adsorpce par, TGA, S_{BET}, MALDI-TOF MS, SERS

CONTENT

1 INTRODUCTION

Presented doctoral thesis deals with the preparation, characterization and the detailed study of properties of ionic π-conjugated polyacetylene type linear polymers and polymer networks prepared via catalyst-free quaternization polymerization of ethynylpyridine based derivatives. Here, the general introduction to the polyacetylene type polymers is provided.

1.1 Polyacetylene type polymers

Conjugated polymers (CPs) and Conjugated polyelectrolytes (CPEs)

Materials labeled as π-conjugated polymers (CP)s include in their structure alternating double C=C bond and single C-C bond which allow the delocalization of π-electrons along molecular backbone (**Figure 1**). The properties originating from the electron delocalization open up wide variety of applications,[1-7] including light-emitting diodes (LEDs),[8] light-emitting electrochemical cells (LECs),[9] plastic lasers,[10] solar cells,[11] field-effect transistors (FETs)[12] The best known π-conjugated polymer is the classic insoluble polyacetylene, discovered in 1976 by Shirakawa and co-workers.[13] Discovery of the conjugated polymers led to the 2000 Nobel Prize in Chemistry awarded to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa. By the mid-eighties, many research teams in both academia and industry were investigating π-conjugated polymers for their nonlinear optical properties and their semiconducting properties and thus the field of plastic electronics and photonics was established.[14]

The π-conjugated structure could be also found in materials derived from poly(arylene)s, poly(paraphenylenevinylene)s, poly(para-phenyleneethynylene)s, polyanilines, polypyridines, polythiophenes etc. However, polymers discussed in presented doctoral thesis are based on polyacetylene derivatives exclusively. According to the substitution of hydrogen atom of main chain the polyacetylenes could be divided into three categories: (i) non-substituted, (ii) monosubstituted and (iii) disubstituted (**Figure 1**). Non-substituted acetylene is represented only by classical polyacetylene polymer prepared by Shirakava. The insolubility and difficult processability exhibit the main problems for the further application of this material. The introduction of poly(monosubstituted acetylene)s resulted in a considerable improvement of polymers properties. Despite unquestionable progress in the chemistry of poly(monosubstituted acetylene)s, these promising materials still suffer mainly from limited stability.[15-17] On the contrary, their disubstituted counterparts are reported to be much more stable with respect to oxygen and elevated temperature.[18] Particular problem concerning preparation of substituted polyacetylenes derivatives is partial changes in the resulting polymer properties (for example conductivity loss).

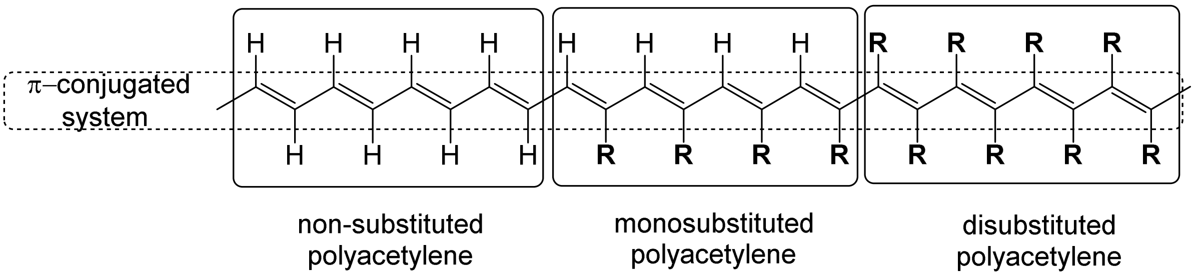


Figure 1 The structure of π-conjugated polyacetylene chain.

Although the polymerization of acetylene was reported in 1866 by Berthelot and linear polyacetylene was prepared in 1929 by Champetier,[19] no efficient polymerization procedure was developed and only low molecular mass products were prepared by the traditional radical or ionic polymerizations till mid-fifties.[20] The interest in polyacetylenes has increased after the Natta et al. described the synthesis of π-conjugated polymers with relatively high molar mass using Ziegler-Natta catalyst in 1957.[19] However, Ziegler-Natta catalysts could only polymerize sterically unhindered monosubstituted acetylenes into insoluble polymers and/or soluble oligomers. The demand on effective polymerization procedure led to the significant growth of interest in this area. Thus, during last few decades, transition-metal based catalytic systems have been studied in details and an effective polymerization processes were established. Methods of coordination polymerization applying either metathesis catalysts or insertion catalysts are used for the preparation of these materials.[5,21-28] Despite a number of new catalytic systems prepared and tested, the coordination polymerization using transition-metal catalyst still suffers from low tolerance to the polar groups and the sensitivity for moisture and oxygen. The later discovery of the functionality-tolerant organorhodium based catalysts[29,30] was a thrilling advance in the area, but the catalysts work for only limited types of monomers, e.g. arylacetylene derivatives, through an insertion mechanism.[31] Since the polyacetylene chemistry is an important part of polymer science, a number of articles and reviews dealing with the new polymerization approaches are published every year. For example, reviews compiled by Percec,[19] Tang[1,32-34] or Masuda[5,35] were published on this topic.

Polymers comprise π-conjugated main chain and ionic and/or ionizable groups are labeled as ionic π-conjugated polymers or as π-conjugated polyelectrolytes (CPE). Unlike the majority of neutral CPs, CPEs additionally exhibit (i) solubility in polar solvents as water, aqueous solutions, alcohols, and others environmentally friendly solvents,[36,37] [38] (ii) amphiphilic nature, which gives CPE macromolecules capability of self-assembling in solutions and ability to interact specifically with particular species inducing measurable optical and/or electrical responses and (iii) simultaneous electronic and ionic conductivity[39] reducing the electron-injection barrier from high work-function metal electrodes into polymer based optoelectronic devices.[40,41] These properties predetermine CPEs as promising optically and/or redox responsive materials for the construction of various devices and sensors.[42] Ionic π-conjugated polyacetylenes are mainly prepared by postpolymerization modifications of conjugated polymers via ionization of polymer side groups. The direct synthesis of ionic π-conjugated polyacetylenes is used rarely, mainly due to the sensitivity of the polymerization catalysts (initiators) to the ionic groups of the monomer molecules.

Polymer networks

Porous polymer networks have attracted significant interest due to the broad field of the potential applications. Porous networks for the gas storage and separation,[43-45] heterogeneous catalysis,[46] sensors and detectors[47,48] have been prepared by various methods. The π-conjugated porous polymer networks are of particular interest.[49-51] The sp^2 and sp hybridization of the carbon atoms in π-conjugated porous networks stands for the rigid character of the network segments that contributes to the formation of the porous texture of the networks. Moreover, the delocalized electronic structure of π-conjugated chains enables them to exhibit strong absorption and emission in UV/vis region, which opens variety of applications in the field of optoelectronics and sensors.[52,53,48]

The preparation of conjugated polymer networks is mostly performed as step-growth homo-coupling, cross-coupling and polycyclotrimerization,[32,34] or chain-growth polymerization[32,35] of monomers with higher functionalities e.g. multiethynylarenes, multihaloarenes, multiazidoarenes. As mentioned in the part dealing with the π-conjugated polymers, most of the synthetic pathways require transition-metal catalysis, which exhibit limited compatibility to the monomer structure. Moreover, the efficient purification of the insoluble polymer networks is difficult and the materials could be contaminated by catalyst residues. Obviously, the direct, transition-metal catalyst free preparation of π-conjugated polymer networks would be beneficial for the product purity and would open up a new opportunity for the applications of these materials.

Reactivity of triple bond

The polyacetylene type polymers are prepared mainly via polymerization of the acetylenic monomers – monomers containing internal or terminal triple bond. Triple bond is shorter (120.3 pm) compared to the double bond (133.9 pm), on the other hand, the triple bond exhibits higher dissociation energy. The energy required for homolytic bond cleavage at 298 K, which is by definition the bond dissociation enthalpy of the molecule DH_{298}, also called bond-dissociation energy was determined for acetylene (HC≡CH) and ethylene ($H_2C{=}CH_2$) to DH_{298} = 230 kcal/mol and DH_{298} = 174 kcal/mol respectively.[54] However, the triple bond is not completely dissociated during the polymerization process and thus the acetylenic monomer reactivity is determined by the π-bond energy and by the triple bond electron density. Acetylene has a 54 kcal/mol π-bond energy, whereas for ethylene it is of 65 kcal/mol. Moreover, due to the sp-type hybridization, the carbon atoms in acetylene are less distant from each other than in ethylene. This peculiarity, together with the cylindrical symmetry of π-electron distribution with respect to the molecular axis, lead to an increase of the triple bond π-electron density. Consequently, the π-electron polarizability decreases; electrophilic attack at the triple bond is hindered and nucleophilic attack is favored. These are reasons for the acetylene's ability to form π-complexes and metal acetylides. Therefore, acetylenes should be more easily polymerized by coordination polymerizations.[26]

Polymerization of ethynylpyridines

Although the polymerizations of various acetylenic monomers are broadly explored and efficient approaches were established, the polymerization of ethynylpyridines is still not sufficiently probed, mainly due to N atom that complicate the application of commonly used transition metal catalysts.

In 1964, 2-ethynylpyridine (2EP) was firstly thermally polymerized by Okamoto to give a low yield of polymer with low molecular weight.[55] The polymerization of 2-, 3- and 4-ethynylpyridines were also briefly mentioned by Simionescu and Percec in the book "Progress in Polymer Science",[19] unfortunately, the original articles are not available even in printed version. Polymerizations of 2EP induced by transition metal (Pd, Pt) chloride and organoaluminum compounds were presented in article published in 1988, in the journal "Polymer Korea" but article is written in Korean language.[56] Since there is no further citation associated to the mentioned article, we assume that published results were not astonishing. It's worth to mention that transition-metal catalysts (W and Mo based - working in metathesis mode) were also used for the copolymerization of 2EP with phenylacetylenes and various halogen-substituted acetylenes. Reported copolymers were obtained only in low to moderate yield. The homopolymerization of 2EP is also mentioned in this article, however, the closer description of polymerization procedure and characteristics of resulting poly(2EP) is missing. Only ^{13}C NMR spectrum of poly(2EP) with characteristic three distinguished maxima was presented.[57]

However, a few papers reporting the polymerization of ethynylpyridines using transition-metal catalyst have been published. The electro-optical properties of poly(2EP) prepared via polymerization of 2EP using the catalyst of WCl_6-$EtAlCl_2$ is described in article written by Gal et al.[58] Prepared polymer was soluble in polar solvents and exhibited photoluminescence with maximum located at 581 nm. Also polymerization of 3-ethynylpyridine (3EP) using Rh based catalyst $[[Rh(cod)Cl]_2$, $[Rh(nbd)Cl]_2$ or $Rh^+[\eta^6\text{-}C_6H_5(nbd)B^-(C_6H_5)_3]]$ gave linear polymers (PPyA), which were consequently modified via quaternization into corresponding ionic polyelectrolytes type polymers (CPE). The authors proposed that fully quaternized *N*-methyl-meta-ethynylpyridinium halides (PPyA-MX) were obtained via reaction of PPyA with methyl iodide and methyl bromide.[59]

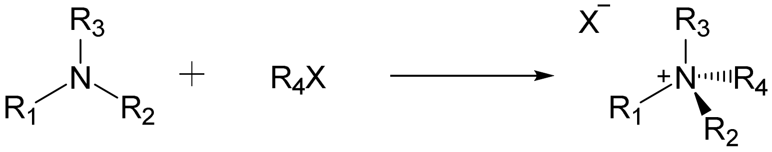
Polymerization of vinylpyridines

As the quaternization polymerization of vinylpyridines is also discussed in the introduction in connection with quaternization polymerization, the traditional polymerization approaches of vinylpyridines should be also briefly mentioned. From a large number of derivatives of vinylpyridine, only three monomers, 2-vinylpyridine, 4-vinylpyridine and 2-vinyl-6-methyl-pyridine have become commercially important. Poly(vinylpyridine)s are of particular interest because they can act as polyelectrolytes and furthermore, because they can form complexes at the basic nitrogen atom. Vinylpyridine shows a polymerization tendency similar to that observed for styrene and thus can be polymerized via radical polymerization initiated by peroxides or azo compounds. Also free radical polymerization in emulsion and controlled radical polymerization in presence of TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl or (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl] were described in the literature. Due to the high electronegativity of nitrogen atom, vinylpyridine can also undergo anionic polymerization. The polymerization can be initiated by carbanions, by electron-transfer initiators, electrochemically, by sodium in liquid amonia, by magnesium (mainly Grignard reagent), beryllium, and lithium compounds, or by transition-metal allyl compounds.[60]

1.2 Menshutkin reaction and quaternization polymerizations of vinylpyridines

1.2.1 Quaternization reaction

Nitrogen is an element of *p*-group with electron configuration $1s^2\,2s^2\,2p^3$ carrying 5 valence electrons. Most of the bonds in nitrogen containing compounds are formed by the electrons of $2p^3$ orbital. However, the lone pair of $2s^2$ orbital is crucial for the quaternization reaction. In 1890, Russian chemist Nikolai Menshutkin discovered the reaction of converting the tertiary amine into quaternary ammonium salts (**Scheme 1**).[61,62] Nowadays, in his honor, this reaction is known by his name. Menshutkin reaction is a special kind of S_N2 (nucleophilic substitution) reaction where the reactants are uncharged, in contrast to the most usual S_N2 reaction where one of the reactant is charged.[63] In this process, the tertiary amine is reacted with alkyl halide, which withdraws one of the electron of the lone pair of nitrogen atom resulting in positively charged ammonium and the negatively charged halide.



Scheme 1 Quaternization reaction, also labeled as Menshutkin reaction.

The tertiary amines are also included in the nitrogen containing aromatic heterocyclic compounds e.g. azirene, azete, pyrrole, pyridine, azepine, quinoline etc. Because of its chemical properties, the pyridine is broadly used as a raw material in the chemical industry and thus the most examined nitrogen containing heterocylic compound (**Figure 2**).

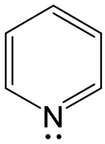
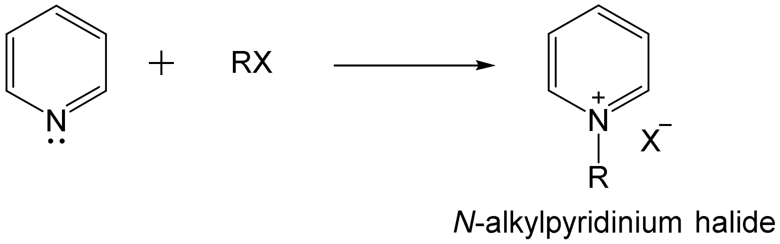


Figure 2 Structure of pyridine with lone electron pair.

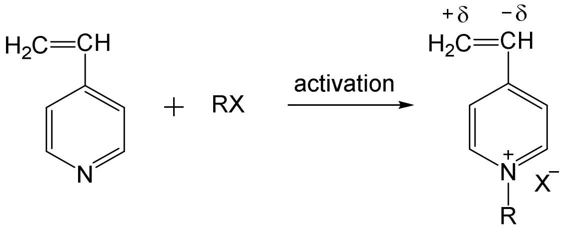
Similarly to benzene, pyridine has conjugated system of π-electrons delocalized over the ring. As the nitrogen atom contains sp^2-hybridized lone pair, the electron density is not equally distributed. Lone pair does not contribute to the aromatic system, however, the lone pair influences the chemical properties and reactivity of pyridine. Due to the lone pair, pyridine could easily undergo e.g. protonation or as mentioned earlier, Menshutkin reaction. In this reaction is pyridine reacted with alkyl halide and the *N*-alkylpyridinium halide is obtained as a product (**Scheme 2**).[64] Pyridinium salts compounds are referred to be used in various areas ranging from biological to industrial applications. [63,65]



Scheme 2 Quaternization of pyridine with alkyl halide results in *N*-alkylpyridinium halide.

1.2.2 Polymerization of activated vinylpyridines

When the pyridinium salt is formed, the positive charge on the nitrogen atom influences the *π*-conjugated system and the electron density is redistributed over the pyridine ring. The redistribution of electron density affects the positional reactivity of pyridine ring and also the reactivity of pyridine pendants. In the 1966 Russian chemists Kargin and Kabanov applied this phenomenon on the pyridine derivative 4-vinylpyridine (4VP).[66] The double bond of vinyl group of 4VP is in conjugation with the delocalized *π*-electron structure of pyridine ring. Thus, when 4VP is reacted with alkyl halide and *N*-alkyl-4-vinylpyridinium halide is formed, the electron density of the double bond of vinyl group is also influenced. Consequently, partial charges on *α* and *β* carbons of double bond are formed. The reaction of 4VP with alkyl halide is depicted in **Scheme 3**.



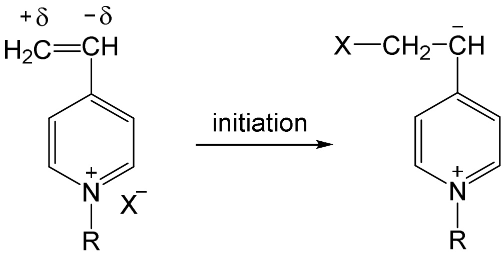
Scheme 3 Quaternization of 4-vinylpyridine with alkyl halide results in *N*-alkyl-4-vinylpyridinium halide accompanied with the formation of partial charges on vinyl group.

The quaternized form of 4VP is denoted as activated species. For further discussion, more precise labeling is an activated monomer. Generally, the chemical activation of a monomer is ascribed to the redistribution of electron density among the intramolecular bonds caused by the interaction between monomer and activation agent, in this case alkyl halide. As the activation proceeds as Menshutkin reaction resulting into quaternized species, the activation agent is generally labeled as quaternizing agent (QA).

When Kargin and Kabanov had reacted 4VP with alkyl halide, the high-molecular mass amorphous substances, which do not contain free pyridine base groups was obtained instead of monomeric quaternary salts. Thus, the spontaneous polymerization of 4VP takes place, which was later labeled as quaternization polymerization (QP). According to Kargin and Kabanov, the mechanism of QP of vinylpyridines involves three steps: activation, initiation and propagation.[66,67] Activation step proceeds as mentioned above, by

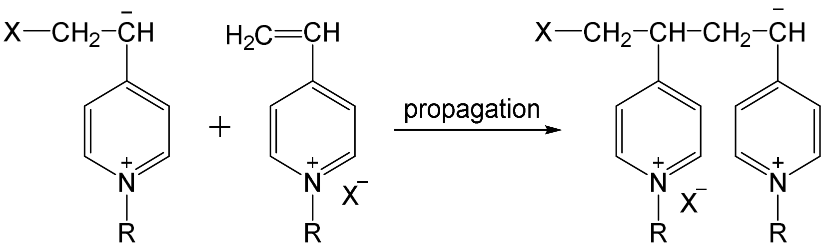
Menshutkin reaction in which the *N*-alkyl-vinylpyridinium salt is formed (**Scheme 3**). The activation could be caused by the alkyl halide or by the strong acid.[68]

As a result of the electron density redistribution after the quaternization of N atom of pyridyl, π-electrons of the double bonds are appreciably displaced towards the pyridine ring. This is being accompanied by a sharp increase of the electrophilicity of the double bond. The activated monomer now readily reacts even with weak nucleophilic agents. The role of such agent in the initiation step is fulfilled by the anion X^- resulting into the zwitter-ion as depicted in **Scheme 4**.



Scheme 4 Initiation of activated monomer with halide anion.

The propagation is proposed as a chain-growth polymerization, where the activated monomer reacts with the zwitter-ionic form of monomer and the polymer chain with ionic pendants is formed. (**Scheme 5**)



Scheme 5 Propagation proceeds via reaction of initiated and activated monomers.

When strong inhibitors of radical polymerization (benzoquinone, diphenylpicrylhydrazyl, and *N*-oxides) were added into the reaction mixture, no retardation of the reaction and no affect on the viscosity of prepared polymers were observed. Thus, the radical mechanism of polymerization was excluded. When the reaction of 4VP and ethyl bromide was carried out in acrylonitrile and in styrene, the resulting polymers do not contain nitrile and styrene units, respectively. Under the reaction conditions both styrene and acrylonitrile behave as solvents and do not copolymerize with 4VP. Thus, it could be possible to eliminate the usual anionic and cationic mechanisms. In the presence of the excess of 4VP over the alkyl halide, the formation of the polymer occurred until the all alkyl halides have been used up and unreacted 4VP remained in the system. Therefore, the specific mechanism, where only monomers activated by Menshutkin reaction were polymerized, was proposed. The formed polymer was fully quaternized with general formula shown in **Figure 3**. The obtained polymer contains charged pendants of the main chains, thus, according to the IUPAC classification, this material could be regarded as polyelectrolyte.[69] The ionic character stands for the good solubility of polymer in the polar solvents.

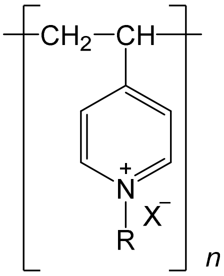


Figure 3 The general formula of ionic poly(4-vinylpyridine) prepared via quaternization polymerization of 4VP activated with alkyl halide.

In accordance with the mechanism examined above, it could be expected that of 3-vinylpyridines and its derivatives exhibited lower tendency towards spontaneous polymerization, due to the electron density redistribution over the pyridine ring. Really, the polymerization reactions of 2-methyl-5-vinyl-pyridine with ethyl bromide, methyl iodide, dimethyl sulphate, and others QA in organic solvents (acetone, ethyl acetate, etc.) did not occur and only crystalline pyridinium salts were obtained.[66]

In 1967, the mechanism of the QP of 1-methyl-2-vinylpyridinium methylsulphate and 1-methyl-4-vinylpyridinium methylsulphate in aqueous solution was described. The authors proposed that the monomeric slats create ordered aggregates, which are consequently polymerized into the polymers.[67] The same assumption is applied on the “matrices” polymerization reported in the article.[68] The 4VP is reacted with polystyrenesulphonic acid (PSSA) in agues solution. PSSA act as matrices for the nascent polymers composed of vinylpyridinium units. Similarly to the usual QP, 4VP is activated with QA, in this case –SO_3H and the resulting polymer is a stoichiometric half-salt. The authors proposed that initiated 4VP monomers have sufficient mobility to migrate along the chain of the PSSA macromolecules. However, SO_3^- pendants of the PSSA could be also compensated by the H_3O^+ cations and thus the length of the poly(vinylpyridinium) chain is determined by the number of the neighboring 4VP fixed on the PSSA. The model of PSSA and 4VP is depicted in **Figure 4** and the structure of prepared ionic polymer is depicted in **Figure 5**.

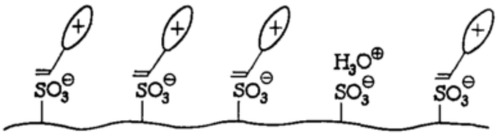


Figure 4 The “matrice” polymerization of 4VP activated with polystyrenesulphonic acid (PSSA). The mechanism proposed certain mobility of 4VP to migrate along the PSSA chain. (Kargin, Kabanov; 1967)[68]

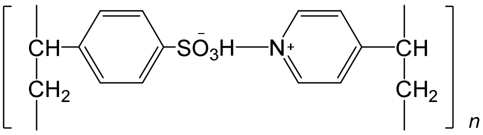
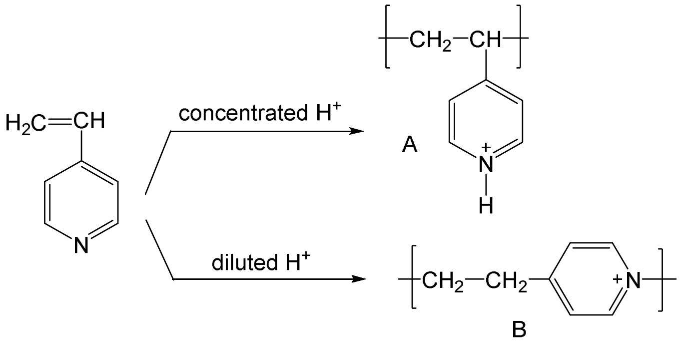


Figure 5 The proposed structure of ionic polymers prepared via “matrice” polymerization of 4VP activated with PSSA.

As mentioned above, vinylpyridine monomers could be activated with alkyl halide or with strong acids. When the strong acid is used as an activation agent, the polymerization mechanism depends on the concentration of H_3O^+ ions in selected media. When highly concentrated solution of acid is used, the poly(vinylpyridinium salt) is obtained. However, when diluted solution of strong acid is applied, polymerization leads to the poly(1,4-pyridiniumdiylethylene salts) in which the pyridinium units are involved in the polymer main chain (**Scheme 6**). This process appeared to be a step-growth hydrogen-transfer polymerization which gave low molecular weight ionene polymers.[70,71] (Ionene polymer is polyquaternary ammonium compounds with the ammonium ion integral in the backbone of the polymer chain – author’s note)



Scheme 6 The QP of 4VP activated with strong acid. When concentrated solution of strong acid is used, the poly(vinylpyridinium salt) is formed (product A). When diluted solution of strong acid is used, the poly(1,4-pyridiniumdiylethylene salts) is formed (product B).

A number of articles concerning the influence of the reaction conditions on the product, the detailed studies of the matrices polymerizations with various polyacids or the mechanism of inhibition were published.[66,72-76] Mostly 4-vinylpyridine or 2-vinylpyridine and their derivatives were used as a starting materials. Reported reactions were carried out in various organic media (e.g. benzene, nitrobenzene, acetonitrile, dimethyl sulfoxide, sulpholane and methanol) or in the aqueous solution in the case of polymerizations of vinylpyridines activated with strong acid. Various *n*-alkyl halides (e.g. ethyl bromide, butyl bromide, methyl iodide, etc.) benzyl halides, low molecular weight acids (hydrochloric, sulphonic, hydrobromic, perchloric or acetic acid, etc.) and poly-acids were used as QA. The reactions were performed usually in sealed glass ampoule under inert atmosphere at the temperature from -5 °C to 70 °C. The products of QP reaction were characterized mainly by means of UV/vis spectroscopy and viscosimetry or rarely by the GPC (reported by Salamone et al.[70]).

Polymerization of vinylpyridinium salts

In order to synthesize fully quaternized ionic polymer with tunable *N*-alkyl moiety, the polymerization of variety of stable *N*-alkyl-4-vinylpyridinium trifluoromethanesulfonates salts was performed. In this case, the polymerizations of activated vinylpyridinium slats were initiated by the elevated temperature or with radical (AIBN - azobisisobutyronitrile) or base (pyridine) initiators.[77,78]

Kinetic study of the quaternization reaction

Fuoss and coworkers have proposed a kinetic model of the quaternization reaction of pyridine with various QA. According to obtained data, the reactions followed second order kinetic with no evidence for side products.[65,79] However, the kinetic of the quaternization polymerization, unlike the simple quaternization reaction, was not consistently described. In articles[66,80] is the reaction described satisfactory by a first order kinetic equation with respect to monomer (vinylpyridine). The first order kinetic illustrated mainly the initiation of the QP. However, alternative kinetic model has been proposed later in article, where the second order kinetic was suggested.[67] The QP activated with low molecular weight acids followed third order kinetic with respect to the monomer. In contrast, second order kinetic was previously found for quaternization matrices polymerizations.[76]

Preparation of polymer networks via one step quaternization polymerization

The quaternization polymerization of 4-vinylpyridine activated with 1,4-dibromo-2-butene in the absence of organic solvents was presented in article written by Mondal et al.[81] The bifunctional character of quaternizing agent caused the cross-linking of product and consequent network formation. Prepared ionic polymer networks exhibited superior ion exchange, antibacterial properties and high thermal stability.

Modifying of the poly(vinylpyridine)s – postpolymerization modification via quaternization reactions

Postpolymerization modifications are generally summarized in the book: “History of Post-Polymerization Modification“.[82] The postpolymerization modification is not the topic of the presented work. However, let us briefly discuss the main features of the modification by the quaternization reaction. The attention was focused mainly on the modification of the poly(vinylpyridine)s prepared by radical polymerization. For example, the kinetic and the rate constant of the quaternization modification were studied.[83] The results of reactions with various QA and at a various concentrations and temperatures were analyzed according to the neighboring-group model. This kinetic model is based on the quantity of already reacted (quaternized) neighbors (could be 0, 1 or 2) indicate that the retardation of the quaternization is predominantly caused by the steric effects. Later, the kinetic studies with variety of QA and solvents were reported, e.g. in articles.[84-88]

In comparison with quaternization polymerization, the quaternization modification of prepared polymer allows the superior polymer characterization, especially the length of the polymer chain: (i) molecular weight is controlled by the proper polymerization method and, (ii) the characterization of the polymers could be performed by means of traditional methods (e.g. SEC chromatography).

Cross-linking of poly(vinylpyridine)s

The quaternization modification of existing poly(vinylpyridine)s with bifunctional QA (e.g. dichloroalkane) leads to cross-linking of polymer chains and consequent network formation.[89] Polymeric core-shell stars with a novel fluorescent, cross-linked and swollen core was prepared by the postpolymerization modification of di-block copolymer (polystyrene-*b*-polyvinylpyridine). The poly(vinylpyridine) blocks were quaternized with propargyl chloride, which activated the ethynyl of propargyl resulting in the cross-linking of poly(vinylpyridine) blocks and the network formation.[90]

Application of poly(vinylpyridine)s

It has been reported that cationic polymers of quaternary ammonium salt-type possess excellent flocculation, corrosion inhibition, and sterilization functions, which open up the broad variety of applications.[91,92]

1.3 Quaternization polymerizations of ethynylpyridines

This section deals with the quaternization polymerization of ethynylpyridines. The quaternization polymerizations reported in the literature are summarized in **Figure 11** (Quaternization polymerization chart), **Table 1** (for characteristics of reported polymers) and **Table 2** (for elemental analysis of reported polymers). For better clarity, the reported polymers are labeled with **PNo.** (Polymer number), which refers to the mentioned **Figure 11**, **Table 1** and **Table 2**.

A new polymerization method for substituted acetylenes

In 1964, W.A. Little presented the review on the superconductive polymers. Proposed polymer model contained extensively conjugated polyacetylene chain with repeating units in which one of the hydrogen atoms was substituted with a positively charged side group. The positive charges were reached by the quaternization of the nitrogen atoms of the side groups and compensated by the negative charge of the halide. The proposed structure is shown in **Figure 6**.[93]

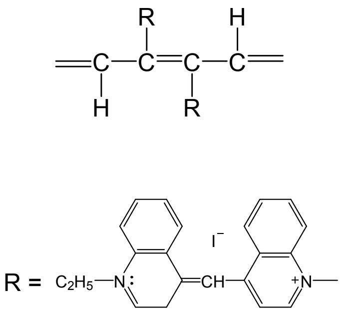


Figure 6 Model of superconductive polymer proposed by Little. Polymer contained conjugated main chain with charged pendants.

In 1991, based on the study of superconductivity reported by Little et al., Blumstein and Subramanyam synthesized π-conjugated polyacetylene type polymers bearing positively charge side groups with similar architecture to the one proposed by Little. Prepared materials were briefly mentioned in the book “Organic Superconductivity”[94] and then discussed in detail in article.[95] To prepare this kind of polymers, Blumstein and Subramanyam used the quaternization polymerization method frequently applied on the vinylpyridines: via one-step quaternization polymerization, the polyacetylenic type polymers containing π-conjugated backbone, bearing various ionic pendants, also labeled as conjugate polyelectrolytes (CPE)s, were obtained with general structure depicted in **Figure 7**.

A series of mono- and bi-pyridylacetylene based monomers was activated with various quaternizing agents and mainly the linear polymers were obtained (**PNo. 1-5**, **7**, **8**). However, when 1,2-bis(4-pyridyl)acetylene was reacted with nonena-1,9-bis(methanesulfonate) the insoluble cross-linked product was obtained (**PNo. 75**). The reaction of 1,4-bis(4-pyridyl)butadiyne with 1-bromododecane also resulted in a insoluble, highly cross-linked polymer (**PNo. 9**). Prepared materials were characterized by means of elemental analysis, IR, UV/vis and photoluminescence spectroscopies, TGA and DSC analysis and by the inherent viscosity in methanol. Moreover, according to the Sondheimer,[96] the relation between the absorption maxima λ_{max} and the number of C=C double bonds in conjugation, *n*, based on the Lewis-Calvin equation[97] was proposed.[98] Detailed study on preparation and characterization of prepared ionic polymers was published later in articles.[95,99]

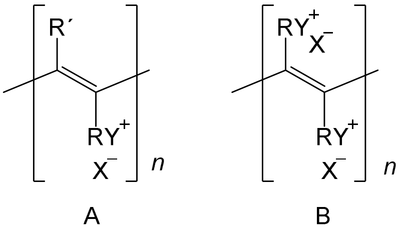
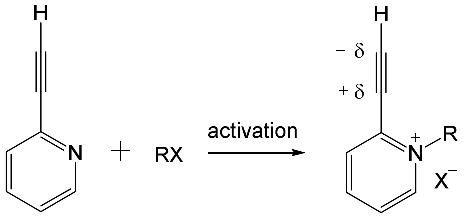


Figure 7 Structure of ionic polymers prepared via quaternization polymerization of mono-pyridylacetylene based monomers (A) and bi-pyridylacetylene based monomers (B) activated with quaternizing agent YX.

Blumstein presented this approach as a novel method for polymerization of 2-ethynylpyridines (2EP) and 4-ethynylpyridines (4EP) similar to that applied by the Kargin and Kabanov on the quaternization polymerization of vinylpyridines.[66] The reaction involved a quaternization reaction followed by spontaneous, rapid polymerization resulting in ionic π-conjugated polyacetylenes that were highly soluble in the polar solvents. This method provide a powerful tool for polymerizing acetylenic triple bonds attached either directly or via a sequence of conjugated carbon-carbon double bonds to nitrogen atom capable to undergo a quaternization reaction. The molecular weights of polymers prepared from ethynylpyridines were higher than those obtained from the QP of vinylpyridines.

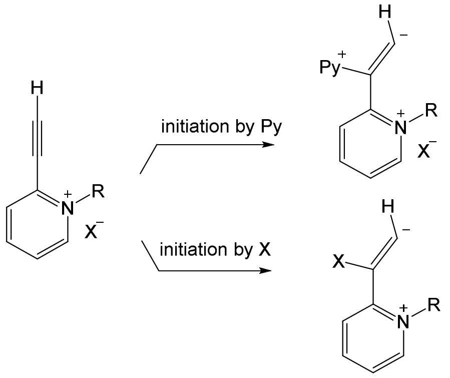
Proposed mechanism of quaternization polymerization of ethynylpyridines

A free-radical mechanism of the QP was precluded (similarly to the radical mechanism for the quaternization polymerization of vinylpyridines[67]) due to the observations: (i) inhibitors of free-radical polymerization (such as oxygen) do not interfere with the polymerization process and (ii) only quaternized monomeric species were found to participate in the polymerization process. The special kind of ionic polymerization mechanism, similar to the mechanism described by Kargin and Kabanov for the polymerization of vinylpyridines, was proposed. Generally, the quaternization polymerization could be described via three-step mechanism involving activation, initiation and propagation. The activation step of quaternization polymerization is represented by the formation of *N*-alkylpyridinium salt via a Menshutkin reaction as depicted in **Scheme 7**. The redistribution of electron density due the quaternization of N atom of pyridyl ring causes the polarization of carbons of ethynyl group. Blumstein et al.[100] assumed that *α*-carbon of C≡C bond carries positive partial charge and the *β*-carbons of C≡C bond carries the negative partial charge. However, it is worth to mention that also opposite partial charges on C≡C carbons were proposed in the process of quaternization polymerization.[101]



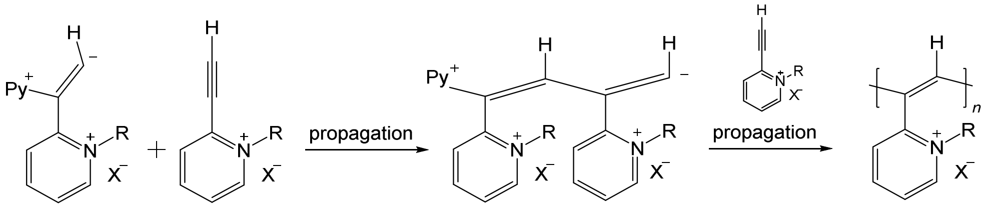
Scheme 7 The activation of 2EP with alkyl halide (RX) and formation of *N*-alkylpyridinium salt.

The initiation step involves a nucleophilic attack on *α*-carbon of C≡C bond of activated monomer (monomeric salt) by either the nitrogen atom of unreacted 2-ethynylpyridine monomer and/or the halide anion of quaternizing agent (**Scheme 8**). When halide anion take place in this step, the molecule contains two ions is formed. Since this type of molecule is labeled as zwitter-ion, the quaternization polymerization is also labeled as zwitterionic polymerization in the literature.[40]



Scheme 8 Initiation step of quaternization polymerization of 2EP. The initiation of monomer could proceeds via unreacted monomer (Py represent pyridyl group of non-quaternized monomer) or by the halide anion X^{-}.

Propagation step involves a nucleophilic attack of the resulting carbanion on the triple bond of quaternized (activated) monomer molecule (**Scheme 9**). Moreover, the authors assumed that the vinylic carbanion could also undergo alkylation by the quaternizing agent, which would result in chain terminations.[99] This mechanism was described in detail in article reported by Blumstein et al.[100] According to Gal et al. the activated monomer could be initiated by addition of nucleophiles such as pyridines, halide anions and also by the tertiary amines. Thus the quaternization polymerization seems to proceed via anionic mechanism.[102]



Scheme 9 The propagation steps of quaternization polymerization of 2EP, in which initiated monomer reacts with activated monomer resulting into ionic polymer.

Quaternization polymerizations of ethynylpyridines activated with molecular bromine and strong acid

Mainly alkyl halides were used for the activation of the monomers via quaternization reaction. However, the alternative quaternizing agents were also reported. The formation of a donor-acceptor complex between the pyridine ring of the monomer and bromine provided sufficient activation of the acetylenic triple bond allowing spontaneous polymerization (**PNo. 10**, **11**).[100] The extensively conjugated ionic polyacetylene bearing protonated pyridinium side groups was also prepared by the spontaneous polymerization of the acetylene bond in 2-ethynylpyridine in concentrated hydrochloric acid (**PNo. 12**).[98] The polymer structure formed by the activation with molecular bromine (Br_2) was analogous to the structure of ionic polymers obtained via the activation with alkyl halides, however, the alkyl was replaced by the bromide in this case (**Figure 8**). This assumption is also in good agreement with the Br/N mole ratio 1.83 of resulting polymer (see **Table 2**, **PNo. 10**), which indicates that major part, but not all, of monomeric units bound two Br atoms.

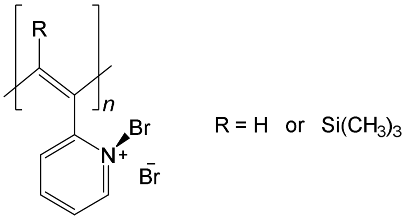
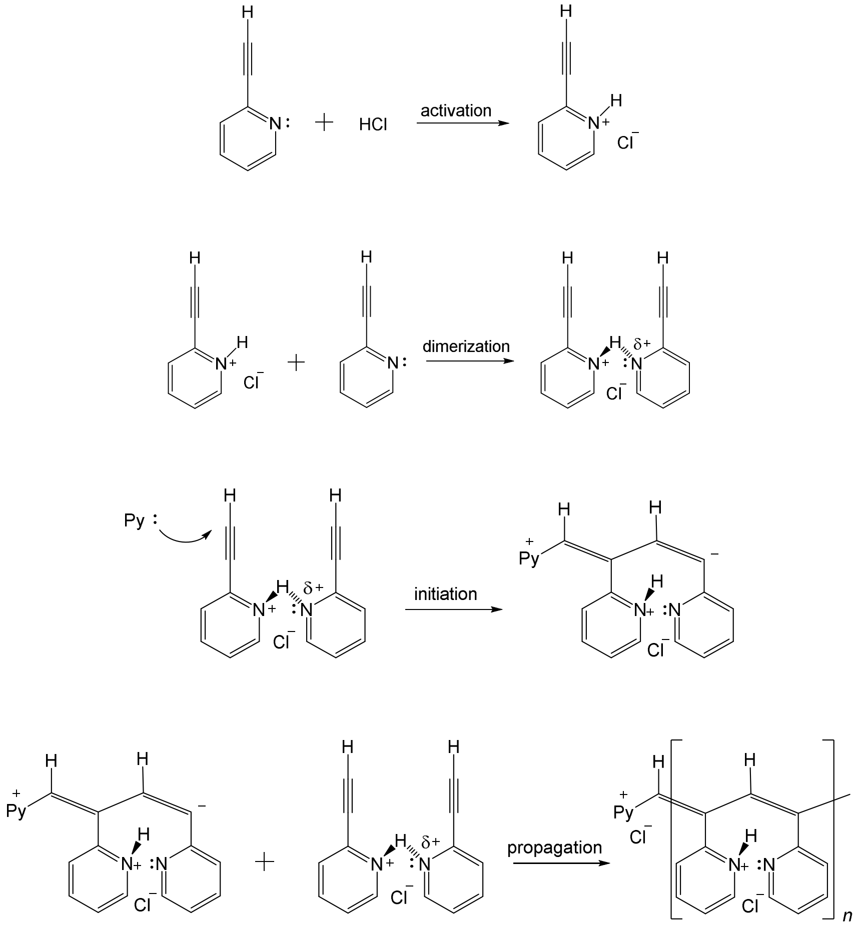


Figure 8 Proposed structure of ionic polymer prepared via quaternization polymerization of 2EP activated with Br_2.

On the contrary, the different composition of the polymer was obtained from the reaction with the strong acid. The side reaction step incorporated between activation and initiation steps was proposed in this case.[103] The activated (quaternized) monomer reacted with the non-quaternized monomer resulting into dimer, which contains two monomers activated with one hydrochloric acid molecule. The mechanism proposed in the mentioned article regards the dimer as a single unit, which undergoes initiation and propagation steps according to the mechanism proposed for the QP activated with alkyl halide. Therefore, the polymer with a structure wherein only 50% of pyridine rings in the polymer contain quaternary nitrogen is obtained. This is also in good agreement with Cl/N mole ratio 0.43 for resulting polymer (see **Table 2**, **PNo. 12**). [95,99,100,103] The mechanism of polymerization of 2EP activated with hydrochloric acid is depicted in **Scheme 10**.



Scheme 10 Quaternization polymerization of 2EP activated with HCl. Unlike the traditional mechanism of QP, the authors proposed the formation of dimer after activation step.

Polymerization of ethynylpyridinium salts

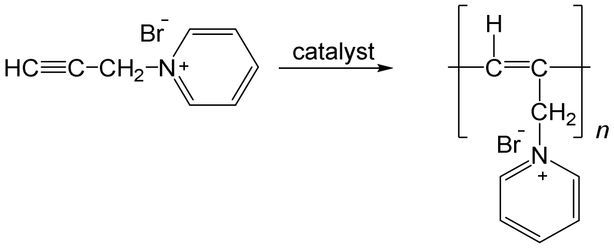
In the presented polymerization process, the activated monomers (ethynylpyridinium salts) are unstable intermediates that are difficult to isolate due to competition between polymerization and *N*-alkylation. With the aim to obtain product with higher molecular weight, it was desirable to separate the overlapping quaternization (activation) and polymerization (propagation) processes. The successful isolation of *N*-methyl-2-ethynylpyridinium triflate and *N*-methyl-2-[(trimethylsily1)ethynyl]pyridinium triflate salts was presented in article.[104] The isolated salts were characterized and further polymerized via initiation by nucleophiles such as pyridine (**PNo. 13**), via free-radical initiator such as AIBN (azobisisobutyronitrile) (**PNo. 14**) or by means of thermal polymerization by heating at 170 °C (**PNo. 15**). The conjugation extent based on spectral data for the ionic polyacetylenes obtained via described nonspontaneous method was larger ($n > 16$) compared to those obtained by methods involving spontaneous processes.[95,99,100] Kinetic and mechanism of presented system was later proposed based on the UV/vis, IR and NMR experiments. [101] The same monomeric salt, *N*-methyl-2-ethynylpyridinium triflate, was used for synthesis of amphiphilic block copolymer with styrene. At first, the polystyrene chain was formed by the living polymerization initiated with *sec*-butyllithium which was further used as macroinitiator (polystyrene Li^+) for the polymerization of the monomeric pyridinium salt.[105] It was also proposed that the ionic 1,4-bis(4-methylpyridinium)butadiyne triflate salts create organized aggregates, due to the charged moieties, which undergo polymerization at temperature of 210 °C for 10 hours into corresponding polymer.[106,107] Later, the isolation, characterization and consequent polymerization of *N*-ethynyl-4-ethynylpyridinium triflate salts initiated by the elevated temperature was also published.[108]

Thermal polymerizations of several substituted phosphonium phenylacetylene monomer using a weak base (pyridine, picoline) as initiator under elevated temperature were also reporter. The quaternization of phosphonium changes the electron density of the ethynyl group in the similar way as in the case of quaternized ethynylpyridines, which makes the activated phosponium phenylacetylene monomer polymerized in presence of pyridine. Since this approach does not involved ethynylpyridine based monomers we don’t discus these reactions in detail.[109]

Preparation of ionic polymers via quaternization polymerization approach

Gal and co-workers had paid great attention to the polymerization of variety of acetylenic compounds. Mostly transition-metal catalyst (e.g. WCl_6, $MoCl_5$, $PdCl_2$, etc. systems) were used for the preparation of π-conjugated polymers based on mono- and di-substituted acetylenes.[110-114] Since the transition-metal catalyst were used for the polymerization of various propargyl monomers[115-118] the propargyl monomers containing N atom in their structure (amine group) were also tested by Gal et al. Compounds such as propargylamine,[119] 1,1-diethylpropargylamine,[119] tripropargylamine,[120] were successfully polymerized by catalyst derived from Mo and W.

After the Blumstein published the quaternization polymerization approaches for preparation of ionic polyacetylene based polymers, Gal inclined to the preparation of ionic polymers. The transition-metal (e.g. $PdCl_2$, $PtCl_2$, $RuCl_3$) catalyzed polymerizations of various propargylpyridinium slats (e.g. propargylpyridinium bromide,[121] dimethylphenylpropargylammonium bromide,[122] 2-ethynyl-*N*-propargylpyridinum bromide,[123,124] 4-dimethylamino-*N*-propargylpyridinium bromide[125]) gave ionic polymers soluble in polar solvent in moderate to high yield (**Scheme 11**).



Scheme 11 Transition-metal catalyzed polymerization of propargylpyridinium bromide into ionic polyacetylene type polymer.

Later, Gal and coworkers used the spontaneous, catalyst free approach reported by Blumstein, for the synthesis of various ionic π-conjugated polymers. First published reaction was the quaternization polymerization of 2EP with propargyl bromide as QA. The resulting ionic π-conjugated polymers bearing propargyl side chains were well soluble in polar solvents, e.g. water (**PNo. 24**).[126,127] Since that, Gal has published a number of articles dealing with the quaternization polymerization of ethynylpyridines activated with various QA. The polymerizations were mostly focused on 2EP and there was no intention to test alternative pyridylacetylene based monomers. However, the systematical study of QP provided comprehensive overview concerning reaction conditions, polymer characterization and polymer testing. The discussion about particular quaternization polymerizations is however unnecessary, since the reported articles exhibit similar procedure and characterization of products.

The quaternization polymerizations reported in the literature are summarized in the Quaternization polymerization chart in **Figure 11**. Here, we provide the general discussion about the reaction conditions of quaternization polymerizations and characterization of prepared materials.

1.3.1 Reaction conditions

General procedure of quaternization polymerization

The quaternization polymerizations reported in the literature were performed mainly under inert atmosphere (e.g. N_2, Ar) in glass ampoule. The products of quaternization polymerization were purified as follows: the resulting polymer solution was diluted with additional solvent and precipitated into an excess amount of less polar solvent (e.g. ethyl ether), followed by filtration. The product was collected as dark (black, brown, red, etc.) powder and dried under vacuum at elevated temperature (e.g. overnight at 40 °C, to constant weight).

Reaction temperature

The quaternization polymerizations were performed mainly at elevated temperature. The only exceptions was the polymerizations activated with bromine (Br_2) and acids (**PNo. 11**, **12**), which were performed at 0 °C. The activated acetylene triple bond of *N*-alkyl-2-ethynylpyridinium halide was found to be susceptible to the polymerization under mild conditions (polymerization preceded at temperature of 50 °C). However, many QP did not proceed fully when the reaction temperature was set below 90 °C.[128-137] Thus the quaternization polymerizations were tested mainly at the temperatures from 90 °C up to 130 °C. The temperature dependence on the yield of the product obtained was investigated in the case of quaternization polymerization of 2EP by using 3-(6-bromohexyloxy)methylthiophene as QA (**PNo. 39**). The reaction did not proceed at temperature of 60 °C. When the reaction was carried out at temperature 80 °C for 24 hours, the yield of polymer reached 53%. When the reaction temperature was elevated up to 110 °C, the polymer yield was 86% and the inherent viscosity increased (0.21 dL/g). When the reaction temperature was set to 130 °C, the polymer yield increased up to 89% and the inherent viscosity was 0.22 dL/g. It was assumed that quaternization reaction (activation) of monomers did not proceed bellow the temperature of 60 °C in this case, moreover, the bulky QA may also limit the incorporation of activated monomers into polymer chains under mild conditions.[133] The influence of the reaction temperature on polymer yield was also investigated in the polymerizations of 2EP activated with 4-(methylthio)benzyl bromide (**PNo. 43**),[138] 2-thiophenecarbonyl chloride (**PNo. 44**)[102] or 2-(bromomethyl)-5-nitrofuran (**PNo. 47**)[122] with the similar results. Generally, both the quaternization (activation) of monomer and also the polymerization of activated monomers require elevated temperature (e.g. thermal polymerization of ethynylpyridinium salt). It was assumed that the polymer yield increases with increasing reaction temperature, however, only in the limited range. The polymer yield increased approximately by 25% when the temperature is elevated from 60 °C to 100 °C, but only negligible increase of polymer yield was observed (5%) when temperature was increased from 100 °C to 130 °C. Moreover, the structure of monomer and QA may be considered: it was reported that considerable amount (35%) of product was insoluble in organic solvent in the case of the quaternization polymerization of 2EP with benzoyl chloride at temperature at of 100 °C, which was probably caused by the thermal cross-linking of side pendants (**PNo. 48**).[139]

Reaction time

The quaternization (activation) of monomer is considered to be the rate determining reaction in the quaternization polymerization. The activated monomer is then polymerized in the propagation step into the polyacetylene type polymer. However, as the both reactions proceed simultaneously (if we do not consider the polymerization of ethynylpyridinium salts) the quaternization polymerization could be seen as complex process. The polymerization of 2EP activated with 6-(*N*-carbazolyl)hexyl bromide (DMF, 90 °C) (**PNo. 25**) was monitored by UV/vis spectroscopy and the yield was determined after 1, 3, 6, 12, 24 and 48 hours. The band at around 381 nm was well observable in UV/vis spectra at time 1 hour. The intensity of this band has increased up to 24 hours, when reached the maximum at 383 nm with absorption edge around 750 nm. The polymer yield was developing alike: 12% at 1 hour, 25% at 3 hours, 40% at 6 hours, 60% at 12 hours and 75% at 24 hours, no further polymer yield increase was observed up to time 48 hours.[128] The same results were obtained when 2EP was polymerized via activation with 4-(methylthio)benzyl bromide (DMF, 60 °C) (**PNo. 43**). This polymerization proceeded well within the first hour (yield = 56%). The polymer yields after 3 and 6 hours were 89 and 93%, respectively, and a plateau (95%) was reached after 12 hours.[138] The same trend could be observed in the case of polymerization of 2EP activated with 2-thiophenecarbonyl chloride (DMF, 60 °C) (**PNo. 44**). The polymer yield increased in the time: 12 hours (67%), 24 hours (79%) and same at time 48 hours and 72 hours (81%).[102]

The polymerization of 2EP with 5-[(5-bromopenthoxy)methyl]-2-norborene (**PNo. 46**) reached the polymer yield of 50% even within the first hour.[140] The similar dependence was also reported in the polymerization of 2EP activated with 2-(bromomethyl)-5-nitrofuran (**PNo. 47**),[122] 1,3-propandiol cyclic sulfate (**PNo. 51**)[141] or benzoyl chloride (**PNo. 48**).[142] From the obtained data, it could be concluded that the quaternization polymerization proceeds in the range of hours and the maximum yield could be reached within the 24 hours. However, the kinetic of the quaternization reaction is affected by the variety of factors, e.g. reaction temperature, type of solvent (or in the bulk), or the nature of reagents (bulkiness, polarity).

Solvent

Quaternization polymerizations were carried out in various polar organic solvents (dimethylformamide, methanol or dimethyl sulfoxide, etc.) or in bulk (without solvent). Due to the variety of reagents used in the quaternization polymerizations, it is complicated to summarize the direct influence of the used solvents on resulting polymer. We can speculate that the quality of solvent may play role in the packing of nascent polymer, which could influence yield, viscosity, degree of quaternization and the conjugation extent of formed polymers. A series of quaternization polymerizations of 2EP activated with 2-thiophenecarbonyl chloride (60 °C, 24 hours) (**PNo. 44**) was carried in the various solvents and the final polymers yields and inherent viscosities were compared. The polymer yield increased in the solvent series: methanol (64%), acetonitrile (67%), pyridine (70%), *N*-methyl-2-pyrrolidone (71%), dimethylformamide (79%) and dimethyl sulfoxide (83%). The inherent viscosity increased in the series: pyridine (0.09 dL/g), acetonitrile (0.11 dL/g), methanol (0.12 dL/g), *N*-methyl-2-pyrrolidone (0.18 dL/g), dimethylformamide (0.20 dL/g) and dimethyl sulfoxide (0.21 dL/g).[102] Similar investigation in case of the polymerization of 2EP with benzoyl chloride (**PNo. 48**) was published in the article.[139]

Initial concentration of monomers

The polymer yield was also monitored with the respect to initial concentration of the monomer. The polymerization of 2EP activated with 4-(methylthio)benzyl bromide (DMF, 60 °C) (**PNo. 43**) was performed at initial monomer concentration 0.50, 0.75 and

1.00 mol/l (the QA/monomer mole ratio was 1 in all the reactions). The resulting polymer yields were 82%, 95% and 99% respectively and the inherent viscosity was 0.15, 0.18 and 0.20 dL/g, respectively.[138] The same trend could be observed in case of polymerization of 2EP activated with 2-thiophenecarbonyl chloride (DMF, 60 °C, 24 hours) (**PNo. 44**). The polymer yield increased in the series of initial monomer concentration: 0.5 mol/l (65%), 1.0 mol/l (79%), 2.0 mol/l (83%) and 2.5 mol/l (85%).[102]

Positional isomerism of pyridylacetylene based monomers

Although mainly 2EP or 4EP were used as a starting monomers, the reactivity of 3-ethynylpyridine (3EP) was also studied in the quaternization polymerization activated with pentyl iodide (PI) (**PNo. 61**). The authors described the lower reactivity of *meta*-positioned ethynylpyridine based monomers in the quaternization polymerization compared to its *ortho*-positioned counterpart. The prepared polymers were characterized by absorption and emission spectroscopies. Comparing the maximum wavelength values of UV/vis and photoluminescence data and absorption edge values, poly(3EPPPI) was clearly blue-shifted up to 100 nm compared to poly(P2EPPI) in all spectral data. This observation was explained by the electronic effect of link position between conjugated polyene and pyridinium group. Both polymers have the same side groups, but it includes the different link position between conjugated polyene and pyridinium moiety. Thus, both polymers have different electronic effect based on resonance concept (mesomeric effect).[95,143,144] The low reactivity of *meta*-positioned ethynylpyridine based monomers was also reported in the case of polymer networks formation. No product was obtained from the reaction of 3EP activated with 1,4-bis(bromomethyl)benzene (**PNo. 78**).[145]

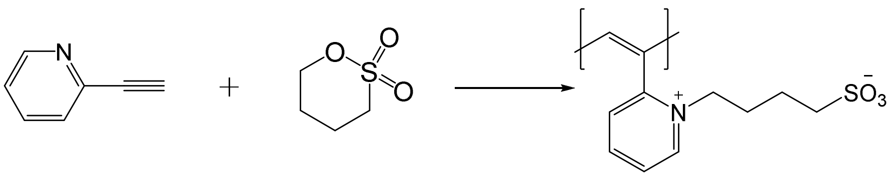
Initial reagents mole ratio and the degree of quaternization of products

One of the basic characteristic of the ionic polymers is the degree of ionization. In the case of discussed polymers, the ionic character is caused by the formation of quaternized species via the Menshutkin (quaternization) reaction, therefore it is denoted as degree of quaternization. Most general expression could be defined by the mole ratio of N^+ to total amount of N expressed as $N^+/(N^++N)$. As it is assumed, the formation of N^+ is caused by the withdrawing of one electron of lone pair by the quaternizing agent (QA) accompanied by the formation of pyridinium salt. The positive charge of pyridinium is compensated by the negatively charged moiety of QA. As the alkyl halides are mainly applied as QA, the negative charge is carried by the halide atom. Therefore, the degree of quaternization of resulting polymers could be expressed as mole ratio of halide to nitrogen X/N.

If the quaternization polymerization of ethynylpyridines containing one pyridyl group activated with alkyl halides is considered, the degree of quaternization may be equal to unity, X/N = 1. This assumption was widely accepted and only quaternized monomeric units were assumed to be present in the polymer. However, the results of elemental analysis of polymers reported in the literature suggest that the X/N mole ratio can drops under 1. For results of elemental analysis of reported polymers see **Table 2**. This may indicate that not strictly quaternized monomeric units were present in the polymers. Two possible explanations could be suggested: (i) the formation of fully quaternized polymer is followed by the dequaternization of monomeric units or (ii) also non-quaternized (activated) monomers are involved in the polymerization process. As the quaternary ammonium salt is consider to be stable, the dequaternization of polymer is not probable to occur, therefore, the later theory may cause the reduction of degree of quaternization.[95]

The initial QA/monomer mole ratio was mostly 1 in quaternization polymerizations reported in the literature. If monomer with two pyridyl groups was applied, the initial QA/monomer mole ratio was set to 2, which correspond to the initial X/N mole ratio 1 (X is halide of QA and N is nitrogen atom of pyridyl).[95,99] However, also alternative initial QA/monomer mole ratios were reported. The QA/monomer mole ratio 0.1 was applied in the polymerization of 2EP with 3rd generation dendritic benzyl bromide (**PNo. 60**). Thus, the resulting ionic polymer was assumed to contain only 10% of quaternized monomeric units.[146] The various X/N mole ratios were applied also in the preparation of polymer networks from 4EP activated with a series of bi-functional QA in article reported recently by our group.[145]

The counter ion could be also involved in the side pendant as it is demonstrated in the QP of 2EP and 1,4-butanesultone in **Scheme 12**. Thus, the monomer units with positively and negatively charged parts are obtained. This type of polymer is denoted as zwitterionic polymer or as a self-doped polymer. The quaternization of monomer proceed by the simultaneous ring opening of quaternizing agent (**PNo. 29**, **42**, **49**, **51**, **57**)[130,137,141,147,148]



Scheme 12 The quaternization polymerization of 2EP with 1,4-butanesultone resulting into self-doped ionic polymers.

1.3.2 Characterization of ionic π-conjugated polyacetylene type polymers

Elemental analysis (EA)

Since the classical polyacetylene contains only carbon and hydrogen atoms, the elemental analysis do not provide any important characteristics of these materials. However, to prepare ionic polymers via quaternization polymerization mechanism, monomers containing pyridyl group(s) (N atom) and quaternizing agent containing (mainly) halide(s) (X atom) are required. Thus, the X/N mole ratio of product can imply the basic compositional characterization of prepared materials. Although the X/N mole ratio provides important information about the product, the results of elemental analysis were not available for all ionic polymers prepared via quaternization polymerizations reported in the literature. **Table 2** summarizes the results of elemental analysis of reported quaternization polymerizations found in the literature. Its worth to mention that the data were available only for 23 from 84 reported products.

Fourier transform infrared spectroscopy (FT-IR)

Prepared ionic polymers were typically characterized by the FT-IR spectroscopy. Since the quaternizing agents used in the quaternization polymerizations posses various pendants, it is not meaningful to discuss all IR bands. Thereby, only IR vibration common for all ionic polymers are discussed here. The formation of polyacetylene type polymers is supported mainly by the absence of C≡C-H and C≡C stretching vibration, which are present in the IR spectra of monomers from 3120 to 3290 $\mathrm{cm^{-1}}$ (C≡C-H stretching vibration) and from 2090 to 2110 $\mathrm{cm^{-1}}$ (C≡C stretching vibration). A new absorption bands of double bonds of conjugated system are observed in the IR spectra from 1634 to

1590 cm^{-1}, or this absorption bands were more intense than those ascribed to C=C and C=N stretching vibrations of 2EP itself. The N^{+}=C stretching vibration of pyridiniumyl units are observed in the region from 1620 to 1634 cm^{-1}. The broad absorption band around 3400 cm^{-1} is assigned to C=C-H stretching vibration of conjugated polymer main chain. Peaks at 3032 and 1572 cm^{-1} are assigned to C-H and C=C stretching vibration of the pyridinium rings.[149]

Nuclear magnetic resonance spectroscopy (NMR)

^{1}H NMR and ^{13}C NMR experiments were carried out in polar solvents, mainly in DMSO-*d*$_6$. Similarly to the FT-IR spectroscopy, only the common characteristics for all polymers are discussed here. The pyridyl protons and the vinyl protons of the conjugated polymer backbone are demonstrated in ^{1}H NMR in the range from 3.7-4.8 ppm[150] to 5.5-10.8 ppm.[151] The poly(2-ethynylypridine) prepared using transition-metal catalyst exhibits ^{13}C NMR spectrum with three characteristic maxima (**Figure 9**).[57] The signals in the region 118-126 ppm are assigned to C_3 and C_5 carbon atoms, signal at 136 ppm is assigned to the C_4 carbon atoms and signal at 148 ppm is assigned to the C_6 carbon atoms of pyridine ring. The signals at 111 ppm and 126 ppm are assigned to the $C_{\beta\text{-trans}}$ and to the $C_{\beta\text{-cis}}$ carbon atoms. The broad band from 151 to 159 ppm is assigned to the $C_{2\text{-cis}}$, $C_{2\text{-trans}}$, $C_{\alpha\text{-cis}}$ and $C_{\alpha\text{-trans}}$.

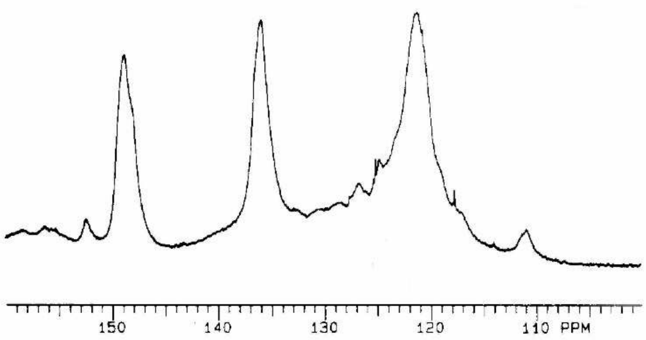


Figure 9 ^{13}C NMR spectra of poly(2-ethynylpyridine) prepared by using transition-metal catalyst. (Leben, Koller; 1994)[57]

However, the structure of the ionic polymers prepared via spontaneous quaternization polymerization is not controlled by any catalyst and thus the significantly broadened and barely resolved NMR spectra are obtained. ^{13}C NMR spectra of ionic polymers showed the multiple peaks at the region of 105-157 ppm, which originate from the aromatic carbons of pyridyl moiety and the vinyl carbons of conjugated polymer backbone. Generally, due to the nonuniform structure of main chain, the signals in NMR spectra were fairly broadened and the detailed assignment was complicated.

Absorption spectroscopy (UV/vis)

UV/vis spectroscopy represents an important method for the characterization of π-conjugated system of polyacetylene mains chains. The absorption spectra of monomers used in the quaternization reaction exhibited absorption edge at around 380 nm. Contrary, the absorption spectra of prepared ionic polymers showed a continuous absorption with absorption edge up to 750 nm originating from the π-π* transition of the π-conjugated polymer backbone. The absorption in the region from 300 nm to 400 nm is usually ascribed to the charge-transfer (CT) absorption of the ion pairs composed of *N*-alkylpyridiniumyl/halide anion.[152] The character of absorption spectra of prepared polymers was influenced by (i) the counter ion and (ii) the *N*-substituent of pyridinium and its ability of interfere with the conjugation of the polymer main chain. The nature of quaternizing agent may also influence the backbone twits (dihedral angles) due to steric factors leading to reduced conjugation.

Photoluminescence (emission) spectroscopy

The photoluminescence spectra of reported ionic polyacetylenes showed broad low-energy band with maxima from 454 to 720 nm. This phenomenon was explained mainly as an intramolecular excimer formation involving the pendant pyridine rings. The stacking between neighboring aromatic side groups and contrary the backbone twist due to steric factors plays also important role in emission properties.[100] Pendant groups stacking seems to be large due to a strong electrostatic interaction of each counterion with two adjacent pyridinium rings.[98] Moreover, the photoluminescence spectra may be affected by main chain conjugation length, which may be also influenced by ionic strength of pyridinium ion because of interaction between pyridinium ion and conjugated polyene.[153]

X-Ray diffraction (XRD)

The morphology of prepared ionic polymers was also investigated by X-Ray diffraction analysis. Because the peaks in the diffraction pattern were broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) was greater than 0.35, it was concluded that prepared ionic polymers are amorphous.[133] This conclusion is also in good agreement with the polymerization mechanism: since the polymerization proceeds without any catalyst that may control the configuration and conformation structure of polyacetylene main chain, the resulting polymer are highly non-uniform.

Cyclic voltammetry (CV)

In order to investigate the electrochemical properties of prepared ionic polymers, the cyclic voltammetry experiments were performed and the oxidation and reduction potentials were determined. Cyclic voltammograms showed that the materials exhibit stable redox process. It was assumed that electrode kinetic, the electrochemical redox reaction on the electrode is controlled by either the electron transfer, or the reactant diffusion process. From the data obtained it was concluded that kinetics of the redox process is very close to a diffusion process.[133,138]

Thermogravimetric analysis (TGA)

The thermal stability of prepared polymers was investigated by the TGA analysis. The thermal decomposition was measured mainly under nitrogen atmosphere with a step 10 °C/min. The polymers weight loss under 100 °C was mainly assigned to the residual moisture in the sample. The decomposition of polymers starts at around 200-300 °C by releasing of quaternizing agents followed by the decomposition of main chain at temperature range 400-800 °C.[140] The thermal cross-linking of reactive side pendants of acetylenic main chain may also increase the thermal stability of materials (residual mass up to 40%) at higher temperatures (700-800 °C).[133,138,141]

Differential Scanning Calorimetry (DSC)

The thermal processes were also investigated with the DSC. However, the results were not discussed in details.[131,140,154]

Surface enhanced Raman spectroscopy (SERS)

The Raman spectroscopy analysis of prepared ionic π-conjugated polyacetylene type polymers is complicated due to their luminescence which is strong enough to preclude the use of conventional techniques. This problem was circumvented by Surface Enhanced Raman Spectroscopy (SERS) approach using colloidal silver particles.[155] The SERS characterization of poly(2-pyridinium hydrochloride-2-pyridylacetylene) and poly(*N*-ethyl-2-ethynylpyridinium iodide) colloidal system with silver nanoparticles was performed, which allowed an improvement in the band assignment of vibrational spectra of prepared ionic polymers.[103,156]

1.3.3 The molecular mass characterization

The determination of molar mass of ionic polymers is complicated due to the ionic nature of polymers, which causes strong interaction of the prepared polymers with standard GPC columns, which could bias obtained results. Moreover, the strongly colored solution of reported ionic materials limits the traditional light scattering characterization method. Thus the alternative approaches were applied.

Estimation of molar-mass characteristics of prepared ionic polymers using Lewis-Calvin equation

In 1939 Lewis and Calvin proposed the correlation between the number of conjugated -CH=CH- bonds, *n*, in molecule and its absorption spectra.[97] The absorption spectra of a series of diphenylpolyenes containing *n* conjugated -CH=CH- bonds ($n = 1\text{-}7$) were measured in mixture ether/alcohol (diethyl ether/ethanol, author's note) at -196 °C. The absorption maxima λ_{max} were better resolved under these conditions compared to the absorption spectra measured at room temperature, which facilitated the λ_{max} determination.

The correlation between n and λ_{max} was described by the equation:

$$\lambda_{max}^2 = kn$$

where λ_{max}^2 is a square of wavelength of absorption maxima, k is coefficient and n is the number of -CH=CH- bonds in conjugation. From the known n of a series of diphenylpolyenes the values k ranging from 15 000 to 22 000 were calculated.[97] This equation was applied on a series of conjugated polyenes with defined n of -CH=CH- bonds in conjugation ($n = 3$-10). The n-values have been plotted against the squares of the wavelength for each of the maxima. The straight lines were obtained as far as $n = 7$ and only slight deviation occurs for $n = 8$-10. The Lewis-Calvin equation was therefore fitted fairly well.[96]

According to the Lewis-Calvin equation, Blumstein proposed the conjugation length from $n = 6$[157] up to $n = 16$[98-100,104] using the k value 17 532. The λ_{max} values plotted versus number of conjugated C=C bond (n) are shown in **Figure 10**.[99] However, the absorption spectra of prepared ionic polymer exhibited generally nearly continuous absorption from 300-750 nm with barely distinguished maxima. Thus, the identification of maxima and calculation of the number of -CH=CH- bonds in conjugation is complicated and could be partly biased. Nevertheless, the main chain effective conjugation length may not refer to the length of polymer chain directly. We can speculate that prepared polymers contain more than one conjugated sequences in the polyacetylene chain.

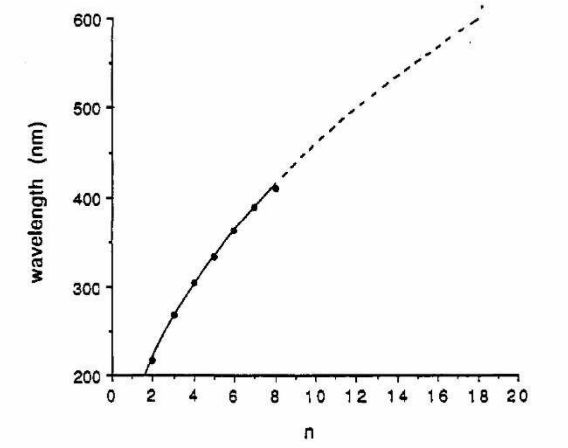


Figure 10 Plot of UV/vis absorption maxima versus the number of conjugated bonds n for unsubstituted polyenes. (Subramanyam, Blumstein; 1991)[99]

Viscosimetry

The intrinsic viscosity $[\eta]$ of a polymer in a certain solvent can be correlated with the molar mass M:[158]

$$[\eta] = K_{[\eta]} M^a$$

This dependence is also referred as the $[\eta]$-M-relationship or the Kuhn-Mark-Houwink-Sakurada equation (KMHS-equation) where $K_{[\eta]}$ and a are constants for a given polymer under selected conditions. The exponent a is related to the solvent quality and therefore for the solution structure of the dissolved polymer. The knowledge of $K_{[\eta]}$ and a allow the easy determination of the molar mass of a polymer by measuring the intrinsic viscosity. This method provides the viscosity average molar mass M_η, which lie between the number average molar mass M_n and the mass average molar mass M_w. The intrinsic viscosity $[\eta]$ is defined as:

$$[\eta] = \lim_{c \to 0}(\eta_{rel} / c)$$

where η_{rel} is relative viscosity and c is the concentration of polymer limiting to zero. However, the determination of constants $K_{[\eta]}$ and a is complicated and mentioned constants are typically not known. This fact limits the application of KMHS equation on the prepared ionic polymers and consequently determining the M_η values.

Thus, the ionic polymers reported in the literature are characterized mostly by the inherent viscosity defined as:

$$\eta_{inh} = (\ln \eta_{rel})/c$$

where ln η_{rel} is the natural logarithm of the relative viscosity and c is the mass concentration of the polymer in g/dL. Thus, the inherent viscosity is given in dL/g. The relative viscosity η_{rel} is defined as:

$$\eta_{rel} = \eta/\eta_0$$

where η is the viscosity of polymer solution and η_0 is the viscosity of solvent.[158]

Generally, the inherent viscosity measurements were performed in polar solvent e.g. dimethyl sulfoxide or dimethylformamide at concentration of 0.5 g/dL. The inherent viscosity obtained for the reported ionic polymers ranged from 0.11 dL/g to 0.29 dL/g.[159,160] However, we can speculate about the relation between inherent viscosity and real polymer length (molecular mass of product) due to the phenomena as coil formation, which distort the viscosity of ionic polymer.

Vapor pressure osmometry

Molecular weight was also determined by vapor pressure osmometry in chloroform at 30 °C or in THF at 45 °C. Calibration was done with low molecular weight polystyrene (M_n = 2000).[98,157]

Gel permeation chromatography – multi angle laser light scattering (GPC-MALLS)

GPC-MALLS system was used to determine the molecular mass of the polymer prepared from the polymerization of pyridine with propargyl bromide. GPC with two PL mix-D columns was equipped with four detectors (UV/vis, viscosity, refraction index, and multi angle laser light scattering), using DMF with LiBr (2 mg/ml) as eluent at a flow rate of 1ml/min at 80 °C.[161] However, as already mentioned, the ionic nature of prepared polymers may bias the mechanism of GPC method, and the results may be seen only as apparent.

1.3.4 Structure of ionic polyacetylene main chain and molecular dynamic simulations

Since the conformation of polymers prepared by spontaneous QP is not controlled by any catalyst, we can speculate about the structure of formed materials. The conformation of monosubstituted ionic polyacetylenes was calculated by the means of molecular dynamic simulation.[162] The poly[(4-*N*-methylpyridiniumyl)acetylene bromide] and its uncharged counterpart poly(4-pyridyl)acetylene, both containing 10 monomeric units, were investigated by this method. The charge distribution of the lone monomer unit was calculated and changed arbitrary according to model structure of polymer. The results shows that the preferred chain conformations of monosubstituted polyacetylene with ionic side groups that are associated with counterions were planar and highly extended, which is in complete contrast to uncharged, monosubstituted polyacetylene. Moreover, the fact that the charged polymer model displayed a long-wavelength fluorescence band in its emission spectrum due to intramolecular excimer formation between the pendant aromatic rings is indicative that the *trans-transoid* conformation is favored over the *cis-transoid* and *trans-cisoid* conformers in these ionic polyacetylene. The charged side groups with the associated counterions in the ionic polyacetylenes play a significant role in the stabilizing an extended, planar backbone in such system. In this case, the electrostatic attractive interactions override the steric repulsion interaction between side groups. Contrary, the repulsion of bulky, uncharged substituent may cause the formation of non-planar structure of uncharged system. However, the model systems do not consider the defects in quaternization of side groups, which may cause serious conformation alteration. Therefore, the results of the molecular dynamic simulation may significantly differ from the native structure of obtained materials. It was concluded that many factors (e.g. the position of N heteroatom in the pyridyl group, the nature of QA, the degree of quaternization, etc.) play role in the final polymer structure.

This is partly confirmed by the ^{13}C NMR spectra of poly(2-ethynylpyridine hydrochloride-*co*-2´-ethynylpyridine) (**PNo. 19**) and poly[(2-*N*-octylpyridinium)acetylene bromide] (**PNo. 17**).[163] First mentioned polymer was prepared by the spontaneous polymerization of 2EP activated with concentrated hydrochloric acid (mechanism see in **Scheme 10**) in bulk (without solvent). In the activation step a complex (dimer) is formed and the authors assumed that complex is locked in the *cis* configuration geometry which sustain during the polymerization process and polymer with highly *cis-cisod* conformation is formed. The two peaks at 149,5 and 136,9 ppm assigned to the main chain carbon of *cis* geometry (according to Masuda et al.[20]) were well manifested in the ^{13}C NMR spectra of this product. On the contrary, no such signals were manifested in ^{13}C NMR spectra of poly[(2-*N*-octylpyridinium)acetylene bromide] prepared by the spontaneous quaternization polymerization of 2EP activated with 1-octylbromide and therefore, the random geometry of product is assumed. The discussion about the polymer main chain configuration was also reported for poly[(2-*N*-bromopyridiniumy1)acetylene bromide] prepared from 2EP activated with Br_2 (**PNo. 10**). However, the evaluation of the *cis* and *trans* content of backbone from C=C stretching bands for the presented polymer was complicated by the fact that the fairly intense band around 1015-1019 cm^{-1} (*trans* C=C) could also arise from symmetrical ring vibration of the side group pyridine rings upon complexation with bromine. The 740 cm^{-1} band (*cis* C=C) is, however, very weak, implying very small *cis* content.[100]

The atomic charge and dipole contribution using molecular orbital theory were calculated for 2EP. The authors reported that the nitrogen with atom electron density 5.1339 on pyridyl ring increases the electron density of β-carbon of ethynyl up to 4.1688.[57]

1.3.5 Special quaternization reactions

Ionic polyacetylene type polymer networks via one step quaternization polymerization

The intention to synthesize the ionic interpenetrating polymer network containing π-conjugated structure led to the modification of the quaternization polymerization process. The polymer network could be obtained when functionality of monomer and/or QA is enhanced. When 1,2-bis(4-pyridyl)acetylene was reacted with nonena-1,9-bis(methanesulfonate) (**PNo. 75**) the insoluble cross-linked product was obtained. The reaction of 1,4-bis(4-pyridyl)butadiyne with 1-bromododecane (**PNo. 9**) also resulted in a insoluble, highly cross-linked polymer.[95,99] The polymerization of 2EP activated with mixture of 1-bromobutane and 1,4-dibromobutane (**PNo. 21**) resulted also into insoluble network. The cross-linking of product was caused by the bifunctional QA, 1,4-dibromobutane, which can simultaneously activate two monomers. The extensive conjugation was revealed by the absorption extending to the visible range in this case.[149] Polymer networks were also prepared via the polymerization of 2EP and 4EP activated with a series of bis(bromomethyl)arenes reported by our group (**PNo. 77-83**). Obtained ionic polymer networks were investigated in a view of photoluminescence behavior and CO_2 capture capacity.[145]

Modification of counterion (ion-exchange reactions)

The various ionic polymers were prepared by the one-step quaternization polymerization, however, the properties of original polymer could be modified by the ion exchange of negatively charged moiety compensating positively charged pyridinium pendant. Thus, the new ionic polymers were prepared via the ion exchange reaction of former polymers. The ion exchange reactions were carried out mainly in methanol under the mild conditions. Poly(2-ethynylpyridinium bromide) with propargyl side chain (PEP-Br) prepared by the direct reaction of 2EP with propargyl bromide was used as a starting material for the ion exchange reaction with sodium tetraphenylborate ($NaBPh_4$) (**PNo. 34**), sodium perchlorate ($NaClO_4$) (**PNo. 35**) and sodium azide (NaN_3) (**PNo. 36**). The prepared corresponding ionic polymers were found to be mostly insoluble in water and methanol, whereas the original polymer was completely soluble in above-mentioned solvents. The counter anions, moreover, influence the UV/vis and photoluminescence properties.[164] The poly(*N*-methylpyridinium iodide) was treated with sodium tetraphenylborate to obtain poly(*N*-methylpyridinium tetraphenylborate) (**PNo. 28**).[165,166] Sodium tetraphenylborate was also utilized for the preparation of corresponding ionic polymers from poly[2-ethynyl-*N*-(*p*-hydroxyphenylethyl)pyridinium bromide] (**PNo. 54**),[167] poly[*N*-(6-azidohexyl)-2-ethynylpyridinium iodide] (**PNo. 55**)[136] or poly(*N*-benzoyl-2-ethynylpyridinium chloride) (**PNo. 62**).[168]

As a modification of counter anion could be also considered the deprotonation of ionic polymer poly(2-pyridinium hydrochloride-2-pyridylacetylene) by the KOH (**PNo. 20**). The deprotonated form exhibited lower conjugation length, compared to the protonated form. Reduced conjugation presumably originated from backbone twist introduced upon deprotonation and was not due to a change in the pyridinium pendent groups. The backbone twist may be attributed to the absence of electrostatic interactions between the counterions and the pyridinium rings that were present in the protonated form and thereby the steric interaction between the side groups becoming a dominating factor.[98]

Two synthetic pathways to almost identical polymers

The experiment, where poly(*N*-octadecyl-2-ethnylpyridinium bromide) was synthesized via two different approaches was reported in article.[157] At first, 2EP was polymerized via one step quaternization polymerization activated with 1-bromooctadecane (**PNo. 22**), second approach include thermal polymerization of 2EP into poly(2-ethynylpyridine) which was further modified by the postpolymerization quaternization with 1-bromooctadecane (**PNo. 23**). Polymer prepared vie one step QP was assumed to be fully quaternized, on the contrary, the polymer prepared via the modification of already existing polymer was assumed to be quaternized from 25 to 30% and therefore was considered as a random copolymer of 2-ethynylpyridine and *N*-octadecyl-2-ethynylpyridinium bromide. The low degree of quaternization of the polymer was probably caused by sterical repulsion between the pyridine ring and the long alkyl chain of 1-bromododecane. However, the elemental analyses of both polymers were not published and we can only speculate about the real degree of quaternization.

In light of this discussion, we can speculate about probability of postpolymerization quaternization of polymer containing pyridine pendent groups. Frere and Gramain investigated the postpolymerization quaternization of poly(4-vinylpyridine).[169] According to the reported conclusions the steric effects play the most important role, which are influenced mainly by the quality of solvent and the volume of alkylating agent. Moreover, other factors as temperature or neighboring group effect (see *Modifying of the poly(vinylpyridine) – postpolymerization modification via quaternization reactions* in section *1.2.2*) are involved in the process. The authors proposed the coil formation which may complicate or retard the quaternization postpolymerization process. The coil formation was also supported by the changes of viscosity during the quaternization reaction of 4-vinylpyridine which passes through maximum at reaction extents 15-30% and then decreases to lower values.[170] Despite the fact that backbone of poly(ethynylpyridine)s is more rigid compared the poly(vinylpyridine)s, the similar behaviors could be expected concerning the sterical effects.

To conclude the postpolymerization quaternization, two models could be assumed: (i) the quaternization of not fully quaternized poly(*N*-alkylethynylpyridine halide)s and (ii) quaternization of uncharged poly(ethynylpyridine)s. The first modification is not probable, due to the sterical effects and coil formation of polymer chain. In the second case, the quaternization of already prepared polymers (uncharged) is broadly reported in the literature, but it is not the topic of presented thesis. However, here we provide few examples of postpolymerization quaternizations of pyridine and ethynylpyridine containing compounds. A series of pyridine/pyridinium containing monomers, oligomers and polymers was quaternized with methyl iodide or methyl triflate to improve the delocalization of π-electrons along the polymer backbone.[171] Similarly, poly(3-ethynylpyridine) was quaternized with methyl iodide (**PNo. 73**) and methyl bromide (**PNo. 74**) to improve the solubility and processability of former polymer.[59]

1.3.6 Associated reactions

Polymerization of propargyl halides via activation of triple bond

The reaction of pyridine and propargyl tosylate in the methanol did not give any polymeric products, but gave only propargylpyridinium tosylate. This means that the propargyl functional group does not undergo polymerization reaction by the simple attack of pyridine.[160] Similarly, the reaction of propargyl chlorides and bromides with pyridines and substituted pyridines gave no polymeric products, but only the corresponding pyridinium salts were isolated.[99] Consequently, it was presumed that the polymerization occurred inefficiently. However, Chen et al. reported the reaction of propargyl bromide with pyridine in methanol (60 °C, 100 hours) that gives the high molecular-mass polymer according to the GPC. The product was characterized by means of elemental analysis, ^{1}H NMR, FT-IR, GPC-MALLS and the fluorescent spectroscopy.[161] The reaction of propargyl bromide with quinoline and acridine (DMF, 60 °C, 100 hours) led also to the ionic polymers containing conjugated main chain.[172]

Thin layer film

The thin layers using Langmuir-Blodgett and layer-by-layer techniques were prepared from the amphiphilic ionic polyacetylene, poly(*N*-octadecyl-2-ethynylpyridinium bromide). The IR studies indicate that the transferred polymer multilayers are organized with the conjugated backbone chains oriented parallel to the substrate. The thickness measurements suggest that the polyacetylene backbones are sandwiched between layers of interlinked octadecyl groups.[173]

Star-shape copolymers

The quaternization polymerization approach was applied also on the star shape architecture copolymers preparation, in which the shell was formed by rigid conductive ionic polyacetylene and the dendrimer core by the spheroidal, aliphatic poly(amidoamine). The polymerization of 2-ethynylpyridinium triflate was initiated with amino group on poly(amidoamine) on a surface of the core unit, therefore the ionic polyacetylene chains emanate from the core. The authors proposed that ionic arms contained from 1 to 16 monomeric units.[40]

Preparation of nanocomposites

The spontaneous polymerization of 2EP induced by Ca^{2+}-montmorillonite (Ca-MMT) in benzene resulted in nanocomposite of Ca-MMT with varying amounts of intercalated 2EPs. In this case the Ca-MMT did not act only as host matrix for the interaction of polymer but also as a surface initiating agent for the formation of ionic conjugated polyacetylene.[174] The alternative approach of preparation nanocomposite from 2EP was described in articles.[175-177] Ionic π-conjugated polyacetylene prepared from 2EP activated with hydrochloric acid and exfoliated aluminosilicate nanoplatelets (saponite) were deposited through electrostatic layer-by-layer deposition technique. The same approach was also used for preparation of poly(*N*-R-2-ethnylypyridinium bromide) (R = hexyl, dodecyl, octadecyl) and saponite multilayer nanocomposite.[178,179] Mentioned multilayer nanocomposite materials were investigated with the purpose of application as an hydrophobic membranes. The resulting hydrophobic barrier efficiently blocked transport of the water molecules and hence showed substantially high barrier properties.[180]

The surface initiated "grafting-from" method was also applied on the preparation of the water-soluble single-walled nanotubes (SWNT). SWNT were functionalized with 4-(2-aminoethyl) pyridine, which act as an initiator for the polymerization of *N*-methyl-2-ethylpyridinium triflate into ionic conjugated polyacetylene chain.[181] The same approach was used for the preparation of multi-walled carbon nanotubes (MWCNTs) covalently functionalized with poly(2-ethynylpyridine).[182] Graphene nanosheets functionalized with ionic polymers were also prepared by catalyst free quaternization polymerization of 2EP activated with thionyl chloride moiety bounded to the graphene.[183]

Surface brushes

The concept of self-templating surface-initiated polymerization for the synthesis of ionic conjugated polymer brushes serving as surface-grafted molecular wires. A newly synthesized bifunctional monomer was used in the controlled photoiniferter-mediated polymerization resulting in the formation of multimonomer surface-grafted chains with polymerizable ethynylpyridine pendant groups (Iniferter is a chemical compound that simultaneously acts as initiator, transfer agent, and termination agent, hence the name ini-fer-ter, author´s note). These groups aligned along the template chains were subsequently polymerized using catalyst-free quaternization polymerization activated with ethyl iodide, leading to charged ladder-like brushes with conjugated poly(*N*-ethyl-2-ethynylpyridinium iodide) chains.[184]

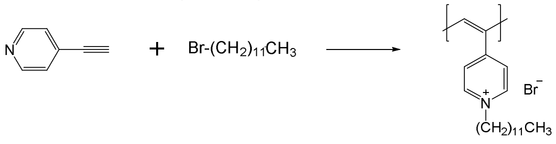
Complexation with metals

A water-soluble ionic polyacetylene, poly(2-ethynyl-*N*-pentylpyridinium iodide) (PEPPI), was prepared by the quaternization polymerization of 2EP activated with 1-iodopentane (**PNo. 45**).[143] PEPPI-iron(III) chloride complex was prepared by the reaction of PEPPI and iron(III) chloride in DMF and its properties were characterized. However, the closer discussion about the modes of Fe coordination to the polymer was missing.[185]

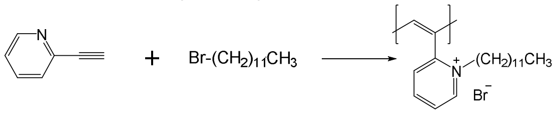
Figure 11 Quaternization polymerization chart. The quaternization polymerizations reported in the literature. Proposed structure – do not reflect real composition and structure. Reactions conditions (Rc:) are taken from the original articles. If more conditions provided – more reactions with the same reactants were performed. **PNo.** – Polymer number used in this work; For reference number of the original article see **Table 1**.

Linear polymers

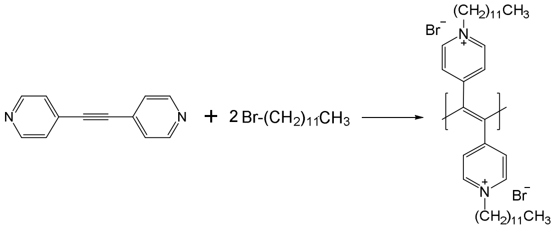
PNo. 1
Rc: acetonitrile, 50 °C, 72 hours.



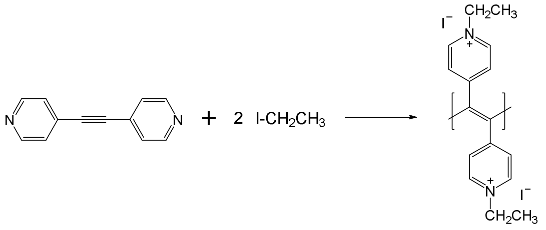
PNo. 2
Rc: acetonitrile, 50 °C, 72 hours.



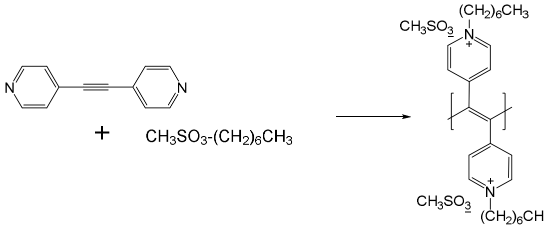
PNo. 3
Rc: acetonitrile, 50 °C, 72 hours.



PNo. 4
Rc: acetonitrile, 50 °C, 72 hours.

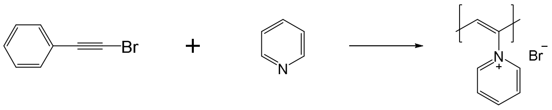


PNo. 5
Rc: acetonitrile, 50 °C, 72 hours.

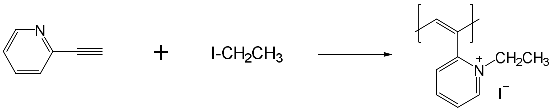


PNo. 6
See Polymer networks

PNo. 7
Rc: acetonitrile, 50 °C, 72 hours.



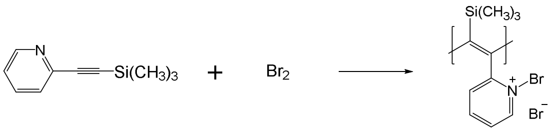
PNo. 8
Rc: acetonitrile, 50 °C, 72 hours.



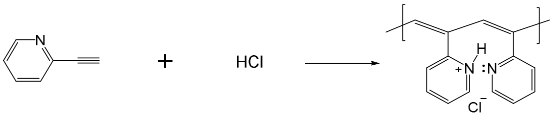
PNo. 9
See Polymer networks

PNo. 10
Rc: bulk, 0 °C.

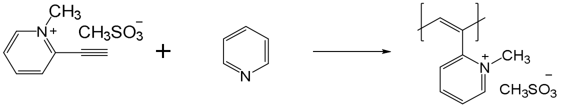
PNo. 11
Rc: bulk, 0 °C.



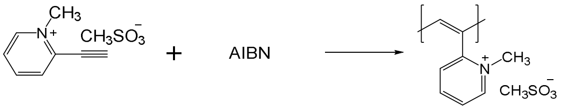
PNo. 12
Rc: bulk, 0 °C.



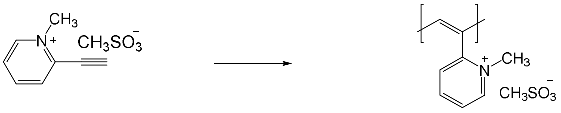
PNo. 13
Rc: acetonitrile (DMSO), 20 ℃, 24 hours.



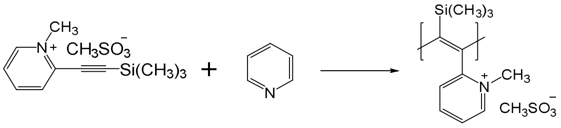
PNo. 14
Rc: 70 ℃, 15 hours.



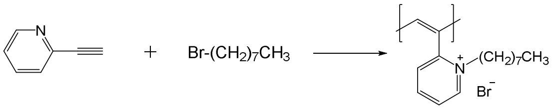
PNo. 15
Rc: 170 ℃, 1 hour.



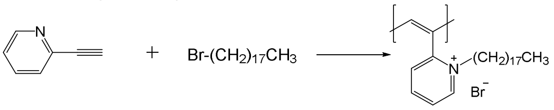
PNo. 16
Rc: acetonitrile (DMSO), 20 ℃, 24 hours.



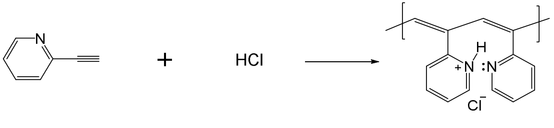
PNo. 17
Rc: bulk, 60 ℃, 72 hours.



PNo. 18
Rc: bulk, 60 ℃, 72 hours.



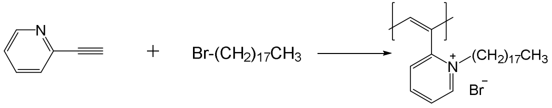
PNo. 19
Rc: ice cooling.



PNo. 20
See Postpolymerization modifications

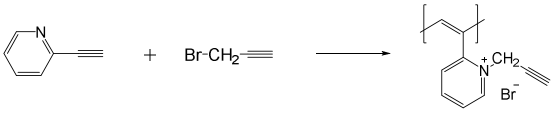
PNo. 21
See Polymer networks

PNo. 22
Rc: THF (toluen, bulk), 80 ℃, 120 hours.

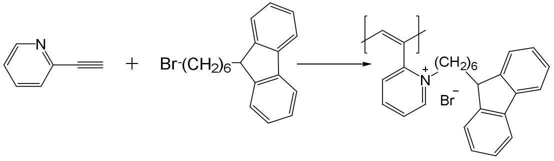


PNo. 23
See Postpolymerization modifications

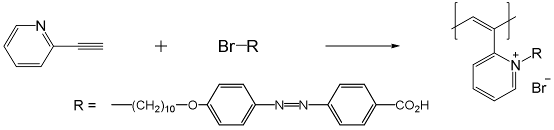
PNo. 24
Rc: methanol, 24 hours.



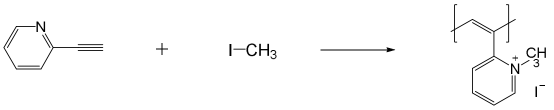
PNo. 25
Rc: DMF (DSMO, nitrobenzene), 90 ℃, 24 hours. (5 reactions)



PNo. 26
Rc: DMF (NMP, DMSO), 120 ℃. (series of reactions)

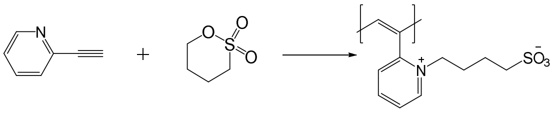


PNo. 27
Rc: methanol, 70 ℃.



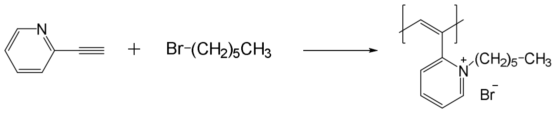
PNo. 28
See Postpolymerization modifications

PNo. 29
Rc: DMF, 130 ℃, 24 hours.



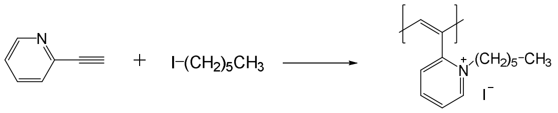
PNo. 30

Rc: methanol, 80 ℃, 24 hours.



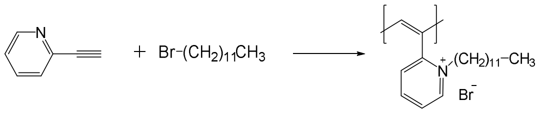
PNo. 31

Rc: methanol, 80 ℃, 24 hours.



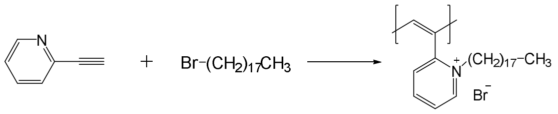
PNo. 32

Rc: DMF, 80 ℃, 24 hours.



PNo. 33

Rc: DMF, 80 ℃, 24 hours.



PNo. 34

See Postpolymerization modifications

PNo. 35

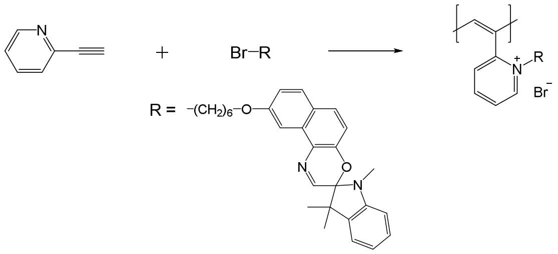
See Postpolymerization modifications

PNo. 36

See Postpolymerization modifications

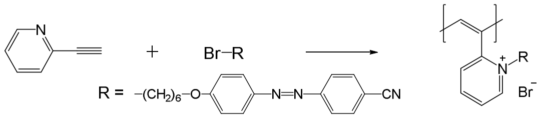
PNo. 37

Rc: DMF, 120 ℃, 24 hours.



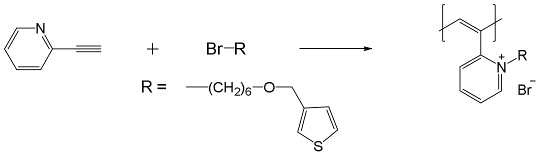
PNo. 38

Rc: DMF, 100 ℃, 24 hours.



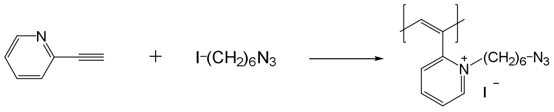
PNo. 39

Rc: DMF, 110 ℃, 24 hours.



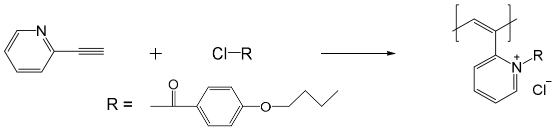
PNo. 40

Rc: methanol, 60 ℃, 24 hours.



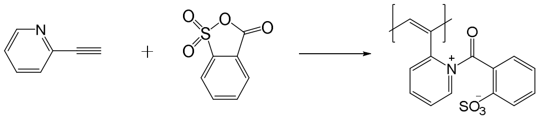
PNo. 41

Rc: DMF, 100 ℃, 24 hours.



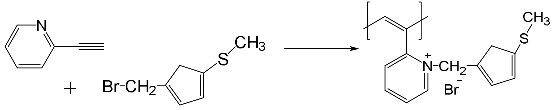
PNo. 42

Rc: DMF, 85 ℃, 24 hours.



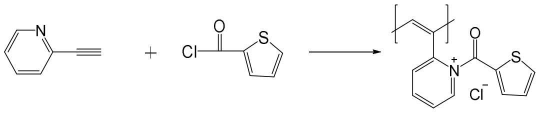
PNo. 43

Rc: DMF (DMSO, pyridine, NMP), 80 ℃ (60 ℃), 24 hours.



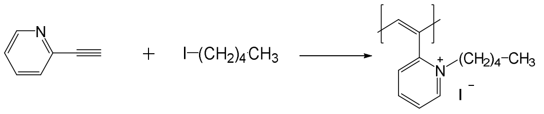
PNo. 44

Rc: DMF, 60 ℃, 24 hours.

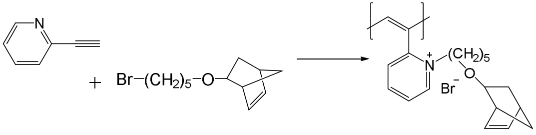


PNo. 45

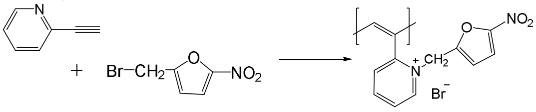
Rc: DMF, 80 ℃, 24 hours.



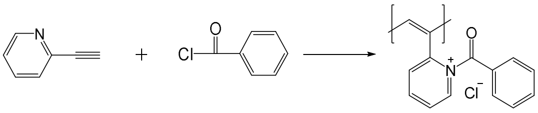
PNo. 46
Rc: DMF (DMSO, NMP), 80 ℃, 24 hours.



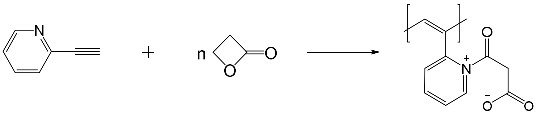
PNo. 47
Rc: DMF (DMSO, NMP), 65 ℃ (80 ℃, 90 ℃), 24 hours.



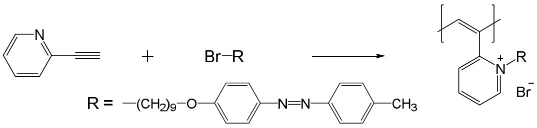
PNo. 48
Rc: DMF (DMSO, NMP, methanol), 80 ℃, 24 hours.



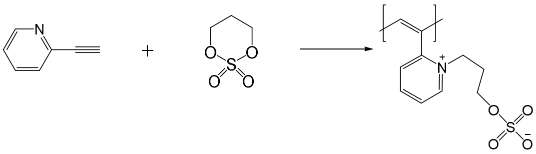
PNo. 49
Rc: DMF, 70 ℃, 24 hours.



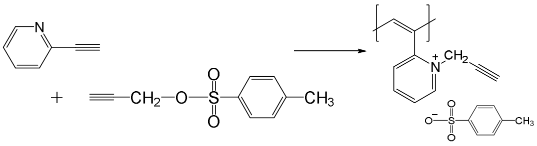
PNo.50
Rc: DMF, 100 ℃ 24, hours.



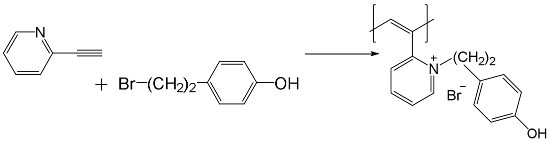
PNo. 51
Rc: DMF, 70 ℃, 24 hours.



PNo. 52
Rc: methanol, 24 hours.



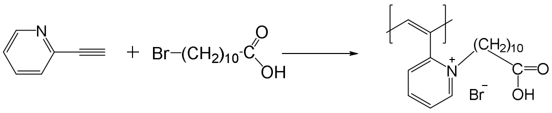
PNo. 53
Rc: DMF, 80 ℃, 24 hours.



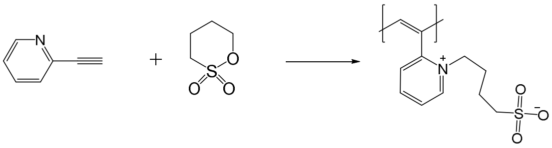
PNo. 54
See Postpolymerization modifications

PNo. 55
See Postpolymerization modifications

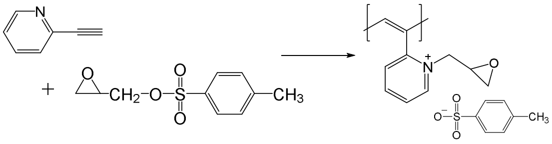
PNo. 56
Rc: DMF, 100 ℃, 24 hours.



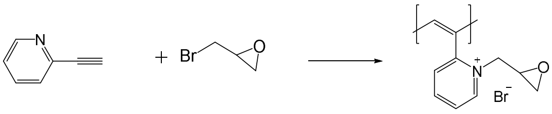
PNo. 57
Rc: DMF, 130 ℃, 24 hours.



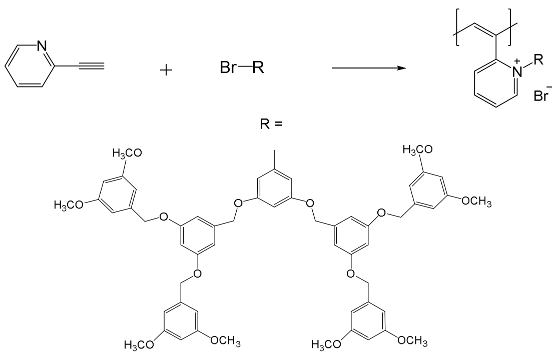
PNo. 58
Rc: methanol, 75 ℃, 24 hours.



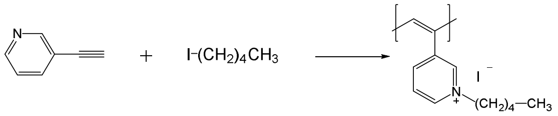
PNo. 59
Rc: methanol, 75 ℃, 24 hours.



PNo. 60
Rc: DMF, 60 ℃, 24 hours.

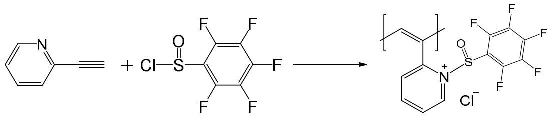


PNo. 61
Rc: DMF, 80 ℃, 24 hours.

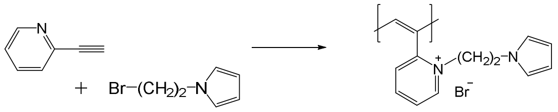


PNo. 62
See Postpolymerization modifications

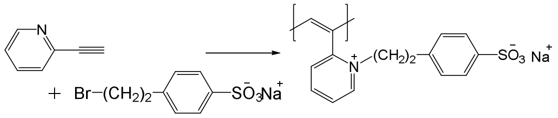
PNo. 63
Rc: DMF, 80 ℃, 24 hours.



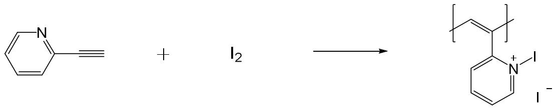
PNo. 64
Rc: DMF, 60 ℃, 24 hours.



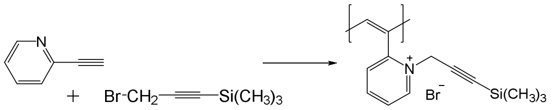
PNo. 65
Rc: DMF, 90 ℃, 24 hours.



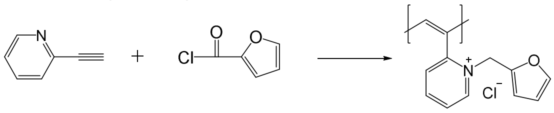
PNo. 66
Rc: DMF, 80 ℃, 24 hours.



PNo. 67
Rc: DMF, 70 ℃, 24 hours.

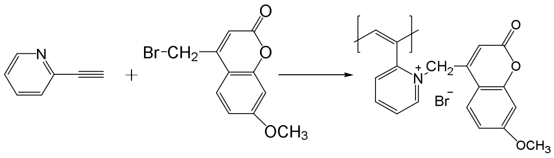


PNo. 68
Rc: DMF, 60 ℃, 24 hours.

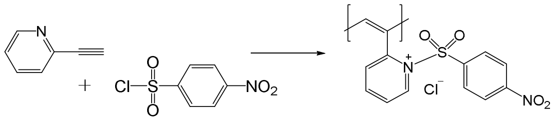


PNo. 69
Rc: methanol, 60 ℃, 24 hours.

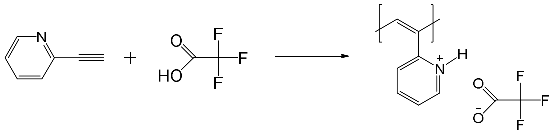
PNo. 70
Rc: DMF, 80 ℃, 24 hours.



PNo. 71
Rc: DMF, 80 ℃, 24 hours.



PNo. 72
Rc: DMF, 0-65 ℃, 3 hours.



PNo. 73
See Postpolymerization modifications

PNo. 74
See Postpolymerization modifications

PNo. 75
See Polymer networks

PNo. 76
See Polymer networks

PNo. 77
See Polymer networks

PNo. 78
See Polymer networks

PNo. 79
See Polymer networks

PNo. 80
See Polymer networks

PNo. 81
See Polymer networks

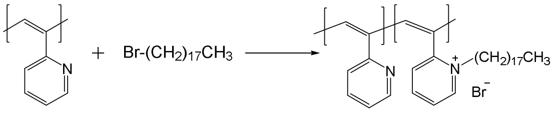
PNo. 82
See Polymer networks

PNo. 83
See Polymer networks

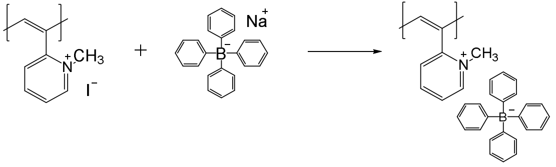
Postpolymerization modifications

PNo. 20
Rc: water, KOH, 12 hours.

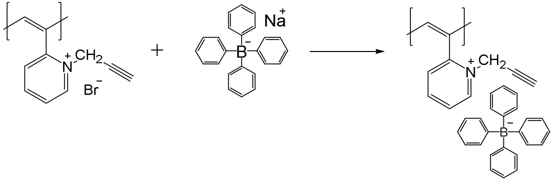
PNo. 23
Rc: THF + toluen, 80 ℃, 150 hours.



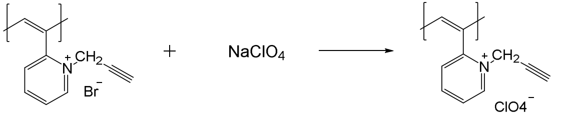
PNo. 28
Rc: methanol. Ion exchange reaction.



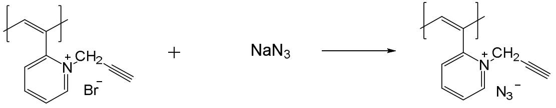
PNo. 34
Rc: methanol. Ion exchange reaction.



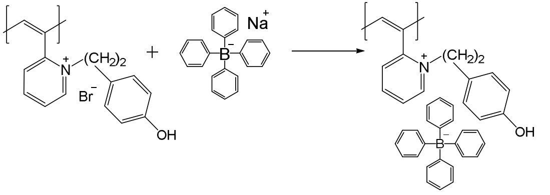
PNo. 35
Rc: methanol. Ion exchange reaction.



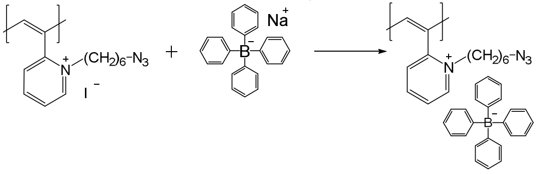
PNo. 36
Rc: methanol. Ion exchange reaction.



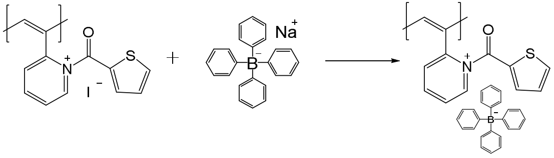
PNo. 54
Rc: methanol. Ion exchange reaction.



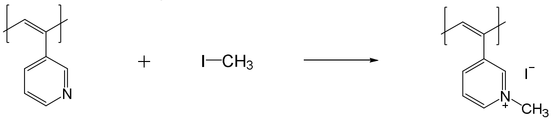
PNo. 55
Rc: methanol. Ion exchange reaction.



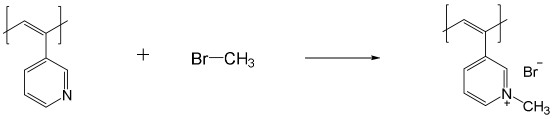
PNo. 62
Rc: methanol. Ion exchange reaction.



PNo. 73
Rc: methanol, 55 ℃.



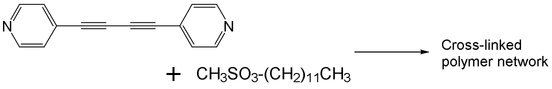
PNo. 74
Rc: methanol, 55 ℃.



Polymer networks

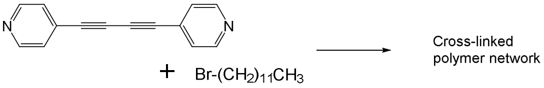
PNo. 6

Rc: acetonitrile, 50 ℃, 72 hours.



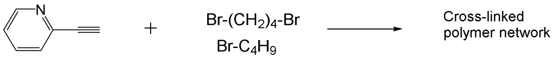
PNo. 9

Rc: acetonitrile, 50 ℃, 72 hours.



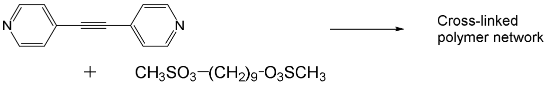
PNo. 21

Rc: toluen, 70 ℃, 72 hours.



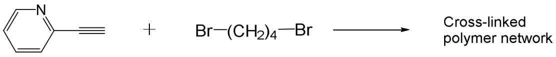
PNo. 75

Rc: acetonitrile, 50 ℃, 72 hours.



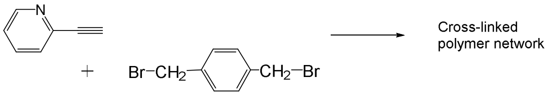
PNo. 76

Rc: toluen, 70 ℃, 72 hours.



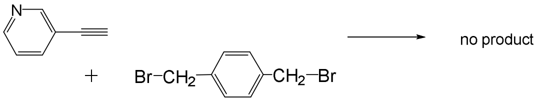
PNo. 77

Rc: DMF, 70 ℃, 72 hours.



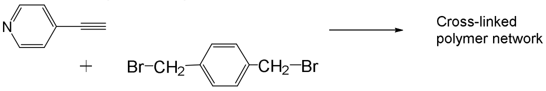
PNo. 78

Rc:DMF, 70 ℃, 72 hours.



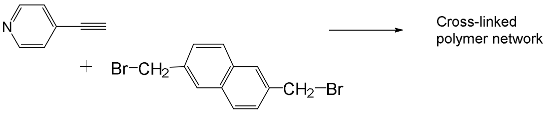
PNo. 79

Rc: DMF, 70 ℃, 72 hours.



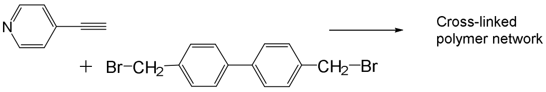
PNo. 80

Rc: DMF, 70 ℃, 72 hours.



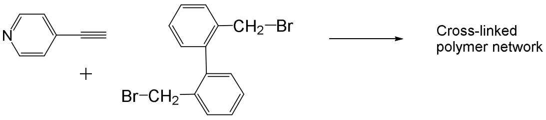
PNo. 81

Rc: DMF, 70 ℃, 72 hours.



PNo. 82

Rc: DMF, 70 ℃, 72 hours.



PNo. 83

Rc: DMF, 70 ℃, 72 hours.

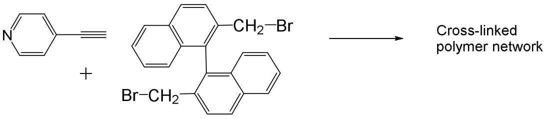


Table 1 The characteristics of polymers prepared via quaternization polymerization reported in the literature. **PNo.** – Polymer number used in this work (1-83) related to the Quaternization polymerization chart (**Figure 11**); Code – code of polymer used in the original article; Yield – yield of reported polymer (%); A_{max} – absorption maxima of reported polymer (nm), two values indicates two maxima, edge – the absorption edge (if determine); PL_{max} – photoluminescence maxima of reported polymer (nm), two values indicates two maxima; Inherent vis. – inherent viscosity (η_{inh}) of reported polymers (dL/g); Solubility – solvents which dissolve reported polymer under the standard conditions; Charact. – characterization method applied on the reported polymer; TGA – thermogravimetric analysis of reported polymer (the value in % determines the residual mass fraction at given temperature); Ref – reference number; n/a – data no available

PNo.	Code	Yield (%)	A_{max} (nm)	PL_{max} (nm)	Inherent vis. (dL/g)	Solubility	Charact.	TGA	Ref.
1	2	n/a	n/a	n/a	0.2-0.5	ethanol, THF, chloroform, acetone	IR, UV/vis, TGA, XRD, DSC	degraded at 250 °C, 20% at 800 °C	[95]
2	4	70	447	n/a	0.2-0.5	ethanol, THF, chloroform, acetone	IR, UV/vis	n/a	[95]
3	6a	94	450	n/a	0.2-0.5	ethanol, methanol, polar organic solvents	IR, UV/vis TGA, XRD, DSC	Deg. at 240 °C comp. deg. at 800°C	[95]
4	6b	n/a	488	n/a	0.2-0.5	water, methanol, ethanol	IR, UV/vis	n/a	[95]
5	6c	69	n/a	n/a	n/a	ethanol, methanol, polar organic solvents:	IR, UV/vis TGA	n/a	[95]
6	8	n/a	n/a	n/a	Cross-linked	Insoluble polymer network	IR, UV/vis	n/a	[95]
7	10	n/a	401	n/a	0.5	ethanol, THF, chloroform, acetone	IR, UV/vis	n/a	[95]
8	2p	53	447	n/a	0.20	ethanol, THF, chloroform, acetone	IR, UV/vis, XRD, DSC	n/a	[99]
9	4p	64	n/a	n/a	Cross-linked	Insoluble polymer network	n/a	n/a	[99]
10	VIp	92	470	560	0.1	alcohol and DMSO	IR, UV/vis, PL, TGA, XRD	degraded at 100 °C	[100]
11	VIIp	n/a	450	n/a	0.1	alcohol, DMSO, chloroform	IR, UV/vis, PL, TGA, XRD	degraded at 150 °C	[100]
12	VIIIp	n/a	530	550, 560	0.2	water, DMSO	IR, UV/vis, TGA, XRD	91% at 150 °C	[98]
13	8pa	n/a	598	n/a	0.25	n/a	IR, UV/vis, TGA, DSC	major loss at 360 °C	[104]
14	8pb	n/a	348	n/a	0.05	n/a	IR, UV/vis, TGA, DSC	major loss at 360 °C	[104]
15	8pc	n/a	900	n/a	0.05	n/a	IR, UV/vis, TGA, DSC	major loss at 360 °C	[104]

PNo.	Code	Yield (%)	A_{max} (nm)	PL_{max} (nm)	Inherent vis. (dL/g)	Solubility	Charact.	TGA	Ref.
16	9p	n/a	610	n/a	0.2	n/a	IR, UV/vis, TGA, DSC	major loss at 360 ℃	[104]
17	3	62	n/a	n/a	n/a	n/a	13C NMR, UV/vis	n/a	[163]
18	4	57	n/a	n/a	n/a	n/a	13C NMR, UV/vis	n/a	[163]
19	1	26	n/a	n/a	n/a	n/a	13C NMR, UV/vis	n/a	[163]
20	2	84	n/a	n/a	n/a	n/a	13C NMR, UV/vis	n/a	[163]
21	PB2EPB	80	n/a	n/a	Cross-linked	Insoluble polymer network	IR, UV/vis, DSC, SEM, TGA	stable up to 200 ℃	[149]
22	PNOEPB	87	480, edge 620	n/a	0.19	THF, chloroform, methanol (partly acetone, acetonitrile).	1H NMR, IR, UV/vis, TGA, DSC, osmometry	stable up to 230 ℃ (98%)	[157]
23	P2EPY-q-octa	n/a	480	n/a	0.13	THF, chloroform, methanol (partly water, acetone, acetonitrile)	1H NMR, IR, UV/vis, TGA, DSC	stable up to 230 ℃ (80%)	[157]
24	polymer	95	524	n/a	0.21	water, methanol, DMSO, DMF	1H NMR, UV/vis, IR	n/a	[126, 127, 186]
25	poly(CHEPB)	34 - 85	383, edge 750	495, 540	0.11-0.21	DMF, DMSO, nitrobenzene, formic acid (partly: water, acetone, methanol)	1H 13C NMR, IR, UV/vis, PL film and solution, TGA, DSC	99% at 200 ℃, 90% at 265 ℃, 22% at 800 ℃	[128]
26	polymer	53	371	454	0.10-0.14	DMF, DMSO, N,N-dimethylacetamide, formic acid	1H NMR, IR, UV/vis PL SS and film, XRD	n/a	[129]
27	PEMPI	78	487	568	n/a	DMF, DMSO, NMP water, methanol	1H NMR, IR, UV/vis, PL, XRD	n/a	[165]
28	PEMMTPB, PEMP-TPB	n/a	379, 486	576	n/a	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, XRD, CV, TGA, DSC	99% at 170 ℃, 94% at 200 ℃, 10% at 700 ℃	[165, 166]
29	PESPB	82	300, edge 770	530	0.26	water, methanol, DMF, DMSO, N,N-dimethylacetamide, or organic acids capable of hydrogen bonding with the sulfonate anion	1H 13C NMR, IR, UV/vis, PL, XRD, CV, dielectric constant	n/a	[130]

PNo.	Code	Yield (%)	A_{max} (nm)	PL_{max} (nm)	Inherent vis. (dL/g)	Solubility	Charact.	TGA	Ref.
30	PEHPB	86	300, 519	603	0.19	methanol, DMF, DMSO, N,N-dimethylacetamide, formic acid (partially soluble in ethanol and acetone)	1H 13C NMR, IR, UV/vis, PL, XRD, SEM, CV	n/a	[153]
31	PEHPI	95	300, 515	611	0.21	methanol, DMF, DMSO, N,N-dimethylacetamide, formic acid, (partially: ethanol and acetone)	1H 13C NMR, IR, UV/vis, PL, XRD, SEM, CV	n/a	[153]
32	polymer	85	516	600	0.14	DMF, DMSO, formic acid	1H 13C NMR, IR, UV/vis, CV, XRD	n/a	[150]
33	polymer	95	520	596	0.22	DMF, DMSO, formic acid	1H 13C NMR, IR, UV/vis, CV, XRD	n/a	[150], [187]
34	PEP-TPB	n/a	534	n/a	0.16-0.29	DMF and DMSO	1H NMR, IR, UV/vis, PL, XRD	n/a	[164]
35	PEP-PC	n/a	broad, edge 650	610	0.16-0.29	DMF and DMSO	1H NMR, IR, UV/vis, PL, XRD	n/a	[164]
36	PEP-AC	n/a	broad, edge 650	720	0.16-0.29	DMF and DMSO	1H NMR, IR, UV/vis, PL, XRD	n/a	[164]
37	PEHSPB	75	400, edge 800	515	0.15	DMF, DMSO,	1H 13C NMR, IR, UV/vis, PL, DSC	stable up to 230 ℃	[131]
38	PEPB	79	400, edge 800	542	0,13	DMF, DMSO,	1H 13C NMR, IR, UV/vis, PL, CV	95% at 178 ℃, 90% at 235 ℃	[132, 188]
39	PETHPB	86	469	510	0.2.	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, TGA, XRD, CV	degraded at 200 ℃, 31% at 800 ℃ (cross-linking at high T)	[133]
40	PAEPI	71	502, edge 790	596	0.11	methanol, water, DMF, DMSO, DMAc	1H 13C NMR, IR, UV/vis, TGA, DSC	97% at 100 ℃, 91% at 200 ℃, 22% at 700 ℃	[159]
41	PBEC	83	476	575, 630	0.18	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, CV	n/a	[189]
42	PEPBS	93	395, 533	545, 585	0.21	water, methanol, DMF, DMSO, N,N-dimethylacetamide, and organic acids capable of hydrogen bonding with the benzoyl sulfonate anion	1H 13C NMR, IR, UV/vis, PL, CV	n/a	[147]

PNo.	Code	Yield (%)	A$_{max}$ (nm)	PL$_{max}$ (nm)	Inherent vis. (dL/g)	Solubility	Charact.	TGA	Ref.
43	PEMBPB	99	446, edge 750	508	0.21	Pyridine, DMF, NMP, DMSO	1H 13C NMR, IR, UV/vis, PL, XRD, CV	under 100 ℃ moisture, 95% at 162 ℃, 90% at 241 ℃, 43% at 700 ℃	[138]
44	PETCPC	79	300, edge 700	573	0.21	methanol, pyridine, DMF, NMP, DMSO.	1H 13C NMR, IR, UV/vis, PL, TGA, XRD, CV	under 100 ℃ moisture, 95% at 200 ℃, 82% at 220 ℃, 29% at 800 ℃	[102]
45	PEPPI	87	337,515, edge 700	583	0.14	water and, DMF, DMSO, NMP.	1H 13C NMR, IR, UV/vis, PL, TGA, CV	97% at 100℃, 95% at 200℃, 25% at 700 ℃	[143]
46	PENPPB	90	460, edge 800	519	0.18	DMF, DMSO, MeOH, N,N-dimethylacetamide, formic acid, water	1H 13C NMR, IR, UV/vis, PL, TGA, DSC, XRD	98% at 189 ℃, 95% at 205 ℃, 90% at 219 ℃, 25% at 700 ℃	[140]
47	PNFMEPB	92	300, edge 700	593	0.19	DMF, DMSO, N,N-dimethylacetamide	1H 13C NMR, IR, UV/vis, PL, CV, XRD	n/a	[122]
48	PBEPC	89	300, edge 750	509	0.18	water, methanol, DMF, DMSO	1H 13C NMR, IR, UV/vis, PL, XRD, CV	n/a	[139]
49	PEPPB	86	338, edge 650	490	0.14	water, methanol, DMF, DMSO, N,N-dimethylacetamide, or organic acids capable of hydrogen bonding with the propionate anion	1H 13C NMR, IR, UV/vis, PL, XRD, CV	n/a	[148]
50	PEMPB	75	359,464, edge 750	539	0.15	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, TGA, CV	95% at 267 ℃, 90% at 295 ℃, 80% at 338 ℃, 29% at 700 ℃	[135]
51	PEPSPB	83	387,521, edge 650	525	0.15	water, pyridine, DMF, NMP, DMSO.	1H 13C NMR, IR, UV/vis, PL, TGA, CV	99% at 160 ℃, 90% at 200 ℃, 41% at 700 ℃	[141]
52	poly(EPT-P)	80	519, edge 700	710	0.29	water, methyl alcohol, formic acid, DMF, DMSO, nitrobenzene	1H NMR, IR, UV/vis, PL, DSC, TGA, XRD	99% at 105 ℃, 95% at 267 ℃, 90% at 302 ℃, 70% at 342 ℃, 50% at 600 ℃	[160]
53	PEHPB	65	512, edge 650	no PL	0.18	DMF, DMSO, acetone, methanol	1H 13C NMR, IR, UV/vis, XRD, TGA	95% at 232 ℃, 80% at 283 ℃, 40% at 379 ℃ 27% at 700 ℃	[167]
54	PEHP-TPB	56	512, edge 650	no PL	0.20	DMF, DMSO, acetone	1H 13C NMR, IR, UV/vis, XRD, TGA	95% at 232 ℃, 80% at 283 ℃, 40% at 379 ℃ 31% at 700 ℃	[167]

PNo.	Code	Yield (%)	A_{max} (nm)	PL_{max} (nm)	Inherent vis. (dL/g)	Solubility	Charact.	TGA	Ref.
55	PAHEP-TPB	n/a	502, edge 750	599	n/a	n/a	UV/vis, PL, CV	n/a	[190]
56	PUEPB	82	502, edge 750	593	0.17	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, XRD, CV	n/a	[136]
57	PESPB	82	389, 480, edge 620	511	0.13	DMF, DMSO, NMP	UV/vis, PL, CV	n/a	[137]
58	PEGPT	52	502, edge 750	710	0.15	methanol, pyridine, DMF, NMP, DMSO	1H 13C NMR, IR, UV/vis, PL, TGA, DSC, CV	99% at 165 ℃, 95% at 223 ℃, 90% at 277 ℃, 22% at 700 ℃	[154]
59	PEGPB	91	515, edge 720	598	0.25	DMF, DMSO, MeOH, N,N-dimethylacetamide, formic acid, and water	IR, UV/vis, PL, CV	n/a	[191]
59	PEPBG	82	500, edge 800	725	0.25	methanol, pyridine, DMF, NMP, DMSO	1H 13C NMR, IR, UV/vis, PL, TGA, CV	99% at 100 ℃, 95% at 173 ℃, 90% at 204 ℃, 27% at 700 ℃	[192]
60	PEPB-DBM	80	499, edge 620	516, 555	0.15	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, CV	n/a	[146]
61	P3EPPI	65	344, 429, edge 590	534	0.10	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, CV, EDX	n/a	[144]
62	poly(Bep-TPB)	n/a	389, 259, edge 750	620	0.15	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, XRD, CV	n/a	[168]
63	PEPBPC	75	333, 580, edge 800	627	0.13	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, TGA, CV, XRD	99% at 100 ℃, 90% at 200 ℃, 52% at 700 ℃	[151]
64	PEPEPB	70	382, 471, edge 730	574	0.14	DMF, NMP, DMSO	1H 13C NMR, IR, UV/vis, PL, XRD, TGA	98% at 100 ℃, 96% at 200 ℃ 6% at 800 ℃	[193]
65	PESEPB	87	382, 469, edge 720	545	0.13	DMF, DMSO	1H 13C NMR, IR, UV/vis, PL, XRD, TGA, EDXW	98% at 100 ℃, 95% at 200 ℃, 70% at 300 ℃ 16% at 700 ℃	[194]
66	PEIPI	87	edge 800	513, 550	0.14	DMF, DMSO, NMP, acetone	1H 13C NMR, IR, UV/vis, PL, XRD, CV, EDS	n/a	[195]
67	PETPPB	89	451, edge 750	518	0.16	water, DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, CV	n/a	[196]

PNo.	Code	Yield (%)	A_{max} (nm)	PL_{max} (nm)	Inherent vis. (dL/g)	Solubility	Charact.	TGA	Ref.
68	PEFPC	81	410, 490, edge 750	578	0.17	DMF, DMSO, NMP	1H 13C NMR, IR, UV/vis, PL, CV, XRD	n/a	[102]
69	PBCEPB	85	327,510, edge 800	n/a	0.15	methanol, DMF, DMSO, water	1H 13C NMR, IR, UV/vis, XRD, CV	n/a	[197]
70	PEMMCPB	75	325, 458, edge 730	512	n/a	methanol, pyridine, DMF, NMP, DMSO	1H 13C NMR, IR, UV/vis, PL, XRD, CV	n/a	[198]
71	PNESPEC	65	332, edge 700	584	0.15	DMF, NMP, DMSO	1H 13C NMR, IR, UV/vis, PL, XRD, CV	n/a	[199]
72	P2EPF	72	300, edge 700	513, 550	n/a	chloroform, benzene	1H 13C NMR, IR, UV/vis, PL, XRD	n/a	[200]
73	PPyA-MI	99	n/a	n/a	n/a	methanol, DMF, DMSO	1H 13C NMR, IR, TGA	95% at 310 ℃, 60% at 400 ℃ 38% at 700 ℃	[59]
74	PPyA-MBr	97	n/a	n/a	n/a	water, methanol, DMF, DMSO	1H 13C NMR, IR, TGA	95% at 279 ℃, 60% at 360 ℃ 38% at 700 ℃	[59]
75	n/a	n/a	n/a	n/a	Cross-linked	Insoluble polymer network	n/a	n/a	[95]
76	PB2EPB	80	470, edge 600	n/a	Cross-linked	Insoluble polymer network	IR, UV/vis,	n/a	[149]
77	EPyNet1	61	700-720	529	Cross-linked	Insoluble polymer network	13C NMR, IR, UV/vis, PL, S_{BET}	n/a	[145]
78	No product	n/a	n/a	n/a	n/a	n/a	n/a	n/a	[145]
79	EPyNet4 (EPyNet2 EPyNet3 EPyNet5)	82 (48 50 79)	600-750	535	Cross-linked	Insoluble polymer network	13C NMR, IR, UV/vis, PL, S_{BET}	n/a	[145]
80	EPyNet6	82	650-750	529	Cross-linked	Insoluble polymer network	13C NMR, IR, UV/vis, PL, S_{BET}	n/a	[145]
81	EPyNet7	82	650-750	529	Cross-linked	Insoluble polymer network	13C NMR, IR, UV/vis, PL, S_{BET}	n/a	[145]
82	EPyNet8	82	700-720	535	Cross-linked	Insoluble polymer network	13C NMR, IR, UV/vis, PL, S_{BET}	n/a	[145]
83	EPyNet9	82	700-720	529	Cross-linked	Insoluble polymer network	13C NMR, IR, UV/vis, PL, S_{BET}	n/a	[145]

Table 2 The results of elemental analysis of polymers reported in the literature. The results of EA were available only for 23 from 83 reported polymers in the literature. **PNo.** – polymer number used in this work; Code – code of polymer in the original article. Ion (X) – the counterion (X of quaternizing agent), or the atom which corresponds to the degree of quaternization; Initial X/N – initial X/N mole ratio in the reaction feed; C, H, N, X, O – the mass fraction of respective chemical element (in %); Total – summation of all mass fractions (in case of polymers 13, 14; 16 and 59 all the elements were not determined); X/N – degree of quaternization expressed as X/N mole ratio calculated from EA; O/N – the mole ratio of oxygen to nitrogen; Ref – reference number; n/a – data not available.

PNo.	Code	Ion [X]	Initial X/N	C	H	N	X	O	total	X/N	O/N	Ref.
1	2	Br	1	64.49	8.21	4.93	22.68		100.31	0.81		[95]
2	4	Br	1	65.84	8.12	5.42	20.44		99.82	0.66		[95]
3	6a	Br	1	63.29	8.87	6.18	18.77		97.11	0.53		[95]
4	6b	I	1	38.95	3.78	5.72	51.49		99.94	0.99		[95]
7	10	Br	1	56.6	2.54	3.48	32.86		95.48	1.65		[95]
10	VIp	Br	2	33.91	2.1	5.57	58.19		99.77	1.83		[100]
12	VIIIp	Cl	1	70.25	4.82	11.8	12.75		99.62	0.43		[96]
13	8pa	S	1	42.55	3.9	6.19	n/a		52.64	n/a		[104]
14	8pb	S	1	39.04	3.13	5.12	11.98		59.27	1.02		[104]
16	9p	S	1	43.53	3.59	6.63	n/a		53.75	n/a		[104]
24	polymer	Br	1	54.01	3.54	6.03	36.15		99.73	1.05		[126, 127, 186]
25	poly(CHEPB)	Br	1	71.2	6.03	3.5	19.27		100.00	0.96		[128]
52	poly(EPT-P)	S	1	64.95	4.80	5.11	10.21	14.93	100.00	0.87	2.56	[160]
59	PEPBG	Br	1	52.13	4.10	6.65	n/a	7.20	70.08	n/a	0.95	[191]
77	EPyNet1	Br	0.5	55.41	4.70	6.71	25.17		91,99	0.66		[145]
79	EPyNet2	Br	0.25	58.88	4.60	7.67	19.19		90,34	0.44		[145]
79	EPyNet3	Br	0.33	56.29	4.43	7.16	22.15		90,03	0.54		[145]
79	EPyNet4	Br	0.5	52.67	4.45	6.64	23.27		87,03	0.61		[145]
79	EPyNet5	Br	1	51.18	4.48	4.35	29.12		89,13	1.18		[145]
80	EPyNet6	Br	0.5	58.56	4.44	6.01	22.28		91,29	0.64		[145]
81	EPyNet7	Br	0.5	63.34	4.25	6.90	20.50		94,99	0.52		[145]
82	EPyNet8	Br	0.5	62.81	4.32	6.90	20.12		94,15	0.51		[145]
83	EPyNet9	Br	0.5	66.51	4.20	6.26	17.94		94,91	0.50		[145]

2 AIMS OF THE THESIS

The Specialty polymers research team at the Department of Physical and Macromolecular Chemistry has been traditionally dealing with the preparation and characterization of variety of functional polymers. Based on the contemporary projects (Czech Science Foundation Projects No. 15–09637S and P108/11/1661) focused on the synthesis, characterization and properties testing of conjugated polyacetylene type polymers, the basic scopes of presented thesis were established.

The spontaneous process involving activation of ethynylpyridine based monomers with alky halides, frequently denotes as quaternization polymerization (QP), is a powerful tool for the preparation of ionic π-conjugated polyacetylene type polymers containing heteroatom in their structure. The advantages of this process (catalyst-free, tolerant to the ionic groups) and advantages of prepared materials (solubility in polar solvents, photoluminescence activity) have been broadly reported in the literature. However, mainly poly(monosubstituted acetylene)s were investigated. This is despite the fact that poly(disubstituted acetylene)s prepared from monomers containing internal ethynyl group generally exhibit better photoluminescence properties and higher thermal stability compared to the poly(monosubstituted acetylene)s. Furthermore, the discussion on the composition and structure of prepared materials via this catalyst-free approach is mostly missing.

Thus, the main aims of presented thesis could be summarized:

- To prepare a series of ionic π-conjugated poly(monosubstituted acetylene)s via quaternization polymerization (QP) of 2-ethynylpyridine under various reaction conditions. In dependence on reaction conditions applied, compare the composition and configurational structure of resulting materials by means of elemental analysis, NMR, IR, UV/vis and photoluminescence spectroscopies. Moreover, to characterize the prepared materials in the form of Ag/polymer nanocomposites by means of Surface enhanced Raman spectra (SERS) method.

- To synthesize a series of disubstituted monomers based on *ortho*-pyridylacetylene and *para*-pyridylacetylene containing one or two internal ethynyl group(s) and one or two pyridyl group(s).

- To prepare linear ionic π-conjugated poly(disubstituted acetylene)s and ionic π-conjugated polyacetylene type polymer networks via the quaternization polymerization (QP) of synthesized monomers using monofunctional or bifunctional quaternizing agent. To characterized products by means of elemental analysis, NMR, IR and MALDI-TOF MS spectroscopies and compare their composition and structure with structure of original monomers and quaternizing agent applied. To test the thermal stability (TGA analysis) and absorption/emission properties (UV/vis and photoluminescence spectroscopies). Moreover, to test the solubility of prepared linear polymers and characterize prepared polymer networks by means of gas (N_2, CO_2) and vapor (ethanol) capture capacity in dependence on the structure.

3 MATERIALS AND METHODS

3.1 Materials

Chemicals

1,4-Bis(bromomethyl)benzene (1,4-BBrMB) (Sigma-Aldrich), bis(triphenylphosphine)palladium(II) dichloride [$Pd(PPh_3)_2Cl_2$] (Sigma-Aldrich), 1,2-diphenylacetylene (anhydrous, 99.8%, Sigma-Aldrich), benzyl bromide (BBr) (Sigma-Aldrich), bromoethane (EtBr, 98%, Sigma-Aldrich), 1-bromononane (NoBr, 95%, Sigma-Aldrich), 1-bromohexadecane (cetyl bromide, CtBr, 95%, Sigma-Aldrich), 2-bromopyridine (Sigma-Aldrich), 4-bromopyridine (Sigma-Aldrich), 1-bromo-4-*tert*-butylbenzene (Sigma-Aldrich), copper(I) iodide (CuI) (Sigma-Aldrich), 1,4-Diethynylbenzene (Sigma-Aldrich, purified by vacuum sublimation), 4,4´-dipyridyl (DIPY) (Across Organics), 2-ethynylpyridine, (2EP, 98%, Sigma-Aldrich), 4-ethynylpyridine (4EP, TCI Europe), iodoethane (EtI, 99%, Sigma-Aldrich), 4-iodopyridine (Across Organics) 1-hexyne (Sigma-Aldrich), phenylacetylene (Sigma-Aldrich), silver nitrate (≥99%) (Sigma-Aldrich), sodium borohydride (grade for analysis, Merck), 4-*tert*-butylphenylacetylene (Sigma-Aldrich). All mentioned chemicals were used as received.

Solvents

Acetone (Sigma-Aldrich), acetonitrile (AN) (Sigma-Aldrich), diethyl ether (Lach-ner), dichloromethane (Sigma-Aldrich), *N*,*N*-dimethylformamide (DMF) (anhydrous, 99.8%, Sigma-Aldrich), dimethyl sulfoxide (DMSO) (Sigma-Aldrich), ethanol (EtOH) (Sigma-Aldrich), ethyl acetate (Lach-ner), methanol (MeOH) (Sigma-Aldrich) hexane (Lach-ner), tetrahydrofuran (THF) (Sigma-Aldrich distilled from $LiAlH_4$), triethylamine (Sigma-Aldrich), toluene (Sigma-Aldrich, distilled from sodium-benzophenone desiccant), water (distilled).

Solvents for spectroscopy

N,*N*-dimethylformamide-d_7 (DMF-d_7, 99.5 atom% D, Armar chemicals), dimethyl sulfoxide-d_6 (DMSO-d_6, 99.5 atom% D, Armar chemicals), chloroform-*d* ($CDCl_3$-*d*, 99.5 atom% D, Armar chemicals), deuterium oxide (D_2O, 99,9 atom% D, Cambridge isotope laboratories), methanol for spectroscopy (Merck).

3.2 Methods

Infrared (IR) spectroscopy

All the Fourier transform infrared (FTIR) spectra were measured on a Nicolet Magna IR 760 using the diffuse reflection mode (DRIFTS), samples were diluted with KBr (128 or more scans at resolution 4 cm^{-1}).

Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR and ^{13}C NMR spectra were measured on a Varian *UNITY*^{INOVA} 400 MHz, Varian *UNITY*^{INOVA} 300 MHz or Bruker Biospin Avance 600 MHz spectrometers using $CDCl_3$-*d*, DMSO-d_6, DMF-d_7 or D_2O as a solvent. Chemical shifts δ are reported in ppm relative to the solvent peak (7.25 ppm (^{1}H); 77.0 ppm (^{13}C) for $CDCl_3$-*d*, 2.50 ppm (^{1}H) 39.52 ppm (^{13}C) for DMSO-d_6, 4.80 ppm (^{1}H) for D_2O and 8.03, 2.92 and 2.75 ppm (^{1}H); 163.15, 34.89 and 29.76 ppm (^{13}C) for DMF-d_7. Coupling constants, *J*, are given in Hz and they were obtained by the first-order analysis. COSY experiments were recorded in absolute value mode using standard two-pulse sequence. HSQC, HMQC and HMBC measurements were performed as gradient experiments.

All the ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectra were measured using a Bruker Avance III HD 500 WB/US NMR spectrometer in a double-resonance 3.2 mm probehead at a spinning frequency of 20 kHz.
Measured by: Ing. Jiří Brus (Academy of Sciences of the Czech Republic, Institute of Macromolecular Chemistry, Heyrovsky sq. 2, Prague, CZ 162 06)

Size-exclusion chromatography (SEC) measurement

SEC analyses of polymers were carried out on a TSP chromatograph (Thermo Separation Product, Florida, USA) equipped with RI and UV/vis detectors and a series of two (Mixed C and Mixed E) PL-gel columns (Polymer Laboratories-Agilent technologies, UK). Dimethylformamide (DMF with addition of 2 mol% of LiCl, flow rate 0.7 ml min^{-1}) was used as the eluent and the column system was calibrated with PMMA standards. Apparent values of weight-averaged molar masses, M_w, are reported relative to PMMA calibration.

Absorption spectroscopy (UV/vis)

UV/vis absorption spectra were measured using Hewlet-Packard 4452 diode-array and Shimadzu UV-2401PC spectrophotometer in methanol for spectroscopy using quartz 10 mm optical path cuvette.

Diffuse reflectance spectra (DR UV/vis) of the solid products (polymer networks) were recorded on a Shimadzu UV-2401PC spectrometer using an integration sphere assembly. The polymers were diluted with $BaSO_4$ (1/10, w/w) before measurements were carried out.

Emission spectroscopy (Photoluminescence, PL)

Photoluminescence emission spectra of soluble samples were measured using a Horiba Jobin Yvon Fluorolog 3 with excitation wavelength of 260, 350 and 420 nm in methanol for spectroscopy in quartz 10 mm optical path cuvette.

Photoluminescence emission spectra of the solid polymers were measured using a Horiba Jobin Yvon Fluorolog 3 instrument using a solid-state holder and excitation wavelength 378 nm or 470 nm. Excitation pulse laser diode Horriba either 378 nm or 470 nm was used also for the measurement of fluorescence decays. Photos of polymer networks emitting in visible region were taken with Nikon D300 digital camera using Micro-Nikkor 55mm f/3.5 lens in a solid-state holder of Horiba Jobin Yvon Fluorolog 3 spectrometer.

Thermogravimetric analysis (TGA)

TGA of polymers was performed using SETSYS Evolution TGA, Setaram Instrumentation, in N_2 atmosphere. TGA measurement procedure: at first, sample was heated to 100 °C with a step of 10 °C min^{-1} and dried for 1 hour (at 100 °C), then the sample was cooled down to 25 °C and heated to 800 °C with a step of 10 °C min^{-1}.
Measured by: Kamila Langerová, Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030/8, Prague, CZ 128 43

Elemental analyses (EA)

Measured by: Zuzana Kálalová Academy of Sciences of the Czech Republic, Institute of Macromolecular Chemistry, Heyrovsky sq. 2, Prague, CZ 162 06

Raman spectroscopy and Surface Enhanced Raman Scattering (SERS)

The preparation of Ag hydrosol

A hydrosol of Ag-NPs stabilized with borate anions was prepared by reduction of $AgNO_3$ with $NaBH_4$ adopting the standard procedure described in refs.[201] An aqueous solution of $NaBH_4$ (10.5 mg) in deionized water (225 ml) was cooled down in the dark to temperature ~ 5 °C and an aqueous solution of $AgNO_3$ (2.2×10^{-3} M, 27 ml) cooled to ~ 5 ºC was dropwise added under vigorous stirring. Resulting mixture was stirred in the dark for 45 min and then warmed up to the room temperature. The obtained bright yellow hydrosol of silver nanoparticles (Ag-NPs) showed the surface plasmon extinction (SPE) band at 395 nm.

Preparation of Ag-NPs/PEP-RX systems

Colloidal system Ag-NPs/sPEP-CtBr was chosen as model system for optimization of Ag-NPs/PEP-RX mole ratio for SERS spectroscopy measurement of others Ag-NPs/PEP-RX. Various polymer (sPEP-CtBr) to Ag-NPs ratios were prepared by a stepwise addition of 20 μl of a polymer solution in DMSO into Ag hydrosol (2 ml). The final concentration of sPEP-CtBr (c_{pol}) in the system varied from ca 5×10^{-8} M to ca

1 x 10^{-4} M (in mol of monomeric unites per dm^3). Changes in prepared colloidal solutions were monitored by the UV/vis spectroscopy. The aggregation of the prepared systems was observed as red-broadening of the plasmon resonance band of Ag-NPs (the solution color changes from yellow to green if an aggregation occurs). Bulk systems of Ag-NPs/PEP-RX for SERS spectroscopy were obtained by evaporation of a drop of the aggregated system onto a microscopic glass slide.

SERS spectra of hydrosols of Ag-NPs/PEP-RX composite systems were recorded with a multichannel Raman spectrometer equipped with a monochromator Jobin-Yvon-Spex 270M (1600 g mm^{-1} grating) and liquid N_2-cooled CCD detector Princeton Instruments (100 x 1340 pixels) in a right angle scattering geometry. Elimination of Rayleigh scattered light was provided by holographic notch-plus filter (Kaiser) located in front of the monochromator input slit. Excitation lines 488 nm and 514 nm (argon laser Innova 300, 250 mW) were used.

SERS spectra of bulk Ag-NPs/PEP-RX composite systems deposited on a glass substrate were recorded on a DXR Raman microscope (Thermo Scientific) interfaced to an Olympus microscope. The 445 nm (diode laser), 532 nm (diode pumped solid state laser) and 633 nm (He-Ne laser) excitation lines were used. The laser power ranged from 0.1 to 0.5 mW. Full range gratings were used (for more details see ref. [201]).
Measured by: Mgr. Libor Slaný, RNDr. Ivana Šloufová Ph.D., author

Matrix-assisted laser desorption/ionization – time-of-flight mass spectrometry (MALDI-TOF MS)

The samples for MALDI-TOF MS were prepared by the dried droplet method: solutions of sample (10 mg ml^{-1}) and of DCTB (trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malonitrile (10 mg ml^{-1}) as a matrix in methanol were mixed in the volume ratio 4:20. 1 µl of the mixture was deposit on the ground-steel target plate. Drop was dried at ambient atmosphere. MALDI-TOF MS analysis was performed with an Ultrafl eXtreme (Bruker Daltonics, Bremen, Germany) in the positive ion reflectron mode. The spectra were the sum of 30 000 shots with a diode-pumped solid-state laser (DPSS), Nd: YAG laser (355 nm, 1000 Hz). Delayed extraction and external calibration was used.

Measured by: Ing. Zuzana Walterová (Academy of Sciences of the Czech Republic, Institute of Macromolecular Chemistry, Heyrovsky sq. 2, Prague, CZ 162 06)

Gas and vapor sorption

Nitrogen adsorption on the polymer networks was determined at 77 K using a Gemini II surface area analyzer (Micromeritics). The samples for adsorption analysis were prepared using a FlowPrep 060 degasser. The degassing procedure was performed at 383 K for 8 hours in flowing helium. Adsorption/desorption isotherms of carbon dioxide were recorded at 293 K using an ASAP 2020 (Micromeritics) volumetric instrument. The samples were degassed at 383 K for 8 hours under a turbomolecular vacuum pump. Since adsorption isotherms of CO_2 on organic polymers can depend on the time allotted to the adsorption measurement,[202] all of the isotherms were recorded using the same equilibration time interval of 5 s (the equilibration time interval represents the time between successive pressure readings during equilibration). The temperature of the sample was maintained with an accuracy of ±0.01 K using an IsoTherm thermostat (e-Lab Services, Czech Republic). Ethanol vapors adsorption measurements were performed at 293 K with an ASAP 2020 instrument. In order to measure isotherms of vapors of liquid ethanol, the instrument was equipped with vapor accessory kit. Before adsorption experiments, possible contaminants such as atmospheric gases or traces of moisture were removed from liquid adsorptives. The samples were degassed according to procedure given in paper.[203] Adsorption isotherms of ethanol vapors were recorded using equilibration time interval of 5 s. The temperature of the sample was maintained with an accuracy of ±0.01 K using an IsoTherm thermostat (e-Lab Services, Czech Republic).

Measured by: Ing. Arnošt Zukal (Academy of Sciences of the Czech Republic, J. Heyrovsky Institute of Physical Chemistry, Dolejskova 3, Prague, CZ 182 23)

Interpreted by: author, Ing. Arnošt Zukal, Doc. Jan Sedláček

3.3 Synthesis of monomers

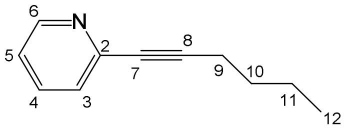
General procedure

Synthesis of monomers was performed as a Sonogashira cross-coupling of **reactant A** (typically aromatic halogen bearing derivative) and **reactant B** (triple bond bearing derivative). [$Pd(PPh_3)_2Cl_2$] (5 mol%) was used as a catalyst, CuI (5 mol%) was used as a cocatalyst. Appropriate amounts of reagents were placed into the Schlenk flask and diluted with **solvent**, which act also as a base. The air was removed by the vacuum/argon cycles and the reaction was stirred under Ar atmosphere at appropriate **temperature**. Reaction course was monitored by thin layer chromatography (TLC – on TLC Silicagel$_{(254nm)}$ sheets Merck, using the mixture of hexane and ethylacetate as a mobile phase, UV detection of products was used in all cases) After the appropriate **time** was reaction mixture cooled down and solvent was evaporated off on vacuum rotary evaporator. In some cases, the reaction time was prolonged to achieve higher conversion (actual conversion was roughly estimated from TLC). Residual solid phase was diluted in diethyl ether and filtered on alumina and concentrated. The desired product was obtained after purification by chromatography on silica gel using appropriate **mobile phase.** The yield of purified product was determined by the gravimetry.

Characterization of prepared monomers

2-(1-Hexynyl)pyridine (2PH)

Reactant A: 2-bromopyridine (1.6 g, 10.1 mmol); reactant B: 1-hexyne (0.8 g, 10.1 mmol); solvent: triethylamine (9 ml); temperature: 50 °C; time: 24 hours. The desired product (1150 mg, yield = 76%) was obtained as a yellowish liquid after purification by chromatography on silica gel with diethyl ether/hexane (5:3) as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.51 (d, $J = 4.9$ Hz, 1H^6); 7.75 (dt, $J = 7.7$, 1.8 Hz, 1H^4); 7.44 (d, $J = 7.8$ Hz, 1H^5); 7.32 (dq, $J =$ 7.0, 1.0 Hz, 1H^3); 2.44 (t, $J = 7.0$ Hz, 2H^9) ; 1.58-1.37 (m, 4H^{10,11}); 0.91 (t, $J = 7.2$ Hz, 3H^{12}).

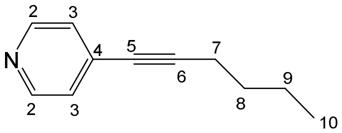
^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 149.8 C^6; 142.9 C^2; 136.5 C^4; 126.8 C^3; 122.8 C^5; 90.4 C^7; 80.8 C^8; 29.9 C^{10}; 21.4 C^{11}; 18.0 C^9; 13.4 C^{12}.

IR [DRIFT, KBr, υ (cm^{-1})]: 3050 (w), 2958 (s), 2933 (s), 2872 (m), 2230 (m, C≡C), 1583 (s), 1561 (s), 1464 (s), 1427 (s), 1328 (m), 1268 (m), 1149 (m), 1091 (w), 988 (m), 779 (s), 740 (m), 629 (m), 403 (m).

The spectra of monomers (^{1}H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.[204]

4-(1-Hexynyl)pyridine (4PH)

Reactant A: 4-bromopyridine (1.0 g, 6.3 mmol); reactant B: 1-hexyne (0.5 g, 6.4 mmol); solvent: triethylamine/toluene (12/6 ml); temperature: 50 °C; time: 48 hours. The desired product (463 mg, yield = 56%) was obtained as a brownish liquid after purification by chromatography on silica gel with ethyl acetate as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.52 (d, $J = 6.1$ Hz, 2H^2); 7.35 (d, $J = 6.1$ Hz, 2H^3); 2.47 (t, $J = 7.0$ Hz, 2H^7); 1.60-1.35 (m, 4H^{8,9}); 0.91 (t, $J = 7.2$ Hz, 3H^{10}).

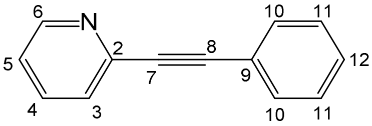
^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 149.8 C^2; 131.2 C^3; 125.5 C^4; 96.0 C^5; 78.4 C^6; 29.9 C^8; 21.4 C^9; 18.3 C^7; 13.4 C^{10}.

IR [DRIFT, KBr, υ (cm^{-1})]: 2958 (m), 2933 (m), 2872 (m), 2234 (w, C≡C), 1593 (s), 1539 (w), 1488 (w), 1466 (w), 1406 (w), 1213 (w), 989 (w), 821 (s), 695 (w), 550 (w).

The spectra of monomers (^{1}H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.[205]

2-(Phenylethynyl)pyridine (2PP)

Reactant A: 2-bromopyridine (1.0 g, 6.3 mmol); reactant B: phenylacetylene (0.65 mg, 6.3 mmol); solvent: triethylamine/toluene (12/10 ml); temperature: 50 °C; time: 48 hours. The desired product (890 mg, yield = 79%) was obtained as a yellouwish solid purification by chromatography on silica gel with hexane/ethyl acetate (2:1) as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.60 (d, J = 4.7 Hz, 1H^6); 7.86 (dt, J = 7.7, 1.8 Hz, 1H^4); 7.68-7.58 (m, 3H$^{5, 10}$), 7.49-7.44 (m, 3H$^{3, 11}$), 7.42 (ddd, J = 7.7, 4.9, 1.2 Hz, 1H^{12}).

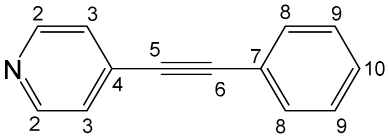
^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 150.2 C^6; 142,2 C^2; 136.8 C^4; 131.6 C^{10}; 129.4 C^3; 128.9 C^{11}; 127.3 C^5; 123.5 C^{12}; 121.4 C^9; 88.9 C^7; 88.3 C^8.

IR [DRIFT, KBr, υ (cm^{-1})]: 3055 (w), 3003 (w), 2221 (m, C≡C), 1598 (m), 1580 (s), 1561 (m), 1491 (s), 1462 (s), 1427 (s), 1282 (w), 1233 (w), 1155 (m), 1089 (w), 1070 (w), 987 (m), 916 (w), 777 (s), 757 (s), 737 (m), 689 (s), 630 (w), 555 (m), 400 (m).

The spectra of monomers (^{1}H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.[206]

4-(Phenylethynyl)pyridine (4PP)

Reactant A: 4-iodopyridine (500 mg, 2.4 mmol); reactant B: phenylacetylene (250 mg, 2.4 mmol); solvent: triethylamine/toluene (12/10 ml); temperature: 70 °C; time: 24 hours. The desired product (362 mg, yield = 83%) was obtained as a yellowish solid after purification by chromatography on silica gel with ethyl acetate as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.64 (s, 2H^2); 7.64-7.59 (m, 2H^3); 7.53 (d, J = 6.0 Hz 2H^8); 7.50-7.42 (m, 3H^{9,10}).

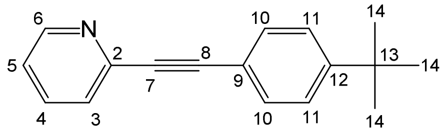
^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 149.9 C^2; 131.7 C^8; 130.1 C^4; 129.7 C^7; 128.9 C^9; 125.4 C^3; 121.2 C^{10}; 93.5 C^5; 86.7 C^6.

IR [DRIFT, KBr, υ (cm^{-1})]: 3074 (w), 3060 (m), 3023 (w), 2223 (m, C≡C), 1600 (m), 1589 (s), 1538 (m), 1492 (m), 1441 (m), 1412 (s), 1216 (m), 1070 (m), 1025 (m), 988 (m), 923 (m), 854 (m), 828 (s), 759 (s), 692 (s), 521 (s).

The spectra of monomers (^{1}H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.[206]

2-(4-Tert-butylphenylethynyl)pyridine (2PT)

Reactant A: 2-bromopyridine (1.0 g, 6.4 mmol); reactant B: 4-tert-butylphenylacetylene (1.0 g, 6.4 mmol); solvent: triethylamine/toluene (8/6 ml); temperature: 50 °C; time: 24 hours. The desired product (956 mg, yield = 66%) was obtained as a brownish solid after purification by chromatography on silica gel with hexane as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.64 (d, J = 7.5 Hz, 1H^6); 7.58 (dt, J = 7.7, 1.9 Hz, 1H^4); 7.61 (d, J = 7.7 Hz 1H^5); 7.54 (d, J = 8.5 Hz, 2H^{10}); 7.47 (d, J = 8.5, Hz, 2H^{11}), 7.41 (dq, J = 4.9, 1.3 Hz, 1H^3); 1.29 (s, 9H^{14}).

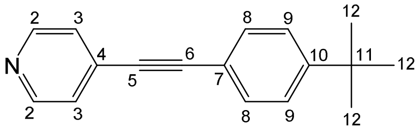
^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 152.2 C^{12}; 150.1 C^6; 142.4 C^2; 136.7 C^4; 131.5 C^{10}; 127.2 C^3; 126.7 C^{11}; 123.4 C^5; 118.4 C^9; 88.5 C^7; 88.4 C^8; 34.6 C^{13}; 30.8 C^{14}.

IR [DRIFT, KBr, υ (cm^{-1})]: 3052 (w), 2960 (m), 2865 (m), 2224 (m, C≡C), 1580 (s), 1561 (m), 1507 (m), 1462 (s), 1427 (s), 1363 (m), 1278 (m), 1107 (m), 1015 (m), 844 (s), 828 (s), 781 (s), 741 (m), 625 (m), 565 (s), 547 (m).

The spectra of monomers (^{1}H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.[207]

4-(4-Tert-butylphenylethynyl)pyridine (4PT)

Reactant A: 4-ethynylpyridine (0.5 g, 4.8 mmol); reactant B: 1-bromo-4-tert-butylbenzene (1.0 g, 4.8 mmol); solvent: triethylamine/toluene (8/6 ml); temperature: 50 °C; time: 24 hours. The desired product (844 mg, yield = 74%) was obtained as a white solid after purification by chromatography on silica gel with ethyl acetate as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.65 (s, 2H^2); 7.57-7.45 (m, 6H^{3,8,9}); 1.29 (s, 9H^{12}).

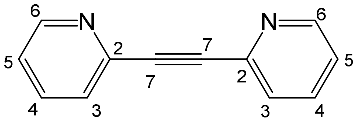
^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 152.5 C^{10}; 149.9 C^2; 131.5 C^8; 130.3 C^4; 126.7 C^7; 125.7 C^9; 118.3 C^3; 93.7 C^5; 86.2 C^6; 34.7 C^{11}; 30.8 C^{12}.

IR [DRIFT, KBr, υ (cm^{-1})]: 3034 (w), 2963 (s), 2868 (m), 2221 (m, C≡C), 1589 (s), 1507 (m), 1402 (s), 1364 (m), 1268 (m), 1104 (m), 989 (w), 836 (s), 822 (s), 566 (m), 548 (m).

To the best of our knowledge, the monomer 4PT was not reported in the literature before the completing this work.

1,2-Bis(2-pyridyl)acetylene (2PM)

Reactant A: 2-bromopyridine (1.6 g, 10.1 mmol); reactant B: 2-ethynylpyrdine (1.1 g, 10.1 mmol); solvent: triethylamine (9 ml); temperature: 50 °C; time: 24 hours. The desired product (922 mg, yield = 48%) was obtained as a yellowish solid after purification by chromatography on silica gel with diethyl ether as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.63 (d, J = 4.8 Hz, 2H^6); 7.88 (dt, J = 7.7, 1.7 Hz, 2H^4); 7.71 (d, J = 7.7 Hz, 2H^5); 7.45 (dq, J = 4.9, 1.0 Hz, 2H^3).

^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 150.3 C^6; 141.5 C^2; 136.9 C^4; 127.7 C^3; 124.1 C^5; 87.5 C^7.

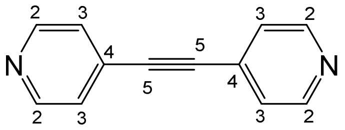
IR [DRIFT, KBr, υ (cm^{-1})]: 3076 (m), 3044 (m), 3003 (m), 2326 (w), 2230 (w, C≡C), 1954 (w), 1579 (s), 1559 (s), 1470 (s), 1425 (s), 1316 (m), 1280 (m), 1148 (m), 1090 (m), 989 (s), 917 (m), 802 (s), 775 (s), 738 (s), 627 (m), 575 (m), 520 (m).

Raman spectra [λexc: 780 nm, υ (cm^{-1})]: 3052 (w), 2230 (s, C≡C), 2176 (w), 1579 (m), 1560 (w), 1459 (w), 1426 (w), 1288 (w), 1180 (m), 1046 (w), 989 (m), 549 (w), 368 (w).

The spectra of monomers (^{1}H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.[208]

1,2-Bis(4-pyridyl)acetylene (4PM)

Reactant A: 4-iodopyridine (800 mg, 3.9 mmol); reactant B: 4-ethynylpyrdine (400 mg, 3.9 mmol); solvent: triethylamine/toluene (12/6 ml); temperature: 90 °C; time: 48 hours. The desired product (440 mg, yield = 63%) was obtained as a white solid after purification by chromatography on silica gel with ethyl acetate as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.68 (dd, $J = 4.5$, 1.7 Hz, 4H^{2}); 7.59 (dd, $J = 4.5$, 1.7 Hz, 4H^{3}).

^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 150.0 C^{2}; 129.0 C^{4}; 125.5 C^{3}; 90.4 C^{5}.

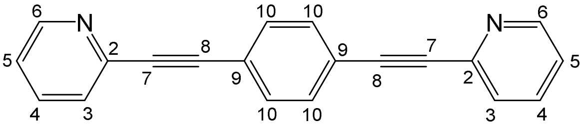
IR [DRIFT, KBr, υ (cm^{-1})]: 3074 (m), 3034 (m), 2979 (m), 2892 (w), 2162 (w), 1944 (w), 1701 (w), 1595 (m), 1541 (m), 1523 (m), 1500 (m), 1413 (s), 1217 (m), 1117 (m), 1088 (m), 994 (m), 857 (s), 827 (s), 736 (m), 553 (s), 529 (s), 516 (m).

Raman spectra [λexc: 780 nm, υ (cm^{-1})]: 2229 (s, C≡C), 2165 (w), 1595 (m), 1494 (w), 1155 (m), 994 (m), 670 (w), 555 (w).

The spectra of monomers (^{1}H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.[209]

1,4-Bis[(2-pyridyl)ethynyl]benzene (2PD)

Reactant A: 2-bromopyridine (1.0 g, 6.2 mmol); reactant B: 1,4-diethynylbenzene (400 mg, 3.1 mmol); solvent: triethylamine/toluene (6/20 ml); temperature: 50 °C; time: 24 hours. The desired product (620 mg, yield = 69%) was obtained as a yellowish solid after purification by chromatography on silica gel with ethyl acetate as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.63 (d, $J = 4.1$ Hz, 2H^{6}); 7.88 (dt, $J = 7.7$, 1.8 Hz, 2H^{4}); 7.69 (s, 6 H^{10}); 7.67 (d, $J = 7.7$ Hz, 2H^{5}); 7.44 (dq, $J = 7.7$, 1.8 Hz, 2 H^{3}).

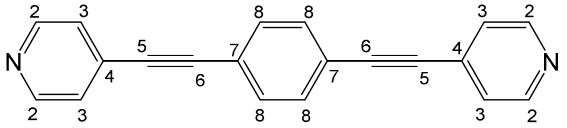
^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 150.2 C^{6}; 142.0 C^{2}; 136.9 C^{4}; 132.0 C^{10}; 127.5 C^{3}; 123.8 C^{5}; 122.2 C^{9}; 91.0 C^{8}; 87.6 C^{7}.

IR [DRIFT, KBr, υ (cm^{-1})]: 3049 (w), 2220 (m, C≡C), 1910 (w), 1585 (m), 1575 (s), 1485 (s), 1459 (m), 1425 (m), 1394 (m), 1069 (m), 1009 (m), 822 (m), 775 (m), 735 (m), 515 (m).

The spectra of monomers (^{1}H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.[210]

1,4-Bis[(4-pyridyl)ethynyl]benzene (4PD)

Reactant A: 4-iodopyridine (1.0 g, 4.8 mmol); reactant B: 1,4-diethynylbenzene (307 mg, 2.4 mmol); solvent: triethylamine/toluene (12/6 ml); temperature: 50 °C; time: 48 hours. The desired product (480 mg, yield = 72%) was obtained as a yellowish solid after purification by chromatography on silica gel with ethyl acetate as a mobile phase.



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.65 (dd, J = 4.5. 1.7 Hz, 4H^2); 7.70 (s, 4H^8); 7.55 (dd, J = 4.5 1.7 Hz, 4H^3).

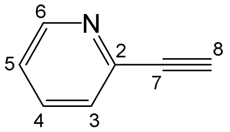
^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 150.0 C^2, 132.1 C^8, 129.8 C^4, 125.4 C^3, 122.2 C^7, 92.7 C^6, 88.9 C^5.

IR [DRIFT, KBr, υ (cm^{-1})]: 3038 (w), 2223 (w, C≡C), 1589 (s), 1512 (w), 1405 (m), 1214 (w), 988 (w), 848 (m), 820 (s), 626 (m), 539 (m).

The spectra of monomers (^{1}H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.[210]

A series of reference quaternization reactions was performed with the aim to support the discussion on quaternization polymerization. As starting compounds were used purchase materials. Since the spectral characterization of these materials is mostly missing, here, we provide the basic NMR characterization of purchased compounds

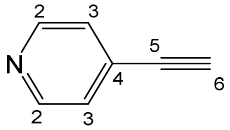
2-Ethynylpyridine (2EP) (Sigma-Aldrich)



^{1}H NMR [300 MHz, DMSO-d_6, δ (ppm)]: 8.56 (d, J = 4.7 Hz, 1H^6); 7.81 (dt, J = 7.7, 1.7 Hz, 1H^4); 7.56 (d, J = 7.9 Hz, 1H^5); 7.41 (dq, J = 4.7, 1.0 Hz, 1H^3); 4.32 (s, 1H^8).

^{13}C NMR [300 MHz, DMSO-d_6, δ (ppm)]: 150.0 C^6; 141.7 C^2; 136.8 C^4; 127.4 C^3; 123.8 C^5; 83.0 C^7; 80.0 C^8.

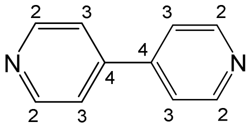
4-Ethynylpyridine (4EP) (TCI Europe)



^{1}**H NMR** [300 MHz, DMSO-d_6, δ (ppm)]: 8.60 (dd, $J = 4.5$, 1.7 Hz, 2H^{2}); 7.45 (dd, $J = 4.5$, 1.7 Hz, 2H^{3}); 4.61 (s, 1H^{6}).

^{13}**C NMR** [300 MHz, DMSO-d_6, δ (ppm)]: 149.9 C^{2}; 129.6 C^{4}; 125.8 C^{3}; 85.5 C^{6}; 80.9 C^{5}.

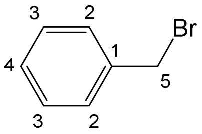
1,4-Dipyridyl (DIPY) (Across Organics)



^{1}**H NMR** [300 MHz, DMSO-d_6, δ (ppm)]: 8.73 (dd, $J = 4.5$, 1.7 Hz, 4H^{2}); 7.83 (dd, $J = 4.5$, 1.7 Hz, 4H^{3}).

^{13}**C NMR** [300 MHz, DMSO-d_6, δ (ppm)]: 150.6 C^{2}; 144.3 C^{4}; 121.3 C^{3}.

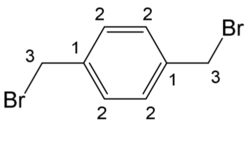
Benzyl bromide (BBr) (Sigma-Aldrich)



^{1}**H NMR** [300 MHz, DMSO-d_6, δ (ppm)]: 7.48-7.28 (m, 5H^{2,3,4}); 4.70 (s, 2H^{5}).

^{13}**C NMR** [300 MHz, DMSO-d_6, δ (ppm)]: 138.5 C^{1}; 129.7 C^{2}; 129.1 C^{3}; 128.8 C^{4}; 34.9 C^{5}.

1,4-Bis(bromomethyl)benzene (1,4-BBrMB) (Sigma-Aldrich)



^{1}**H NMR** [300 MHz, DMSO-d_6, δ (ppm)]: 7.43 (s, 4H^{2}); 4.70 (s, 4H^{3}).

^{13}**C NMR** [300 MHz, DMSO-d_6, δ (ppm)]: 138. C^{1}; 129.6 C^{2}; 34.0 C^{3}

3.4 Quaternization polymerizations

3.4.1 Quaternization polymerizations of 2-ethynylpyridine activated with a series of various alkyl halides

Quaternization polymerizations performed in acetonitrile solution.

Appropriate amount of 2EP (10 mmol) and equimolar amount of quaternizing agent RX (10 mmol) were mixed in acetonitrile (AN) (6 ml) under Ar atmosphere in the thick-wall glass ampoule. Ampoule was carefully sealed and placed into the thermostatic bath. Temperature was set to 60 °C. Reaction mixture change color from light yellow to dark brown. After 10 days, reaction mixture was withdrawn from the thermostatic bath, cooled down and carefully opened. Reaction mixture was immersed with diethyl ether to precipitate the resulting polymer. A brown powder of formed polymer was decanted, washed five times with fresh diethyl ether (5 x 40 ml) and dried in vacuum at room temperature for two or more days to constant weight. Polymer yield was determined by gravimetry. Polymers prepared according to this procedure were labeled as **sPEP-RX**.

Quaternization polymerizations performed in bulk.

Appropriate amount of 2EP (10 mmol) was introduced to the glass ampoule together with equimolar amount of quaternizing agent RX (10 mmol). The ampoule was flushed with Ar and carefully sealed, then placed into the thermostatic bath set to 60 ºC. The ampoule was withdrawn from the thermostatic bath after 10 days, cooled down and carefully opened. Polymers prepared with EtBr and EtI were dissolved in 25 ml of methanol and precipitated with the excess of chloroform (65 ml). Vials with the polymer with excess of chloroform were left overnight at -18 ºC to achieve maximal polymer precipitation. Polymers prepared with the NoBr and CeBr were dissolved in methanol (25 ml) and precipitated with excess of water (65 ml) and left overnight at 4 ºC. The precipitate was always filtered off and washed with the excess of the appropriate cold solvent (chloroform/water, 25/25 ml). The precipitation procedure was three times repeated for polymer purification. Polymers were isolated by the simple filtration as brown powder and dried in reduced pressured to constant weight. Polymer yields were determined by gravimetry. Polymers prepared according to this procedure were labeled as **bPEP-RX**.

3.4.2 Quaternization polymerizations activated with benzyl bromide

Monomers 2EP, 4EP, 2PH, 4PH, 2PP, 4PP, 2PT, 4PT, 2PM, 4PM, 2PD, and 4PD were polymerized via activation with benzyl bromide (BBr) as a quaternizing agent. In a typical experiment, a monomer (200 mg) and two or four equivalents of BBr (Br/N = 2) were mixed in 1.5 mL of DMF under Ar atmosphere in a thick-wall glass ampoule. Ampoule was sealed and reaction mixture was stirred for 2 hours at 100 °C, then the ampoule was placed into the thermostated own at 100 °C. Reaction mixture changes color from light yellow to dark brown or black. After 10 days, the reaction mixture was cooled down, diluted with methanol (2 ml), and poured into diethyl ether (30 ml). Precipitated polymer was separated and washed with diethyl ether (3 × 30 ml). Finally, solid polymer was dried in vacuum at 60 °C for 1 hour and then in vacuum for 48 hours at room temperature to constant weight. Polymers prepared according to this procedure were labeled as **poly(monomer)**.

3.4.3 Quaternization polymerizations activated with 1,4-bis(bromomethyl)benzene

Monomers 2PM, 4PM, 2PD, and 4PD were polymerized via activation with 1,4-bis(bromomethyl)benzene (1,4-BBrMB) as a quaternizing agent. In a typical experiment, a monomer (200 mg) and equimolar amount of 1,4-BBrMB (Br/N = 1) were mixed in 1.5 ml DMF under Ar atmosphere in a thick-wall glass ampoule. Ampoule was flushed with argon, sealed and the reaction mixture was stirred for 2 hours at 100 °C, then the ampoule was placed into the thermostated oven at temperature of 100 °C. Reaction mixture changed color from light yellow to dark brown. After 10 days reaction mixture was cooled down. Formed product was transferred into methanol (30 ml) and stirred for 30 min. Then, the solid was filtered off and repeatedly washed with methanol. Finally, insoluble solid product was dried under vacuum at temperature of 60 °C for 1 hour and then under vacuum at room temperature to constant weight. Polymer networks prepared according to this procedure were labeled as **net(monomer)**.

3.5 Results of elemental analysis

Table 1 Results of elemental analysis of prepared materials.

Sample Code	Wt. %				
	C	H	N	Br	I
sPEP-EtBr	57.62	4.96	8.31	21.74	
sPEP-EtI	50.73	4.14	6.97		33.36
sPEP-NoBr	64.41	6.85	7.20	17.27	
sPEP-CtBr	68.10	8.21	6.7	15.58	
bPEP-EtBr	54.61	4.87	8.21	23.91	
bPEP-EtI	48.47	4.30	6.99		38.90
bPEP-NoBr	64.94	6.81	7.20	16.73	
bPEP-CtBr	67.97	7.86	5.93	15.80	
Poly(2PH)	61,63	5,92	5,06	25,76	
Poly(4PH	60,75	5,55	4,16	27,32	
Poly(2PP)	64,63	4,48	4,47	27,31	
Poly(4PP)	62,46	4,61	3,73	26,84	
Poly(2PT)	65,40	6,21	4,65	22,67	
Poly(4PT)	64,46	5,59	3,70	25,46	
Poly(2PM)	57.30	4.40	6.81	29.49	
Poly(4PM)	65.69	4.30	9.89	15.31	
Poly(2PD)	56.91	3.75	4.95	27.71	
Poly(4PD)	70.11	3.81	6.48	12.76	
Net(2PM)	53.55	3.57	7,03	29,44	
Net(4PM)	48.58	3.74	6,08	35,64	
Net(2PD)	59.415	3.47	4,87	28,91	
Net(4PD)	55.98	3.53	4,37	30,04	
BBr-DIPY-BBr	57.84	4.14	5.55	33.34	
Poly(DIPY-alt-1,4-BBrMB)	48.33	2.91	6.62	31.33	
Poly(2PM)-B	57,49	4,77	6,71	26,26	
Poly(2PM)-C	59,81	4,41	8,23	23,83	
Poly(2PM)-D	54,60	5,27	6,00	30,25	
Net(2PM)-B	48,05	4,01	6,50	25,41	
Net(2PD)-B	56,56	3,77	4,64	28,76	
Poly(2EP)	62,03	4,98	5,95	24,83	
Poly(4EP)	60,20	5,03	4,95	25,30	

The complete characterization of all products is provided in the section *4 RESULTS AND DISCUSSION.*

4 RESULTS AND DISCUSSION

Presented doctoral thesis deals with the quaternization polymerizations of various monomers comprising in their structure ethynyl group(s) and pyridyl group(s) into monosubstituted and disubstituted ionic linear π-conjugated polyacetylene type polymers and ionic π-conjugated polyacetylene type polymer networks. This study involved synthesis of 10 monomers and over 60 quaternization polymerizations accompanied with the full characterization and detailed study of properties and testing of prepared materials. The major part of results was summarized in three research articles published in the impacted journals. However, the present thesis also contains unpublished results.

4.1 The structure and composition of monosubstituted ionic polyacetylene type polymers prepared via quaternization polymerization of 2-ethynylpyridine

Results of this section are summarized in the article:

> Faukner, T., Slaný, L., Šloufová, I., Vohlídal, J., & Zedník, J.; Π-conjugated Polyelectrolytes Derived from 2-Ethynylpyridine: The Effect of Quaternization Agent and Reaction Conditions on the Polymer Structure and SERS Characterization of Nanocomposites with Ag-Nanoparticles. *Macromolecular Research*, **2016**, *24*(5), 441–449. doi:10.1007/s13233-016-40620

labeled as **A1** in Attachments.

This section is focused on the study of structure and composition and detailed characterization of ionic π-conjugated monosubstituted polyacetylene type materials prepared via quaternization polymerization. Since the Blumstein presented this method as a powerful tool for the preparation of ionic polyacetylene type polymers, a number of quaternization polymerizations were reported in the literature. However, only a few articles comprise detailed study of QP and the influence of the reaction conditions on the formed products. The dependence of the polymer yield on the solvent used or temperature applied was reported in the literature (see *INTRODUCTION*), however, the discussion on the polymer structure and composition is mostly missing.

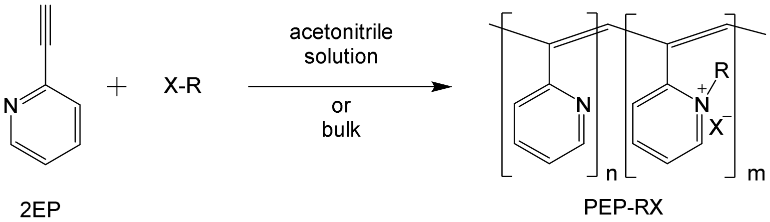
Since the QP is complex system and many factors affects the resulting product, the selection of polymerization conditions was an important aspect influencing polymer properties. The selection of the reaction conditions applied in this study was based on reaction conditions presented by Blumstein et al.[98-100] As a starting monomer was selected 2-ethynylpyridine (2EP), which was the most frequently used monomer for the QP reported in the literature.

The main tasks of this section can be summarized:

(i) The preparation of ionic polymers via QP of 2-ethynylpyridine (2EP) activated with various QA performed in solution as well in bulk (see **Scheme 1**) and characterization of prepared polymers by means of elemental analysis, ^{1}H NMR, IR, UV/vis and photoluminescence spectroscopies.

(ii) In dependence on the reaction conditions (solution or bulk polymerization) and QA applied to compare the degree of quaternization and configurational structure of prepared materials.

(iii) The preparation of Ag/polymer nanoparticles which allow the characterization of prepared polymers by means of Raman SERS spectroscopy.



Scheme 1 Scheme of quaternization polymerization of 2-ethynylpyridine (2EP) activated with a series of alkyl halides resulting into the ionic polymer PEP-RX with various n/m ratio.

The spontaneous quaternization polymerizations of 2EP activated with various QA resulted into ionic π-conjugated polyacetylene type polymers, frequently denoted also as conjugated polyelectrolytes (CPE)s. The influence of the reaction conditions and type of QA on the structure of formed polymers was investigated in a series of eight quaternization polymerizations: 2EP was separately reacted with four quaternizing agents (RX): ethyl bromide (ErBr), nonyl bromide (NoBr), hexadecyl (cetyl) bromide(CeBr) and ethyl iodide (EtI) in acetonitrile solution as well as in bulk. Thus, the influence of (i) the length of aliphatic chain (ethyl, nonyl, hexadecyl), (ii) nature of halide anion (bromide or iodide) and (iii) the effect of solvent (solution or bulk) on the polymer structure could be compared. All QPs were performed in sealed glass ampoule at the temperature of 60 °C for 10 days. The relatively long reaction time was preferred with the aim to reach (i) high conversion of monomer-to-polymer and (ii) highest possible degree of quaternization. For quaternization polymerization procedure see section *3 MATERIALS AND METHODS.*

Table 1 Codes of prepared ionic π-conjugated polymers and alkyl halides (RX) used as quaternizing agents. Polymers prepared in acetonitrile solution are labeled as **sPEP-RX** and polymers prepared in bulk are labeled as **bPEP-RX**.

Polymer Code		**R**		**X**
Materials prepared in acetonitrile solution	**Materials prepared in bulk**			
sPEP-EtBr	bPEP-EtBr	ethyl	(C_2H_5)	Br
sPEP-EtI	bPEP-EtI	ethyl	(C_2H_5)	I
sPEP-NoBr	bPEP-NoBr	nonyl	(C_9H_{19})	Br
sPEP-CtBr	bPEP-CtBr	cetyl	($C_{16}H_{33}$)	Br

The codes of prepared polymers are depicted in **Table 1**. The products were generally labeled as **sPEP-RX** for ionic polymers prepared in acetonitrile solution and **bPEP-RX** for ionic polymers prepared in the bulk. The reaction conditions and characteristics of prepared ionic polymers are summarized in the **Table 2**.

The products prepared via bulk polymerizations, **bPEP-RX**, were obtained in higher yield compared to the products prepared in acetonitrile solution, **sPEP-RX**. Moreover, the yields of **bPEP-RX** were not influenced by the QA aliphatic chain length, which is in contrast with the **sPEP-RX** products, where the yield decreased with the increasing length of aliphatic chain of QA. This could be ascribed to the strongly polar acetonitrile molecules in contrast with aliphatic chain that undoubtedly increase steric demands for enchaining the monomer molecules.

The prepared ionic polymers were characterized also by SEC analysis. However, the determined values of the mass-average, $M_{w,ap}$, and number-average, $M_{n,ap}$, molar masses of **PEP-RX** (relative to PMMA standards) (**Table 2**) should be regarded as the "apparent" ones since ionic polymers are currently adsorbed on the stationary phase, which significantly bias the SEC separation mechanism. We could not ascertain the molar mass values more reliably since these ionic polymers were formed directly in the polymerization process and not by a modification of a non-ionic polymeric precursor of known molar mass (the latter method namely enables much better molar-mass characterization of ionic polymers).[211] An attempt to carry out measurement of light scattering failed due to remarkable absorption of the analyzed solution in selected region of wavelength of laser used (633 nm). Nevertheless, we observed a long time (one week) stability of $M_{w,ap}$ and $M_{n,ap}$ values (within the experimental error ± 10%) for all **PEP-RX** samples, which proves the unexpectedly high stability of these polymers in solution exposed to air. This finding strongly contrasts with the behavior of non-ionic monosubstituted polyacetylenes that mostly visibly degrade in solution exposed to air[15,21] (within a few hours or even during a single SEC measurement).[23] Observed high stability of ionic **PEP-RX** under ambient conditions is important for potential applications of these ionic π-conjugated polyacetylene type polymers.

Degree of quaternization of monosubstituted ionic polymers

The degree of quaternization, defined as X/N mole ratio of products (calculated from the results of elemental analysis data) was found to be around 0.5 (± 0.1) for all prepared polymers, despite that the polymerizations started with equimolar mixtures of 2EP and QA. This indicates that polymer chains were incompletely quaternized, ca. half-quaternized, which may imply alternation of the ionized: [1-(*N*-alkylpyridinium-2-yl)ethane-1,2-diyl] and non-ionized: [1-(pyridine-2-yl)ethane-1,2-diyl] units in the formed polymer chains. It is worth noting that Blumstein et al.[98] as well as Millen et al.[103] reported degree of quaternization of 0.5 for ionic polymers prepared from 2EP activated with HCl. However, in this case was proposed polymerization mechanism in which is firstly formed dimer stabilized by one HCl molecule, which is further transformed into the polymer chain (see *Quaternization polymerization of ethynylpyridines activated with molecular bromine and strong acid* in section *1.3*). This might be reasonably explained by sharing the ionizing proton (cation) by two near-neighboring pyridine rings. In our case, we can only speculate about the real alternating structure of ionized and non-ionized monomeric units, since there are besides the degree of quaternization only indirect evidences for this structure.

The results of the degree of quaternization of polymers prepared via QP activated with alkyl halides (and not with hydrochloric acid) are mostly missing in the literature and fully quaternized ionic polymers are mainly precluded. For the elemental analysis data reported in the literature see **Table 2** in *INTRODUCTION*. The fact that polymers prepared via QP activated with alkylhalide are not fully quaternized is partly surprising and suggests that (i) also non-quaternized (non-activated) monomers are involved in the polymerization process and (ii) the postpolymerization quaternization of formed polymer is not efficient.

Table 2 Reaction conditions of quaternization polymerizations and characteristics of prepared polymers. Yield – isolated polymer yield relative to 2EP, $M_{w,ap}$ - apparent weight-average and $M_{n,ap}$ - apparent number-average molar mass of the polymer, X/N - degree of quaternization of pyridyl side rings defined as X/N mole ratio (calculated from results of elemental analysis, section *3 MATERIALS AND METHODS*).

			Polymerization			**Polymer characterization**	
Sample Code	**X**	**Solvent**	**Temperature [°C]**	**Yield [%]**	**$M_{w,ap}$ x 10^{-3} [g/mol]**	**$M_{n,ap}$ x 10^{-3} [g/mol]**	**X/N**
sPEP-EtBr	Br	acetonitrile	60	53	45	16	0.46
sPEP-EtI	I	acetonitrile	60	50	82	15	0.52
sPEP-NoBr	Br	acetonitrile	60	44	39	23	0.42
sPEP-CtBr	Br	acetonitrile	60	20	33	17	0.45
bPEP-EtBr	Br	none[a)]	60	67	13	10	0.51
bPEP-EtI	I	none[a)]	60	77	21	6	0.61
bPEP-NoBr	Br	none[a)]	60	95	12	6	0.41
bPEP-CtBr	Br	none[a)]	60	82	11	5	0.47

[a)] Quaternization polymerizations performed in bulk.

The structure of monosubstituted ionic polymers

The structures of prepared polymers were investigated by means of ^{1}H NMR, IR and SERS spectroscopies. ^{1}H NMR spectra of all polymers were free of the signal of acetylenic hydrogens (**Figure 1**), which indicates the absence of 2EP as well as its *N*-alkylpyridinium salts in formed polymers. The spectra show a partly resolved multiplet (6.0-9.5 ppm) of aromatic and vinylic protons, a broad signal of protons of CH_2 groups of QA linked to the nitrogen atoms at about 4.5 ppm and a broad signals of others aliphatic protons at around 1.0 ppm. As can be seen, the overall spectral resolution decreases regarding the length of aliphatic chain of QA in the order: Et >> No ~ Ct, which can be ascribed to a decrease in the mobility of pendent groups with increasing length of alkyl chains that prefers mutual attractions of non-polar chains in polar solvent. However, a decrease in the spectral resolution when going from the **sPEP-RX** (polymers prepared by solution polymerization) to the **bPEP-RX** (polymers prepared by bulk polymerization) is much more interesting phenomenon, since it indicates a substantial effect of the reaction conditions on the regularity of polymer chains formed in this catalyst-free polymerization process.

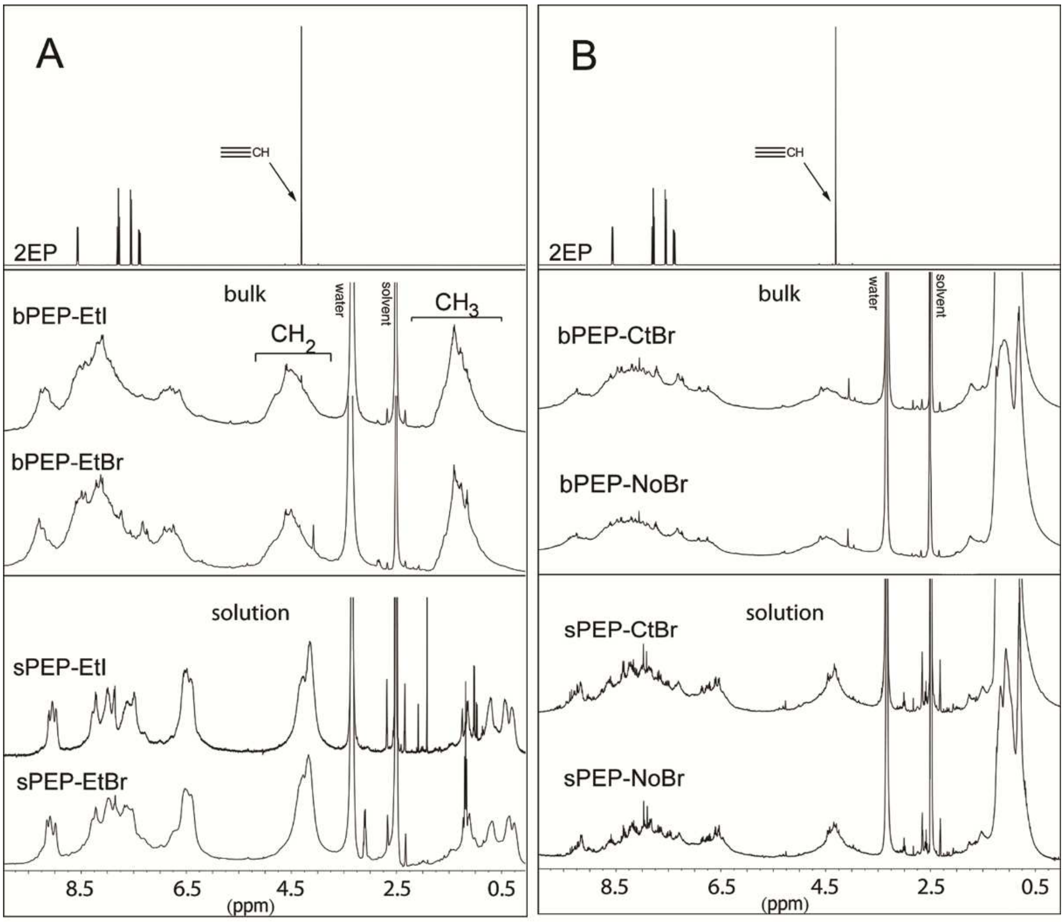


Figure 1 Comparison of ^1H NMR (400 MHz, DMSO-d_6) spectra of monomer 2EP and polymers prepared via quaternization polymerizations of 2EP activated with EtI and EtBr (A) and CtBr and NoBr (B) performed in acetonitrile solution and in bulk.

The most evident difference between ^{1}H NMR spectra of the **sPEP** type and **bPEP** type samples is observed for polymers with *N*-ethylpyridinium-2-yl side groups (**PEP-EtX**). Besides substantially higher spectral resolution, the spectra of the **sPEP-EtX** type samples exhibit well resolved signal at 6.5 ppm, which is typical of the main-chain vinylic protons in high-*cis* polyacetylenes.[21] In contrast, this signal is very weak in the spectra of **bPEP-EtX** type samples, which show a strong signal at around 7.0 ppm that is typical for atactic *cis*/*trans* polyacetylenes. Hence the ^{1}H NMR spectra indicate that the solution polymerizations in acetonitrile give high-*cis* polymers while the bulk polymerizations give atactic *cis*/*trans* polymers.

Although the detailed assignment of bands in IR spectra is complicated due to the complex structure of prepared materials, the characterization of polyacetylene type materials by IR spectroscopy is an important method. The region from 2100 to 2300 cm^{-1} corresponds exclusively to the energy of vibration of triple C≡C bonds (also to the C≡N bonds, but this motive is not expected in the structure of prepared materials) which are well manifested in the IR spectra of acetylenic monomers. The transformation of C≡C bond of monomer into C=C bond of polyacetylene chain is thus well manifested by the diminishing of band at around 2220 cm^{-1}. Furthermore, the C=C bond vibrations of phenyl, pyridyl and polyacetylene chain and C=N bond vibrations of pyridyl can be observed in the region from 1500 to 1700 cm^{-1}.

IR spectra of prepared polymers are in good accordance with the results revealed from the ^{1}H NMR characterization. The transformation of monomers into polyacetylene type polymers is well manifested by the diminishing of C≡C bonds stretching vibration in all IR spectra (see **Figure 2 –** A, B). The most significant IR spectral differences between the **sPEP** type and **bPEP** type polymers are seen in the region around 750 cm^{-1}, which is typical of the out-of-plane ($\gamma_{\text{C-H}}$) vibrational modes of the main-chain hydrogens of monosubstituted polyacetylenes. Well developed band at around 740 cm^{-1} is exclusively observed for polyacetylenes containing long sequences of *cis*-units, typically for polyacetylenes that contain above 80% of *cis*-units. On the other hand, this band is degraded to a shoulder or absent in the IR spectra of atactic *cis*/*trans* or high-*trans* polyacetylenes.[19,212] As it is shown in **Figure 2** - C, D the IR spectra of **sPEP-EtX** show strong band at 740 cm^{-1} that belongs to longer blocks of *cis*-units while the spectra of **bPEP-EtX** show only shoulder shifted to ca. 755 cm^{-1}, which indicates almost absence of the *cis*-blocks.

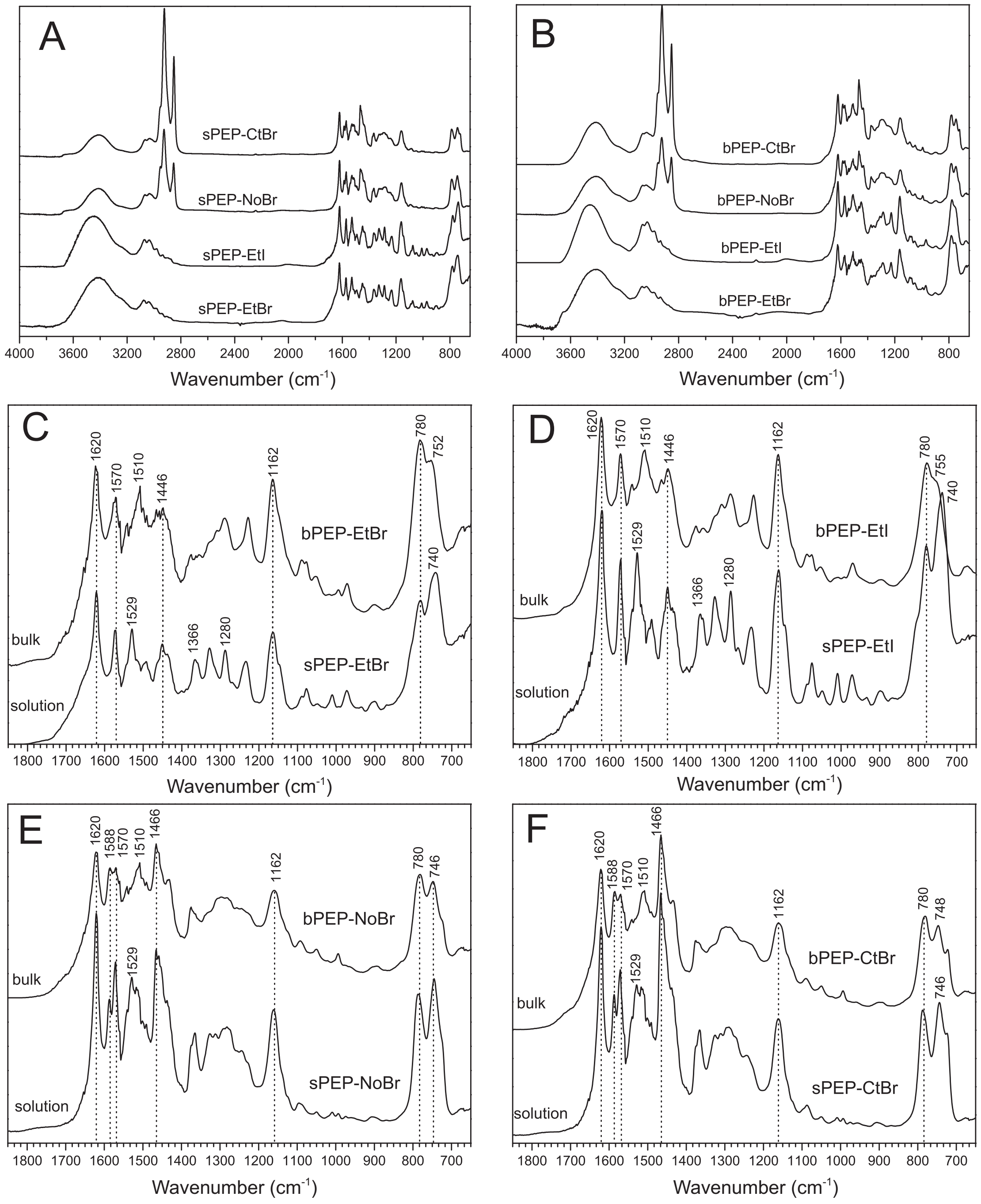


Figure 2 IR spectra of prepared ionic polymers. A – IR spectra of polymers prepared in acetonitrile solution **sPEP-RX**, B – IR spectra of polymers prepared in bulk **bPEP-RX**. C-F - Comparison of the IR spectra of prepared polymers in the region from 700 to 1800 cm^{-1}.

Qualitatively similar though less pronounced spectral differences are seen between **sPEP** type and **bPEP** type polymers comprising longer alkyl chains. Somewhat less apparent IR spectral difference between **sPEP** type and **bPEP** type polymers is seen in the region from 1500 to 1550 cm^{-1}. The band at 1529 cm^{-1} assigned to the $\nu_{\mathrm{C\text{-}C}}$

stretching modes of high-*cis* main chains is well developed (R = Et) or clearly visible (R = No or Ct) only in the spectra of **sPEP** type polymers, whereas the band at ca. 1510 cm^{-1} typical of *trans*-rich polyacetylene main chains dominates this IR spectral region of the **bPEP** type polymers.

In summary, ^{1}H NMR and IR spectra consistently indicate the high-*cis* configuration of polymers prepared by the solution polymerization in acetonitrile and the *cis*/*trans* configuration of the polymers prepared by bulk polymerization. Regarding that both these polymerization methods are the catalyst-free processes, the observed increased *cis*-regularity of **sPEP** type polymers must come from the participation of acetonitrile in the reaction. Coulombic binding of strongly dipolar acetonitrile molecules to growing species should undoubtedly increase steric demands for enchaining the monomer molecules. These demands can be thus regarded as the main reason for the preferred *cis* configuration of polyacetylene chains formed in the presence of acetonitrile.

UV/vis and photoluminescence characterization of monosubstituted ionic polymers

The UV/vis spectra of prepared polymers taken from methanol solutions (**Figure 3**) show almost continuous decrease in absorption from blue to the red region without any distinctive maxima. The shoulders can be seen at around 280 nm and 450 nm; the former should be ascribed to the electronic transitions within pyridine rings while the latter to the transitions in π-conjugated main chains. The absorption in the region from ca. 300 to 400 nm can be also ascribed to the transitions within the charge-transfer (CT) complex formed by the *N*-alkylpyridinium/anion (Br^- or I^-) ion pairs. [152]

As can be seen in **Figure 3**, the high-*cis* **sPEP-EtX** polymers show significantly weaker absorption in the region of the main-chain transitions compared to other samples, which fully corresponds to the reduced delocalization of electrons in high-*cis* polymer chain.

The photoluminescence (PL) spectra of all polymers show emission bands at about 500 nm, regardless the *cis*-content (**Figure 3**). The emission intensities show a correlation with the intensity of absorption bands. The observed uniformity of the emission maxima indicates that the **sPEP** type polymers are composed of the high-*cis* but not all-*cis* chains. As they contain also *trans*-units, they preferably emit light from the excited states located at segments comprising these t*rans*-units, where the excited state energy is lower compared to the *cis* segments.

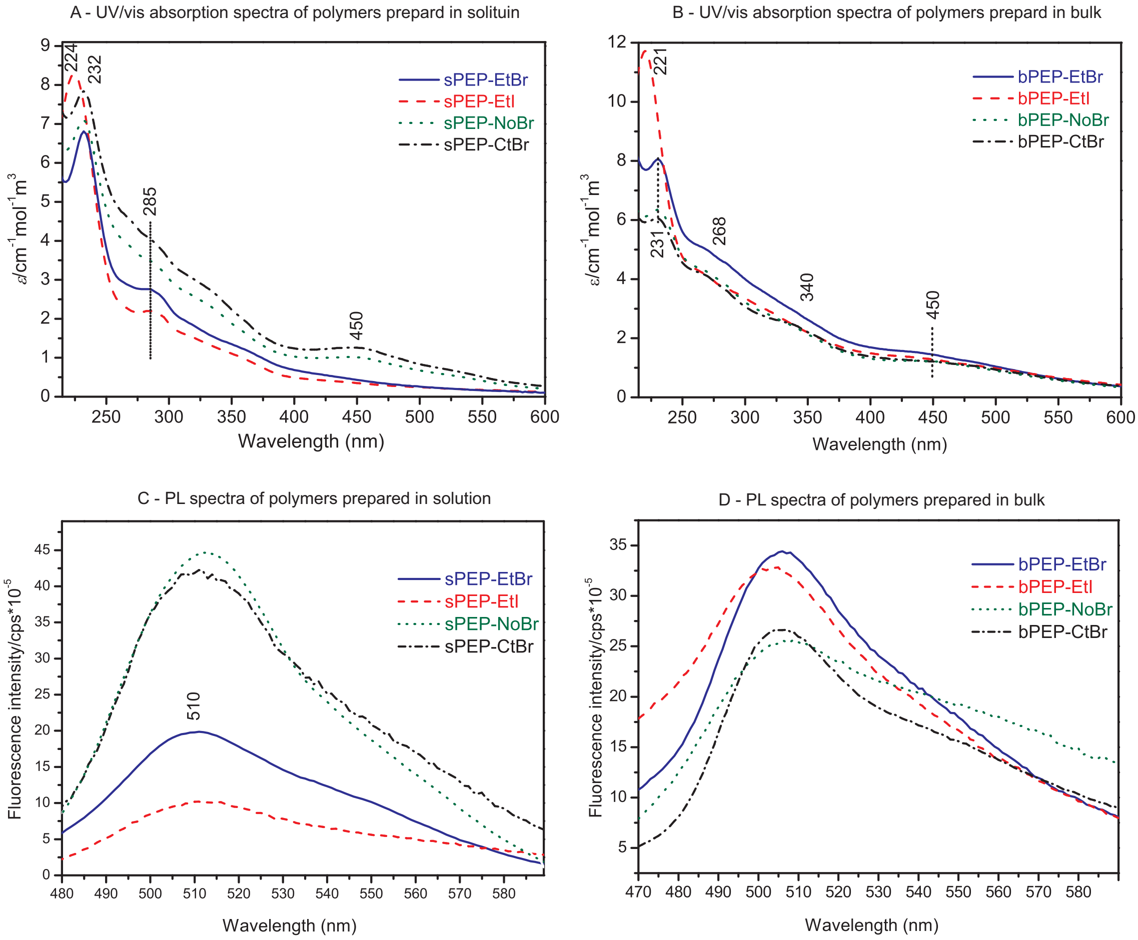


Figure 3 UV/vis absorption spectra and photoluminescence (PL) spectra of prepared ionic polymers measured in methanol solutions; ε is the molar absorption coefficient of the lower energy band. Concentration of samples for PL measurements 5 x 10^{-5} mol dm^{-3} in MeOH, λ_{exc}= 420 nm.

SERS characterization of monosubstituted ionic polymers

Since the luminescence of prepared ionic polymers made impossible direct measurement of Raman spectra, the surface-enhanced Raman scattering (SERS) technique was used, at which the luminescence is damped due to the polymer adsorption on surfaces of silver nanoparticles (Ag-NPs).[201,213]

Moreover, the SERS signal is about several orders of magnitude,[201,213,214] stronger than current enhanced Raman signal. This fact enables measuring the spectra of

Ag-NPs/**PEP-RX** systems. The borate stabilized aqueous Ag colloid (pH of 9.3) possessing negative ζ-potential was used, because cationic **PEP-RX** chains can easily adsorb on the surface of negatively charged Ag-NPs. The concentration of **PEP-RX** in nanocomposites with Ag-NPs was tuned to obtain systems with a strong band of the surface plasmon extinction (SPE), occurring at about 530 nm,[213,215] which indicates the presence of fractal aggregates of Ag-NPs.[156] The optimum concentration was found to be ca. 5×10^{-6} M for all studied **PEP-RX**.

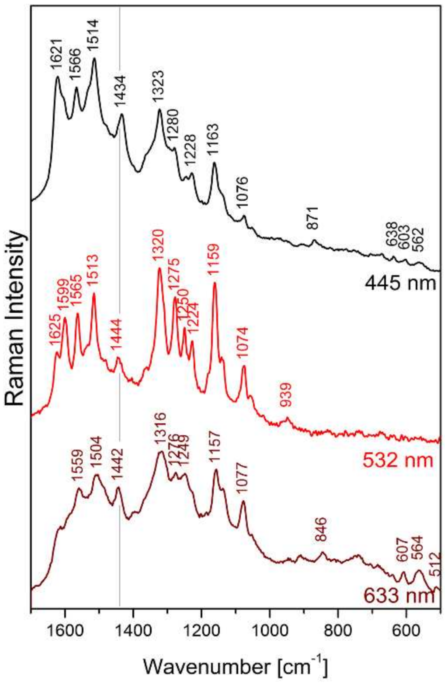


Figure 4 SERS spectra of Ag-NPs/**sPEP-EtI** system studied with excitation wavelength 445 nm, 532 nm and 633 nm.

The SERS spectra of Ag-NPs/**PEP-RX** systems were measured with different excitation wavelengths (see examples in **Figure 4**): (i) $\lambda_{exc} = 445$ nm matches the absorption band of CPEs at 450 nm (see UV/vis spectra in **Figure 3**) and thus fulfills the molecular resonance conditions; (ii) $\lambda_{exc} = 532$ nm matches the surface plasmon extinction (SPE) band of fractal aggregates of Ag-NPs and thus meets the best conditions for the electromagnetic mechanism of the Raman signal enhancement; and (iii) $\lambda_{exc} = 633$ nm does not match any significant band. As can be seen, the best spectral resolution was obtained for the excitation to the SPE band (532 nm), which proves that the electromagnetic mechanism of the SERS gives the highest enhancement. In addition, the spectra taken with different λ_{exc} show small differences in positions of the bands, which is the so called Raman dispersion effect that has already been observed for related polymers including poly(2-ethynylpyridine) and poly(2-pyridinium hydrochloride-2-pyridylacetylene).[103,155,215,216]

The SERS spectra of Ag-NPs/**PEP-RX** systems taken with λ_{exc} = 532 nm (**Figure 5**) exhibit bands assigned to pyridinium ring stretching (at about 1625 cm^{-1} and 1563 cm^{-1}) and C=C-H bending (1157 and 1075 cm^{-1}) modes and the band at 1512 cm^{-1} (**sPEP** type polymers) or 1516 cm^{-1} (**bPEP** type polymers) of the main-chain C=C stretching vibrations.[103,155,156] The spectra of the **sPEP** and **bPEP** type polymers show very similar patterns in the region of stretching bands (1500-1630 cm^{-1}), which can be regarded as characteristic of these polymers. Somewhat lower spectral similarity is seen in the region from 1200 to 1350 cm^{-1} (mainly in-plane deformation modes). The most important are the following features: (i) Raman spectra of the **sPEP** type polymers show better spectral resolution compared to the spectra of the **bPEP** type polymers, which points to increased regularity of the **sPEP** type polymers, and (ii) the band typical for the ring breathing vibrations of non-ionized pyridine rings occurring at around 1005 cm^{-1}[103,216] is practically absent in spectra of all samples, which might be ascribed to strong interactions of the ionized and non-ionized pyridine rings.

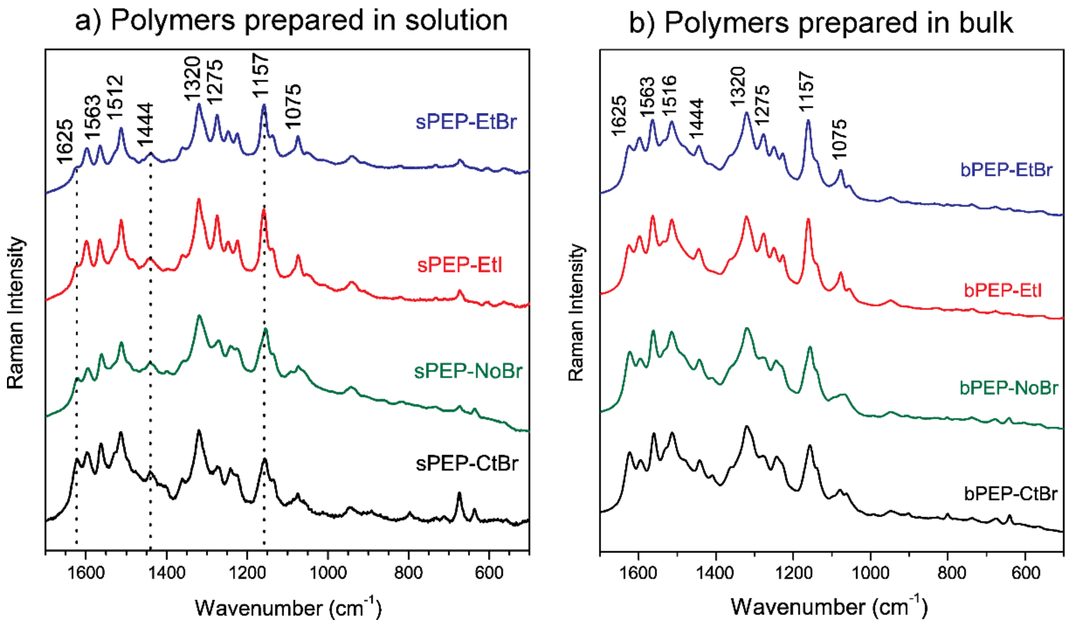


Figure 5 SERS spectra of Ag-NPs/**PEP-RX**. a) Systems based on polymers prepared in acetonitrile solution, b) systems based on polymers prepared in bulk. Excitation wavelength 532 nm.

Solubility of monosubstituted ionic polymers

The solubility of prepared polymers is summarized in **Table 3**. All prepared ionic polymers were soluble in methanol, dimethyl sulfoxide and dimethylformamide, those with ethyl side groups also fully (bromide) or partly (iodide; owing to low hydrophilicity of I^- ions)[217] soluble in water. On the other hand, polymers with longer alkyl side chains were insoluble in water but soluble also in low-polar solvents such as THF and chloroform.

Table 3 The Solubility of prepared ionic polymers. Samples labeled as **sPEP** were prepared in acetonitrile solution and samples labeled as **bPEP** were prepared in bulk.

Solvent	**Sample Code**							
	sPEP-EtBr	**sPEP-EtI**	**sPEP-NoBr**	**sPEP-CtBr**	**bPEP-EtBr**	**bPEP-EtI**	**bPEP-NoBr**	**bPEP-CtBr**
water	Yes	Partly	No	No	Yes	Partly	No	No
methanol	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
dimethyl sulfoxide	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
dimethylformamide	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
tetrahydrofuran	Partly	Partly	Yes	Yes	Partly	Partly	Yes	Yes
chloroform	Partly	Partly	Yes	Yes	Partly	Partly	Yes	Yes

4.2 Preparation of disubstituted ionic polyacetylene type linear polymers and ionic polymer networks via quaternization polymerization

This section represents the main task of presented thesis. The preparation of disubstituted ionic π-conjugated linear polyacetylenes and ionic π-conjugated polyacetylene type networks via quaternization polymerization is investigated in detail. This section is divided into the two parts, according to the character of monomers and quaternizing agents (QA). First, *Part A*, contains optimization of reaction conditions, supporting experiments and polymerization of monomers containing one pyridyl and one internal ethynyl group via quaternization polymerization (QP) activated with monofunctional QA. The results presented in *Part A* were published only partly before the completion of presented work.

The second part, *Part B*, deals with QP polymerization of symmetrical monomers containing two pyridyl groups and one or two internal ethynyl group(s) activated with monofunctional and bifunctional QA.

As it is discussed in *INTRODUCTION*, a number of QPs were reported in the literature since the first Blumstein paper on this topic was published. However, the vide variety of possible monomers suitable for QP is reduce mainly to the 2-ethynylpyrdine (2EP), which contains one pyridyl group and one terminal ethynyl group. This is despite the fact that poly(disubstituted acetylene)s prepared from monomers containing internal ethynyl group generally exhibit better photoluminescence properties and higher thermal stability compared to the poly(monosubstituted acetylene)s. Moreover, the detailed study of reactivity of positional isomers of pyridyl group is missing in the literature. Since the 2EP belongs to the group of monosubstituted acetylenic monomers, the resulting ionic polyacetylenes are also monosubstituted. On the contrary, monomers applied in this section belong to the group of disubstituted acetylenes and thus the ionic disubstituted polyacetylene type polymers result from presented QP.

Two types of QA were applied in this study: benzyl bromide (BBr) as a monofunctional QA and 1,4-bis(bromomethyl)benzene (1,4-BBrMB) as a bifunctional QA. The selection of these QAs was supported by the fact: (i) that the bromide anion appeared as suitable counter ion from the point of view of its reactivity and consequent polymer characterization and (ii) for the rigid structure of the phenyl (phenylene) group, which may play an important role in the case of polymer formation and especially in the case of polymer network formation.

Disubstituted pyridylacetylene based monomers

For the purpose to be subsequently polymerized, a series of disubstituted pyridylacetylene based monomers was prepared. From three positional isomers *ortho*-pyridylacetylene (2P), *meta*-pyridylacetylene (3P) and *para*-pyridylacetylene (4P) were selected only isomers *ortho* and *para*. Since the *meta* isomer exhibited low reactivity in QP process this monomer was not involved in presented study.[95,1431-45]

The synthesis of monomers was performed as a Sonogashira cross-coupling reaction of ethynyl containing species and alkyl halide containing species (see section 3 *MATERIALS AND METHODS*). The solvent was optimized within the preparation of monomers **2PH**, **2PM** and **2PD** (for the abbreviations and monomer structures see **Figure 7**). When reactions were carried out in piperidine, only low yield products were obtained. When triethylamine was used as a solvent, not all the reagents were dissolved, even at elevated temperature. Finally, the mixture of triethylamine and toluene was used as a solvent in reaction process.

The comparison of monomers reactivity was based on two structural variations: the position of N atom of pyridyl (A) and the second pendant of internal ethynyl group (B) as demonstrated in **Figure 6**.

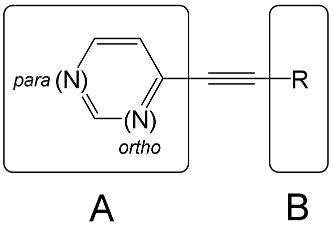


Figure 6 The general structure of monomers used in this study. Two structural variations were considered: A – position of N atom of pyridyl group and B – the second substituent of internal ethynyl group.

Thus, two parallel series for various R pendants were prepared: monomers based on *ortho*-pyridyl (2P) and monomers based on *para*-pyridyl (4P).

The structures of monomers applied in this study are depicted in **Figure 7**. The purchased monosubstituted monomers 2-ethynylpyridine (2EP) and 4-ethynylpyridine (4EP) (in this cases R = H) were used as reference monomers. All disubstituted pyridylacetylene based monomers were synthesized and characterized as a part of presented work (see section *3 MATERIALS AND METHODS*).

The pendant R represent butyl, phenyl, *tert*-butyl phenyl, pyridyl and 4-(ethynylpyridyl)phenyl. Butyl was selected as a simple modification of ethynylpyridines and was also used for the optimization of reaction conditions. Phenyl and *tert*-butylphenyl were selected with the aim to involve the conjugated system of pendant into the conjugated system of formed polyacetylene main chain, which may enhance the absorption and emission properties. *Tert*-butylphenyl may also additionally improve the solubility of prepared polymers. Pyridyl and 4-(ethynylpyridyl)phenyl were selected because of (i) the symmetry of resulting monomer molecules may enhance the possibility of activation of monomer (two pyridyl groups), (ii) the overall conjugated character of monomers [mainly in the case 4-(ethynylpyridyl)phenyl] may positively influenced absorption and emission properties and (iii) also as a promising pendants in the case of network preparation (formation of ionic alternating chains). Phenyl, *tert*-butylphenyl, pyridyl and 4-(ethynylpyridyl)phenyl also provide the rigid structure of monomer and consequently the rigid structure of monomeric unit in formed polymers. Based on the symmetry, prepared monomers could be divided into non-symmetrical and symmetrical. Non-symmetrical monomers contain one pyridyl group and symmetrical monomers contain two pyridyl groups.

The functionality of monomers and quaternizing agents

The functionality is usually understood as the total number of functional groups in the monomer molecule.[218] In the case of monomers used for the QP, the functionality f is represented by ethynyl group (f_{Et}) and by pyridyl group (f_{Py}). The functionality of ethynyl group is the ability of transformation into double bond of polyacetylene chain and the functionality of pyridyl group is the ability to undergo the quaternization reaction. The functionality of QA used in this study is represented by methylbromide group, which can react with nitrogen atom of pyridyl group resulting into *N*-benzylpyridiniumyl bromide. From this point of view, BBr is consider as a monofunctional QA and 1,4-BBrMB as a bifunctional QA.

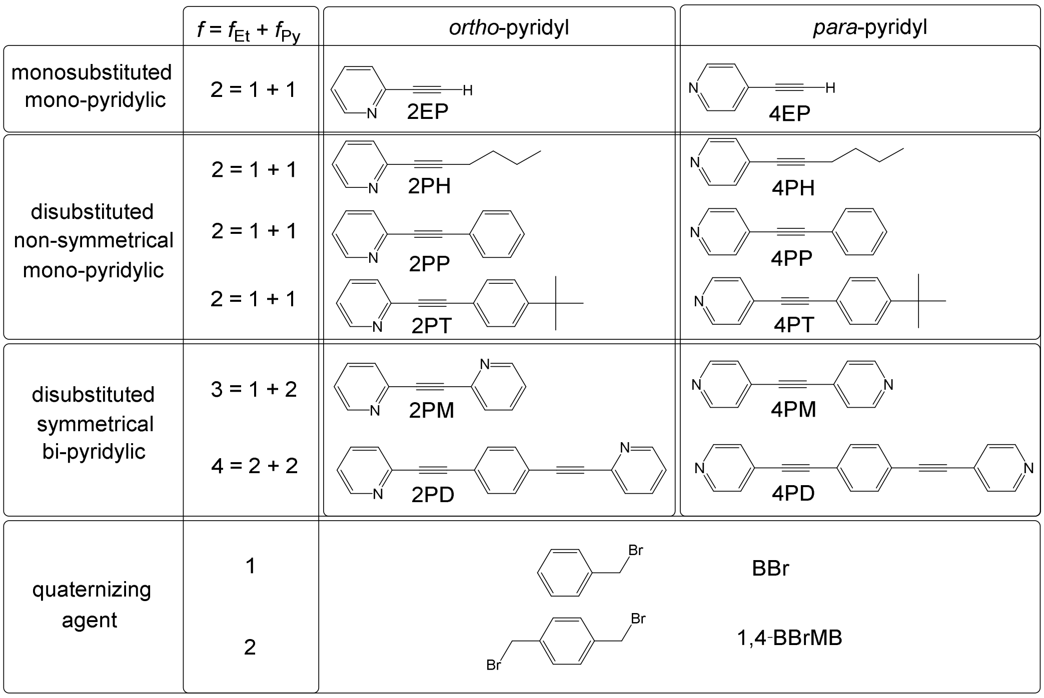


Figure 7 The structures of monomers and quaternizing agents (QA) with appropriate labels used in this study. f – total functionality of compounds, f_{Et} – functionality originating from ethynyl group(s), f_{Py} – functionality originating from pyridyl group(s).

The formulas and codes of monomers are depicted in **Figure 7**. Digits in the codes specify the positional isomerism of the pyridyl substituents (2 – *ortho*-positioned N atom of pyridyl group, 4 – *para*-positioned N atom of pyridyl group). The letters characterized the structure of monomer: EP stands for ethynylpyridine, PH stands hexynylpyridine, PP stands for phenylethynylpyridine, PT stands for *tert*-butylphenylethynylpyridine, PM stands for the monoacetylenic character of bi-pyridylic monomer, PD stands for the diacetylenic character of the bi-pyridylic monomer.

4.2.1 Part A – Optimization of reaction conditions, supporting experiments and quaternization polymerization of non-symmetrical disubstituted monomers

Prior the QPs of synthesized disubstituted pyridylacetylene based monomers the optimization of reaction conditions and a series of supporting experiments were performed.

4.2.1.1 Reaction conditions

A number of QP of mainly monosubstituted monomers activated with various QA under variety of reaction conditions were described in the literature. For the reaction conditions reported in the literature see **Figure 11** (Quaternization polymerization chart) in *INTRODUCTION*. In this study, we have partly assumed the conditions reported in the literature, however, the further optimization was necessary.

The quaternization polymerizations in this study were performed in sealed glass ampoule under the Ar atmosphere (see section *3 MATERIALS AND METHODS*).

Solvent for the QP of disubstituted pyridylacetylene based monomers

The polymers prepared in previous section *4.1* were partly compared with the results reported by Blumstein and thus the reaction conditions described in Blumstein articles were adopted and acetonitrile was used as a solvent.[99,100] However, acetonitrile is not only solvent used for the QP and also alternative polar solvents were described as suitable for QP (see section *1 INTRODUCTION*). Since the selection of solvent influence the product yield, the other possible solvents were considered. Dimethylformamide (DMF) was one of the most frequently applied solvent for the QP reported in the literature resulting in high polymer yields. Thus, the QP of monomer **2PH** was performed in the acetonitrile as well as in DMF under the same conditions. As the product yield in acetonitrile was 39% and in DMF 76%, we decided to use DMF as a solvent for the QP of disubstituted monomers in this work.

Reaction temperature

The QPs reported in this work were carried out at temperature of 100 °C. From the data reported in the literature (see section *1 INTRODUCTION*), the elevated reaction temperature positively influence the reaction kinetic and the polymer yield. Although the QP carried out under temperature higher than 100 °C were also reported in the literature, we have decided not to exceed 100 °C. The high temperature (> 100 °C) may possibly cause the degradation of product (especially when polymer is dissolved in the solution). However, the elevated temperature (100 °C) may cause the side reactions during the polymerization process. To ascertain whereas the reagents could, or could not, individually react under selected conditions, the monomer **2PH** and QA (BBr) were separately heated in DMF under the temperature of 100 °C (blank experiments). The assumption that monomer could thermally polymerize under these conditions was not approved and only unreacted monomer was founded in the reaction mixture after 10 days. However, new signal at 4.68 ppm in ^{1}H NMR spectra was revealed in the second reaction mixture after 10 days. As the only DMF and BBr were present in the reaction mixture, we assigned this signal to the protons of CH_2 group of BBr, which quaternize DMF. This observation indicates that BBr could attack DMF under selected conditions and this reaction could accompany the quaternization polymerization. However, according to ^{1}H NMR measurement this reaction is supposed to proceed only in low extent.

Reaction time

Although the quaternization polymerization is considered to fully proceed in range of days, we have decided to set the reaction time up to 10 days with the aim to achieve: (i) highest possible monomer-to-polymer conversion, (ii) the highest possible degree of quaternization and (iii) the highest possible cross-linking in the case of polymer networks preparation.

Monomer and quaternizing agent mole ratio

According to the proposed mechanism of QP, the BBr activates monomer via quaternization of N atom of pyridyl with Br-CH_2- group. Thus, it is assumed that bromine is present in the form of Br^- anions compensating the positive charge of the *N*-benzylpyridinium moieties and the degree of quaternization of formed polymers is defined as Br/N mole ratio calculated from the results of elemental analysis.

The initial reagents mole ratio was mostly defined as QA/monomer mole ratio in the reaction reported in the literature. However, mainly monomers with one pyridyl group and QA with one halogen atom (functional group) were tested. As the monomers with two pyridyl groups and quaternizing agent with two halogen (Br) atoms are also investigated in this study (see section *4.2.2 Part B*), more precise definition for the initial reagents ratio is defined as Br/N mole ratio (generally X/N mole ratio) rather then QA/monomer mole ratio.

Although the quaternization polymerization proceeds without any catalyst that may control the polymerization process, the resulting product can be partially tuned via the selection of reaction conditions. As mentioned in the previous section, mainly the dependence of polymer yield on the reaction temperature, reaction time and solvent used was described in the literature and the discussion on the degree of quaternization of prepared materials was published rarely. The initial X/N mole ratio was 1 in majority of QP reported in literature. However, the data related to the degree of quaternization of products were mostly missing and fully quaternized products were generally presumed. According to the partial data obtained from the literature, we can however speculate that formed polymers were not fully quaternized in all reported QP (see **Table 2** in *INTRODUCTION*). The formation of only partly quaternized monosubstituted polyacetylene polymers was well demonstrated in the previous section *4.1*, where ionic polymers with degree of quaternization ~ 0.5 were obtained via QP of the stoichiometric mixture of 2EP and alkyl halides (see *Degree of quaternization of monosubstituted ionic polymers* in section *4.1*). The dependence of the degree of quaternization of products on the initial reagents mole ratio was also reported in the article published by our group.[145] It was suggested that the degree of quaternization could be tuned via the QA/monomer (Br/N) mole ratio in the feed. A series QP of 2EP activated with 1,4-bis(bromomethyl)benzene with initial Br/N mole ratio ranging from 0.25 to 1.00 gave polymer networks with Br/N mole ratio ranging from 0.43 to 1.02 (see **Table 4**).

Table 4 The initial Br/N mole ratio and Br/N mole ratio of product resulting from the QP of 2EP activated with 1,4-bis(bromomethyl)benzene.

Sample Code	Initial Br/N mole ratio in feed	Br/N mole ratio of product	Ref.
EPyNet2	0.25	0.43	[145]
EPyNet3	0.33	0.54	[145]
EPyNet4	0.50	0.62	[145]
EpyNet5	1.00	1.02	[145]

It is assumed that the degree of quaternization depends on the monomer and QA used and also on the reaction conditions. When the reaction conditions were already optimized, we have decided to test the relation between initial Br/N mole ratio and the Br/N mole ratio of resulting product. As a model compound was selected monomer **2PM**, which was reacted with BBr with various initial Br/N mole ratio. As it is shown in **Table 5**, the QP with initial Br/N mole ratio 1 gave product **poly(2PM)-C** with Br/N mole ratio 0.51, QP with initial Br/N mole ratio 2 gave product **poly(2PM)-A** with Br/N mole ratio 0.75 and QP with initial Br/N mole ratio 4 gave product **poly(2PM)-D** with Br/N mole ratio 0.88.

Table 5 The initial Br/N mole ratio and Br/N mole ratio of products resulting from the QP of monomer **2PM** activated with benzyl bromide.

Sample Code	Run Code	Initial Br/N mole ratio	Br/N mole ratio of product
Poly(2PM)	C	1	0.51
	A	2	0.75
	D	4	0.88

The increased degree of quaternization is also well observable in IR spectra of products **poly(2PM)-C**, **poly(2PM)-A** and **poly(2PM)-D** shown in **Figure 8**. The $N^+=C$ stretching vibration of pyridiniumyl units at 1620 cm^{-1} is well observed in the IR spectra of all products, however, the intensity of the N=C stretching vibration of non-quaternized pyridyl units at 1574 cm^{-1} decreasing the series **poly(2PM)-C** > **poly(2PM)-A** > **poly(2PM)-D**, which is in good agreement with the decreasing of degree of quaternization in this series (0.88 >0.75 > 0.51).

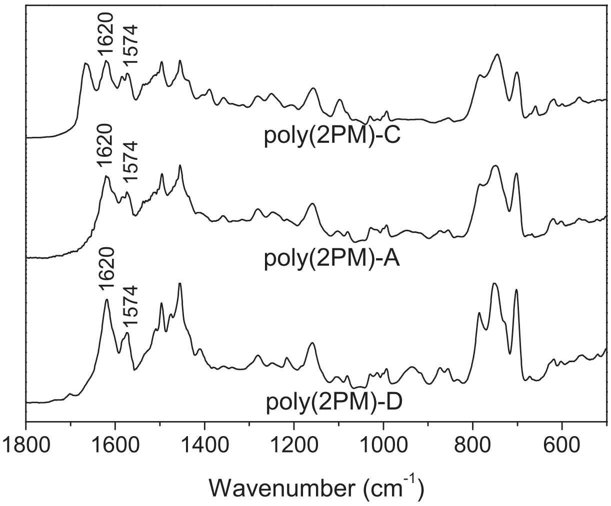


Figure 8 IR spectra of polymers with various degree of quaternization Br/N: Br/N$_{\mathbf{poly(2PM)\text{-}C}}$ = 0.53, Br/N$_{\mathbf{poly(2PM)\text{-}A}}$ = 0.75 and Br/N$_{\mathbf{poly(2PM)\text{-}D}}$ = 0.88.

Based on the results obtained from this experiments, we can assume that Br/N mole ratio of product could be partly tuned via the initial Br/N mole ration. However, the fully quaternized polymer was not obtained from the symmetrical disubstituted monomers even the initial Br/N mole ratio was 4. Thus, we have decided to apply the initial Br/N mole ratio 2 in case of QP activated with BBr with the aim to support the quaternization of monomers. On the contrary, in case of QPs activated with 1,4-BBrMB, which were suppose to results into the polymer networks, the Br/N mole ratio was reduce to 1 with the aim to reach the high cross-linking of polymer structure via ionic alternating chains (resulting from step-growth polymerization, see section *4.2.2 Part B*).

4.2.1.2 Supporting experiments

With the aim to support the discussion on the structure of prepared polymers, a series of additional experiments was performed. Model compounds were reacted under the conditions of quaternization polymerizations and the products were characterized by means of elemental analysis, ^{1}H NMR, IR spectroscopies and MALDI-TOF MS.

Quaternization reaction of DIPY and tolan with BBr.

As it was demonstrated previously in the section *The functionality of monomers and quaternizing agents* (**Figure 7**), monomers applied in this study comprise two types of functional groups (functionalities) in one molecule: (i) pyridyl groups and (ii) internal ethynyl group(s). In order to verify that the presence of both types of functional groups in the monomer is essential for the quaternization polymerization to proceed we have performed experiments in which 4,4-dipyridyl (DIPY) and 1,2-diphenylacetylene (tolan) were separately reacted with an excess of benzyl bromide (BBr) under conditions of the polymerization experiments (see section *3 MATERIALS AND METHODS*). No reaction proceeded in the system tolan/BBr heated at 100 °C for 10 days. On the contrary, the total transformation of DIPY into 4,4′-bis(*N*-benzyl)dipyridinium bromide (BBr-DIPY-BBr), however, no polymer formation was observed in the DIPY/BBr system. The quaternized product BBr-DIPY-BBr was isolated and characterized by means of ^{1}H NMR, MALDI-TOF MS, IR spectroscopies and elemental analysis.

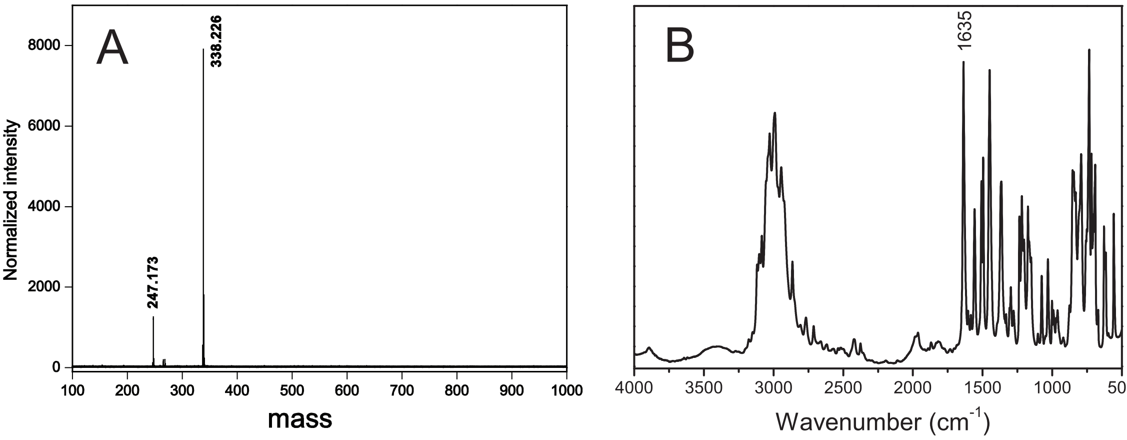


Figure 9 MALDI-TOF MS spectrum (A) and IR spectrum (B) (DRIFTs diluted with KBr) of 4,4´-bis(*N*-benzyl)dipyridinium bromide (BBr-BIPY-BBr).

The results of the elemental analysis (see section *3 MATERIALS AND METHODS*) were in agreement with the theoretical stoichiometry of BBr-DIPY-BBr (Br/N = 1.05, **Table 6**). Also the stretching vibration of the N$^+$=C bonds at 1635 cm^{-1} in the IR spectrum is in good agreement with literature[145] and support the discussion concerning the IR spectra of prepared polymers (the vibration of the N$^+$=C bonds of the polymers is observed in the region 1619-1629 cm^{-1}). The MALDI-TOF MS provided spectrum contains a dominant bromine-free signal with the molar mass of 338 Da which refers to the cationic form of BBr-DIPY-BBr. Moreover, obvious decrement of mass of 90 Da corresponding to benzyl group is observed in the spectrum (for MALDI-TOF MS spectrum and IR spectrum see **Figure 9**). ^{1}H NMR spectrum corresponds to those reported for BBr-DIPY-BBr in the literature.[219] **Figure 10** shows the presumed structure of BBr-DIPY-BBr and ^{1}H NMR spectra of A) BBr-DIPY-BBr, B) 4,4′-dipyridyl (DIPY), and C) benzyl bromide (BBr). The quaternization of the nitrogen atoms in DIPY caused shifts of the ^{1}H NMR signals of the DIPY protons from 8.71 to 9.59 ppm and from 7.84 to 8.81 ppm, respectively. The bonding of the benzyl group to DIPY nitrogen resulted in the shift of the signals of CH_2 protons from 4.70 to 6.01 ppm. These shifts in ^{1}H NMR spectra are typical for the quaternization of pyridyl units with benzyl bromide.[219]

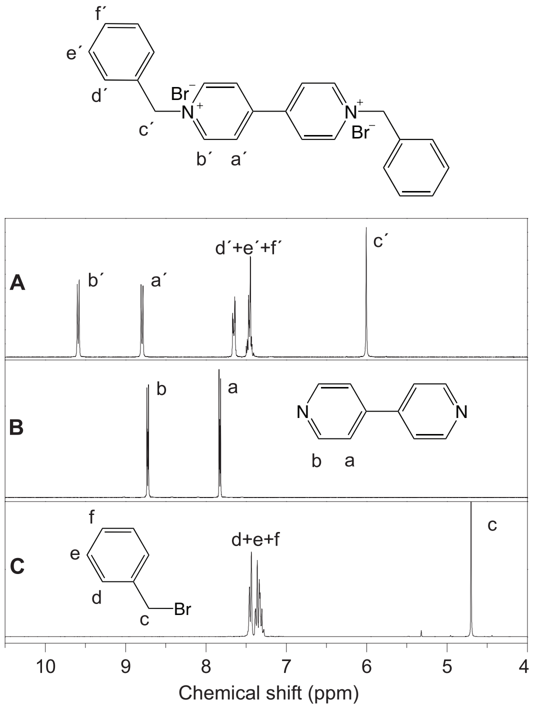


Figure 10 The structure of 4,4′-bis(*N*-benzyl)dipyridinium bromide (BBr-DIPY-BBr) and ^{1}H NMR spectra of A) BBr-DIPY-BBr, B) 4,4′-bipyridyl (DIPY), C) benzyl bromide (BBr), 300 MHz, DMSO-d_6.

The experiments described in this paragraph confirmed that for the polymerization to proceed, the simultaneous presence of pyridyl and ethynyl groups in one monomer molecule is necessary. Moreover, it has been shown that nitrogen atoms of 4-pyridyl groups of DIPY are totally quaternized (by an excess of QA) under the applied conditions although only a partial quaternization of the nitrogen atoms of *para*-pyridyl groups is observed in the case of prepared polymers from symmetrical bi-pyridylacetylene based monomers under the application of the same QA excess (see discussion in section *4.2.2 Part B*).

Moreover, a slight dependence of the position of the ^{1}H NMR signals on the concentration of ionic BBr-DIPY-BBr in the solution has been revealed. It is obvious from **Figure 11** that increasing concentration of BBr-DIPY-BBr in the DMSO-d_6 solution causes a downfield shift of the signals of the protons adjacent to N^+ atoms. We ascribe this behavior to the change of the ionic strength when concentration of polar BBr-DIPY-BBr is increased in the solution.

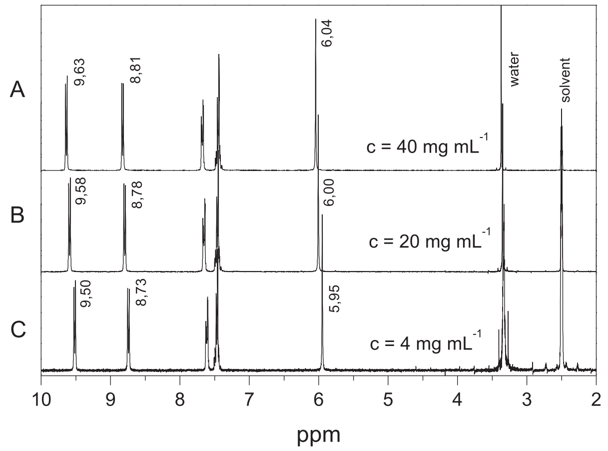


Figure 11 ^{1}H NMR spectra of 4,4´-bis(*N*-benzyl)dipyridinium bromide (BBr-DIPY-BBr), 300 MHz, DMSO-d_6. The influence of the sample concentration on the ^{1}H NMR shifts. A) Concentration of BBr-DIPY-BBr, c = 40 mg ml^{-1}. B) Concentration of BBr-DIPY-BBr, c = 20 mg ml^{-1}. C) Concentration of BBr-DIPY-BBr, c = 4 mg ml^{-1}.

Quaternization reaction of DIPY with 1,4-BBrMB – formation of ionic alternating chains

With the aim to prepare polymer networks, a series of monomers was reacted with bifunctional QA, 1,4-bis(bromomethyl)benzene (1,4-BBrMB). For related discussion see section *4.2.2 Part B*. It was assumed that the network structure results from the simultaneous formation of two types of chains: (i) polyacetylene chain and (ii) ionic alternating chain. To ascertain whether the second type of chains can be formed under selected conditions, the DIPY was also reacted with 1,4-BBrMB. The resulting ionic alternating oligomer poly[*N,N´*-(4,4´-dipyridiniumyl)-*alt*-1,4-dimethylenephenylene dibromide] poly(DIPY-alt-1,4-BBrMB) confirmed the successful formation of this type of alternating chains. The proposed structure of poly(DIPY-alt-1,4-BBrMB) together with ^{1}H NMR spectra of DIPY, 1,4-BBrMB and poly(DIPY-alt-1,4-BBrMB) are depicted in **Figure 12**.

The similar shifts of hydrogen atoms in ^{1}H NMR spectra as in the case of BBr-DIPY-BBr (**Figure 10**) were observed. However, the closer characterization of specific signals was necessary for the determination of the approximate length of oligomeric poly(DIPY-alt-1,4-BBrMB). Thus a series of NMR experiments was performed. The model compound DIPY was reacted with 1,4-BBrMB in variety of initial DIPY/1,4-BBrMB mole ratios (0.25, 0.5, 1, 2, and 4), which consequently allows to assign the ^{1}H NMR signals. Reactions were carried out at room temperature in NMR cuvettes in the DMSO-d_6 that allows the continuous monitoring of process of quaternization.

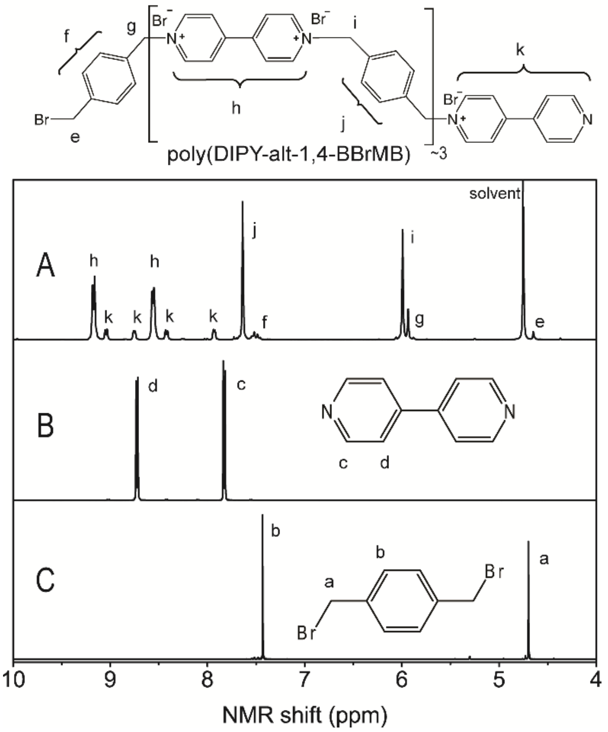


Figure 12 Proposed structure of poly(DIPY-alt-1,4-BBrMB) and ^{1}H NMR spectra (300 MHz): A: poly(DIPY-alt-1,4-BBrMB) in D_2O; B: 4,4´-dipyridyl (DIPY) in DMSO-d_6; C: 1,4-bis(bromomethyl)benzene (1,4-BBrMB) in DMSO-d_6.

The abundance of 1,4-BBrMB in the reaction DIPY/1,4-BBrMB with initial mole ratio 0.25 enables to detect residual 1,4-BBrMB and fully quaternized DIPY in the ^{1}H NMR spectra. With the aim to study the rate of the quaternization, the reaction mixture was monitored at given times: 2 min, 10 min, 15 min, 20 min, 25 min, 1 hour and 3 hours (**Figure 13**). Spectrum at time 2 min shows signals of DIPY (signals “c” and “d”), modified DIPY (signals “k”), aromatic protons of non-reacted 1,4-BBrMB (signal “b”) and aromatic protons of reacted 1,4-BBrMB (signals “f”), protons of CH_2 group of reacted 1,4-BBrMB (signal “g”) and protons of CH_2 group of non-reacted 1,4-BBrMB (signal “a”). Thus, we can assume that immediately after the mixing of reagents, the quaternization of DIPY with 1,4-BBrMB is initiated. Signals of DIPY (“c” and “d”) and modified DIPY (signal “k”) decreasing up to time 25 minutes and up to time 1 hour, respectively. New signals “h” are observed at time 10 min, which remain as only signals of DIPY at time 3 hours. Therefore, we assigned these signals to di-quaternized form of DIPY.

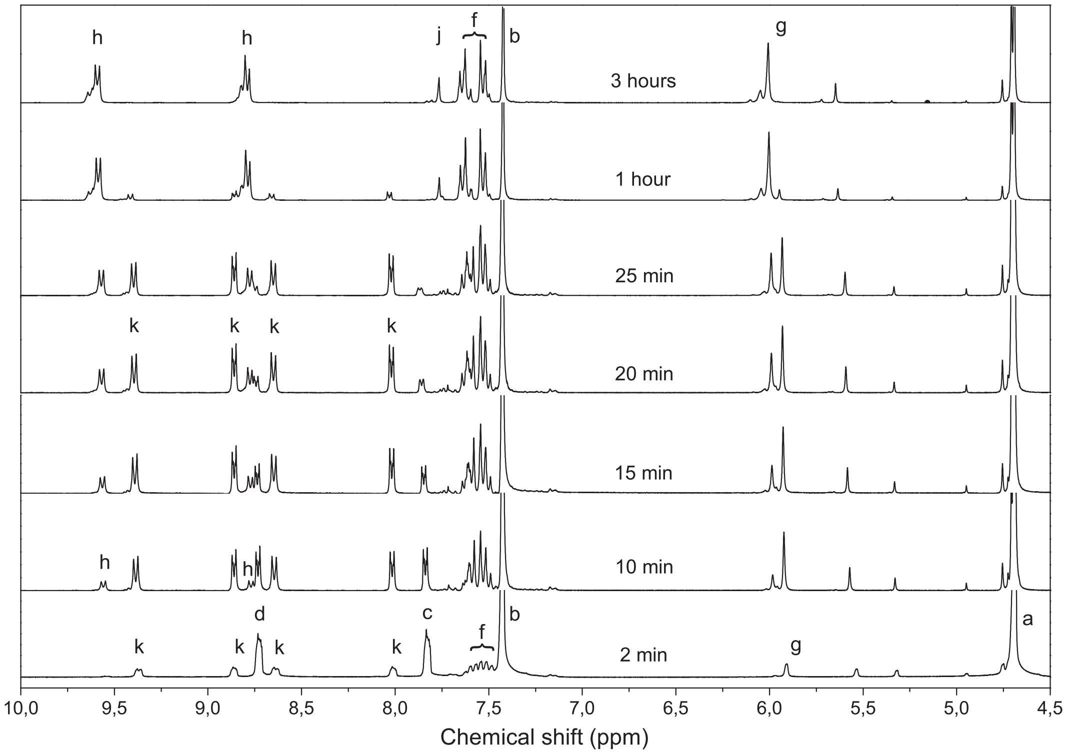


Figure 13 The comparison of ^{1}H NMR spectra of reaction system DIPY/1,4-BBrMB (initial mole ratio 0.25) at times: 2 min, 10 min, 15 min, 20 min, 25 min, 1 hour and 3 hours, 300 MHz, DMSO-d_6.

Since the quaternization reaction with initial DIPY/1,4-BBrMB mole ratio 0.25 fully proceeded at time 3 hours, we have selected this reaction time for the comparison of another reaction systems. The spectra of reactions with initial DIPY/1,4-BBrMB mole ratios 0.25, 0.5, 1, 2 and 4 are depicted in **Figure 14** (the labeling of spectra correspond to the initial DIPY/1,4-BBrMB mole ratios). Signals of fully quaternized DIPY (signals "h") are well manifested in reactions with the abundance of 1,4-BBrMB (spectrum 0.25 and 0.5). On the contrary, in the spectrum of reaction with abundance of DIPY over the 1,4-BBrMB (spectrum 4, **Figure 14**) only fully reacted form of 1,4-BBrMB (signals "j" and "i"), non-reacted DIPY (signals "c" and "d") and modified-DIPY (signals "k") should be observed. Thus, we can assume that signal "j" is assigned to the aromatic protons and signal "i" to protons of CH_2 groups of fully reacted 1,4-BBrMB. Four signals "k" in the spectra 1, 2 and 4 are assigned to the mono-quaternized DIPY, which is in accordance with their intensities and their appearance in the spectra. Similarly, signals "f" in the spectra 0.25, 0.5 and 1 are assigned to aromatic protons of 1,4-BBrMB bounded to DIPY only via one CH_2 group.

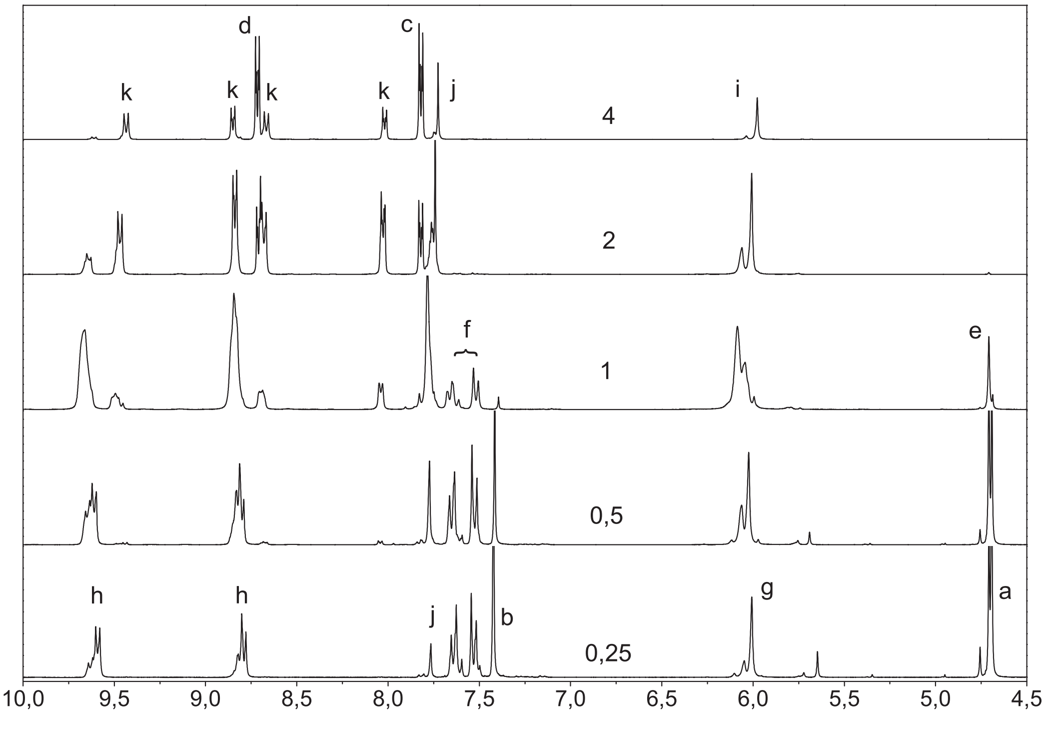


Figure 14 The comparison of ^{1}H NMR spectra of reaction systems DIPY/1,4-BBrMB at time 3 hours. The values 0.25, 0.5, 1, 2 and 4 represent the initial DIPY/1,4-BBrMB mole ratio in the reaction system, 300 MHz, DMSO-d_6.

When the equal DIPY/1,4-BBrMB mole ratio was applied, the only reacted form of both DIPY and 1,4-BBrMB should be present in the reaction mixture. This is partly confirmed in spectrum 1 in **Figure 14**, where no signals of DIPY (expected signals “d” and “c”) and only weak signals of 1,4-BBrMB are observed (signals “a” and “b”).

Moreover, signal of CH_2 protons of 1,4-BBrMB could be present in the reaction mixture in 4 forms: (i) fully reacted 1,4-BBrMB, (ii) non-reacted 1,4-BBrMB, (iii) non-bounded CH_2 group of reacted 1,4-BBrMB and (iv) bounded CH_2 group of reacted 1,4-BBrMB. According to the intensities of these signals in spectra 0.25, 0.5 and 1, we can assign specific protons to the appropriate signals [“i” (i), “a” (ii), “e” (iii) and “g” (iv)]. The assignment of signals to the appropriate protons of presumed structure is depicted in **Figure 12**.

As could be seen in both **Figure 13** and **Figure 14**, the chemical shifts of signals in ^{1}H NMR spectra are slightly shifted. We can speculate that this is caused by the various concentrations of quaternized molecules which may influence the ionic strength of solvent in the same way as it was demonstrated previously in **Figure 11**.

Since all signals in ^{1}H NMR spectra of reaction DIPY with 1,4-BBrMB were assigned, the appropriate length of ionic alternating chain can be estimate from the intensities of specific signals. Poly(DIPY-alt-1,4-BBrMB) was, however, not fully soluble in DMSO-d_6 and therefore the sample was measured in D_2O. The alteration of solvent may influence the chemical shift, but the mutual position and intensities remains the same.

Signals at 9.16 ppm and 8.55 ppm in **Figure 12** were ascribed to the protons of pyridiniumyl units of di-quaternized DIPY (signals “h”). Signals of internal 1,4-BBrMB units (bound by both methylene groups to two different pyridiniumyl groups) were observed in the spectra at 7.64 ppm and 5.99 ppm (signals “j” and “i” respectively). The end groups of the chains were formed by mono-quaternized DIPY groups (signals “k”) as well as 1,4-BBrMB groups (signals “e”,”f” and “g”). According to the ^{1}H NMR signal’s intensity the occurrence of DIPY as an end groups in the oligomer was twice as higher than that of 1,4-BBrMB (**Figure 12**). The intensity of the signals of di-quaternized and mono-quaternized species in ^{1}H NMR spectrum also allowed estimating the length of the alternating chains: the chains consisting of four DIPY units and three to four 1,4-BBrMB units were prevailingly present in poly(DIPY-alt-1,4-BBrMB). This is also in good agreement with Br/N = 0.83 mole ratio (**Table 6**) calculated from the results of elemental analysis (see section *3 MATERIALS*

AND METHODS). The formation of alternating oligomer poly(DIPY-alt-1,4-BBrMB) by the reaction of 1,4-BBrMB and DIPY indicates that the ionic alternating chains of a similar architecture could be formed also in the polymerization systems containing **2PM**, **4PM**, **2PD** and **4PD** monomers and 1,4-BBrMB (see section *4.2.2 Part B*).

Table 6 The initial Br/N mole ratio and Br/N mole ratio of products BBr-DIPY-BBr and poly(DIPY-alt-1,4-BBrMB).

Sample Code	Initial Br/N mole ratio	Br/N mole ratio in product
BBr-DIPY-BBr	2	1.05
Poly(DIPY-alt-1,4-BBrMB)	1	0.83

Reproducibility of performed quaternization polymerizations

To the best of our knowledge, the reproducibility of spontaneous quaternization polymerizations was not reported in the literature previously. Thus, we have decided to perform duplicate experiments. With the aim to verify the results obtained in this work, selected quaternization polymerizations were performed under identical conditions twice. One series of quaternization polymerization activated with benzyl bromide resulting into the linear polymers and two series of quaternization polymerizations activated with 1,4-bis(bromomethyl)benzene resulting into polymer networks were performed. The products of duplicate reactions were characterized only by means of elemental analysis and IR spectroscopy.

Table 7 The initial Br/N mole ratio and Br/N mole ratio of products resulting from the duplicate quaternization polymerizations A and B.

Sample Code	Run Code	Initial Br/N mole ratio	Br/N mole ratio of product
Poly(2PM)	A	2	0.75
	B	2	0.69
Net(2PM)	A	1	0.74
	B	1	0.69
Net(2PD)	A	1	1.04
	B	1	1.09

The Br/N mole ratio of products calculated from results of elemental analysis (see section *3 MATERIALS AND METHODS*) together with the initial Br/N mole ratio in the feed are demonstrated in the **Table 7**. The products labeled as **A** (Run Code) are the prime reaction and theirs characteristics and properties are discussed further in this work (see section *4.2.2 Part B*) and the products labeled as **B** refers to the duplicate reactions. The Br/N mole ratio of the products **A** and products **B** of particular sample differ by 5-8% and thus we can conclude that product with similar Br/N mole ratios were obtained under identical conditions.

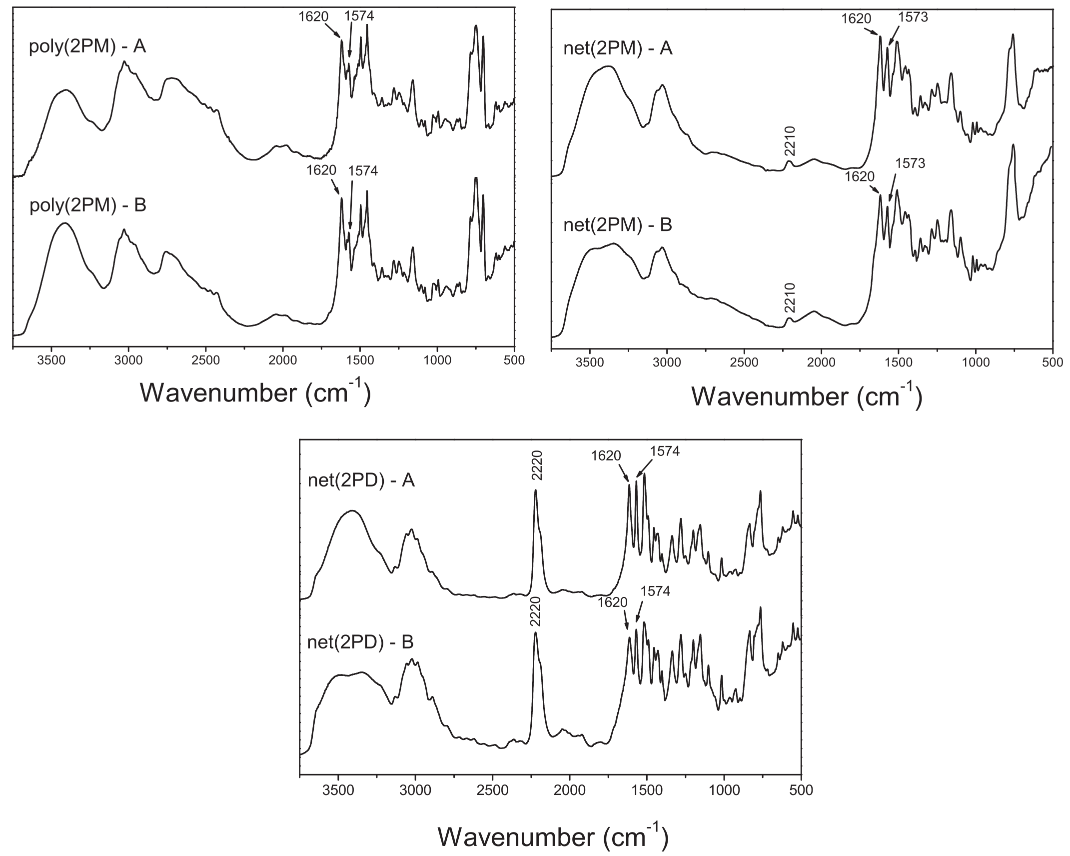


Figure 15 IR spectra of products obtained from duplicate quaternization polymerizations **A** and **B** for samples **poly(2PM)**, **net(2PM**) and **net(2PD)**. DRIFTs, diluted with KBr.

The identical compositions of products **A** and **B** were also well supported by the IR spectroscopy. According to the IR spectra depicted in **Figure 15**, we can assume that products **A** and products **B** contain almost identical structural elements, which is well demonstrated mainly in the finger-print region. Similar degree of quaternization is well demonstrated by comparable ratio of N=C stretching vibrations (1573 cm^{-1} and

1574 cm^{-1}) and N^+=C stretching vibrations (1620 cm^{-1}) intensities in the spectra of products **A** and products **B**. The similar conversion of acetylenic triple bonds into polyacetylene main chain is also well demonstrated by comparable intensities of C≡C stretching vibrations at around 2220 cm^{-1} in spectra of products **A** and products **B** in case of polymer networks **net(2PM)** and **net(2PD)**.

These experiments proved that the quaternization polymerizations exhibit high reproducibility and highly similar products are obtained under identical conditions in the case of preparation of both linear polymers and polymer networks.

4.2.1.3 Quaternization polymerization of 4-ethynylpyridine and 2-ethynylpyridine activated with benzyl bromide

Since the benzyl bromide (BBr) was not reported as a QA in literature previously, it was necessary to clarify its suitability for the QP. Thus the BBr was firstly reacted with 4-ethynylpyridine (4EP) and 2-ethynylpyridine (2EP). 4EP and 2EP are considered as structurally basic monomeric compounds, which can be polymerized via QP. Since the QPs of 4EP and 2EP activated with BBr were supposed to result in linear monosubstituted polyacetylene type polymer, which are generally consider as less stable then theirs disubstituted counterparts, the reaction temperature was reduced to 75 °C. QP of 4EP and 2EP were carried out in DMF for 10 days according to the general procedure (see section *3 MATERIALS AND METHODS*).

In both cases, the solid dark materials were obtained in high yield after purification labeled as **poly(4EP)** and **poly(2EP)**. Both polymers, well soluble in polar solvents such as ethanol, methanol, dimethyl sulfoxide and dimethylformamide, were characterized by means of elemental analysis, IR, ^{1}H NMR and UV/vis spectroscopies.

The elemental analysis of poly(2EP) and poly(4EP)

The elemental analysis proved the presence of bromine in both products [24.8% in **poly(2EP)** to 25.3% in **poly(4EP)**] (see section *3 MATERIALS AND METHODS*). The degree of quaternization (Br/N mole ratio) 0.73 and 0.88 respectively, suggested that highly, but not fully, quaternized monomeric units were present in the prepared materials.

NMR and IR characterization of poly(2EP) and poly(4EP)

Although the NMR is one of the basic characterization of polymeric materials, it is difficult to obtain appropriate and complex information concerning the polymers structure. This is caused mainly by the nonuniformity of formed polymers and consequent broadening of NMR signals. However, a slight difference in ^{1}H NMR spectra of **poly(4EP)** and **poly(2EP)** could be identified (**Figure 16**). Generally, the broad signal at 6.5-10.0 ppm in spectra of both polymers can be ascribed to the aromatic protons of pyridyl and/or pyridiniumyl pendant groups of the polymer main chains and to the phenyl groups of QA. The broad signal at 5.3-6.3 ppm in spectra of **poly(2EP)** and signal at 5.5-6.2 ppm in spectra of **poly(4PE)** were ascribed to the protons of CH_2 groups of *N*-benzylpyridiniumyl moieties as well as to protons of polyene main chain. The overall higher resolution of **poly(4EP)** spectra may be ascribed to higher structural uniformity compared to the **poly(2EP)**. For the relation between ^{1}H NMR spectra and configurational structure see *The structure of monosubstituted ionic polymers* in section *4.1*.

Similarly to the discussion on the IR spectra of ionic polymers prepared in the previous sections *4.1*, the transformation of triple bond into double bonds of polymer main chain is well manifested by absence of band of C≡C bond stretching vibration (around 2100 cm^{-1}) in IR spectra of both **poly(4EP)** and **poly(2EP)** (see **Figure 16**). Formation of *N*-benzylpyridiniumyl units is confirmed by the N^+=C stretching vibration at 1634 cm^{-1} and 1620 cm^{-1} in spectra of **poly(2EP)** and **poly(4EP)**, respectively.[92]

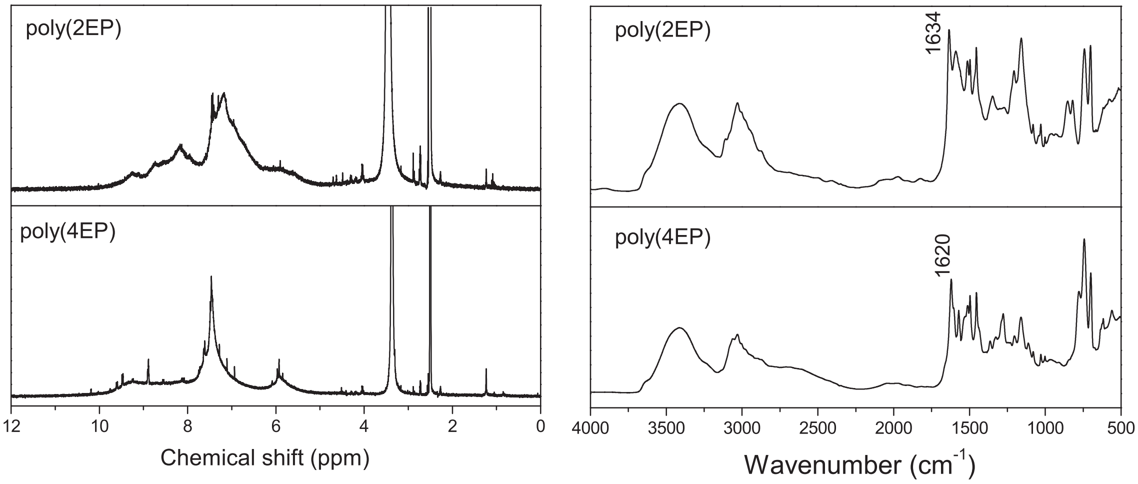


Figure 16 ^{1}H NMR (300 MHz, DMSO-d_6) and IR spectra (DRIFTs, diluted with KBr) of polymers **poly(2EP)** and **poly(4EP)**.

UV/vis characterization of poly(2EP) and poly(4EP)

The absorption spectra of **poly(2EP)** and **poly(4EP)** are shown in **Figure 17**. The formation of π-conjugated segments is well demonstrated by broad absorption up to 650 nm in spectra of both polymers. Generally, as mentioned previously (see section *4.1.*), the absorption up to 350 nm is ascribable charge-transfer (CT) absorption of the ion pairs composed of *N*-benzylpyridinium/bromide anion.[152] The absorption in visible region can be ascribed to π→π* transitions in the polyacetylene main chains.[18] The comparison of UV/vis spectra indicated that **poly(4EP)** exhibits higher extent of conjugation compared to the **poly(2EP)**. We can speculate that the benzyl moieties that quaternize the nitrogen atoms in the pyridine rings in *para*-position [**poly(4EP)**] are distant from the polyacetylene main chains and thus the main chains can possess the microstructure convenient for an achievement of a high conjugation extent. Contrary, the bulky benzyl groups in the vicinity to the polyacetylene main chains in *ortho*-position [**poly(2EP)**] may complicate the optimization of microstructure toward high extent of the main-chain conjugation.

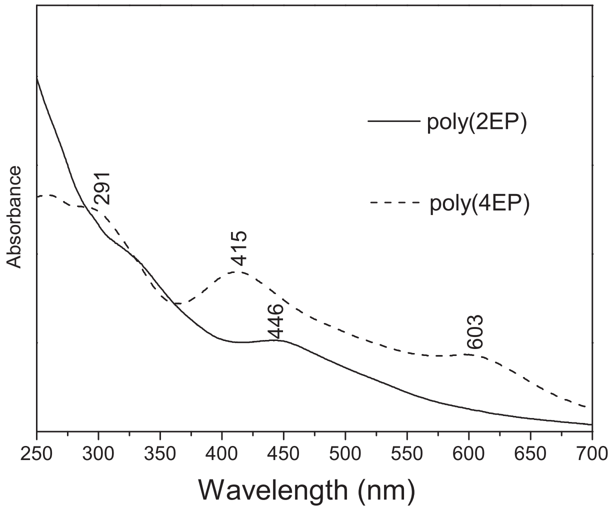


Figure 17 UV/vis absorption spectra of polymers **poly(2EP)** and **poly(4EP)**, measured in methanol. Concentration of samples 2.0 × 10^{-2} mg ml^{-1}.

The successful preparation of ionic π-conjugated monosubstituted polyacetylene type polymers via quaternization polymerization of 2EP and 4EP activated with BBr, proved that BBr is a suitable QA and could be therefore applied as QA also for QP of disubstituted pyridylacetylene based monomers prepared in this work. These experiments have also shown that only monomers with fully transformed acetylenic groups are present in the products. Moreover, the structure dependence on the position of N atom of pyridyl was suggested. The less broadened signals in ^{1}H NMR spectra of **poly(4EP)** may be ascribed to the higher uniformity of formed polymer chain compared to the **poly(2EP)**, which is in good agreement with absorption spectra. **Poly(4EP)** exhibits intense absorption with maxima up to 603 nm ascribed to the higher π-conjugation of polyene main chain.

4.2.1.4 Quaternization polymerization of non-symmetrical disubstituted monomers activated with benzyl bromide

The quaternization polymerizations of six non-symmetrical disubstituted pyridylacetylene based monomers via activation with BBr are discussed in this section. For the monomers structure see **Figure 7 in** *The functionality of monomers and quaternizing agents* in section *4.2*.

QPs are divided into two groups according to the monomers used: products obtained from QP of *ortho*-pyridylacetylene based monomers and products obtained from the QP of *para*-pyridylacetylene based monomers.

The quaternization polymerization of three *ortho*-pyridylacetylene based monomers: 2-(1-hexynyl)pyridine (**2PH**), 2-phenylethynylpyridine (**2PP**) and 2-(4-*tert*-butylphenylethynyl)pyridine (**2PT**) activated with benzyl bromide (BBr) proceeded according to standard procedure (see section *3 MATERIALS AND METHODS*). In all cases, the dark solid products in moderate to high yield labeled as **poly(2PH)**, **poly(2PP)** and **poly(2PT)** were obtained. The prefix “poly” is in this case understood as product of quaternization polymerization and do not refer directly to the polymeric character of materials. The elemental analysis proved the presence of bromine in all products [from 22.7% in **poly(2PT)** to 27.3% in **poly(2PH)**].

The quaternization polymerization of three *para*-pyridylacetylene based monomers: 4-(1-hexynyl)pyridine (**4PH**), 4-phenylethynylpyridine (**4PP**) and 4-(4-*tert*-butylphenylethynyl)pyridine (**4PT**) activated with BBr proceeded according to standard procedure (see section *3 MATERIALS AND METHODS*). In all case, the dark solid products in moderate yield labeled as **poly(4PH)**, **poly(4PP)** and **poly(4PT)** were obtained. Similarly to the *ortho*-pyridyl derived products, the prefix “poly” is in this case understood as product of quaternization polymerization and do not refer directly to the polymeric character of materials. The elemental analysis proved the presence of bromine in all products [from 25.5% in **poly(4PT)** to 28.6% in **poly(4PP)**].

NMR and IR characterization of materials prepared via QP of non-symmetrical monomers

^{1}H NMR spectra of products prepared from *ortho*-pyridylacetylene based monomers are shown in **Figure 18**. As compared to ^{1}H NMR spectra of polymers prepared from 2EP and 4EP [**poly(2EP)** and **poly(4EP)**], ^{1}H NMR spectra of **poly(2PH)**, **poly(2PP)** and **poly(2PT)** exhibit significantly better resolved signals. This could be ascribed to the (i) high structural uniformity of products or (ii) the formation of low molecular mass products. The second explanation may be preferred and only oligomers were assumed as products, since the spontaneous quaternization polymerization proceeded without any catalyst that might control the configurational structure of products.

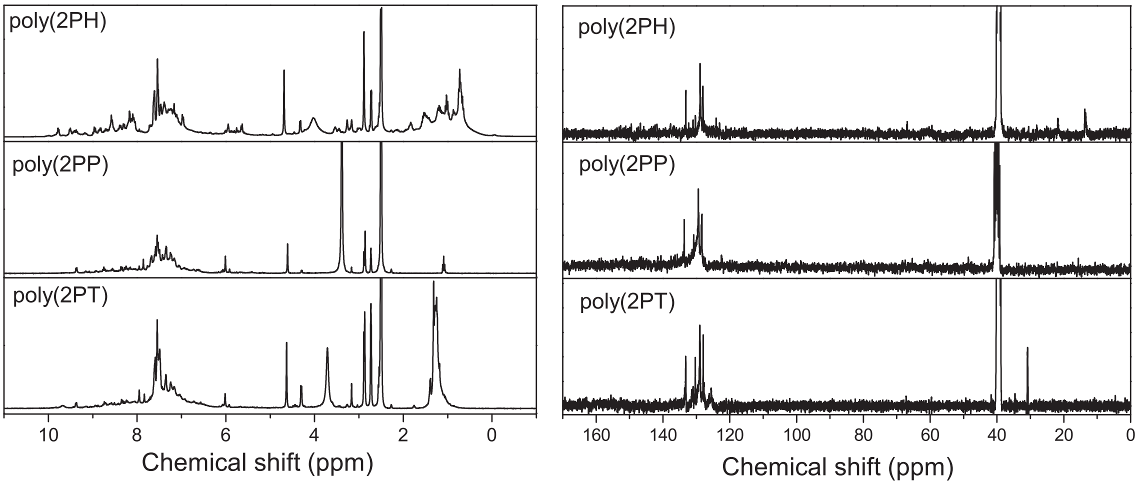


Figure 18 ^{1}H NMR and ^{13}C NMR spectra of products **poly(2PH)**, **poly(2PP)** and **poly(2PT)**, 300 MHz, DMSO-d_6.

However, the dependence of the formed product on the second pendant of ethynyl group could be discussed. The partly broadened ^{1}H NMR spectra of **poly(2PH)** may be ascribed to the formation of short oligomeric chains. The same tendency, however less apparent, could be observed in the case of ^{1}H NMR spectra of **poly(2PP)** and **poly(2PT)**. Generally, the signal at 6.5-10.0 ppm in spectra of all polymers can be ascribed to the aromatic protons of pyridyl and/or pyridiniumyl pendant groups of the polymer main chains and the phenyl groups of QA. The signal at around 6.0 ppm ascribed to the CH_2 group of BBr proved that the major part of monomers was successfully quaternized (activated) with BBr. The signals around 1.0 ppm in the spectra of **poly(2PH)** and **poly(2PT)** are ascribed to the aliphatic protons of butyl or *tert*-butyl pendants, respectively. Signals at 4.6, 2.8 and 2.7 ppm are ascribed to the quaternized form of DMF, which formation was discussed above in the section *4.2.1.1 Reaction conditions*.

^{13}C NMR spectra of products are shown in **Figure 18**. The detailed assignment is, however, complicated, due to the non-uniformity of prepared materials and consequent broadening of signals. Signals at about 130 ppm can be ascribed to the resonance of carbons of (i) conjugated acetylenic backbone, (ii) phenyl groups of *N*-benzylpyridiniumyl moieties, and (iii) pyridyl/pyridiniumyl pendent groups. Since the only low molecular mass products were obtained, the contribution of carbons of conjugated backbone to this signal is, however, speculative. Signals at 13 and 21 ppm in the spectra of **poly(2PH)** are ascribed to the aliphatic carbons of butyl and signal at 30 ppm and 34 ppm in the spectra of **poly(2PT)** are ascribed to the carbons of *tert*-butyl pendants.

^{1}H NMR and ^{13}C NMR spectra of products derived from *para*-pyridylacetylene based monomers exhibit even more resolved signals compared to the spectra of products derived from *ortho*-pyridylacetylene based monomers. Thus, we can speculate that mainly quaternized monomers and/or low molecular mass products were obtained in this case.

^{1}H NMR spectral resolution increases in series **poly(4PH)** < **poly(4PT)** < **poly(4PP)** which indicates that in the case of **poly(4PT)** and **poly(4PH)** the formation of short chains can be considered. Since the spectra of **poly(4PP)** exhibit well resolved signals we have decided to performed two-dimensional NMR experiment (COSY, HSQC and HMBC) with the aim to assign the signals to the proposed structures. From the obtained data, three types of molecules were identified in the product: quaternized monomers (BBr-4PP), quaternized DMF (BBr-DMF) and free BBr. The non-quaternized 4PP was not identified in the product via the performed NMR experiments.

^{1}H NMR and ^{13}C NMR spectra of **poly(4PP)** and presumed structures of BBr-4PP and BBr-DMF are depicted in **Figure 19** and **Figure 20**, respectively. Product also contained free BBr molecules, which is demonstrated by the signal of CH_2 group in both spectra at 4.70 ppm and 35.8 ppm respectively. The signals of phenyl group of free BBr are in the same region as the signals of phenyl groups of BBr-4PP and BBr-DMF. For structure of BBr and corresponding NMR spectra see section *3 MATERIALS AND METHODS*.

The signals around 9.00 ppm and 8.40 ppm in ^{1}H NMR spectrum were assigned to the protons of pyridyl groups of BBr-4PP. The signal at 7.91 ppm is ascribed to the proton of -CH=O of BBr-DMF. The closer assignment of signals in the region from 7.46 to 7.81 ppm was complicated, however, these signals are generally ascribed to the aromatic protons of phenyl groups of BBr-4PP as well as phenyl groups of BBr-DMF and BBr. The signal at 5.90 ppm was assigned to the protons of CH_2 groups of BBr-4PP. Signal at 4.70 ppm was assigned to the protons of CH_2 groups of BBr-DMF and free BBr and signal at 2.89 ppm was assigned to the protons of CH_3 groups of BBr-DMF.

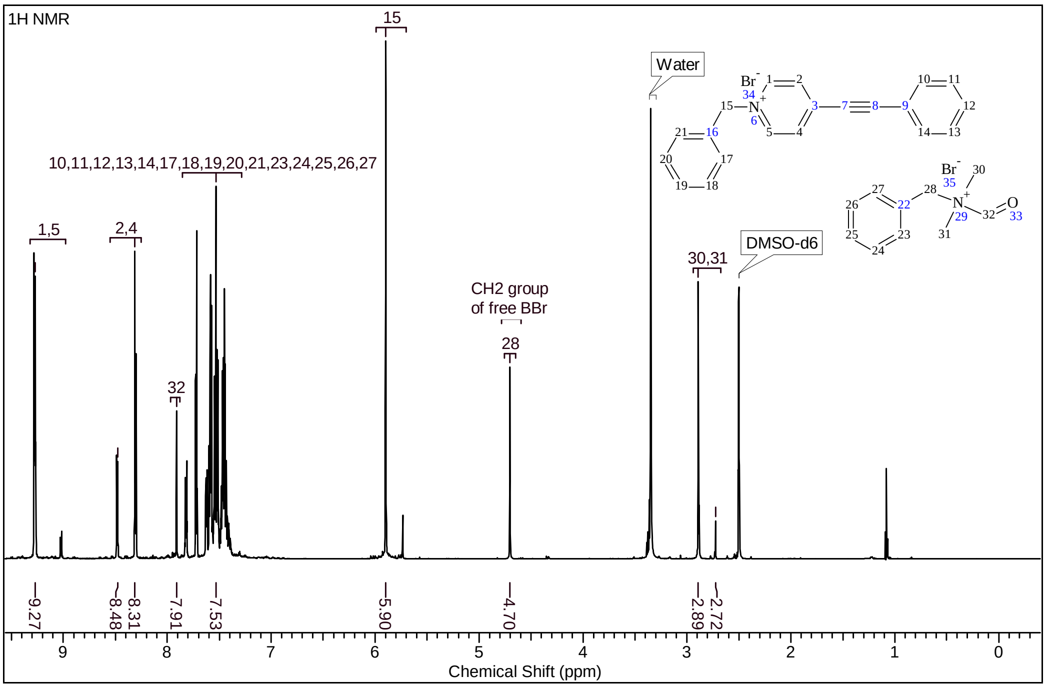


Figure 19 ^{1}H NMR spectrum of **poly(4PP)** with proposed structure of compounds identified in the product. The assignment of signals is based on the two-dimensional NMR experiments.

The signals around 145 ppm in ^{13}C NMR spectrum (**Figure 20**) were assigned to the carbons of pyridyl groups (neighboring to the nitrogen atom) of BBr-4PP and signals at around 139 and 134 ppm were assigned to the quaternary carbons of pyridyl groups and to the quaternary carbons of phenyl groups of BBr pendant, respectively. The signals in the region from 126 to 133 ppm were assigned to the carbons of pyridyl (remote from the nitrogen atom) and to the carbons of phenyl groups. The signal at 119 ppm was assigned to the quaternary carbons of phenyl pendant of 4PP. The carbons of triple bond were demonstrated in the spectra at 103 ppm and 85 ppm. The signal at 63 ppm was assigned to the carbons of CH_2 groups of BBr-4PP, signals at 152 ppm, 67.2 ppm and 48.4 ppm were assigned to the BBr-DMF and signal at 35 ppm to the carbons of CH_2 group of free BBr.

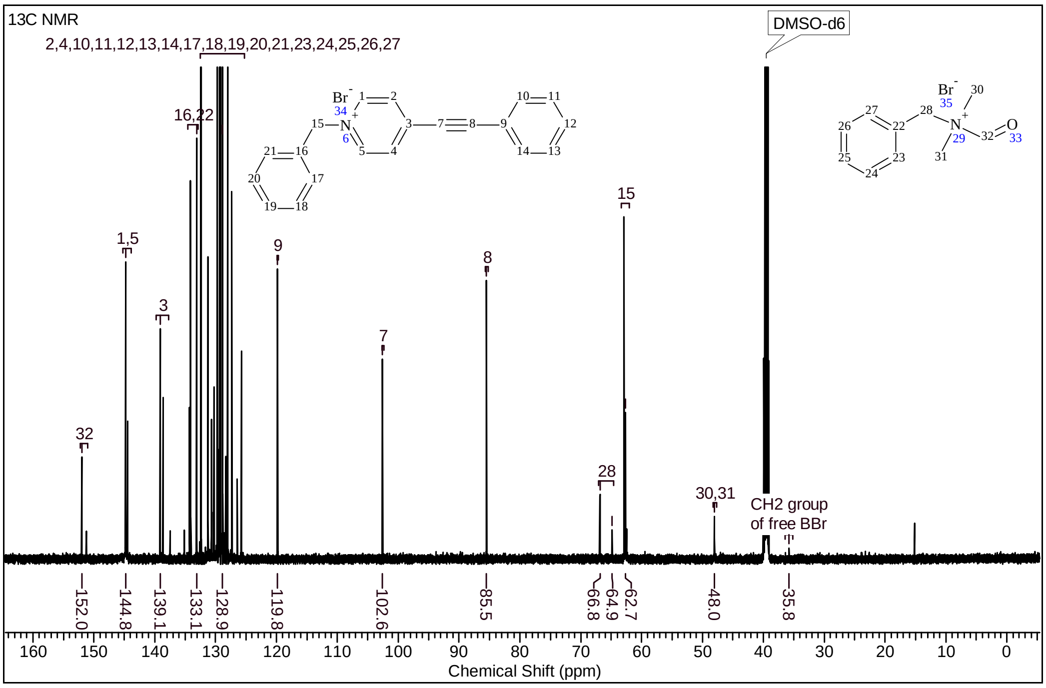


Figure 20 ^{13}C NMR spectrum of **poly(4PP)** with proposed structure of compounds identified in the product. The assignment of signals was based on the two-dimensional NMR experiment.

Since the signals of the triple bond carbons were well demonstrated in the spectra (**Figure 22**), we can assume that mainly quaternized monomers instead of expected polyacetylene type polymers were present in the product. The formation of low molecular weight product was also supported by the resolution of NMR spectra. In the case of polymer formation, the much broadened NMR spectra would be expected. The NMR spectra also confirmed the formation of quaternized form of DMF and the contamination of product by the free BBr, which bias the calculation of degree of quaternization from elemental analysis. The intention to purify the product via washing with diethyl ether resulted only in the reduction of yield and not in the removing of contaminants. This is probably caused by the low molecular character of product BBr-4PP and to its physical interaction with the other components present in the product. As only low molecular product instead of polymer was obtained in this case, the purification process was not optimized.

^{1}H NMR and ^{13}C NMR spectra of **poly(4PH)** and **poly(4PT)** are shown in **Figure 21**. The presented ^{1}H NMR spectra are similar to the spectrum of **poly(4PP)**, however, the spectra of **poly(4PH)** and **poly(4PT)** exhibit partial broadening in the region from 6.5 to 10.0 ppm, which may indicate the formation of short polyacetylene chains. The assignment of signals in NMR spectra is similar to the assignment of NMR spectra of **poly(4PP)**. Additionally, the signals of butyl (1.0 ppm in ^{1}H NMR spectra and 13 ppm and 21 ppm in ^{13}C NMR spectra) in the case of **poly(4PH)** and signal of *tert*-butyl (at 1.0 ppm in ^{1}H NMR spectra and 30 ppm and 34 ppm in ^{13}C NMR spectra) in the case of **poly(4PT)** were observed. Similarly to the **poly(4PP)** we assume that both **poly(4PH)** and **poly(4PT)** were also contaminated with residual BBr-DMF and free BBr.

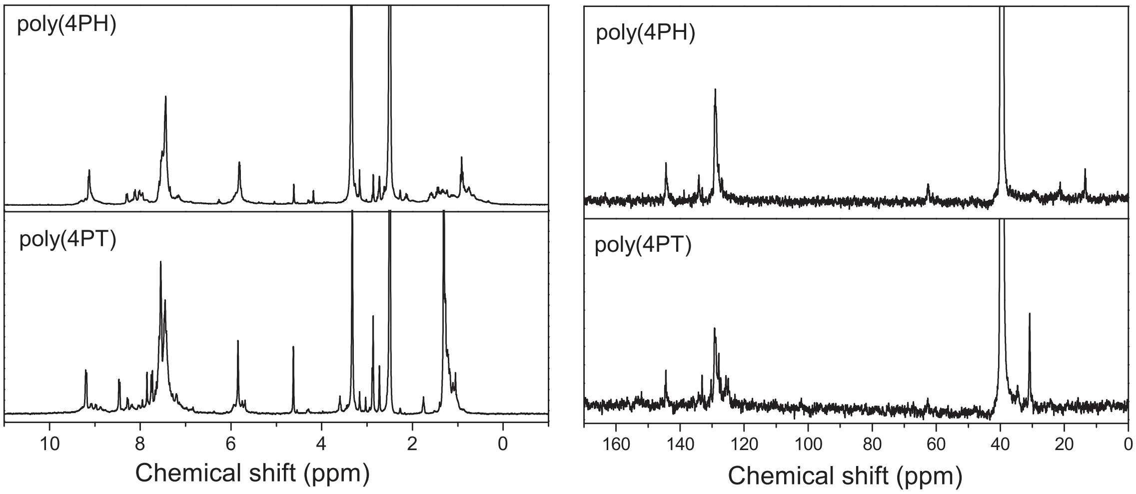


Figure 21 ^{1}H NMR and ^{13}C NMR spectra of products **poly(4PH)** and **poly(2PT)**, 300 MHz, DMSO-d_6.

Figure 22 shows the IR spectra of prepared product **poly(2PH)**, **poly(2PP)** and **poly(2PT)**. The transformation of ethynyl groups of monomer into polymer main chain was well manifested by diminishing of C≡C bond stretching vibration in the case of **poly(2PH)**. However, the low intensity signal at 2219 cm^{-1} and 2221 cm^{-1}in spectra of

poly(2PP) and **poly(2PT),** respectively, was ascribed to the C≡C bond stretching vibration of residual monomer molecules, which were not incorporated into polymer main chains. According to the intensities of these signals, we can assumed that not-transformed monomer molecules are present in the product as a minor part. However, the separation of monomer molecules from low molecular mass product was difficult and thus also free monomers were present in the resulting product. Considering that free monomer molecules were quaternized, the separation from the ionic, low molecular mass product is nearly impossible. This is partly supported by the N^+=C stretching vibration of *N*-benzylpyridiniumyl units (at 1619 or 1620 cm^{-1}) observed in the IR spectra of all products, which imply that highly quaternized products (monomeric units and/or monomers) were formed.

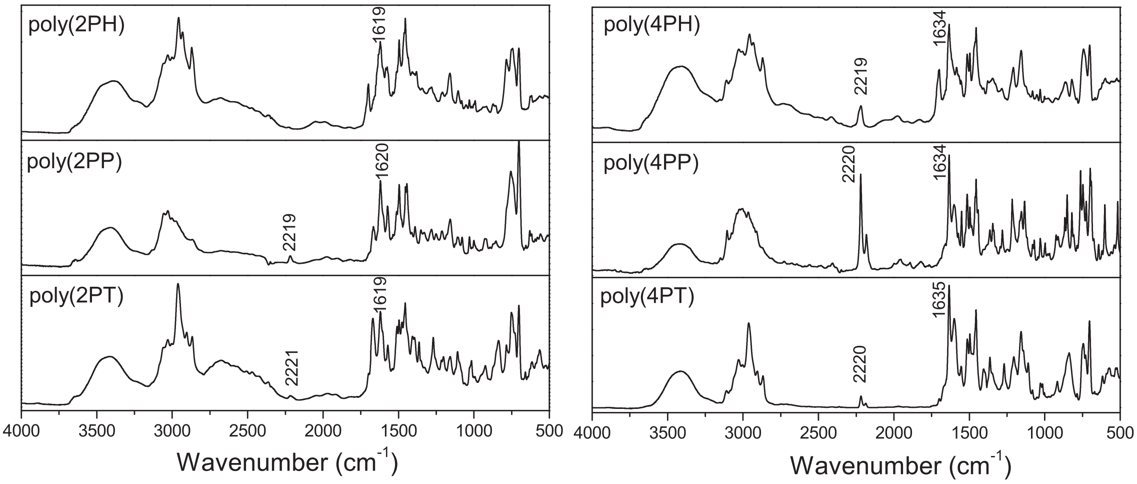


Figure 22 IR spectra of **poly(2PH)**, **poly(2PP)**, **poly(2PT)**, **poly(4PH)**, **poly(4PP)**, and **poly(4PT)**. DRIFTS, diluted with KBr.

IR spectra of products **poly(4PH)**, **poly(4PP)** and **poly(4PT)** are shown in **Figure 22**. In all IR spectra of products were observed significant bands at 2220 cm^{-1} ascribed to the C≡C bond stretching vibration. This may imply that triple bonds were not fully transformed into the double bounds of polyene chain. The intensity of C≡C bond stretching vibration increases in series **poly(4PT)** < **poly(4PH)** < < **poly(4PP)**, which is in good accordance with NMR spectra resolution and imply that only quaternized monomers was formed in the case of **poly(4PP)**. IR spectra of **poly(4PH)** and **poly(4PT)** indicate that triple bonds were partially transformed into a polyacetylene chain, however, we can only speculate about the conversion. The N^+=C stretching vibration of *N*-benzylpyridiniumyl units at around 1634 cm^{-1} presented in all IR spectra suggest that fully or highly quaternized products (monomeric units and/or monomers) were formed.

UV/vis and photoluminescence characterization of materials prepared via QP of non-symmetrical monomers

The UV/vis absorption and photoluminescence spectra of products **poly(2PH)**, **poly(2PP)** and **poly(2PT)** measured in MeOH solution are shown in **Figure 23**. Only the structured UV bands with absorption maximum at wavelength around 300 nm were observed in the spectra of monomers. Similarly to the UV/vis spectra discussed above in section *4.2.1.3* concerning **poly(2EP)** and **poly(4EP)**, the UV/vis spectra of **poly(2PH)**, **poly(2PP)** and **poly(2PT)** contain a partly resolved band at λ_{max} of 336, 339 and 349 nm, respectively, ascribable to the charge-transfer (CT) absorption of the ion pairs composed of *N*-benzylpyridiniumyl/bromide anion[152] which is in good agreement with high content of quaternized monomeric units. However, only low intensity band ascribed to the π→π* transitions in the polyacetylene main chains is observed in the spectra of all products which imply low extent of conjugation of product. **Poly(2PP)** and **poly(2PT)** exhibit absorption with a shoulder up to 390 nm compared to the **poly(2PH)**. We ascribed this to the phenyl and *tert*-butylphenyl pendants which may be involved in the conjugation of main chain.

The monomer **2PH** exhibits no photoluminescence after irradiation and monomers **2PP** and **2PT** exhibit low intensity photoluminescence with maxima at 324 nm and 338 nm respectively. On the contrary, all the prepared products emit in the region from 345 to 470 nm (**Figure 23**). The emission of the products probably originate from the excitation of the partly conjugated polymer chains of polyacetylene type[18] and/or the transition of the CT complex *N*-benzylpyridinium/bromide anion.[220,221] Since the prepared products exhibit only low conjugation, we ascribe the photoluminescence mainly to the CT complex, which is obvious especially in the case of **poly(2PH)**.

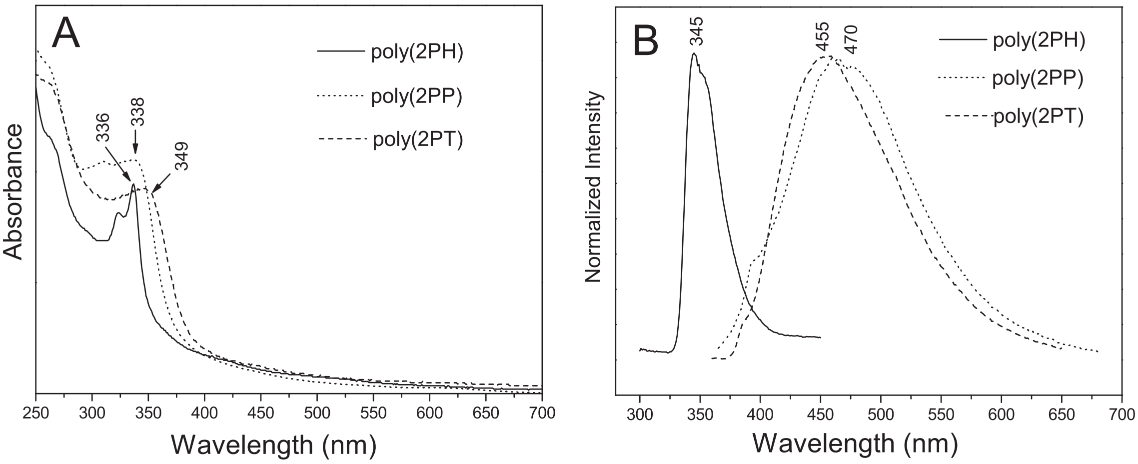


Figure 23 UV/vis (A) and photoluminescence (PL) (B) spectra of **poly(2PH)**, **poly(2PP)** and **poly(2PT)** measured in MeOH. Concentration of samples for UV/vis measurements 2.0×10^{-2} mg ml^{-1}. Concentration of samples for PL measurements was 3.3×10^{-3} mg ml^{-1}, excitation wavelength 260 nm [**poly(2PH)**] and 350 nm [**poly(2PP)** and **poly(2PT)**] was used.

The UV/vis absorption and photoluminescence spectra of products **poly(4PH)**, **poly(4PP)** and **poly(4PT)** measured in MeOH solution are shown in **Figure 24**. Only the structured UV band with absorption maximum at 249 nm (**4PH**), 281 nm (**4PP**) and 306 nm (**4PT**) were observed in the spectra of monomers.

The UV/vis spectrum of **poly(4PH)** exhibits partly resolved bands at λ_{max} of 287, 408 and 520 nm. Similarly, the spectrum of **poly(4PT)** exhibits bands at λ_{max} of 352 and 507 nm. On the contrary, spectrum of **poly(4PP)** exhibit only one band at $\lambda_{max} = 338$ nm. Similarly to the spectra of *ortho*-pyridyl based products, the absorption in UV region, which is observed in all spectra, is ascribed to the CT complex of the ion pairs composed of *N*-benzylpyridinium/bromide anion[152] and the absorption in vis region, observed only in spectra of **poly(4PH)** and **poly(4PT)**, is ascribed to $\pi \rightarrow \pi^*$ transitions in the polyacetylene main chains.[18] This is in good agreement with the assumption that in the case of **poly(4PP)** only quaternized monomer was formed. The low intensity band in vis region in the case of **poly(4PH)** and **poly(4PT)** imply partial conjugation of low molecular products. Higher absorption intensity of *para*-pyridyl based polymers compared to the *ortho*-pyridyl based polymers may be caused by the position of N atom of pyridyl. Similarly to the discussion on UV/vis spectra of **poly(2EP)** and **poly(4EP)**, the bulky benzyl group in *para*-position may allow microstructural optimization toward the conjugation compared to the *ortho*-positioned benzyl group.

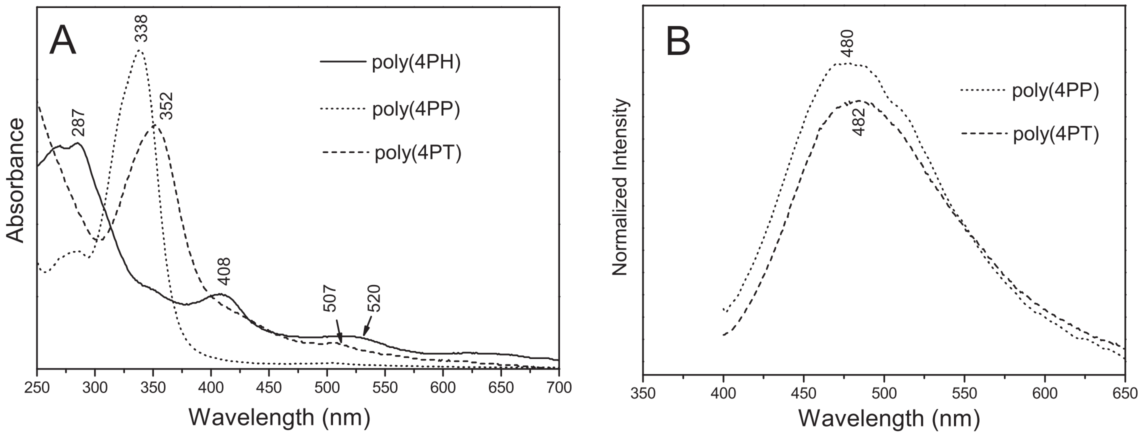


Figure 24 UV/vis (A) and photoluminescence (PL) (B) spectra of **poly(4PH)**, **poly(4PP)** and **poly(4PT)** measured in MeOH. **Poly(4PH)** exhibits no emissions. Concentration of samples for UV/vis measurements 2.0×10^{-2} mg ml^{-1}. Concentration of samples for PL measurements was 3.3×10^{-3} mg ml^{-1}, excitation wavelength 350 nm was used.

The monomers **4PH** and **4PT** exhibit no photoluminescence after irradiation and monomer **4PP** exhibit low intensity photoluminescence with maxima at 346 nm. **Poly(4PH)** exhibits similarly to monomers no photoluminescence and **poly(4PT)** only low intensity photoluminescence with maxima $\lambda_{max} = 482$ nm. However, products **poly(4PP)** exhibit photoluminescence with maxima $\lambda_{max} = 480$ nm (**Figure 24**). Since the product **poly(4PP)** is considered to be a mixture of quaternized monomers (BBr-4PP), quaternized DMF (BBr-DMF) and free BBr we ascribed the emission mainly to the CT complex *N*-benzylpyridinium/bromide anion in junction with the conjugated system of pyridyl-ethynyl-phenyl in the molecule of BBr-4PP.[220,221] From the point of view of absorption and emission properties, the selection of phenyl group as a second pendant of acetylene group confirmed the advantages of interconnection of conjugated system in the monomer structure. The absorption and emission characteristic of prepared ionic materials are summarized in **Table 8**.

Table 8 UV/vis absorption and photoluminescence characteristics of prepared materials.

Sample Code	UV region λ_{max} [nm][a]	Vis region λ_{max} [nm][b]	Excitation [nm][c]	Emission λ_{max} [nm]
Poly(2PH)	336	n/a	260	345
Poly(4PH)[d]	287	408, 520	350	n/a
Poly(2PP)	338	n/a	350	470
Poly(4PP)[d]	352	507	350	480
Poly(2PT)	349	n/a	350	455
Poly(4PT)[d]	352	507	350	482

[a] Position of absorption in UV region; [b] Position of absorption in vis region; [c] Excitation wavelength; [d] Only low molecular mass products or quaternized monomers were obtained.

The overall character of the products prepared from the QP of *ortho*-positioned and *para*-positioned non-symmetrical mono-pyridylacetylene based monomers activated with BBr can be summarized. Since the *ortho*-pyridyl products are considered to be low molecular mass oligomers, the *para*-pyridyl based products are considered to be mostly quaternized monomer molecules. The suggested character of products, based on NMR, IR and UV/vis spectroscopies is depicted on the illustrative diagram in **Figure 25**. However, the proposed character of products may be considered as only apparent.

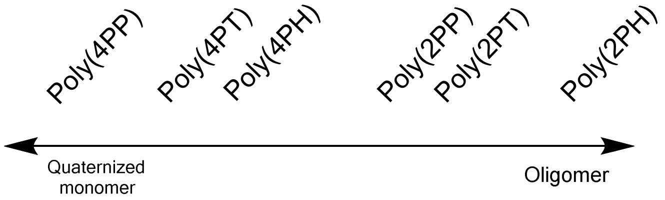


Figure 25 The apparent polymeric character of prepared products from QP of a series of non-symmetrical mono-pyridylacetylene based monomers activated with BBr.

Degree of quaternization of materials prepared via QP of non-symmetrical monomers

Although all the products were characterized by means of elemental analysis and bromine was proved in all prepared materials, the calculation of degree of quaternization is disposable only for *ortho*-pyridylacetylene based products, which exhibit the oligomeric character. Since the *para*-pyridylacetylene based products are considered to be mainly quaternized monomers contaminated with residual reactant, the calculated Br/N mole ratio may not refer to the native degree of quaternization. However, according to the results of EA the content of Br atoms in the product is higher then that of N atoms in all *para*-pyridyl products.

As given in **Table 9**, the resulting degree of quaternization defined as Br/N mole ratio for *ortho*-pyridyl products was close unity and thus we can assume that monomers were inbuilt mostly in quaternized form.

Thermal stability of materials prepared via QP of non-symmetrical monomers

As the mainly quaternized monomers were prepared from *para*-pyridylacetylene based monomers, the TGA curves do not refer to the polymer stability and thus we present only the stability of *ortho*-positioned products. TGA curves recorded for the products **poly(2PH)**, **poly(2PP)** and **poly(2PT)** in N_2 atmosphere are given in **Figure 26**. Two characteristics of the products have been ascertained from these curves: (i) the temperature at which the weight loss of 5 wt% was detected ($t_{95\%}$) and (ii) the weight loss at temperature of 800 °C. The results are summarized in **Table 9**. According to the Reynolds and co-workers[36] studied the thermal stability of quaternized and non-quaternized (dialkylamino)ethoxy-substituted poly(phenylene)s and concluded that the quaternization deteriorated the thermal stability at the onset of the TGA experiment. The authors also proved that the thermal decomposition of quaternized polymers started with releasing hydrogen halide and quaternizing agent at a temperature >150 °C.

Poly(2PH), **poly(2PP)** and **poly(2PT)** exhibit similar $t_{95\%}$ (from 207 °C to 225 °C), however, the mass loss at temperature of 800 °C differ depending on (i) degree of quaternization (ii) character of side pendants. The highest mass loss of **poly(2PH)** presumably associated with the low thermal stability of the alkyl chain and the higher thermal stability of **poly(2PT)** compared to the **poly(2PP)** may be caused by the lower content of BBr units in the molecule, which may be released under elevated temperature.

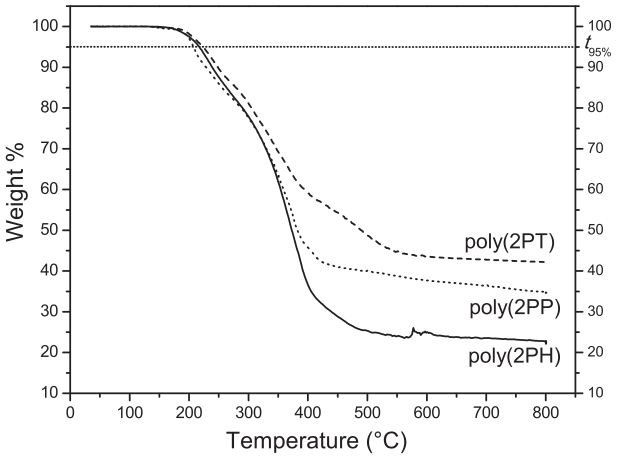


Figure 26 TGA curves of products **poly(2PH)**, **poly(2PP)** and **poly(2PT)** in N_2, step 10 °C min^{-1}.

Table 9 The characterization of prepared products. Yield – products yield after purification, Br/N mole ratio – degree of quaternization of prepared materials calculated from elemental analysis. Characteristics of products from the TGA analysis in N_2 atmosphere, step 10 °C min^{-1}. n/a – data no available due to the low molecular mass character of products.

Sample Code	Yield [%]	Br/N mole ratio in product	TGA	
			$t_{95\%}$ [°C]	Weight loss at 800 °C
Poly(2PH)	73	0.85	217	77
Poly(4PH)	61	n/a	n/a	n/a
Poly(2PP)	74	0.98	207	65
Poly(4PP)	58	n/a	n/a	n/a
Poly(2PT)	81	0.84	225	58
Poly(4PT)	64	n/a	n/a	n/a

Solubility of materials prepared via QP of non-symmetrical monomers

The non-substituted polyacetylene is a totally insoluble polymer. Both mono and disubstituted polyacetylenes with nonionic substituents are mostly reported as well soluble, however, in nonpolar solvents only.[43] The substitution of the polyacetylene chains with ionic groups is a promising way to obtain polyacetylenes soluble in polar solvents. The solubility of products prepared in this section is summarized in **Table 10**. Although, in the case of *para*-pyridylacetylene based monomers the mainly quaternized monomers were obtained instead of ionic polymers, we have also tested the solubility of these products. The solubility of product is influenced mainly by the second pendant of acetylenic groups and not by the molecular mass of the products (oligomer vs. quaternized monomer). All products were well soluble in polar solvents and confirmed the solubility of ionic polymers. Prepared materials were fully soluble in ethanol, methanol, acetonitrile, dimethyl sulfoxide, dimethylformamide and partly soluble in water. The additional solubility of **poly(2PT)** and **poly(4PT)** in THF and acetone was presumably caused by the presence of *tert*-butyl pendants in these materials that generally improved solubility.

Table 10 Solubility of prepared products in solvents of various relative polarity.

Solvent	**Relative polarity of solvent**[a]	**Sample code**					
		Poly(2PH)	**Poly(4PH)**	**Poly(2PP)**	**Poly(4PP)**	**Poly(2PT)**	**Poly(4PT)**
Water	1	Partly	Partly	Partly	Partly	No	No
Methanol	0.762	Yes	Yes	Yes	Yes	Yes	Yes
Ethanol	0.654	Yes	Yes	Yes	Yes	Yes	Yes
Acetonitrile	0.460	Yes	Yes	Yes	Yes	Yes	Yes
Dimethyl sulfoxide	0.444	Yes	Yes	Yes	Yes	Yes	Yes
Dimethylformamide	0.386	Yes	Yes	Yes	Yes	Yes	Yes
Acetone	0.355	Partly	Partly	Partly	Partly	Yes	Yes
Dichloromethane	0.309	Yes	Yes	Yes	Yes	Yes	Yes
Tetrahydrofuran	0.207	No	No	No	No	Yes	Yes
Toluene	0.099	No	No	No	No	No	No
Hexane	0.009	No	No	No	No	No	No

[a] Relative polarity values of solvents taken from literature.[222]

4.2.2 Part B – Quaternization polymerization of symmetrical disubstituted monomers

This section deal with the quaternization polymerization of four symmetrical bi-pyridylacetylene based monomers activated with benzyl bromide as well as 1,4-bis(bromomethyl)benzene into linear ionic π-conjugated polyacetylene type polymers and ionic π-conjugated polyacetylene type polymer networks together with the detailed characterization and testing of prepared materials. The experiments and results of this section are summarized in articles:

Faukner, T., Trhlíková, O., Zedník, J., & Sedláček, J.; Ionic π-Conjugated Polyelectrolytes by Catalyst Free Polymerization of Bis(pyridyl)acetylenes and Bis[(pyridyl)ethynyl]benzenes. *Macromolecular Chemistry and Physics*, **2015**, *216*(14), 1540–1554. doi:10.1002/macp.201500147
labeled as **A2** in Attachments

and

Faukner, T., Zukal, A., Brus, J., Zedník, J., & Sedláček, J.; Ionic π-Conjugated Polymer Networks by Catalyst-Free Polymerization, Photoluminescence and Gas Sorption Behavior. *Macromolecular Chemistry and Physics*, **2016** 0–13. doi:10.1002/macp.201600092
labeled as **A3** in Attachments.

Symmetrical bi-pyridylacetylene based monomers

In the previous section *4.2.1 Part A*, the reaction conditions of quaternization polymerizations were optimized, moreover the quaternization polymerization of disubstituted non-symmetrical mono-pyridylacetylene based monomers was performed. It was concluded that non-symmetrical monomers with butyl, phenyl and *tert*-butylphenyl as a second pendant of triple bond suffered from low polymerization activity and only short oligomers or quaternized monomers were obtained. This section deals with quaternization polymerizations of four symmetrical bi-pyridylacetylene monomers containing as a second substituent pyridyl or 4-(ethynylpyridyl)phenyl.

Similarly to the monomers prepared in previous section *4.2.1 Part A*, both type of monomers were synthesized based on *ortho*-pyridylacetylene and *para*-pyridylacetylene and thus, four monomers were investigated: 1,2-bis(2-pyridyl)acetylene (**2PM**), 1,2-bis(4-pyridyl)acetylene (**4PM**), 1,4-bis[(2-pyridyl)ethynyl]benzene (**2PD**) and 1,4-bis[(4-pyridyl)ethynyl]benzene (**4PD**). The structures of monomers are depicted in **Figure 7** in section *4.2 Disubstituted pyridylacetylene based monomers*.

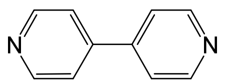
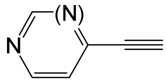
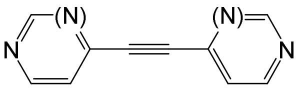
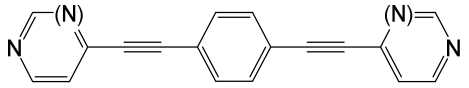
Quaternization polymerization modes

Prior the discussion on the prepared materials let us briefly consider on the possible polymerization modes and resulting products. The chain-growth polymerization of monofunctional acetylenic monomers (e.g. phenylacetylene) by common catalytic polymerization approaches (e.g. with Rh based catalysts) leads to the linear polymer [e.g. poly(phenylacetylene)]. The polymer network could be obtained when the monomer with higher functionality is used (e.g. diethynylbenzene is polymerized into the polyacetylene-type π-conjugated polymer network consisting of ethynylaryl-substituted polyene main chains that are cross-linked by arylene linkers).

Considering quaternization polymerization approach, the structure of product could be tune by the selection of monomer (monomer with various functionality f) as well as the selection of quaternizing agent (QA). The overall relation between monomer and QA structures and product obtained in the quaternization reaction see **Table 11**.

When monomer with two pyridyl groups and no ethynyl group ($f = 2$) is reacted with monofunctional QA ($f = 1$), the only quaternized monomer is assumed to be formed. This is well demonstrated in the reaction of 1,4-dipyridyl (DIPY) with monofuctional benzyl bromide (BBr). No polymerization occurs in this case and only fully quaternized DIPY, 4,4´-bis(*N*-benzyl)dipyridinium bromide, is obtained (see section *4.2.1.2 Supporting experiments*). As shown in **Table 11**, DIPY is a compound with functionality $f = 2$, however, both functionalities originate from the pyridyl groups.

Table 11 The overall relation between monomer and quaternizing agent (QA) structure and product obtained in the quaternization reaction. f_{Et} – ethynyl functionality, f_{Py} – pyridyl functionality, f_{QA} – quaternizing agent functionality.

Monomer		f_{Et}	f_{Py}	**QA**	f_{QA}	**Product**	**Type of chain(s)**	**Ref.**
DIPY		0	2	BBr	1	quaternized monomer	no chain is formed	A2
				1,4-BBrMB	2	linear oligomer	ionic alternating chain	A3
EP		1	1	BBr	1	linear polymer	polyacetylene chain	this work
				1,4-BBrMB	2	polymer network	polyacetylene chain with short cross-links	[145]
PM		1	2	BBr	1	linear polymer	polyacetylene chain	A2
				1,4-BBrMB	2	polymer network	polyacetylene chain and ionic alternating chain	A3
PD		2	2	BBr	1	linear polymer (5% pol.net.)	2 polyacetylene chains	A2
				1,4-BBrMB	2	polymer network	2 polyacetylene chains and 1 ionic alternating chain	A3

The quaternization polymerization of ethynylpyridines (EP)s containing one pyridyl and one terminal ethynyl group ($f = 2$), via activation with BBr leads to the linear ionic polymer, where the linear backbone is formed by π-conjugated polyacetylene type chain. The results of this QP are discussed in section *4.2.1.3 Quaternization polymerization of 4-ethynylpyridine and 2-ethynylpyridine activated with benzyl bromide*. Similarly to DIPY, EP is compound with $f = 2$, however, one functionality originates from ethynyl group and one from pyridyl group.

When monomer with two pyridyl groups and one ethynyl group (e.g. bispyridylacetylene, PM type monomers) ($f = 3$) is reacted with monofunctional BBr, no branching comes into consideration and linear product is obtained. When monomer possessing two pyridyl groups and two ethynyl groups [e.g. bis(pyridylethynyl)benzene, PD type monomers] ($f = 4$) is reacted with monofunctional BBr, the cross-linking comes into the consideration. This assumption presumes that both triple bonds of single monomeric unit are transformed into polyene chain. However, the network formation occurs only in a little part (see section *4.2.2.1 Quaternization polymerization of symmetrical bi-pyridylacetylene based monomers* and related discussion). This could be attributed mainly to the steric effects that could play important role in spontaneous quaternization polymerization.

In mentioned examples QA act only as activation agent allowing quaternization polymerization to proceeds. However, when QA posses more than one alkylhalide [e.g. 1,4-bis(bromomethyl)benzene (1,4-BBrMB)] ($f = 2$), QA could act also as a cross-linker and/or as a monomeric unit. The formation of short cross-links (one cross-link connect two polyacetylenic chains) is assumed when monomer with one pyridyl and one ethynyl group (EP type monomers, $f = 2$) is activated with bifunctional QA. This was lately describe on QP of 2EP with various bifunctional QA in article reported by our group.[145] However, the formation of longer cross-links – ionic alternating chains under selected conditions was not discussed previously in the literature. Thus, the formation of ionic alternating chains of similar composition was studied in the independent experiment in which 1,4-BBrMB was reacted with DIPY. The formation and characterization of obtained oligomeric product, poly[*N*,*N*´-(4,4´-dipyridiniumyl)-*alt*-1,4-dimethylenephenylene dibromide] [poly(DIPY-alt-1,4-BBrMB)] is discussed in the section *4.2.1.2 Supporting experiments*. The formation of structure with similar composition with long cross-links is thus assumed also when monomers possessing one or two ethynyl group(s) and two pyridyl groups (monomers with $f = 3$ or 4, PM and PD type monomers) are activated with bifunctional 1,4-BBrMB. The short cross-links and long cross-links (ionic alternating chains) are demonstrated in **Figure 27**.

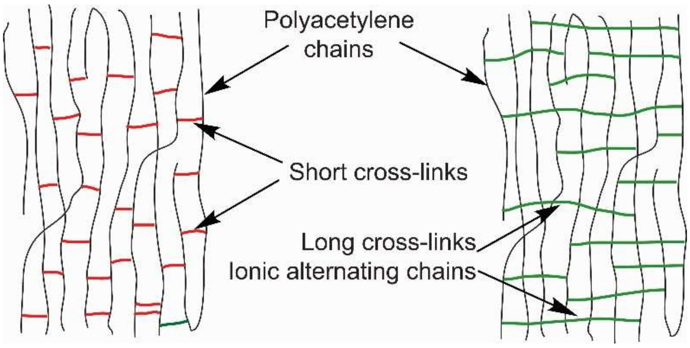


Figure 27 The demonstration of short cross-links resulting from the QP of mono-pyridylacetylene based monomers activated with bifunctional QA (1,4-BBrMB) and long cross-links (ionic alternating chains) resulting from the QP of bi-pyridylacetylene based monomers activated with bifunctional QA (1,4-BBrMB).

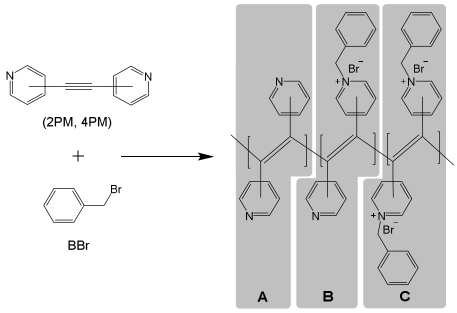
4.2.2.1 Quaternization polymerization of symmetrical bi-pyridylacetylene based monomers activated with benzyl bromide and 1,4-bis(bromomethyl)benzene

Monomers synthesized in this study were polymerized via activation with benzyl bromide (BBr) and 1,4-bis(bromomethyl)benzene (1,4-BBrMB) resulting into linear ionic π-conjugated polyacetylene type polymers labeled as **poly(monomer)** and ionic π-conjugated polymer networks labeled as **net(monomer)**, respectively.

Linear polymers

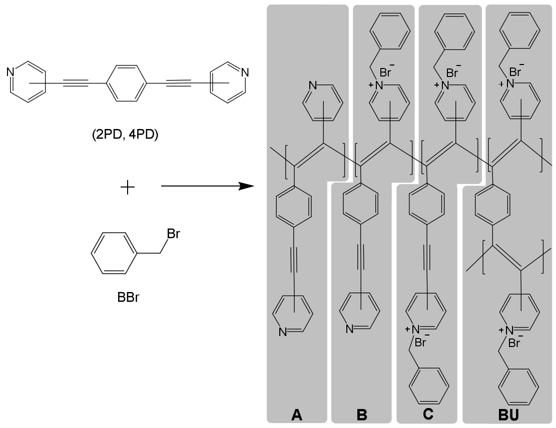
Linear polymers were prepared via quaternization polymerization of four monomers **2PM**, **4PM**, **2PD** and **4PD** activated with BBr as a QA without any additional catalyst or initiator according to the procedure described in section *3 MATERIALS AND METHODS*. Structure, thermal stability, absorption/emission properties and solubility of linear polymers were determined by means of various methods. With the aim to support (i) the activation (quaternization) of monomers and (ii) the degree of quaternization of obtained linear polymers, the initial Br/N mole ratio was set to 2 that corresponded to the QA/monomer mole ratio 4. The discussion on the initial Br/N mole ratio and Br/N mole ratio of products see section *4.2.1.1 Reaction conditions*.

In all cases the dark solid polymers were obtained in high yield labeled as **poly(2PM)**, **poly(4PM)**, **poly(2PD)**, and **poly(4PD)**. In the case of quaternization polymerization of **2PM** and **4PM** monomers, linear polymers possessing monomeric units of various degrees of quaternization can be expected as the product. Three types of monomeric units can be present in polymer: A) non-quaternized units, B) mono-quaternized units, and C) di-quaternized units (**Scheme 2**).



Scheme 2 Quaternization polymerization of PM type monomers with benzyl bromide. A, B, and C are the contemplated monomeric units in the polymer.

In the case of quaternization polymerization of **2PD** and **4PD** monomers a chain-branching comes into consideration, which could possibly lead to the network formation (**Scheme 3**). This may be expected due to the presence of two ethynyl groups in one monomer molecule, since both these ethynyl groups can be transformed into the polyacetylene type backbone. Really, the products **poly(2PD)** and **poly(4PD**) contained an insoluble fraction (about 5 wt%), which can be ascribed to the cross-linking of the polymer chains. As the content of the insoluble fraction in both polymers was very low we have dealt only with the major soluble parts of **poly(2PD**) and **poly(4PD)**. Before all the characterization of **poly(2PD)** and **poly(4PD)**, the minor insoluble part was removed by filtration. The formation of only linear or branched polymers in the case of PD base products may be ascribed to the sterical properties of growing polymer chains, which complicate the transformation of both triple bonds into polymer chain.



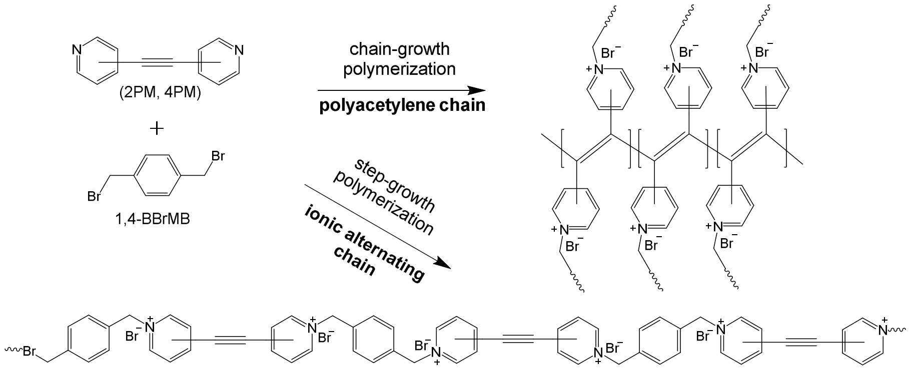
Scheme 3 Quaternization polymerization of PD type monomers with benzyl bromide. A, B, and C are contemplated linear monomeric units of polymer. BU represents an example of branching unit in the polymer.

Polymer networks

With the aim to prepare the ionic π-conjugated polyacetylene type polymer networks instead of linear polymers we have decided to enhance the functionality of QA. Various bifunctional quaternizing agents were tested in article reported by our group[145] and 1,4-bis(bromomethyl)benzene (1,4-BBrMB) appeared as a most suitable for the network formation. Thus, the same series of monomers, **2PM**, **4PM**, **2PD** and **4PD**, as in case of preparation of linear polymers, was polymerized via quaternization polymerization activated with 1,4-BBrMB as a QA. In all cases the dark solid insoluble materials were obtained in high yield as only product labeled as **net(2PM)**, **net(4PM)**, **net(2PD)** and **net(4PD)**. Structure, thermal stability, absorption/emission properties and surface characterization of polymer networks were determined by means of various methods.

When the bifunctional QA is reacted with the monomers possessing two pyridyl groups, the process of step-growth polymerization, in which QA act as a monomer, is assumed (see *Quaternization polymerizations modes* in section *4.2.2*). Therefore, with the aim to achieved the high cross-linking of polymer networks the initial Br/N mole ratio was reduced to 1, which correspond to the one pyridyl group per one methylbromide group.

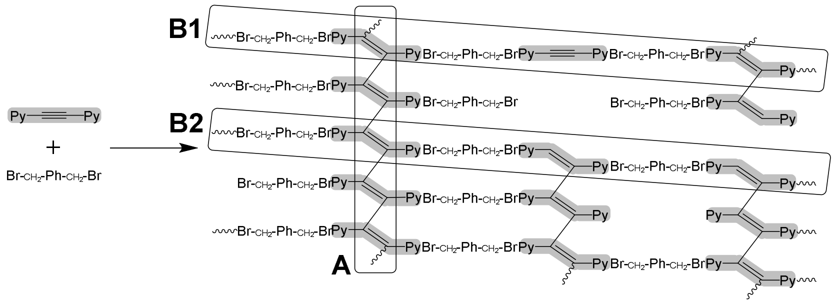
All the monomers discussed in this section contain two pyridyl groups in one molecule. Together with the bifunctional character of QA the formation of two different types of polymer chains can be assumed in **net(2PM)**, **net(4PM)**, **net(2PD)** and **net(4PD)**: the polyacetylene type chains and ionic alternating chains. The polyacetylene type chains result from the chain-growth polymerization of activated ethynyl groups of the monomer molecules, which are transformed into vinylene groups of the main chains. The ionic alternating chains result from the step-growth quaternization interconnecting of pyridine moieties of the monomer with haloalkyl groups of 1,4-BBrMB. The formation of two types of polymer chains is depicted in **Scheme 4** for the polymerization of PM type monomers.



Scheme 4 Quaternization polymerization of PM type monomers activated with 1,4-BBrMB. Two types of main chains can be simultaneously formed: polyacetylene chains and ionic alternating chains.

Polymer networks prepared from PM type monomers

The proposed structure of polymer networks prepared from PM type monomer with 1,4-BBrMB is shown in **Scheme 5**. The π-conjugated polyacetylene type chains are labeled as A and ionic alternating chains are labeled as B1 and B2. As each molecule of PM type monomer contains one ethynyl group and two pyridyl groups, each PM molecule can potentially give rise to a branching unit in the polymer. If all the groups of a PM monomer are involved in the polymerization four chains will emanate from the monomeric unit.

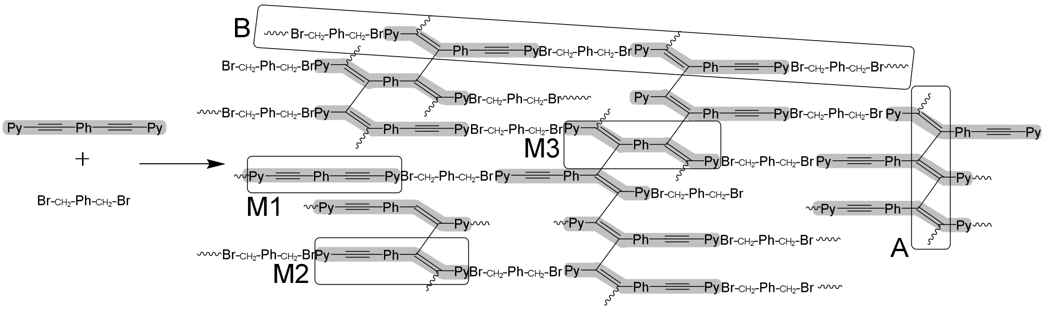


Scheme 5 Proposed structure of the polymer networks obtained from the quaternization polymerization of **2PM** and **4PM** into **net(2PM)** and **net(4PM)**, respectively. A - polyacetylene type chain, B1 and B2 - ionic alternating chains. Ph - 1,4-phenylene, Py - pyridyl, Br - bromine that was not involved into quaternization, PyBr (BrPy) - pyridiniumyl bromide.

However, we can speculate that the real extent of branching in **net(2PM)** and **net(4PM)** is lower and that two types of ionic alternating chains (B1 and B2) could be present in these polymers. Chain B1 in **Scheme 5** represents the ionic alternating chain containing monomeric units incorporated into polyacetylene chains (branching units) and also monomeric units which are not incorporated into polyacetylene chains (linear units). Contrary, chain B2 contains only monomeric units incorporated into polyacetylene chains (branching units). The presence of B1 and B2 chains in **net(2PM)** and **net(4PM)** is discussed in connection with the occurrence of signals of ethynyl groups in ^{13}C NMR an IR spectra of prepared polymer networks in section 4.2.2.2 *Structural characterization of linear polymers and polymer networks*

Polymer networks prepared from PD type monomers

The proposed structure of the polymer networks prepared from PD monomers is shown in **Scheme 6**. Similarly to the polymerization of PM type monomers, the quaternization polymerization of PD type monomers most probably leads to the polymer networks containing polyacetylene type chains (labeled as A) and ionic alternating chains (labeled as B). Since PD monomers contain two ethynyl groups, three different types of monomeric units can be included in the ionic alternating chains: (i) units in which none of the ethynyl groups are incorporated into polyacetylene chain (linear units labeled as M1 from which two chains emanate), (ii) units in which one of the ethynyl groups is incorporated into polyacetylene chain (branching units M2 from which four chains emanate) and (iii) units in which both ethynyl groups are incorporated into polyacetylene chains (branching units M3 from which six chains emanate).



Scheme 6 Proposed structure of the polymer networks obtained from the quaternization polymerization of **2PD** and **4PD** into **net(2PD)** and **net(4PD)**. A - polyacetylene type chain, B - ionic alternating chain, M1, M2, and M3 - possible monomeric units present in the network. Ph - 1,4-phenylene, Py - pyridyl, Br - bromide, PyBr (BrPy) - pyridiniumyl bromide.

The structure of linear polymers and polymer networks

The results of the elemental analysis (EA) of linear polymers **poly(2PM)**, **poly(4PM)**, **poly(2PD)**, and **poly(4PD)** proved the presence of bromine in all the products [from 12.8 wt% in **poly(4PD)** to 29.5 wt% in **poly(2PM)**]. The bromine is assumed to be present in the form of Br^- anions compensating the positive charge of the

N-benzylpyridinium moieties in the same way as in the polymers prepared via polymerization of 2EP and 4EP induced by quaternization with benzyl bromide various alkyl halides (see section *4.2.1.3 Quaternization polymerization of 4-ethynylpyridine and 2-ethynylpyridine activated with benzyl bromide*).

Although the initial BBr/monomer mole ratio in the feed was constant for all the polymerizations, the degree of quaternization (calculated from the results of EA see section *3 MATERIALS AND METHODS*) of the prepared linear polymers varied significantly in dependence on the type of the monomer applied. Polymers based on *ortho*-pyridyl, **poly(2PM)** and **poly(2PD)**, were highly quaternized Br/N = 0.77 and 1.00, respectively. On the other hand, polymer based on *para*-pyridyl, **poly(4PM)** and **poly(4PD)**, exhibit the degree of quaternization Br/N = 0.27 and 0.34, respectively, which imply that prepared polymers differ in the composition of monomeric units. The highly quaternized **poly(2PM)** and **poly(2PD)** should contain mainly C-type monomeric units (see **Scheme 2** and **Scheme 3**). On the other hand, the less quaternized **poly(4PM)** and **poly(4PD)** should unambiguously contain non-quaternized monomeric units of the A-type (see **Scheme 2** and **Scheme 3**) in combination with the quaternized units (both B- and C-types units are under consideration). The weight of the polymers isolated from the reaction mixture and the results of EA allowed determining the conversion of the acetylenic monomer into the polymer. As given in **Table 12**, high monomer-to-polymer conversions ranging from 61% to 81% were achieved in the reported polymerizations.

Similarly to linear polymers the EA proved the presence of bromine in all the polymer networks [Br content from 28.9 wt.% in **net(2PD)** to 35.6 wt.% in **net(4PM)**]. The initial 1,4-BBrMB/monomer mole ratio and corresponding initial Br/N mole ratio in the feed were equal to unity in all the polymerizations. As it is evident from **Table 12**, the Br/N mole ratio in the networks (Br/N = 0.74-1.20) was close to that of the polymerization feeds. This finding shows that molecules of 1,4-BBrMB and monomers were incorporated into the networks with a similar efficiency. Bromine can be present in the networks (i) in the same way as in the linear polymers - in the form of Br^- anions compensating the positive charge of the *N*-benzylpyridinium moieties and, (ii) moreover, as Br atoms in non-reacted $Br\text{-}CH_2\text{-}$ groups of 1,4-BBrMB (end groups). Providing that the majority of pyridyl groups of the monomeric units were quaternized in the networks we can assume that bromine is present in these networks prevailingly in the form of Br^- anions. In the case of **net(4PD)** (Br/N = 1.20) we can, however, assume (based on the EA) that some amount of Br is present in the form of Br-CH_2- groups because the content of Br in the network exceeds that of N.

The weight of the polymer networks isolated from the reaction mixture and the results of EA allowed determining the conversion of the acetylenic monomer into the polymer network. High monomer-to-polymer network conversions ranging from 71% to 90% were achieved in the reported polymerizations, see **Table 12**.

Table 12 Characterization of prepared linear polymers and polymer networks.

Sample Code	Product[a)]	Yield [%]	Initial Br/N mole ratio	Br/N mole ratio of product[b)]	Ref.
Poly(2PM)	Linear polymer	81	2	0.77	A2
Net(2PM)	Polymer network	71	1	0.74	A3
Poly(4PM)	Linear polymer	73	2	0.27	A2
Net(4PM)	Polymer network	90	1	1.03	A3
Poly(2PD)	Linear polymer	63	2	1.00	A2
Net(2PD)	Polymer network	77	1	1.04	A3
Poly(4PD)	Linear polymer	61	2	0.34	A2
Net(4PD)	Polymer network	73	1	1.20	A3

[a)] Character of prepared materials; [b)] Calculated from results of elemental analysis (see section *3 MATERIALS AND METHODS*).

Degree of quaternization of linear polymers and polymer networks

Table 12 summarizes the degree of quaternization of prepared linear polymers and polymer networks defined as Br/N mole ratio. As it is discussed in the *INTRODUCTION*, Blumstein and co-workers proposed that the propagation of the quaternization polymerization of pyridyl-substituted acetylenes proceeds as a consecutive addition of the quaternized (activated) monomer molecules to the growing polymer chain.[95] Thus, the fully quaternized polymers should be formed via polymerizations of mono-pyridylacetylenes. The discussion on the degree of quaternization for monosubstituted ionic polyacetylenes see *Degree of quaternization of monosubstituted ionic polymers* in section *4.1*. The bi-pyridylacetylenes can be activated by either single or double quaternization. The polymerizations of bi-pyridylacetylenes should therefore provide polymers with degree of quaternization Br/N = 1 (for double quaternization) and Br/N = 0.5 (for single quaternization).[99,100]

The prepared linear polymers differ significantly in the degree of quaternization. **Poly(4PM)** and **poly(4PD)** posses the degree of quaternization Br/N < 0.5 that means i) totally non-quaternized monomeric units A (see **Scheme 2** and **Scheme 3**, *Linear polymers* in section *4.2.2.1*) have been inbuilt into the chains of **poly(4PM)** and **poly(4PD)** and ii) the non-quaternized monomeric units have not undergone a postpolymerization quaternization. On the other hand, **poly(2PM)** and **poly(2PD)** exhibit a high degree of quaternization, indicating that prevailingly double quaternized monomeric units have been inbuilt into the polymers. Nevertheless, an alternative explanation can be proposed based on the postpolymerization quaternization of originally less quaternized **poly(2PM)** and **poly(2PD)**.

In order to decide which of these reaction modes prevails we conducted the polymerization of **2PM** activated with BBr (BBr/**2PM** mole ratio = 4) in DMF-d_7 (at room temperature) and monitored the reaction course by ^{1}H NMR spectroscopy. Resulting ^{1}H NMR spectra are given in **Figure 28** together with the reaction scheme of the two-step quaternization of **2PM** monomer.

^{1}H NMR spectrum recorded immediately after mixing the reaction components showed signals of **2PM** and BBr (protons a, b, c, d, f, g, h, see **Figure 28** for the proton labeling). After 1 hour of the reaction, new signals at 9.76 and 6.40 ppm appeared in the spectrum that can be attributed to protons a′ and e′, respectively, of the mono-quaternized **2PM**. The positions of signals of a′ and e′ protons in ^{1}H NMR spectrum were slightly downfield shifting with reaction time due to the increasing ionic character of the reaction mixture (see section *4.2.1.2 Supporting experiments*). Other new signals (at 9.85 and 6.55 ppm) were detectable in the spectrum at the reaction time of 1 day. We ascribed these signals to the protons a″ and e″, respectively, of the di-quaternized **2PM**. The intensity of these signals increased with the reaction time at the expense of the intensity of a′ and e′ signals. This indicates a continuous transformation of mono-quaternized **2PM** into di-quaternized **2PM**. The signals of non-quaternized **2PM** were nearly absent in ^{1}H NMR spectrum after 1 day of the reaction. The intensities of the narrow signals characteristic of mono- and di-quaternized **2PM** monomers (protons a′, e′, a″ and e″) began to decline after ca. 4 days of the reaction which we attribute to the transformation of the quaternized **2PM** into microstructurally nonuniform **poly(2PM)**.

It can be thus concluded that the high extent of quaternization of **poly(2PM)** is due to the high extent of the prepolymerization quaternization of the monomers. The same conclusions can be expected to apply to the high quaternization extent of **poly(2PD)**.

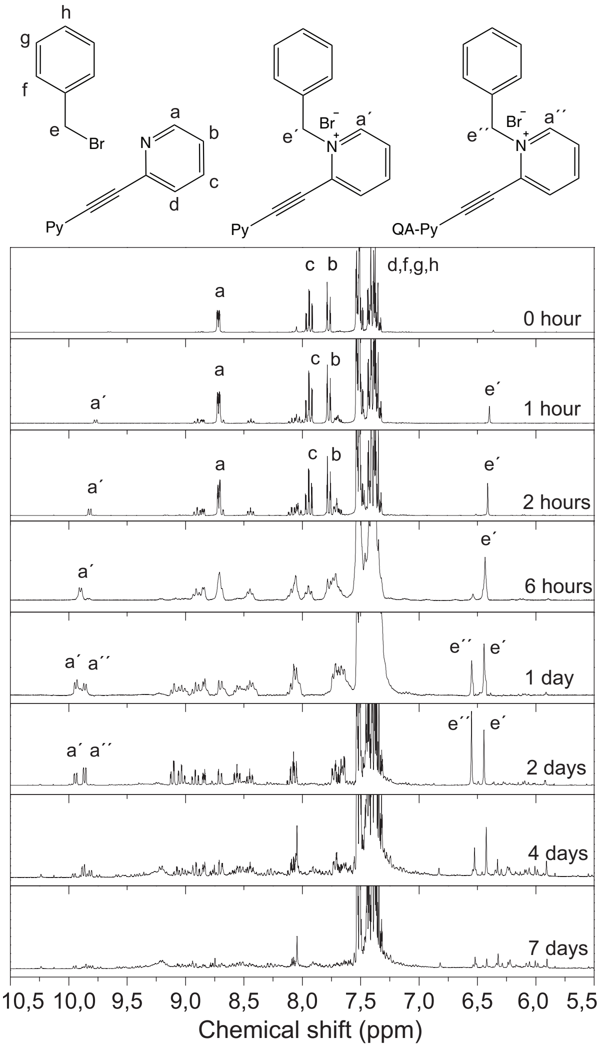
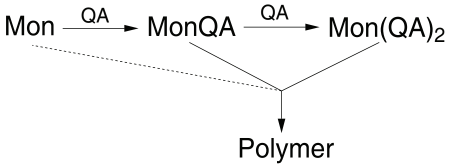


Figure 28 ^{1}H NMR spectral study of the reaction of monomer **2PM** with benzyl bromide, 300 MHz, DMF-d_7, room temperature.

The simplified **Scheme 7** shows (i) the quaternization of monomer (Mon) into mono- and di-quaternized molecules, MonQA and Mon(QA)$_2$, respectively, and (ii) copolymerization of MonQA, Mon(QA)$_2$, and, eventually, non-quaternized Mon. From the kinetic point of view, the consecutive quaternization of Mon and MonQA and the polymerization of Mon and MonQA represent competitive reactions, although for the polymerization to proceed, some amount of the monomer must first be activated via quaternization. Nevertheless, the quaternized monomer can copolymerize with non-quaternized monomer, at least in the case of monomers **4PM** and **4PD**. The low extent of quaternization of **poly(4PM)** and **poly(4PD)** may reflect that the rate of polymerization is higher than the rate of quaternization so that the Mon and MonQA molecules are inbuilt into the chains before they are fully quaternized. The postpolymerization quaternization of **poly(4PM)** and **poly(4PD)** is clearly inefficient. The reason for this may lie in the (assumed) coil conformation of the **poly(4PM)** and **poly(4PD)** chains in the reaction mixture that makes the non-quaternized pyridyl groups of the chains difficult to be accessed by QA molecules.[169] In accordance with the above interpretation, the high extent of the quaternization of **poly(2PM)** and **poly(2PD)** should reflect that the rate of polymerization is lower than the rate of quaternization in this case so that the majority of the monomer molecules can be highly quaternized before they are inbuilt into the polymer chains. The steric effect of the quaternized pyridine nitrogen in the vicinity to the ethynyl group may be responsible for the low rate of the polymerization of the quaternized **2PM** and **2PD** molecules.



Scheme 7 Quaternization and polymerization of monomer (Mon). Mon stands for non-quaternized monomer, MonQA stand for mono-quaternized monomer, and Mon(QA)$_2$ stands for di-quaternized monomer.

The degree of quaternization of *ortho*-pyridyl base polymer networks [**net(2PM)** and **net(2PD)**] did not differ from the degree of quaternization of their linear counterparts [**poly(2PM)** and poly**(2PD)**].

We can speculate that degree of quaternization (Br/N ~ 0.75) for both **2PM** based materials **poly(2PM)** and **net(2PM)** is a limiting degree of quaternization attained under selected conditions (see *Monomer and quaternizing agent mole ratio* in section *4.2.1.1 Reaction conditions*). It is assumed that quaternization of pyridyl in *ortho*-position may be sterically hindered and thus the formation of fully quaternized products is not probable.

The degree of quaternization (Br/N ~ 1) for **2PD** based materials, **poly(2PD)** and **net(2PD),** indicates that fully quaternized monomers were inbuilt into the polymer in both linear polymers and polymer networks. We assume that different degree of quaternization of **2PM** and **2PD** based materials originates from the monomer structure. The pyridyl groups in **2PD** molecule are more distant, compared to the **2PM** molecule, which make the N atom of **2PD** molecule more easily accessible for QA even if the molecule is already mono-quaternized. The diameters of monomers are demonstrated in **Figure 29**.

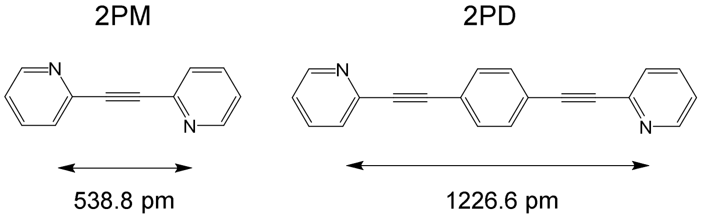
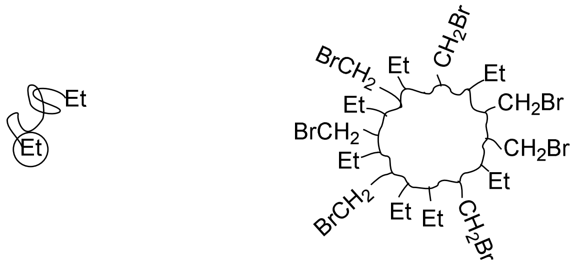


Figure 29 The structure of monomers 2PM and 2PD. The distance between N atoms of pyridyl groups calculated by GaussView 5.0 (Gaussian, Inc., www.gaussian.com).

The polymer networks prepared from **4PM** and **4PD** exhibit significantly higher degree of quaternization compared to their linear counterparts. The low degree of quaternization of **poly(4PM)** and **poly(4PD)** was explained by higher polymerization rate than that of quaternization in case of 4P based monomers activated with BBr discussed previously. However, the alternative explanation of higher degree of quaternization of networks could be proposed based on the bifunctional character of 1,4-BBrMB. Since the formation of two types of polymer chains is assumed to proceed simultaneously, the growing polymer networks could be seen as a clue with a two types of functional groups (active centers) emanating from its surface. **Figure 30** demonstrate the model of growing linear polymer and growing polymer networks. Although the both ends of linear polymer are represented by ethynyl group, the initiation of monomers (see *Proposed mechanism of quaternization polymerization of ethynylpyridines* in section *1 INTRODUCTION*) may allow to grow of polymer chain only in one direction. Thus, the growing linear polymer contains one active center represented by ethynyl (Et) group and the diffusing monomer could be attached exclusively to this active center via incorporation of acetylenic triple bond into the polyacetylene chain. Considering polymer network formation, the system is more complex compared to the linear polymers. The growing polymer network contains a number of active centers represented by ethynyl groups (Et) and Br-CH_2- groups (pendant groups of 1,4-BBrMB). Although, the N atom of pyridyl group may be also considered as an active center, since the formation of ionic alternating chains was confirmed, we do not involved pyridyl in this mechanism, because it is not reactive partner for the diffusing monomer. Thus, the molecules of non-quaternized monomer which diffuse to the vicinity of growing polymer network come to the part of the reaction system with a high concentration of Br-CH_2- groups. That is why the probability of quaternization of monomer molecules is significantly enhanced before the monomer is incorporated into polymer network through the polyacetylene type chain.



Model of growing linear polymer

Model of growing polymer network

Figure 30 The model of growing linear polymer and growing polymer network. Et – the active center represented by ethynyl group of monomer, Et in the ring – the initiated ethynyl group, which is not consider as an active center, $BrCH_2$ – the active center represented by methylbromide group of 1,4-BBrMB.

4.2.2.2 Structural characterization of linear polymers and polymer networks

NMR characterization of prepared linear polymers and polymer networks

The prepared linear polymers were characterized by means of ^{1}H NMR and ^{13}C NMR spectroscopies. The insolubility of prepared polymer networks excluded the characterization of samples in solution and thus only ^{13}C CP/MAS NMR spectra were recorded. Generally, the NMR spectra confirmed the polymeric character of formed products, however, only limited suggestions concerning obtained structure. The broad and poorly resolved spectra reflect the low covalent and configurational uniformity of prepared polymers. As discussed previously, since the polymerizations proceeded without any catalyst that might control the configuration structure of the product, the double bonds of both *cis* and *trans* configuration and single bonds of both *cisoid* and *transoid* configuration are most probably distributed in the polymer chains.

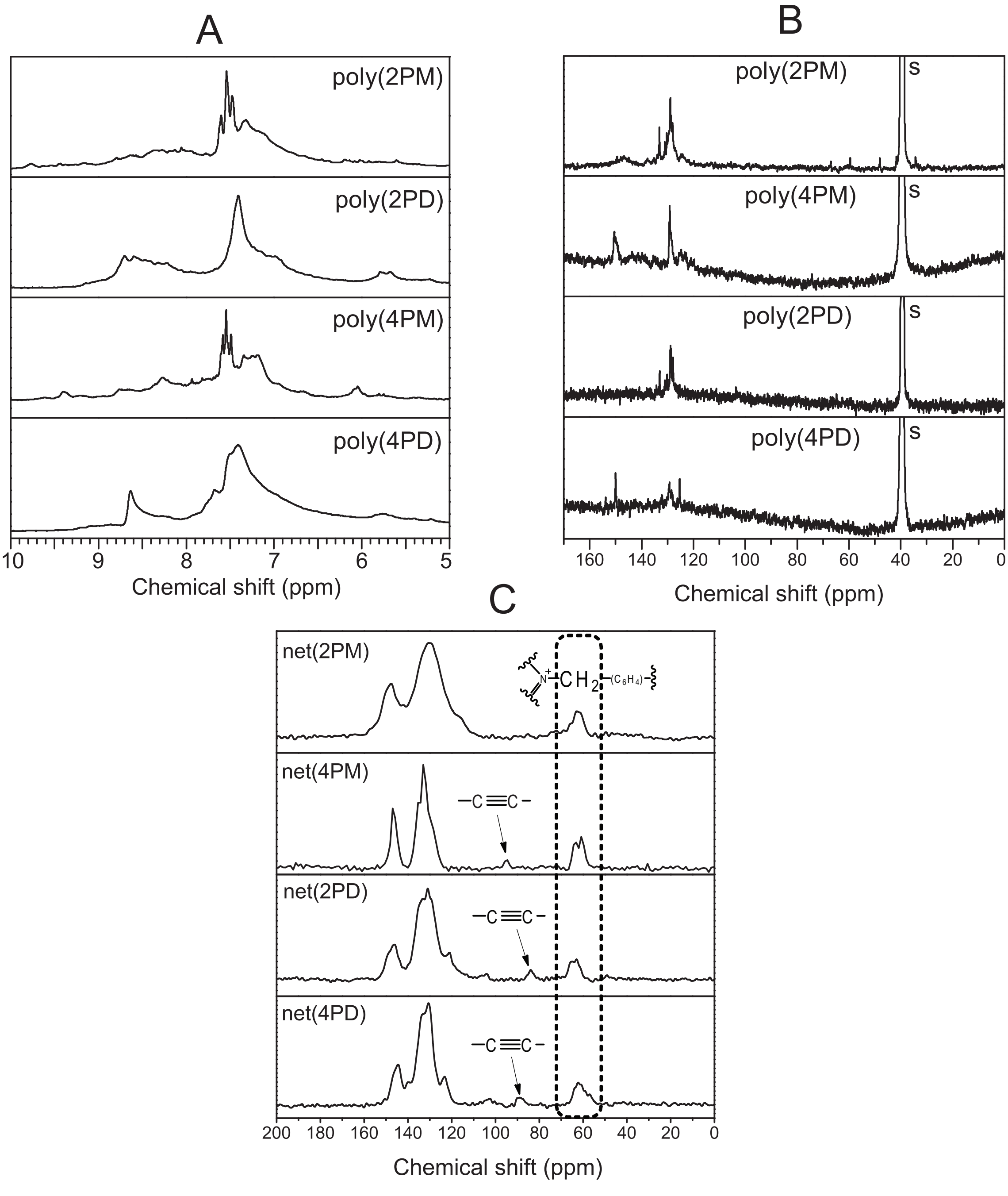


Figure 31 ^{1}H NMR (A) (300 MHz, DMSO-d_6) and ^{13}C NMR (B) (400 MHz, DMSO-d_6, S – solvent) spectra of **poly(2PM)**, **poly(4PM)**, **poly(2PD)**, and **poly(4PD)**. ^{13}C CP/MAS NMR (C) spectra of polymer networks **net(2PM)**, **net(4PM)**, **net(2PD)**, and **net(4PD)**.

The broad signal at 6.5–9.1 ppm in ^{1}H NMR spectra in **Figure 31** of all linear polymers can be ascribed to the aromatic protons of pyridyl and/or pyridiniumyl pendent groups of the polymer main chains and the phenyl groups of BBr. A more precise specification is possible in the case of ^{1}H NMR spectra of **poly(4PM)** and

poly(4PD) where a partly resolved signal at about 8.6 ppm most probably corresponds to the aromatic protons of 4-pyridyl/4-pyridiniumyl rings. The worse resolution or absence of this signal in the spectra of polymers derived from 2P type monomers may reflect a lower symmetry of 2-pyridyl/2-pyridiniumyl groups. Protons of CH_2 groups of *N*-benzylpyridiniumyl moieties are manifested as broad signal at around 6.1 ppm (polymers derived from 2P type monomers) and 5.8 ppm (polymers derived from 4P type monomers) in ^{1}H NMR spectra.

Due to the low uniformity of prepared linear polymers, it was complicated to obtain relevant ^{13}C NMR. However, the signal at about 130 ppm in ^{13}C NMR spectra of all linear polymers (**Figure 31**) can be ascribed to the resonance of carbons of (i) conjugated acetylenic backbone, (ii) phenyl groups of *N*-benzylpyridiniumyl moieties, and (iii) pyridyl/pyridiniumyl pendent groups. The broad signal at about 150 ppm in the ^{13}C NMR spectra of **poly(2PM)**, **poly(4PM)**, and **poly(4PD)** most probably corresponds to the carbon atoms adjacent to nitrogen in non-quaternized pyridyl groups.

^{13}C CP/MAS NMR spectra of polymer networks **net(2PM)**, **net(4PM)**, **net(2PD)** and **net(4PD)** are shown in **Figure 31**. Although the highly cross-linked polymer networks were obtained in this case, similar structural pattern to the linear polymers can be observed. Spectra of all networks contain a broad signal at 100–160 ppm, which is assigned to carbons of (i) conjugated polyacetylene chains, (ii) phenylene groups in moieties formed from 1,4-BBrMB, **2PD** and **4PD** and (iii) pyridiniumyl/pyridyl groups. The signals of non-reacted ethynyl groups are well observable in the case of both PD based networks, **net(2PD)** and **net(4PD)**, at 83.9 ppm and 88.9 ppm, respectively and also in case of **net(4PM)** at 95.7 ppm. As the non-reacted ethynyl groups are observable in ^{13}C CP/MAS NMR spectrum of **net(4PM)**, we can assume that both B1 and B2 motives (**Scheme 5**, *Polymer networks prepared from PM type monomers* in section *4.2.2.1*) of ionic alternating chains are present in **net(4PM)**. On the other hand, no signal of ethynyl groups was observed in ^{13}C CP/MAS NMR spectrum of **net(2PM)**. It can be concluded that **net(2PM)** did not comprise NMR detectable amount of **2PM** units with preserved ethynyl group in ionic alternating chains. Therefore, we assume that **net(2PM)** contains predominantly the B2 structure motive (**Scheme 5**) of ionic alternating chains.

The presence of signals of non-reacted ethynyl groups in ^{13}C CP/MAS NMR spectra of **net(2PD)** and **net(4PD)** shows that ethynyl groups were not fully transformed into polyacetylene chain. As the PD type monomers possesses two ethynyl groups, we assume that only one ethynyl group of the monomer molecule is prevailingly transformed into segment of the polyacetylene chain (via chain-growth polymerization) and the second ethynyl group may remain preserved (branching units M2 in **Scheme 6,** *Polymer networks prepared from PD type monomers* in section *4.2.2.1*). However, the **net(2PD)** and **net(4PD)** can contain also units in which both ethynyl groups of PD monomeric units were preserved (linear units M1 in **Scheme 6**) or both ethynyl groups are transformed into polyacetylene chains (branching units M3 in **Scheme 6**). As the cross-linking is concerned we speculate that (i) the content of M3 units in the networks is not high due to the steric difficulties that should accompany their formation and (ii) the M2 units are mainly responsible for the cross-linking of **net(2PD)** and **net(4PD)**.

The carbons of methylene groups in $-N^+-CH_2-(C_6H_4)-$ units of 1,4-BBrMB that quaternize pyridyl moieties are well manifested as a signal at about 63 ppm in the ^{13}C CP/MAS NMR spectra of all the networks. On the contrary, no signal ascribable to the carbons of non-reacted $Br-CH_2-$ groups of $Br-CH_2-(C_6H_4)-CH_2-N^+-$ units (expected at ca. 30 ppm) was detected in the spectra of the prepared networks. This points that both $Br-CH_2-$ groups are mostly transformed to the 1,4-BBrMB units incorporated into the networks. However, the absence of the signal of $Br-CH_2-$ groups in ^{13}C CP/MAS NMR spectrum of **net(4PD)**, where a small content of these groups is assumed according to Br/N mole ratio (see **Table 12** and related discussion), may indicate that ^{13}C CP/MAS NMR is not sensitive enough to detect small amounts of $Br-CH_2-$ groups in the analyzed networks.

IR characterization of prepared linear polymers and polymer networks

The polymerization of **2PM** and **4PM** (monomers with one triple bond per monomer molecule) activated with BBr is assumed to lead to linear polyacetylene type polymers in which triple bonds of monomers are transformed into double bonds of the polymer main chains (**Scheme 2**, *Linear polymers* in section *4.2.2.1*). This assumption is well confirmed by absence of band of the C≡C bond stretching vibration (around 2220 cm^{-1}) in IR spectra of **poly(2PM)** and **poly(4PM)** (**Figure 32**). As prevailingly soluble polymers were obtained in the polymerization of **2PD** and **4PD** (monomers with two triple bonds per monomer molecule) activated with BBr, it is not expected that both triple bonds of the monomer were transformed into the polyacetylene main chains. The total transformation of both triple bonds of the monomer should lead to a hyper cross-linked insoluble product. The IR spectrum of **poly(4PD)** is in accord with this assumption since it exhibits a band at 2220 cm^{-1} that corresponds to the stretching C≡C vibration of non-reacted internal ethynyl groups. However, such a band has not been detected in the IR spectrum of **poly(2PD)** (**Figure 32**) although this polymer should contain the internal ethynyl groups too. This may be explained by the complete quaternization of pyridyl groups in **poly(2PD)** [Br/N = 1.00, see **Table 12**] which could make the C≡C bond stretching vibration less IR active or inactive. We attempted to detect the internal ethynyl groups in **poly(2PD)** by means of Raman spectroscopy. However, no reliable Raman spectrum was obtained due to the photoluminescence of **poly(2PD)**.

The N^+=C stretching vibration of pyridiniumyl units (region from 1619 to 1629 cm^{-1}) is well observed in the IR spectra of all linear polymers (**Figure 32**).[92] The bands in the region from 1592 to 1598 cm^{-1} well observed only in the IR spectra of **poly(4PM)** and **poly(4PD)** corresponds to (i) stretching vibration of C=C bonds of phenyl groups and acetylenic backbone and (ii) stretching vibration of N=C bonds of non-quaternized pyridyl groups.[223] The ratio of the intensities of 1619-1629 cm^{-1} and 1592-1598 cm^{-1} vibration bands in the IR spectra correlates with the degree of quaternization of the polymers. In the spectra of highly quaternized polymers **poly(2PM)** and **poly(2PD)** the 1619-1629 cm^{-1} band is observed mainly, whereas in the spectra of less quaternized **poly(4PM)** and **poly(4PD)**, both 1619-1629 cm^{-1} and 1592-1598 cm^{-1} vibration bands are well developed.

IR spectra of prepared polymer networks **net(2PM)**, **net(4PM)**, **net(2PD)** and **net(4PD)** are shown in **Figure 32**. Contrary to the linear polymers, the structure of polymer networks is not formed exclusively by the polyacetylene chains, but also via the formation of the ionic alternating chains. Thus, the complete transformation of ethynyl groups of PM type monomers into double bonds of polyacetylene chains was not assumed.

This assumption was confirmed by the low intensity bands of C≡C bond stretching vibration at 2210 cm^{-1} and 2229 cm^{-1} detected in the case of **net(2PM)** and **net(4PM)**, respectively. The residual bands of C≡C bond stretching vibration are assigned to ethynyl groups of monomeric units incorporated into B1 segments (**Scheme 5**, *Polymer networks prepared from PM type monomers* in section *4.2.2.1*) of the ionic alternating chains of **net(2PM)** and **net(4PM)**.

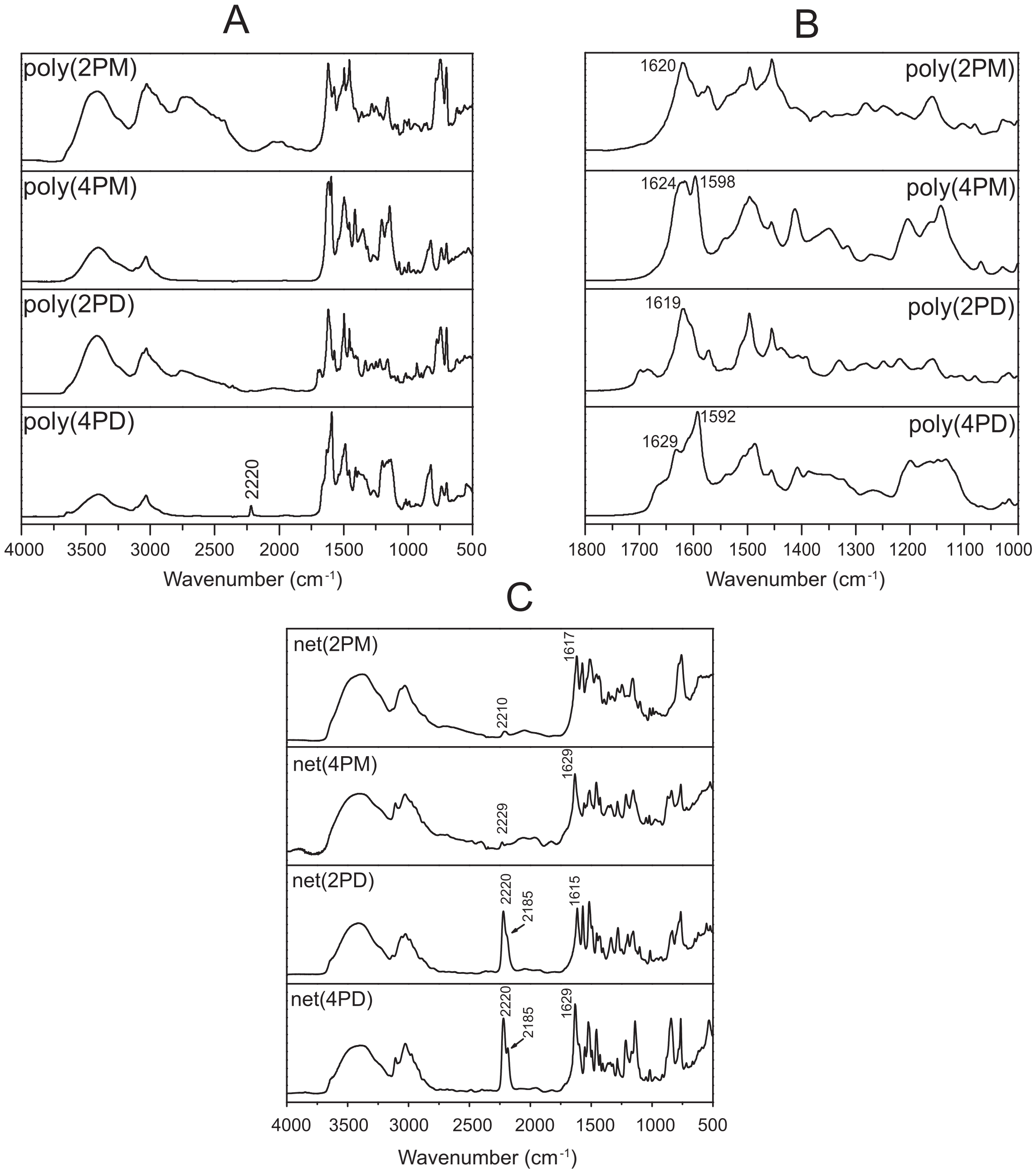


Figure 32 A) IR spectra of linear polymers **poly(2PM)**, **poly(4PM)**, **poly(2PD)**, and **poly(4PD)**, B) IR spectra of linear polymers region 1800 cm^{-1} – 1000 cm^{-1}. C) IR spectra of prepared polymer networks **net(2PM)**, **net(4PM)**, **net(2PD)**, and **net(4PD)**. DRIFTs, diluted with KBr.

As mentioned above in case of linear polymers, the total or close to total transformation of both ethynyl groups of PD types monomers into polyacetylene chain of polymer networks was not expected. This is due to the steric effects, which may be even more evident when bifunctional 1,4-BBrMB is used as an QA. The formation of ionic alternating chain may limit the adjustment of monomers in the optimal positions, which is essential for the transformation of ethynyl groups into the segments of the polyacetylene chains.

This assumption is confirmed by strong bands due to the C≡C bond stretching vibration at 2220 cm^{-1} in the IR spectra of both networks prepared from PD type monomers, **net(2PD)** and **net(4PD)** (**Figure 32**). The shoulders at 2220 cm^{-1} bands [at about 2185 cm^{-1} for **net(2PD)** and **net(4PD)** in **Figure 32**] most probably indicate a non-uniform structure of the monomeric units containing ethynyl group(s).

Probably the most important structural difference is evident from a comparison of units M1 and M2 in **Scheme 6** (*Polymer networks prepared from PD type monomers* in section *4.2.2.1*): these units differ in the number of the preserved ethynyl groups. It should be noted that the symmetrical shoulder-free bands (2222 cm^{-1}) due to the C≡C bond stretching vibration were present in the IR spectra of **2PD** and **4PD** monomers (see section *3 MATERIALS AND METHODS*).

Similarly to the IR spectra of linear polymers the N^{+}=C stretching vibration of pyridiniumyl units (region from 1615 cm^{-1} to 1629 cm^{-1}) corresponding the high degree of quaternization was well observable in the IR spectra of all the polymer networks.[92]

The characterization of linear polymers by MALDI-TOF MS

The determination of the molecular mass and the composition of linear ionic polymers is generally complicated and only apparent values are usually published, e.g. inherent viscosity or estimation of effective conjugation via Lewis-Calvin equation. The traditional methods are limited because of: (i) the ionic pendants of polymers may interact with the stationary phase of column and significantly bias the SEC separation mechanism, which disable the application of GPC method and (ii) the strongly colored solution of samples with absorption up to 650 nm disables the application of light scattering method.

Although the characterization of ionic polymers by MALDI-TOF MS is not generally clear mainly due to the complicated process of the sample ionization that is not understood enough nowadays,[224] we have decided to support the discussion on their composition and structure proposed in **Scheme 2** and **Scheme 3** (*Linear polymers* in section *4.2.2.1*) by this method. Before the characterization of prepared polymers, the MALDI-TOF MS analysis of low-molecular-weight model compound, 4,4′-bis(*N*-benzyl)dipyridinium bromide (BBr-DIPY-BBr) was performed. The

MALDI-TOF MS provided spectrum contains a dominant bromine-free signal with the molar mass of 338 Da which refers to the cationic form of BBr-DIPY-BBr (**Figure 9** in section *4.2.1.2 Supporting experiments*). Moreover, obvious decrement of mass of 90 Da corresponding to benzyl group was observed in the spectrum. Similarly, all the MALDI-TOF spectra of prepared polymers provide only the bromine-free signals with increment corresponding to the polymer structure. Unfortunately, we are not able to explain the absence of bromide anion in the spectra.

The MALDI-TOF MS spectra of polymers derived of PM type monomers exhibit distinct series of signals with an increment of 90 Da (**Figure 33**). The molecular mass of the **2PM** and **4PM** monomers is 180 Da and molecular mass of the benzyl group is 90 Da. Hence, the series of the signals in mean distance of 90 Da could be attributed to the combinations of these two masses. The steps consistent with the proposed polymer structure are presented in the spectra in **Figure 33**. As far as the resolution of the spectra of **poly(2PM)** and **poly(4PM)** are processible, a signals corresponds to particles containing 5 molecules of the monomer (5Mon) quaternized with 7 benzyl groups (7BG) (mass 1530) for **poly(2PM)** and signal corresponds to particles containing more than 7 molecules of the monomer (7Mon) quaternized with 4 benzyl groups (4BG) (mass 1640) for **poly(4PM)** were observed. This Mon/BG mole ratio is in agreement with Br/N value of 0.77 for **poly(2PM)** and with Br/N value of 0.27 for **poly(4PM)** ascertained from the elemental analysis.

The MALDI-TOF spectra of PD type polymer are less concise, which may be attributed to the high compositional and structural diversity of the monomeric units of these polymers. As far as the resolution of the MALDI-TOF MS spectrum of **poly(2PD)** is processible (**Figure 33**), a signal with mass of 1893 was detected that corresponds to particles containing more than 4 molecules of the monomer (4Mon) quaternized with 8 benzyl groups (8BG). This Mon/BG mole ratio is in agreement with the total quaternization of this polymer ascertained from the elemental analysis. Moreover, the mass increment of 460 Da corresponding to cationic part of di-quaternized monomeric unit (see C-type monomeric unit in **Scheme 3**, *Linear polymers* in section *4.2.2.1*) is observed in the spectrum (**Figure 33**).

The same evaluation of the MALDI-TOF MS spectrum of **poly(4PD)** provides a signal with mass 2320 (**Figure 33**). This signal corresponds to particles containing more than 7 molecules of the monomer (7Mon) quaternized with 4 benzyl groups (4BG). This Mon/BG mole ratio is in agreement with Br/N value of 0.34 ascertained from the elemental analysis. Moreover, the mass increment of 1390 Da corresponding to the sum of the masses of cationic part of monomeric units (combination of monomeric unit types: A + 3B or 2A + B + C in **Scheme 3**, *Linear polymers* in section *4.2.2.1*) is observed in the MALDI-TOF MS spectrum of **poly(4PD)**.

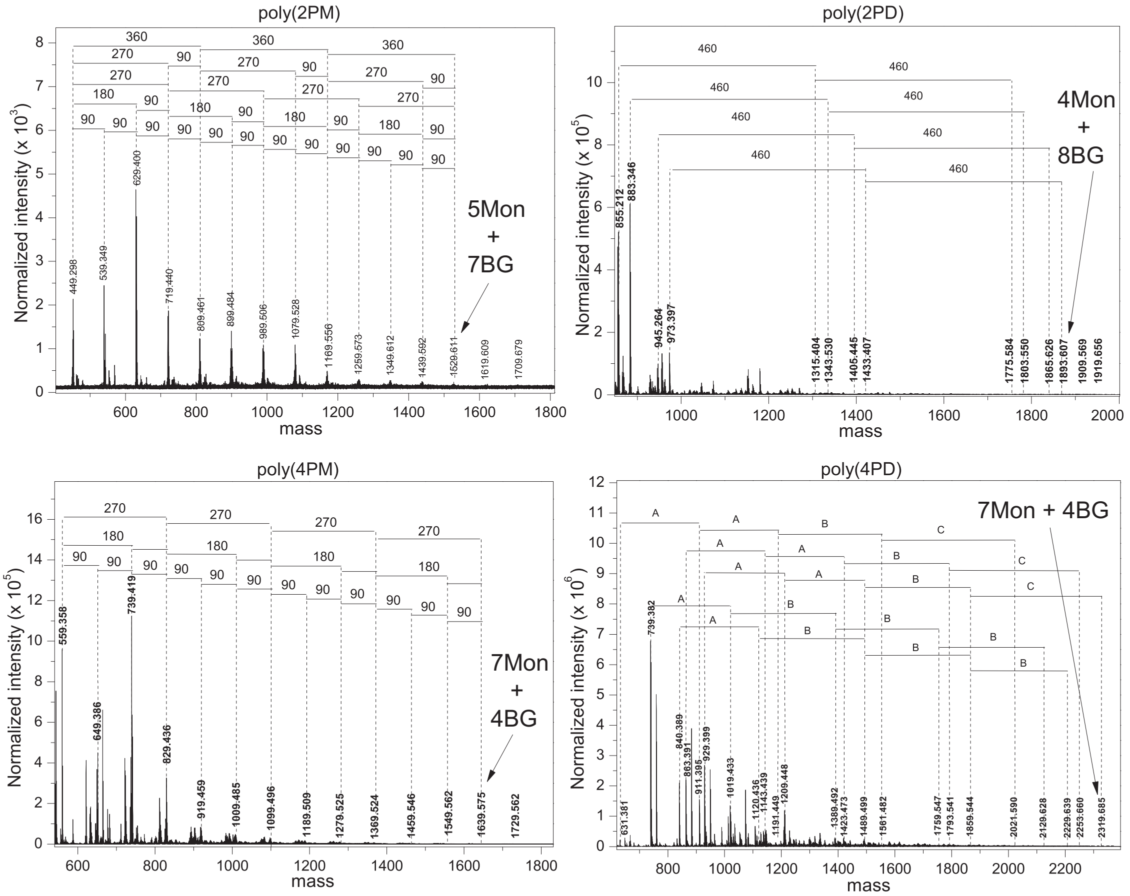


Figure 33 MALDI-TOF MS spectra of ionic linear polymers **poly(2PM)**, **poly(4PM)**, **poly(2PD)**, and **poly(4PD)**.

4.2.2.3 The properties of linear polymers and polymer networks

UV/vis and photoluminescence characterization of prepared linear polymers and polymer networks

Both linear polymers and polymer network exhibit interesting absorption and emission properties originating from the junction of ionic character of side pendants and π-conjugated system of polyacetylene chains. Although the structural patterns are common for both polymer types, the detailed comparison of their spectra may be misleading due to the method applied. The absorption and emission spectra of linear soluble polymers were obtained from the samples dissolved in solution, on the contrary, the absorption and emission spectra of insoluble polymer networks were obtained from the solid state measurements.

Only a structured UV band with absorption maximum at wavelengths (λ_{max}) of 297 nm (**2PM**), 274 nm (**4PM**), 320 nm (**2PD**), and 318 nm (**4PD**) is observed in the spectra of monomers. Since emission properties of prepared polymers were also investigated, the photoluminescence activity of starting monomers was tested. All the monomers applied in this study except for **2PM** exhibit photoluminescence in the UV region (emission maxima at 350-360 nm when excited by UV light of 280 nm).

The structure bands of monomers remains preserved in the spectra of linear polymers (from 255 to 307 nm) (**Figure 34**). Besides these bands, all the linear polymers also exhibit the absorption in the lower energy regions. According to the absorption properties, the linear polymers could be divided into two groups: *ortho*-pyridyl based (2P) and *para*-pyridyl base (4P) materials. The UV/vis spectra of **poly(2PM)** and **poly(2PD)** contain a partly resolved band at λ_{max} of 334 and 341 nm, respectively, ascribable to the charge-transfer (CT) absorption of the ion pairs composed of *N*-benzylpyridinium/bromide anion.[152]. This transition is less apparent in the spectra of **poly(4PM)** and **poly(4PD)** most probably due to the lower degree of quaternization of these polymers (see **Table 12** for degree of quaternization in *The structure of linear polymers and polymer networks* in section *4.2.2.1*). The absorption in visible region can be ascribed to π→π* transitions in the polyacetylene main chains. The comparison of UV/vis spectra indicated that **poly(4PM)** and **poly(4PD)** exhibit higher extent of conjugation than their **poly(2PM)** and **poly(2PD)** counterparts.

As discussed previously, the benzyl moieties that quaternize nitrogen atoms of pyridine rings the in *para* position are distant from the polyacetylene main chains in the case of **poly(4PM)** and **poly(4PD)**. The main chains can thus possess the microstructure convenient for an achievement of a high conjugation extent. On the other hand, the optimization of microstructure toward high extent of the main-chain conjugation is less easy for **poly(2PM)** and **poly(2PD)** that possess bulky benzyl groups in the vicinity to the polyacetylene main chains. This assumption in good accordance with the absorption spectra of linear polymer prepared from 2EP and 4EP activated with benzyl bromide. (see section *4.2.1.3 Quaternization polymerization of 4-ethynylpyridine and 2-ethynylpyridine activated with benzyl bromide*).

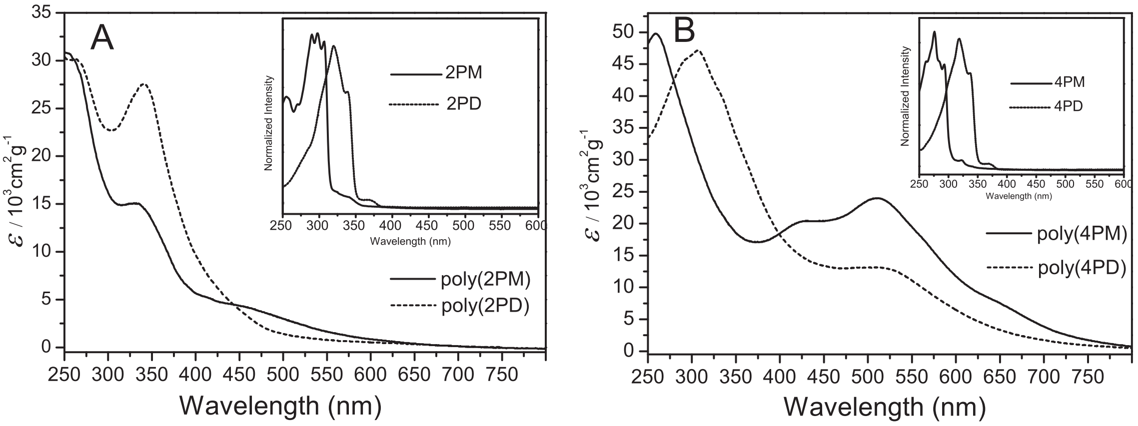


Figure 34 UV/vis absorption spectra of polymers A) **poly(2PM)**, **poly(2PD)** and monomers **2PM** and **2PD** and UV/vis spectra of polymers B) **poly(4PM)** and **poly(4PD)** and monomers **4PM** and **4PD** measured in MeOH, concentration 2.0×10^{-2} mg mL^{-1},ε - specific absorptivity.

All the linear polymers emit the visible light upon the UV excitation (**Figure 35**). Due to the non-uniform structure of prepared polymer, the detailed assignment of each single light emitting group is complicated. We can, however, speculate that the emission of the linear polymers can originate from the excitation of the partly conjugated polymer chains of polyacetylene type[18] and/or from the transition of the charge-transfer (CT) complex *N*-benzylpyridinium/bromide anion.[220,221]

The emission spectrum of **poly(2PM)** shows maximum in the yellow region ($\lambda_{\max}$ = 560 nm). By the comparison of absorption and excitation luminescence spectra, it is assumed that the emission originates prevailingly from the main polyene chains. The shape of the emission spectra remains unchanged whether the excitation proceeds in the region of absorption of the CT complex (350 nm) or the polyacetylene main chain (470 nm).

Poly(2PD) exhibits emission maxima in the violet region ($\lambda_{\max}$ = 407 nm). The origin of the emission is attributed mainly to the absorption of the CT complex since the absorption due to the polyacetylene main chains is weak in **poly(2PD)**. Samples **poly(4PM)** and **poly(4PD)** emit in the blue region ($\lambda_{\max}$ = 453 and 490 nm, respectively) when excited at 350 nm. On the other hand, the excitation in the wavelength region 470-500 nm leads only to a barely measurable emission around 550-600 nm. Evidently, the CT complexes and not the polyacetylene chains represent the photoluminescently most active components of **poly(4PM)** and **poly(4PD)** despite the low contribution of the CT complexes to the overall absorption of the polymers. The photoluminescence characteristics of linear polymers are summarized in **Table 13** together with fluorescence decay components. As it shown all prepared linear polymers exhibit only short fluorescent lifetimes.

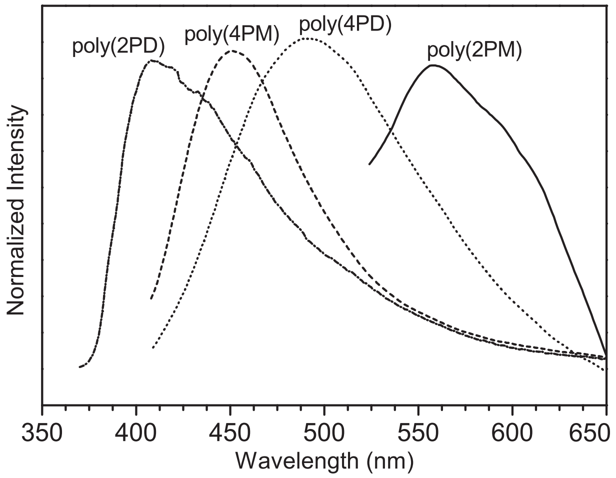


Figure 35 Photoluminescence spectra of prepared linear polymers **poly(2PM)**, **poly(4PM)**, **poly(2PD)** and **poly(4PD)** measured in MeOH. Concentration of all samples was 3.3×10^{-3} mg mL^{-1}, excitation wavelength 350 nm was used.

Table 13 UV/vis and photoluminescence characteristics of linear polymers.

Sample Code	UV λ_{max} [nm]a)	UV λ_{max} [nm]b)	Vis λ_{max} [nm]c)	λ_{exc} [nm]d)	$\lambda_{E(max)}$ [nm]e)	τ_1 [ns]f)	τ_2 [ns]f)	τ_3 [ns]f)
Poly(2PM)	255	334	460	350	560	2.21 (30)	7.12 (64)	0.21 (6)
Poly(4PM)	259	n/a	427, 512	350	407	2.60 (57)	4.15 (33)	0.42 (10)
Poly(2PD)	264	341	n/a	350	453	0.5 (86)	1.9 (14)	--
Poly(4PD)	307	n/a	521	350	490	1.82 (58)	0.24 (10)	4.58 (32)

a) Position of the high energy absorption maximum in the UV region; b) Position of the low energy absorption maximum in the UV region (corresponds to the charge-transfer band); c) Position of the absorption maximum in the Vis region; d) Excitation wavelength; e) Maxima of emission of the linear polymer networks; d) The luminescence decay components obtain from the time resolved luminescence measurements; n/a data no available.

The absorption spectra of the prepared polymer networks are shown in **Figure 36**. All the networks exhibited continuous absorption in the visible region with absorption maximum in the interval from 540 to 690 nm and with absorption edge over 800 nm. Similarly to the linear polymers, the observed absorption could be ascribed to the partly conjugated polyacetylene chains in junction with *N*-benzylpyridiniumyl pendant groups. The polymer networks absorption may also be affected by the charge-transfer (CT) absorption of the ion pairs composed of *N*-benzylpyridinium/bromide anion.[225,226]

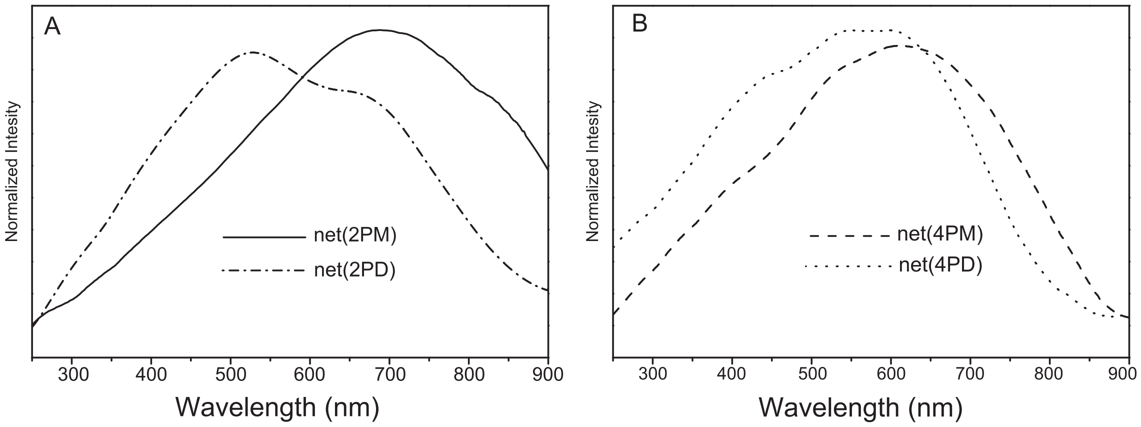


Figure 36 UV/vis absorption spectra of prepared polymer networks. A) **net(2PM)** and **net(2PD)**, B) **net(4PM)** and **net(4PD)**. Samples were diluted with $BaSO_4$.

All the prepared polymer networks emit in visible or infrared/near infrared region (**Figure 37**). We assume that origin of emission is also ascribed to the partly conjugated polyacetylene chains and/or the transition of the CT complex *N*-benzylpyridiniumyl/bromide anion as it was discussed in case of linear polymers. Based on the character of emission, the polymer networks can be divided into two groups: *ortho*-pyridyl based (2P) and *para*-pyridyl based (4P) materials. The polymer networks based on 2P type monomers emit in the red to near infrared region when excited at 470 nm. **Figure 37** shows broad emission bands of these networks with emission maxima at 735 nm for **net(2PD)** and 798 nm for **net(2PM)**. The polymer networks based on 4P type monomers strongly emit in the visible region when excited at 378 nm. **Figure 37** shows emission bands of these networks with maxima at 431 nm (blue region) for **net(4PM)** and 566 nm (greenish yellow region) for **net(4PD)**.

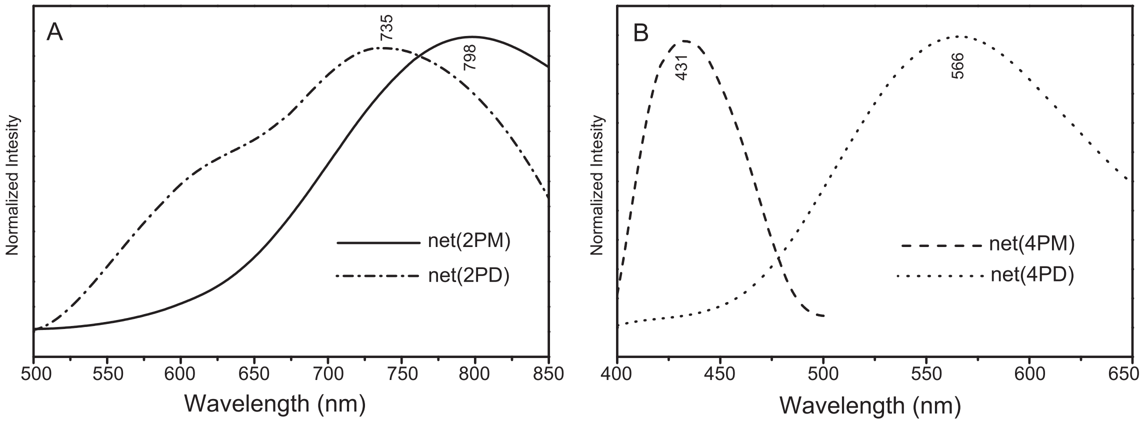


Figure 37 Photoluminescence spectra of prepared polymer networks. A) **net(2PM)** and **net(2PD)** excitation wavelength: 470 nm; B) **net(4PM)** and **net(4PD)**, excitation wavelength: 378 nm.

The strong visible emissions of 4P based polymer networks were successfully captured using digital camera (see section *3 MATERIALS AND METHODS*). The photos of the strong photoluminescence emissions of **net(4PD)** and **net(4PM)** after excitation by radiation of wavelength 378 nm are shown in **Figure 38**. As it is evident, the shade of the emitted color is in good agreement with the color calculated from obtained data (photoluminescence measurements) using CIE1931 color space. The CIE1931 chromaticity coordinates being x = 0.143, y = 0.052 for **net(4PM)** and x = 0.425, y = 0.494 for **net(4PD)**.

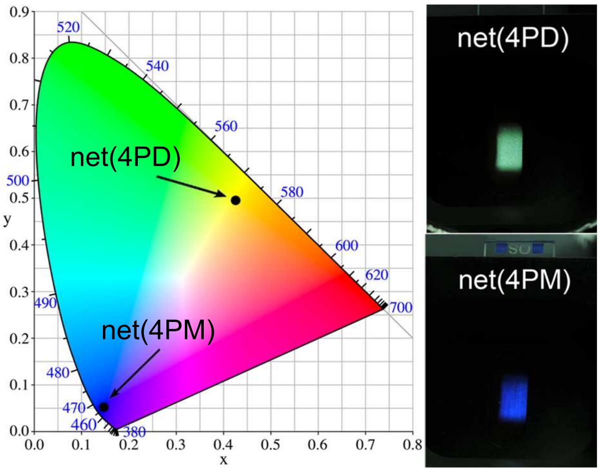


Figure 38 Chromaticity coordinates of the emissions observed in **net(4PM)** and **net(4PD)** in CIE1931 diagram. Photos of **net(4PD)** and **net(4PM)**, excited at 378 nm.

It is shown that the positional isomerism of pyridiniumyl groups in the networks importantly affects the luminescence behavior of these networks. The structure of the polymer networks containing *para*-pyridiniumyl moieties could be more flexible compared to the structure of the networks with *ortho*-pyridiniumyl moieties. The difference in the flexibility of the networks could cause various extents of geometrical changes of the segments of particular networks after excitation and consecutive emissions.

Table 14 summarized the absorption and photoluminescence characteristics of prepared polymer networks together with fluorescence decay components. The PM type networks show remarkably shorter lifetimes compared to the PD type networks. The prolonged lifetimes of the PD type networks (corresponding to the phosphorescence) may be ascribed to an intersystem crossing (ISC) process.[227] ISC may originate from the ionic character of networks in connection with the 1,4-phenylene groups present in the monomeric units formed from PD type monomers.

Table 14 UV/vis and photoluminescence characteristics of prepared polymer networks.

Sample Code	**$\lambda_{A(max)}$ [nm]$^{a)}$**	**λ_{exc} [nm]$^{b)}$**	**$\lambda_{E(max)}$ [nm]$^{c)}$**	**τ_1 [ns]$^{d)}$**	**τ_2 [ns]$^{d)}$**	**τ_3 [ns]$^{d)}$**
Net(2PM)	690	470	798	0.1 (87)	0.5 (13)	---
Net(4PM)	620	378	431	0.2 (26)	1.1 (54)	3.7 (20)
Net(2PD)	537	470	735	1.0 (20)	13.0 (31)	92.0 (49)
Net(4PD)	580	378	566	2.0 (5)	11.0 (18)	102.0 (77)

$^{a)}$ Absorption maxima of polymer networks, DRIFTs, sample diluted with $BaSO_4$; $^{b)}$ Excitation wavelength; $^{c)}$ Maxima of emission of the polymer networks; $^{d)}$ The luminescence decay components obtain from the time resolved luminescence measurements.

Thermal stability of prepared linear polymers and polymer networks

The thermal stability is an important quality of polymer materials, mainly due to the further processing and potential application of these materials. The stability can be defined as (i) thermal decomposition, which is a process of extensive chemical species change caused by heat and (ii) thermal degradation, which is a process whereby the action of heat or elevated temperature on a material, product, or assembly cause a loss of physical, mechanical or electrical properties.[228] The prepared linear polymers and polymer networks are discussed from the point of view of thermal decomposition.

TGA curves recorded for the prepared linear polymers and polymer networks in N_2 atmosphere are given in **Figure 39**. Two characteristics of the materials have been ascertained from these curves: (i) the temperature at which the weight loss of 5 wt% was detected ($t_{95\%}$) and (ii) the weight loss at temperature of 800 °C (see **Table 15**). Similarly to the discussion on thermal stability in *Thermal stability of materials prepared via QP of non-symmetrical monomers* in section *4.2.1.4*, we assume that the thermal decomposition of prepared polymers starts with a gradual release of HBr and/or benzyl bromide from the polymers at temperature > 150 °C. [36]

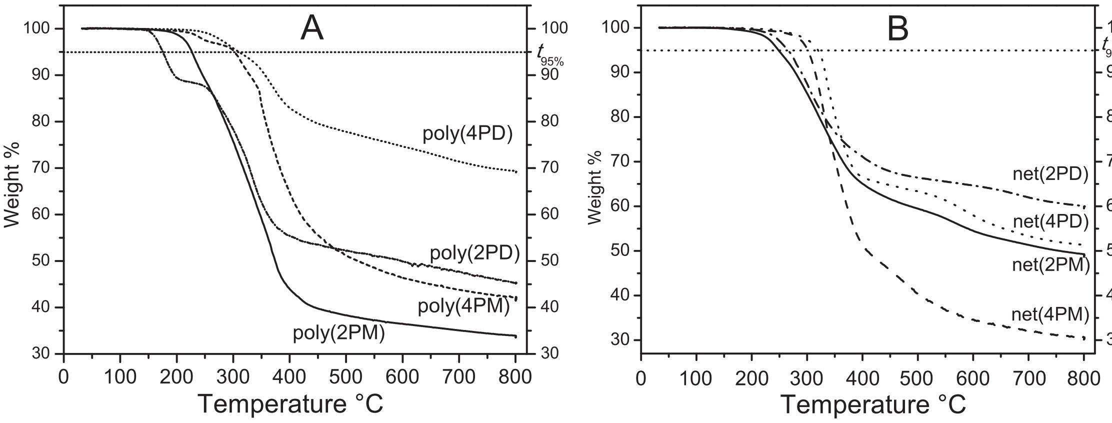


Figure 39 TGA curves of A) linear polymers **poly(2PM)**, **poly(4PM)**, **poly(2PD)**, **poly(4PD)** and B) polymer networks **net(2PM)**, **net(4PM)**, **net(2PD)**, and **net(4PD)** in N_2 atmosphere, step 10 °C min^{-1}.

The values of $t_{95\%}$ ascertained for the linear polymers range from 175 to 320 °C and increase in the order: **poly(2PD)** < **poly(2PM)** << **poly(4PM)** < **poly(4PD)**. The high values of $t_{95\%}$ determined for **poly(4PM)** and **poly(4PD)** are most probably connected with the low extent of quaternization of these polymers; on the other hand, the high extent of quaternization of **poly(2PD)** and **poly(2PM)** is most probably responsible for the lower values of $t_{95\%}$ of these polymers. The terminal parts of TGA curves (temperature > 500 °C) of linear polymers confirm a higher thermal stability of **poly(4PD)** and **poly(2PD)** compared to the samples **poly(4PM)** and **poly(2PM)**. This may be due to the presence of ethynyl groups in **poly(4PD)** and **poly(2PD)** and absence of these groups in **poly(4PM)** and **poly(2PM)**. The thermal transformation of ethynyl groups can lead to the cross-linking of the polymer chains resulting in the enhanced thermal stability of **poly(4PD)** and **poly(2PD)** at higher temperature.[7]

It was assumed that the thermal stability of the polymer networks may exceed the thermal stability of the linear polymers due to the high cross-linked structure.[229] However, the overall higher content of Br-CH_2- groups in the polymer networks, which are mainly released under elevated temperature, reduced the positive effect of the cross-linked architecture on the thermal stability. Thus, the thermal stability of prepared linear polymers and polymer networks did not differ significantly.

The values of $t_{95\%}$ ascertained for the polymer networks range from 248 °C to 320 °C and increase in the order: **net(2PM)** < **net(2PD)** << **net(4PM)** < **net(4PD)** (**Table 15**) The degradation of **net(4PM)** and **net(4PD)** started at the temperature higher by 50 °C compared to their **net(2PM)** and **net(2PD)** counterparts (**Figure 39**). Similarly to the decomposition of linear polymers, we assume that the thermal decomposition of polymer networks started with a gradual release of HBr and/or 1,4-BBrMB from the network at temperature higher than 150 °C. The terminal parts of TGA curves (temperature > 500 °C) confirm that the polymer networks **net(2PD)** and **net(4PD)** were more stabile than their counterparts prepared from PM type monomers, **net(2PM)** and **net(4PM)**, respectively. This can be explained by the high content of ethynyl groups in **net(4PD)** and **net(2PD)** and the low content or absence of these groups in **net(4PM)** and **net(2PM)**. Similarly to the higher thermal stability of linear polymers prepared from PD type monomers, the ethynyl groups may be thermally transformed into additional cross-links in the networks,[7] which could enhance the thermal stability of **net(4PD)** and **net(2PD)** at higher temperature.

Table 15 Characteristics of prepared linear polymers and polymer networks obtained from TGA analysis in N_2 atmosphere, step 10 °C min^{-1}.

Sample Code	$t_{95\%}$ [°C]	Weight loss at 800 °C [%]
Poly(2PM)	227	66
Net(2PM)	248	51
Poly(4PM)	303	58
Net(4PM)	301	69
Poly(2PD)	175	54
Net(2PD)	265	40
Poly(4PD)	320	31
Net(4PD)	320	48

Solubility of prepared linear polymers

The linear polymers prepared via the quaternization polymerization approach are generally well soluble in polar solvent due to the ionic character of side pendants, which was also approved in the section *4.1* dealing with monosubstituted ionic polyacetylene type polymers.

Table 16 Solubility of prepared polymers in solvents of various relative polarity.

Solvent	Relative polarity of solvent[a)]	Sample Code			
		poly(2PM)	poly(4PM)	poly(2PD)	poly(4PD)
water	1	Yes	Yes	No	No
methanol	0.762	Yes	Yes	Yes	Yes
ethanol	0.654	Yes	Yes	Partly	Yes
acetonitrile	0.460	Yes	Yes	Partly	Yes
dimethyl sulfoxide	0.444	Yes	Yes	Yes	Yes
dimethylformamide	0.386	Yes	Yes	Yes	Yes
acetone	0.355	No	Partly	No	No
dichloromethane	0.309	Partly	Partly	Partly	Partly
tetrahydrofuran	0.207	No	No	No	No
toluene	0.099	No	No	No	No
hexane	0.009	No	No	No	No

[a)] Relative polarity values of solvents taken from literature.[222]

The solubility and related processability in environmentally friendly solvents is one of the advantages of prepared materials. As it is evident from **Table 16**, all prepared linear polymers were well soluble in methanol, ethanol, acetonitrile, dimethyl sulfoxide, and dimethylformamide and **poly(2PM)** and **poly(4PM)** were also soluble even in water. The water-insolubility of **poly(2PD)** and **poly(4PD)** may be due to the presence of the nonpolar 1,4-phenylene segments in the monomeric units of these polymers. All polymers are insoluble in non-polar solvents as hexane or toluene.

4.2.2.4 Gas and vapor adsorption on prepared polymer networks

N_2 and CO_2 adsorption on prepared polymer networks

Net(2PM), **net(2PD)**, **net(4PM)** and **net(4PD)** are highly cross-linked networks possessing high content of rigid segments. Since this structure was promising for the formation of the porous texture of the networks we characterized all the prepared networks by means of N_2 (at 77 K) and CO_2 (at 293 K) gas adsorption (**Table 17**). However, only low BET (Brunaer-Emmett-Teller) specific surface areas, (S_{BET}, values up to 27 m^2 g^{-1}) and broad pore size distribution were revealed by nitrogen adsorption at 77 K for **net(2PD)**, **net(4PM)** and **net(4PD)**. The N_2 adsorption/desorption isotherms on these networks are given in **Figure 40**.

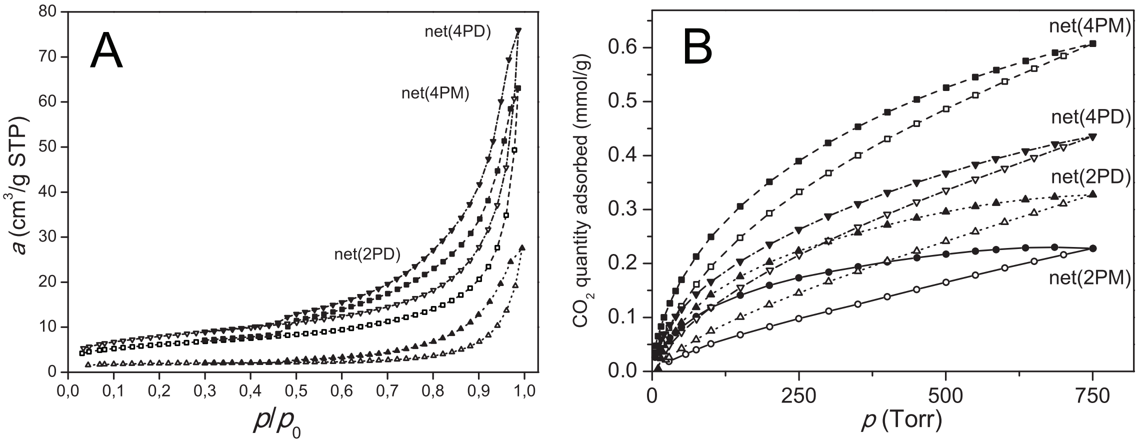


Figure 40 A) - N_2 adsorption isotherm (77 K) of prepared polymer networks **net(2PD)**, **net(4PM)** and **net(4PD)**. Adsorption of **net(2PM)** was under detection limit. Empty symbols - adsorption, filled symbols – desorption. B) - CO_2 adsorption/desorption isotherms (293 K) on polymer networks net(2PM), net(2PD), net(4PM) and net(4PD). Empty symbols - adsorption, filled symbols - desorption.

No porosity was revealed by N_2 adsorption at 77 K for the network **net(2PM)**. It should be noted that **net(2PM)** was the only network in which no free ethynyl groups were detected by ^{13}C CP/MAS NMR (see *NMR characterization of prepared linear polymers and polymer networks* in section *4.2.2.2*). This indicates a tight interconnecting of the segments of **net(2PM)** network that can be responsible for the inactivity of **net(2PM)** in N_2 adsorption at 77 K. Despite the low S_{BET} values, all the polymer networks including **net(2PM)** exhibited certain efficiency in CO_2 capturing at 293 K.

Table 17 The texture characteristics of networks resulting from N_2 adsorption/desorption isotherms (77 K) and CO_2 and ethanol capture capacities.

Sample Code	S_{BET} **[m^2/g]**	**Volume of pores [cm^3/g]**	**Diameter of pores [nm]**$^{a)}$	$a_{CO2,\ 750\ Torr}$ **[mmol/g]**$^{b)}$	$a_{ethanol,\ 750\ Torr}$ **[wt.%]**$^{c)}$
Net(2PM)	---$^{d)}$	---$^{d)}$	---$^{d)}$	0.23	---$^{e)}$
Net(4PM)	21	0.11	4 - 20	0.61	19.8
Net(2PD)	7	0.05	4 - 30	0.33	24.5
Net(4PD)	27	0.11	4 - 20	0.43	19.5

$^{a)}$ Pore size distribution was obtained by Barrett-Joyner-Halenda (BJH) method; $^{b)}$ Amount of CO_2 captured on 1 g of polymer network at 293 K; $^{c)}$ Amount of ethanol (in wt.%) captured on the polymer network at 293 K.; $^{d)}$ Under detection limit; $^{e)}$ Too slow equilibration that did not allow to continue with the measurement up to 750 Torr.

The CO_2 adsorption/desorption isotherms of the polymer networks are given in **Figure 40**. The efficiency of the networks in CO_2 capture could be ascribed to (i) the specific interactions between ionic groups of the networks and CO_2 molecules and (ii) the partial flexibility of the segments of the networks.[145] The assumed flexibility of the network structure can originate from the conformational changes of *N*-benzylpyridiniumyl moieties owing to a partial rotation around bonds of N-CH_2-C segments. The extent of conformational changes should increase with increasing temperature, i.e. while the changes in the network conformation can significantly contribute to CO_2 adsorption at 293 K they may play significantly reduced role at the temperature of 77 K at which N_2 adsorption on the networks was studied. Thanks to the conformational flexibility of the networks at room temperature the penetration of CO_2 into these networks can (i) induce formation of temporary pores via the swelling mechanism as discussed by our group recently[202] or (ii) facilitate filling of pores with restricted access as proposed by Weber et al.[230] The CO_2 uptake increased in the polymer network series **net(2PM)** < **net(2PD)** < **net(4PD)** < **net(4PM)**. The higher CO_2 uptake of *para*-pyridyl based (4P) networks compared to the *ortho*-pyridyl based (2P) networks could be explained by the various flexibilities of 4P and 2P networks: the bonds in N-CH_2-C segments may be less restricted in rotation in the 4P type networks (containing *para*-positioned pyridiniumyl groups) compared to the 2P type networks (containing *ortho*-positioned pyridiniumyl groups).

Ethanol vapor adsorption on prepared polymer networks

Despite the low specific surface area revealed by N_2 adsorption at 77 K, the polymer networks exhibited exceptional ethanol vapor capture capacity at 293 K (see **Table 17** for the ethanol uptake). The ethanol vapors adsorption isotherms are shown in **Figure 41**. The ethanol uptake of 24.5 wt.% determined for **net(2PD)** is comparable with highly structurally organized materials, e.g. MOFs or zeolites.[231,232] However, the ethanol capture on the studied networks suffered from the long-term equilibration at particular p/p_0 during the experiments. The time needed for recording ethanol adsorption isotherms on **net(4PM)**, **net(2PD)** and **net(4PD)** was about 40 hours. In the case of **net(2PM)**, the ethanol adsorption isotherm was only measurable up to $p/p_0 = 0.2$ due to the extremely slow equilibration. The long term equilibration points to the exceptionally slow penetration of ethanol molecules into the polymer networks. The tardiness of penetrating process could be explained by the dissolution of ethanol vapor in the solid polymer network instead of the adsorption on the network surface.

Figure 41 shows the difference between the ethanol adsorption isotherms on 2P type networks and the same isotherms on 4P type networks. The isotherm on **net(2PD)** as well as the measurable part of the isotherm on **net(2PM)** are nearly linear. This finding is in accord with the idea of dissolving of ethanol vapor in the networks in the course of the capture process. The ethanol adsorption isotherms on 4P type networks with similar capture capacity of 19.5 wt.% and 19.8 wt.%, respectively, at $p/p_0 = 0.95$ are close to the isotherm of the Type II according to the IUPAC classification.[233] Since **net(4PM)** and **net(4PD)** exhibit higher S_{BET} values than the **net(2PM)** and **net(2PD)** counterparts we speculate that the capture of ethanol vapor on **net(4PM)** and **net(4PD)** may proceed as a combination of ethanol vapor dissolving and adsorption on the network surface.

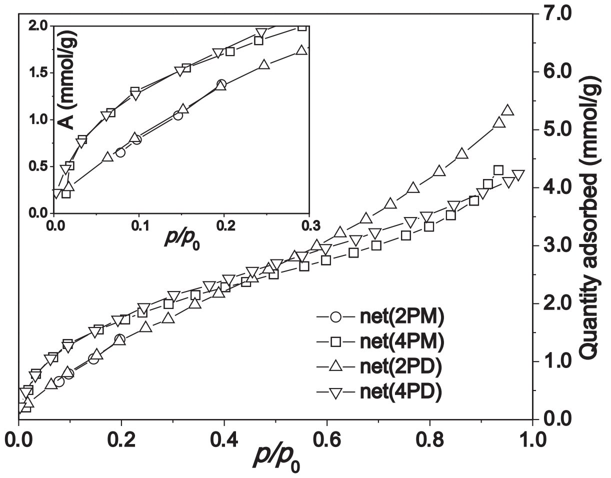


Figure 41 Ethanol vapors adsorption isotherm on **net(2PM)**, **net(2PD)**, **net(4PM)** and **net(4PD)** (293 K). Insert: the onset of the isotherms.

5 CONCLUSIONS

Conclusions concerning **poly(monosubstituted acetylene)s**

- Quaternization polymerization of the equimolar mixture of 2-ethynylpyridine activated with various alkyl halides (RX = ethyl bromide, ethyl iodide, nonyl bromide and hexadecyl bromide) performed in acetonitrile solution as well as in bulk gives an ionic π-conjugated poly(monosubstituted acetylene)s with approximately half of pyridine rings quaternized by corresponding RX. This indicates partly surprising alternation of the quaternized: [1-(*N*-alkylpyridinium-2-yl)ethane-1,2-diyl] and non-quaternized: [1-(pyridine-2-yl)ethane-1,2-diyl] units along polymer chains. The degree of quaternization (X/N mole ratio) of polymers implies that also non-quaternized monomers were involved in the process of QP. Due to the ionic character, prepared polymers were well soluble in polar solvents such as methanol, dimethyl sulfoxide and dimethylformamide. Polymers with short, ethyl side chains were in addition soluble in water while those with longer alkyl chains (nonyl, cetyl) also in low polar solvents.

- The interesting phenomenon is the dependence of configurational structure of monosubstituted polyacetylene main chain on the reaction conditions applied in this spontaneous, catalyst-free polymerization process. The QPs in acetonitrile solution gave the high-*cis* polymers while bulk polymerizations gave more expected irregular *cis*/*trans* polymers. Differences in the configurational structure were well observed in the ^{1}H NMR, IR as well as Raman (SERS) spectral patterns. As there was no other difference between these polymerization processes, this effect shall be ascribed to the presence of acetonitrile. Increased steric demands for an enchainment of a monomer molecule resulting from Coulombic binding of polar acetonitrile molecules to ionic growing polymer are suggested as the reason for the preferred *cis* configuration of polyacetylene chains formed in the presence of acetonitrile.

- The prepared ionic poly(monosubstituted acetylene)s were easily mixed with an aqueous sol of borate-stabilized Ag nanoparticles (Ag-NPs) to give nanocomposites in which quite strong luminescence of polymers that prevents measuring of their Raman spectra is quenched. Nanocomposites exhibiting strong surface enhancement of the Raman signal can be easy obtained by proper tuning the composition of these systems and allow the SERS characterization of ionic π-conjugated monosubstituted polyacetylene type polymers.

Conclusions concerning **poly(disubstituted acetylene)s**

- A series of QP of symmetrical bi-pyridylacetylene based monomers resulted into new ionic disubstituted polyacetylene type polymers and polymer networks in high yield. It is therefore obvious that the mechanism of quaternization activation frequently used for the polymerization of ethynylpyridines into ionic poly(monosubstituted acetylene)s is efficient also for the polymerization of symmetrical bi-pyridylacetylene type monomers of various composition and architecture into ionic poly(disubstituted acetylene)s materials.

- Although the quaternization polymerization proceeds without any catalyst, that may control the polymerization process, we have proved surprisingly high reproducibility of performed spontaneous polymerizations.

- The extent of quaternized pyridiniumyl units (degree of quaternization - Br/N mole ratio) in the prepared materials could be partly tuned via the reagents initial mole ratio. A series of QPs with initial Br/N mole ratio ranging from 1 to 4 resulted into ionic polymers with Br/N mole ratio from 0.53 to 0.88, respectively.

- The quaternization polymerization of a series of symmetrical bi-pyridylacetylene based monomers derived from *ortho*-pyridylacetylenes [1,2-bis(2-pyridyl)acetylene (2PM) and 1,4-bis[(2-pyridyl)ethynyl]benzene (2PD)] and *para*-pyridylacetylenes [1,2-bis(4-pyridyl) acetylene (4PM) and 1,4-bis[(4-pyridyl)ethynyl]benzene (4PD)] resulted into corresponding ionic materials. The structure of resulting material can be easily tuned via character of quaternizing agent applied. When monofunctional benzyl bromide was applied as quaternizing agent the linear ionic π-conjugated polyacetylene type polymers were obtained. When bifunctional 1,4-bis(bromomethyl)benzene was applied the quaternization polymerizations resulted into ionic π-conjugated polyacetylene type polymer networks. The network structure was formed by interconnected polyacetylene chains and the ionic alternating chains. Owing to the ionic nature, all linear polymers were well soluble in common polar solvents (e.g., methanol, dimethyl sulfoxide, and dimethylformamide) and those with one ethynyl group [poly(2PM) and poly(4PM)] were soluble even in water.

- Although the initial Br/N mole ratio in the feed was equal to 2 in the case of linear polymers preparation, the materials based on symmetrical *ortho*-pyridylacetylene monomers exhibit high degree of quaternization [Br/N = 0.77-1.00] and the linear polymers based on symmetrical *para*-pyridylacetylene monomers were less quaternized [Br/N = 0.27-0.34]: in this case a not negligible amount of monomer molecules has been inbuilt into the polymer in the non-quaternized form. The incomplete quaternization of linear polymers derived from monomers with *para*-pyridyl groups thus most probably reflects a high rate of the propagation step of the polymerization that exceeds the rate of the monomer quaternization (activation).

- The polymer networks prepared from symmetrical *ortho*-pyridylacetylene based monomers exhibit similar degree of quaternization [Br/N = 0.74-1.04] to their linear counterparts, which may reflect the limiting quaternization of monomeric units under selected conditions due to the sterical effects in case of *ortho*-pyridyl based materials. The apparently higher degree of quaternization of polymer networks derived from symmetrical *para*-pyridylacetylene based monomers compared to their linear counterparts was presumably caused by the bi-functional character of quaternizing agent. The molecules of non-quaternized monomer which diffuse to the vicinity of growing polymer network come to the part of the reaction system with a high concentration of Br-CH_2- groups of quaternizing agent. That is why the probability of quaternization of monomer molecules is significantly enhanced before the monomer is incorporated into polymer network via the polyacetylene type chain.

- The positional isomerism of the N atom of pyridyl groups (*ortho* or *para*) in the monomer structure also affects the extent of conjugation of the linear polymers. The linear polymers based on *para*-pyridyl monomers possess a high extent of conjugation manifested by a distinct absorption in the visible region with maximum around 550 nm. The linear polymers based on *ortho*-pyridyl monomers were less conjugated most probably due to the presence of the quaternized moiety in the close vicinity to the polyene main chains may complicate the optimization of microstructure toward high extent of the main-chain conjugation

- All prepared materials exhibit good thermal stability. It was assumed that the stability of the polymer networks may exceed the thermal stability of the linear polymers, due to the high cross-linked structure. However, the overall higher content of Br-CH_2- groups in the networks, which are mainly released under elevated temperature, reduced the positive effect of the cross-linked architecture on the thermal stability. Thus, the thermal stabilities of prepared linear polymers and polymer networks did not differ significantly.

- Both linear polymers and polymer networks exhibit photoluminescence originating most probably from the partly π-conjugated segments in connection with the charge-transfer complexes composed of *N*-benzylpyridiniumyl group and bromide anion. All linear polymers exhibit emission from violet to yellow region (407-560 nm) with no respect to the position of N atom of pyridyl group. On the contrary, the emission of polymer networks significantly differs in dependence on the position of N atom of pyridyl. *Ortho*-pyridylacetylene based polymer networks exhibit broad photoluminescence in red to near infra-red region [net(2PM) and net(2PD)] and *para*-pyridylacetylene based polymer networks exhibit strong photoluminescence in blue region [net(4PM)] and in greenish yellow region [net(4PD)]. The strong emission in visible region probably originate from high degree of quaternization (Br/N = 1.03-1.20) in connection with sterically convenient position of *para*-pyridyl based units resulting in enhanced conjugation of polyacetylene chains of net(4PM) and net(4PD).

- Despite low specific surface revealed by N_2 adsorption at 77 K, all the prepared polymer networks exhibit moderate efficiency in CO_2 capture at 293 K (up to 13.6 $cm^3(CO_2)/g$ at 750 Torr). The capture of CO_2 in the networks at room temperature is assumed to proceed under the formation of temporary pores and/or “opening” of pores with restricted access. This may be enabled by the partial flexibility of the segments of the networks originating from the presence of CH_2 groups in the network structure. Moreover, the prepared networks exhibit high efficiency in ethanol vapor capture (up to 24.5 wt%) that is mainly ascribable to the dissolution of the ethanol vapor in the networks rather than the adsorption of the ethanol vapor on the surface of the networks.

- Although the benzyl bromide was proved as a suitable quaternizing agent in case of quaternization polymerization of symmetrical disubstituted bi-pyridylacetylene based monomers, the quaternization polymerization of a series of non-symmetrical disubstituted mono-pyridylacetylene based monomers activated with benzyl bromide resulted into low molecular mass products. The quaternization polymerization of three *ortho*-pyridylacetylene based monomers: 2-(1-hexynyl)pyridine (2PH), 2-phenylethynylpyridine (2PP) and 2-(4-*tert*-butylphenylethynyl)pyridine (2PT) gave a low molecular mass oligomers and the quaternization polymerization of three *para*-pyridylacetylene based monomers: 4-(1-hexynyl)pyridine (4PH), 4-phenylethynylpyridine (4PP) and 4-(4-*tert*-butylphenylethynyl)pyridine (4PT) gave mostly quaternized monomers. The advantage of disubstituted structure of polyacetylene monomers was, however, partly confirmed in the case oligomeric products prepared from disubstituted *ortho*-pyridyl based monomers: the prepared materials exhibit good thermal stability and photoluminescence activity. Owing to the ionic character, all prepared materials were well soluble in polar solvents.

6 LIST OF ABBREVIATIONS

1,4-BBrMB	1,4-bis(bromomethyl)benzene
2EP	2-ethynylpyridine
2VP	2-vinylpyridine
3EP	3-ethynylpyridine
4EP	4-ethynylpyridine
4VP	4-vinylpyridine
BBr	benzyl bromide
Br/N	Br/N mole ratio
CIE diagram	full name CIE 1931 XYZ color space is the color space defined by International Commission on Illumination (from French name Commission internationale de l'éclairage) in 1931
CP	conjugated polymers
CPE	conjugated polyelectrolytes
CT	charge-transfer complex
CtBr	cetyl bromide (1-bromohexadecane)
Da	unified atomic mass unit (Dalton)
DIPY	1,4-dipyridyl
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
EtBr	ethyl bromide
EtI	ethyl iodide
f	functionality of compound
f_{Et}	functionality represented by ethynyl group
f_{Py}	functionality represented by pyridyl group
f_{QA}	functionality of quaternizing agent
ISC	intersystem crossing process
IUPAC	The International Union of Pure and Applied Chemistry
$\mathrm{M}_{\mathrm{n,ap}}$	apparent number-average molar mass of the polymer
$\mathrm{M}_{\mathrm{w,ap}}$	apparent weight-average average molar mass of the polymer
NMP	*N*-ethyl-2-pyrrolidone
NoBr	nonyl bromide (1-bromononane)
$p/p0$	relative pressure
PNo.	Polymer number used in Introduction
QA	quaternizing agent
QP	quaternization polymerization
$\mathrm{S}_{\mathrm{BET}}$	specific surface are determined via (BET) Brunauer–Emmett-Teller theory ($\mathrm{m}^2\mathrm{g}^{-1}$)
$t_{95\%}$	the temperature at which the weight loss of 5 wt% occur
THF	tetrahydrofuran

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8 LIST OF PUBLICATIONS

A1 Faukner, T., Slaný, L., Šloufová, I., Vohlídal, J., & Zedník, J.; Π-conjugated Polyelectrolytes Derived from 2-Ethynylpyridine: The Effect of Quaternization Agent and Reaction Conditions on the Polymer Structure and SERS Characterization of Nanocomposites with Ag-Nanoparticles. *Macromolecular Research*, **2016**, *24*(5), 441–449, doi:10.1007/s13233-016-40620.

A2 Faukner, T., Trhlíková, O., Zedník, J., & Sedláček, J.; Ionic π-Conjugated Polyelectrolytes by Catalyst Free Polymerization of Bis(pyridyl)acetylenes and Bis[(pyridyl)ethynyl]benzenes. *Macromolecular Chemistry and Physics*, **2015** *216*(14), 1540–1554, doi:10.1002/macp.201500147.

A3 Faukner, T., Zukal, A., Brus, J., Zedník, J., & Sedláček, J.; Ionic π-Conjugated Polymer Networks by Catalyst-Free Polymerization, Photoluminescence and Gas Sorption Behavior. *Macromolecular Chemistry and Physics*, **2016**, 0–13. doi:10.1002/macp.201600092

9 ATTACHMENTS

A1 Faukner, T., Slaný, L., Šloufová, I., Vohlídal, J., & Zedník, J.; Π-conjugated Polyelectrolytes Derived from 2-Ethynylpyridine: The Effect of Quaternization Agent and Reaction Conditions on the Polymer Structure and SERS Characterization of Nanocomposites with Ag-Nanoparticles. *Macromolecular Research*, **2016**, *24*(5), 441–449, doi:10.1007/s13233-016-40620.

A2 Faukner, T., Trhlíková, O., Zedník, J., & Sedláček, J.; Ionic π-Conjugated Polyelectrolytes by Catalyst Free Polymerization of Bis(pyridyl)acetylenes and Bis[(pyridyl)ethynyl]benzenes. *Macromolecular Chemistry and Physics*, **2015** *216*(14), 1540–1554, doi:10.1002/macp.201500147.

A3 Faukner, T., Zukal, A., Brus, J., Zedník, J., & Sedláček, J.; Ionic π-Conjugated Polymer Networks by Catalyst-Free Polymerization, Photoluminescence and Gas Sorption Behavior. *Macromolecular Chemistry and Physics*, **2016**, 0–13. doi:10.1002/macp.20160009