

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

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Abstract: The reaction of 2-ethynylpyridine (2EP) with stoichiometric equivalent of an alkyl halide RX (R is ethyl, nonyl, or hexadecyl and X is Br or I) gives a poly(*N*-alkyl-2-ethynylpyridinium halide) type ionic polymer that belongs to the family of π -conjugated polyelectrolytes (CPEs). Reaction conditions significantly influence configuration of the polymer main chains: polymerization in acetonitrile solution gives polymers with high content of *cis* units while bulk polymerization provides irregular *cis/trans* polymers. Increased regularity of the high-*cis* polymers is documented by the NMR and IR as well as SERS (surface enhanced Raman scattering) spectra measured on Ag-nanoparticles/CPE systems. Both polymerization processes give polymers in which 2EP monomeric units are ionized only from ca one half, which exhibit good stability in air and good solubility in polar solvents such as MeOH, DMF, and DMSO and those with *N*-ethylpyridinium groups even in water.

Keywords: conjugated polymers, ethynylpyridine, SERS, silver colloid, zwitterionic polymerization, silver nanocomposites, quaternization polymerization, ionic polymers.

Introduction

Conjugated polymers have attracted remarkable interest due to their promising functional properties in last few decades. These polymers found applications in various fields of modern research, such as organic light emitting diodes, photovoltaic cells, field-effect transistors, fluorescent sensors, gas storage and gas separation.^{1,2} The best known π -conjugated polymer is the insoluble polyacetylene, discovered by Shirakawa *et al.*,³ which upon doping can exhibit nearly metallic conductivity. The insolubility makes processing of unsubstituted polyacetylene difficult. Implementation of poly(substituted acetylene)s provided well processable polymers which, however, show worse conductivity and, mainly poly(monosubstituted acetylene)s suffer from limited stability.^{4,6} In contrast, poly(disubstituted acetylene)s are reported to be much more resistant to oxygen and elevated temperatures.⁷

Coordination polymerizations of the insertion and metathesis class are generally used for preparation of polymers of substituted acetylenes.⁶ The exceptional method of the preparation of polyacetylenes is the “catalyst-free” polymerization of ethynylpyridines induced with alkyl halide or esters of strong acids. Suggested mechanism of this type of ethynylpyri-

dine polymerization (usually classified as quaternization polymerization) presumes the addition of the quaternizing agent - alkyl halide, which changes the electron density on the terminal ethynyl groups thus allowing spontaneous polymerization of appropriate ethynylpyridine derivative.⁸ The procedure provides ionic conjugated polymers of the polyelectrolyte type: π -conjugated polyelectrolytes (CPEs).⁸⁻¹¹ Major advantages of CPEs are: (i) solubility in polar solvents such as water, alcohols and others environmentally friendly solvents (processing advantages), (ii) amphiphilic nature giving to CPE macromolecules capability of self-assembling in solutions and ability to interact specifically with particular species under measurable optical and/or electrical responses, and (iii) simultaneous electronic and ionic conductivity.¹² CPEs are regarded as promising functional polymeric materials¹³ reducing the electron-injection barrier from high work-function metal electrodes into polymer in optoelectronic devices,¹⁴⁻¹⁸ optically and/or redox responsive materials for various sensors and also as promising matrix materials for conjugated polymer composites with noble-metal plasmonic nanoparticles (NPs) that comprise hot spots strongly enhancing a local electrical field. Since the polymers of ethynylpyridines might well interact with noble-metal NPs through pyridyl and/or pyridiniumyl pendant groups, they are worth examining as matrices for conjugated nanocomposites comprising these NPs.

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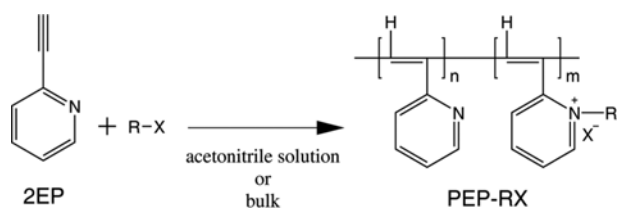


Figure 1. Scheme of polymerizations of 2-ethynylpyridine (2EP) activated with alkyl halide (RX).

Many polymers based on ethynylpyridines, in particular those derived from 2-ethynylpyridine (2EP), have been reported by Blumstein *et al.*^{16,19,15} and Gal *et al.*²⁰⁻²⁴ Recently also the syntheses of novel conjugated networks suitable for CO₂ storage using quaternization polymerization approach has been reported.²⁵ Our earlier study²⁶ on poly(2EP) quaternized with iodoethane revealed that the SERS intensity, *i.e.*, extent of the surface-induced enhancement of electric field, strongly depends on the polymer/Ag-NPs ratio in the composite system. A high SERS enhancement has been achieved by a proper tuning of the colloidal system and the enhancement remained preserved in a coagulated bulk composite system. Other studies on composites of polythiophene CPE with ionic-liquid-like cationic pendant groups and negatively charged plasmonic Ag and Au NPs have shown a key role of Coulombic interactions in the formation of SERS-active systems.²⁷⁻²⁹

In this paper we report preparation of eight CPEs derived from 2-ethynylpyridine by quaternization polymerization with various alkyl halide - RX (R is ethyl, nonyl, or hexadecyl and X is Br or I) in acetonitrile solution and in bulk (see Figure 1). Although polymers prepared with EtI, EtBr as well as long-chain alkyl halides (octadecyl)^{10,26,30} are already known, to our best knowledge, no systematic survey of their structure, properties and spectral characteristics (¹H NMR, IR, UV/vis, Raman) as a function of the preparation method (the nature of quaternizing agents, bulk *vs.* solution polymerization) has been reported in detailed. Tuning of polymer nanocomposites with silver nanoparticles for obtaining surface enhancement of the Raman scattering is also reported.

Experimental

Measurements. FTIR spectra were recorded on a Nicolet Magna-IR 760 instrument equipped with an Inspector IR Microscope using diffuse reflectance technique (DRIFT) (128 or more scans at resolution 4 cm⁻¹) and KBr-diluted samples. NMR spectra were measured on a Varian Unity INOVA 400 spectrometer using DMSO-*d*₆ (Armar Chemicals) as solvent. SEC analyses of polymers were carried out on a TSP chromatograph (Thermo Separation Product, Florida, USA) equipped with an RI and UV/vis detectors and a series of Mixed C and Mixed E columns (Polymer Laboratories, UK). DMF (Sigma-Aldrich) with added LiCl (Sigma-Aldrich) (2 mol%) was used as the eluent at flow rate 0.7 mL/min and the column

system was calibrated with PMMA standards (Polymer Laboratories). The UV/vis spectra of polymers were measured on a Hewlett-Packard 4452 diode-array and Shimadzu UV-2401 instruments using quartz cuvettes with optical path of 10 mm. Fluorescence spectra were taken on a Spex FluoroLog-3 spectrometer (Jobin Yvon Instruments S. A., Inc., USA) using samples dissolved in methanol (Sigma-Aldrich) and excitation wavelength of 420 nm. Elemental analyses were carried out on a Perkin Elmer PE 2400 Series II CHNS/O Analyzer (1999). Raman 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 (1,600 g mm⁻¹ grating) and liquid N₂-cooled CCD detector Princeton Instruments (100 × 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. Raman spectra of bulk Ag-NPs/PEP-RX composites 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 refs).³¹⁻³⁴

Materials. The following chemicals: 2-ethynylpyridine (2EP), iodoethane (EtI), bromoethane (EtBr), 1-bromononane (NoBr), 1-bromohexadecane (CtBr) and silver nitrate (≥99%), as well as the chromatography grade solvents: dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile and methanol were all supplied by Sigma-Aldrich. Sodium borohydride (grade for analysis) was supplied by Merck. All chemicals were used as supplied.

Polymerization Procedures. Polymerizations in acetonitrile solution were carried out as follows: Equimolar amounts of 2EP (1.03 g, 10 mmol) and RX (10 mmol) were dissolved in acetonitrile (6 mL) in an ampoule, the solution was flushed with argon, carefully sealed under decreased pressure and placed into a bath thermostated to 60 °C. After 10 days, the ampoule was opened, the reaction mixture poured into diethyl ether to precipitate the formed polymer as a brown powder, which was then extensively washed with diethyl ether (5×40 mL) using the decantation and filtration approach and finally dried in vacuum at room temperature for two or more days to the constant weight. The polymer yield was determined by gravimetry. Thus prepared CPEs are labeled by the prefix “s”, in general: sPEP-RX.

Bulk polymerization were carried out similarly; equimolar amounts of 2EP and RX were mixed in an ampoule that was then flushed with argon, sealed and kept at 60 °C for 10 days. Thus prepared CPEs are labeled by the prefix “b” (bPEP-RX). Polymers bPEP-EtBr and bPEP-EtI were primarily purified by dissolving in methanol (25 mL) and precipitation by diethyl ether (150 mL) and reprecipitated from the system methanol

(25 mL)/chloroform (65 mL); the dispersion formed was left overnight at $-18\text{ }^{\circ}\text{C}$ to achieve maximal polymer sedimentation. Polymers with longer alkyl side groups bPEP-NoBr and bPEP-CeBr were also dissolved in methanol (25 mL) but precipitated in water (65 mL) and the primary dispersion was kept overnight at $4\text{ }^{\circ}\text{C}$. The precipitation procedure was three times repeated and polymers finally washed with diethyl ether, isolated by filtration and dried under reduced pressure to the constant weight.

Preparation of Ag Hydrosols. A hydrosol of silver nanoparticles (Ag-NPs) stabilized with borate anions was prepared by reduction of AgNO_3 with NaBH_4 adopting the standard procedure described earlier.³⁴ An aqueous solution of NaBH_4 (10.5 mg) in deionized water (225 mL) was cooled down in the dark to temperature $\sim 5\text{ }^{\circ}\text{C}$ and an aqueous solution of AgNO_3 ($2.2 \times 10^{-3}\text{ M}$, 27 mL) cooled to $\sim 5\text{ }^{\circ}\text{C}$ 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 Nanocomposite Systems. Colloidal nanocomposite system of various polymer to Ag-NPs ratios were prepared by the adding a measured volume of a stock solution of a polymer in DMSO into Ag hydrosol (2 mL). The final polymer concentration in the system varied from $5 \times 10^{-8}\text{ M}$ to $1 \times 10^{-4}\text{ M}$ (mol of monomeric units per dm^3). Changes in prepared colloidal solutions were monitored by the UV/vis spectroscopy. Bulk nanocomposite systems were prepared by evaporating solvents from a drop of the aggregated system deposited onto a microscopic glass slide.

Results and Discussion

Synthesis and Basic Characterization of Polymers. Ionic polymers of 2EP carrying various alkyl groups attached to the nitrogen of pyridinium rings and bromide or iodide counterions (Table I) were prepared by spontaneous quaternization

polymerization of 2EP activated with corresponding alkyl halides (RX) without any catalyst or initiator, adopting the one-pot procedure described earlier.²⁶ Crude polymers contained a remarkable amount of the unreacted RX agent and traces of non-polymerized quaternary ammonium salts which had to be removed by re-precipitation and extensive washing. All polymers are soluble in methanol, DMSO and DMF, those with ethyl side groups also fully (bromide) or partly (iodide; owing to low hydrophilicity of Γ ions³⁵) soluble in water. On the other hand, polymers with longer alkyl side chains are insoluble in water but soluble also in low-polar solvents such as THF and chloroform.

As a rule, the bulk polymerization provided a higher yield but lower molar mass of the polymer as compared to the polymerization in acetonitrile solution (Table I). The degree of polymer ionization, α_{ion} , defined as the fraction of ionized monomeric units (calculated from elemental analysis data; see Supporting Information) was found to be around $0.5 (\pm 0.1)$ for all prepared polymers, despite that the polymerizations started with equimolar mixtures of 2EP and RX. This indicates that polymer chains are incompletely ionized, ca half-ionized. This indicates alternation of the ionized: [1-(*N*-alkylpyridinium-2-yl)ethene-1,2-diyl] and non-ionized: [1-(pyridin-2-yl)ethene-1,2-diyl] units in the formed polymer chains. It is worth noting that Blumstein *et al.*⁸ as well as Millen *et al.*³⁶ reported the value of $\alpha_{ion} \sim 0.5$ for hydrochlorinated P2EP, which might be reasonably explained by sharing the ionizing proton (cation) by two near-neighboring pyridine rings.³⁶

The determined values of the weight-average, $M_{w,ap}$, and number-average, $M_{n,ap}$, molar masses of PEP-RX (relative to PMMA standards) (Table I) should really 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 char-

Table I. Isolated Yield, Y , the Weight-Average, $M_{w,ap}$, and Number-Average, $M_{n,ap}$, Apparent Molar Mass, Degree of Ionization, α_{ion} , and Solubility of Prepared Polymers

Polymer Code	Y (%)	$M_{w,ap}$ (kg/mol)	$M_{n,ap}$ (kg/mol)	α_{ion}	Polymer Solubility					
					H ₂ O	MeOH	DMF	DMSO	THF	CHCl ₃
sPEP-EtI	50	82	15	0.52	partly	+	+	+	partly	partly
sPEP-EtBr	53	45	16	0.46	+	+	+	+	partly	partly
sPEP-NoBr	44	39	23	0.42	no	+	+	+	+	+
sPEP-CtBr	20	33	17	0.45	no	+	+	+	+	+
bPEP-EtI	77	21	6	0.61	partly	+	+	+	partly	partly
bPEP-EtBr	67	13	10	0.51	+	+	+	+	partly	partly
bPEP-NoBr	95	12	6	0.41	no	+	+	+	+	+
bPEP-CtBr	82	11	5	0.47	no	+	+	+	+	+

acterization of ionic polymers²⁷). The attempts to determine real M_w values by the light scattering method failed due to the light absorption by polymers. The most interesting and important output of the SEC measurements is the unexpectedly long-term stability (for at least one week) of these polyelectrolytes in solutions exposed to air (experimental error $\pm 10\%$). This strongly contrasts with the behavior of non-ionic monosubstituted polyacetylenes that mostly visibly degrade in solutions exposed to air^{4-6,37-41} within a few hours or even during a single SEC measurement.⁴² Such stability of PEP-RX at ambient conditions is important for their potential applications.

Configurational Structure of Polymers (¹H NMR and IR spectra). ¹H NMR spectra of all polymers are free of the signal of acetylenic hydrogens (Figure 2), which indicates the absence of 2EP as well as its *N*-alkylpyridinium salts in polymers. The spectra show each a partly resolved multiplet (6.0–9.5 ppm) of aromatic and vinylic protons, a broad signal of protons of CH₂ groups linked to nitrogen atoms at about 4.5 ppm and a broad signal of others aliphatic protons at around 1.0 ppm. As can be seen, the overall spectral resolution decreases in the order: Et \gg No \sim Ct, which can be ascribed to a decrease in the mobility of pendant 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 s-samples (those prepared by solution polymerization) to the b-samples (those 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.

The most striking difference between the ¹H NMR spectra of the s-type and b-type samples is observed for polymers with *N*-ethylpyridinium-2-yl side groups. Besides substantially higher spectral resolution, the spectra of the s-type samples exhibit well resolved strong signal at 6.5 ppm, which is typical of the main-chain vinylic protons in high-cis polyacetylenes.⁶ In contrast, this signal is very weak in the spectra of b-type samples, which show a strong signal at around 7.0 ppm that is typical of atactic cis/trans polyacetylenes. Hence the ¹H NMR spectra indicate that the solution polymerizations in acetonitrile give cis-rich polymers while the bulk polymerizations give atactic cis/trans polymers.

The measured IR spectra strongly support conclusions drawn from ¹H NMR spectra of prepared polymers. The complete IR spectra of prepared polymers are presented in Supporting

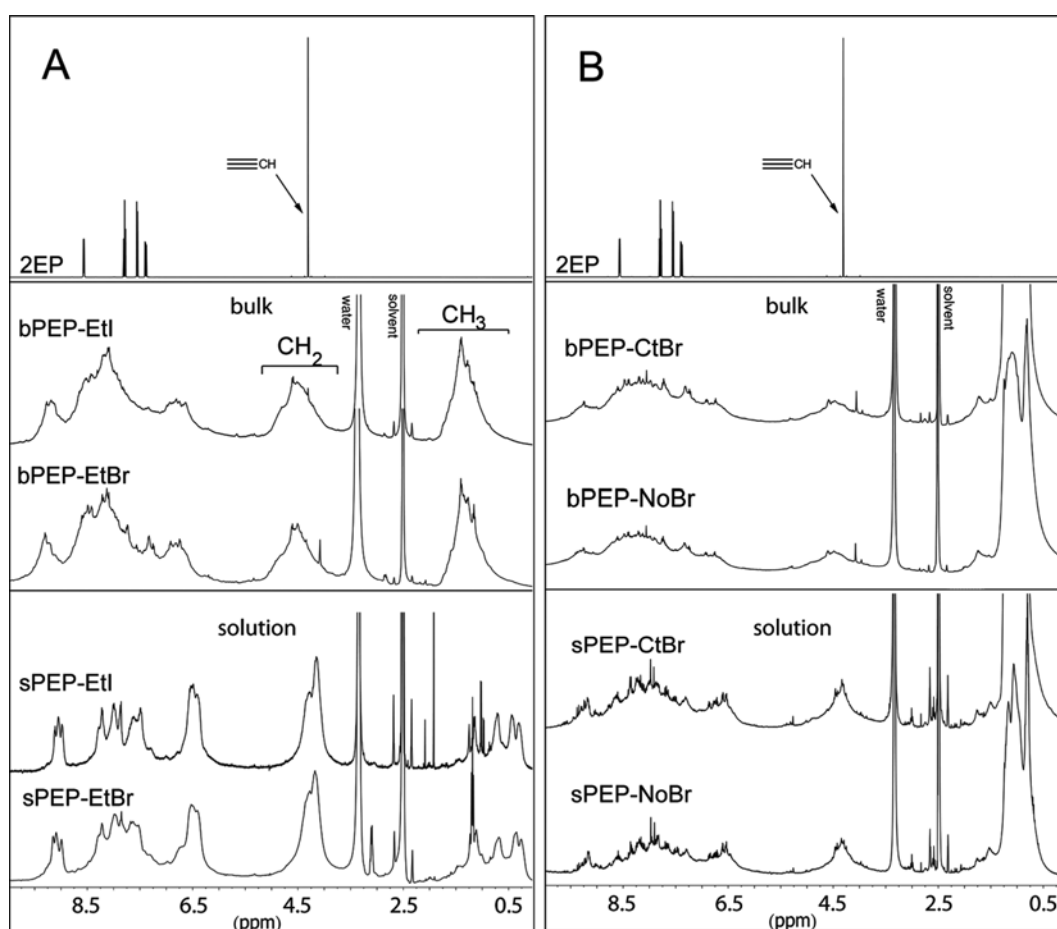


Figure 2. Comparison of ¹H NMR (400 MHz, DMSO-*d*₆) spectra of monomer 2EP and polymers prepared by reactions of 2EP with EtI and EtBr (A) and CtBr and NoBr (B).

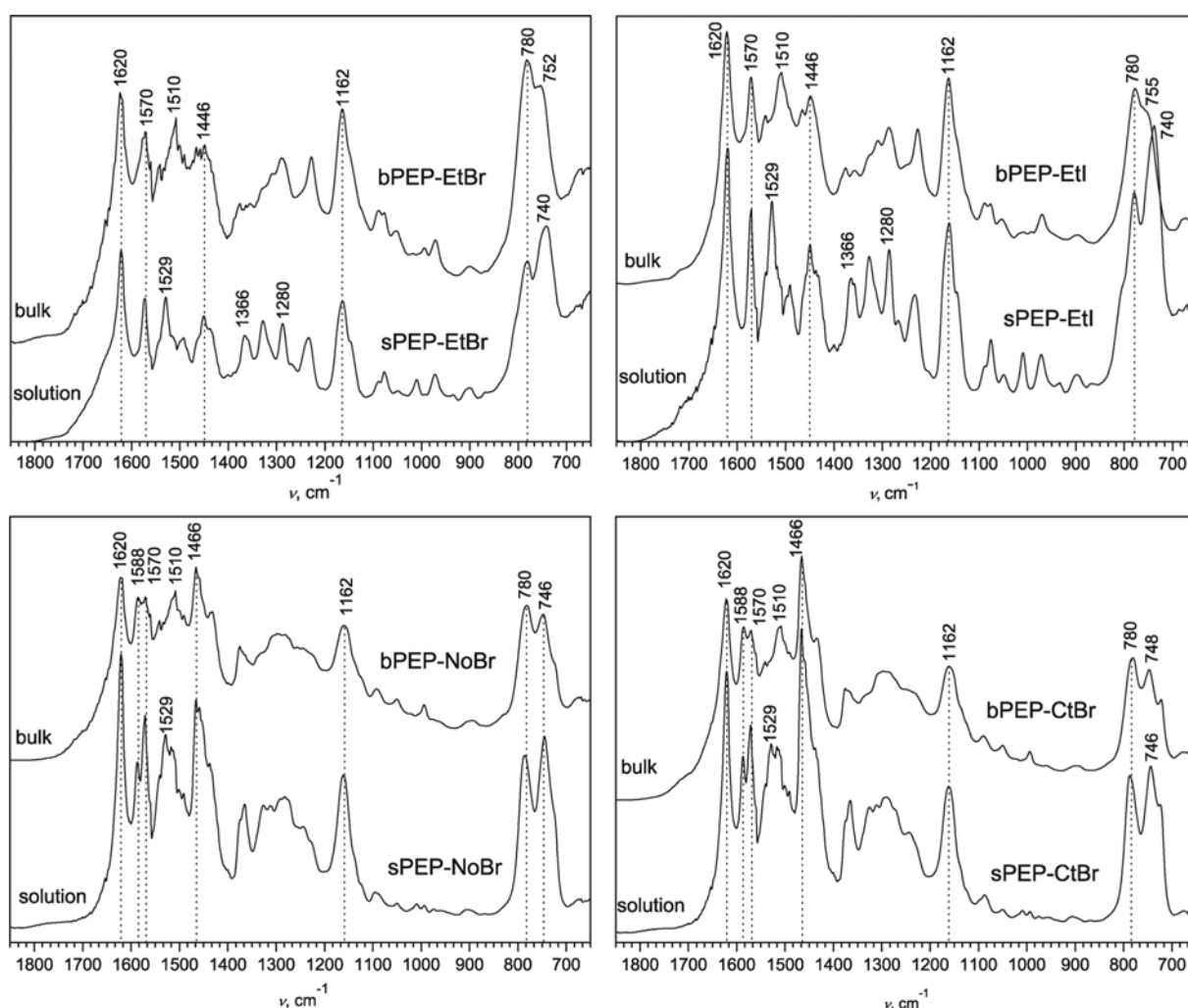


Figure 3. Comparison of the IR spectra of PEP-RX polymers prepared by the bulk (bPEP-RX) and acetonitrile solution (sPEP-RX) polymerizations.

information Figures S1 and S2. The overall IR spectra of the s-type samples are substantially better resolved than the spectra of the b-type samples (Figure 3), which also indicates increased structure regularity of the s-type samples. Nevertheless, the most significant IR spectral differences between the s- and b-type samples 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 polymers of monosubstituted acetylenes. 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.^{40–42} One can see from Figure 3 that 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. Qualitatively similar though less pronounced

spectral differences are seen between the s- and b-type samples comprising longer alkyl chains.

Somewhat less apparent IR spectral difference between s-type and b-type samples is seen in the region from 1500 to 1550 cm^{-1} . The band at 1529 cm^{-1} assigned to the $\nu_{\text{C-C}}$ stretching modes of high-cis main chains is well developed (when R is Et) or clearly visible (R is No or Ct) only in the spectra of s-type samples, whereas the band at ca 1510 cm^{-1} typical of trans-rich polyacetylene main chains dominates this IR spectral region of the b-type samples.

In summary, the ^1H NMR and IR spectra consistently indicate the cis-rich configuration of polymers formed by the solution polymerization in acetonitrile and the cis/trans configuration of the polymers formed by the bulk polymerization. Regarding that both these polymerization methods are the catalyst-free processes, the observed increased cis-regularity of s-samples must come from the participation of acetonitrile in the overall reaction. Coulombic binding of strongly dipolar acetonitrile

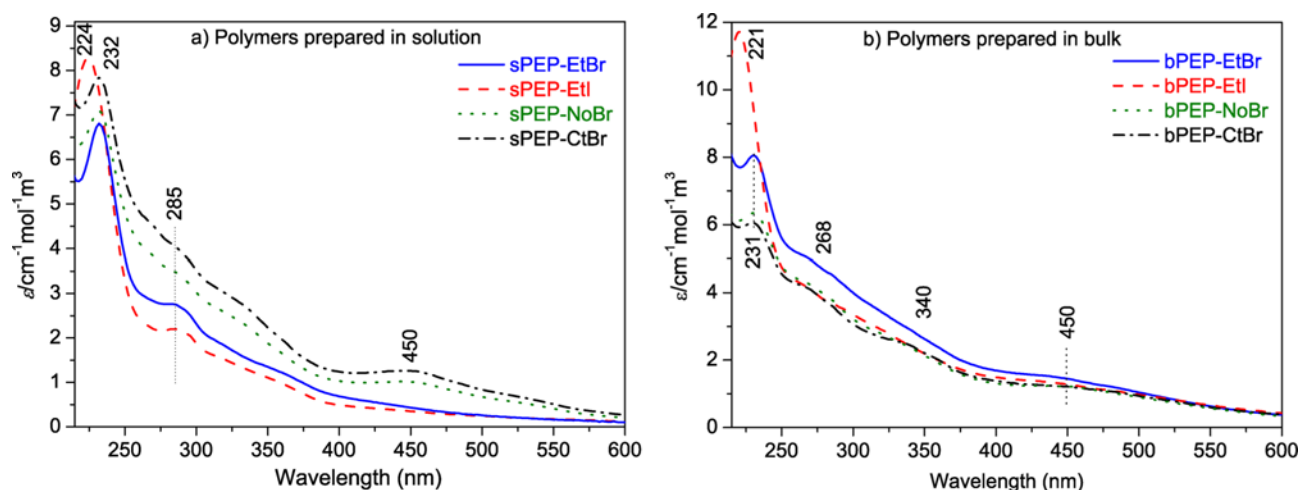


Figure 4. UV/vis spectra of prepared polymers in methanol solutions; ϵ_i is the molar absorption coefficient.

molecules (dipol moment of *ca.* 11.5 Debye) to zwitterionic 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.

Electronic Spectra of Polymers. The UV/vis spectra of prepared polymers taken from methanol solutions (Figure 4) show the almost continuous decrease in optical absorption from blue to the red region without any distinctive band. Distinct shoulders are 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 conjugated main chains. The absorption in the region from *ca.* 300 to 400 nm can be ascribed to the transitions within the charge-transfer complex formed by the *N*-alkylpyridinium/(Br⁻ or I⁻) ion pairs described recently in the literature.⁴³ As can be seen from Figure 4, 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* chains.

The solution photoluminescence spectra of all polymers (methanol, conc. 5×10^{-5} mol dm⁻³, Figures S3 and S4 in the Supporting Information) show emission bands at about 500 nm, regardless the *cis*-content. The emission intensity shows a correlation with the intensity of absorption bands. The observed uniformity of the emission maxima indicates that the *s*-type polymers are composed of the *cis*-rich but not all-*cis* chains. As they contain also *trans* units, they preferably emit light from the excited states located at segments comprising these *trans*-units, where the excited state energy is lower compared to the all-*cis* segments.

Surface Enhanced Raman Scattering (SERS). The luminescence of prepared CPEs made impossible direct measurement of Raman spectra. Therefore, the SERS was used, at which the luminescence is damped due to the polymer adsorption

on surfaces of silver nanoparticles (Ag-NPs). Moreover, the SERS signal is about several orders of magnitude,^{29,34,44} stronger than current enhances the Raman signal, which enables measuring the spectra of Ag-NPs/CPE systems with the polymer concentration is as low as 5×10^{-8} M. The borate stabilized aqueous Ag colloid (pH of 9.3) possessing negative ζ -potential^{45,46} was used, because cationic CPE chains can easily adsorb on the surface of negatively charged Ag-NPs. The concentration of CPE 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,⁴⁷⁻⁴⁹ which indicates the presence of fractal aggregates of Ag-NPs.²⁶ The optimum concentration was found to be *ca.* 5×10^{-6} M for all studied CPEs (Figure S5 in Supporting Information).

The SERS spectra were measured with different excitation wavelengths (see examples in Figure 5): (i) $\lambda_{exc}=445$ nm matches the absorption band of CPEs at 450 nm (Figure 4) 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).^{36,47-50}

The SERS spectra taken with $\lambda_{exc}=532$ nm (Figure 6) exhibit bands assigned to pyridinium ring stretching (at about 1625 and 1563 cm⁻¹) and CCH bending (1157 and 1075 cm⁻¹) modes and the band at 1512 cm⁻¹ (*s*-samples) or 1516 cm⁻¹ (*b*-samples) of the main-chain C=C stretching vibrations.^{26,36,49} The spectra

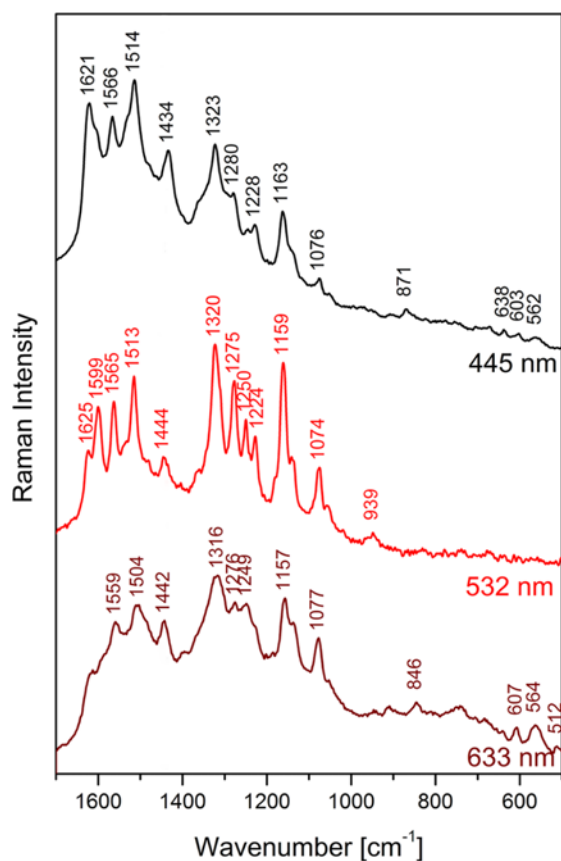


Figure 5. SERS spectra of the Ag-NPs/sPEP-EtI system taken with different excitation wavelength.

of the s- and b-type samples show very similar patterns in the region of stretching bands (1500 to 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 s-type samples show better spectral resolution compared to the spectra of the b-samples, which points to increased regularity of the s-type polymers, and (ii) the band typical of the ring breathing vibrations of non-ionized pyridine rings occurring at around 1005 cm^{-1} ^{36,50} is practically absent in spectra of all samples, which might be ascribed to strong interactions of the ionized and non-ionized pyridine rings.

Conclusions

The obtained results show that the thermally induced spontaneous polymerization of the equimolar mixture of 2EP and alkyl halide RX (EtBr, EtI, NoBr and CtBr) in acetonitrile solution or in bulk gives a π -conjugated polyacetylene-type polyelectrolytes (CPEs) with ca half of pyridine rings ionized by corresponding *N*-alkyl substituent, PEP-RX. This indicates partly surprising alternation of the ionized: [1-(*N*-alkylpyridinium-2-yl)ethene-1,2-diyl] and non-ionized: [1-(pyridin-2-yl)ethene-1,2-diyl] units along polymer chains. The presence of ionic side groups gives to polymers good solubility in polar solvents such as MeOH, DMF and DMSO. Polymers with short, ethyl side chains are in addition soluble in water while those with longer alkyl chains (nonyl, cetyl) also in low polar sol-

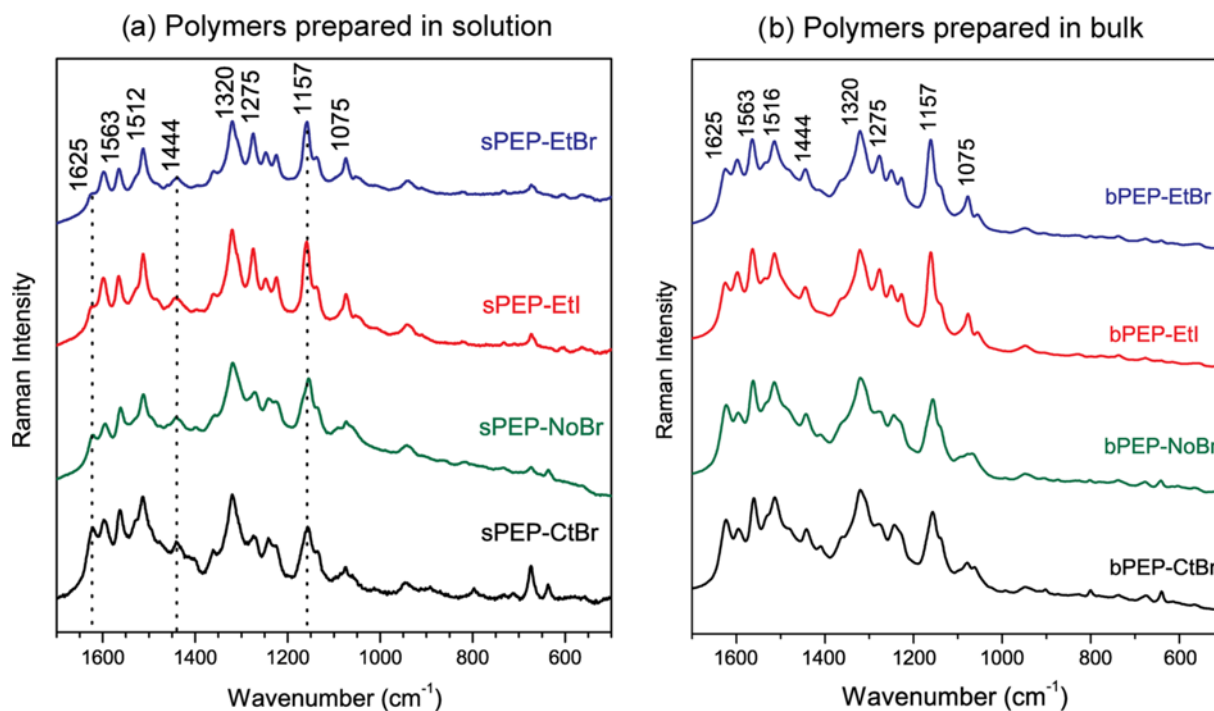


Figure 6. SERS spectra of Ag-NPs/PEP-RX systems taken with the excitation wavelength of 532 nm.

vents.

An interesting phenomenon revealed is the configurational structure controlling effect of acetonitrile when used as a solvent in this catalyst-free polymerization process. The solution polymerizations in acetonitrile surprisingly gave the cis-rich polymers while bulk polymerizations gave more expected irregular cis/trans polymers. Differences in the configurational structure are well seen in the ¹H NMR, IR as well as Raman spectral patterns, which all are substantially better resolved for the cis-rich compared to the cis/trans polymers. 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 zwitterionic growing species are suggested as the reason for the preferred cis configuration of polyacetylene chains formed in the presence of acetonitrile.

The prepared cationic polyelectrolytes are easily mixed with an aqueous sol of borate-stabilized 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 easily obtained by proper tuning the composition of these systems.

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Supporting Information: Information is available regarding to Results of Elemental Analysis of Prepared Polymers, IR spectra, luminescence spectra of prepared polymers and examples of Examples of the extinction spectra of Ag-NPs/sPEP-CtBr systems. The materials are available *via* the Internet at <http://www.springer.com/13233>.

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Supporting Information

Elemental Analysis.

Table SI. Results of Elemental Analysis of Prepared Polymers

Polymer Code	Polymerization Solvent	wt%				
		C	H	N	Br	I
sPEP-EtBr	AN solution ^a	57.62	4.96	8.31	21.74	X
sPEP-EtI	AN solution ^a	50.73	4.14	6.97	X	33.36
sPEP-NoBr	AN solution ^a	64.41	6.85	7.20	17.27	X
sPEP-CtBr	AN solution ^a	68.10	8.21	6.07	15.58	X
bPEP-EtBr	none ^b	54.61	4.87	8.21	23.91	X
bPEP-EtI	none ^b	48.47	4.30	6.99	X	38.90
bPEP-NoBr	none ^b	64.94	6.81	7.20	16.73	X
bPEP-CtBr	none ^b	67.97	7.86	5.93	15.80	X

^aAcetonitrile solution. ^bBulk (without solvent).

Spectral Characteristics.

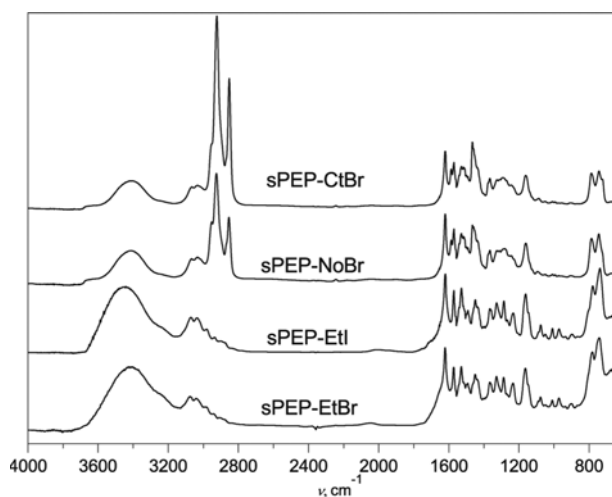


Figure S1. IR spectra of polymers prepared in acetonitrile solution. Samples were diluted in KBr, DRIFT.

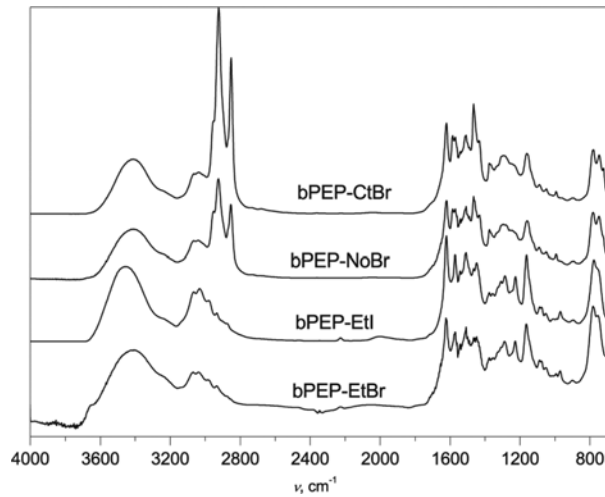


Figure S2. IR spectra of polymers prepared in bulk. Samples were diluted in KBr, DRIFT.

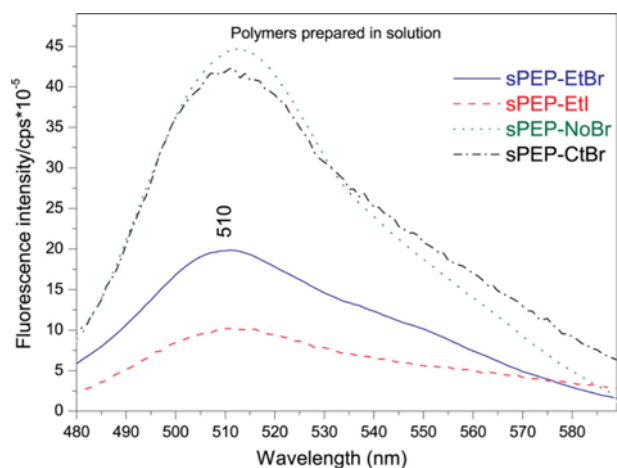


Figure S3. Emission spectra of polymers prepared in acetonitrile solution (concentration 5×10^{-5} mol dm⁻³ in MeOH, λ_{exc} =420 nm).

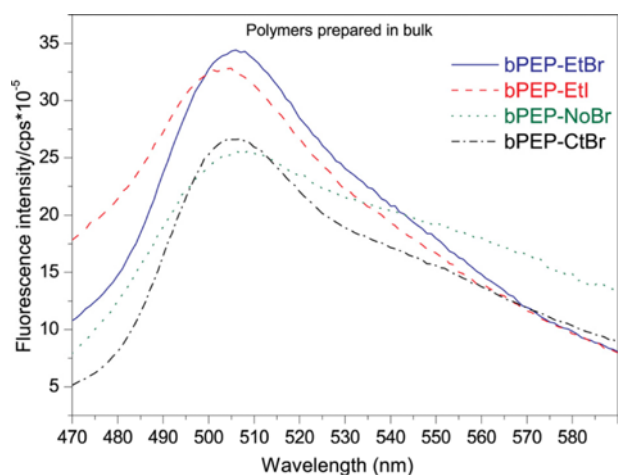


Figure S4. Emission spectra of polymers prepared in bulk (concentration 5×10^{-5} mol dm⁻³ in MeOH, λ_{exc} = 420 nm).

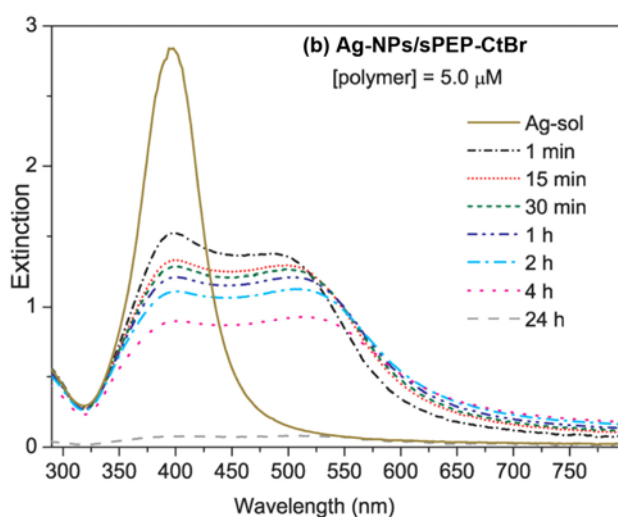
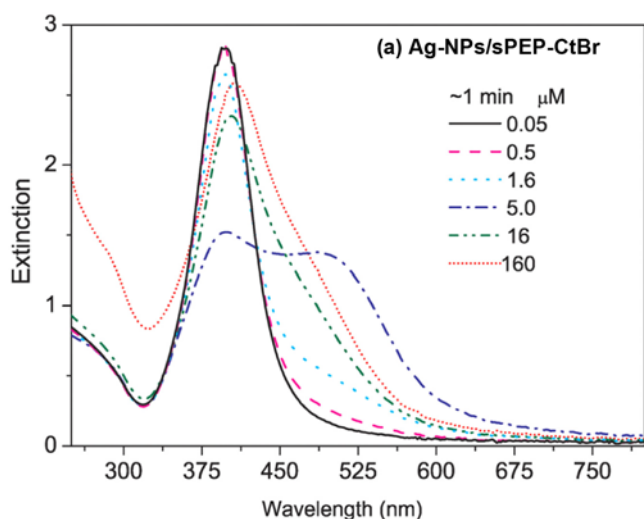
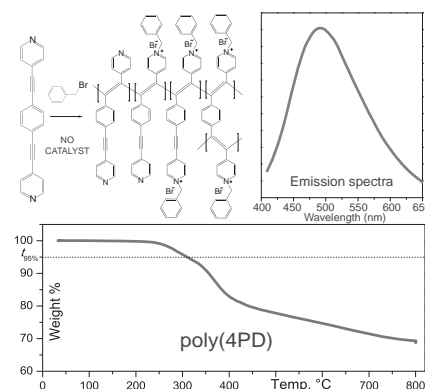


Figure S5. Examples of the extinction spectra of Ag-NPs/sPEP-CtBr systems: (a) different concentrations of sPEP-CtBr, aging time of 1 min. (b) optimum concentration (5×10^{-6} M), different aging times - a decrease in the absorption is due to the sedimentation of nano-composite aggregates to the bottom of cuvette. Thus obtained solid systems were used in the SERS experiments.

Ionic π -Conjugated Polyelectrolytes by Catalyst Free Polymerization of Bis(pyridyl)acetylenes and Bis[(pyridyl)ethynyl]benzenes

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The spontaneous, catalyst free polymerization of four monomers of the bis(pyridyl)acetylene and bis[(pyridyl)ethynyl]benzene types containing either 2-pyridyl or 4-pyridyl groups via activation with benzyl bromide leads to ionic π -conjugated polyacetylene-type polyelectrolytes (CPEs). All polymers are characterized by means of NMR, IR, UV/vis and photoluminescence spectroscopies, thermogravimetric analysis (TGA) and matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS). The position of the pyridyl groups in the monomer influences the degree of quaternization and the extent of conjugation of CPEs. Monomers with 4-pyridyl groups provide CPEs with a low extent of quaternization [$N^+/(N^+ + N) = 0.27\text{--}0.34$] and high extent of conjugation. On the other hand, the CPEs derived from 2-pyridyl-containing monomers are highly quaternized [$N^+/(N^+ + N) = 0.77\text{--}1.00$], however, possess lower conjugation of the main chains. The mechanism assuming quaternization and polymerization as competitive reactions is proposed to explain the difference in the extent of quaternization of CPEs. Prepared CPEs i) are well soluble in polar solvents, e.g., water, methanol, dimethyl sulfoxide, and dimethylformamide, ii) exhibit photoluminescence (emission in the violet to yellow region), and iii) possess high thermal stability.



1. Introduction

The π -conjugated polymers (CP), e.g., polyacetylenes, poly(arylene)s, poly(*para*-phenylenevinylene)s, and poly(*para*-phenyleneethynylene)s have become an important class of

materials with a wide variety of applications,^[1–8] including light-emitting diodes (LEDs),^[9] light-emitting electrochemical cells (LECs),^[10] plastic lasers,^[11] solar cells,^[12] field-effect transistors (FETs)^[13] and porous materials.^[14,15]

The π -conjugated polyelectrolytes (CPEs) represent a special subclass of CPs.^[16] The CPE polymers comprise π -conjugated main chains and ionic and/or ionizable groups. Unlike the majority of neutral CPs, CPEs additionally exhibit i) solubility in polar solvents as water, aqueous solutions, alcohols, and others environmentally friendly solvents,^[17–19] ii) amphiphilic nature, which gives CPE macromolecules capability of self-assembling in solutions and ability to interact specifically with particular species under measurable optical and/or electrical responses, and iii) simultaneous electronic and ionic conductivity^[20] reducing the electron-injection barrier

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from high work-function metal electrodes into polymer in optoelectronic devices.^[21] These properties predetermine CPEs as promising optically and/or redox responsive materials for the construction of various devices and sensors.^[22]

CPEs are mainly prepared by postpolymerization modifications of conjugated polymers via ionization of the side groups. The direct synthesis of CPEs is used rarely, mainly due to the sensitivity of the polymerization catalysts (initiators) to the ionic groups of the monomers.

In 1991, Subramanyam and Blumstein published the one step synthesis of CPEs from mixtures of either 2- or 4-ethynylpyridine with alkyl halides without any additional catalyst or initiator.^[23] This polymerization yielded the ionic conjugated polyacetylene-type CPEs bearing *N*-alkylpyridiniumyl pendants. This reaction is often denoted as (spontaneous) quaternization polymerization. The propagation of this chain-growth polymerization is assumed to proceed via quaternization of the monomer molecule with alkyl halide followed by the addition of the quaternized (activated) monomer molecule to the end of the growing polyene chain. A wide variety of CPEs of this type have been prepared and investigated.^[24–27] For example, Gal et al. presented a series of CPEs, prepared from 2-ethynylpyridine and various functionalized quaternizing agents as β -propiolactone, 1-iodopentane, or 4-(methylthio) benzyl bromide.^[28–30] Recently, we reported quaternization polymerization of 2- and 4-ethynylpyridines with bifunctional quaternizing agents [e.g., 1,4-bis(bromomethyl)benzene] into porous CPE-type networks.^[26] However, only few experiments dealt with the quaternization polymerization of monomers comprising in the molecule pyridyl group(s) and internal ethynyl group. These experiments were reported by Subramanyam and Blumstein (1991) in the article^[23] which however deal mainly with polymerization of terminal-ethynyl-group containing pyridine monomers. Nevertheless Blumstein presented also the quaternization polymerization of 1,2-bis(4-pyridyl)acetylene with 1-bromododecane and with 1-heptylmethanesulfonate. These polymerizations resulted in water soluble ionic CPEs.^[23] The same polymerization with nonane-1,9-bis(methanesulfonate) led to insoluble cross-linked product.^[23] However, to our best knowledge, no further research has been focused on the quaternization polymerization of pyridyl groups containing internal alkynes. This is despite the fact that i) poly(disubstituted acetylene)s generally exhibit better photoluminescence properties compared to the poly(monosubstituted acetylene)s^[31] and ii) that the presence of two pyridiniumyl pendants per one monomeric unit may have a positive impact on the solubility of the polymers in polar solvents.^[32–34]

In this paper we report the spontaneous, catalyst free polymerization of four bis(pyridyl)acetylenes containing one (PM type monomers) or two (PD type monomers) internal ethynyl groups (PM stands for monoacetylenic type of monomer, PD stands for diacetylenic type of monomer). Resulting well soluble, photoluminescent, and thermally stable CPEs were characterized by elemental analysis, matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS), IR, NMR, UV/vis, and photoluminescence spectroscopies. The relation between the composition and architecture of the monomer on one side and extent of the ionization of the polymer, its thermal stability, and photoluminescence properties on the other side is discussed.

2. Experimental Section

2.1. Materials

Acetone, acetonitrile, 2-ethynylpyridine (2EPy), 2-bromopyridine, benzyl bromide, bis(triphenylphosphine)palladium(II) dichloride [Pd(PPh₃)₂Cl₂], dichloromethane, copper(I) iodide (CuI), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), 1,2-diphenylacetylene (anhydrous, 99.8%), ethanol, hexane, methanol, tetrahydrofuran (THF), triethylamine (all from Sigma-Aldrich), DMF-*d*₇ (99.5 atom% D), DMSO-*d*₆ (99.5 atom% D) (both from Armar chemicals), methanol for spectroscopy (Merck), diethyl ether, ethyl acetate (both from Lach-ner), 4,4'-bipyridyl, 4-iodopyridine (both from Across Organics), and 4-ethynylpyridine (TCI Europe) were used as obtained. 1,4-Diethynylbenzene from Sigma-Aldrich was purified by vacuum sublimation. Toluene from Sigma-Aldrich was distilled from sodium-benzophenone desiccant.

2.2. Methods

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. The ¹H NMR and ¹³C NMR spectra were measured using a Varian Unity Inova 400 and Varian Unity Inova 300 spectrometer in DMSO-*d*₆ as a solvent. Photoluminescence emission spectra were measured using a Horiba Jobin Yvon Fluorolog 3 with excitation wavelength of 350 nm in methanol. UV/vis absorption spectra were measured using Shimadzu UV-2401PC spectrophotometer in methanol. Thermogravimetric analysis (TGA) of polymers was performed using SETSYS Evolution TGA, Setaram Instrumentation, in N₂ atmosphere. TGA measurement procedure: at first, sample was heated to 100 °C with a step of 10 °C min⁻¹ and dried for 1 h (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. 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 μ L of the mixture was deposit on the ground-steel target plate. Drop was dried

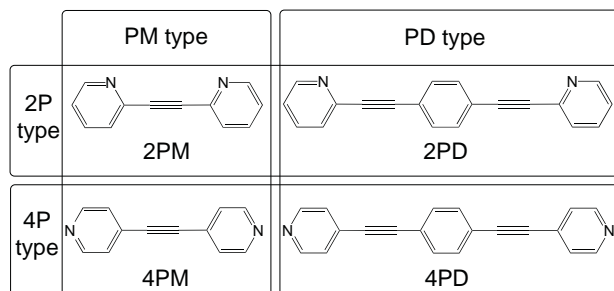


Figure 1. Monomers: 1,2-bis(2-pyridyl)acetylene (2PM), 1,2-bis(4-pyridyl)acetylene (4PM), 1,4-bis[(2-pyridyl)ethynyl]benzene (2PD), and 1,4-bis[(4-pyridyl)ethynyl]benzene (4PD).

at ambient atmosphere. MALDI-TOF MS analysis was performed with an UltrafleXtreme (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.

Elemental analyses of the products were done at the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic.

2.3. Monomers Synthesis

On the purpose to be subsequently polymerized, a series of four symmetrical acetylenic monomers with pyridyl groups has been synthesized and characterized: 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 formulas and codes of the monomers are presented in Figure 1. Digits in the codes specify the positional isomerism of the pyridyl substituents (2P – *ortho*-positioned pyridyl groups, 4P – *para*-positioned pyridyl groups), M stands for the monoacetylenic character of the monomer, D stands for the diacetylenic character of the monomer.

Synthesis of monomers was performed as a Sonogashira cross-coupling reaction. In case of PM type monomers, 2-bromopyridine or 4-iodopyridine was coupled with equimolar amount of respective ethynylpyridine. In case of PD type monomers, 2.1 equivalents of proper halopyridine were coupled with one equivalent of 1,4-diethynylbenzene. Pd(PPh₃)₂Cl₂ (5 mol%) was used as a catalyst, CuI (5 mol%) was used as a cocatalyst and mixture of toluene and triethylamine as solvent and as a base. Procedure: reaction mixture in Schlenk flask was stirred on magnetic stirrer under Ar atmosphere at temperature of 50 °C. After 24 h the reaction mixture was cooled down and solvent was evaporated. The desired product was obtained as solid after purification by column chromatography [silica gel, diethyl ether (PM type monomers) or ethyl acetate (PD type monomers) as a mobile phase].

The spectra of monomers (¹H NMR, ¹³C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.^[35–37] For details on preparation and spectral characterization of monomers see the Supporting Information.

2.4. Quaternization Polymerization

Monomers 2PM, 4PM, 2PD, and 4PD were polymerized via activation with benzyl bromide as quaternizing agent (QA).^[26] In a typical experiment, a monomer (200 mg) and four equivalents of QA were mixed in 1.5 mL of DMF under Ar atmosphere in a thick-wall glass ampule. Ampule was sealed and reaction mixture was stirred for 2 h at 100 °C, then the ampule was placed into the thermostated oven at 100 °C. Reaction mixture changes color from light yellow to dark brown or black. After 10 d, 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 h and then in vacuum for 48 h at room temperature.

3. Results and Discussion

3.1. Polymerization

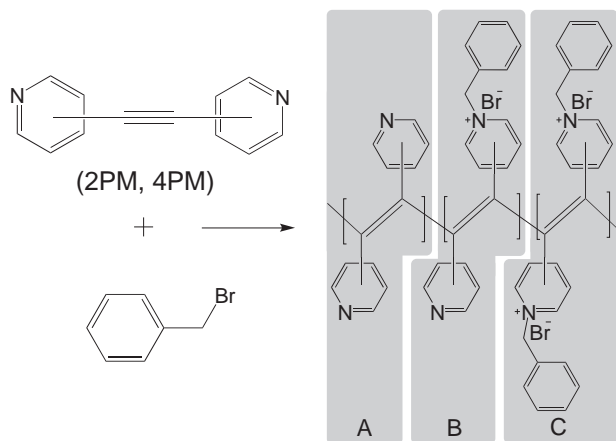
Monomers 2PM, 4PM, 2PD, and 4PD were polymerized into the respective polymers poly(2PM), poly(4PM), poly(2PD), and poly(4PD) by means of quaternization polymerization with benzyl bromide as a QA without any additional catalyst or initiator. In all cases the dark, solid polymers were obtained.

In the case of quaternization polymerization of 2PM and 4PM monomers, linear polyacetylene-type polymers possessing monomeric units of various degrees of quaternization can be expected as the product. Three types of monomeric units can be present in the polymer: A) nonquaternized units, B) monoquaternized units, and C) diquaternized units (Scheme 1).

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 (see Scheme 2). 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, 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.

3.2. Extent of Quaternization of the Pyridine Rings in the Polymers

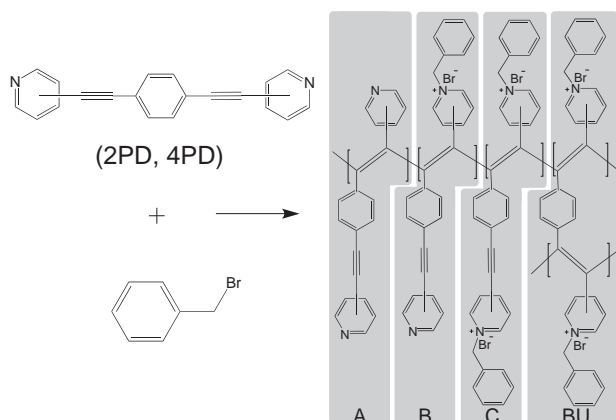
Table S1 in the Supporting Information summarizes the results of the elemental analysis (EA) of polymers prepared in this study, poly(2PM), poly(4PM), poly(2PD), and poly(4PD). The EA proved the presence of bromine in all



Scheme 1. Quaternization polymerization of PM type monomers with benzyl bromide. A, B, and C are the contemplated monomeric units in the polymer.

the polymers [from 12.8 wt% in poly(4PD) to 29.5 wt% in poly(2PM)]. We assume bromine 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 well-known polymers prepared via polymerization of 2-ethynylpyridine and 4-ethynylpyridine induced by quaternization with various alkyl halides.^[23]

The initial mole ratio of QA/monomer in the feed was equal to 4 in all the polymerizations that corresponded to the initial Br/N mole ratio equal to 2. The excess of QA over the amount of pyridine nitrogen atoms was applied with the aim to support the quaternization of the pyridine rings. Taking into account Schemes 1 and 2, one can assume the maximum value of the Br/N mole ratio in the polymer to be equal to unity. All the pyridine rings are quaternized in such a case, i.e., the degree of quaternization defined as $N^+/(N^+ + N)$ is equal to unity (N^+ and N stand for amounts of quaternized and nonquaternized nitrogen atoms in the



Scheme 2. 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, respectively). As it is evident from Table 1, regardless of the constant Br/N mole ratio in the feed the degree of quaternization of the polymers varied significantly in dependence on the type of the monomer applied. Based on the $N^+/(N^+ + N)$ values, the polymers can be divided into two groups: i) highly quaternized polymers based on 2P type of monomers and ii) less quaternized polymers based on 4P type of monomers. The highly quaternized polymers of the first group, poly(2PM) and poly(2PD), should contain mainly C-type monomeric units (see Schemes 1 and 2). On the other hand, the less quaternized poly(4PM) and poly(4PD) exhibit the degree of quaternization of 0.27 and 0.34, respectively, i.e., only a quarter to a third of pyridine rings are quaternized in these polymers. Poly(4PM) and poly(4PD) thus unambiguously contain nonquaternized monomeric units of the A-type (see Schemes 1 and 2) in combination with the quaternized units (both B- and C-types units are under consideration).

The weight of the polymer isolated from the reaction mixture and the results of EA allowed to determine the conversion of the acetylenic monomer into the polymer. As given in Table 1, high monomer-to-polymer conversions ranging from 61% to 81% were achieved in the reported polymerizations.

3.3. NMR and IR Spectra of the Polymers

The ^1H NMR spectra of polymers are shown in Figure 2. The spectra are characteristic with broad and poorly resolved signals that may reflect low covalent and configurational uniformity of the polymers. All the samples except for poly(2PD) are in fact copolymers (most probably random) composed of monomeric units differing in the degree of quaternization (see Schemes 1 and 2). Moreover, chain-branching is to be assumed in the case of samples poly(2PD) and poly(4PD).

As the configurational structure is concerned 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 since the polymerizations proceeded without any catalyst that might control the configuration structure of the product. That is why only a rough assignment of the signals of ^1H NMR spectra in Figure 2 can be done. Generally, the broad signal at 6.5–9.1 ppm in ^1H NMR 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. A more precise specification is possible in the case of ^1H 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

Table 1. Polymerization of 2PM, 4PM, 2PD, and 4PD (200 mg of the monomer in the feed is same for all polymerizations) with benzyl bromide as QA (initial mole ratio QA/monomer = 4).

Sample code	Weight ^{a)} [mg]	Monomer conversion ^{b)} [%]	N ⁺ /(N ⁺ + N) ^{c)}	Composition of polymer ^{d)}
Poly(2PM)	367	81	0.77	<u>C</u> + A and/or B
Poly(4PM)	230	73	0.27	<u>A</u> + B and/or C
Poly(2PD)	256	63	1.00	C
Poly(4PD)	188	61	0.34	<u>A</u> + B and/or C

^{a)}Weight of isolated polymers; ^{b)}Monomer-to-polymer conversion; ^{c)}Degree of quaternization of the polymer based on the Br/N mole ratio in the polymers. ^{d)}Possible monomeric units in the polymers (see Schemes 1 and 2), the prevailing units are underlined.

lower symmetry of 2-pyridyl/2-pyridiniumyl groups. Protons of CH₂ 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 the ¹H NMR spectra (vide infra).

Due to the microstructural nonuniformity of all the samples, it was difficult to obtain their relevant ¹³C NMR spectra. Nevertheless, recorded ¹³C NMR spectra of all polymers (see Figure 3) show signal at about 130 ppm that can be ascribed to the resonance of carbons of i) conjugated acetylenic backbone, ii) phenyl groups of *N*-benzylpyridiniumyl moieties, and iii) pyridyl/pyridiniumyl pendant groups. The broad signal at about 150 ppm in the

¹³C NMR spectra of poly(2PM), poly(4PM), and poly(4PD) most probably corresponds to the carbon atoms adjacent to nitrogen in nonquaternized pyridyl groups.

The polymerization of 2PM and 4PM (monomers with one triple bond per monomer molecule) with QA is assumed to lead to linear polyacetylenic-type polymers in which triple bonds of monomers are transformed into double bonds of the polymer main chains (Scheme 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) (see Figure 4).

As prevalently soluble polymers were obtained in the polymerization of 2PD and 4PD (monomers with two triple bonds per monomer molecule) with QA, it is not expected

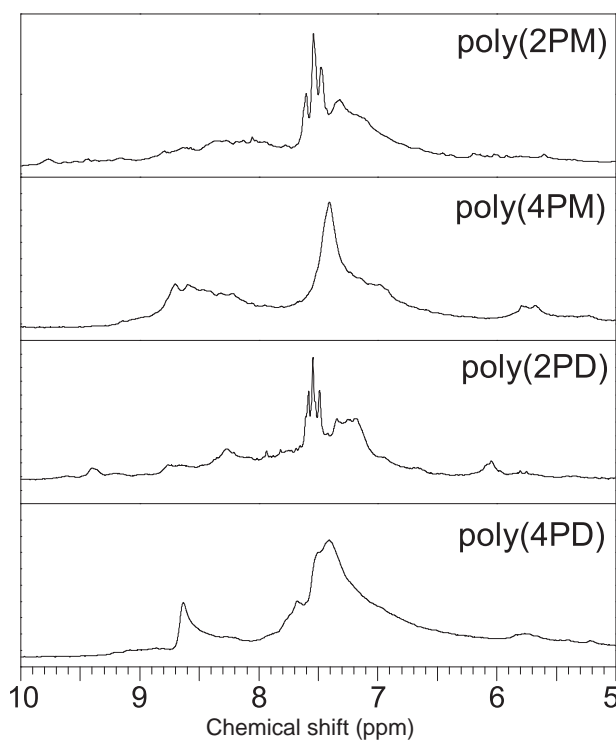


Figure 2. ¹H NMR spectra of poly(2PM), poly(4PM), poly(2PD), and poly(4PD), 300 MHz, DMSO-*d*₆.

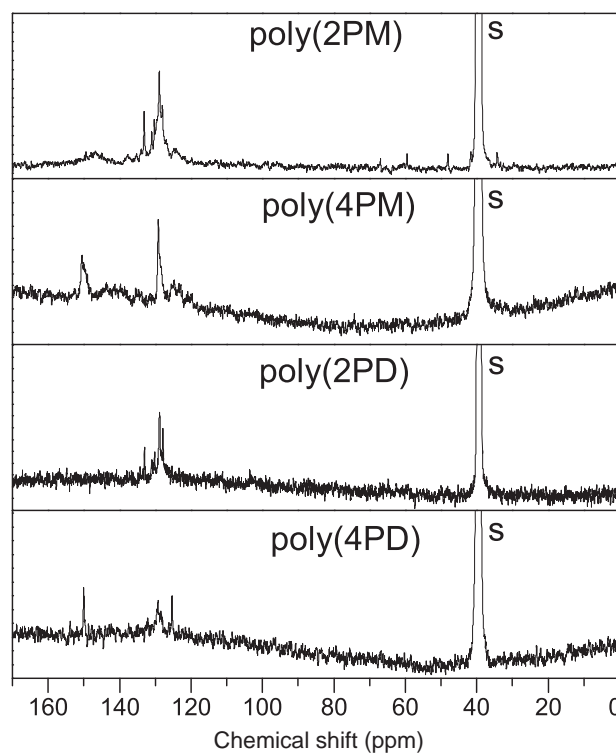


Figure 3. ¹³C NMR spectra of poly(2PM), poly(4PM), poly(2PD), and poly(4PD), 400 MHz, DMSO-*d*₆, S – solvent.

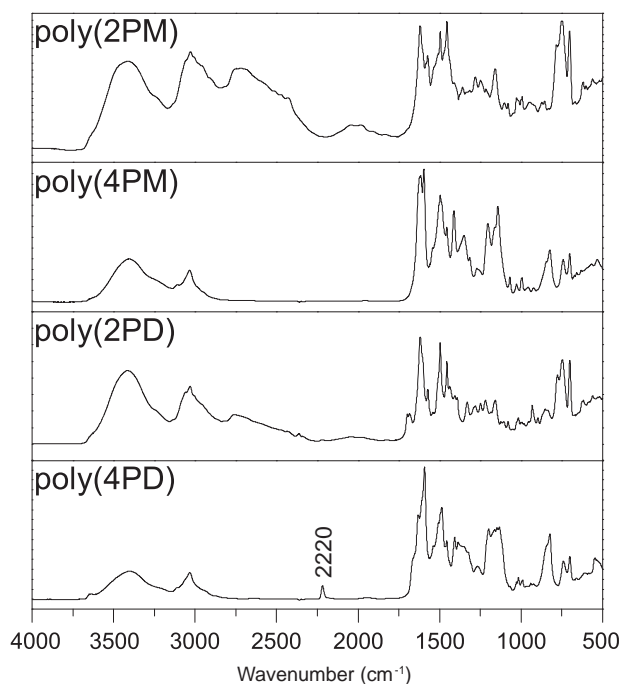


Figure 4. IR spectra of poly(2PM), poly(4PM), poly(2PD), and poly(4PD). DRIFTS, diluted with KBr.

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 $\text{C}\equiv\text{C}$ vibration on nonreacted internal ethynyl groups. However, such a band has not been detected in the IR spectrum of poly(2PD) (Figure 4) although this polymer should contain the internal ethynyl groups too. This may be explained by the complete quaternization of pyridyl groups in poly(2PD) [$\text{N}^+ / (\text{N}^+ + \text{N}) = 1$, see Table 1] which could make the $\text{C}\equiv\text{C}$ bond stretching vibration less IR active or inactive. We attempted to detect the internal ethynyl groups in poly(2PD) by means of Raman spectroscopy (for the instrumentation of Raman spectroscopy see literature.^[38] However, no reliable Raman spectrum was obtained due to the photoluminescence of poly(2PD) (vide infra).

The $\text{N}^+=\text{C}$ stretching vibration of pyridiniumyl units (region from 1619 to 1629 cm^{-1}) is well observed in the IR spectra of all polymers (Figure 5).^[39] 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 $\text{C}=\text{C}$ bonds of phenyl groups and acetylenic backbone and ii) stretching vibration of $\text{N}=\text{C}$ bonds of nonquaternized pyridyl groups.^[40] 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

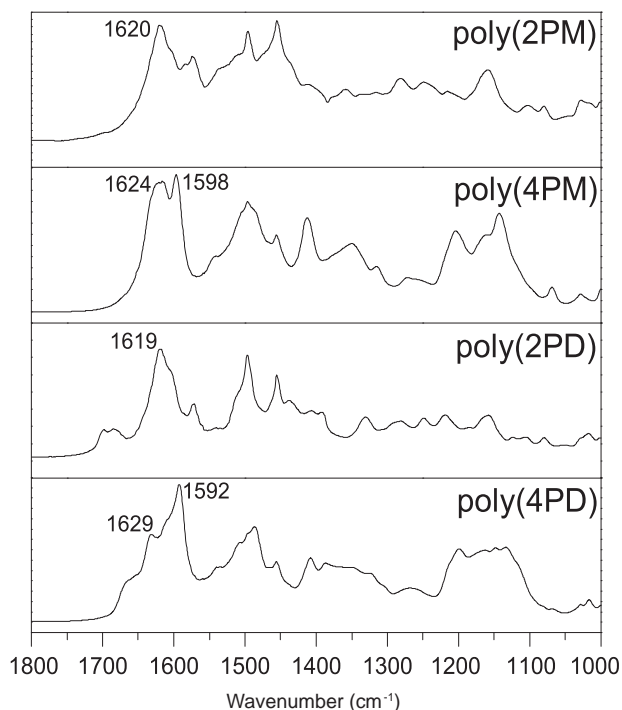


Figure 5. IR spectra of poly(2PM), poly(4PM), poly(2PD), and poly(4PD). DRIFTS, diluted with KBr, 1800 cm^{-1} – 1000 cm^{-1} .

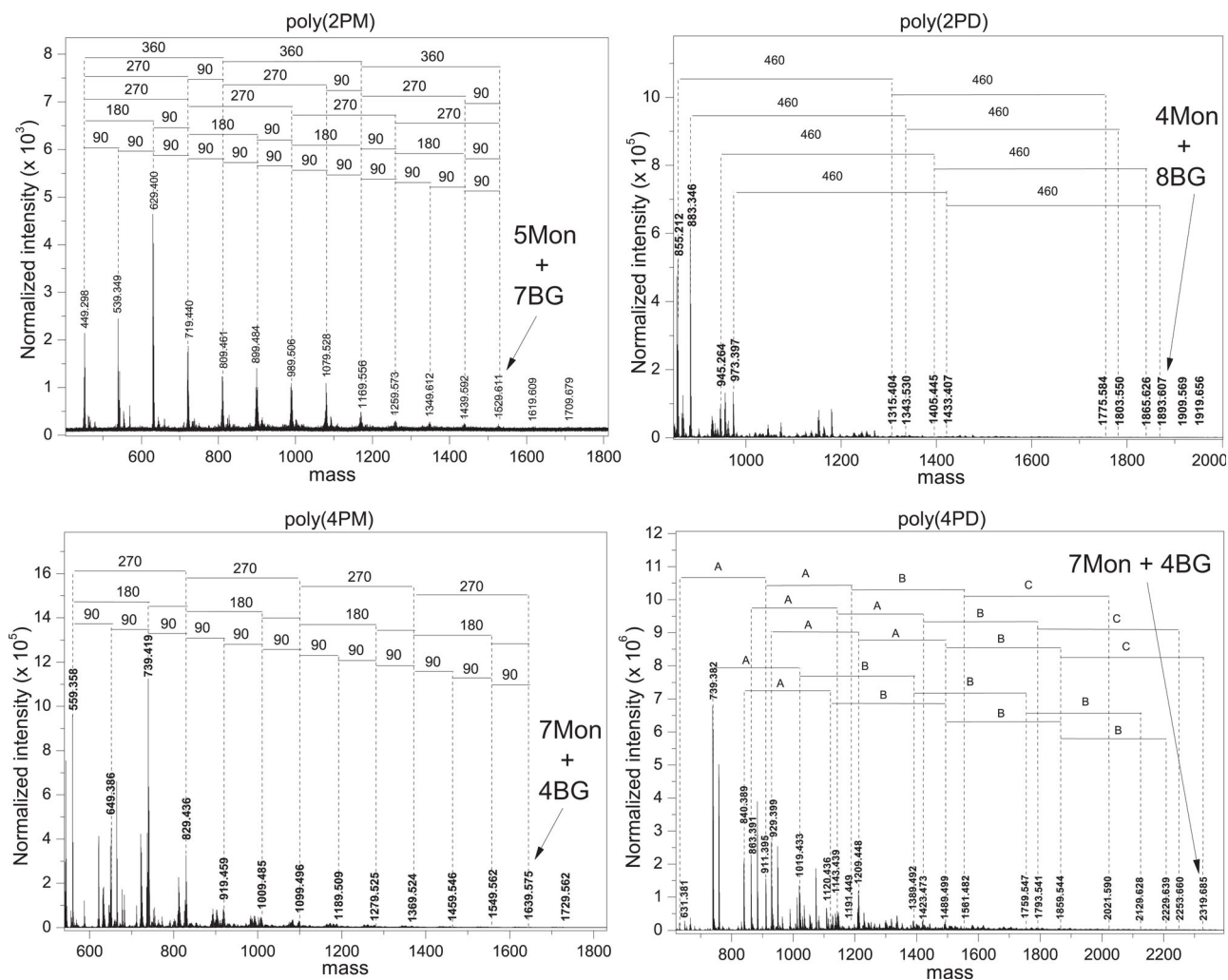
highly quaternized polymers poly(2PM) and poly(2PD) the 1619 – 1629 cm^{-1} band is observed mainly, whereas in the spectra of less quaternized poly(4PM) and poly(4PD), both 1619 – 1629 cm^{-1} and 1592 – 1598 cm^{-1} vibration bands are well developed.

3.4. MALDI-TOF MS Analysis of the Polymers

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.^[41] At this time we provide the interpretation of MALDI-TOF MS spectra of our polymers to support their composition and structure proposed in Schemes 1 and 2.

The MALDI-TOF MS spectra of polymers derived of PM type monomers exhibit distinct series of signals with an increment of 90 Da . 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 (see Figure 6).

As far as the resolution of the spectrum of poly(2PM) (Figure 6) is processible, a signal corresponding to particles containing five molecules of the monomer (5Mon) quaternized with 7 benzyl groups (BG) (mass 1530) is detected. This Mon/BG mole ratio is in agreement with



■ Figure 6. MALDI-TOF MS spectra of poly(2PM), poly(4PM), poly(2PD), and poly(4PD).

the $N^+/(N^+ + N)$ value of 0.77 ascertained from the elemental analysis.

The same evaluation of the MALDI-TOF MS spectrum of poly(4PM) (Figure 6) provides a signal with mass 1640. This signal corresponds to particles containing more than seven molecules of the monomer (7Mon) quaternized with 4 BG. This Mon/BG mole ratio is in agreement with $N^+/(N^+ + N)$ value of 0.27 ascertained from the elemental analysis.

The MALDI-TOF MS spectra are less concise in the case of polymers derived of the PD type monomers. This could be attributed to the high compositional and structural diversity of the monomeric units of these polymers (see Scheme 2). As the resolution of the MALDI-TOF MS spectrum of poly(2PD) (see Figure 6) is processible, a signal with mass of 1893 was detected that corresponds to particles containing more than four molecules of the monomer (4Mon) quaternized with 8 BG. 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 monomeric unit C (see Scheme 2 for the diquaternized monomeric unit) is observed in the spectrum (Figure 6).

The same evaluation of the MALDI-TOF MS spectrum of poly(4PD) (Figure 6) provides a signal with mass 2320. This signal corresponds to particles containing more than seven molecules of the monomer (7Mon) quaternized with 4 BG. This Mon/BG mole ratio is in agreement with $N^+/(N^+ + N)$ 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 A + 3B or 2A + B + C in Scheme 2) is observed in the MALDI-TOF MS spectrum of poly(4PD).

Although all the polymers contain a high amount of bromide anions we did not succeed in revealing the bromine-containing particles in the MALDI-TOF MS spectra. Probably, further optimization of the ionization process would be necessary. It should be noted that

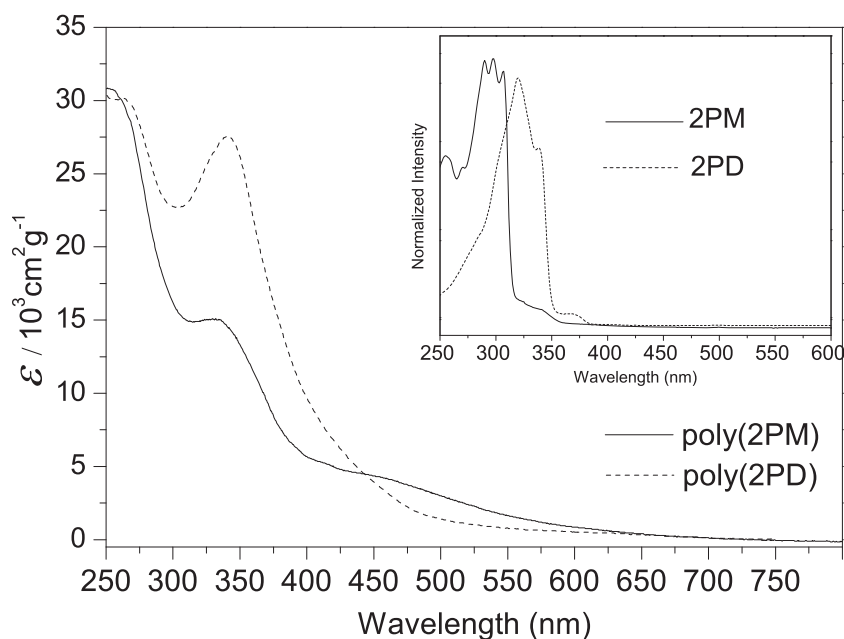


Figure 7. UV/vis spectra of polymers poly(2PM) and poly(2PD) and monomers 2PM and 2PD, measured in MeOH, concentration 2.0×10^{-2} mg mL⁻¹, ϵ – specific absorptivity.

also the MALDI-TOF analysis of a low-molecular-weight model compound, 4,4'-bis(*N*-benzyl)dipyridinium bromide, provides only bromine-free MS signals. The MALDI-TOF MS spectrum contains a dominant signal with the molar mass of 338 Da which refers to the cationic form of 4,4'-bis(*N*-benzyl)dipyridinium bromide. Moreover, obvious decrement of mass of 90 Da corresponding to benzyl group is observed in the spectrum. For the MALDI-TOF MS spectrum of 4,4'-bis(*N*-benzyl)dipyridinium bromide see the Supporting Information.

3.5. UV/vis and Photoluminescence Characteristics of the Polymers

The UV/vis spectra of the polymers and corresponding monomers (all in methanol) are shown in Figures 7 and 8, the respective UV/vis spectral characteristics of polymers are summarized in Table 2. 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. These bands remains preserved in the spectra of polymers although they are slightly shifted to the higher energy region (λ_{max} from 255 to 307 nm, see Table 2).

Besides these bands, all the polymers also exhibit the absorption in the lower energy regions. 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 and bromide anion.^[42] 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 1).

The absorption in the visible region can be ascribed to $\pi \rightarrow \pi^*$ transitions in the polyacetylene main chains. The comparison of UV/vis spectra in Figures 7 and 8 indicates that poly(4PM) and poly(4PD) exhibit higher extent of conjugation than their poly(2PM) and poly(2PD) counterparts. In the case of poly(4PM) and poly(4PD), the benzyl moieties that quaternize the nitrogen atoms in the pyridine rings are distant from the polyacetylene main chains. 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.

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). On the contrary, all the polymers emit the visible light upon the UV excitation (see Figure 9 for the photoluminescence emission spectra of the polymers).

Table 2. UV/vis absorption characteristics of polymers in MeOH.

Sample code	UV region $\lambda_{\text{max}}^{\text{a)}$ [nm]	UV region $\lambda_{\text{max}}^{\text{b)}$ [nm]	Vis region $\lambda_{\text{max}}^{\text{c)}$ [nm]	Wavelength of absorption edge [nm]
Poly(2PM)	255	334	460	564
Poly(4PM)	259	N/A	427, 512	777
Poly(2PD)	264	341	N/A	490
Poly(4PD)	307	N/A	521	685

^{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.

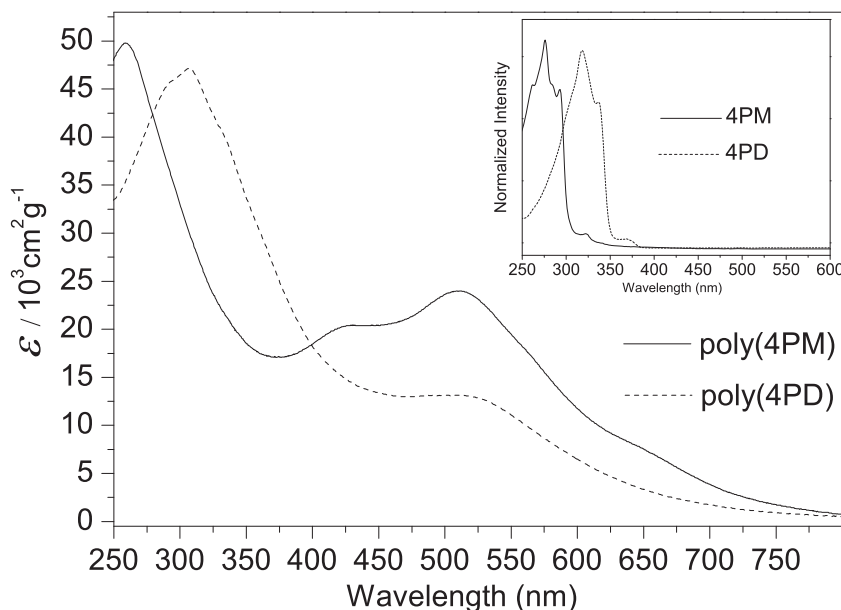


Figure 8. UV/vis spectra of polymers poly(4PM) and poly(4PD) and monomers 4PM and 4PD, measured in MeOH, concentration 2.0×10^{-2} mg mL⁻¹, ϵ – specific absorptivity.

The emission of the polymers can originate from the excitation of the partly conjugated polymer chains of polyacetylene type^[43] and/or the transition of the CT complex *N*-benzylpyridinium/Br⁻.^[44,45]

The emission spectrum of poly(2PM) shows maximum in the yellow region ($\lambda_{\text{max}} = 560$ nm) (see Figure 9). By the comparison of absorption and excitation luminescence spectra (see the Supporting Information) it is assumed that the emission originates prevalingly 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

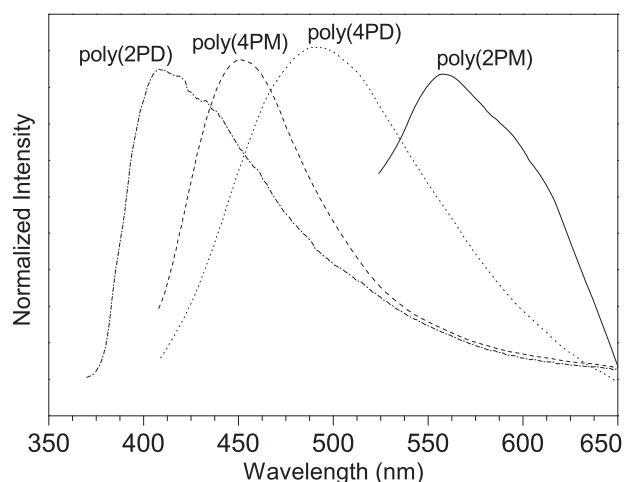


Figure 9. Photoluminescence spectra of prepared polymers measured in MeOH. Concentration of all samples was 3.3×10^{-3} mg mL⁻¹, excitation wavelength 350 nm was used.

the polyacetylene main chain (470 nm). Poly(2PD) exhibits emission maxima in the violet region ($\lambda_{\text{max}} = 407$ 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 ($\lambda_{\text{max}} = 453$ 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 (see the Supporting Information for the excitation spectra). 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.

3.6. Thermal Stability of the Polymers

The TGA curves recorded for the polymers in N₂ atmosphere are given in Figure 10. Two characteristics of the polymers 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 the temperature of 800 °C (see Table 3). The values of $t_{95\%}$ 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. This assumption is supported, e.g., by Reynolds and co-workers^[17] who studied the thermal stability of quaternized and nonquaternized (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. Similarly, we assume that the thermal decomposition of our polymers starts with a gradual release of HBr and/or benzyl bromide from the polymers at temperature >150 °C. This process is more pronounced in the case of highly quaternized poly(2PM) and poly(2PD) than in the case of less quaternized poly(4PM) and poly(4PD).

The terminal parts of TGA curves (temperature > 500 °C) confirm a higher thermal stability of poly(4PD)

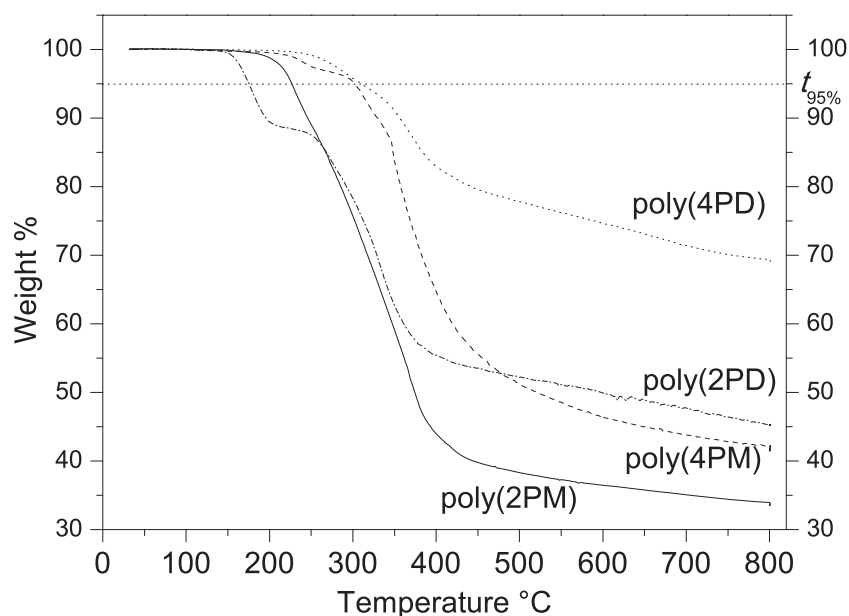


Figure 10. TGA curves of polymers in N_2 , step 10 °C min^{-1} .

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.

3.7. Solubility of the Polymers

The nonsubstituted 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.^[1] The substitution of the polyacetylene chains with ionic groups is a promising way to polyacetylenes soluble in polar solvents. As it is evident from Table 4, this assumption is confirmed for all our quaternized polymers: the polymers are mostly well soluble in methanol, ethanol, acetonitrile, dimethyl sulfoxide, and dimethylformamide. Water dissolves

Table 3. Characteristics of polymers from the 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%
Poly(4PM)	303	58%
Poly(2PD)	175	54%
Poly(4PD)	320	31%

only poly(2PM) and poly(4PM) and not poly(2PD) and poly(4PD) polymers. 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.

3.8. The Mechanism of the Quaternization Polymerization

The monomers applied in this study comprise two types of functional groups 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 polymerization to proceed we have performed experiments in which 4,4'-bipyridyl (BIPY) and 1,2-diphenylacetylene (tolan) were separately reacted with an excess of benzyl bromide (QA) under conditions

of the polymerization experiments (see the Experimental Section). No reaction proceeded in the system tolan/QA heated at 100 °C for 10 d. On the contrary, the total transformation of BIPY into 4,4'-bis(*N*-benzyl)dipyridinium bromide (QA-BIPY-QA), however, no polymer formation was observed in the BIPY/QA system. The quaternized product QA-BIPY-QA was isolated and characterized by $^1\text{H NMR}$, MALDI-TOF MS, IR spectroscopy and elemental analysis (see the Supporting Information). The results of the elemental analysis are in agreement with the theoretical stoichiometry of QA-BIPY-QA. Also the vibration of the $\text{N}^+=\text{C}$ bonds at 1635 cm^{-1} in the IR spectrum is in good agreement with literature^[26] and support the discussion on the IR spectra of prepared polymers (the vibration of the $\text{N}^+=\text{C}$ bonds in the polymers is observed at $1619\text{--}1629\text{ cm}^{-1}$, vide supra). The MALDI-TOF MS spectrum of QA-BIPY-QA (Supporting Information) has been discussed above. $^1\text{H NMR}$ spectrum corresponds to those reported for QA-BIPY-QA in the literature.^[47] Figure 11 shows $^1\text{H NMR}$ spectra of A) 4,4'-bis(*N*-benzyl)dipyridinium bromide, B) 4,4'-bipyridyl, and C) benzyl bromide. The quaternization of the nitrogen atoms in BIPY caused shifts of the $^1\text{H NMR}$ signals of the BIPY protons from 8.71 to 9.59 ppm and from 7.84 to 8.81 ppm, respectively. The bonding of the benzyl group to BIPY nitrogen resulted in the shift of the signals of CH_2 protons from 4.70 to 6.01 ppm. These shifts in $^1\text{H NMR}$ spectra are typical for the quaternization of pyridyl units with benzyl bromide as it has been discussed earlier in connection with the $^1\text{H NMR}$ spectra of the polymers (see Figure 2).^[47] Moreover, a slight dependence of the position of the $^1\text{H NMR}$ signals on the concentration of ionic QA-BIPY-QA in the solution has been

Table 4. 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.^[46]

revealed. It is obvious from Figure S7 in Supporting Information that increasing concentration of QA-BIPY-QA in the DMSO-*d*₆ solution causes a downfield shift of the signals of the protons adjacent to N⁺ atoms.

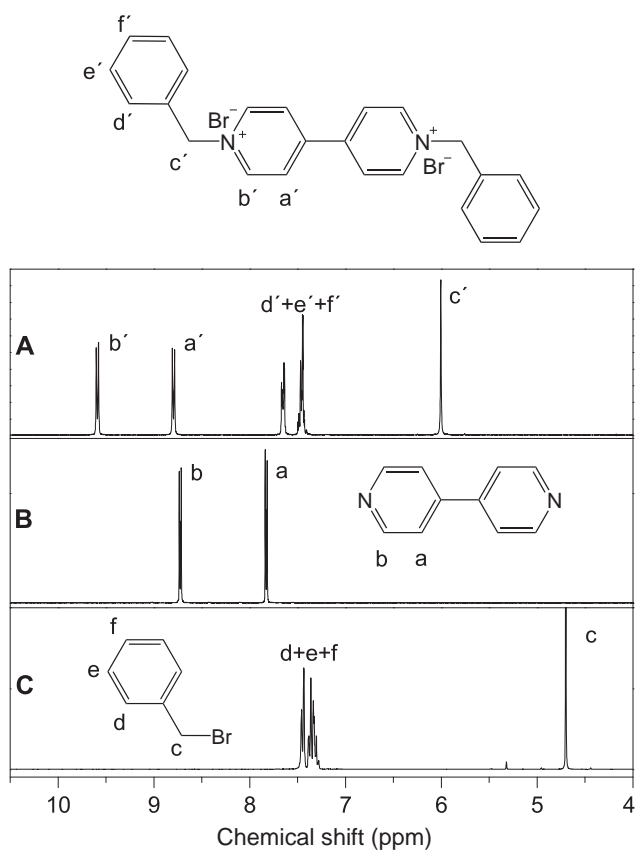


Figure 11. ¹H NMR spectra of A) 4,4'-bis(N-benzyl)dipyridinium bromide, B) 4,4'-bipyridyl, C) benzyl bromide, DMSO-*d*₆.

The experiments reported in this paragraph confirmed i) 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 BIPY are totally quaternized (by an excess of QA) under the applied conditions although only a partial quaternization of the nitrogen atoms of 4-pyridyl groups is observed in the case of poly(4PM) and poly(4PD) polymers prepared under the application of the same QA excess.

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.^[48] As a result, the fully quaternized polymers should be formed via polymerizations of monopyridylacetylenes. The dipyridylacetylenes can be activated by either single or double quaternization. The polymerizations of dipyridylacetylenes should thus provide polymers with degree of quaternization, N⁺/(N⁺ + N), ranging from 0.5 to 1 according to the original assumption of Blumstein and co-workers.^[48,49] As already stated in the Introduction, only the polyacetylene-type CPEs derived from monopyridylacetylenes have been intensively studied. Despite the extensive literature on this topic, the data and the discussion on the degree of quaternization are mostly missing and the authors presume the total quaternization of the polymers. Nevertheless, Blumstein and co-workers admitted the degree of quaternization of only 0.5 in the case of polymers prepared from 2-ethynylpyridine activated with hydrochloric acid.^[49] Recently, we determined the degree of quaternization to drop to the value of 0.43 in the case of polymer networks prepared from 2- or 4-ethynylpyridines and

1,4-bis(bromomethyl)benzene.^[26] The polymers reported in this article differ significantly in the degree of quaternization. Poly(4PM) and poly(4PD) possess the degree of quaternization <0.5 , i.e., i) totally nonquaternized monomeric units A (see Schemes 1 and 2) have been inbuilt into the chains of poly(4PM) and poly(4PD) (see Table 1) and ii) the nonquaternized 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 prevalently 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 with QA (QA/2PM mole ratio = 4) in DMF-*d*₇ (at room temperature) and monitored the reaction course by ¹H NMR spectroscopy. Resulting ¹H NMR spectra are given in Figure 12 together with the reaction scheme depicting the two-step quaternization of 2PM. The ¹H NMR spectrum recorded immediately after mixing the reaction components showed signals of 2PM and benzyl bromide (protons a, b, c, d, f, g, h, see Figure 12 for the proton labeling). After 1 h 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 monoquaternized 2PM. The positions of signals of a' and e' protons in ¹H NMR spectrum were slightly downfield shifting with reaction time due to the increasing ionic character of the reaction mixture (vide supra). Other new signals (at 9.85 and 6.55 ppm) were detectable in the spectrum at the reaction time of 1 d. We ascribed these signals to the protons a'' and e'', respectively, of the diquaternized 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 monoquaternized 2PM into diquaternized 2PM. The signals of nonquaternized 2PM were nearly absent in ¹H NMR spectrum after 1 d of the reaction. The intensities of the narrow signals characteristic of mono and diquaternized 2PM monomers (protons a', e', a'' and e'') began to decline after ca 4 d 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 monomer. The same conclusions can be expected to apply to the high quaternization extent of poly(2PD).

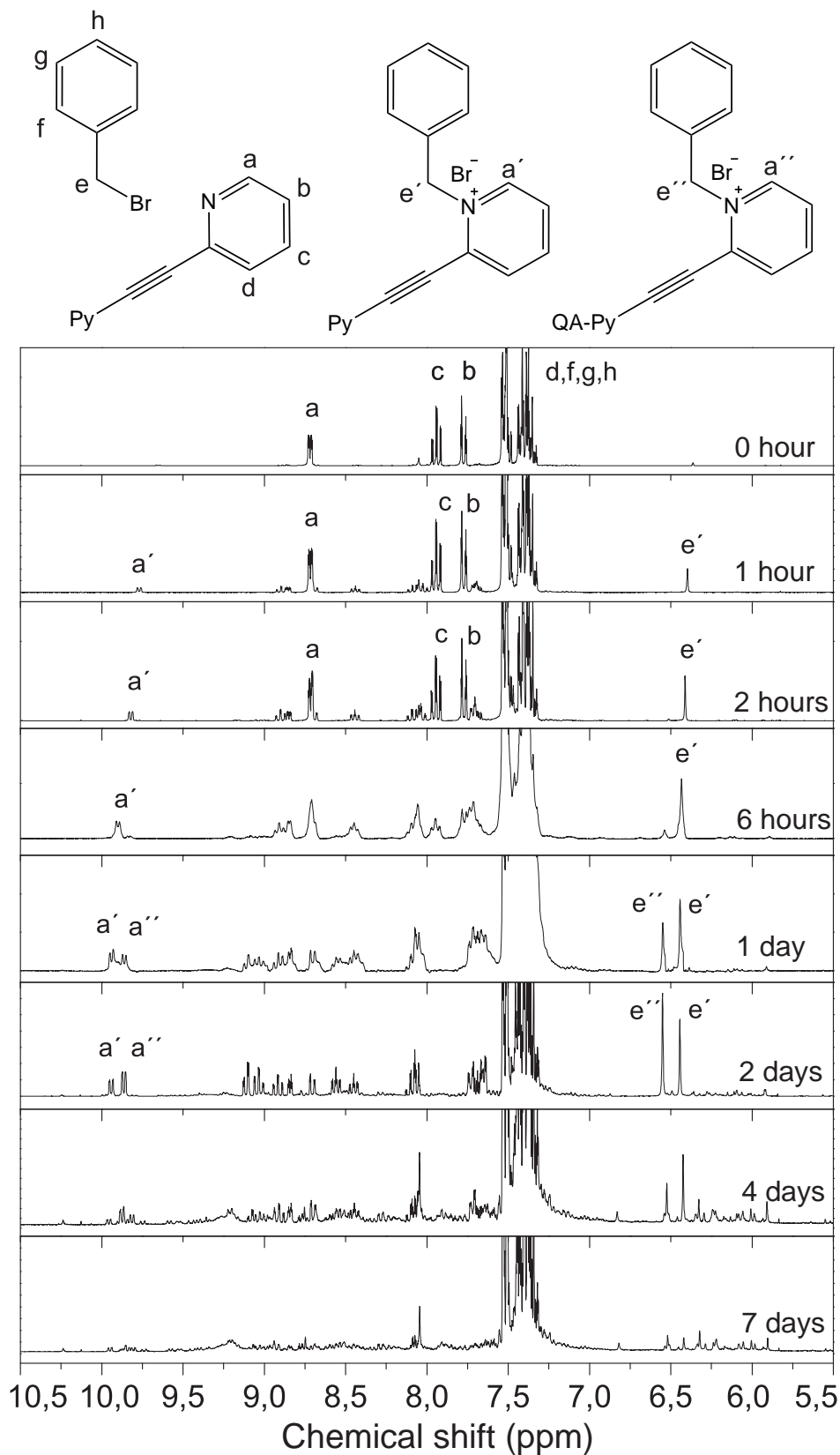
The simplified Scheme 3 shows i) the quaternization of monomer (Mon) into mono and diquaternized molecules, MonQA and Mon(QA)₂, respectively, and ii) copolymerization of MonQA, Mon(QA)₂, and, eventually, nonquaternized Mon. From the kinetic point of view, the

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 nonquaternized 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 nonquaternized pyridyl groups of the chains difficult to be accessed by QA molecules.^[50] 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.

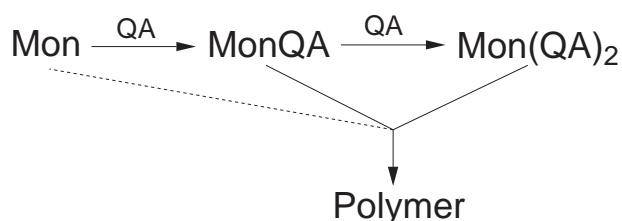
4. Conclusions

Four various monomers containing either one or two internal ethynyl groups and either 2-pyridyl or 4-pyridyl substituents have been polymerized under activation with benzyl bromide into respective linear or branched ionic π -conjugated polyacetylene-type polyelectrolytes (CPEs) without any addition of catalyst or initiator. It is therefore obvious that the quaternization polymerization which is frequently used for the polymerization of monopyridylacetylenes in the literature is efficient also for the polymerization of bispyridylacetylene type monomers of various composition and architecture.

The polymers prepared from 1,2-bis(2-pyridyl)acetylene and 1,4-bis[(2-pyridyl)ethynyl]benzene exhibit a high degree of quaternization [$N^+/(N^+ + N) = 0.77-1.00$]. On the other hand, the polymers derived from 1,2-bis(4-pyridyl)acetylene and 1,4-bis[(4-pyridyl)ethynyl]benzene are less quaternized [$N^+/(N^+ + N) = 0.27-0.34$]: in this case a not negligible amount of monomer molecules has been inbuilt into the polymer in the nonquaternized form. We suppose that the pre-polymerization quaternization of the monomer molecules and not the postpolymerization quaternization of the polymer chains predominantly contribute to the extent of the polymer quaternization. The incomplete quaternization of polymers derived from monomers with



■ Figure 12. ^1H NMR spectral study of the reaction of 2PM with benzyl bromide, $\text{DMF-}d_7$, room temperature.



Scheme 3. Quaternization and polymerization. Mon – nonquaternized monomer, MonQA – monoquaternized monomer, and Mon(QA)₂ – diquaternized monomer.

4-pyridyl groups thus most probably reflects a high rate of the propagation step of the polymerization that exceeds the rate of the monomer quaternization.

The positional isomerism of the pyridyl groups in the monomers affects also the extent of conjugation of the polymers. The polymers derived from 1,2-bis(4-pyridyl)acetylene and 1,4-bis[(4-pyridyl)ethynyl]benzene possess a high extent of conjugation manifested by a distinct vis absorption maximum at about 550 nm. The polymers derived from 1,2-bis(2-pyridyl)acetylene and 1,4-bis[(2-pyridyl)ethynyl]benzene are less conjugated most probably due to the presence of the quaternized moiety in the close vicinity to the polyene main chains that sterically hinder these chains to assume an optimal conjugated conformation.

All the polymers exhibit photoluminescence in the violet to yellow region. The photoluminescence most probably originates at the partly conjugated polymer chains and/or charge transfer complexes composed of *N*-benzylpyridiniumyl group and bromide anion.

Owing to the ionic nature, the reported polymers are well soluble in common polar solvents (e.g., methanol, dimethyl sulfoxide, and dimethylformamide). Polymers derived from monomers with one ethynyl group are, moreover, soluble in water.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Supporting Information

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Ionic π -Conjugated Polyelectrolytes by Catalyst Free
Polymerization of Bis(pyridyl)acetylenes and
Bis[(pyridyl)ethynyl]benzenes

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Supporting Information for

Full paper

Ionic π -conjugated Polyelectrolytes by Catalyst Free Polymerization of Bis(pyridyl)acetylenes and Bis[(pyridyl)ethynyl]benzenes

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1. Synthesis and characterization of the monomers

1.1. 2PM, 1,2-bis(2-pyridyl)acetylene

Synthesis of 2PM monomer was performed as a Sonogashira cross-coupling of 1 ml 2-bromopyridine (1.6 g, 10.1 mmol) and 2-ethynylpyridine (1.1 g, 10.1 mmol). Bis(triphenylphosphine)palladium dichloride (350 mg, 5 mol %) was used as a catalyst, CuI (96 mg, 5 mol %) was used as a cocatalyst and triethylamine (9 ml) as solvent and as a base. Reaction was performed in Schlenk flask and stirred under Ar atmosphere at temperature 50 °C. After 24 hours was reaction could down and solvent was evaporated. Residual solid phase was diluted in diethyl ether and filtered on alumina and concentrated. The desired product (Yield: 922 mg, 48%) was obtained as a yellowish solid after purification by chromatography on silica gel with diethyl ether as a mobile phase. The spectra of monomers (¹H NMR, ¹³C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.^[1]

^1H NMR (300 MHz, $\text{DMSO-}d_6$, δ (ppm)): 7.45 t (2 $\text{H}_{\text{pyridine}}$); 7.70 d (2 $\text{H}_{\text{pyridine}}$); 7.88 t (2 $\text{H}_{\text{pyridine}}$); 8.63 d (2 $\text{H}_{\text{pyridine}}$).

^{13}C NMR (300 MHz, $\text{DMSO-}d_6$, δ (ppm)): 88.1 (triple bond); 124.6; 128.2; 137.4; 142.0; 150.8.

IR spectrum: see Figure S1.

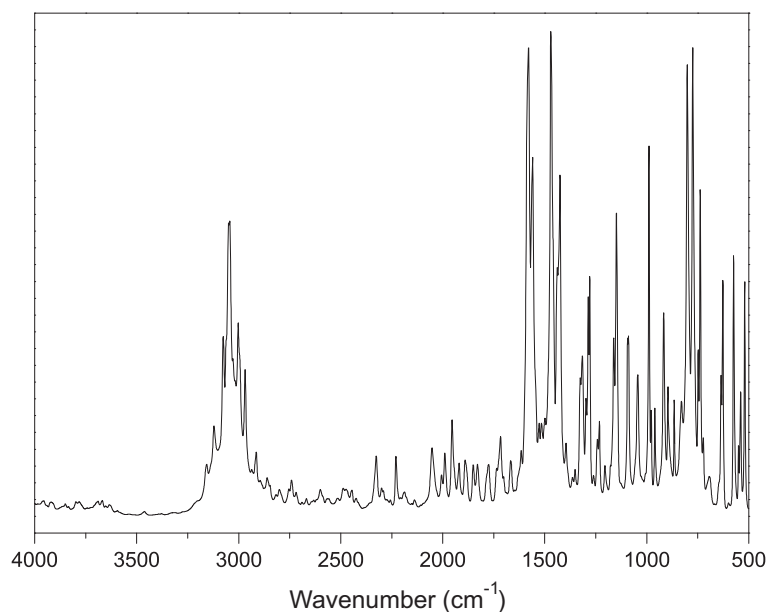


Figure S1 IR spectrum of monomer 2PM, DRIFT, diluted with KBr.

1.2. 4PM, 1,2-bis(4-pyridyl)acetylene

Synthesis of 4PM monomer was performed as a Sonogashira cross-coupling of 4-iodopyridine (800 mg, 3.9 mmol) and 4-ethynylpyridine (400 mg, 3.9 mmol). Bis(triphenylphosphine)palladium dichloride (82 mg, 3 mol %) was used as a catalyst, CuI (22 mg, 3 mol %) was used as a cocatalyst and mixture triethylamine/toluene (12/6 ml) as solvent and as a base. Reaction was performed in Schlenk flask and stirred under Ar atmosphere at temperature 90 °C. After 48 hours was reaction could down and solvent was evaporated. Residual solid phase was washed with diethyl ether, filtered on alumina and

concentrated. The desired product (Yield: 440 mg, 63%) was obtained as a white solid after purification by chromatography on silica gel with ethyl acetate as a mobile phase. The spectra of monomers (^1H NMR, ^{13}C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.^[2]

^1H NMR (300 MHz, $\text{DMSO-}d_6$, δ (ppm)): 7.59 d (4 $\text{H}_{\text{pyridine}}$); 8.67 d (4 $\text{H}_{\text{pyridine}}$).

^{13}C NMR (300 MHz, $\text{DMSO-}d_6$, δ (ppm)): 90.4 (triple bond); 125.5; 129.0; 150.0.

IR spectrum: see Figure S2.

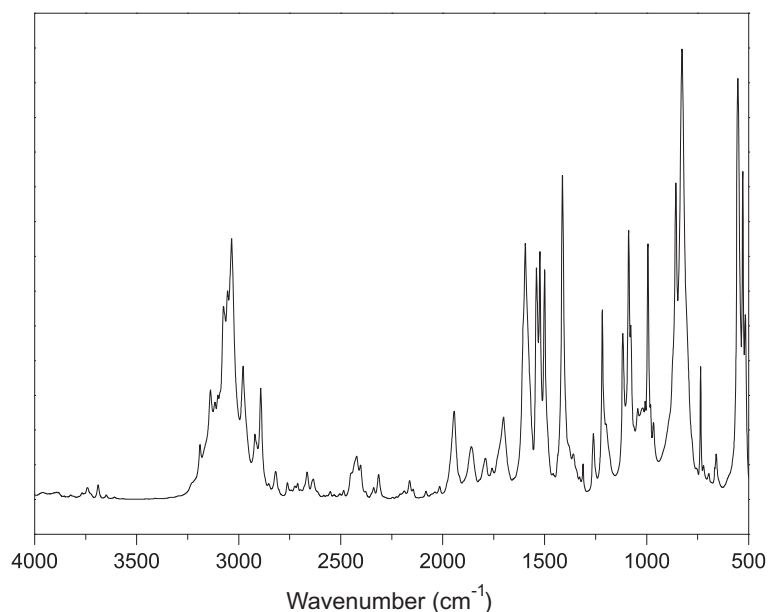


Figure S2 IR spectrum of monomer 4PM, DRIFT, diluted with KBr.

1.3. 2PD, 1,4-bis[(2-pyridyl)ethynyl]benzene

Synthesis of 2PD monomer was performed as a Sonogashira cross-coupling of 2-bromopyridine (1.0 g, 6.2 mmol) and 1,4-diethynylbenzene (400 mg, 3.1 mmol). Bis(triphenylphosphine)palladium dichloride (133 mg, 3 mol %) was used as a catalyst, CuI (36 mg, 3 mol %) was used as a cocatalyst and mixture triethylamine/toluene (6/20 ml) as

solvent and as a base. Reaction was performed in Schlenk flask and stirred under Ar atmosphere at temperature 50 °C. After 24 hours was reaction could down and solvent was evaporated. Residual solid phase was washed with diethyl ether, filtered on alumina and concentrated. The desired product (Yield: 620 mg, 69%) was obtained as a yellowish solid after purification by chromatography on silica gel with ethyl acetate as a mobile phase. The spectra of monomers (¹H NMR, ¹³C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.^[3]

¹H NMR (300 MHz, DMSO-*d*₆, δ (ppm)): 7.44 t (2 H_{pyridine}); 7.69 m (6 H_{pyridine, aroma}); 7.88 t (2 H_{pyridine}); 8.62 d (2 H_{pyridine}).

¹³C NMR (300 MHz, DMSO-*d*₆, δ (ppm)): 87.6 (triple bond); 91.0 (triple bond); 122.2; 123.8; 127.5; 132.0; 136.9; 141.9; 150.2.

IR spectrum: see Figure S3.

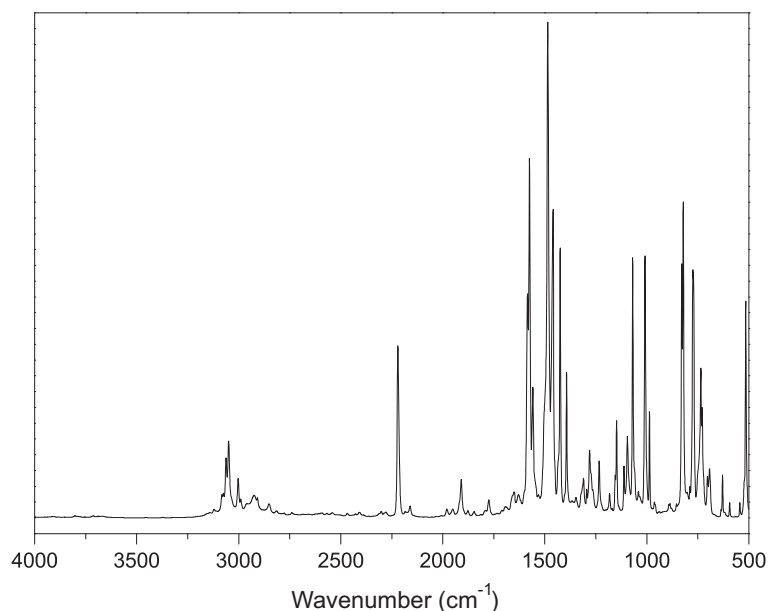


Figure S3 IR spectrum of monomer 2PD, DRIFT, diluted with KBr.

1.4. 4PD, 1,4-bis[(4-pyridyl)ethynyl]benzene

Synthesis of 4PD monomer was performed as a Sonogashira cross-coupling of 4-iodopyridine (1.0 g, 4.8 mmol) and 1,4-diethynylbenzene (307 mg, 2.4 mmol). Bis(triphenylphosphine)palladium dichloride (103 mg, 3 mol %) was used as a catalyst, CuI (27 mg, 3 mol %) was used as a cocatalyst and mixture triethylamine/toluene (12/6 ml) as solvent and as a base. Reaction was performed in Schlenk flask and stirred under Ar atmosphere at temperature 50 °C. After 48 hours was reaction could down and solvent was evaporated. Residual solid phase was washed with diethyl ether, filtered on alumina and concentrated. The desired product (Yield: 480 mg, 72%) was obtained as a yellowish solid after purification by chromatography on silica gel with ethyl acetate as a mobile phase. The spectra of monomers (¹H NMR, ¹³C NMR, IR) were in good agreement with the spectra of respective compounds available in the literature.^[3]

¹H NMR (300 MHz, DMSO, δ (ppm)): 7.55 d (4 H_{pyridine}); 7.70 s (4 H_{aroma}); 8.65 d (4 H_{pyridine}).

¹³C NMR (300 MHz, DMSO, δ (ppm)): 88.9 (triple bond); 92.7 (triple bond); 122.2; 125.4; 129.8; 132.1; 150.0.

IR spectrum: see Figure S4.

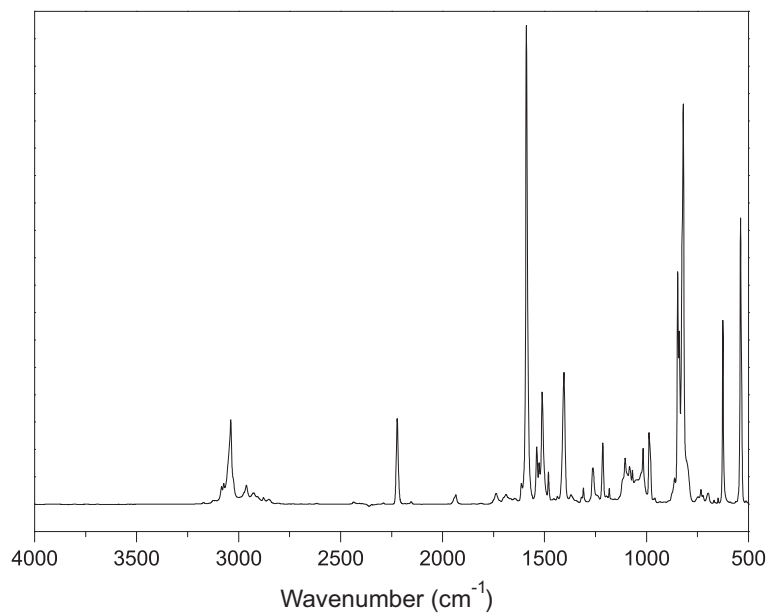


Figure S4 IR spectrum of monomer 4PD, DRIFT, diluted with KBr.

2. Elemental analysis of the polymers

Table S1 Elemental analysis of prepared polymers, weight % found in the samples.

Sample code	Wt%			
	C	H	N	Br
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

3. Photoluminescence

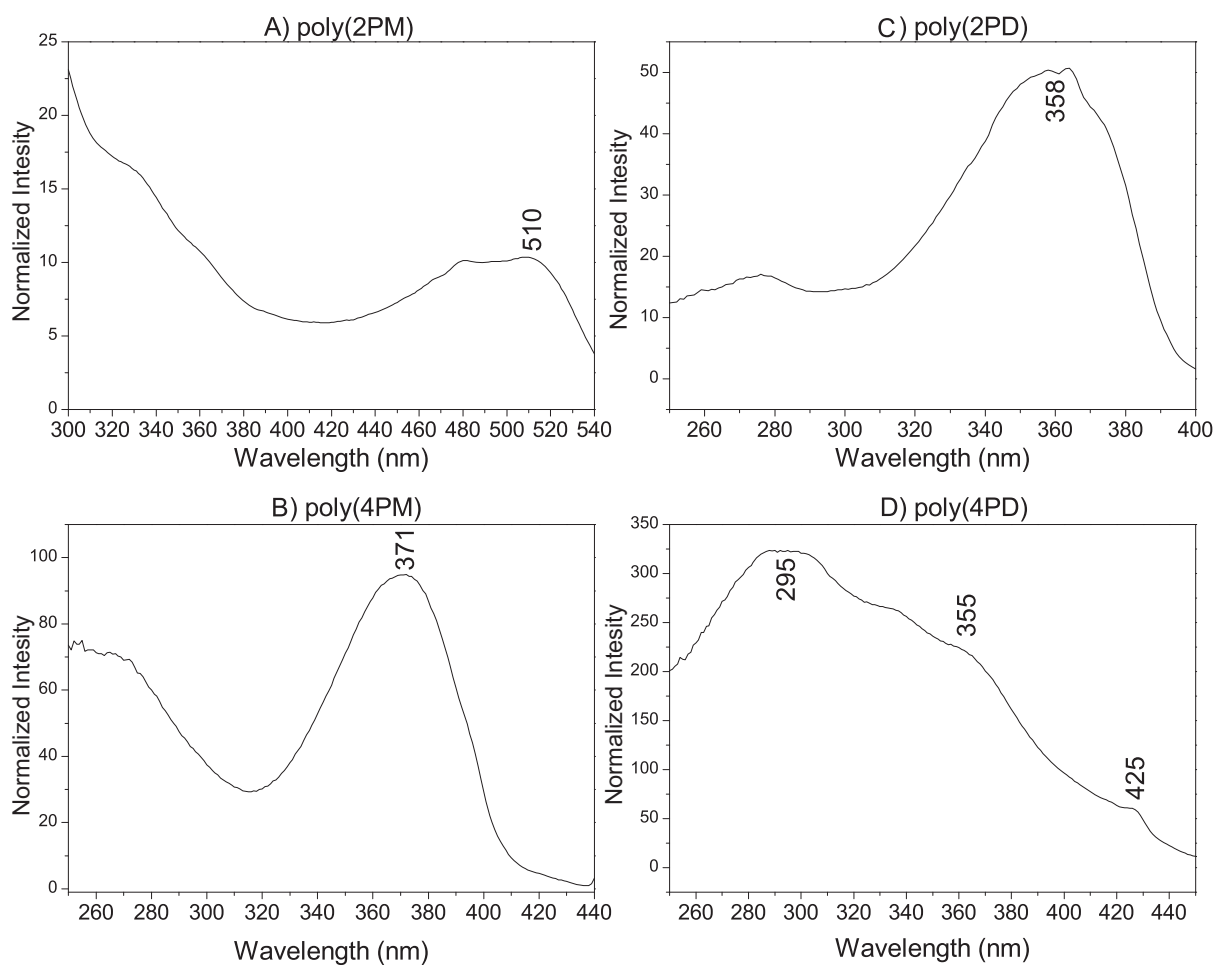


Figure S5 Excitation photoluminescence spectra of polymers A) poly(2PM), B) poly(4PM), C) poly(2PD) and D) poly(4PD). Emission monochromator was set to the emission maxima.

Table S2 Fluorescence decays.

Sample code	τ_1 (ns) [rel.amp %]	τ_2 (ns) [rel.amp %]	τ_3 (ns) [rel.amp %]
poly(2PM)	2.21 (30)	7.12 (64)	0.21 (6)
poly(4PM)	2.6 (57)	4.15 (33)	0.42 (10)
poly(2PD)	0.5 (86)	1.9 (14)	--
poly(4PD)	1.82 (58)	0.24 (10)	4.58 (32)

Concentration of all samples was $3.3 \times 10^{-3} \text{ mg mL}^{-1}$. Time resolved decays were measured with 378 nm Horriba laser diode, τ_1 , τ_2 , and τ_3 : lifetimes of the fluorescence components (their contributions are given in parentheses).

4. Sythesis and characterization of QA-BIPY-QA

4,4'-Bis(*N*-benzyl)dipyridinium bromide (QA-BIPY-QA) was prepared by quaternization of 4,4-bipyridyl (BIPY) with benzyl bromide (QA). 200 mg of BIPY and four equivalents of QA were mixed in 1.5 mL of DMF under Ar atmosphere in a thick-wall glass ampule. Ampule was sealed and reaction mixture was stirred for 2 hours at 100 °C, then the ampule was placed into the thermostated own at 100 °C. After 10 days, the reaction mixture was cooled down, and washed with acetone (3 x 30 mL). Finally, the solid product was recrystallized from ethanol and dried in vacuum for 48 hours. QA-BIPYQA was obtained as yellow solid in the yield of 89%.

Table S3 Elemental analysis of QA-BIPY-QA, weight % found in samples.

Code	Wt%			
	C	H	N	Br
QA-BIPY-QA	57.84	4.14	5.55	33.34

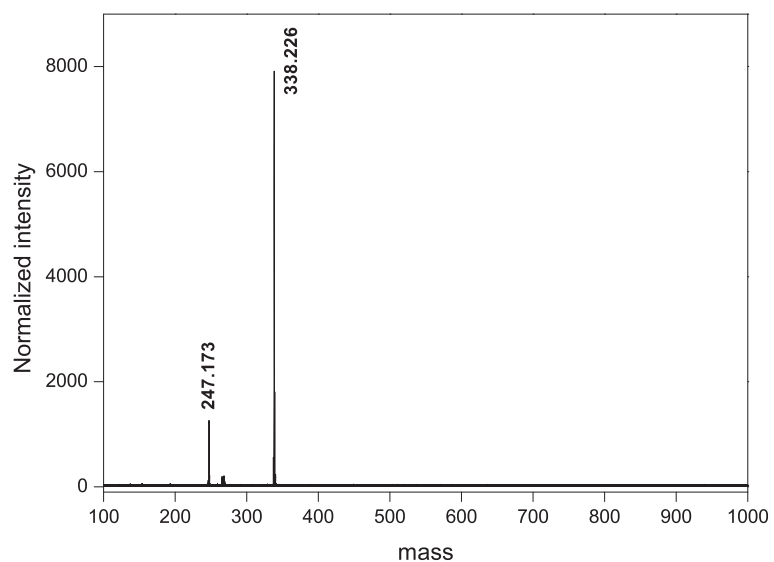


Figure S6 MALDI-TOF MS spectrum of 4,4'-bis(*N*-benzyl)dipyridinium bromide (QA-BIPY-QA).

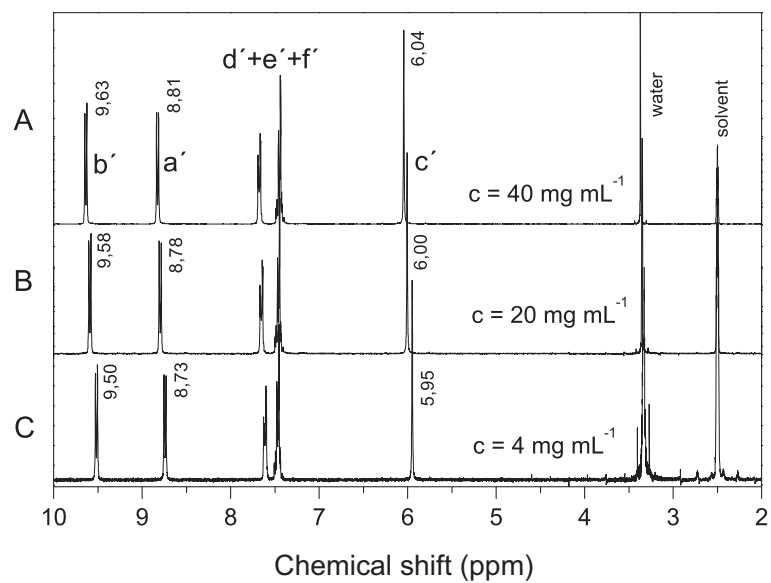
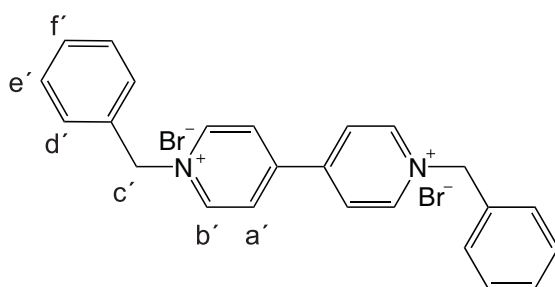


Figure S7 ^1H NMR spectra of 4,4'-bis(*N*-benzyl)dipyridinium bromide (QA-BIPY-QA) in $\text{DMSO-}d_6$. The influence of the sample concentration on the ^1H NMR shifts. A) Concentration of QA-BIPY-QA, $c = 40 \text{ mg mL}^{-1}$. B) Concentration of QA-BIPY-QA, $c = 20 \text{ mg mL}^{-1}$. C) Concentration of QA-BIPY-QA, $c = 4 \text{ mg mL}^{-1}$.

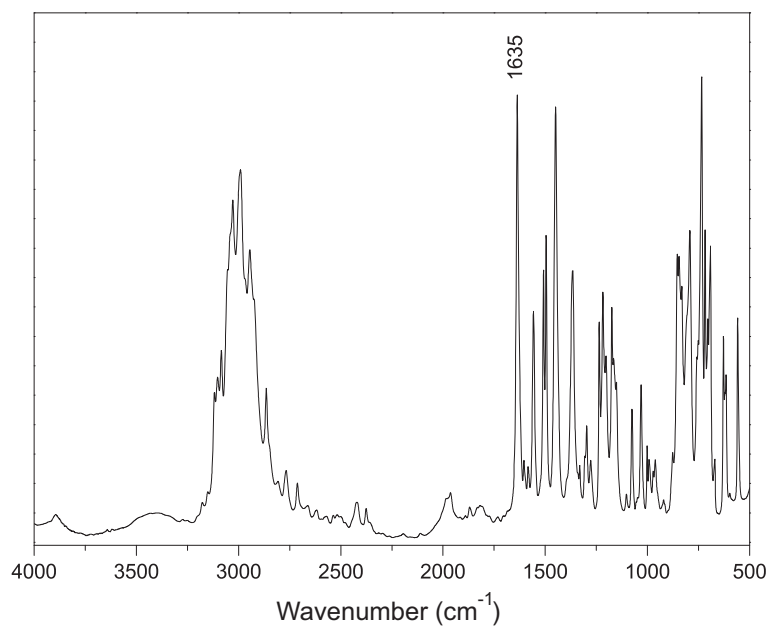


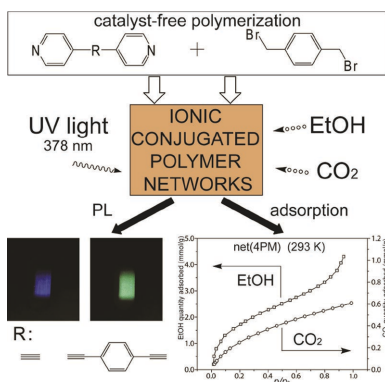
Figure S8 IR spectrum of 4,4'-bis(*N*-benzyl)dipyridinium bromide (QA-BIPY-QA), DRIFT, diluted with KBr.

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Full Paper

Catalyst-free preparation of ionic π -conjugated polyelectrolyte (CPE) type polymer networks via quaternization polymerization of bis(pyridyl)acetylenes and bis[(pyridyl)ethynyl]benzenes. Prepared CPE networks show exceptionally high ethanol vapors capture efficiency up to 24.5 wt% (293 K), moderate efficiency in CO₂ sorption up to 13.6 cm³ g⁻¹ (STP) and strong photoluminescence in the visible region.



Ionic π -Conjugated Polymer Networks by Catalyst-Free Polymerization, Photoluminescence and Gas Sorption Behavior

T. Faulkner,* A. Zukal, J. Brus, J. Zedník, J. Sedláček*

Macromol. Chem. Phys. **2016**, *217*, 000–000

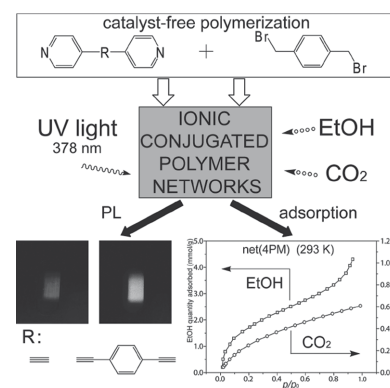


Early View Publication; these are NOT the final page numbers, use DOI for citation !!

Ionic π -Conjugated Polymer Networks by Catalyst-Free Polymerization, Photoluminescence and Gas Sorption Behavior

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Four monomers of the bis(pyridyl)acetylene and bis[(pyridyl)ethynyl]benzene types containing either 2-pyridyl or 4-pyridyl groups are polymerized into respective networks of the conjugated polyelectrolyte (CPE) type by catalyst-free polymerization via activation with 1,4-bis(bromomethyl)benzene as quaternization agent (QA). Prepared CPE networks are characterized by elemental analysis (EA), TGA analysis, ^{13}C cross-polarization magic-angle spinning NMR, IR, UV/vis, and photoluminescence spectroscopies. Highly cross-linked network structure containing both π -conjugated polyacetylene type chains and ionic alternating type chains is proposed. According to EA analysis, the mole ratio of units derived from monomer molecules and QA molecules is close to unity in all prepared networks. The CPE networks based on 4-pyridyl monomers exhibit strong photoluminescence in the visible region after irradiation with light of wavelength of 378 nm. Prepared CPE networks also show moderate efficiency in CO_2 sorption up to $13.6 \text{ cm}^3 \text{ g}^{-1}$ (STP) and exceptionally high ethanol vapor capture efficiency up to 24.5 wt% (293 K). The specific interactions of ionic network and adsorbed molecules and also temporary pores formation are assumed to play important role in sorption processes.



1. Introduction

Porous polymer networks have recently attracted significant interest due to the broad field of the potential applications. Porous networks for the gas storage and

separation,^[1–3] heterogeneous catalysis,^[4] and sensors and detectors^[5,6] have been prepared by various methods. The π -conjugated porous polymer networks are of a particular interest.^[7] 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 networks enables them to exhibit strong absorption and emission in UV/vis region, which opens variety of applications in the field of optoelectronics and sensors.^[6,8,9] The preparation of conjugated polymer networks is mostly performed as step-growth homo-coupling, cross-coupling, and polycyclotrimerization,^[10,11] or chain-growth polymerization^[10,12] of monomers with higher functionalities, e.g., multiethynylarenes, multihaloarenes, multi-azidoarenes, and others. Most of the mentioned synthetic pathways require transition-metal catalysis. However, the efficient purification of the insoluble polymer networks is

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difficult and the networks could be contaminated by catalyst residues. Obviously, the 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.

The spontaneous, catalyst-free polymerization of ethynylpyridines with alkyl halides as quaternization agents (QAs) introduced by Blumstein in 1991 resulted in the linear ionic polymers containing π -conjugated polyacetylene main chains with *N*-alkylpyridiniumyl pendants classified as conjugated polyelectrolytes (CPEs).^[13] This reaction is often denoted as a (spontaneous) quaternization polymerization. The propagation of this chain-growth polymerization is assumed to proceed via quaternization of the monomer molecule with alkyl halide followed by the addition of the quaternized (activated) monomer molecule to the end of the growing polyene chain. A wide variety of both linear and cross-linked CPEs of this type have been prepared and investigated.^[14–20] For example, Gal et al. presented a series of linear CPEs, prepared from 2-ethynylpyridine and various functionalized QAs as β -propiolactone, 1-iodopentane, or 4-(methylthio)benzyl bromide.^[21–23] Recently, we have reported quaternization polymerization of 2- and 4-ethynylpyridines with a series of bifunctional QAs [e.g., 1,4-bis(bromomethyl)benzene and 2,6-bis(bromomethyl)naphthalene] into ionic π -conjugated polyacetylene type networks.^[16]

However, monomers containing one terminal ethynyl group and one pyridine ring in the molecule are mostly used as starting materials for the synthesis of CPEs. Only few experiments dealt with the quaternization polymerization of monomers comprising in the molecule an internal ethynyl group and two pyridyl groups. These experiments have been mentioned by Blumstein et al.^[13]: the polymerization of 1,2-bis(4-pyridyl)acetylene with either 1-bromododecane or 1-heptylmethanesulfonate resulted in water soluble linear CPEs. The polymerization of the same monomer with nonane-1,9-bis(methanesulfonate) led to insoluble cross-linked CPE product.

Little interest is devoted to the quaternization polymerization of the monomers comprising in the molecule two pyridyl groups and an internal ethynyl group. This is despite the fact that (i) poly(disubstituted acetylene)s generally exhibit better photoluminescence properties and thermal and oxidizing stability compared to poly(monosubstituted acetylene)s,^[24] (ii) the presence of two pyridiniumyl pendants per one monomeric unit may have a positive impact on the solubility of the linear CPEs (prepared with monofunctional QAs) in polar solvents.^[25–28] On the other hand, the presence of two pyridiniumyl pendants per one monomeric unit may enhance efficiency of (desirable) interchain cross-linking if bifunctional QAs are used for the quaternization.

In our recent paper, we have confirmed the advantages of bis(pyridyl)acetylenes as the monomers for the synthesis of linear CPEs.^[28] bis(pyridyl)acetylenes containing one internal ethynyl group, 1,2-bis(2-pyridyl)acetylene, 1,2-bis(4-pyridyl)acetylene, were efficiently spontaneously polymerized via activation with benzyl bromide as a QA to give well soluble photoluminescent CPEs. The same polymerization of bis(pyridyl)acetylenes containing two internal ethynyl groups, 1,4-bis[(2-pyridyl)ethynyl]benzene, and 1,4-bis[(4-pyridyl)ethynyl]benzene, was also reported^[28] that was aimed at the synthesis of CPE networks. However, despite the fact that monomers contained two polymerizable groups, the soluble (linear or branched, however not cross-linked) CPEs resulted in this case. Evidently, for the cross-linking to be achieved in CPEs derived from bis(pyridyl)acetylenes an alternative strategy was necessary.

In this contribution, we report the preparation of extensively cross-linked ionic π -conjugated polymer networks via quaternization polymerization of bis(pyridyl)acetylenes activated with 1,4-bis(bromomethyl)benzene (1,4-BBrMB) serving as a bifunctional QA. The resulting photoluminescent networks were characterized by elemental analysis (EA), TGA, and various spectroscopic techniques including time-resolved photoluminescence spectroscopy. Moreover, as the networks were active in gas and vapor capture, the efficiency in the N_2 , CO_2 , and ethanol capture on the networks was investigated.

2. Experimental Section

2.1. Materials

1,4-Bis(bromomethyl)benzene (1,4-BBrMB), bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$), 2-bromopyridine, copper(I) iodide (CuI), *N,N*-dimethylformamide (DMF) (anhydrous, 99.8%), 2-ethynylpyridine, methanol, triethylamine (all Sigma–Aldrich, used as received), DMSO- d_6 (99.5 at% D, Armar chemicals), deuterium oxide (D_2O , 99.9 at% D, Cambridge isotope laboratories), diethyl ether, ethyl acetate (Lachner, Czech Republic, used as received), 4-iodopyridine, 4,4'-dipyridyl (DIPY) (Across Organics), and 4-ethynylpyridine (TCI Europe) were used as obtained. 1,4-Diethynylbenzene from Sigma–Aldrich was purified by vacuum sublimation. Toluene from Sigma–Aldrich was distilled from sodium-benzophenone.

All the Fourier transform IR (FTIR) spectra were measured on a Nicolet Magna IR 760 using the diffuse reflection mode (DRIFTS). Samples were diluted with KBr. 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. The 1H NMR spectra were measured using a Varian Unity Inova 300 spectrometer in DMSO- d_6 or D_2O as a solvent. Diffuse reflectance spectra of the solid polymers were recorded on a Shimadzu UV-2401PC spectrometer using an integration sphere



assembly. The polymers were diluted with BaSO₄ (1/10, w/w) before measurements were carried out. 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 or 470 nm. Excitation pulse laser diode Horriba either 378 or 470 nm was used 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 spectrometr. 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 h 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 h under a turbomolecular vacuum pump. Since adsorption isotherms of CO₂ on organic polymers can depend on the time allotted to the adsorption measurement,^[29] 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.^[30] 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). TGA of polymer networks was measured using SETSYS Evolution TGA, Setaram Instrumentation, in N₂ atmosphere. TGA measurement procedure: sample was heated to 100 °C with a step of 10 °C min⁻¹ and dried for 1 h (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. EA of the products were done at the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic.

2.2. Monomer Synthesis

Details on the preparation and spectral characterization of monomers, 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), are presented in the article.^[28] The spectra of the monomers (¹H NMR, ¹³C NMR, IR) were in a good agreement with the spectra available in the literature.^[31–33]

2.3. Quaternization Polymerization Procedure

Monomers 2PM, 4PM, 2PD, and 4PD were polymerized via activation with 1,4-bis(bromomethyl)benzene (1,4-BBrMB) as a QA. In

a typical experiment, a monomer (200 mg) and proper amount of 1,4-BBrMB (Br/N = 1:1) were mixed in 1.5 mL DMF under Ar atmosphere in a thick-wall glass ampule. Ampule was flushed with argon, sealed and the reaction mixture was stirred for 2 h at 100 °C, then the ampule was placed into the thermostated oven at temperature 100 °C. Reaction mixture changed color from light yellow to dark brown. After 10 d 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 h and then under vacuum at room temperature to constant weight.

3. Results and Discussions

3.1. Preparation of Polymer Networks

In order to be subsequently polymerized, a series of four symmetrical acetylenic monomers with two pyridyl groups has been synthesized and characterized: 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 formulae and codes of the monomers are presented in Figure 1. Digits in the codes specify the positional isomerism of the pyridyl substituents (2P—*ortho*-positioned pyridyl groups, 4P—*para*-positioned pyridyl groups), M—stands for the monoacetylenic character of the monomer, D—stands for the diacetylenic character of the monomer. The synthesis of the monomers is described in the article.^[28]

Monomers 2PM, 4PM, 2PD, and 4PD were polymerized into the respective polymer networks net(2PM), net(4PM), net(2PD), and net(4PD) by activation with 1,4-bis(bromomethyl)benzene (1,4-BBrMB) as a QA without any catalyst or initiator. The initial mole ratio monomer to 1,4-BBrMB in the polymerization mixtures was equal to unity. In all cases, dark insoluble networks were obtained as the only products.

The role of a monofunctional QA of the alkyl halide type in polymerization of ethynylpyridines is known.^[13]

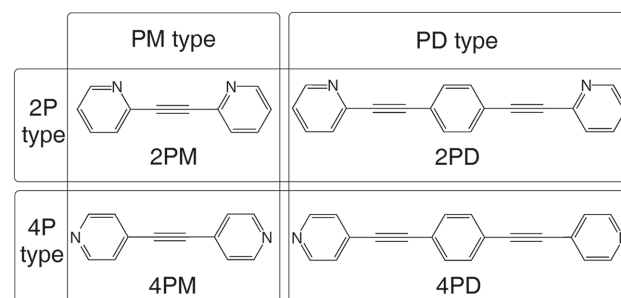
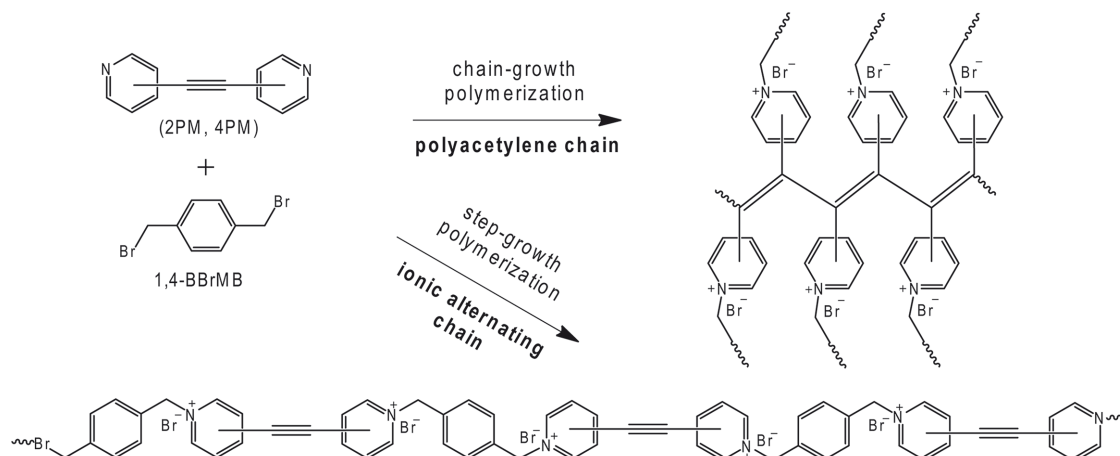


Figure 1. Monomers 1,2-bis(2-pyridyl)acetylene (2PM), 1,2-bis(4-pyridyl)acetylene (4PM), 1,4-bis[(2-pyridyl)ethynyl]benzene (2PD), and 1,4-bis[(4-pyridyl)ethynyl]benzene (4PD).



Scheme 1. 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.

QA molecules quaternize pyridyl part of the monomer molecules that enables the chain polymerization of the ethynyl group into polyene chains. If a bifunctional QA (e.g., 1,4-BBrMB) is used, the cross-linking of the polymer can be expected. All the monomers discussed here contain two pyridyl groups in one molecule. Due to this fact, 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 1 for the polymerization of PM type monomers.

To support the idea of the formation of ionic alternating chains in the reported polymerization systems, an independent experiment has been performed in which 1,4-BBrMB was reacted with 1,4-dipyridyl (DIPY) under the conditions of the polymerization experiments (see the Experimental Section). DIPY is a compound containing two interconnected pyridyl groups and no ethynyl group. The reaction of 1,4-BBrMB with DIPY led to the ionic alternating oligomer poly[*N,N'*-(4,4'-dipyridiniumyl)-*alt*-1,4-dimethylenephylene dibromide] [poly(DIPY-*alt*-1,4-BBrMB)]. Figure 2 shows the proposed structure of poly(DIPY-*alt*-1,4-BBrMB). The ^1H NMR spectra of DIPY, 1,4-BBrMB, and poly(DIPY-*alt*-1,4-BBrMB) are presented in Figure 2. Signals at 9.16 and 8.55 ppm in Figure 2A were ascribed to the protons of pyridiniumyl units of di-quaternized DIPY (signals "h"). Signals of internal 1,4-BBrMB units (bonded by both methylene groups to two different pyridiniumyl groups) were observed in the

spectra at 7.64 and 5.99 ppm (signals "j" and "i" respectively). The end groups of the chains were formed by monoquaternized DIPY groups (signals "k") as well as 1,4-BBrMB groups (signals "e", "f," and "g"). According to the ^1H NMR (Figure 2A) signals intensity the occurrence of DIPY as an end groups in the oligomer was twice higher than that of 1,4-BBrMB. The intensity of the signals of

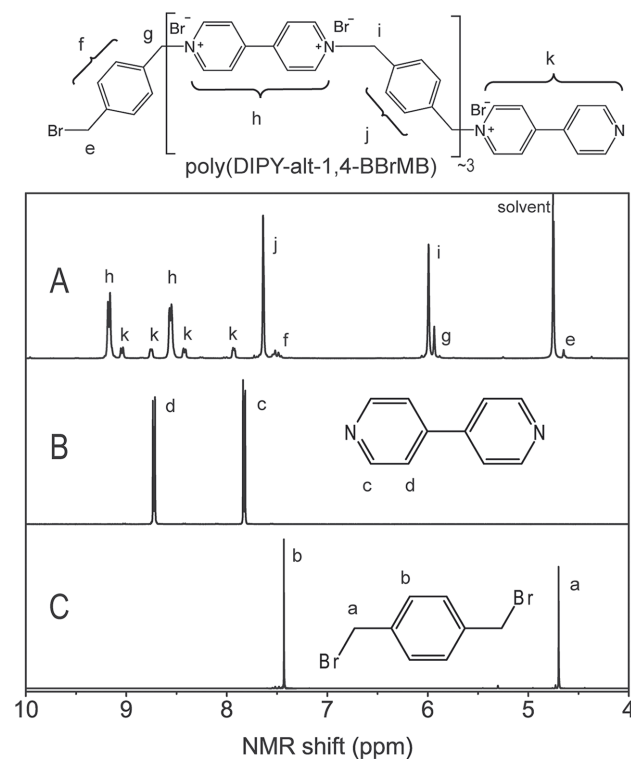
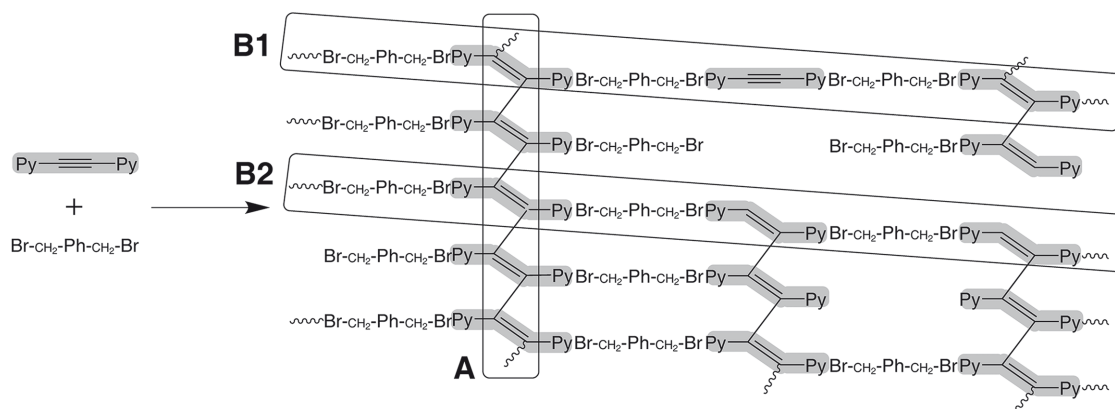


Figure 2. Proposed structure of poly(DIPY-*alt*-1,4-BBrMB) and ^1H NMR spectra (300 MHz): A) poly(DIPY-*alt*-1,4-BBrMB) in D_2O ; B) 4,4'-dipyridyl (DIPY) in $\text{DMSO}-d_6$; C) 1,4-bis(bromomethyl)benzene (1,4-BBrMB) in $\text{DMSO}-d_6$.





Scheme 2. Proposed structure of the 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—bromo group that was not involved into quaternization, PyBr (BrPy)—pyridinium bromide.

di-quaternized and mono-quaternized species in the ^1H NMR spectrum (Figure 2A) also allowed to estimate the length of the alternating chains: the chains consisting of four DIPY units and three to four 1,4-BBrMB units were prevailing present in poly(DIPY-alt-1,4-BBrMB). 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.

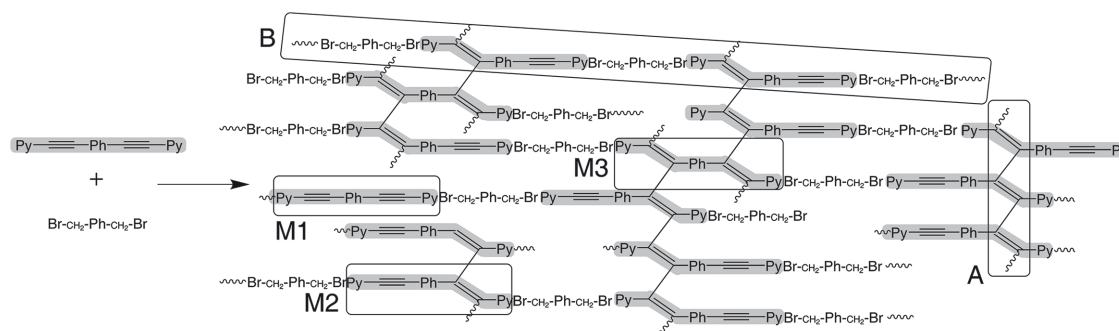
3.2. Quaternization Polymerization of PM Type Monomers

Scheme 2 shows the proposed structure of networks formed by quaternization polymerization of PM type monomers with 1,4-BBrMB: π -conjugated polyacetylene type chains are labeled as A and ionic alternating chains are labeled as B1 and B2. Each molecule of PM type monomer contains one ethynyl and two pyridyl groups, i.e., 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. We nevertheless speculate that the extent of branching is lower in net(2PM) and net(4PM) and that two types of ionic alternating chains (B1 and B2) could be present in these polymers. Chain B1 in Scheme 2 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 and IR spectra of prepared polymer networks (*vide infra*).

3.3. Quaternization Polymerization of PD Type Monomers

The proposed structure of the networks prepared from PD monomers is shown in Scheme 3. Similarly to the polymerization of PM type monomers, the quaternization



Scheme 3. Proposed structure of the networks obtained from the quaternization polymerization of 2PD and 4PD into net(2PD) and net(4PD), respectively. 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)—pyridinium bromide.

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, Scheme 3), (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).

3.4. Characterization of the Networks by Elemental Analysis

Table S1 in the Supporting Information summarizes the results of the EA of net(2PM), net(4PM), net(2PD), and net(4PD). The EA proved the presence of bromine in all the networks [Br content from 28.9 wt% in net(2PD) to 35.6 wt% in net(4PM)]. Results of EA were used to determine the mole ratio Br/N in the networks (see Table 1). The initial mole ratio 1,4-BBrMB/monomer and corresponding initial ratio Br/N in the feed were equal to unity in all the polymerizations. This mole ratio was chosen with the aim to support the cross-linking of the products via step-growth formation of ionic alternating chains. As it is evident from Table 1, the Br/N mole ratio in the networks (from 0.74 to 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) as Br atoms in non-reacted Br—CH₂— groups of 1,4-BBrMB (end groups) and (ii) in the form of Br⁻ anions compensating the positive charge of the *N*-benzylpyridinium moieties. Providing that the majority of pyridyl groups of the monomeric units were quaternized in the networks one can assume that bromine is present in these

Table 1. Polymerization of 2PM, 4PM, 2PD, and 4PD (always 200 mg of the monomer in the feed) with 1,4-bis(bromomethyl)benzene (1,4-BBrMB) as a QA (initial mole ratio 1,4-BBrMB/monomer = 1).

Sample code	Weight ^{a)} [mg]	Monomer conversion ^{b)} [%]	Br/N ^{c)}
Net(2PM)	315	71	0.74
Net(4PM)	460	90	1.03
Net(2PD)	318	77	1.04
Net(4PD)	334	73	1.20

^{a)}Weight of the isolated polymer network; ^{b)}Monomer-to-polymer network conversion; ^{c)}Mole ratio Br/N in the networks obtained from the EA.

networks prevailing in the form of Br⁻ anions. In the case of net(4PD) (Br/N = 1.20) we can, however, assume (on the base of EA) that some amount of Br is present in the form of Br—CH₂— groups because the content of Br in the network exceeds that of N.

The overall higher degree of quaternization of reported networks, compared to the quaternization of their linear counterparts prepared via quaternization polymerization of the same monomers activated with (monofunctional) benzyl bromide reported previously,^[28] is presumably caused by the bifunctional character of 1,4-bis(bromomethyl)benzene applied as a QA in the synthesis of networks. The molecules of nonquaternized monomer which diffuse to the vicinity of growing polymer chains come, in fact, to the part of the reaction system with a high concentration of Br—CH₂— groups (pendant groups of growing polymer chains). That is why the probability of quaternization of monomer molecules is significantly enhanced. It should be noted that during the formation of the linear polymers^[28] the situation is different since no free Br—CH₂— groups are present at the growing polymer chains.

The weight of the polymer network 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 1.

3.5. NMR Spectra of Prepared Polymer Networks

¹³C CP/MAS NMR spectra of polymer networks net(2PM), net(4PM), net(2PD), and net(4PD) are shown in Figure 3. 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 nonreacted ethynyl groups are well observable in the case of both PD based networks, net(2PD) and net(4PD), at 83.9 and 88.9 ppm, respectively, and also in case of net(4PM) (95.7 ppm). As the nonreacted ethynyl groups are observable in ¹³C CP/MAS NMR spectrum of net(4PM), we can assume that both B1 and B2 motives (Scheme 2) of ionic alternating chains are present in net(4PM). On the other hand, no signal of ethynyl groups was observed in ¹³C 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 2) of ionic alternating chains.

The presence of signals of nonreacted ethynyl groups in ¹³C CP/MAS NMR spectra of net(2PD) and net(4PD) shows that ethynyl groups were not fully transformed

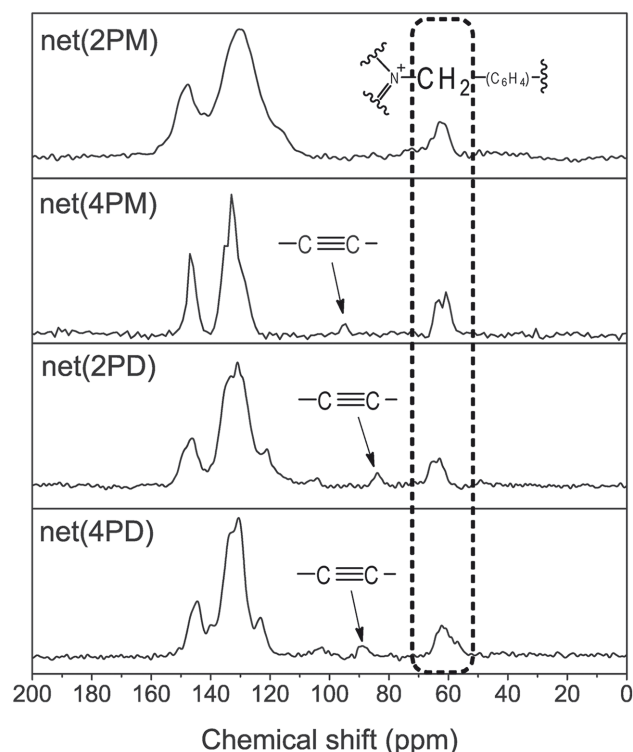


Figure 3. ^{13}C CP/MAS NMR spectra of polymer networks net(2PM), net(4PM), net(2PD), and net(4PD).

into polyacetylene chain. As the PD type monomers possess two ethynyl groups, we assume that only one ethynyl group of the monomer molecule is prevalently transformed into segment of the polyacetylene chain (via chain growth polymerization) and the second ethynyl group may remain preserved (branching units M2 in Scheme 3). 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 3) or both ethynyl groups are transformed into polyacetylene chains (branching units M3 in Scheme 3). 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 $-\text{N}^+-\text{CH}_2-(\text{C}_6\text{H}_4)-$ units of 1,4-BBrMB that quaternize pyridine 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 nonreacted $\text{Br}-\text{CH}_2-$ groups of $\text{Br}-\text{CH}_2-(\text{C}_6\text{H}_4)-\text{CH}_2-\text{N}^+$ units (expected at ca. 30 ppm) was detected in the spectra of the prepared networks. This points that both $\text{Br}-\text{CH}_2-$ groups are mostly transformed to the 1,4-BBrMB units incorporated into the networks. However, the absence of the signal of $\text{Br}-\text{CH}_2-$ groups in ^{13}C CP/MAS NMR spectrum

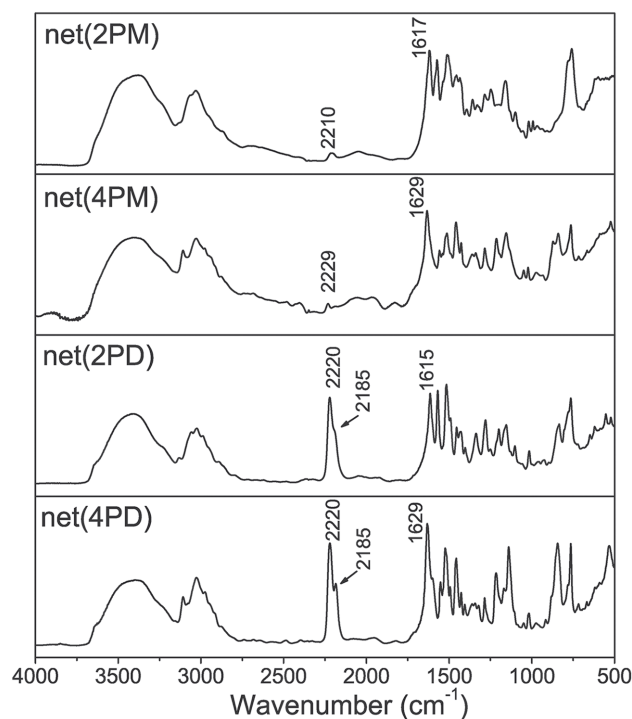


Figure 4. IR spectra (DRIFTS, diluted with KBr) of prepared polymer networks net(2PM), net(4PM), net(2PD), and net(4PD).

of net(4PD), where a small content of these groups is assumed according to the results of EA (see Table 1 and related discussion), may indicate that ^{13}C CP/MAS NMR is not sensitive enough to detect small amounts of $\text{Br}-\text{CH}_2-$ groups in the analyzed networks.

3.6. IR Spectra of Prepared Polymer Networks

IR spectra of net(2PM), net(4PM), net(2PD), and net(4PD) are shown in Figure 4. The $\text{N}^+=\text{C}$ stretching vibration of pyridiniumyl units (region from 1615 cm^{-1} to 1629 cm^{-1}) is well observable in the IR spectra of all the networks.^[34] Only low intensity bands of $\text{C}\equiv\text{C}$ bond stretching vibration at 2210 and 2229 cm^{-1} were detected in the case of net(2PM) and net(4PM), respectively. This indicates a high extent of the transformation of ethynyl groups of 2PM and 4PM monomers into polyacetylene chains. The residual bands of $\text{C}\equiv\text{C}$ bond stretching vibration are assigned to ethynyl groups of monomeric units incorporated into B1 segments (Scheme 2) of the ionic alternating chains of net(2PM) and net(4PM).

As already mentioned above, in case of polymerization of PD type monomers (monomers containing two ethynyl groups), the total or close to total transformation of ethynyl groups into polyacetylene chain was not expected due to the steric effects that may complicate the transformation of both ethynyl groups of one monomer molecule 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) (see Figure 4). The shoulders at 2220 cm^{-1} bands [at about 2185 cm^{-1} for net(2PD) and net(4PD) in Figure 4] most probably indicate a nonuniform 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 3 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.^[28]

3.7. Thermal Stability of the Polymer Networks

The TGA curves recorded for the polymer networks in N_2 atmosphere are given in Figure 5. Two characteristics 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 the temperature of $800\text{ }^\circ\text{C}$ (see Table 2). The values of $t_{95\%}$ range from 248 to $320\text{ }^\circ\text{C}$ and increase in the order: net(2PM) < net(2PD) << net(4PM) < net(4PD). The degradation of net(4PM) and net(4PD) started at the temperature higher by $50\text{ }^\circ\text{C}$ compared to their net(2PM) and net(2PD) counterparts (see Figure 5). We assume that the thermal decomposition of our polymer networks started with a gradual release of HBr and/or 1,4-BBrMB from the network at temperature higher than $200\text{ }^\circ\text{C}$.^[35] The terminal parts of TGA curves (temperature > $500\text{ }^\circ\text{C}$) confirm that the networks net(2PD) and net(4PD) were more stable 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). The ethynyl groups may be

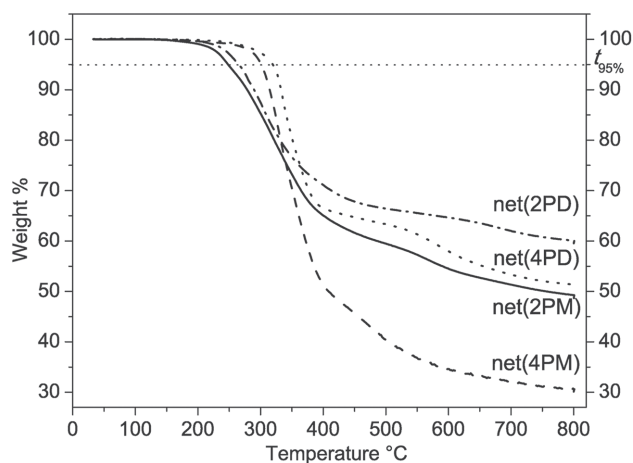


Figure 5. TGA curves of polymer networks net(2PM), net(4PM), net(2PD), and net(4PD) in N_2 atmosphere, step $10\text{ }^\circ\text{C min}^{-1}$.

Table 2. Characteristics of polymer networks obtained from TGA analysis in N_2 atmosphere, step $10\text{ }^\circ\text{C min}^{-1}$.

Sample code	$t_{95\%}$ [$^\circ\text{C}$]	Weight loss at $800\text{ }^\circ\text{C}$
Net(2PM)	248	51%
Net(4PM)	301	69%
Net(2PD)	265	40%
Net(4PD)	320	48%

thermally transformed into additional cross-links in the networks,^[36] which could enhance the thermal stability of net(4PD) and net(2PD) at higher temperature.

We have assumed that the thermal stability of the networks reported in this paper may exceed the thermal stability of the linear polymers of similar composition^[37] reported previously.^[28] However, the higher content of Br- CH_2 - groups in the networks reduced the positive effect of the cross-linked architecture on the thermal stability. Consequently, the thermal stabilities of linear and network-type polymers prepared from bis(pyridyl)acetylenes did not differ significantly.

3.8. UV/Vis and Photoluminescence Characteristics of Prepared Polymer Networks

The absorption and emission characteristics of the prepared networks are summarized in Table 3. As all products of the polymerizations were insoluble solids, the spectral characteristics were measured in the solid state (see the Experimental Section).

The absorption spectra of the prepared polymer networks are shown in Figure 6. 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 . 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) of free electron pair from bromide anion to nitrogen atom of the pyridiniumyl units.^[38,39] Similarly to Kawai et al.^[40] we assume the bromide anion to be in close proximity to strongly electron withdrawing nitrogen atom of the pyridiniumyl units.

All the monomers applied in this study except for 2PM exhibit photoluminescence in the UV region (emission maxima at $350\text{--}360\text{ nm}$).^[28] On the contrary, all the polymer networks emit in visible or visible/near IR region (see Figure 7). The emission of the networks probably originates from the partly conjugated polyacetylene chains^[41] and/or the transition of the CT complex *N*-benzylpyridiniumyl bromide (vide supra). However, the strong overlapping of absorption and photoluminescence

Table 3. The absorption and emission characteristics of prepared polymer networks net(2PM), net(4PM), net(2PD), and net(4PD).

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

^a)Absorption maxima of polymer networks, DRIFTs, sample diluted with BaSO₄; ^b)Excitation wavelength; ^c)Maxima of emission of the polymer networks; ^d)The luminescence decay components obtain from the time-resolved luminescence measurements; ^e)Excitation wavelength was chosen regarding to the emission band of the samples.

bands complicates the closer characterization of the emitting system. The polymer networks based on 2P type monomers (*ortho*-positioned pyridyl) emit in the red to near IR region when excited at 470 nm. Figure 7A 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 (*para*-positioned pyridyl groups) strongly emit in the visible region when excited at 378 nm. Figure 7B 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). 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 8. As it is evident from Figure 8, the shade of the emitted color is in good agreement with the color calculated from obtained data 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). 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 compare 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.

The fluorescence decay components measured for the networks are summarized in Table 3. 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.^[42] 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.

3.9. N₂ and CO₂ Adsorption on Prepared Polymer Networks

Net(2PM), net(2PD), net(4PM), and net(4PD) are highly cross-linked networks possessing high content of rigid

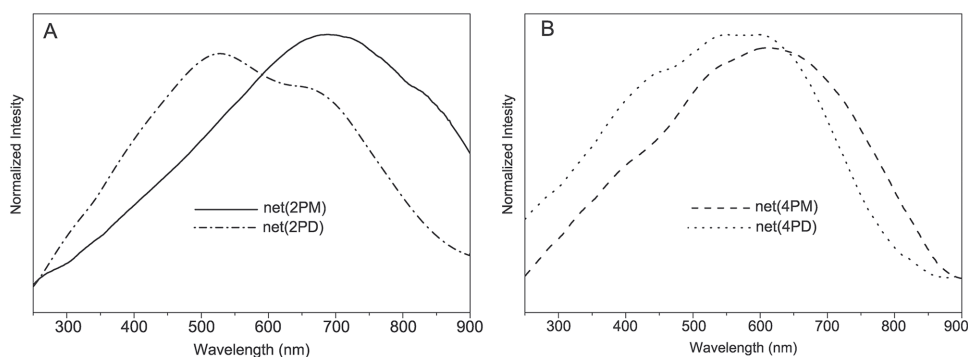


Figure 6. Absorption spectra of prepared polymer networks. A) net(2PM) and net(2PD), B) net(4PM) and net(4PD). Samples were diluted with BaSO₄.

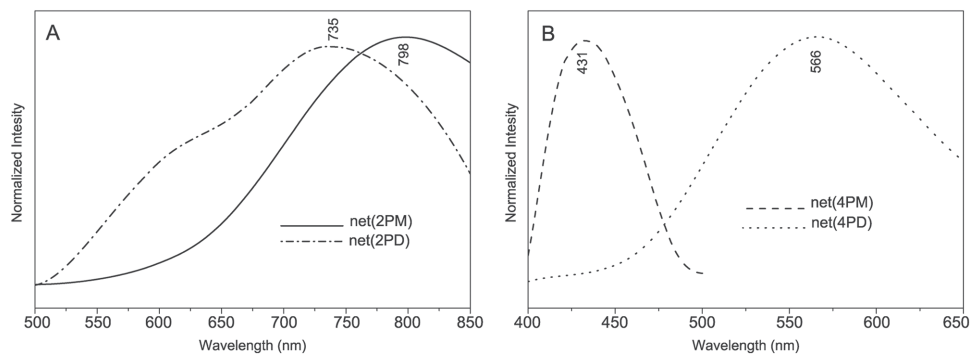


Figure 7. Emission spectra of prepared polymer networks. A) net(2PM) and net(2PD) excitation wavelength: 470 nm; B) net(4PM) and net(4PD), excitation wavelength: 378 nm.

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) adsorption (Table 4). However, only low Brunauer–Emmett–Teller (BET) specific surface areas (S_{BET} , values up to $27 \text{ m}^2 \text{ g}^{-1}$) 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 the Supporting Information, Figure S1. 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 (vide supra). 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. The CO_2 adsorption/desorption isotherms on the networks are given in Figure 9. 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 network.^[16] 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 $N\text{—}CH_2\text{—}C$ 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 us recently^[29] or (ii) facilitate filling of pores with restricted access as proposed by Weber et al.^[43] The CO_2 uptake increased in the polymer network series net(2PM) < net(2PD) < net(4PD) < net(4PM). The higher CO_2 uptake of 4P type networks compared to the 2P type networks could be explained in terms of various flexibilities of 4P and 2P networks: the bonds in $N\text{—}CH_2\text{—}C$ 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).

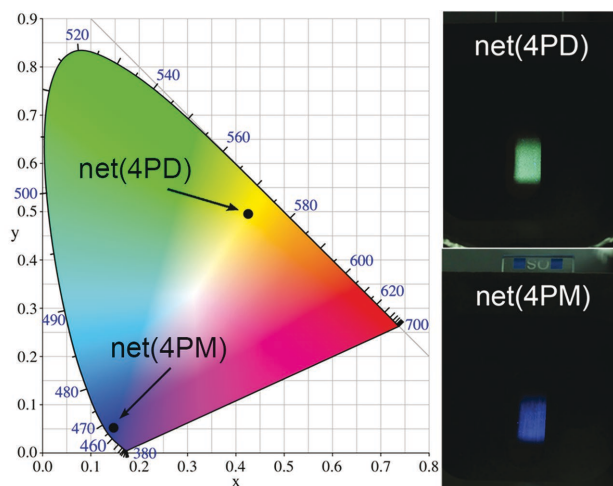


Figure 8. Chromaticity coordinates of the emissions observed in net(4PM) and net(4PD) in CIE1931 diagram. Photos of net(4PD) and net(4PM), excited at 378 nm.

3.10. Ethanol 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 4 for the ethanol uptake). The ethanol vapors adsorption isotherms are shown in Figure 10. The ethanol uptake of 24.5 wt% determined for net(2PD) is comparable with highly structurally organized materials, e.g., MOFs or zeolites.^[44,45] 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),

Table 4. 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} [$m^2 g^{-1}$]	Volume of pores [$cm^3 g^{-1}$]	Diameter of pores ^{a)} [nm]	$a_{CO_2, 750 Torr}$ ^{b)} [$mmol g^{-1}$]	$a_{ethanol, 750 Torr}$ ^{c)} [wt%]
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.

and net(4PD) was about 40 h. 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 10 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 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.^[46] 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.

4. Conclusions

The polymerization of acetylenic monomers with two pyridyl groups and one or two internal ethynyl groups, namely 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) via activation with 1,4-bis(bromomethyl)benzene (1,4-BBrMB) as QA without any addition of catalyst or initiator leads to the corresponding ionic π -conjugated polymer networks: net(2PM), net(4PM), net(2PD), and net(4PD). The quaternization polymerization used frequently for the preparation of the linear ionic polyacetylenes has thus been shown to be effective also for the preparation of ionic π -conjugated polyacetylene type polymer networks in high yields. The network structure is formed by interconnected π -conjugated polyacetylene

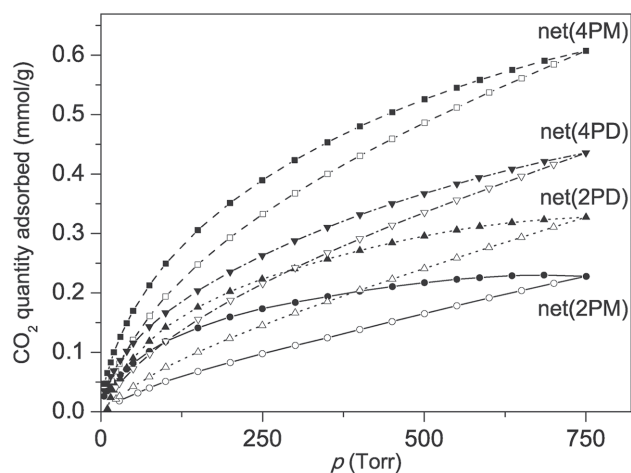


Figure 9. CO_2 adsorption/desorption isotherms (293 K) on polymer networks net(2PM), net(2PD), net(4PM), and net(4PD). Empty symbols—adsorption, filled symbols—desorption.

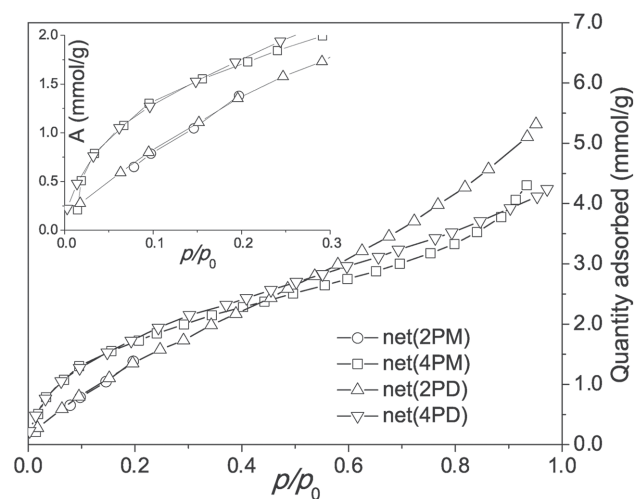


Figure 10. Ethanol adsorption isotherm on net(2PM), net(2PD), net(4PM), and net(4PD) (293 K). Insert: the onset of the isotherms.

type chains and the ionic alternating chains. The proposed polymer network structure is supported mainly by the EA, ^{13}C CP/MAS NMR, and FTIR spectroscopies.

In dependence on the positioning of pyridyl groups in the networks the prepared networks exhibit photoluminescence in either red to near infra-red region [net(2PM) and net(2PD)] or visible region [net(4PM) and net(4PD)]. The emission most probably originates from the partly π -conjugated polymer chains and/or CT complexes composed of *N*-benzylpyridiniumyl group and bromide anion. The time-resolved photoluminescence indicated an ISC process in the case of PD type polymer networks.

Despite low specific surface revealed by N_2 adsorption at 77 K, all the polymer networks exhibit moderate efficiency in CO_2 capture at 293 K (up to $13.6 \text{ cm}^3(\text{CO}_2)/\text{g}$ 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 $-\text{CH}_2-$ 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. We assume that the specific interactions between the ionic polymer network and the polar ethanol molecules may play important role in the capture process.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Supporting Information

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Ionic π -Conjugated Polymer Networks by Catalyst-Free Polymerization, Photoluminescence and Gas Sorption Behavior

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Jan Sedláček***

Supporting information

Ionic π -conjugated polymer networks by catalyst-free polymerization, photoluminescence and gas sorption behavior.

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Table S1 Elemental analysis of prepared materials.

Sample code	wt %			
	C	H	N	Br
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

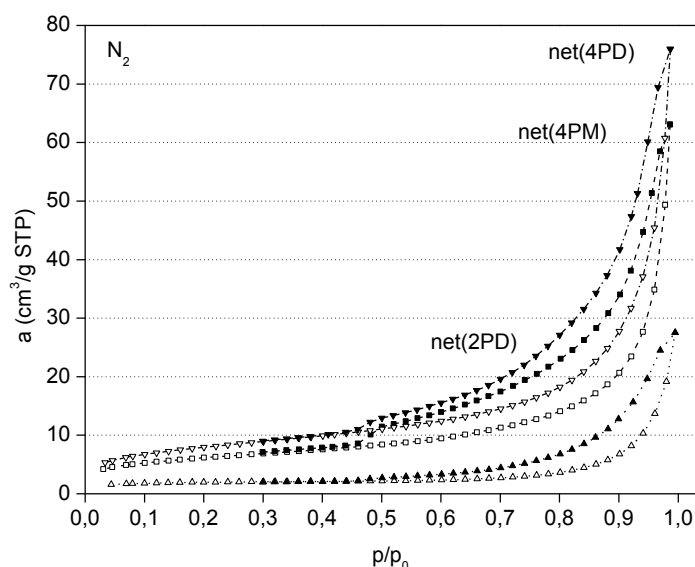


Figure S1 N₂ adsorption isotherm (77 K) of prepared polymer networks net(2PD), net(4PM) and net(4PD). Adsorption of net(2PM) was under detection limit. Empty symbols – adsorption, filled symbols – desorption.