Charles University in Prague
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Study program: Macromolecular Chemistry

Synthesis and characterization of new polymers of substituted acetylenes

Ph.D. Thesis

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Declaration

I hereby declare that this submission is my own work except where acknowledgement is made in the text. To the best of my knowledge and belief, it contains neither material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the University or other Institute of higher education, except for the already published results, which are included in the list of references.

Prague,18.7.2016

Radoslava Sivkova

To make a prairie it takes a clover and one bee,
One clover, and a bee.
And revery.
The revery alone will do,
If bees are few.

Emily Dickinson

Acknowledgement

At this place, I would like to thank to my supervisor Prof. Jiří Vohlídal for his constant support and helpful guidance during my study. It had been an honour to work with You.

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Abstract

New procedures for preparation of polyacetylenes with highly luminescent naphthalimide groups that might be potentially utilized in optoelectronics and sensors are developed within the framework of present doctoral thesis. The procedures provide luminescent *a)* linear polyacetylenes that can be processed from solutions, and *b)* mesoporous network polyacetylenes with high pore volume.

Two paths to soluble polyacetylenes are used: *(i)* copolymerization of ethynyl-functionalized naphthalimide (monomer **PN)** and a monoethynyl aromate catalyzed with [Rh(nbd)acac], and *(ii)* modification of poly(disubstituted acetylene)s carrying ω-chloroalkyl pendants involving the exchange of chlorine atoms for azido groups and subsequent "click"-reaction of Huisgen type of azido groups with ethynyl groups of **PN**.

The **PN** does not homopolymerize but copolymerizes with ethynylaromates. The highest possible molar fraction of the **PN** units in copolymers is of 0.5, which suggests the absence of **PN** dyads or longer sequences in copolymers and the alternating arrangement of **PN** units in the copolymers of the composition of 0.5. Surprisingly, ethynylarenes that give insoluble homopolymers gave soluble copolymers with **PN**.

The modification procedure requires knowledge on the effect of the monomer structure symmetry and substituent bulkiness on its polymerizability and solubility of resulting polymer. This study made with new diarylacetylenes revealed negative effect of the structure symmetry on the solubility of linear polydiarylacetylenes that can even cancel solubilizing effect of the attached alkyl groups. Therefore, the soluble luminescent polymers have been exclusively prepared by modifications of polymers of asymmetric monomers carrying 4-chlorobutyl pendants. These precursor polymers were also modified by the reaction with *N*-methylimidazole giving novel conjugated polyelectrolytes that are soluble in green solvents, including aqueous methanol (50 % by vol.), but not in pure water. Although the modification procedure is more work-demanding, the resulting polymers have the advantage of higher stability in air compared to the copolymers of monosubstituted acetylenes.

The luminescent mesoporous networks prepared by copolymerization of **PN** and 4,4′-diethynylbiphenyl with [Rh(nbd)acac] catalyst shows a very high specific surface of ca 1 000 m^2/g (BET).

All prepared copolymers show luminescence emission originating from **NP** type units which proves the excitation energy transfer from their main chains onto pendent naphthalimide moieties. Extremely high Stokes shift (up to 13 700 cm^{-1}) is observed if the luminescence is excited with the light beam absorbed by polymer main chains.

Keywords: conjugated polymer; coordination polymerization; modified polymer; luminescence; naphthalimide; network polymer; polyacetylenes; polyelectrolytes.

Abstrakt

V rámci předkládané disertační práce byly vyvinuty nové postupy přípravy polyacetylenů s luminescenčně účinnými naftalimidovými skupinami, které mohou najít potenciální využití v optoelektronice a sensorech. Tyto postupy poskytují luminescenční: *a)* lineární polyacetyleny zpracovatelné z roztoků; *b)* mesoporézní polyacetylenové sítě s velkým objemem pórů.

Rozpustné luminiscentní polyacetyleny byly připraveny dvěma syntetickými cestami: *(i)* kopolymerizacemi ethynyl derivátů naftalimidu (**PN**) s ethynylaromáty indukovanými katalyzátorem [Rh(nbd)acac] a *(ii)* modifikacemi poly(disubstituovaných acetylen)ů obsahujících ω-chloralkylové skupiny, spočívajícími v nukleofiní substituci chloru za azidové skupiny a následné “click” reakci Huisgenova typu (azido skupin s ethynylovými skupinami **PN).**

PN sice netvoří homopolymery, avšak je možné tento monomer kopolymerizovat s ethynylaromáty, přičemž nejvyšší dosažená molární frakce **PN** jednotek v kopolymeru je 0.5. Toto pozorování indikuje absenci diád a delších sekvencí **PN** jednotek v řetězcích kopolymerů. Implikuje tedy alternační strukturu řetězců s ekvimolárním obsahem jednotek. Zajímavé je, že ethynylareny poskytující nerozpustné homopolymery vytvářejí s **PN** rozpustné kopolymery.

Studie provedená na sérii nových diarylacetylenů ukázala negativní efekt strukturní symetrie monomeru na rozpustnost lineárních poly(diaryl acetylen)ů, který zastiňuje pozitivní vliv alkylových skupin vázaných v bočních skupinách. Rozpustné luminiscenčně aktivní polymery byly proto připraveny z asymetrických monomerů, v našem případě s 4-chlorbutylovými vedlejšími skupinami. Tyto chlor-substituované polymery byly také modifikovány reakcí s *N*-methylimidazolem a takto získány nové konjugované polyelektrolyty byly rozpustné v polárních rozpouštědlech, včetně 50 %-ního vodného methanolu, avšak ne v samotné vodě. Zvolená metoda modifikace je sice pracnější než přímá kopolymerizace, ale oproti kopolymerům poly(monosubstitutovaných acetylen)ů jsou takto získané polymery značně odolnější vůči oxidaci vzdušným kyslíkem.

Součástí předkládané práce je též příprava luminiscenčně aktivních mesoporézních sítí, ketré byly připraveny přímou kopolymerizací monomeru **PN** s 4,4´-diethynylbifenylem. Reakce byla katalyzována [Rh(nbd)acac] komplexem. Získané polymerní sítě vykazují velmi vysoký specifický povrch až 1 000 m^2/g (stanovený z izoterm metodou BET).

Všechny připravené kopolymery vykazují luminiscenci emitovanou z jednotek **NP**, což svědčí o účinném přenosu excitační energie z konjugovaných polymerních řetězců na naftalimidové skupiny bočních substituentů. Při excitaci luminiscence zářením absorbovaným hlavními polymerními řetězci dosahuje Stokesův posun extrémně vysoké hodnoty až cca 13 700 cm^{-1}.

Klíčová slova: konjugované polymery; koordinační polymerizace; luminiscence; modifikace polymerů; naftalimidy; polyacetyleny; polyelektrolyty; polymerní sítě.

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List of abbreviations

PN- *N*-(prop-1-yn-3-yl)-4-(piperidine-1-yl)-1,8-naphthalimide
PN1- *N*-(pent-1-yn-5-yl)-4-nitro-1,8-naphthalimide
[Rh(nbd)acac]- Acetylacetonato(norborna-2,5-diene)rhodium(I)
THF- tetrahydrofuran
$CHCl_3$- chloroform
CH_2Cl_2- dichloromethane
SC- Sonogashira coupling
SEC- size-exclusion chromatography
UV/vis- ultraviolet-visible spectroscopy
IR- infrared spectroscopy
NMR- nuclear magnetic resonance
M_w- weight-average molecular weight
M_n- number -average molecular weight
Đ- dispersity
Y- polymer yield
BET - Brunauer–Emmett–Teller method

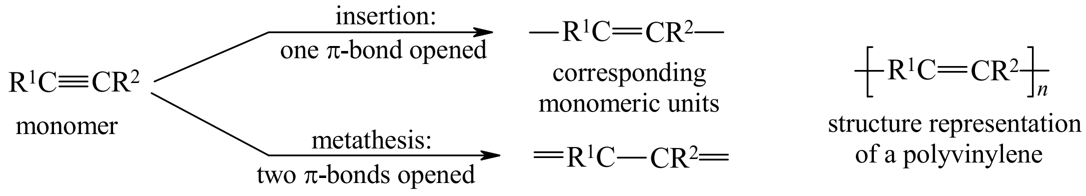
1. INTRODUCTION

Conjugated polymers are the subject of permanent interest as materials with properties that are potentially usable in areas of organic and hybrid organic/inorganic electronics such as light-emitting diodes,[1-6] photovoltaic cells,[7,8] field-effect transistors,[9] sensors[10] and also in the fields of gas storage[11] and separation.[12,13] Properties of conjugated polymers can be tuned towards desired functions through the chemical constitution, regularity and configurational structure of their main chains and by the choice and modifications of substituents (side groups) affecting their electrical, optical and mechanical properties as well as solubility that is of key importance for processing of conjugated polymers.[13-19] Polyacetylenes are perhaps the most known conjugated polymers.[20-22] The discovery of the metallic conductivity of doped polyacetylene films has opened up a new area of research – research of ‘‘synthetic metals’’.[23-28]

1.1. Polymerization of acetylenes

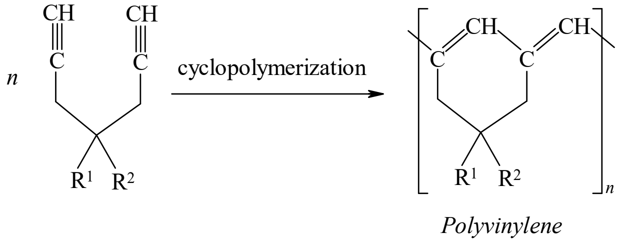
Polyacetylenes are defined as polymers prepared from acetylene monomers by polymerizations involving triple bonds or carbon atoms of triple bonds bond,[29] i.e., by processes which open one, two or all three bonds constituting the triple bond(s) of the monomer molecule or by processes in which the substitution on the triple bond(s) is accomplished. The main types of such processes are described below.

The most known processes of this type are coordination polymerizations of that give polyacetylenes of the polyvinylene structure, i.e., with main chains consisting of a linear sequence of conjugated double bonds.[29] These polymerizations proceed by: *(i)* the insertion (Ziegler-Natta) mechanism, at which only one π-bond of the monomer triple bond is opened, or by *(ii)* the metathesis polymerizations,[30] at which two π-bonds of the monomer triple bond are opened (see **Scheme 1**). These polymerization modes, when taking place on the same monomer, give polymers of the same repeating structure (**Scheme 1**) that, in ideal case, eventually differ only in the end-groups.



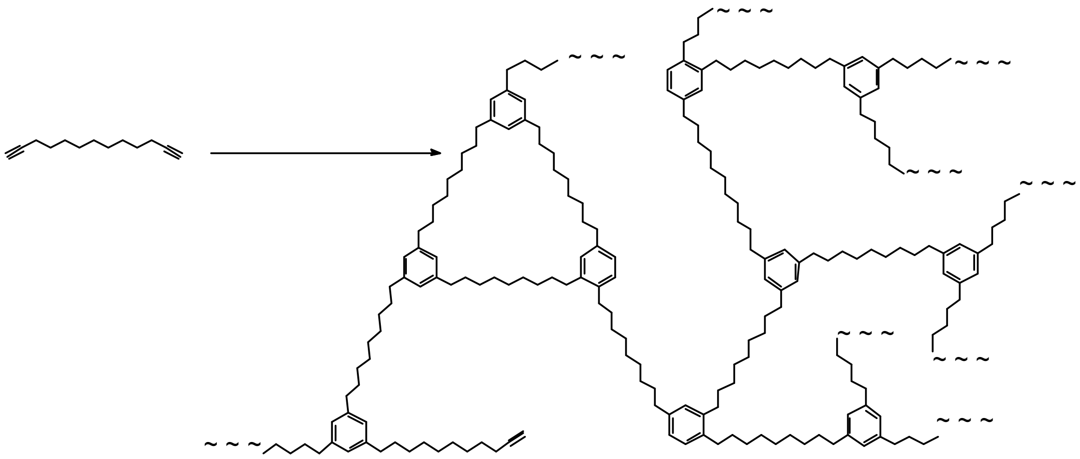
Scheme 1. Difference between the insertion and the metathesis polymerization of an acetylene monomer to polyvinylene (R^1 and R^2 are hydrogen, alkyl, aryl, hetaryl etc.).

Special examples of coordination polymerizations are the polymerizations of the cyclopolymerization type, i.e., polymerizations at which new rings are formed.[31] Those are mainly: polymerizations of geminal dipropargyl derivatives that give polyvinylenes with cyclic main-chain units



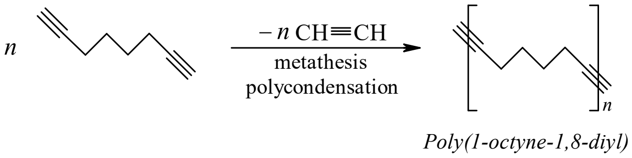
Eq. 1

and cyclopolymerizations based on cyclotrimerization of ethynyl groups of monomers with two or more ethynyl groups yielding branched or network polymers with benzene rings as branch and/or knot points



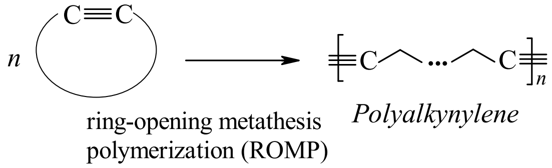
Scheme 2. Cyclotrimerization of ethynyl end-groups

Acetylenes can be further polymerized by reactions preserving triple bonds that thus give polymers containing main-chain triple bonds.[31] Such reactions are: *(i)* metathesis polycondensations of isolated diynes that typically gives non-conjugated polymers together with an alkyne (mostly acetylene) as side product:



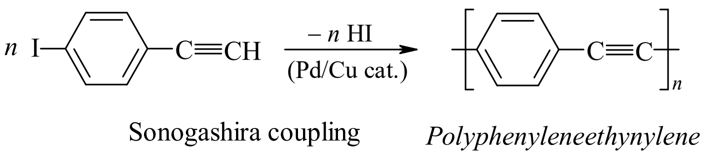
Eq. 2

(ii) metathesis ring-opening polymerization of cycloalkynes giving polyacetylenes of the same structure type without a release of a side product:



Eq. 3

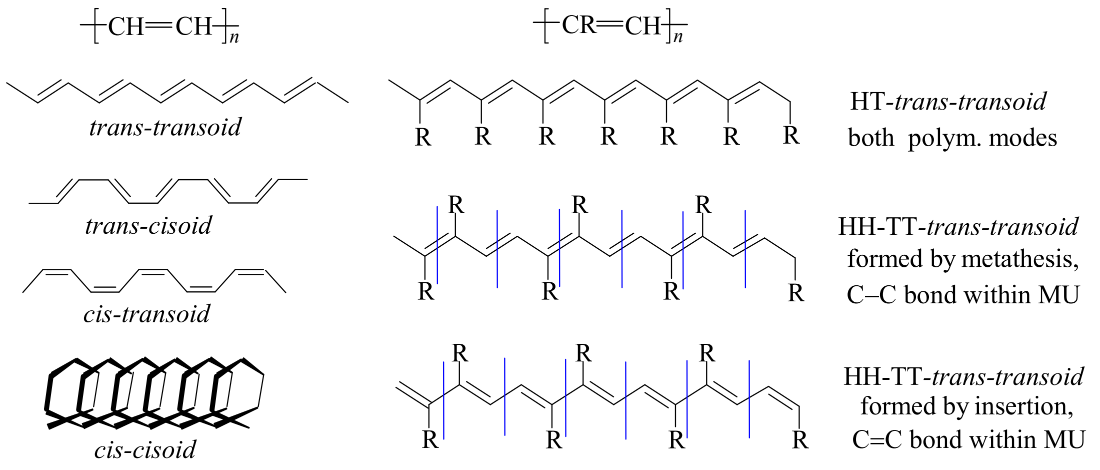
and Sonogashira coupling of alkynes bearing a halogen-substituted group or cross-coupling of a diethynyl compound and dihalogenated compound, which is mostly used for preparation of conjugated polymers of the polyaryleneethynylene type:[32-34]



Eq. 4

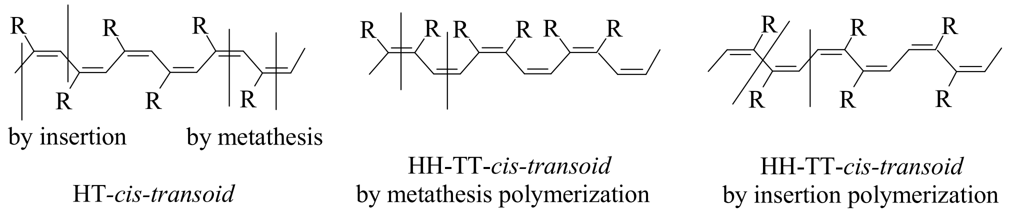
1.2. Isomerism of polyvinylene macromolecules

The isomerism of polyvinylene chains includes the cis-trans (*Z-E*) configurational isomerism of double bonds and the constitutional isomerism of the regio-regularity type, usually referred to as head-tail (H-T) isomerism. Since conjugation restricts free rotation along the main-chain C–C single bonds, polyvinylenes exhibit so called *cisoid–transoid* isomerism in addition to the isomerism originating from the presence of double bonds.[35-37] Therefore, there are four basic configurations of polyvinylene chains (**Scheme 3**).



a) basic configurational isomers

b) head–tail isomers of a trans-transoid chain



c) head–tail isomers of a cis-transoid chain

Scheme 3. Configurational and head-tail isomerism of polyvinylene chains (taken from ref.[38])

Taking into account also regio-regularity, three different H-T isomers can be derived for each basic configuration of a polyvinylene with asymmetric repeating units, depending also on the polymerization mode (insertion or metathesis; see isomers of a *trans-transoid* chain, **Scheme 3*b***). Therefore, there are in total twelve possible regular structures of a polyvinylene chain that is composed of asymmetric monomeric units of one kind.[38] Rh(diene) catalysts typically provide the only one: HT-*cis-transoid* form, out of all twelve possible basic isomeric forms and virtually infinite number of their combinations, which clearly shows their unique product selectivity in polymerization of acetylenic monomers. Other catalysts show much lower stereo-selective propagation.[39]

1.3. Catalytic polymerization of acetylenes to polyvinylenes

First it should be noted that radical or ionic polymerizations of acetylenic monomers to polyvinylenes are practically impossible owing to the delocalization of corresponding active species along growing conjugated chains. Actually, radicals and ions are active centers of the type of a defect in the electronic structure of a molecule and thus they can easily delocalize along a conjugated chain and consequently loss its reactivity. Therefore, these polymerization experiments give only mixtures of oligomers. In contrast, the active centers of coordination polymerizations - transition metal complex species - cannot be delocalized and thus can keep their activity regardless the delocalization of electrons along conjugated chains linked to these complex species. Therefore, they can provide polyacetylenes with high-molar-mass.

Successful polymerization of acetylene was first reported by G. Natta et al.[40] who obtained an insoluble powdered poly(acetylene) by polymerization induced with Ti-based catalysts. The insolubility together with impossibility of thermal processing made this non-processable polymer uninteresting for further research. The direct preparation of a poly(acetylene) film by the polymerization of gaseous acetylene on the surface of a solution Z-N catalyst system discovered by H. Shirakawa[41,42] represented an important progress that about five years later, upon the discovery of this film doping, opened boom of organic electronics. Those finding returned the interest to synthesis and study of the polymers derived from acetylene derivatives and today they are one of the most important and widely studied classes of conductive polymers. From the synthetic point of view, two key-points can be mentioned: *(i)* direct synthesis of poly(acetylene) membrane by Shirakawa using concentrated solution of $Ti(O\text{-}nBu)_4/Et_3Al$ catalyst[43,44], and *(ii)* modification of the catalyst aging method that gives a poly(acetylene) with less defects.[45]

Early unsuccessful attempts to polymerize substituted acetylenes led to conclusions that only monosubstituted acetylenes with sterically unhindered triple bond can be polymerized with Ziegler-type catalysts to give high molecular weight polymers and/or soluble oligomers.[46] However, in 1974, Masuda et al.[47] found that group 6 transition metal chlorides, WCl_6 and $MoCl_5$, are quite active in the polymerization of phenylacetylene (PhA) and phenylpropyne giving polymers with molar masses over 100 kg/mol. They suggested that these polymerizations proceed by the metathesis mechanism. Actually, the system WCl_6 + PhA has been often used as the catalyst for ring-opening metathesis polymerization of cycloalkenes.[30] After this fundamental step, many metathesis catalysts have been developed that are very effective in polymerization of various substituted acetylenes including disubstituted acetylenes with sterically crowded triple bond. Those are mainly complexes or, mostly *in situ* formed active species with W, Mo, Ta and Nb central atoms. Tantalum and niobium based catalysts are especially active in polymerizations of acetylenes with two bulky substituents while tungsten based catalysts polymerize disubstituted acetylenes with less bulky substituents. Complexes of W, Ta and Mo are also active in polymerization of monosubstituted acetylenes. Complexes of Ti, Fe, Ni, Ru and Rh are very active catalysts only for polymerization of monosubstituted acetylenes.

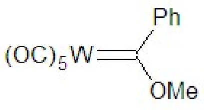
Mo and W catalysts

Those catalysts are proved to show a good ability to polymerize a wide scope of substituted acetylenes. They can be divided into the following three main categories:

Metal halides. $MoCl_5$ and WCl_6 and oxide-halide $WOCl_4$ give high yields of polymers of monosubstituted acetylenes, especially those carrying bulky substituents. In polymerizations of sterically low crowded monomers such as phenylacetylene and mainly alk-1-ynes, these single compounds give polymers in relatively low yields owing to the formation of cyclotrimer byproducts. However, when applied in a combination with cocatalysts such as alkylaluminium or alkyl(aryl)tin compounds they form very active systems providing high polymer yields.[38,48-53] On the other hand, acetylenes with bulkier substituents such as *tert*-butylacetylene and ortho-substituted phenylacetylenes polymerize with $MoCl_5$ as well as WCl_6 to polymers with high molar mass.[54]The addition of organometallic cocatalysts such as $EtAlCl_2$, Ph_3Sn, Bu_4Sn, Ph_3Bi, Ph_3Sb, etc. is needed for obtaining active species for polymerizations of disubstituted acetylenes.[55,56]

Metal carbonyl catalysts. Mo and W hexacarbonyl complexes alone do not polymerize acetylenes. However, when dissolved in a halogenated solvent such as CCl_4 and UV irradiated, they polymerize various substituted acetylenes to polymers with extremely high molar mass.[57] The main advantage of these catalysts is their stability in air, which makes the polymerization protocol easier. A halogenated solvent plays a key role in the formation of active species by replacing carbonyl for halogen-ligands, and thus cannot be replaced by another solvent such as toluene that is widely used as medium for acetylene polymerizations. In some cases a catalytic amount of Ph_2CCl_2 can substitute the use of halogenated solvent and polymerization can be carried out in toluene.

Metal carbene catalysts. First Fisher (**1**) and Casey (**2**) carbenes were used for polymerization of phenylacetylene, *tert*-butylacetylene and cyclooctyne in low yields.[58] Irradiation and adding of Lewis acids is proved to help the generating of active species. The Fisher carbene is more stable but less active than the Casey carbene catalyst. Later metal-carbene complexes developed by Schrock and Hoveyda (**3**) also act as good catalysts for living polymerization of ortho-substituted phenylacetylenes[59,60] and α,ω-diynes.[61,62]



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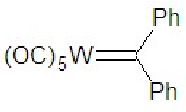

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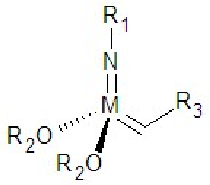
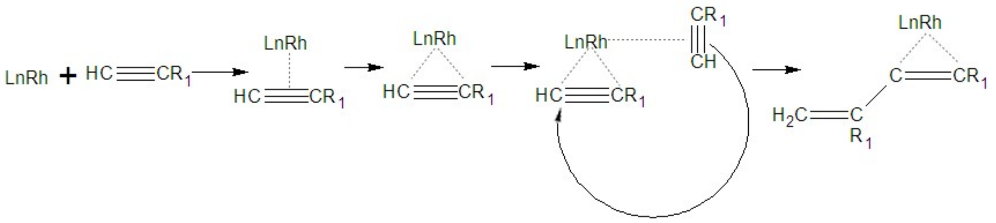


3

Rhodium catalysts

Rhodium complexes are known to catalyze polymerization of acetylenes by the insertion mechanism. Main advantage of these catalysts is their very high activity in the polymerization of monosubstituted acetylenes to stereoregular (*cis-transoid*) high molar mass polymers.[63,64] In addition, Rh catalysts are tolerant to various functional groups such as amino-, hydroxy-, azo-, carbonyl and others.[38] Therefore, Rh-catalyzed polymerizations can be carried out in many different solvents such as benzene, THF, ethanol, CH_2Cl_2 and Et_3N.[65,66] They can be accomplished even in water with a water-soluble Rh-catalyst or in an ionic liquids.[67,68]



Scheme 4. Mechanism of insertion polymerization of monosubstituted acetylenes

Rhodium catalysts polymerize acetylenes by the insertion mechanism.[69,70] The fact that they polymerize only monosubstituted acetylenes gave rise to the proposal of the polymerization mechanism that suggests a transfer of the acetylenic hydrogen from the coordinated monomer molecule to the last monomeric unit of the growing polymer chain (see **Scheme 1**). This mechanism is in a good agreement with the fact that the polymerizability of monosubstituted acetylenes is always higher for monomers with more acidic acetylenic hydrogen.[71,72]

Nb and Ta catalysts

The niobium and tantalum chlorides in combination with tetraphenylbismuth and some other cocatalysts were introduced as the effective catalysts for polymerizations of disubstituted acetylenes to the polymers with high molar mass.[73,74] Besides, they were found as highly efficient catalysts for cyclotrimerization of monosubstituted acetylenes and/or cyclo-polymerizations of these monomers.[75] Also, it is known that bulky substituents must be incorporated to the triple bond of the monomer for the successful polymerization with those catalyst- they are suitable just for polymerization of disubstituted acetylenes.

$NbCl_5$ and $TaCl_5$ can readily polymerize 1-trimethylsilyl-1-propyne without the need of co-catalyst giving polymer with high molecular weight (M_W 10^5-10^6).[73] On the other side, 1:1 mixture of $TaCl_5$ and Ph_3Bi gives polymer with even higher M_W (~ 4 x 10^6). This MW is the highest among those of poly(substituted acetylene)s synthesized till now.

$NbCl_5$ and $TaCl_5$ alone cannot polymerize diphenylacetylenes, but in combination with suitable co-catalysts such as n-Bu_4Sn and Et_3SiH polymers in good yields are achieved. The derivatives of diphenylacetylene with p-Me_3Si, p-tBu, and other substituents can polymerize in similar conditions.[49]

1.4. Polymers of substituted acetylenes - applications

With the inherent nature of electronic unsaturation or π-conjugation and their great structural diversity, the acetylenic polymers are presumed to exhibit an array of functional properties that are difficult to realize by conventional condensation and vinyl polymers. Many groups have been working on the development of advanced functional materials based on the acetylenic polymers. As a result, a variety of novel electrical, optical, photonic, magnetic, and biological properties has been reported for this class of polymeric materials. Poly(substituted acetylene)s are known to be photoconductive[76], optically active[77], to exhibit liquid crystallinity[78], fluorescence sensing[79], optical nonlinearity[80] and gas permeability.[81] Some aspects of their applicability will be shortly given below.

Gas-permeable polyacetylenes

The most intensively studied application of substituted acetylenes is their usage as gas-permeable materials for gas separation and gas storage. Initial catalyst for this interest is poly(1-trimethylsilyl-1-propyne)[73,82] - the most permeable material among all existing polymers which oxygen permeability (P_{oxygen} = 4000-9000 barrels) is about ten times larger than those of poly(dimethylsiloxane). In addition it can give a free standing film and shows a gas permeation mechanism different than that of poly(dimethylsiloxane).

Many examples of gas-permeable poly(disubstituted acetylene)s can be given. Among them, many of the polymers with large P_{oxygen} values contains bulky spherical substituents such as *t*-Bu or Me_3Si.[49,81] On the other hand, poly(disubstituted acetylene)s with long *n*-alkyl substituents usually have a lower gas-permeability. The high gas permeability of the polyacetylenes is usually attributed to the high free volume and unusual free volume distribution in the materials, which is presumed to be derived from their low cohesive energy structure, stiffness of their conjugated main chains and bulkiness of their spherical substituents.

Poly(diphenylacetylene)s with bulky ring substituents also show a high gas permeability and, in addition, they are thermally very stable and also able to form polymer films.[81] It is possible to tune the permeability as well as the solubility of those polymers by varying the type and size of the ring substituents. It is also known that poly(diphenylacetylene)s have a higher gas permeability than poly(phenylacetylene)s.

Luminescent polyacetylenes

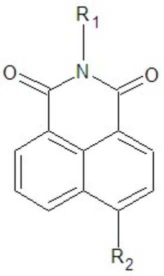
The study of luminescence properties of π-conjugated polymers is a topic of great interest in last decades. Little work had been done on the development of light-emitting polyacetylenes in the early days of their research, because polyacetylene itself is a very poor luminophore. Modifications of molecular structure of polyacetylenes, such as attachments of the pendent groups with different electronic and steric effects have been examined in tuning the extent of delocalization of electrons along conjugated polyene backbone and the excitation energy transfer between polymer chains. These approaches have worked well and led to generation of a large variety of luminescent polyacetylenes with high quantum yields of photoluminescence and good electroluminescence efficiency.[83-89] In these materials, the emitting center can be either the pendent groups or the polymer backbone by itself. The excitation energy can be transferred from pendants to the backbone or from the backbone to pendants, and thus the emission color can occur at different wavelength scale, which is tunable by changing the backbone and pendant structures.[83,84,90]

It is known that, if the hydrogen atom in the repeating unit of a poly(1-alkyne) is replaced by a bulky aromatic substituent, the polymer chains become more twisted but simultaneously more resistant to oxidation with air oxygen and thus more stable. The involved steric effect, however, shorten the effective delocalization of electrons in the resultant poly(disubstituted acetylene)s, hence widening their band gap and giving blue shift to their emission.[38,91] Indeed, poly(1-phenyl-1-alkyne)s emit strongly in the blue region. A systematic investigation of the luminescence of poly(1-phenyl-1-alkyne)s revealed that these polymers have strong photoluminescence around 455 nm and electroluminescence around 470 nm. For poly(diphenylacetylene)s the range is 530 and 550 nm.[92] Green and blue emissions are generally observed for electroluminescent devices based on various poly(diphenylacetylene)s and poly(1-phenyl-1-alkyne)s as emission layers.[93,94]

Aggregation of conjugated polymer chains in the solid state often results in the formation of less-emissive or low-emissive species such as excimers and exciplexes, which partially or almost completely quench the luminescence of the polymers. This aggregation-caused quenching effect has been a thorny problem in the development of efficient polymer light-emitting diodes (PLEDs) because the conjugated polymers are typically used as thin solid films in electroluminescent devices.

1.5. Derivatives of 1,8-naphthalimide as fluorescent compounds

The fluorescent organic compounds have wide applicability in novel technologies. They are largely used in optoelectronics, liquid-crystalline systems, as active media in lasers, light collectors, as photo layers for investigations of cell membranes, as markers in medicine, etc. The class of derivates of 1,8-naphthalimide is amongst the most popular organic dyes. They are known for their high stability and because of this and their low molecular weight they are preferable for usage in electronics[95] and laser techniques.[96-98] This class of fluorophores has also significant application as dichroic dyes in liquid-crystalline systems of the host-guest type.[99,100]



The 1,8-napthalimide derivatives that contain alkoxy- or amino-group at the C4 position of the naphthalene unit aromatic ring usually exhibit medium to strong fluorescence.[101] The spectral characteristics of the chromophores depend mainly on the polarization of the molecule due to the donor-acceptor interaction between the substituent at carbon C4 and the carbonyl groups of the imide moiety.[102-104] Depending on the type of the substituent and its electron-donating properties, the chromophores are divided into two subclasses: *(i)* optical whiteners showing blue fluorescence, which can be represented by the alkoxy-derivatives, and *(ii)* fluorescent dyes which can be represented by the amino-derivatives of naphthalimide. Some of naphthalimide chromophores show solvatochromism, which indicates their nonlinear optical properties.[105]

4-Amino- and 4-alkylamino-derivatives of 1,8-naphthalimide have a good photostability and good fluorescence efficiency. Their absorption maxima λ_A are within the visible spectral region (around 410-440 nm) and emission maxima in the range of 515-540 nm depending on the substitution. The quantum yield of fluorescence varies in a wide range from 0.04 to 0.85.[106,107] If a polymerizable group is introduced onto naphthalimide molecule the resulting chromophoric monomer can be polymerized. There is a number of papers in the literature that deal with polymerization of vinylic naphthalimide chromophores to polymers and dendrimers with fluorescence properties comparable to the properties of initial monomer.[108,109]

The optical and photophysical properties of 1,8-naphthalimides can be tuned through the substitution on the aromatic ring. For example, introduction of amino type groups to the positions 3, 4, 5 or 6 gives compounds with internal charge transfer (ICT) complex.[110] The resulting ICT absorption band is shifted to the visible region and shows a significant solvatochromic effect. Many of the compounds are also strongly fluorescent, with a marked Stokes shift. The emission is mostly in the green part of the spectrum but can be directed further towards the red by altering the nature of the ring substituent or that of the imide.[111] This yields particularly attractive derivatives since they can partially overcome auto-fluorescence and light scattering from any biological environments. Tunable photophysical properties make naphthalimides excellent compounds to probe the microenvironment of biological systems. They also found applications in the field of supramolecular chemistry in anion sensing[112] and as the fluorescence brighteners[113,114], solar energy collectors[115] and laser dyes.[116,117] Naphthalimides brominated at the 3 and 4 positions of the ring have been proposed as good candidates for the photochemical therapeutic inhibition of enveloped viruses in the blood and blood products since they are powerful photo-reagents which can induce lesions in DNA molecules and has the ability to kill cells when photo-activated.[118] This opens up possible applications in photo-therapy. Finally it should again be emphasized that an important feature of 1,8-naphthalimides is that they are relatively easy to be synthesized in high purity on a large scale.[119]

2. AIMS OF THE THESIS

The target of my dissertation project has been the development of the synthetic paths to new luminescent materials based on conjugated polymers that might be potentially utilized in optoelectronics and field of sensors. The highly luminescent naphthalimide group has been chosen as the main luminophore and conjugated polymers of substituted acetylenes as the group carriers. The partial goals were set as follows:

(i) Development of the catalytic processes that are tolerant to naphthalimide groups and give soluble linear polyacetylenes comprising naphthalimide side groups.

(ii) Development of the synthetic paths based on consecutive modifications of polyacetylenes prepared with catalysts that are not tolerant to naphthalimide groups, which finally provide soluble luminescent polymers that can be processed from solutions.

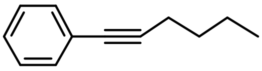
(iii) Determining of the effects of the structure symmetry and substituent bulkiness of disubstituted acetylenes on their polymerizability and solubility of resulting polymers, as the key point for preparing polymers for the modifications set out in paragraph *(ii)*. (Modifications of poly(monosubstituted acetylene)s are not too promissing owing to increased reactivity of their main-chain double bonds and sensitivity to air).

(iv) Synthesis of mesoporous network polyacetylenes with naphthalimide side groups and sufficiently high pore volume, which might be potentially used in gas or vapor sensors.

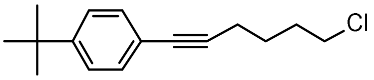
3. *RESULTS AND DISCUSSION*

3.1. Preparation of monomers

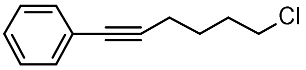
Monomers polymerized within this project and their codes are shown in **Chart 1**. Commercially available monomers **M0** and **M3** to **M9** were used as supplied or, if needed, purified by distillation or sublimation and dried. Disubstituted acetylene monomers **M1**, **M2**, **M10** to **M13** as well as naphthalimide monomers **PN, PN1** were prepared by the procedures described briefly below and more detailed in the Experimental part.



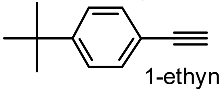
hex-1-yn-1-yl-benzene **M0**



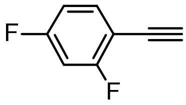
1-(6-chlorohex-1-yn-1-yl)-4-(*t*-butyl)benzene **M1**



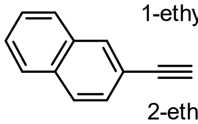
(6-chlorohex-1-yn-1-yl)benzene **M2**



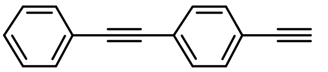
1-ethynyl-4- *t*-butylbenzene **M3**



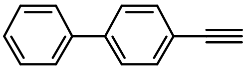
1-ethynyl-2,4-difluorobenzene **M4**



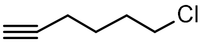
2-ethynylnaphthalene **M5**



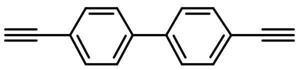
1-phenylethynyl-4-ethynylbenzene **M6**



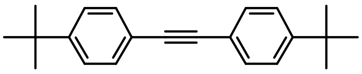
4-ethynylbiphenyl **M7**



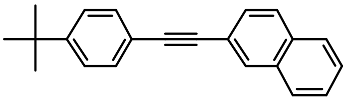
6-chlorohex-1-yne **M8**



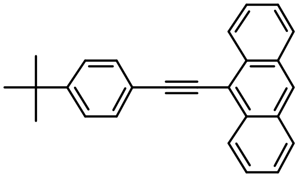
4,4'-diethynylbiphenyl **M9**



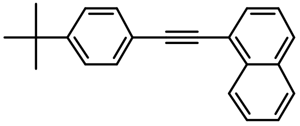
1,2-bis-(4-*t*-butylphenyl)ethyne **M10**



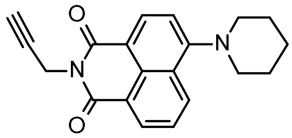
2-[(4-*t*-butylphenyl)ethynyl)]naphthalene **M11**



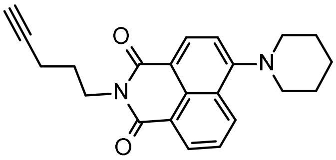
9-[(4-*t*-butylphenyl)ethynyl)]anthracene **M12**



1-[(4-*t*-butylphenyl)ethynyl)]naphthalene **M13**



N-(prop-1-yne-3-yl)-4-(piperidine-1-yl)-1,8-naphthalimide **PN**



N-(pent-1-yne-3-yl)-4-(piperidine-1-yl)-1,8-naphthalimide **PN1**

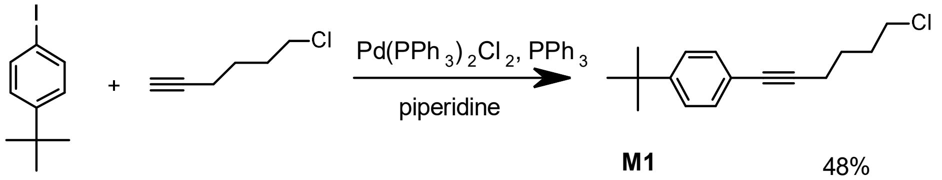
Chart 1. Monomers polymerized within this dissertation project and their codes.

The structures of the synthesized disubstituted acetylene monomers were designed with the following aims:

- Monomers with ω-chloroalkyl side groups: 1-(6-chlorohex-1-yn-1-yl)-4-(*tert*-butyl)benzene (**M1**) and (6-chlorohex-1-yn-1-yl)benzene (**M2**) to provide (after polymerization) corresponding monomeric units containing Cl atom that can be by substitution transformed into side groups that contain naphthalimide or ionic groups or, potentially, other groups giving to prepared polymers different functional properties.

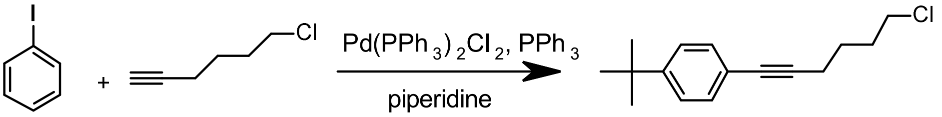
- Monomers with 4-(*tert*-butyl)phenyl group (**M1**, **M3** and **M10** to **M13**) that facilitates spectroscopic resolving of the corresponding monomeric units from the units derived from monomers **M0**, **M2** and **M4** to **M9**, which is useful for the determination of the composition of copolymers.

Monomers **M1**, **M2** and **M10** to **M13** were prepared using the Sonogashira coupling approach from the appropriate, commercially available reactants: **M1** and **M2** from 6-chlorohexyne and appropriate iodobenzenes:



M1 48%

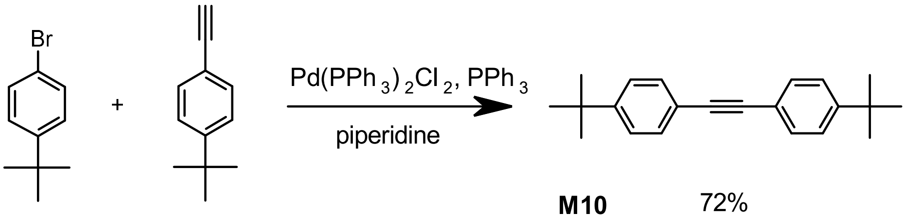
Eq. 5



M2 51%

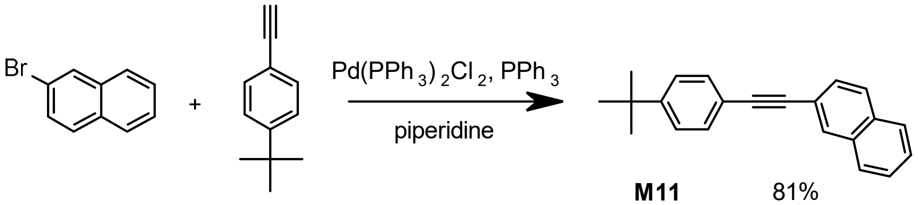
Eq. 6

while **M10** to **M13** from 1-(*tert*-butyl)-4-ethynylbenzene (monomer **M3**) and appropriate bromoaromatics.



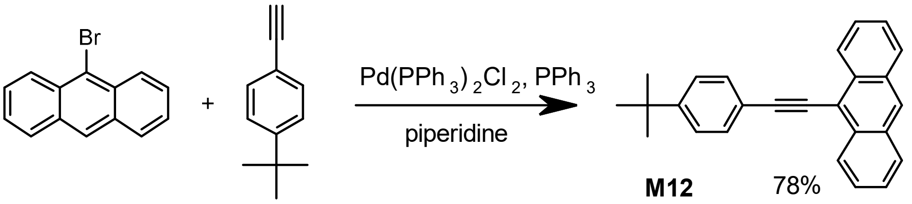
M10 72%

Eq. 7



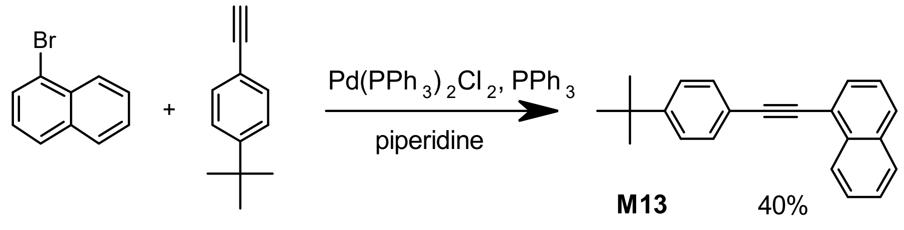
M11 81%

Eq. 8



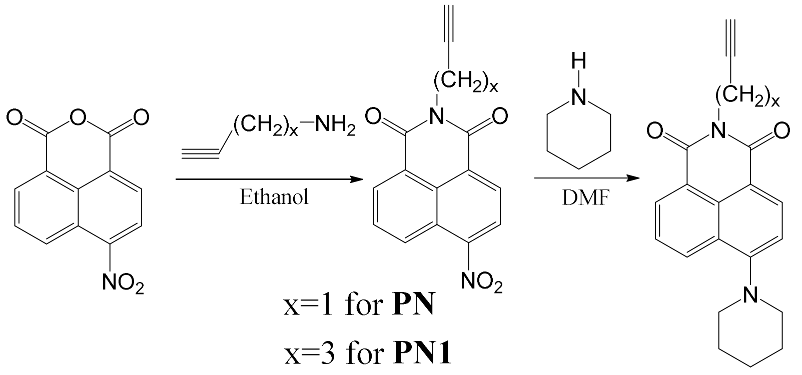
M12 78%

Eq. 9



Eq. 10

The Sonogashira coupling reactions were carried out in piperidine, which was applied as the reaction solvent as well as the base, and catalyzed by the [Pd(PPh$_3$)$_2$Cl$_2$]/CuI catalyst system that is currently used for these reactions. Crude **M1** and **M2** (oils) were purified by column chromatography, crude **M10** to **M13** by recrystallization. The prepared compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, UV/vis spectroscopy, elemental analysis and melting point determination. Luminescent monomers **M11-M13** were also characterized by the fluorescence emission and excitation spectra.



Scheme 5. Synthesis of naphthalimide monomers.

Monomers comprising highly luminescent naphthalimide group: *N*-(prop-1-yn-3-yl)-4-(piperidine-1-yl)-1,8-naphthalimide (**PN**) and *N*-(pent-1-yn-5-yl)-4-nitro-1,8-naphthalimide, **PN1**, were prepared in high isolated yields (~90%) from commercially available 4-nitro-1,8-naphthalic anhydride by the two-step process shown in **Scheme 5**. In the first preparative step, 4-nitro-1,8-naphthalic anhydride was reacted with the corresponding triple bond containing amine: (prop-1-yn-3-yl)amine or (pent-1-yn-5-yl)amine in ethanol under reflux for 5 hours. The obtained crude product was purified by repeated washing with 0.1M solution of NaOH in order to remove unreacted anhydride. In the second step of preparation, 1,8-naphthalimide was reacted with piperidine for 24 hours in *N,N*-dimethylformamide (DMF) at room temperature. The final product was purified by re-precipitation from ethanol; isolated overall yields were 90% for **PN** and 84% for **PN1**. High reproducibility of the overall process was found.

3.2. Electronic spectra of new monomers

Monomers **M1** and **M2** are colorless non-fluorescent oils with absorption bands in the UV-region (λ_{max} ~260 nm in $CHCl_3$ solution). The UV/vis spectra of monomers **M10-M13** are shown in **Figure 1** together with verticals whose position indicate the DFT calculated wavelength and height the oscillator strength of the absorption band. Spectral characteristics of monomers are summarized in **Table 1** and shapes of calculated HOMO and LUMO orbitals are presented in **Figure 2**.

As can be seen from Fig. 1, spectra of all monomers show an intensive absorption band in the UV region and only **M12** also a band in the visible region, in accord with the results of the TD-DFT calculations. The bandgap energy values estimated from the low energy onset of spectra increases from 2.85 to 3.94 eV in the following sample order: **M12** < **M13** < **M11** < **M10**.

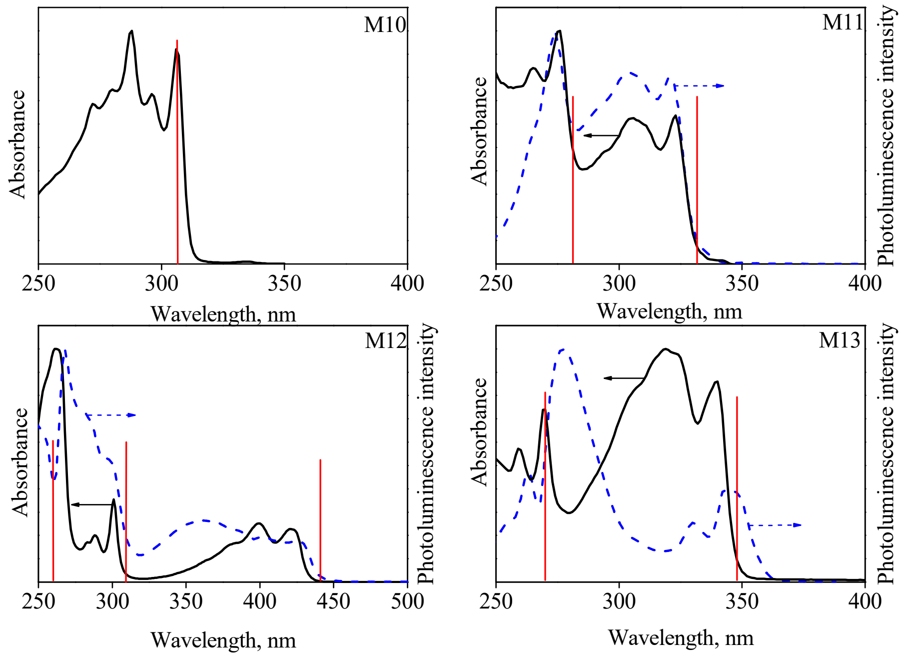


Figure 1. UV/vis absorption (full line) and excitation luminescence (dashed line) spectra of monomers **M10** to **M13**.

For fluorescent monomers, also excitation luminescence spectra are shown in Fig. 1. The best agreement between the absorption and excitation spectrum shows

M11, a bit worse agreement is seen for **M12** and a significant difference for **M13**. Monomers **M11** and **M12** exhibit a high quantum yield of fluorescence, ϕ, (see **Table 1**) while ϕ of **M13** is rather low (18 %), indicating a non-radiative decay of excited states, which might be the reason for this difference.

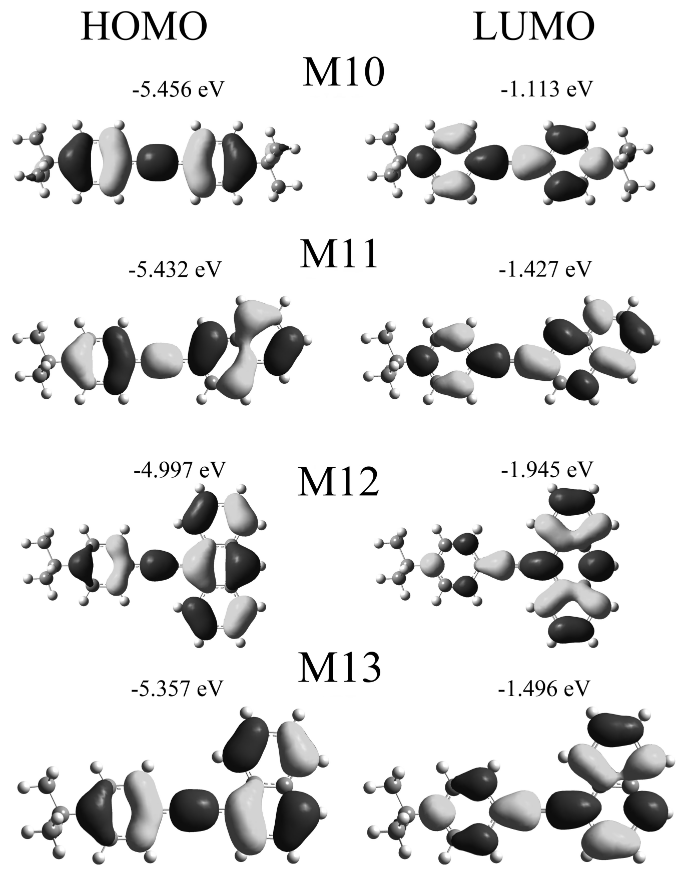


Figure 2. Electronic density contours for HOMO (left) and LUMO (right) of monomers **M10-M13** obtained using DFT calculations.

The TD-DFT calculations for **M10** found only one significant electronic transition with λ_{calc} located in the lower energy part of the broad experimental UV band (Fig. 1). In Fig. 2 could be seen that the orbitals of **M10** are delocalized mainly on the aromatic rings connected to the triple bond. The TD-DFT calculations for **M11** and **M13** revealed two electronic transitions whose wavelengths correspond to the positions of the bands in the experimental spectra. In the case of **M12** three electronic transitions were found by the calculations in accordance with the measured spectra. The replacement of *tert*-butylphenyl group in **M10** by a bigger naphthyl or anthryl group (**M11**, **M12**, **M13**) results in lowering the bandgap energy that is particularly significant for **M12**. Positional isomers **M11** and **M13** show only small difference in the bandgap energy value of about 0.18 eV (higher for **M11**), which can be explained from the calculated shapes of molecular orbitals shown in Fig. 2. The changed molecular geometry resulting from different connecting position of the naphthyl group slightly influences the shape of the molecular orbitals and thus also delocalization of electrons within the monomer molecule.

Table 1. Spectral characteristics of monomers (**M10**-**M13** in THF, **PN** and **PN1** in $CHCl_3$); λ_A absorption maximum; λ_{cut} cut off wavelength, ε_λ molar absorption coefficient; E_g band gap energy; λ_F emission maximum; φ_F quantum yield of fluorescence (excitation at 270 nm for **M10**-**M13** and 420 nm for **PN** and **PN1**); values calculated by the TD-DFT method are labelled by the subscript calc.

Monomer	λ_A [nm]	$\lambda_{A,calc}$ [nm]	ε_λ x 10^{-3} [$m^2.mol^{-1}$]	λ_{cut} [nm]	E_g [eV]	λ_F [nm]	$\lambda_{F;calc}$ [nm]	φ_F
M10	288	307	3.46	315	3.94	---	---	---
M11	306	332	1.86	333	3.72	342	359	0.81
	276	281	2.98					
M12	399	441	2.51	435	2.85	430	477	0.95
	301	309	3.53					
	262	257	9.98					
M13	319	348	2.05	350	3.54	361	380	0.18
	270	270	1.52					
PN	417		16.39	479	2.59	508		0.72
PN1	415		8.43	475	2.61	506		0.4

Normalized luminescence spectra of three luminescent monomers are shown in **Figure 3**. As can be seen, monomers **M11** and **M13** emit light with maxima in the region 340 - 370 nm while **M12** emits light with two resolved peaks at ca 430 and 460, i.e., at about ca 100 nm longer wavelengths. The DFT calculated emission wavelengths (see **Table 1**) are in a good accordance with the experimental ones, showing an increase in $\lambda_{F,calc}$ along the sample order **M11** < **M13** < **M12**.

The experimental UV/vis and emission spectra of the **PN** type monomers (**Figure 4**) exhibit two absorption bands: the first one at about 290 nm and the second one at around 415 nm (λ_{max} = 417 nm for **PN** and 415 nm for **PN1**). The emission maxima of **PN** (508 nm) and **PN1** (506 nm) are also close to each other and both **PN** and **PN1** show a good fluorescence quantum yield (72 % for **PN** and 40% for **PN1**).

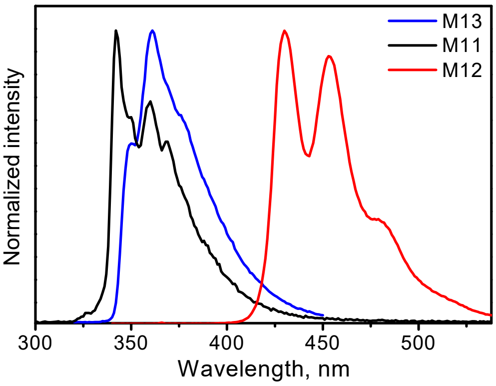


Figure 3. Luminescence spectra of monomers **M11** to **M13**.

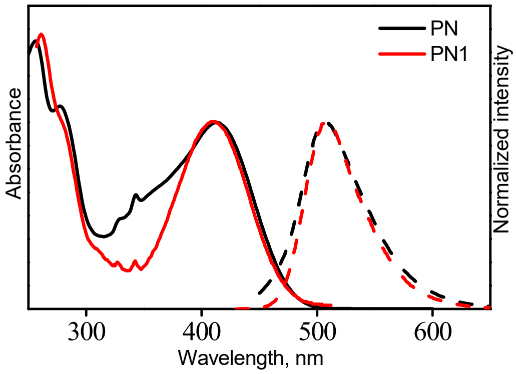


Figure 4. UV/vis and luminescence spectra of **PN** and **PN1**

3.3. Polymerizations of disubstituted acetylenic monomers

3.3.1. Polymerizations of new monomers with $TaCl_5/Bu_4Sn$ catalyst

Polymerizations catalyzed by $TaCl_5/Bu_4Sn$ system were done in a glove box using the Schlenk technique. Monomers were dried by repeated azeotropic distillation of their toluene solutions to remove residues of moisture and the resulting monomer solution was always properly degassed. Polymerizations were qualitatively monitored through color changes of the reaction mixture. A color of the activated catalyst system solution is dark brown. Any opalescence signalizes the presence of either moisture or oxygen, which cause decomposition of the active catalytic species. After the addition of monomer solution, the color of the reaction mixture changes to dark red-violet. However, if moisture is present, an opalescence of the particles of deactivated catalyst appears.

Polymerizations were terminated by pouring the reaction mixture into ca tenfold excess of methanol and the crude precipitated polymer was filtered, repeatedly washed with methanol and dried to the constant weight to determine the polymer yield by weighing. Further purification of the crude polymer from residual impurities was carried out by re-precipitation from the THF/MeOH solvent system, till no traces of the monomer or other impurities were seen on the SEC (RI and DAD detection) records as well as in ^{1}H-NMR spectra.

Table 2. Yield and molar mass characteristics of polymers (oligomers) prepared with $TaCl_5/Bu_4Sn$ catalyst system; M_w (kg/mol) is the mass-average molar mass and $Đ$ the dispersity of polymers.

Polymer	Yield (%)	M_w	$Đ$
P(M10)	71	insoluble	
P(M11)	44	250	5.8
P(M12)	20	1.3	-
P(M13)	16	10	4.1

Experimental data concerning the polymerizations of monomers **M10** to **M13** are summarized in **Table 2**. It is well known that diphenylacetylene polymerizes in precipitation mode, because the resulting polymer is absolutely insoluble in all current solvents.[120] An introduction of alkyl pendants onto conjugated main chains is well known to increase the polymer solubility.[121] Monomer **M10** can be regarded as an analogue of diphenylacetylene carrying two identical alkyl substituents at identical positions (para) of both aromatic rings. Despite this substitution, the resulting polymer is totally insoluble even at elevated temperatures. Consequently, this insoluble polymer is hard to purify from the monomer and catalyst residua, since it can be done only by repeated polymer washing with solvents.

Based on the results of polymerization of other disubstituted acetylenes,[122,123] it can be suggested that the solubility of the substituted polydiphenylacetylenes is mainly influenced (achieved) by introducing a non-symmetry into the structure of their monomeric units, i.e., by introducing different substituents on the aromatic rings of monomer molecules. Molecules of **M10** are namely highly-symmetric bearing identical substituents in para positions of both benzene rings. This gives monomeric units with high symmetry that allows compact packing of polymer chains in the solid state giving an insoluble polymer. The idea on the relation between the polymer solubility and the symmetry of its monomer units is strongly supported by the fact that homopolymers of non-symmetric monomers **M11** and its isomers **M13** are well soluble in various solvents.

Polymerizability of asymmetric monomers **M11**, its isomers **M13,** and **M12** with substituents R_1= *tert*-butylphenyl and R_2 other aromatic group significantly depends on the structure of the R_2 substituent. **M11** and **M13** are positional isomers containing 1- or 2-naphthyl group as R_2. The 1-naphthyl monomer is significantly less reactive then the 2-naphthyl group (proved by several polymerization experiments). This could be explained by different sterical hindrance of the reactive triple bond in the monomers and its possibility to coordinate to the active centers. The isomeric polymers **P(M11)** and **P(M13)** also show substantially different apparent molar masses (ca 250 000 for **P(M11)** and ca 10 000 for **P(M13)** as determined by the SEC technique. The dispersity $Đ = M_w/M_n$ was found to be similar for both prepared polymers. Polymer **P(M11)** is a yellow fine powder while polymer **P(M13)** precipitates as orange globes, which most probably reflects differences in molar masses of these polymers. Despite that, both polymers exhibit very good solubility in THF and $CHCl_3$.

Monomer **M12** exhibited a very low polymerizability giving only oligomers of the average molar mass of ca 1300. It should be noted here that the related monomer with the only one bulky substituent, 9-ethynylanthracene, is known to polymerize very well with WCl_6 and $MoCl_5$ catalysts.[124] This indicates that the simultaneous presence of two bulky substituents, 4-*tert*-butylphenyl and 9-anthryl, yields so high steric hindrances that they make the internal triple bond insertion into a growing polymer chain very difficult.

Soluble homopolymers **P(M11)** and **P(M13)** were characterized by the ^{1}H-NMR spectroscopy. The spectra showed very broad signals which did not allow a detailed assignment (0.7-1.4 ppm for aliphatic substituent and non-resolved broad multiplets for the aromatic protons between 5 and 8 ppm). The observed high signal broadening confirms that these polymers are highly irregular. Nevertheless, the obtained spectra allowed to estimate the ratio of aromatic and aliphatic protons in **P(M11)** and **P(M13)**, which was found to be in accord with the expected structure of the polymers.

The UV/vis spectra of soluble polymers are shown in **Figure 5**. As compared with the spectra of monomers, spectra of polymers contain a broad band in the visible region indicating the transformation of monomer triple bonds into conjugated polymer chain. The values of the absorption coefficients of those bands are summarized in **Table 3**. The position of the band shifts to higher wavelengths in the order **P(M11)<P(M13)**, similar to the order in band position for the monomers **M11<M13**. Despite the fact that **P(M13)** has a significantly lower molar mass than **P(M11)** (M_w=10 000 to M_w=250 000), the position of the UV/vis band of **P(M13)** is red shifted with respect to the band of **P(M11)**. Hence it is quite clear that it is not the

molar mass but the positional isomerism of the substituent R2 that plays a key role in the extent of delocalization of electrons along polymer chains.

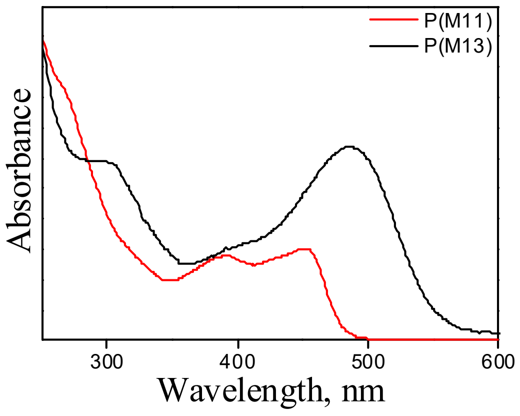


Figure 5. UV/vis spectra of soluble polymers P(M11) and P(M13)

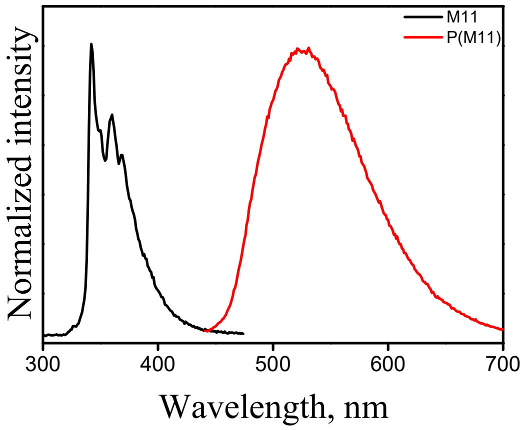


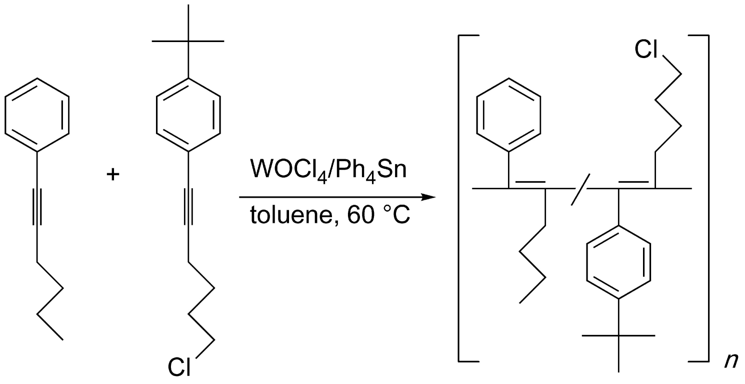
Figure 6. Emission spectra of M11 and P(M11)

The emission spectra of **P(M11)** and the monomer **M11** are shown in **Figure 6** and the emission spectral characteristics including quantum yields and lifetimes are given in Table 3. The emission of the polymer in contrast with the emission of the monomer doesn't have fine vibrational structure. The quantum yield of fluorescence is significantly lower for the polymer compared to the monomer. In comparison polymer **P(M13)** is not fluorescent. The differences in fluorescent properties between **P(M11)** and **P(M13)** could be described by the influence of the naphthalene pendants to the extent of the radiative and non-radiative electronic transitions. For **P(M13)** the radiative process is completely suppressed and no fluorescence occurs.

Table 3. Spectral characteristics of soluble polymers **P(M11)** and **P(M13)** in THF solution; ε_λ, is molar absorption coefficient at $\lambda_{max,}$ absorption maximum; λ_0, cut off wavelength; λ_F fluorescence emission maximum; τ_F, lifetime of excited states (excitation at 370 nm); $\boldsymbol{\Phi}_F$ fluorescence quantum yield relative to fluorescein solution in 0.1 M NaOH (excitation at 420 nm).

Polymer	λ_{max}, nm	ε_λ x 10^{-3} [$m^2.mol^{-1}$]	λ_0 [nm, eV]	λ_F [nm]	τ_F [ns]	Φ_F
P(M11)	452	0.52	488, 2.54	514	0.76 (100%)	0.14
P(M13)	486	0.25	562, 2.21	-	-	-

3.3.2. Copolymerization of monomers M0 and M1 with WOCl₄/Ph₄Sn catalyst



Scheme 6. Scheme of copolymerizations.of M0 and M1

Two homopolymers (**A0** and **A4**) and three copolymers (**A1** to **A3**) were prepared by polymerizations of monomers **M0** and **M1** induced with the metathesis catalyst system $WOCl_4/Ph_4Sn$ (**Scheme 6**). This system is known to polymerize not only monosubstituted acetylenes but, at elevated temperatures, also disubstituted acetylenes.[125-127] The homo- and copolymers were obtained in the medium to high isolated yields (50 - 90 %, **Table 4**) as yellowish solids with a blue fluorescence.

Table 4. Data for polymerizations of monomers **M0** and **M1** with $WOCl_4/Ph_4Sn$ catalyst to homo- and copolymers **A0 to A4**; f_{M1} is the feed mole fraction of **M1**, F_{M1} the mole fraction of **M1** units in polymer, M_w mass-average molar mass, $Đ$ dispersity and Y isolated yield of polymer.

Polymer	f_{M1}	F_{M1} elemental analysis	F_{M1} ^{1}H NMR	Y, %	M_w kg/mol	**$Đ$**
A0	0	0	0	89	300	2.8
A1	0.25	0.22	0.18	91	350	3.2
A2	0.5	0.27	0.24	70	120	2.8
A3	0.75	0.48	0.50	74	110	2.5
A4	1	1	1	46	75	2.8

Poorly resolved ^{1}H NMR spectra (**Figure 7**) proved irregularity of all these polymers, which might consist in the configurational (*cis-trans*) as well as orientational (head-tail) non-uniformity of their chains. Irregularity is typical of polyacetylenes prepared with W, Ta and Nb based catalysts.[125-127] The NMR spectra contain a broad undefined signals of aromatic (6 to 8 ppm) and aliphatic (0.5 to 2 ppm) protons and, except for the spectrum of **A0**, also relatively well resolved signal of protons of CH_2Cl groups at 3.2 ppm. This allows to determine the molar fraction of **M1** units in the prepared polymers, $F_{\mathbf{M1}}$, using the formula: $F_{\mathbf{M1}} = 2.5\ I_{CH2Cl}/(I_{Ar} + 0.5\ I_{CH2Cl})$, where I_{CH2Cl} and I_{Ar} is the signal intensity of CH_2Cl and aromatic protons, respectively. Values of F_{M1} obtained from NMR spectra correspond to those obtained from elemental analysis (**Table 4**).

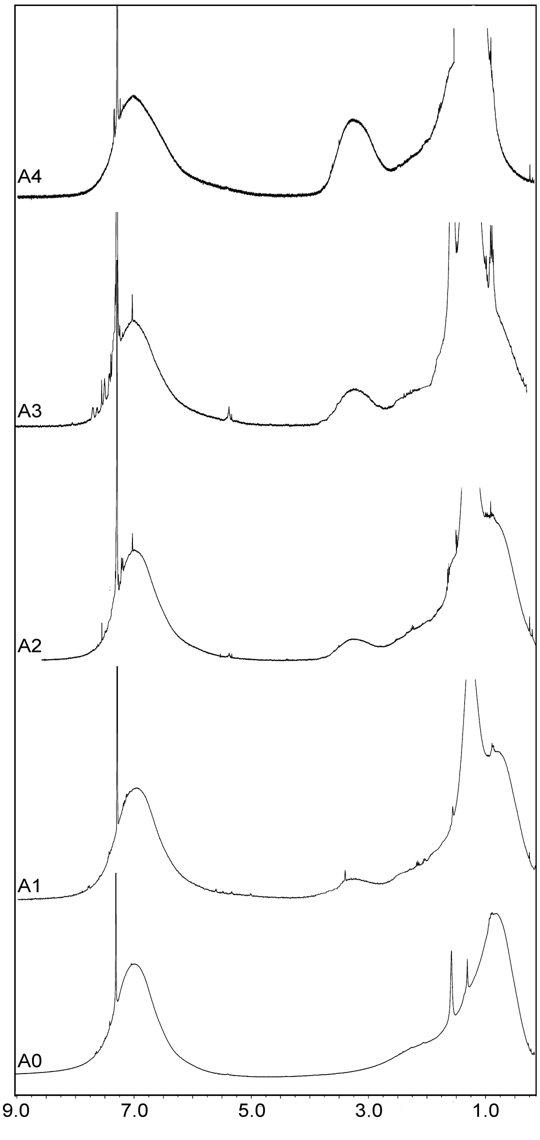


Figure 7. ^{1}H NMR spectra of type A copolymers.

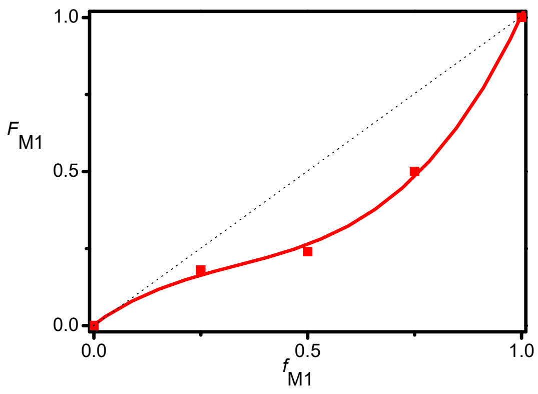


Figure 8. Molar fraction of **M1** units in a polymer, F_{M1}, as a function of the molar fraction of **M1** in the feed monomer mixture; f_{M1}, for copolymerizations of **M0** and **M1** with $WOCl_4/Ph_4Sn$ catalyst.

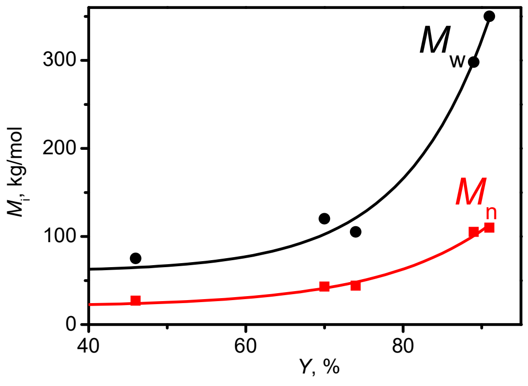


Figure 9. Number-average, M_n, and weight-average, M_w, molar masses of polymers **A0** to **A4** as a function of the isolated polymer yield achieved after 24 hours of polymerization

The dependence of the molar fraction of monomeric units of **M1,** F_{M1}, on the molar fraction of **M1** in the feed monomer mixture, f_{M1}, is shown in **Figure 8**. The dependence shows that **M1** is less reactive than **M0.** The reason for it could be seen in the electron-donating effect of *tert*-butyl group linked to benzene ring of **M1** rather than steric effects. A continuous growth of M_w and M_n values with increasing polymer yield (i.e., with monomer conversion, see **Figure 9**) indicates practical absence of the kinetic chain-transfer reaction in the (co)polymerization of **M0** and **M1**.

The transformation of **M0** and **M1** into homo- and copolymers **A0** to **A4** is confirmed by the absence of the band at 2230 cm^{-1} ($\nu_{C\equiv C}$) in IR spectra of **A0** to **A4** (**Figure 10**). Gradual change in the composition from A0 to A4 homopolymers via copolymers **A1**, **A2** and **A3** is accompanied by (i) the changes of intensities of the bands in the region from ca 3100 to 2850 cm^{-1} belonging to $\nu_{C\text{-}H}$ modes in aromatic and aliphatic groups ($\nu_{C\text{-}H}$ aromatic are weak while $\nu_{C\text{-}H}$ aliphatic strong for (4-*tert*-butyl)phenyl groups of **M1** units constituting **A4**), and (ii) weakening to disappearance of bands at 1597, 1575, 1491 and 1441 cm^{-1} ($\nu_{C\text{-}C}$ phenyl), 907 cm^{-1} ($\nu_{C\text{-}H}$ phenyl), 695 cm^{-1} ($\nu_{\text{ring puckering}}$) and at 1377 cm^{-1} ($\nu_{CH3,\ \text{tert-butyl}}$) that all belong to units **M0**, together with the occurrence of a strong band at 1506 cm^{-1} ($\nu_{C\text{-}C}$ 1,4-phenylene and/or $\nu_{C\text{-}C}$ chain), medium to strong bands at 1394 and 1363 cm^{-1}

($\nu_{\text{CH3-tert-butyl}}$) and bands at 736 and 654 cm^{-1} ($\nu_{\text{C-Cl}}$) that all are typical of units **M1**. The IR spectrum of **A3** shows enormously enhanced bands in the region from 1300 to 750 cm^{-1}. This feature was observed reproducibly and it might originate from the nearly equal content of **M0** and **M1** units in **A3**.

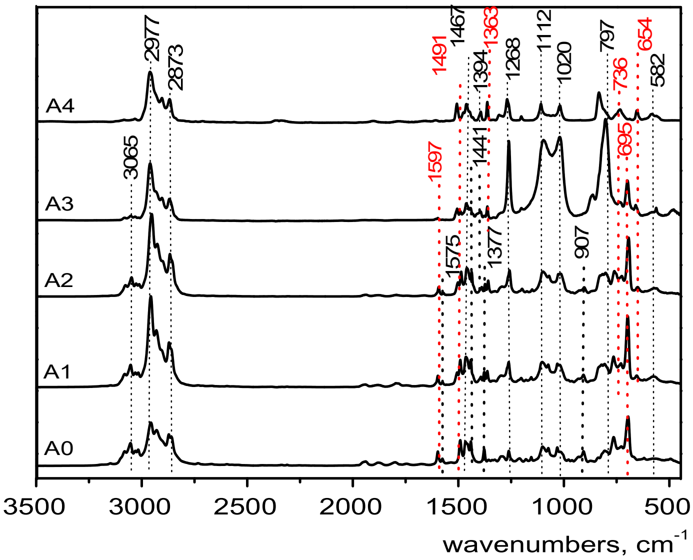


Figure 10. IR spectra of polymers of type **A**.

Raman spectra of **A0** to **A4** (**Figure 11**) provide additional proof of the changes in the composition of samples **A0** to **A4**: increasing intensity of the bands at 1606 cm^{-1} ($\nu_{\text{C-C,arom}}$) and 1108 cm^{-1} ($\delta_{\text{C-H}}$ *tert*-Bu) and a decrease in the intensity of the band at 1002 cm^{-1} (phenyl ring breathing). Spectral properties of polymers **A0-A4** are discussed more in detailed in ***Chapter 3.3.3***.

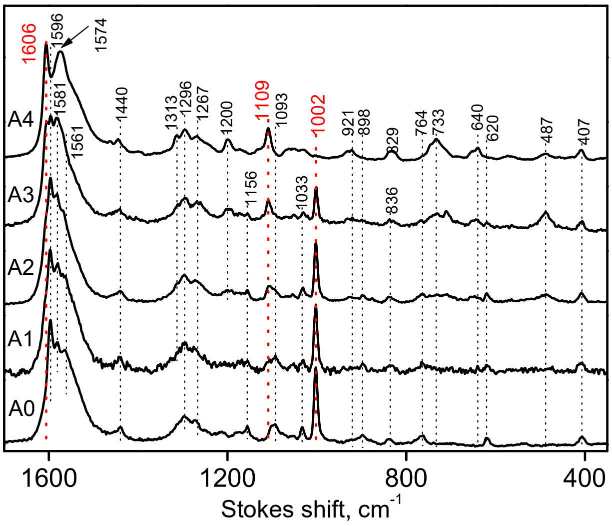
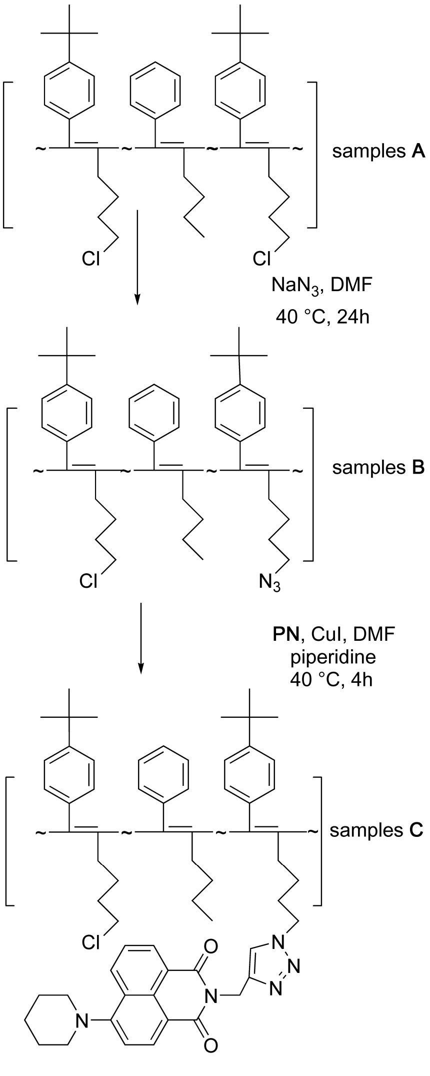


Figure 11. Raman spectra of polymers of type **A** (excitation wavelength of 633 nm).

3.4. Modifications of poly(disubstituted acetylene)s

3.4.1. Modification of chloro to azido side groups



Scheme 7. Two-step modification of primary polymers.

Polymers **A1** to **A4** were reacted with NaN$_3$ in order to replace chlorine atoms of side groups in **M1** units with N$_3$ groups (**Scheme 7**). The modified polymers **B1** to **B4** were obtained in the isolated yields from 75 to 90 % (**Table 5**); the product loss should be ascribed to the purification procedure. Elemental analysis of **B1** to **B4** revealed that the substitution of Cl with N$_3$ groups did not take place quantitatively on any poly(disubstituted acetylene) **A1** to **A4** despite tenfold molar excess of NaN$_3$ (with respect to Cl) taken into the reaction. Hence the modified polymers **B1** to **B4** each contained some portion of non-modified units **M1** carrying Cl atom besides the modified units carrying N_3 group (further labeled **M1B** and their molar fraction F_{M1B}). This seems to be a general feature of this modification since other authors have also reported incompleteness of the conversion of $-CH_2Cl$ to $-CH_2N_3$ groups on polymer chains.[128,129] The ratio $\boldsymbol{F_{M1B}/F_{M1}}$ is equal to the degree of substitution of Cl atoms with N_3 groups.

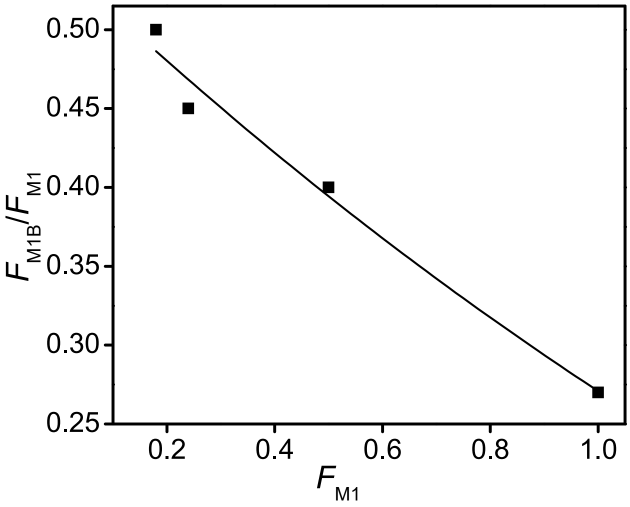


Figure 12. Efficiency of conversion of a polymer of type **A** to the corresponding polymer of type **B** as a function of the molar fraction of **M1** units in the starting polymer of type **A**, $\boldsymbol{F_{M1}}$; $\boldsymbol{F_{M1B}}$ is molar fraction of **M1B** units in the modified polymer of type **B**.

The dependence in **Figure 12** shows that the degree of substitution monotonously decreases with increasing molar fraction of $-CH_2Cl$ groups, F_{M1}, in the initial polymer (**A1** to **A4**). This indicates that an already bound group N_3 prevents binding of another N_3 group in its neighborhoods. Comparison of the molar-mass characteristics of the corresponding **A** and **B** polymers (Table 4 and 5) showed that the substitution only slightly affected the molar mass and dispersity of the polymers and, vice versa, that the molar mass and dispersity of the initial (co)polymer has no significant effect on the degree of substitution of Cl atoms with N_3 groups.

The substitution of Cl atoms with N_3 groups as well as its incompleteness was conclusively proven by IR spectra of **B** polymers, which each comprised the band at 2096 cm^{-1} belonging to the $\nu_{N=N}$ stretching mode, as well as residual $\nu_{C\text{-}Cl}$ bands at 736 and 654 cm^{-1} confirming incompleteness of the substitution (see **Figure 12**). On the other side, ^1H NMR spectra did not provide so conclusive evidence for this substitution, because they showed only slight upfield shift of the broad signal at δ =

3.2 ppm (CH_2Cl) to δ = 3.08 ppm due to merging the signals of protons -CH_2Cl and -CH_2N_3 groups (**Figure 13**, spectra of **A4** and **B4**). Raman spectra also did not provide a conclusive evidence of the substitution discussed; a weak band of the $\nu_{N=N}$ of azide group at 2098 cm^{-1} was detectable only in Raman spectra of **B3** and **B4**.

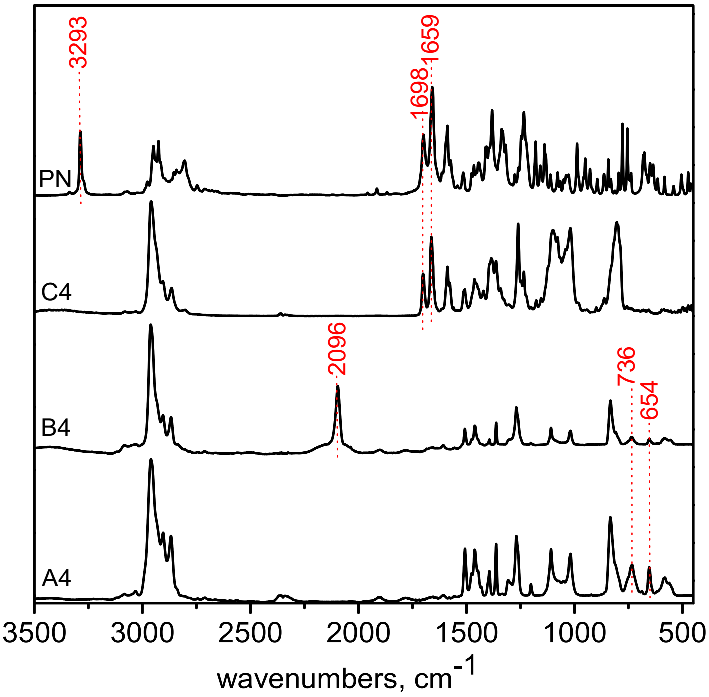


Figure 13. IR spectra of polymers **A4**, **B4**, **C4** and free fluorophore **PN**

3.4.2. Introduction of naphthalimide side groups.

In order to introduce naphthalimide fluorophores to polymer chains, polymers **B1** to **B4** were reacted with **PN** that was so attached via 1,2,3-triazole rings formed in the "click"-reaction of N_3 group of an **M1B** unit and –C≡CH group of a **PN** molecule (**Scheme 7**). So modified monomeric units (**M1C**) in the type **C** poly(disubstituted acetylene)s contain {4-[4-(piperidine-1-yl)-1,8-naphthalimide]-*N*-yl-methyl}-1,2,3-triazole-1-yl groups instead N_3 groups present in initial units **M1B**. The absence of $\nu_{N=N}$ band at 2096 cm^{-1} in IR spectra of polymers **C** (**Figure. 13**) proves that the modification took place quantitatively. The isolated yield of polymers **C1** to **C4** is in the range from 53 to 86 % (**Table 6**) due to the loss of material during its purification. However, thorough purification was necessary for a complete removal of traces of copper ions and non-reacted **PN** as these impurities could affect the fluorescence properties of the type **C** polymers.

Table 5. Characteristics of modified polymers from **B1** to **B4** $F'_{\mathbf{M1}}$ is the mole fraction of non-modified **M1** units (with Cl atom), $F_{\mathbf{M1B}}$ is the mole fraction of units carrying N_3 group, M_w is the mass-average molar mass and *Đ* dispersity of polymers of type **B**.

Starting polymer	$F_{\mathbf{M0}}$ / $F_{\mathbf{M1}}$ **in polymers A**	**Modified polymer**	$F_{\mathbf{M0}}$ / $F'_{\mathbf{M1}}$ / $F_{\mathbf{M1B}}$ **in polymers B**	M_w **kg/mol**	***Đ***
A1	0.82 / 0.18	**B1**	0.82 / 0.09 / 0.09	310	2.4
A2	0.76 / 0.24	**B2**	0.76 / 0.13 / 0.11	110	2.6
A3	0.50 / 0.50	**B3**	0.50 / 0.30 / 0.20	72	2.5
A4	0.00 / 1.00	**B4**	0.00 / 0.73 / 0.27	81	2.8

The **B** to **C** type polymer modification was always accompanied by a decrease in the molar mass and increase in dispersity of the polymer (compare M_w and ***Đ*** values of the **B** and **C** type polymers in Tables 5 and 6). These changes indicate that copper ions which catalyze this modification also induce cleavage of the polymer main chains. The above-mentioned complete disappearance of the $\nu_{N=N}$ IR band at 2096 cm^{-1} represents the main prove of transformation of a **B** polymer to the corresponding polymer **C** (Fig. 13). The IR spectra of **C1** to **C4** also contain bands at 1698 and 1659 cm^{-1} ($\nu_{C=O}$) and 1588 cm^{-1} ($\nu_{C=C,arom}$) typical of **PN** moiety, the intensity of whose increases with increasing content of **PN** moieties in the **C** polymer (**Figure 15**).

Table 6. Characteristics of polymers (**C1** to **C4**) prepared by modification of polymers **B1** to **B4** with **PN** in piperidine at 40°C (reaction time 4 h); *Y* is the isolated polymer yield, M_w is the weight-average molar mass and *Đ* dispersity of polymers of the type **C**.

Starting polymer	**Modified polymer**	***Y*, %**	M_w **kg/mol**	***Đ***
B1	**C1**	82	100	3.9
B2	**C2**	86	62	2.9
B3	**C3**	58	50	3.4
B4	**C4**	53	39	3.7

Raman spectra (**Figure 16**) also show an increase in the content of **PN** fluorophores from **C1** to **C4** through increasing intensity of bands typical of **PN** (~1700, ~1660, 1396, 1367, 1339, 1222, 1077, 831 and 500 cm^{-1}) when going from **C1** to **C4**. Assignment of Raman bands of **PN** according to calculations is the following: 1694 and 1658 cm^{-1} symmetrical and antisymmetrical $\nu_{C=O}$ modes, 1396 and 1367 cm^{-1} $\nu_{C=C}$ of the naphthalene skeleton, 1077 cm^{-1} ring-breathing mode of the conjugated skeleton.

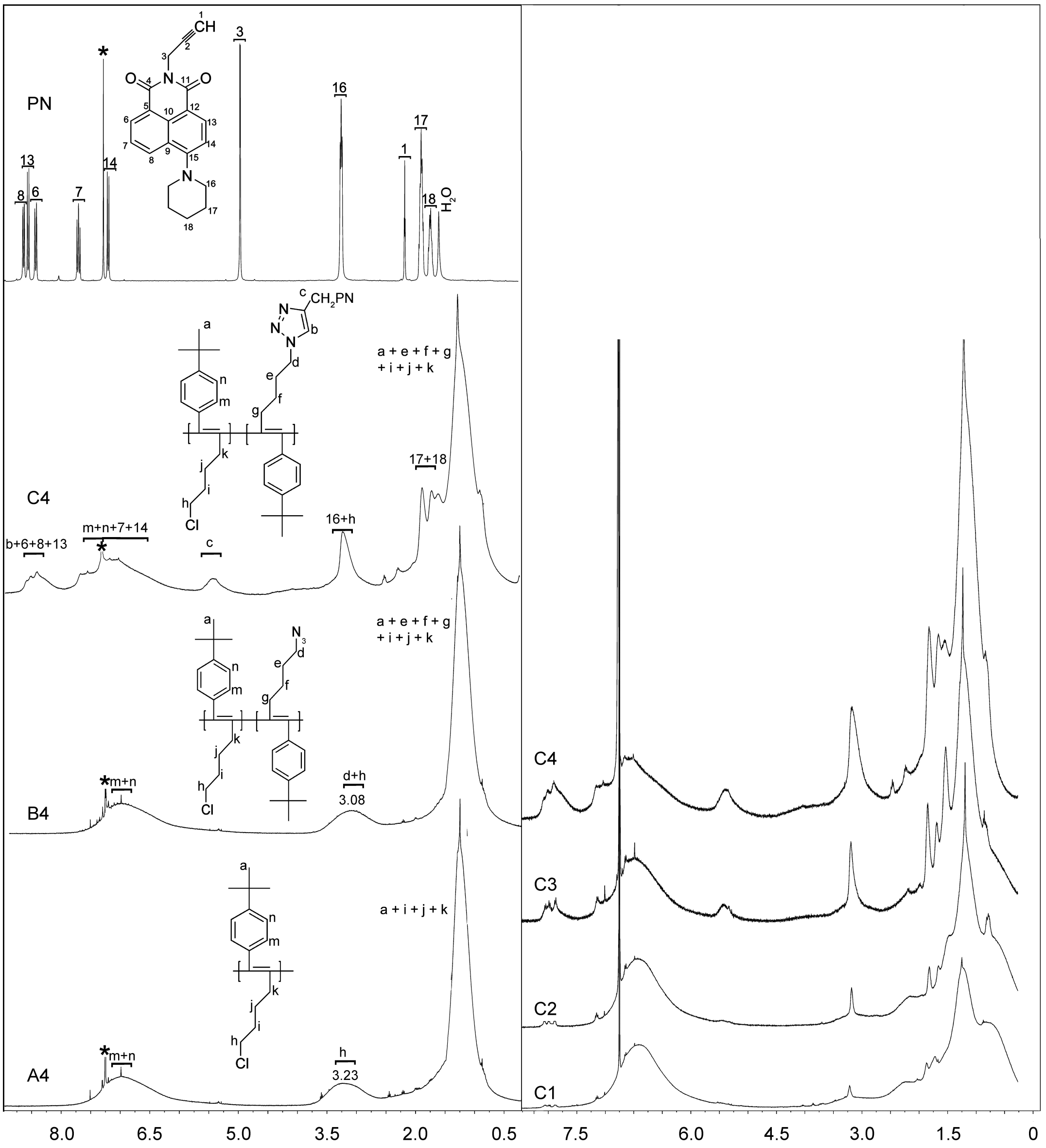


Figure 14. Comparison of ^{1}H NMR spectra of polymers **A4**, **B4**, **C4** and free fluorophore **PN** showing a progress in modification (left); and polymers **C1** to **C4** showing the extent of final modification (right).

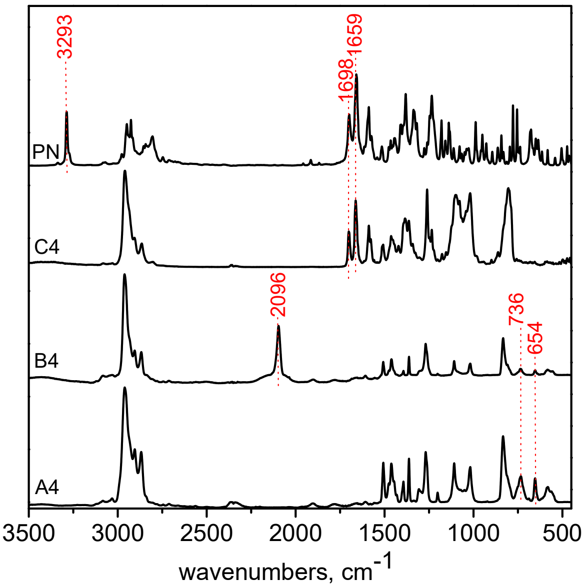


Figure 15. IR spectra of the polymers of type **C.**

^{1}H NMR spectra (**Figure 14**) provided evidence of the **B** to **C** type conversion of polymers by appearance of new signals in the spectra of polymers **C** (compared to **B**): (i) 0.5-2.2 and 3.2 ppm, piperidine CH$_2$ groups (ii) 5.4 ppm, CH$_2$ spacer between triazole ring and naphthalimide skeleton, and (iii) 8.5 ppm, naphthalimide protons.

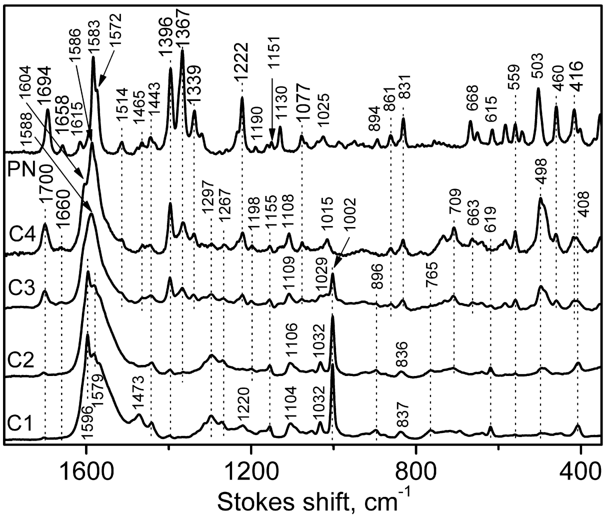


Figure 16. Raman spectra of polymers of type C and free fluorophore PN (excitation at 780 nm)

3.4.3. UV/vis absorption spectra

The absorption spectra of polymers A4, B4, C4 and free PN are compared in Figure 17. The band pertaining to π-π* transition in polymer main chains appears at 320 nm (λmax) and its edge at ca 400 nm (spectra of A4 and B4). The same features show spectra of other polymers of the type A and B. This proves that the extent of delocalization of π-electrons in the conjugated main chains is nearly independent of the molar mass and composition of the type A and B (co)polymer, (including the degree of substitution of Cl atoms with N3 groups). The spectrum of C4 is a weighed superposition of the spectra of B4 and PN (**Figure 26**) and spectra of C1 to C3 can be characterized analogously. The longer-wavelength band of free PN (λmax = 417 nm) is little blue-shifted to 409 nm in spectra of modified polymers C1 to C4, which might be due to its overlap with the π-π* band of main chains.

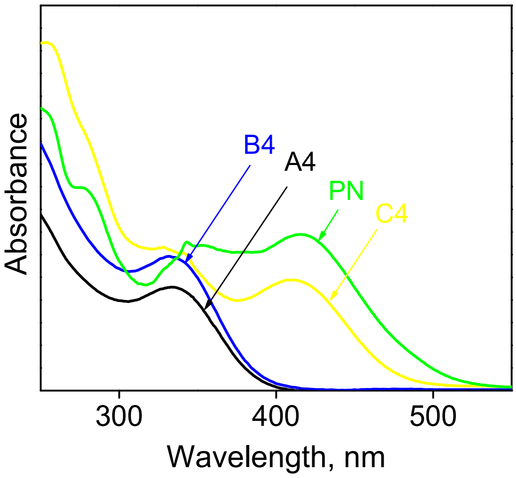


Figure 17 UV/vis spectra of polymers A4, B4, C4, and the free chromophore PN

In order to obtain a better insight into electronic transitions in the studied copolymers we have calculated the transitions in selected **A0, A4** and **C4** oligomers (all-trans H-T dimers, tetramers and octamers) using the TD-DFT computational method.[130] Calculations were conducted for the following oligomers: (i) dimers: 1,3-diphenyl-2,4-di(but-1-yl)-buta-1,3-diene ($A0_{n=2}$), 1,3-bis(4-*tert*-butylphenyl)-2,4-bis(4-chlorobut-1-yl)-buta-1,3-diene ($A4_{n=2}$), (ii) tetramers: 1,3,5,7-tetraphenyl-2,4,6,8-tetra(but-1-yl)-octa-1,3,5,7-tetraene ($A0_{n=4}$), 1,3,5,7-tetrakis(4-*tert*-butyl-phenyl)-2,4,6,8-tetrakis(4-chlorobut-1-yl)-octa-1,3,5,7-tetraene ($A4_{n=4}$), 1,3,5,7--tetrakis(4-tert-butylphenyl)-2,6,8-tris(4-chlorobut-1-yl)-4-(4-PN-but-1-yl)-octa-1,3,5,7-tetraene ($^{PN1}C4_{n=4}$), 1,3,5,7-tetrakis(4-*tert*-butylphenyl)-2,6-bis(4-chlorobut-1-

yl)-4,8-bis(4-PN-but-1-yl)-octa-1,3,5,7-tetraene ($^{PN2}C4_{n=4}$), (iii) octamers: 1,3,5,7,9,11,13,15-octaphenyl-2,4,6,8, 10,12,14,16-octa(but-1-yl)-hexadeca-1,3,5,7,9,11,13,15-octaene ($A0_{n=8}$), 1,3,5,7,9,11,13,15-octakis(4-*tert*-butylphenyl)-2,4,6,8,10,12,14, 16-octakis(4-chlorobut-1-yl)-hexadeca-1,3,5,7,9,11,13,15-octaene ($A4_{n=8}$), 1,3,5,7,9,11,13,15-octakis(4-*tert*-butylphenyl)-2,4,6,10,12,14,16-heptakis(4-chlorobut-1-yl)-8-(4-PN-but-1-yl)-hexadeca-1,3,5,7,9,11,13,15-octaene ($^{PN1}C4_{n=8}$), and (iv) free **PN** moiety.

Table 7. Calculated wavelengths of electronic transitions in selected oligomers and **PN** moiety.

Dimers		**Tetramers**				**Octamers**			**PN (free)**
$A0_{n=2}$	**$A4_{n=2}$**	**$A0_{n=4}$**	**$A4_{n=4}$**	**$^{PN1}C4_{n=4}$**	**$^{PN2}C4_{n=4}$**	**$A0_{n=8}$**	**$A4_{n=8}$**	**$^{PN1}C4_{n=8}$**	
λ (nm) of main chain transition									
280	285	328	333	324	323	349	355	361	
λ (nm) of PN transition									
				388	387 390			390	393

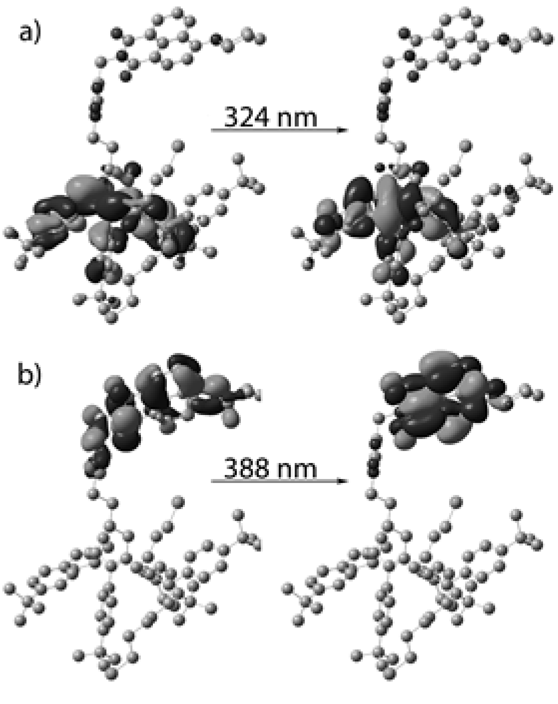


Figure 18. Electronic density contours for orbitals involved in the electronic transition at a) 324 nm and b) 388 nm in $^{PN1}\mathbf{C4}_{n=4}$.

Calculated wavelengths of the high-oscillator-strength electron transitions in the above oligomers are given in **Table 7**. The orbital contours diagrams for tetramer $^{PN1}C4_{n=4}$ (**Figure 18**) showed that the orbitals contributing the band at 324 nm are localized on the main chain, while the orbitals involved in transitions contributing the band at 388 nm are exclusively localized on the **PN** fluorophore. An overlap of these orbitals is very small, which is in accord with the experimentally observed slight blue shift of the band of bound **PN** groups (in **C4**) compared to its position in free **PN**. Vice versa, the λ value of the band of the π-π* transitions in the main chain is almost independent on the side group substituents (see λ values of tetramers and octamers in Table 9). As expected, the wavelength of the π-π* transitions in main chains shows an attenuated growth with increasing chain length: the difference in λ between dimers and tetramers is 48 nm while that between tetramers and octamers is only 21 nm. This indicates that λ growth towards the limit value for an infinite chain.

3.4.4. Fluorescence characteristics

The steady-state fluorescence spectra taken from $CHCl_3$ solutions of the type A and poly(disubstituted acetylene)s B using excitation at 330 nm were similar to each other (**Figure 19**) and they showed nearly equal fluorescence characteristics: emission maximum $\lambda_F \sim 460$ nm; quantum yield $\phi_F \sim 0.10$ (9,10-diphenylanthracene as standard). Time-resolved measurements revealed two-exponential fluorescence decay with relaxation times (τ) and contributions as follows: $\tau_1 = 0.6$ ns (30 %), $\tau_2 = 2.0$ ns (70 %), for all **A** and **B** samples. It proves that neither co-monomeric composition nor degree of substitution of Cl atoms with N3 groups influence fluorescence characteristics of the type **A** and **B** polymers. Hence it is clear that the fluorescence originates from the conjugated main chains as it was already claimed for others poly(disubstituted acetylene)s.[91] The observed occurrence of two fluorescence components with different lifetimes might be ascribed to the *cis-trans* isomerism of the polymer main chains.

Fluorescence of free **PN** is characterized by $\lambda_F = 508$ nm, $\phi_F = 0.72$ (excitation at 420 nm) and $\tau = 9.2$ ns (excitation at 450 nm, denoted as τ_3 in **Table 8**). The stationary emission spectra of the PN-modified samples **C1** to **C4** resemble the spectrum of **PN** (Table 8, **Figure 20**). However, their time-resolved emission spectra revealed three-exponential fluorescence decay of which two faster decaying components showed lifetimes nearly equal to those of **PN**-free poly(disubstituted acetylene)s of the type **A** and **B** (τ_1 and τ_2 of main chains). The third component most contributes (55-83 %) to the total fluorescence of samples **C** and its lifetime (τ_3 = 8.6 - 8.9 ns) is nearly equal to that found for free **PN** (9.2 ns). The emission maxima (λ_F = 507 - 513 nm) found for the type **C** polymers correspond to that of **PN** (λ_F = 507 nm), and the fluorescence quantum yield of the type **C** polymers (ϕ_F = 0.45-0.62) is tolerably lower compared to free **PN** (ϕ_F = 0.72).

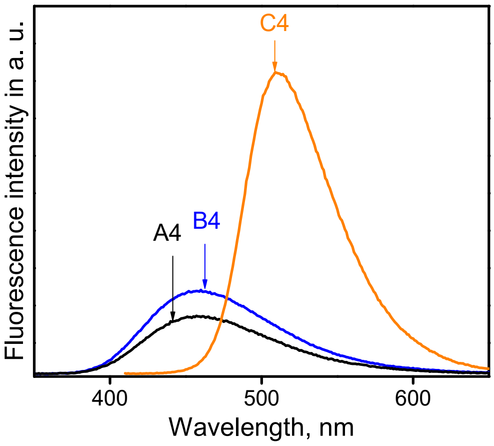


Figure 19. Fluorescence emission spectra of polymers **A4**, **B4**, (excitation at 330 nm), **C4** excitation at 420 nm).

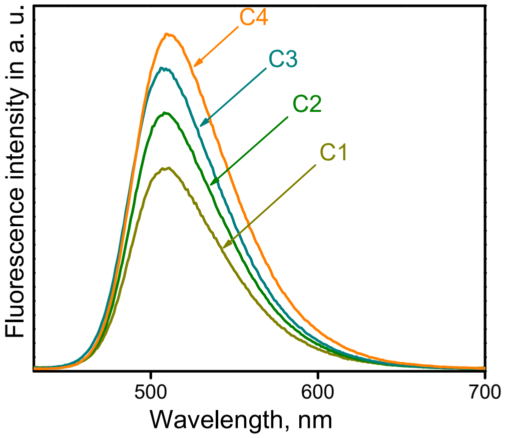


Figure 20. Fluorescence emission spectra of polymers **C1-C4**and free **PN** (excitation wavelength 420 nm). Concentration of all samples was 0.01 mg mL $^{-1}$.

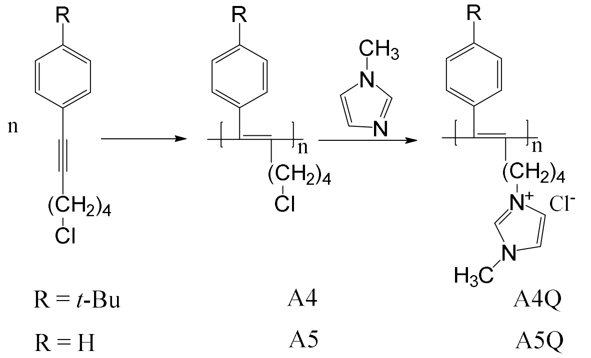
High complexity of the fluorescence-decay kinetics for a fluorophore bound to a polymer chain is known from literature.[131,132] As can be seen (Table 8), the values of both λ_F and τ_3 increase in the sequence: **C1** < **C2** < **C3** < **C4** < **PN**. This means that the fluorescence behaviour of the type C polymers approaches that of the free PN as the content of PN groups in the polymers increases. Growth of the content of bulky PN groups should increase conformational rigidity of polyacetylene chains,[133-135] which might be possible reason for the observed behavior.

The time-resolved fluorescence was also measured with excitation at 330 nm on the **PN**-modified polymer **C4** with the aim to check the excitation-energy transfer from conjugated main chains (donors) to pendant **PN** groups (acceptors). The measured fluorescence decay curves obeyed three-exponential function with parameters: τ_1 = 0.16 ns (46 %), τ_2 = 1.5 ns (34 %) and τ_3 = 5.7 ns (20 %) The lifetimes τ_1 and τ_2 should be ascribed to the fluorescence of **C4** main chains and τ_3 to that of the **PN** groups. Values of τ_1 and τ_2 for **C4** are considerably shorter than corresponding values observed for **B4**: τ_1 = 0.6 ns (30 %) and τ_2 = 2.0 ns (70 %). The decay acceleration indicates possible participation of the excitation energy transfer to **PN**. Notable is fundamental change in contributions of those two fluorescence components to the total fluorescence of poly(disubstituted acetylene)s: that with τ_1, minority component (30 %) of the fluorescence of **B4** has become the major component (46 %) of the fluorescence of **C4**, while that with τ_2 - the majority component (70 %) of the fluorescence of **B4** has became the minority component (34 %) of the fluorescence of **C4**. This also indicates the presence of the excitation-energy transfer from polyacetylene main chains to the **PN** side-chain-capping groups.

Table 8. Fluorescence data for polymers **C1** to **C4** and free **PN** in $CHCl_3$ solutions; λ_F is the wavelength of the fluorescence emission maximum; ϕ_F fluorescence quantum yield (standard: fluorescein in aqueous NaOH (0.1 M)); τ_1, τ_2 and τ_3 - lifetimes of the fluorescence components (contributions are in parentheses). Excitation at 420 nm for the stationary and 450 nm for the time-resolved measurements.

	λ_F (nm)	ϕ_F	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
C1	507	0.45	0.2 (12%)	1.9 (33%)	8.6 (55%)
C2	509	0.50	0.2 (12%)	1.9 (20%)	8.6 (68%)
C3	511	0.59	0.3 (9%)	3.6 (20%)	8.6 (71%)
C4	513	0.62		5.3 (17%)	8.9 (83%)
PN	508	0.72			9.2

3.5. Modification of polymers with chloroalkyl groups to conjugated polyelectrolytes.



Scheme 8. Reaction of **A4** and **A5** with N-methylimidazole

Homopolymers **P(M1)** (i.e., **A4**) and **P(M2)** (**A5**) were allowed to react with *N*-methylimidazole in the methanol and THF (15% by volume, to swell the starting polymer) mixed solvent at 60°C for 48 hours. During that time a complete dissolving of the polymer was achieved. Then the temperature was increased to 65° and the reaction mixture was allowed to react for next 48 hours to complete the ionization process. The obtained ionic polymers are further labelled as **A4Q** (ionized **A4**) and **A5Q** (ionized **A5**). The difference between these polymers consists in the presence of *tert*-butyl substituent on the benzene ring of **A4Q** that is supposed to lower the solubility of **A4Q** as compared to **A5Q** in polar solvents and water.

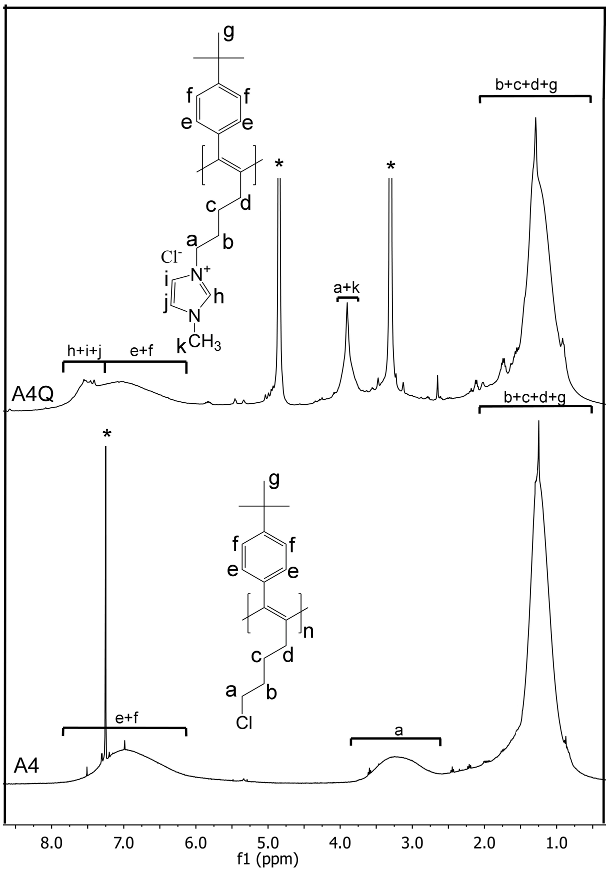


Figure 21. ^{1}H-NMR spectra of polymer **A4** (in $CDCl_3$) and **A4Q** (in CD_3OD)

^{1}H-NMR spectra of modified polymers confirm the expected polymer structure (**Figure 21**). The bands of aromatic (6 to 8 ppm) as well as aliphatic (1 to 2 ppm) protons are broad and poorly resolved. Nevertheless, the transformation of chloromethyl- side groups into (imidazolium-*N*-yl)methyl- capped side groups is good evidenced in the spectra by disappearance of the signal centered at 3.2 ppm and appearance of the new signal at 4.2 ppm together with the signals belonging to protons of the imidazolium ring in the region 7.2 to 7.7 ppm. Broadening of these new bands proves binding of imidazolium moieties to polymer chains. The purity of the prepared polymers from the free non-bonded N-methylimidazole could be easily determined because free methylimidazole gives rise to sharp signals.

The IR spectra of **A4** and **A4Q** are compared in **Figure 22**. The ionization of **A4** is evidenced by the disappearance of the band at 736 cm^{-1} ($\nu_{C\text{-}Cl}$) that is typical of **M1** units and the presence (occurrence) of the bands belonging to the imidazole moiety ($\nu_{C=N}$ at 1717 cm^{-1}, $\nu_{C\text{-}H,imi}$ 3141 cm^{-1}, $\nu_{C\text{-}H}$ alifatic at 2850 cm^{-1}, 1571 and 1336 imidazolium ring stretching). The IR spectra of **A5** and **A5Q** show analogous differences. Both polymers are well soluble in low alcohols such as methanol and ethanol and in polar solvents (DMSO, DMF, acetonitrile), but not in water. Thus the expected significant difference in solubility between **A4Q** and **A5Q** due to the presence of *tert*-butyl moiety was not confirmed. Both polymers are soluble in the mixtures of methanol and water up to 1:1 volume ratio.

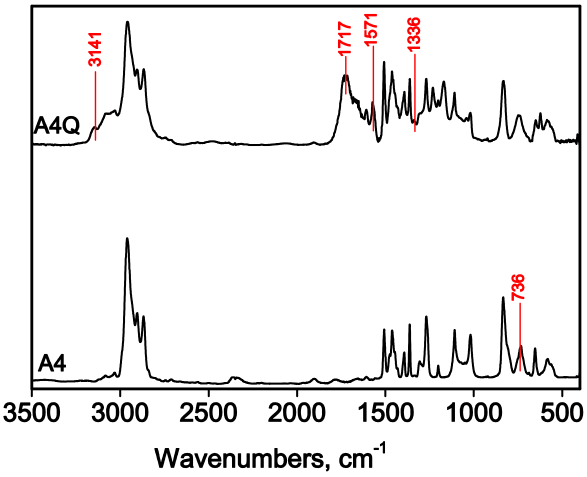


Figure 22. FTIR spectra of polymers **A4** and **A4Q**

3.5.1. Spectral properties of the resulting polymers.

As can be seen from **Figure 23**, the UV/vis spectra of **A4Q** are almost identical with the spectra of **A4**, which proves that the HOMO-LUMO transitions take place in the chain backbones and the change of the side-chain-capping groups has no significant impact on these transitions. Unlike conjugated polyelectrolytes with polythiophene backbone,[136] the ionic poly(disubstituted acetylenes) do not show solvatochromism (change in the shape and/or band positions with the solvent). The polymer **A5Q** exhibits closely similar properties.

Both polymers have shown blue fluorescence (in **Figure 24** shown the emission spectra of **A4** and **A4Q** at excitation wavelength 330 nm) practically identical with that of the initial polymers **A4** and **A5** with emission maxima around 450 nm. Again no shift in the maxima position and no change in the shape of the emission band occur in different solvents.

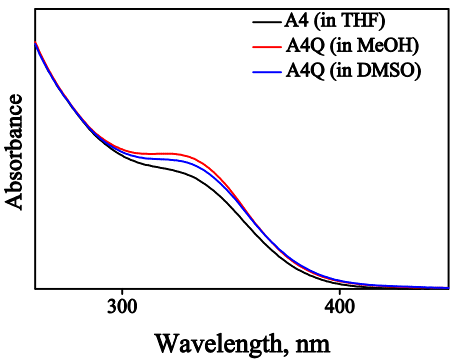


Figure 23. UV/vis spectra of polymers **A4** and **A4Q**

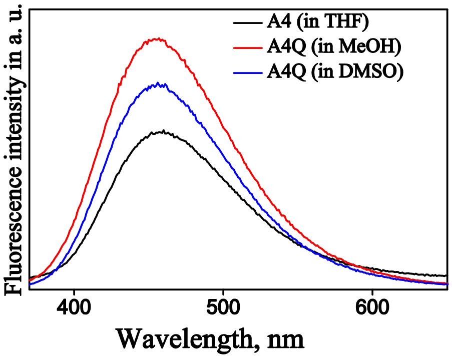
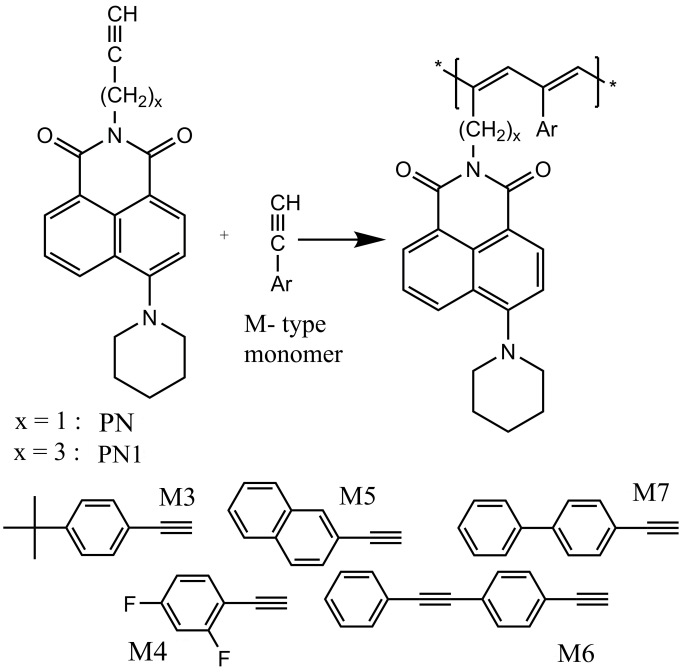


Figure 24. Emission spectra of polymers A4 and A4Q in different solvents, excitation wavelength 330 nm

3.6. Polymerizations catalyzed by [Rh(nbd)acac]



Scheme 9. Copolymerization of **PN** and **PN1** with various monosubstituted acetylenes

3.6.1. Homopolymerization of PN and PN1

Two naphthalimide-type monomers with terminal ethynyl groups, *N*-(prop-1-yne-3-yl)-4-(piperidine-1-yl)-1,8-naphthalimide (**PN**) and *N*-(pent-1-yne-5-yl)-4-(piperidine-1-yl)-1,8-naphthalimide (**PN1**) (see **Scheme 9**) have been prepared in high yields by the procedure described in Chapter 3.1.

The monomers have identical structure except for the number of methylene groups in the alkanediyl spacer, $(CH_2)_n$, separating triple bond and imide nitrogen: $n = 1$ for **PN** while $n = 3$ for **PN1**. The attempts were made to homopolymerize monomers **PN** and **PN1** with [Rh(nbd)acac] catalyst in CH_2Cl_2 (**Table 9**) in order to prepare polyacetylene-type homopolymers with 1,8-naphthalimide pendants. However, homopolymerizations (**Table 9,** No 1 and 2) were unsuccessful: only traces of oligomers with the molar mass of about 700 (by SEC technique, PS calibration) were obtained. But, despite the presence of the amino and imino groups in **PN** and **PN1**, these monomers did not deactivate the catalyst. This fact was confirmed by adding phenylacetylene (known to polymerize easily with this Rh catalyst) to the **PN**/catalyst and **PN1**/catalyst reaction mixtures aged for 24 h. The formation of a high-molar-mass polymer ($M_w \sim 70\,000$) was confirmed by the SEC analysis of samples withdrawn from reaction mixtures one hour after the phenylacetylene addition.

Since **PN** and **PN1** do not decompose the catalyst, the other reason(s) for the failure of **PN** and **PN1** homopolymerization has to be assumed: low reactivity of ethynyl groups of **PN** and **PN1** monomers due to the electron-donating effect of $(CH_2)_n$ spacer decreasing formal acidity of the acetylenic hydrogen. A “sufficiently” high acidity of the acetylenic hydrogen of the terminal alkynes is namely considered to be a crucial factor for the monomer reactivity in the initiation and/or propagation stage of the Rh-catalysed polymerizations.[71,72,137,138] The low acidity of acetylenic hydrogen of **PN** and **PN1** (compared to the acidity of the acetylenic hydrogen of phenylacetylene) can be confirmed from the values of ^{1}H NMR chemical shifts of -C≡CH[139] which are (in $CDCl_3$) 2.16 ppm (**PN**), 1.97 ppm (**PN1**), and 3.06 ppm (phenylacetylene).

Table 9. Data on the homo- and copolymerizations of PN and PN1 monomers with [Rh(nbd)acac] catalyst in CH_2Cl_2 at room temperature. Overall initial concentration of monomers 0.15 mol/L; catalyst concentration 7.5 mmol/L; Y is polymer yield calculated with respect to the weight of applied monomer(s), M_w and M_n are mass-average and number-average molar masses of polymers in kg/mol, t is the reaction time, f_A the molar fraction of monomer A in the feed, F_A is the mole fraction of monomeric units A in the polymer.

No	Polymer code	Monomer A[a)]	Monomer B[a)]	f_A	t h	Y %	F_A	M_w kg/mol	M_n kg/mol
1		**PN1**	-	1	24	~ 0	--	--	--
2		**PN**	-	1	24	~ 0	--	--	--
3	**P(M3)**	--	**M3**	0	3	93	0	130	46
4	**P(PN1/M3)**	**PN1**	**M3**	0.2	24	63	0.06	76	33
5	**P(PN/M3)**	**PN**	**M3**	0.2	24	87	0.14	107	55
6	**P(M4)**	--	**M4**	0	3	~100	0	910	340
7	**P(PN/M4a)**	**PN**	**M4**	0.2	24	91	0.20	210	110
8	**P(PN/M4b)**	**PN**	**M4**	0.4	24	70	0.35	53	20
9	**P(PN/M4c)**	**PN**	**M4**	0.6	24	48	0.51	13	6
10	**P(M5)**	--	**M5**	0	24	91	0	Insol	Insol
11	**P(M6)**	--	**M6**	0	24	90	0	Insol	Insol
12	**P(M7)**	--	**M7**	0	24	72	0	Insol	Insol
13	**P(PN/M5)**	**PN**	**M5**	0.2	24	83	0.17	86	40
14	**P(PN/M6)**	**PN**	**M6**	0.2	24	74	0.18	130	36
15	**P(PN/M7)**	**PN**	**M7**	0.2	24	75	0.20	170	65
16	**P(M6/M8a)**	**M8**	**M7**	0.2	24	59	0.15	Insol	Insol
17	**P(M6/M8b)**	**M8**	**M7**	0.8	24	68	0.36	43	22

a) for the monomer codes see Chart 1

3.6.2. Copolymerization of PN and PN1 with (4-tert-butylphenyl)acetylene

(4-*tert*-Butylphenyl)acetylene (**M3**) easily homopolymerizes with [Rh(nbd)acac] giving polyacetylenes with a very high molar mass. Therefore, monomers **PN1** and **PN** were each separately copolymerized with **M3** using the conditions given in **Table 9** (entry 4 and 5, see also Scheme 9). The mole fraction of **PN1** or **PN** co-monomers in the feed (f_A) was 0.2. Contrary to the failure of **PN1** and **PN** homopolymerizations, both copolymerizations provided high yields of high molecular weight copolymers labeled **P(PN1/M3)** and **P(PN/M3).** It should be noted, that the reaction rate of the copolymerations was decreased compared to the rate of homopolymerization of **M3**.

The yield of **P(M3)** homopolymer of 93 % was attained within 3 h, however, to achieve satisfactory yields of **P(PN1/M3)** and **P(PN/M3)** copolymers, the reaction time had to be increased to 24 h. The polymer yield vs. reaction time curves for experiments No 3, 4 and 5 from Table 9 are given in **Figure 25**. The mole fractions of the naphthalimide-type monomeric units in **P(PN1/M3)** and **P(PN/M3)**, F_A, were 0.06 and 0.14 respectively. The values of F_A were determined from the nitrogen content in the copolymers as obtained by the elemental analysis. Undoubtedly, both **PN1** and **PN** were inbuilt into the polyacetylene chains in the course of the copolymerizations with **M3**.

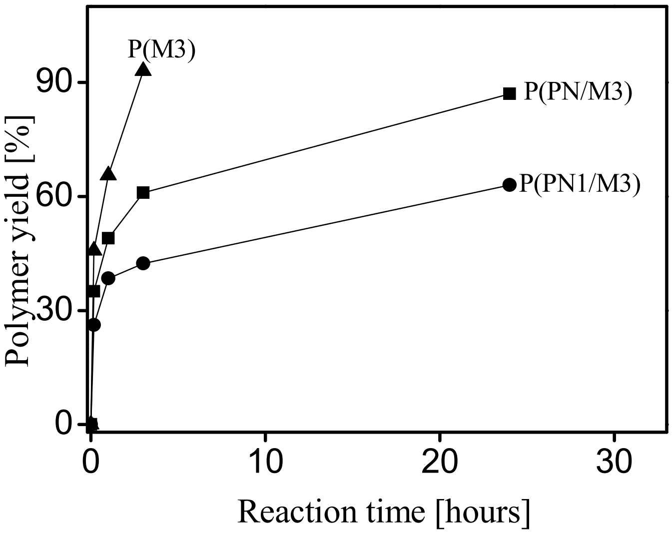


Figure 25. Polymer yield vs. reaction time curves recorded in the course of synthesis of **P(M3)**, **P(PN1/M3)** and **P(PN/M3)**.

Figure 26 shows the results of the characterization of P(PN/M3) by SEC/DAD technique (SEC coupled with a UV/vis Diode Array Detector). The UV/vis spectra recorded for various positions of the SEC chromatogram of **P(PN/M3)** were identical and exhibited absorption maximum at about 400 nm which is contributed by absorption of the 4-(piperidine-1-yl)-1,8-naphthalimide part of the PN monomer. It confirms that the co-monomeric composition of **P(PN/M3)** is practically uniform along the whole molar mass distribution, i.e., the **PN** monomeric units are equally distributed along the short as well as long polymer chains. The SEC/DAD analysis of **P(PN1/M3)** did not provide reliable results in this respect probably due to a low content of the naphthalimide-type monomeric units in the copolymer.

Figure 27 shows the ^{1}H NMR spectra of copolymers **P(PN1/M3)** and **P(PN/M3)** and homopolymer **P(M3)** together with the proton labelling scheme. ^{1}H NMR spectrum of **P(M3)** is typical of polyarylacetylene homopolymers with a high microstructure uniformity and prevailing *cis*-configuration of the main chain double bonds.[140] The signals at 6.97 ppm and 6.55 ppm correspond to the aromatic protons of the pendant phenyl groups and the sharp signal at 5.81 ppm is due to the protons of the *cis* vinylene groups of the main chains. The pendant *tert*-butyl groups of **P(M3)** are manifested by a sharp signal at 1.15 ppm in the ^{1}H NMR spectrum. The same character of the ^{1}H NMR spectrum with the sharp signals is preserved in the case of **P(PN1/M3)** in agreement with the low content of monomeric units derived from **PN1** in the copolymer ($F_A = 0.06$). The presence of the monomeric units derived from **PN1** is manifested in the spectrum of P**(PN/M3)** by signals at: 8-9 ppm. The signals of other aromatic protons of **PN** units are overlapped with signals of the aromatic protons of **M3**.

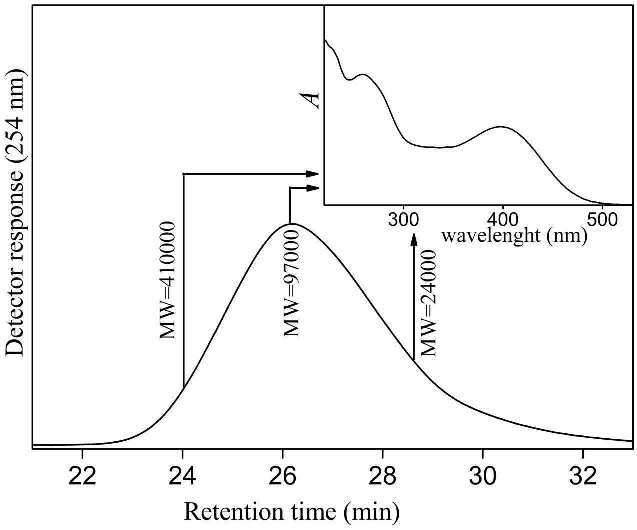


Figure 26. SEC chromatogram of **P(PN/M3)** (detector response at 254 nm) and UV/vis spectrum of SEC fractions for various elution times showing uniformity of the polymer composition.

The spectral resolution as well as signal sharpness in the aromatic region is considerably disturbed in the ^{1}H NMR spectrum of **P(PN/M3).** This spectrum is typical of a random copolymer with comparable contents of individual comonomeric units. The signals of aliphatic protons are strongly influenced by the random linking of the comonomeric units in chains due to which multiplets are poorly resolved. A broad multiplet at 4.2 ppm is ascribed to hydrogens in the CH_2 linker connecting naphthalimide to the main polymer chain.

The broad unresolved multiplets around 3.0 ppm and 1.0 – 2.0 ppm are ascribed to hydrogens CH_2^8 and $CH_2^{9,10}$ of piperidine moiety. A significant suppression of the signal at about 5.8 ppm in the ^{1}H NMR spectrum of **P(PN/M3)** may indicate the absence of sufficiently long sequences of *cis* units in the copolymer chains. This might be ascribed either to the decreased catalyst selectivity towards formation of high-*cis* polyacetylene chains due to the bulkiness of the **PN** substituent or to the *cis*-to-*trans* isomerization taking place during polymerization.[141] It should be noted that the ^{1}H NMR signal of the protons of the main chain *trans*-vinylene groups is, as usually, overlapped with the signals of aromatic protons.[141, 142]

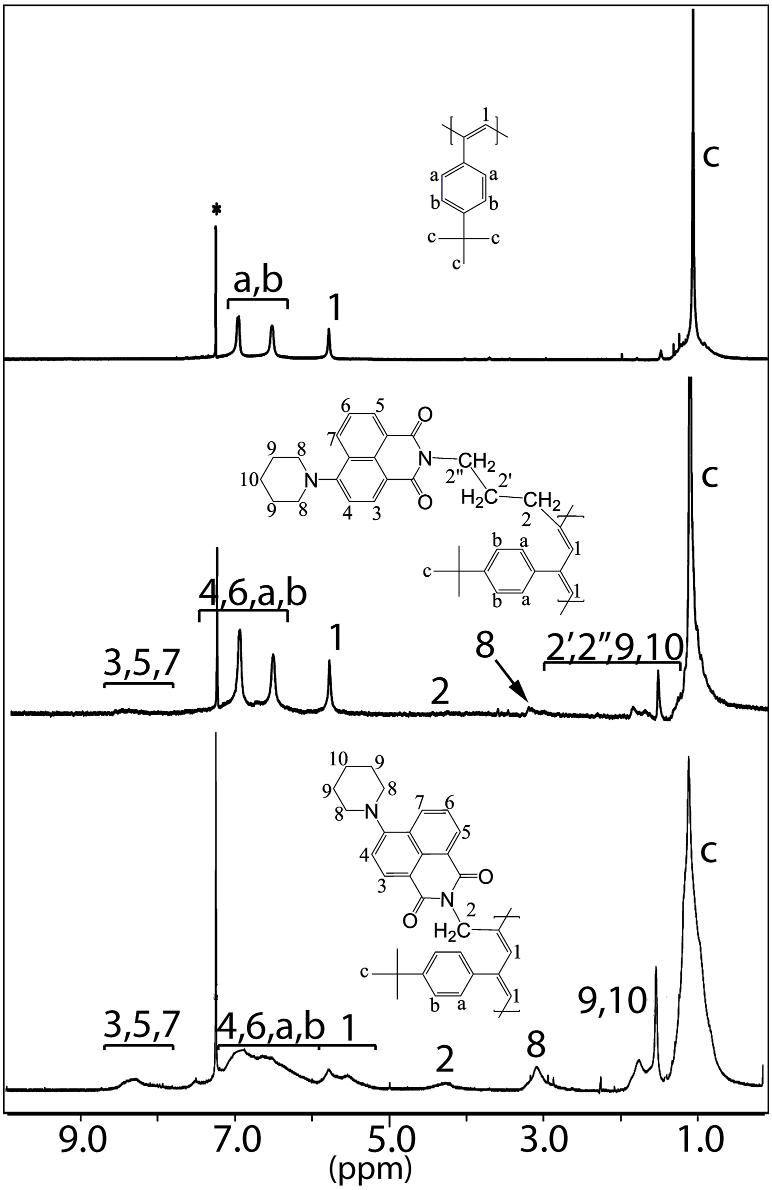


Fig. 27. ^{1}H NMR spectra (in $CDCl_3$) of **P(M3), P(PN/M3)** and **P(PN1/M3).**

3.6.3. Copolymerization of PN with various monosubstituted arylacetylenes

As shown above, **PN** readily copolymerizes with **M3** while **PN1** is inbuilt into the respective **P(PN1/M3)** copolymer with a significantly lowered efficiency. Therefore, we had taken only the **PN** monomer for further studies on copolymerization of naphthalimide monomer with monosubstituted acetylenes. The most complete results were obtained with (2,4-difluorophenyl)acetylene (**M4**) that easily homopolymerized with [Rh(nbd)acac] catalyst and gave polyacetylene **P(M4)** with very high molar mass of M_w = 910 kg/mol (Table 9, entry 6).

Copolymerizations of **PN** with **M4** were performed using three different feed ratios f_A = 0.2; 0.4; 0.6, and provided respective copolymers denoted as **P(PN/M4a)**, **P(PN/M4b)** and **P(PN/M4c)** with F_A values equal to 0.20; 0.35 and 0.51, respectively. As it can be seen (i) the composition of the copolymers may be partly controlled by the composition of the feed and (ii) a quite high content of the **PN** units in the copolymer (~ 50 mol. %) may be achieved. It is necessary to mention here that the copolymer yield decreased with increasing **PN** molar fraction in the feed so that only a moderate copolymer yield of 48 % was attained in the synthesis of **P(PN/M4c)** (F_A = 0.51). This is undoubtedly connected with the increased content of PN units, which hardly undergo homopolymerization, in copolymeric chains. **Figure 28** shows the SEC chromatograms (detector response at 254 nm) of samples withdrawn from the reaction mixtures with feeding ratios f_A = 0; 0.20; 0.35 and 0.51 (Table 9, entries 6 to 9) just before termination of the polymerization. Each SEC chromatogram contains a peak of polymer chains of which average molar mass decreases with increasing f_A, a peak of unreacted monomers (elution time of 39 min) and a significant peak corresponding to oligomers (molar mass ~ 0.7 kg/mol) the intensity of which increases with increasing f_A. The formation of undesirable oligomers ultimately contributes to a reduction of the copolymer yields. We did not succeed in the preparative separation of the oligomers from their mixtures with monomers. Nevertheless, the SEC/DAD spectra strongly indicate the presence of **PN**- units in these oligomeric chains.

As can be seen from **Figure 28** and Table 9, the molar mass of copolymers prepared from **PN** and **M3** decreases significantly with increasing content of the **PN** units: while M_w of 210 kg/mol was attained in the case of **P(PN/M4a)** with F_A = 0.2 the M_w value of only 13 kg/mol resulted for **P(PN/M4c)** with F_A = 0.51. This may be connected with the low rate of propagation on the **PN** growing species (*vide supra*) which may increase the probability of the termination and/or transfer reactions whose reduce the molecular weight of the copolymers significantly.

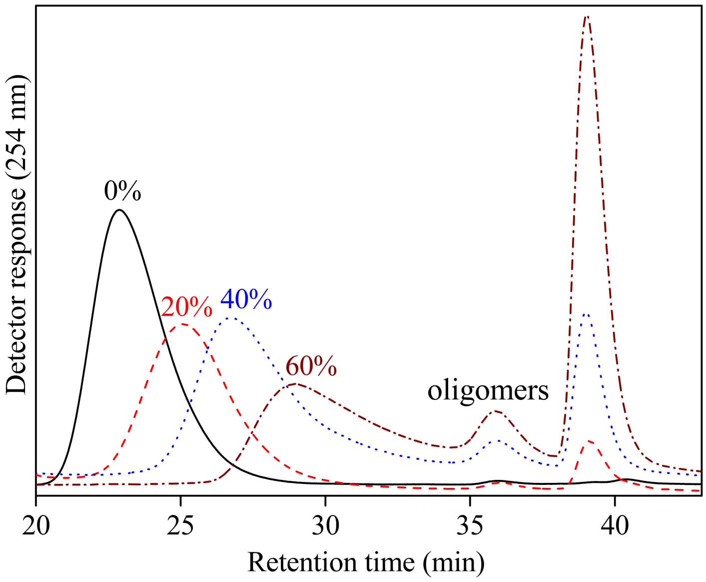


Figure 28. SEC records of the **M4** / **PN** polymerization mixtures just before their termination. The numbers denote the feed molar fraction of **PN** monomer (in mol %); Table 11, entries 6 – 9.

Figure 29 shows the ^{1}H NMR spectra of **P(M4)** homopolymer and **P(PN/M4)** copolymers together with the signal assignment. It is obvious that with increasing F_A value of the copolymers the resolution of ^{1}H NMR signals is decreasing as a result of increasing non-uniformity in the covalent and most probably also configurational structure.

The IR spectra of **P(M4)** and copolymers of **PN** with **M4** are shown **Figure 30**. The presence of the **PN** units in copolymers is proved by the presence of IR bands at 1663 and 1701 cm^{-1} ($\nu_{C=O}$). The detailed study of the low-energy region of the FTIR spectra shows an increase in the intensity of the 760 cm^{-1} band and a parallel decrease in the intensity of the 732 cm^{-1} band with increasing content of **PN** units in the copolymers. The IR bands in this region are being ascribed to the vibrations of the main chain double bonds in the case of polyacetylenes. For example, the configuration of the unsubstituted poly(phenylacetylene)s can be qualitatively evaluated from the intensities of the IR bands at 740 cm^{-1} and 760 cm^{-1} that correspond to the vibration of the main chain vinylene groups with *cis* and *trans* configuration, respectively.[143,144] It is probable that the above mentioned IR bands at 732 cm^{-1} and 760 cm^{-1} in the FTIR spectra of copolymers of **PN** with **M4** may be connected with the configurational structure of the copolymers in a similar way: the former band may correspond to the *cis* main-chain double bonds while the latter to the *trans* main-chain double bonds. The intensity increase of the band at 760 cm^{-1} and a parallel decrease in the intensity of the 732 cm^{-1} band which accompanies the the increased content of **PN** units in copolymers may reflect the increase of the presence of *trans* main-chain double bonds in the copolymers, as it has already been shown on the basis of the ^{1}H NMR spectra.

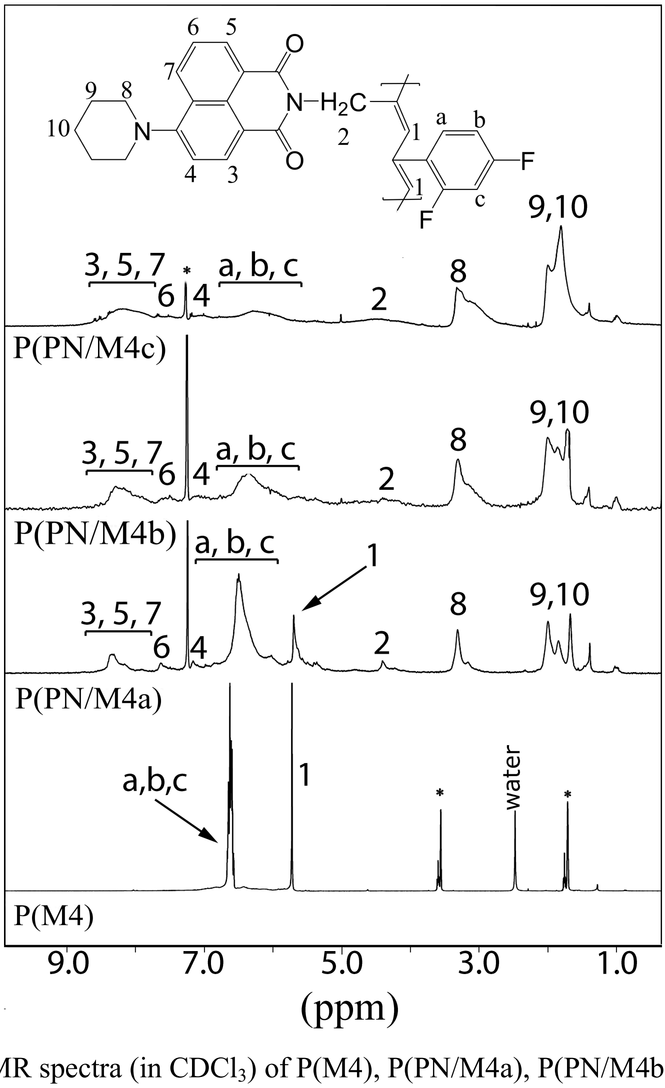


Figure 29. ^{1}H NMR spectra (in CDCl$_3$) of P(M4), P(PN/M4a), P(PN/M4b) and P(PN/M4c).

All copolymers of **PN** with either **M3** or **M4** are well soluble in CH_2Cl_2, $CHCl_3$ and THF. This finding led us to the idea to test the impact of the **PN** monomeric units on the solubility of copolymers prepared from **PN** and acetylene monomers that provide totally insoluble homopolymers under the homopolymerization conditions. Three monomers of this type were selected: (naphthyl-2-yl)acetylene (**M5**), [4-(phenylethynyl)phenyl]acetylene (**M6**) and (biphenyl-4-yl)acetylene (**M7**)

(Scheme 9). The homopolymerization of **M5**, **M6** and **M7** provided high yields (72 - 91 %) of insoluble polyacetylene type homopolymers (see Table 9 No. 10-12). The FTIR spectra of homopolymers (**Figure 31**) show a total disappearance of signals of C≡CH groups of the monomers (bands at 2105 cm^{-1}, $\nu_{C\equiv C}$ and at about 3285 cm^{-1}, $\nu_{\equiv C-H}$) due to the polymerization. In the case of the **M6** monomer, only the terminal ethynyl groups were transformed in the polymerization while the internal ones remained preserved (band at 2217 cm^{-1}, $\nu_{C\equiv C}$). If **M5**, **M6** and **M7** were (separately) copolymerized with **PN** (f_A = 0.2), well soluble (CH_2Cl_2, $CHCl_3$ and THF) high-molar-mass copolymers were obtained in the yields ranging from 74 to 83 % (see Table 9, entries 13-15). The values of F_A of the copolymers were from 0.17 to 0.20, i.e. the incorporation of the units derived from **PN** into the chains of the copolymers was effective.

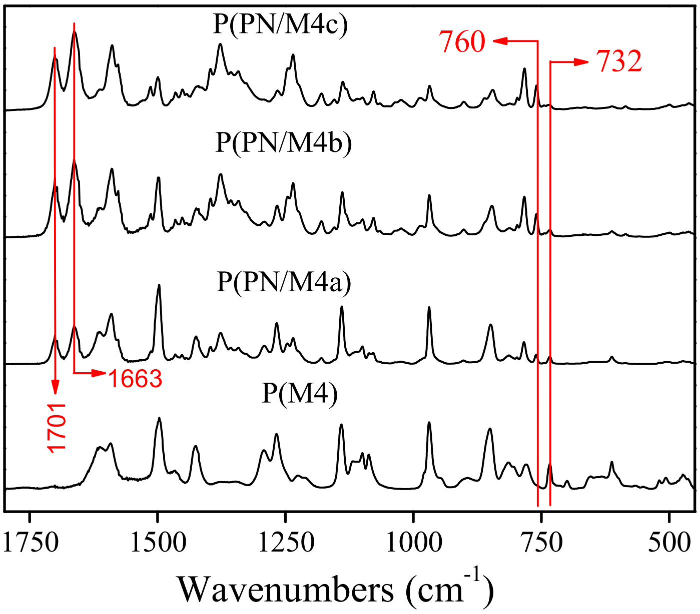


Figure 30. FTIR spectra of P(M4), P(PN/M4a), P(PN/M4b) and P(PN/M4c).

The FTIR spectra of the copolymers **P(PN/M5)**, **P(PN/M6)** and **P(PN/M7)** are given in **Figure 31** together with the spectra of the corresponding homopolymers. Unfortunately, the high complexity of the spectra in the region 700 – 800 cm^{-1} does not allow to speculate on the configurational structure of the analysed homo- and copolymers. The ^{1}H NMR spectra of copolymers and the signal assignment are given in **Figure 32**. The broad character of ^{1}H NMR signals corresponds to the polyacetylenes with low microstructure uniformity possessing both *cis* and *trans* main-chain double bonds in the main chains.

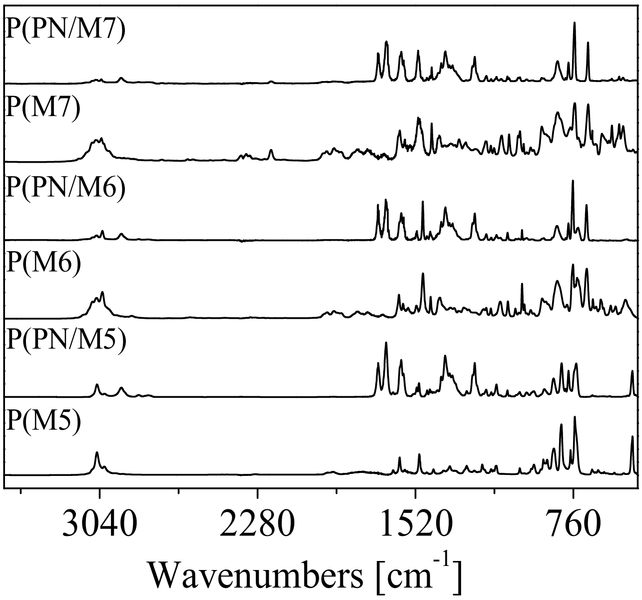


Figure 31. FTIR spectra of P(M5), P(PN/M5), P(M6), P(PN/M6), P(M7) and P(PN/M7).

The insolubility of **P(M5)**, **P(M6)** and **P(M7)** is probably due to the tight, regular packing of the polymer chains in the solid state which is induced by the symmetry and/or rigidity of the pendant groups [naphthyl-2-yl, 4-(phenylethynyl)phenyl and biphenyl-4-yl] of the homopolymers. The solid-state packing of the chains of **P(PN/M5)**, **P(PN/M6)** and **P(PN/M7)** copolymers should be less tight and thus less rigid according to the presence of the units with non-symmetric slightly polar pendant groups derived from **PN**. This ultimately allows the copolymers to be dissolved in proper solvents (*vide supra*). The comonomer (biphenyl-4-yl)acetylene (**M7**) was also copolymerized with (4-chlorobutyl)acetylene (**M8**) (Table 9 No 16 and 17) with the aim to prepare a comparative sample for the fluorescence study (*vide infra*). The comonomer feed containing 20 mol % **M7** provided copolymer, **P(M8/M9a)**, with $F_A = 0.15$ (ascertained from the chlorine content in the copolymer). This copolymer was, however, insoluble. It is therefore clear that the impact of **M8** monomeric units on the solubility of the copolymer is not as great as the impact of **PN** units. Nevertheless, the co-monomer feed containing 80 mol % of **M7** provided a well soluble copolymer, **P(M8/M7b)**, ($F_A = 0.36$) of M_w = 43 000 (Table 9 No 17).

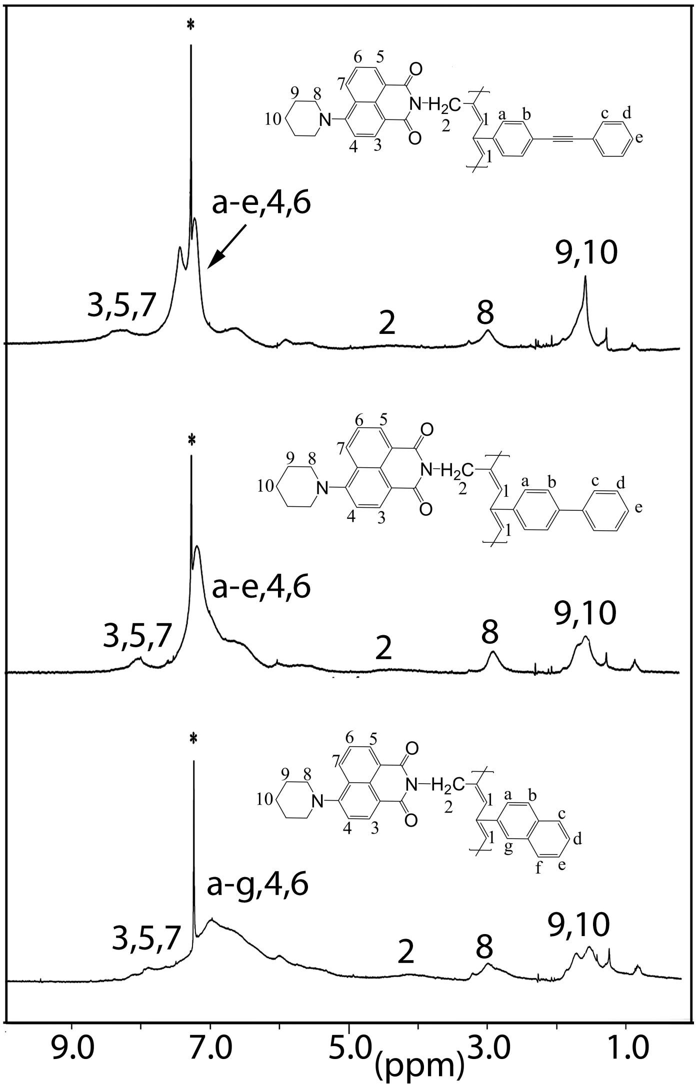


Figure 32. ^{1}H NMR spectra (in $CDCl_3$) of **P(PN/M5)**, **P(PN/M6)** and **P(PN/M7).**

3.6.4. UV/vis absorption and fluorescence characteristics of PN copolymers

The UV/vis absorption spectra of monomers **M3** to **M7** and **PN** are compared in **Figure 32**. The spectra of monomers **M3**, **M4** show only single band with absorption maximum at wavelengths λ_{max} of about 240 nm. Monomer **M6** also shows a single band but with maximum at 270 nm and **M7** absorb at higher wavelengths (λ_{max} = 298 and 272 nm, respectively) due to the higher extent of delocalization of electrons in their rod-like substituents [4-(phenylethynyl)phenyl and biphenyl-4-yl]. Monomer **PN** exhibits two absorption bands: the first one in the region from 260 to 315 nm and the second one in the region from 315 to 530 nm (λ_{max} = 417 nm).

Figure **33** shows UV/vis absorption spectra of copolymers **P(PN/M3)**, **P(PN/M4a)**, **P(PN/M5)**, **P(PN/M6)** and **P(PN/M7)**. All the copolymers contain similar fraction of PN units (F_A from 0.14 to 0.20, Table 11 No 5, 7, 13, 14, 15). The spectrum of each copolymer contains two bands, one in the UV region and the other in the visible region. The UV bands in spectra of copolymers reflect mainly the absorption of pendant groups of monomeric units derived from **M3** to **M7** monomers. The UV/vis bands in the spectra of copolymers are contributed by the electronic transitions within (i) pendant groups of the **PN** units, and (ii) conjugated polyacetylene mains chains. The UV/vis absorption band positions $\lambda_{\max}$ are clearly a function of co-monomeric units to the **PN** units: 396 nm for **P(PN/M3)**; 398 nm for **P(PN/M4a)**; 405 nm for **P(PN/M5)**; 402 nm for **P(PN/M7)**. The UV/vis band of **P(PNM6)** does not exhibit a distinguishable maximum but only a shoulder in the region 380 – 500 nm. All copolymers show almost the same value of the absorption edge.

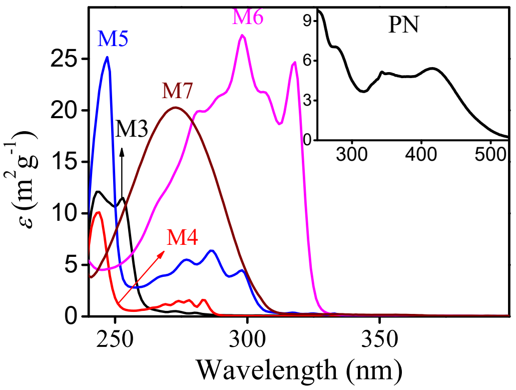


Figure 32. UV/vis spectra of **PN**, **M3**, **M4**, **M5**, **M6** and **M7** solutions in chloroform

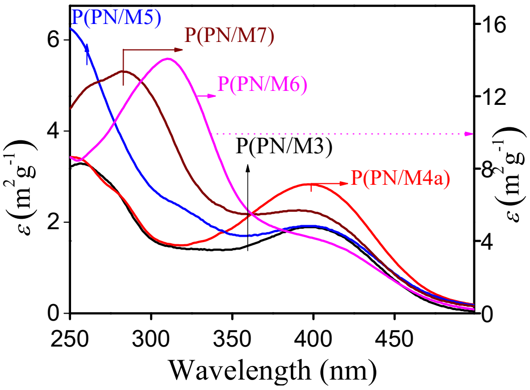


Figure 33. UV/vis spectra of **PN**, **P(PN/M3)**, **P(PN/M4a)**, **P(PN/M5)**, **P(PN/M6)** and **P(PN/M7)** solutions in chloroform

Figure 34 shows the steady-state fluorescence spectra (excitation wavelength, λ_{exc} = 420 nm) taken from CHCl$_3$ solutions of (i) **P(PN/M3)**, **P(PN/M4a)**, **P(PN/M5)**, **P(PN/M6)** and **P(PN/M7)** copolymers (F_A from 0.14 to 0.20, Table 9, entries 5, 7, 13, 14, 15) and (ii) **PN** monomer. It is evident that all the copolymers exhibit fluorescence with the emission maximum λ_F from 507 to 510 nm (**Table 10**) that is identical or nearly identical with the emission maximum of the **PN** monomer (λ_F = 508 nm), i.e. the fluorescence of **PN** has retained after its incorporation into copolymer chains. Unfortunately, the fluorescence quantum yield of enchained **PN** could not be determined due to the simultaneous excitation light (λ_{exc} = 420 nm) absorption by **PN** groups and polyacetylene main chains. Only excited **PN** groups emit fluorescence.

The monomer **PN** exhibits a monoexponential fluorescence decay (τ_1 = 9.2 ns). The time-resolved emission spectra of all the copolymers discussed in this paragraph revealed three-exponential fluorescence decays in which, however, the longest time component belonging to the 1,8-naphthalimide significantly prevails. The high complexity of the fluorescence kinetics of the fluorophore inbuilt into the polymer chains is known from the literature.[131,132] Consequently, the explanation of all the processes participating on the fluorescence decay of the studied polymers is difficult to almost impossible.

Table 10. Fluorescence characteristics of copolymers and PN monomer in $CHCl_3$. λ_F is the wavelength of the emission maximum (λ_{exc} = 420 nm). τ_1, τ_2 , and τ_3 are lifetimes of the fluorescence components (λ_{exc} = 378 nm). The contributions of τ_1, τ_2, and τ_3 lifetimes are given in parentheses.

Polymer code	**λ_F (nm)**	**τ_1 (ns)**	**τ_2 (ns)**	**τ_3 (ns)**
P(PN/M3)	509	8.7 (78%)	3.7 (10%)	0.4 (12%)
P(PN/M4a)	507	9.0 (87%)	2.5 (7%)	0.5 (6%)
P(PN/M5)	508	8.7 (77%)	2.0 (15%)	0.2 (8%)
P(PN/M6)	510	8.7 (69%)	2.2 (20%)	0.4 (11%)
P(PN/M7)	507	8.7 (74%)	2.5 (18%)	0.3 (8%)
PN	508	9.2 (100%)	--	--

Copolymers **P(PN/M5)**, **P(PN/M6)** and **P(PN/M7)** contain (in addition to 1,8-naphthalimide fluorophore emitting in the visible region) aromatic fluorophores [naphthyl-2-yl, 4-(phenylethynyl)phenyl and biphenyl-4-yl] which are known to emit in the UV region. Therefore, the fluorescence behavior of the copolymers was studied more in detail.

The steady-state fluorescence spectrum (λ_{exc} = 300 nm) taken from $CHCl_3$ solution of **P(PN/M7)** is shown in **Figure 35**. The spectrum exhibits two emission maxima with λ_F of 380 nm and 510 nm that can be assigned to the biphenyl-4-yl and

1,8-naphthalimide fluorophores, respectively. To evaluate the fluorescence behavior of a polyacetylene containing biphenyl-4-yl as the sole fluorescent group, the soluble copolymer **P(M8/M7b)** has been prepared (see Table 9 No 17). **P(M8/M7b)** contains the biphenyl-4-yl groups and non-fluorescent 4-chlorobutyl groups.

The fluorescence spectrum of **P(M8/M7b)** (Figure 35, λ_{exc} = 300 nm) exhibits only single emission maximum at 380 nm due to the biphenyl-4-yl pendants. Other fluorescence experiment was performed with **P(PN/M4a)** sample. This copolymer contains in addition to 1,8-naphthalimide fluorophores the non-fluorescent 2,4-difluorophenyl groups. The **P(PN/M4a)** copolymer provided no fluorescence response when excited with the radiation of wavelength 300 nm. It is obvious that the radiation with such a low wavelength is not capable to induce directly the fluorescence of the 1,8-naphthalimide fluorophore bonded to the polyacetylene chains.

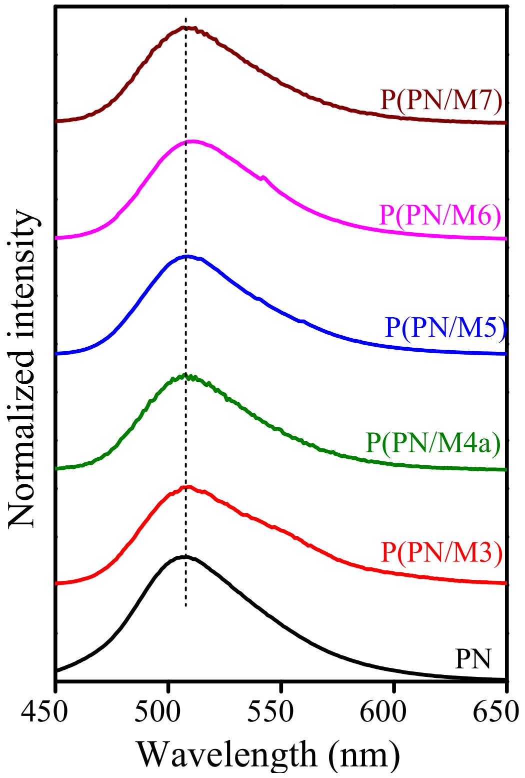


Figure 34. Fluorescence emission spectra of **PN**, **P(PN/M3)**, **P(PN/M4a)**, **P(PN/M5)**, **P(PN/M6)** and **P(PN/M7)** solutions in $CHCl_3$; λ_{exc} = 420 nm.

The fluorescence spectrum of **P(M8/M7b)** (Figure 35, λ_{exc} = 300 nm) exhibits only single emission maximum at 380 nm due to the biphenyl-4-yl pendants. Other

fluorescence experiment was performed with **P(PN/M4a)** sample. This copolymer contains in addition to 1,8-naphthalimide fluorophores the non-fluorescent 2,4-difluorophenyl groups. The **P(PN/M4a)** copolymer provided no fluorescence response when excited with the radiation of wavelength 300 nm. It is obvious that the radiation with such a low wavelength is not capable to induce directly the fluorescence of the 1,8-naphthalimide fluorophore bonded to the polyacetylene chains.

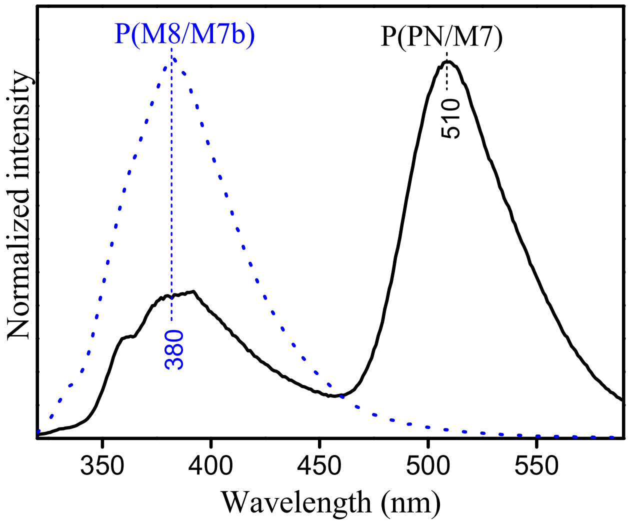
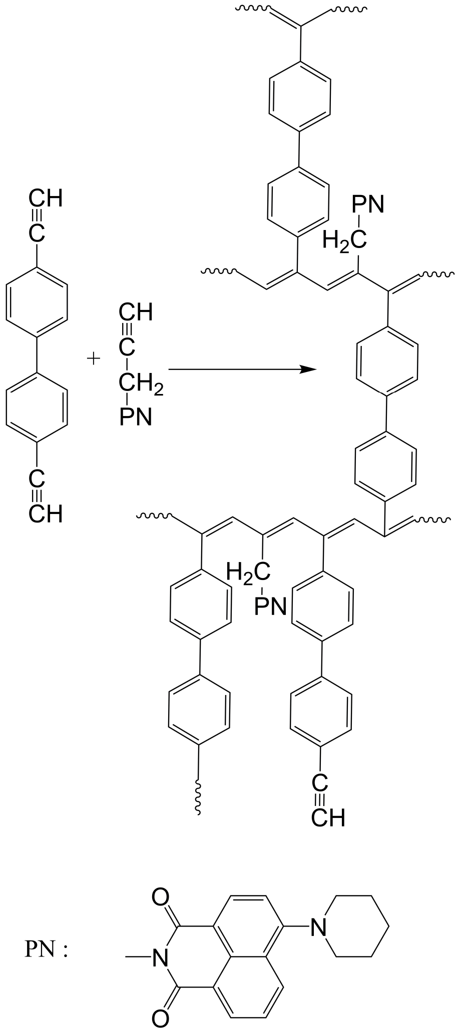


Figure 35. Fluorescence emission spectra of **P(PN/M7)** and **P(M8/M7b)** in $CHCl_3$, $\lambda_{exc} = 300$ nm.

Summarizing the above results we conclude that the observed fluorescence emission of **PN** groups ($\lambda_F = 510$ nm) in **P(PN/M7)** copolymer excited with $\lambda_{exc} = 300$ nm was enabled by the energy transfer from the biphenyl-4-yl fluorophores to the 1,8-naphthalimide fluorophores. In this process the biphenyl-4-yl fluorophore serves as an energy donor for 1,8-naphthalimide fluorophore that is an energy acceptor. The time-resolved emission spectra of 1,8-naphthalimide fluorophore in **P(PN/M7)** ($\lambda_{exc} =$ 300 nm) revealed three-exponential fluorescence decay [parameters: $\tau_1 = 9.3$ ns (60%), $\tau_2 = 3.7$ ns (30%), $\tau_3 = 0.1$ ns (10%)] that is similar to the decay ascertained for 1,8-naphthalimide fluorophore in **P(PN/M7)** excited directly ($\lambda_{exc} = 420$ nm), see Table 10. The fluorescence decay of the biphenyl-4-yl fluorophore in **P(PN/M7)** (λ_{exc} = 300 nm) was too rapid (lifetime < 0.01 ns) to be evaluated reliable. Consequently the character of the energy transfer from the biphenyl-4-yl donor to 1,8-naphthalimide could not be studied in details.

The fluorescence emission of PN groups (λ_F ~ 510 nm) caused by the energy transfer from the fluorophores of the aromatic hydrocarbon type to PN groups was revealed also in the case of copolymers **P(PN/M4)** and **P(PN/M5)** containing naphthyl-2-yl and 4-(phenylethynyl)phenyl pendant groups, respectively.

3.7. Incorporation of PN units into polyacetylene network



Scheme 10. Synthesis of porous networks with PN units.

The Rh catalysed chain-growth polymerization of monomers with one terminal ethynyl group in the molecule (i.e. ethynyl functionality, φ = 1) leads to the linear polyacetylene-type homo- and copolymers. The same type polymerization of monomers with two and more ethynyl groups, i.e., if the average ethynyl functionality of the monomers is properly enhanced, can give hyper-cross-linked polyacetylene networks. Diethynylarenes such as 1,4-diethynylbenzene and 4,4′-diethynylbiphenyl have been either homopolymerized (φ = 2)[145,146] or copolymerized with monoethynylarenes (φ = 1.5).[147] The networks prepared under optimized conditions exhibited micro- or micro/mesoporous texture with the Brunauer-Emmett-Teller (BET) surface, S_{BET}, up to 1470 m^2/g.[146]

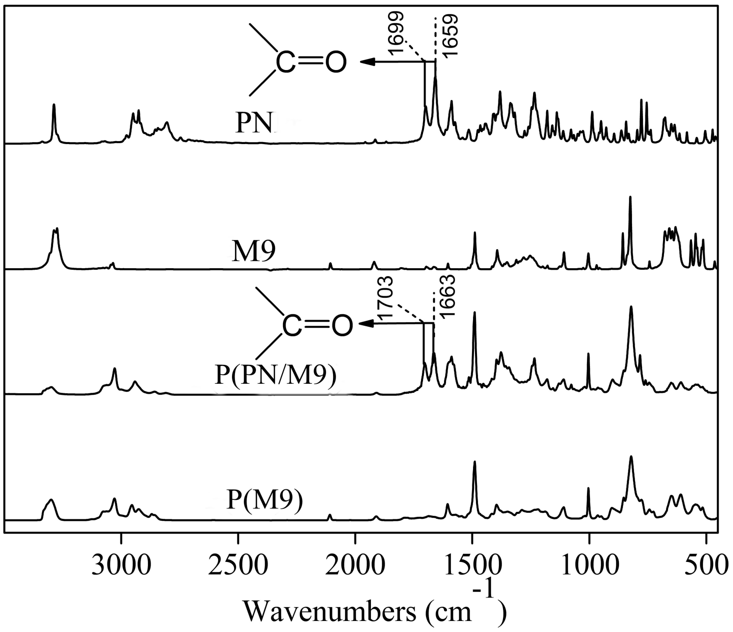


Figure 36. FTIR spectra of **P(M9)**, **P(PN/M9)** and monomers **PN** and **M9**

Successful incorporation of the **PN** units into a porous polyacetylene network via copolymerization of **PN** (f_A = 0.1) with 4,4′-diethynylbiphenyl (**M9**) (φ = 1.9) was performed (**Scheme 10**). The copolymerization was catalysed with [Rh(nbd)acac] and performed under conditions optimized in ref. [146]. Besides, a comparative homopolymerization of **M9** was performed under the same conditions (see **Table 11**). Both reactions gave high yields of insoluble products: the copolymer network **P(PN/M9)** and the homopolymer network **P(M9)**. According to the elemental analysis, the **P(PN/M9)** contained 8 mol. % units derived from **PN**. Three types of monomeric units can be assumed in **P(PN/M9)**: (i) branching units derived from **M9** (both ethynyl groups of **M9** have reacted), (ii) linear units derived from **M9** (only one ethynyl group of **M9** has reacted) and (iii) linear units derived from **PN**.[147] The distribution of particular monomeric units can not, however, be ascertained. The branching and linear units derived from **M9** shall be assumed in the homopolymer network **P(M9)**.[147] This assumption has been confirmed by FTIR spectroscopy. The

FTIR spectra of both **P(PN/M9)** and **P(M9)** (**Figure 36**) contain bands at 3299 cm^{-1} ($\nu_{\equiv C\text{-}H}$) due to the presence of some non-reacted pendant ethynyl groups. The presence of units derived from **PN** in **P(PN/M9)** is well manifested by bands at 1663 and 1703 cm^{-1} ($\nu_{C=O}$). The networks **P(M9)** and **P(PN/M9)** were characterized by N_2 adsorption/desorption at 77 K. The N_2 adsorption/desorption isotherms are given in **Figure 37**, the texture parameters of **P(M9)** and **P(PN/M9)** are summarized in Table 11.

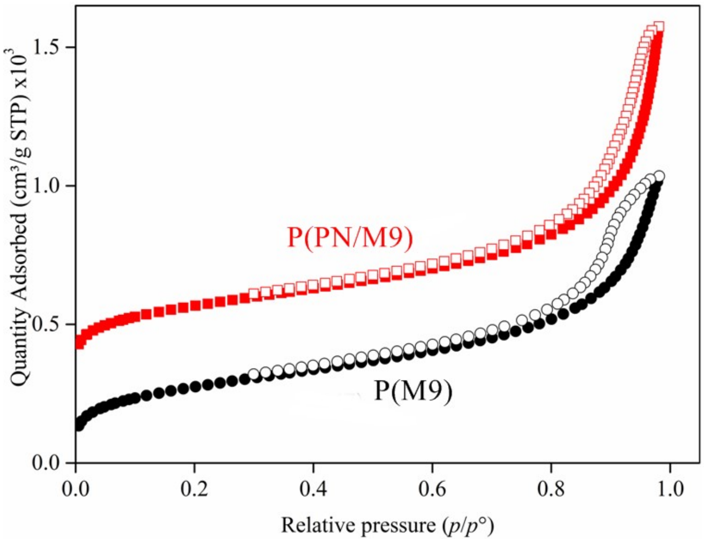


Figure 37. N_2 adsorption and desorption isotherms on P(PNPr/M7) and P(M7) at 77 K. Curve P(PNPr/M7) was shifted vertically by 300 cm^3/g for better clarity; solid points denote adsorption and empty points denote desorption

Table 11. Synthesis of polyacetylene-type networks (Scheme 10) catalysed with [Rh(nbd)acac] in CH_2Cl_2 at 75ºC, reaction time 72 h. Overall initial concentration of monomers in the feed: 0.6 mol/L. Initial concentration of catalyst: 18 mmol/L. Yield of polymer is calculated with respect to the weight of applied monomer(s). φ is average functionality of the monomers in the feed. f_A is the mole fraction of comonomer A in the feed, F_A is the mole fraction of comonomeric units derived from comonomer A in the product. S_{BET} is the specific surface area, V_{mic} and V_{mes} is the volume of micro- and mesopores, respectively.

Polymer code	Monomer A	Monomr B	φ	f_A	Yield in %	F_A	S_{BET} in m^2/g	V_{mic} cm^3/g	V_{mes} cm^3/g
P(PN/M8)	**PN**	**M8**	1.9	0.1	95	0.08	1001	0.24	1.84
P(M8)	--	**M8**	2	0	96	0	995	0.23	1.35

A high S_{BET} value of 995 m^2/g found for **P(M9)** is in accord with the S_{BET} values of the polyacetylene networks prepared from various diethynylarenes and reported previously (Eva's article again). Nevertheless, equally high S_{BET} value was found for the network copolymer **P(PN/M9)**. Both networks show micropores and mesopores (the average mesopore diameter is 20 nm). The micropore volumes of **P(M9)** and **P(PN/M9)** are identical (Table 11). The copolymer network **P(PN/M9)** exhibits a slightly higher mesopore volume (1.84 cm^3/g) than **P(M9)** (1.35 cm^3/g). Thus it can be concluded that the incorporation of units of monofunctional **PN** in amount of 8 mol. % into the network based on the bifunctional monomer **M9** did not alter significantly the micro/mesoporous texture of the network (Figure 23). We admit, however, that the attempt to incorporate a higher amount of units derived from **PN** into this network while maintaining the porosity of the network has failed. The copolymerization of **PN** (f_A = 0.5) with **M9** (φ = 1.5) provided insoluble network (F_A = 0.31, yield 72 %) that was nonporous.

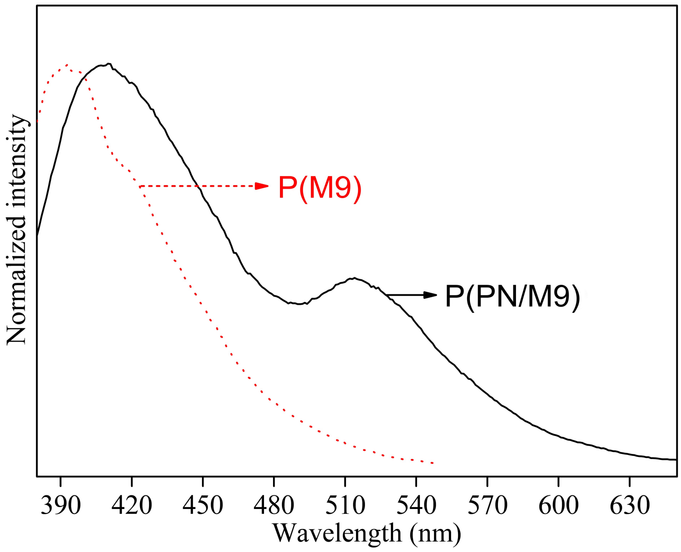


Figure 38. Solid state emission spectra of **P(M9)** and **P(PN/M9)**, excitation wavelength 340 nm

Both networks **P(M9)** and **P(PN/M9)** exhibit fluorescence when excited in the solid state with λ_{exc} = 340 nm. The fluorescence spectrum of **P(M9)** (**Figure 38**) exhibits single emission maximum at λ_F = 395 nm. The biphenyl-4,4′-diyl and biphenyl-4-yl segments of the network are most probably responsible for this fluorescence. The fluorescence spectrum of **P(PN/M9)** exhibits two emission maxima with λ_F of 410 nm and a broad shoulder with λ_F of 515 nm. The former maximum is ascribable to biphenyl-4,4′-diyl and biphenyl-4-yl fluorophores, the latter one reflects the presence of the 1,8-naphthalimide fluorophores in the network. The network

P(PN/M9) and the linear copolymer **P(PN/M7)** contain the same two types of luminescent moieties: 1,8-naphthalimide fluorophores and biphenyl-type fluorophores. As evident from Figure 9 and 11, **P(PN/M9)** and **P(PN/M7)** exhibit similar fluorescence responses on the UV irradiation, regardless of the fundamental difference in the architecture of these copolymers. Owing to the complexity of the solid-state fluorescence measurement we can not specify the mechanism of the excitation of 1,8-naphthalimide fluorophores in the **P(PN/M9)** network. Nevertheless, at least a partial energy transfer from the biphenyl-type to 1,8-naphthalimide fluorophores seems to be reasonable.

4. Summary

At the beginning of the project we tried to prepare a conjugated polymer containing highly luminescent naphthalimide groups. Therefore, the new monomer **PN** has been designed, synthesized and subjected to polymerizations with various catalysts, however, without a significant success. Therefore we decided to try to introduce naphthalimide groups to conjugated polymers by the modification approach. As polymers of low air-stable reactive monosubstituted acetylenes are not too suitable for modifications, the attention was turned to polymers of disubstituted acetylenes.

In the first part of the project, the effects of the structure symmetry and substituent bulkiness on the polymerizability of diarylacetylenes and solubility of resulting polymers were examined. For these purposes, a series of new diarylacetylene monomers with spectrally easily recognizable substituents has been designed, prepared, characterized and then polymerized. The results obtained show that the structure symmetry of monomeric units negatively affects solubility of linear polydiphenylacetylenes to such an extent that it cancels the expected positive effect of alkyl groups attached to phenyl pendants in para positions: insolubility of poly[1,2-bis(4-*tert*-butyl)phenylacetylene]. These results well corresponds with the results of Masuda et al. who reported a good solubility of poly{1-[(4-*tert*-butyl)phenyl]-2-phenylacetylene with non-symmetrically substituted monomeric units that contrasts with insolubility of poly(diphenylacetylene). On the other hand, the results obtained have shown that an increase in the steric hindrances of pendant groups decreases the polymerizability of a diarylacetylene monomer as expected; the reactivity of 4-(*t*-Bu)Ph-C≡C-Aryl monomers decreases in the expected Aryl order: 4-*tert*-butylphenyl > naphthalen-2-yl > naphthalen-1-yl > anthracen-5-yl.

Other interesting observations found within the above research are: *(i)* long-term stability of polydiarylacetylenes when exposed to air in solutions, which strongly contrasts with rather fast degradation of overwhelming majority of the polymers of monosubstituted acetylenes under comparable conditions, *(ii)* absence of fluorescence found for poly[4-(*t*-Bu)Ph-C≡C-naphthalen-1-yl] as well as low fluorescence efficiency of the corresponding monomer, which both strongly contrast with fluorescence behavior of corresponding isomers with naphthalen-2-yl side group, and *(iii)* blue shift of the UV/vis band about ca 35 nm and a drop of the absorption coefficient to one half when going from the polymer with naphthalen-1-yl to that with naphthalen-2-yl groups. The latter two points emphasize the importance of the positional isomerism of pendent aryl on the delocalization of electrons in a π-conjugated system.

In the next part of the project we have shown that the polymer-modification strategy represents a feasible path for incorporation of naphthalimide groups that are incompatible with polymerization catalysts onto chains of polymers of disubstituted acetylenes. A new monomer: 1-(6-chlorohex-1-yn-1-yl)-4-(*tert*-butyl)benzene has been designed and prepared, which provides monomeric units carrying *(i)* 6-chlorobutyl groups that can be modified by a nucleophilic substitution, and *(ii) tert*-butyl groups that facilitate good spectroscopic detection of the corresponding monomeric units in copolymers. The two step modifications of copolymers of this monomer and (hex-1-yn-1-yl)benzene consisting in the exchange of chlorine atoms of pendent groups with azido groups and subsequent Huisgen "click" reaction of azido groups with ethynyl groups of the naphthalimide monomer **PN** has been performed as a good method for preparing polymers of disubstituted acetylenes with significantly enhanced fluorescence efficiency. The UV/vis and stationary as well as time resolved luminescence spectra of the **PN** modified polymers have shown that the luminescence properties of the **PN** chromophores are preserved upon binding **PN** to polymer chains. A convergence of the fluorescence characteristics towards those of the free **PN** was found with increasing degree of the polymer modification, which is ascribed to the increasing conformational rigidity of the **PN**-rich chains. The time-resolved measurements proved considerable participation of the excitation-energy transfer from the conjugated polymer main chains to the pendant **PN** groups in the overall luminescence process.

Homopolymers of disubstituted acetylenes carrying hexyl side groups with terminal chlorine atoms (polymers of **M1** and **M2**) were, in addition, modified by the reaction with *N*-methylimidazole to obtain novel conjugated polyelectrolytes. The obtained polymers are soluble in polar aprotic as well as protic solvents, including low alcohols such as methanol and ethanol, but not in water, in contrast to the analogous polymer with polythiophene backbone and identical pendant groups. Nevertheless, both these polyacetylenes were found to be soluble in the water/methanol mixtures of the compositions up to 1/1 by volume. Surprisingly, no significant difference in solubility has been observed between the polymers with and without *tert*-butyl group attached to the phenyl ring of the constitutional repeating unit. Unlike the related conjugated polyelectrolyte with polythiophene backbone the here reported polyelectrolytes do not exhibit solvatochromism.

Successful introduction of naphthalimide groups into conjugated chains has encouraged us to extend the experiments with the direct polymerization of monomers **PN** and **PN1** about their copolymerization with other monomers carrying the terminal ethynyl groups. Copolymerizations with monoethynyl monomers with [Rh(nbd)acac] catalyst carried out at various comonomer mole ratios were found to provide well soluble, mostly high-molar-mass polyacetylenes comprising up to one half of the naphthalimide monomeric units despite the fact that naphthalimide monomers alone do not polymerize. The observed limiting polymer composition: up to 50 % of **PN** units indicates the alternating sequence of monomeric units in the most **PN**-loaded copolymer chains and a need of the presence of the another, more reactive monomer in the polymerization mixture, which ensures the creation and/or maintaining of the active catalyst species that can give rise to sufficiently long polymer chains in these reaction systems. The optical spectral properties of naphthalimide groups remained preserved in these new polymers, same as in the case of naphthalimide-functionalized copolymers of disubstituted acetylenes. Luminescence spectra of these new polymers induced with excitation at 420 nm (absorption band of the **PN** chromophore) are practically the same as the spectra excited at 300 nm (band of aromatic side groups, typically biphenyl groups), which proves efficient energy transfer from the aromatic onto naphthalimide pendant groups. Taking into account that the copolymer emission bands are centered at 510 nm, a very high Stokes shifts up to ca 13 700 cm^{-1} are achieved for these copolymers. Another very interesting result is that the new copolymers are well soluble while the homopolymers of comonomers to **PN** are insoluble in tetrahydrofurane.

The **PN** monomer has also been copolymerized with 4,4′-diethynylbiphenyl using the same rhodium-based catalyst and average functionality of monomers in the mixture above 1.5. This copolymerization gave an insoluble micro/mesoporous network polymer of a very high BET specific surface of ca 1 000 m^2/g, which contains inbuilt PN monomeric units and thus exhibits luminescence band centered at 510 nm that is characteristic of the naphthalimide chromophore. The network can be applied in the construction of a fluorescence sensor based on the micro/mesoporous sorbents.

5. Experimental part

5.1. Materials

- *Precursors for monomer synthesis and monomers*

4-Nitro-1,8-naphthalic anhydride (95%), 1-phenyl-1-hexyne (99%) 6-chloro-1-hexyne (98%), 1-bromo-4-tert-butylbenzene (97%), 1-iodo-4-tert-butylbenzene (98%), iodobenzene (98%), sodium azide NaN3 (99%), phenylacetylene (98%), (4-tert-butylphenyl)acetylene (96%), (2,4-difluorophenyl)acetylene (97%), 2-ethynyl-naphthalene (97%), (biphenyl-4-yl)acetylene (97%), (4-chlorobutyl)acetylene (98%), 9-bromoanthracene (97%), 2-bromonaphthalene (98%), 1-bromo-4-tert-butylbenzene (97%) were bought from Sigma-Aldrich; [4-(phenylethynyl)phenyl]acetylene (98%) and 4,4′-diethynylbiphenyl (98%)- from TCI Europe. All chemicals were used as obtained except (2,4-difluorophenyl)acetylene which was purified by vacuum sublimation.

- *Catalysts and cocatalysts used in polymerizations and Sonogashira couplings (SC):*

Acetylacetonato(norborna-2,5-diene)rhodium(I) [Rh(nbd)acac] (97%), dichlorobis(triphenylphosphine)palladium [$PdCl_2(PPh_3)_2$] (99%), triphenylphosphine PPh_3 (99%), copper (I) iodide CuI (99.5%), tungsten(V) chloride $WOCl_4$ (98%), tantalum (V) chloride (99.8%), tetrabutyltin Bu_4Sn (93%) and tetraphenyltin Ph_4Sn (97%) were all purchased from Sigma-Aldrich and used as obtained.

- *Reaction solvents*

Toluene (Lachner) was distilled from sodium/acetophenone drying system under nitrogen just before use. Tetrahydrofuran (Sigma-Aldrich) was distilled from $LiAlH_4$ drying system under nitrogen before use. Dichloromethane (Sigma-Aldrich) was distilled from P_2O_5 drying system before use. Piperidine (Acros Organic), dimethylformamide (DMF), methanol (Sigma-Aldrich), chloroform (Lachner) were all used as obtained.

5.2. Methods

- *Size-exclusion chromatography*

Size-exclusion chromatography (SEC) analyses were carried out using an HP 1100 (Agilent) instrument with a UV detector operating at 254 nm and a series of SEC columns (mixed-B, mixed-C, and mixed-E, Polymer Laboratories, Bristol). THF (flow rate 0.7 mL min^{-1}) was used as a mobile phase. The number-average, M_n and weight-average, M_w, molar masses and dispersity, $Đ$, ($Đ = M_w/M_n$) relative to polystyrene standards are reported.

- *Nuclear magnetic resonance spectroscopy*

^{1}H and ^{13}C NMR spectra were measured on a Varian $^{\mathrm{UNITY}}$INOVA 400 instrument using samples dissolved in *d*-$CDCl_3$ and d_4-MeOD. Chemical shifts are reported in ppm relative to tetramethylsilane (^{1}H) or the solvent peak. Coupling constants, *J* (in Hz), were obtained by the first-order analysis. Two-dimensional NMR experiments were performed for a detailed assignment of the structures of low-molar-mass compounds: COSY experiments were recorded in absolute value mode using standard two-pulse sequence, HSQC, HMQC and HMBC measurements were made as gradient experiments.

- *Infrared and Raman spectroscopy*

FTIR spectra were recorded on a Thermo Nicolet 6700 FTIR instrument using diffuse reflectance technique (128 scans at resolution 4 cm^{-1}) and undiluted as well as KBr-diluted samples. Raman spectra were recorded on a DXR Raman microscope (Thermo Scientific) using excitation at 633 and 780 nm and undiluted samples.

- *UV/vis absorption spectroscopy*

UV/vis absorption spectra were recorded on a Shimadzu UV-2401 spectrometer using quartz cuvettes and spectroscopic grade solvents.

- *Emission spectroscopy*

Fluorescence emission spectra were measured on a Fluorolog 4 Jobin Yvon Spex instrument (Jobin Yvon Instruments S. A., Inc., USA) using four-window quartz cuvette (1 cm). Time resolved fluorescence decays were measured on an ED 299 T (Edinburgh Instruments) spectrometer equipped with laser diodes with excitation wavelength 330 nm or 450 nm using the time correlated single-photon-counting technique.

Fluorescence emission spectra of the solid polymer networks were measured on the same apparatus using a solid-state film holder (22.5 degrees angle) and excitation wavelength of 340 nm. Samples for the measurements were prepared as follows: approximately 10 mg of finely powdered polymer was mixed with three drops of microscope glue (Entellan PB 5265, Euromex Microscopes, Holland). Mixture was transferred to the fresh surface of pyrolitic graphite slide (NT-MDT comp.). Slide of the pyrolitic graphite was previously adjusted on the microscopic glass slide. Prepared samples were left in the oven (50˚C for 15 min) to harden the glue.

- *Adsorption/desorption isotherms*

Nitrogen adsorption/desorption isotherms on the polymer networks were recorded at 77 K using an ASAP 2020 (Micromeritics) volumetric instrument. The micropore volume was determined using the semi-empirical Horvath-Kawazoe method. The mesopore volume and average mesopore diameter were determined by the BJH method. All adsorption/desorption isotherms were measured by Dr. M. Kubů and Dr. M. Polášek at J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the CzechRepublic)

- *Elemental analysis*

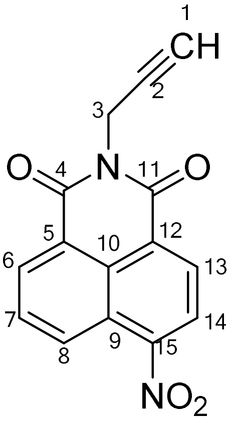
Elemental analyses of the polymers were done by Ing. Zuzana Kálalové at the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic.

5.3. Synthesis:

Preparation of luminescent monomers PN and PN1

- *N-(prop-1-yne-3-yl)-4-Nitro-1,8-naphthalimide*

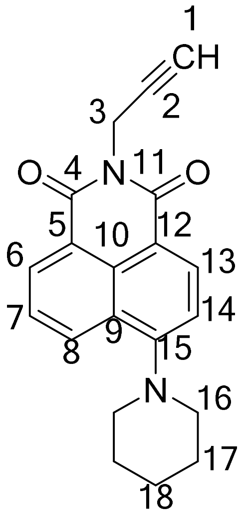
4-Nitro-1,8-naphthalic anhydride (2 g, 8.22 mmol), propargylamine (0.45 g, 8.22 mmol) and ethanol (15 ml) were inserted into a round-bottom flask equipped with a reflux condenser. The mixture was stirred at 60 °C for 24 hours, then the solvent was evaporated, crude product several times washed with aqueous NaOH (0.1M) to remove the anhydride residua, then with water and cold ethanol, and finally it was dried to the constant weight. Isolated yield: 1.72 g (75 %) of a pink solid. Melting point 215.6°C; ^1H NMR (400 MHz, $CDCl_3$, δ (ppm)): 2.22 (bs, $1H^1$), 4.96 (d, $J = 2.5$ Hz, $2H^3$), 8.00 (dd, $J_1 = 7.4$ Hz, $J_2 = 8.7$ Hz, $2H^7$), 8.41 (d, $J = 8.0$ Hz, $1H^{14}$), 8.73 (d, $J = 8.0$ Hz, $1H^{13}$), 8.78 (dd, $J_1 = 7.3$ Hz, $J_2 = 0.9$ Hz, $1H^6$), 8.85 (dd, $J_1 = 8.7$ Hz, $J_2 = 0.9$ Hz, $1H^7$). ^{13}C NMR (100 MHz, $CDCl_3$, δ (ppm)): 29.8 C^3, 71.1 C^1, 77.8 C^2, 122.6 C^9, 123.7 C^5, 123.9 C^{14}, 126.6 C^{12}, 129.15 C^{10}, 129.9 C^8, 130.0 C^7, 130.2 C^{13}, 132.9 C^6, 149.8 C^{15}, 161.8 C^4, 162.5 C^{11}, for atoms numbering see Scheme. Anal. calculated for $C_{15}H_8N_2O_4$ (%): C 64.29, H 2.88, N 10.00, Found: C 64.52, H 2.89, N 9.91. IR (drift, KBr-diluted), cm^{-1}: 3269 ($\nu_{\equiv C-H}$), 1537 and 1335 (ν_{NO2}), 1712 and 1677 ($\nu_{C=O}$), 1583 ($\nu_{C=C,arom}$)



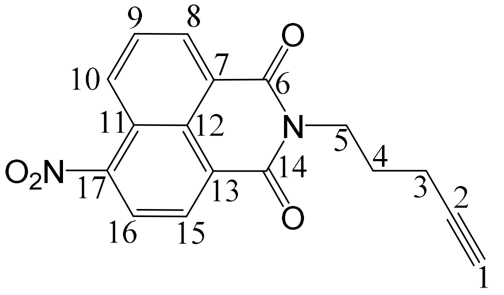
- *N-(prop-1-yne-3-yl)-4-(Piperidine-1-yl)-1,8-naphthalimide* ***PN***

N-(prop-1-yne-3-yl)-4-Nitro-1,8-naphthalimide (1 g, 3.5 mmol) was inserted into a glass vial, dissolved in DMF (6 ml), and piperidine (330 mg, 4.2 mmol) was added. The mixture was allowed to react at room temperature for 24 h, then the solvent was evaporated and crude product recrystallized from ethanol. Isolated yield: 968 mg (87 %) of a yellow solid. Melting point 176.2°C; ^1H NMR (400 MHz, $CDCl_3$, δ (ppm)): 1.70 – 1.76 (m, $2H^{18}$), 1.85 – 1.92 (m, $4H^{17}$), 2.16 (bs, $1H^1$) 3.23 (m, $4H^{16}$), 4.95 (d, *J*

= 2.4 Hz, 2H^3), 7.17 (d, *J* = 8.2 Hz, 1H^{14}), 7.65 – 7.70 (m, 1H ^{7}), 8.40 (bd, *J* = 8.1, 1H^6), 8.53 (d, *J* = 8.2 Hz, 1H^{13}), 8.60 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H^8). ^{13}C NMR (100 MHz, CDCl$_3$, δ (ppm)): 24.3 C^{18}, 26.35 C^{17}, 29.4 C^3, 54.5 C^{16}, 70.0 C^1, 78.9 C^2, 114.3 C^{12}, 114.7 C^{14}, 115.5 C^5, 122.8 C^9, 125.3 C^7, 130.1 C^{10}, 131.1 C^6, 131.4 C^8, 133.1 C^{13}, 157.7 C^{15}, 163.1 C^4, 163.8 C^{11}, for atoms numbering see Scheme 1. HRMS *m/z* 318: measured 318.1378 ; theoretical 318.1368; $C_{20}H_{18}N_2O_2$. IR (drift, KBr-diluted), cm^{-1}: 3287 ($\nu_{\equiv C-H}$), 2120 ($\nu_{C\equiv C}$, very weak), 1698 and 1659 ($\nu_{C=O}$), 1588 ($\nu_{C=C,arom}$).

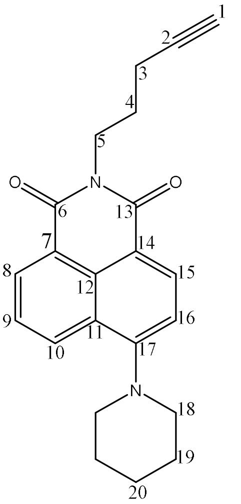


- *N-(pent-1-yne-5-yl)-4-Nitro-1,8-naphthalimide*



4-Nitro-1,8-naphthalic anhydride (2 g, 8.22 mmol), 4-pentyn-1-amine (0.68 g, 8.22 mmol) and ethanol (15 ml) were inserted into a round-bottom flask equipped with a reflux condenser. The mixture was stirred at 60 °C for 24 hours, then the solvent was evaporated, crude product several times washed with aqueous NaOH (0.1M) to remove the anhydride residua, then with water and cold ethanol, and finally it was dried to the constant weight. Isolated yield: 2.05 g (80 %) of a pinkish solid. Melting point 140.2°C ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.82 (d, J = 8.7 Hz, 1H^{9}), 8.72 (d, J = 7.2 Hz, 1H^{8}), 8.67 (d, J = 8.0 Hz, 1H^{15}), 8.38 (d, J = 8.0 Hz, 1H^{16}), 7.97 (dd, J_1 = 8.6, J_2 = 7.4 Hz, 1H^{10}), 4.33 – 4.26 (m, 2H^{5}), 2.33 (td, J_1 = 7.0, J_2 = 2.6 Hz, 2H^{3}), 2.03 – 1.94 (m, 2H^{4}), 1.91 (t, J = 2.6 Hz, 1H^{1}). ^{13}C NMR (CDCl$_3$, 150 MHz, δ (ppm)): 163.6 C^{14}, 162.8 C^{6}, 149.8 C^{17}, 132.7 C^{8}, 130.2 C^{15}, 130.1 C^{9}, 129.6 C^{10}, 129.3 C^{12}, 127.1C^{14}, 124.1C^{16}, 123.8C^{7}, 123.2 C^{7}, 83.4 C^{2}, 68.9C^{1}, 40.2C^{5}, 26.8 C^{3}, 16.6 C4. IR (drift, KBr-diluted), cm^{-1}: 3264 ($\nu_{\equiv C-H}$), 1523 and 1362 (ν_{NO2}), 1696 and 1655 ($\nu_{C=O}$), 1583 ($\nu_{C=C,arom}$)

- *N-(pent-1-yne-5-yl)-4-(Piperidine-1-yl)-1,8-naphthalimide* ***PN1***



N-(pent-1-yne-3-yl)-4-Nitro-1,8-naphthalimide (1 g, 3.2 mmol) was inserted into a glass vial, dissolved in DMF (10 ml), and piperidine (330 mg, 4.2 mmol) was added. The mixture was allowed to react at room temperature for 24 h, then the solvent was evaporated and crude product recrystallized from ethanol. Izolated yield 1.10 g (84%) of orange-yellow solid. Melting point 160.9°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.55 (d, J = 7.2 Hz, 1H^{10}), 8.48 (d, J = 8.1 Hz, 1H^{15}), 8.37 (d, J = 8.3 Hz, 1H^{8}), 7.66 (t, J = 7.8 Hz, 1H^{9}), 7.16 (d, J = 8.1 Hz, 1H^{16}), 4.31 – 4.22 (m, 2H^{5}), 3.27 – 3.16 (m, 4H^{18}), 2.32 (td, J = 7.2, 2.4 Hz, 2H^{3}), 1.97 (m, 3H^{4+1}), 1.91 – 1.82 (m, 4H^{19}), 1.72 (d, J = 5.1 Hz, 2H^{20}). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 164.5 C^{13}, 164.0 C^{6}, 157.2 C^{17}, 132.6C^{15}, 132.5 C^{10}, 131.0C^{10}, 130.8C^{8}, 130.6C^{8}, 130.5C^{12}, 129.8C^{12}, 126.1 C^{9}, 125.3 C^{11}, 125.2 C^{11}, 123.0C^{7}, 115.7C^{16}, 114.6C^{14}, 83.5 C^{2}, 83.4 C^{2}, 68.5 C^{1}, 68.4 C^{1}, 54.4 C^{18}, 39.3C^{3+5}, 26.9C^{4}, 26.1C^{19}, 24.2C^{20}, 16.14C^{4}. HRMS *m/*z 346: measured

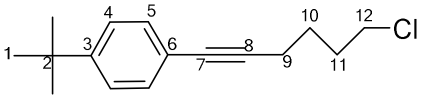
346.1672 ; theoretical 346.1681; $C_{22}H_{22}N_2O_2$. IR (drift, KBr-diluted), cm^{-1}: 3255 ($\nu_{\equiv C-H}$), 2114 ($\nu_{C\equiv C}$, very weak), 1689 and 1647 ($\nu_{C=O}$), 1587 ($\nu_{C=C,arom}$).

Preparation of monomers by Sonogashira coupling

General Procedure

Weighed amounts of $[Pd(PPh_3)_2Cl_2]$, CuI and PPh_3 were introduced into a dried Schlenk flask with a magnetic stir bar, air was removed in three vacuum-argon cycles, solutions of terminal triple bond containing precursor and halogenoarene in piperidine were added under argon and the reaction mixture was allowed to react under stirring at 50°C for 24 h (in case of iodoarenes- at room temperature). After $CHCl_3$ (50 mL) was added, the resulting solution was successively washed three times with 200 mL of 0.1M HCl and two times with 100 mL of brine, then dried over $MgSO_4$ and concentrated on a rotary evaporator to give the crude product.

- *Preparation of 1-(6-chlorohex-1-yn-1-yl)-4-(t-butyl)benzene **M1***

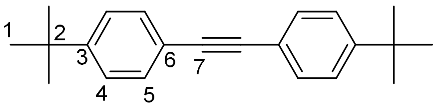


Weighed amounts of $[Pd(PPh_3)_2Cl_2]$ (265 mg, 0.38 mmol), CuI (72 mg, 0.38 mmol) and PPh_3 (297 mg, 1.13 mol) were introduced into a dried Schlenk flask with a magnetic stir bar, air was removed in two vacuum-argon cycles, solutions 1-bromo-4-tert-butylbenzene (2.68 g, 12.6 mmol) and 6-chlorohex-1-yne (1.47 g, 12.6 mmol) in piperidine (10 ml) were added under argon and the reaction mixture was allowed to react under stirring at 50 °C for 24 h. After chloroform (50 ml) was added, the resulting solution was successively washed three times with 200 ml of 0.1M HCl and two times with 100 mL of brine, then dried over $MgSO_4$ and concentrated on a rotary evaporator to give the crude product. The crude product was purified by chromatography (silica; n-hexane). Isolated yield: 1.5 g (48 %) of colorless oil. ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.30 (s, 9 H^1), 1.58 – 1.70 (m, 4 H^{10+11}), 2.41 – 2.47 (m, 2 H^9), 3.60 (t, J = 6.6 Hz, 2 H^{12}), 7.29 – 7.33 (m, 4 H^{4+5}). ^{13}C NMR (100 MHz, $CDCl_3$, δ (ppm)): 19.4 C^9, 26.9 C^{10}, 31.2 C^1, 31.6 C^{11}, 34.7 C^2, 44.6 C^{12}, 81.2 C^7, 89.0 C^8, 120.9 C^6, 125.2 C^4, 131.2 C^5, 150.7 C^3, IR (drift, KBr, cm^{-1}): 2230 vw ($\nu_{C\equiv C}$), 1606 vw and 1505 s ($\nu_{C=C,arom}$), 835 vs ($\nu_{C-H,arom}$), 653 m (ν_{C-Cl}). Anal. calc. for $C_{16}H_{21}Cl$ (%): C 76.80, H 8.40, Cl 14.20, found: C 76.72, H 8.52, Cl 14.31

- *Preparation of (6-chlorohex-1-yn-1-yl)benzene* ***M2***

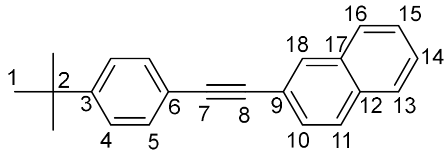
M2 was prepared following the general SC procedure from 1-iodo-benzene (2.57 g, 12.6 mmol), 6-chlorohex-1-yne (1.47 g, 12.6 mmol), copper(I) iodide (72 mg, 0.38 mmol), [$PdCl_2(PPh_3)_2$] (265 mg, mmol) and PPh_3 (297 mg, mmol). The crude product was purified by column chromatography on silica gel using hexane as eluent. Isolated yield: 1.24 g (51 %) of colorless oil. ^1H NMR spectra were in accordance with literature.[148] IR (drift, KBr-diluted) cm^{-1}: 2230 vw ($\nu_{C\equiv C}$), 1606 vw and 1505 s ($\nu_{C=C,arom}$), 835 vs ($\nu_{C-H,arom}$), 653 m (ν_{C-Cl}).). Anal. calc. for $C_{12}H_{13}Cl$ (%): C 74.81, H 6.75, Cl 18.44, found: C 74.69, H 6.81, Cl 18.47

- *1,2-Bis(4-t-butylphenyl)ethyne* ***M10***



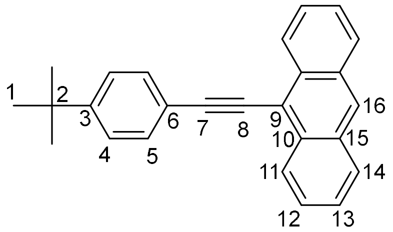
M10 was prepared following the general procedure from (4-*t*-butylphenyl) acetylene (2.0 g, 12.6 mmol), 1-bromo-4-t-butylbenzene (2.68 g, 12.6 mmol), [$Pd(PPh_3)_2Cl_2$] (265 mg, 0.38 mmol) CuI (72 mg, 0.38 mmol), PPh_3 (297 mg, 1.13 mmol) and piperidine (10 mL). The crude product was purified by double recrystallization from n-hexane. 2.63 g of **M10** was obtained aswhite crystals (yield 72%; m.p. 191.5 °C). ^1H NMR($CDCl_3$, 400 MHz, d): 1.32 (s, H^1, 18H), 7.35 (m, H^4, 4H), 7.46 (m, H^5, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, d): 31.18 (C^1), 34.76 (C^2), 88.84 (C^7), 120.47 (C^6), 125.29 (C^4), 131.28 (C^5), 151.31 (C^3); IR (DRIFT, KBr): 591 cm^{-1} (w), 562 cm^{-1} (s), 669 cm^{-1} (w), 737 cm^{-1} (w), 838 cm^{-1} (s), 927 cm^{-1} (w), 948 cm^{-1} (w), 1016 cm^{-1} (m), 1109 cm^{-1} (s), 1202.5 cm^{-1} (m), 1268 cm^{-1} (s),1310 cm^{-1} (w), 1369 cm^{-1} (s), 1391 cm^{-1} (m), 1463 (s), 1521 (s), 1663 cm^{-1} (w), 1911 cm^{-1} (w), 2865 cm^{-1} (s), 2904 cm^{-1} (s), 2959 cm^{-1} (s), 3032 cm^{-1} (m), 3086 cm^{-1} (m); Anal. calc. for $C_{22}H_{26}$: C 90.98, H 9.02; found: C 90.96, H 9.00.

- *2-[(4-t-Butylphenyl)ethynyl]naphthalene* ***M11***



M11 was prepared following the general procedure from (4-*t*-butylphenyl)acetylene (0.85 mL, 4.7 mmol), 2-bromonaphthalene (1.0 g, 4.8 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (169 mg, 0.24 mmol), CuI (85 mg, 0.4 mmol), PPh$_3$ (63 mg, 0.24 mmol) and piperidine (5 mL). The crude product was purified by double recrystallization from n-hexane. (yield 81%; m.p. 131.7 °C). ^{1}H NMR (400 MHz, CDCl$_3$, d): 1.34 (s, H^1, 9H), 6.76–6.79 (m, H^4, 2H), 7.30–7.33 (m, H^5, 2H), 7.36–7.46 (m, H$_{arom,}$ 6H), 7.75–7.77 (m, H^{18}, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, d): 31.2 (C^1), 34.5 (C^2), 88.3 (C^8), 88.9 (C^7), 116.2 (C^6), 119.2, 120.6 (C^9), 125.5, 127.9 (C^4),130.4, 132.5, 132.6, 135.6 (C^5), 151.2, 155.6 (C^3); IR (DRIFT, KBr): 480 (s), 537(w), 561(s),627(w), 644(w),659(w),745(s), 829(vs), 840(m), 867 (m), 899 (s), 923 (w), 950 (m), 965 (m), 1015 (s), 1023 (s), 1102 (m), 1116 (s), 1141 (w), 1191 (w), 1200 (s), 1265 (s), 1303 (m), 1345 (w), 1358 (s), 1366 (s), 1407 (m), 1429 (w), 1438 (w), 1459 (s), 1506 (s), 1570 (s), 1593 (s), 1625 (m), 1913 (m), 2870 (m), 2905 (m), 2963 (vs), 3020 (w), 3037 (w), 3053cm_1 (m); Anal. Calc. for $C_{22}H_{20}$: C 92.91,H 7.09; found: C 92.86, H 7.14.

- *9-[(4-t-Butylphenyl)ethynyl]anthracene* ***M12***



M12 was prepared following the general procedure from (4-*t*-butylphenyl)acetylene (2.0 g, 12.6 mmol), 9-bromoanthracene (3.23 g, 12.6 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (265 mg, 0.38 mmol), CuI (72 mg, 0.38 mmol), PPh$_3$ (297 mg, 1.13 mmol) and piperidine (10 mL). The crude product was purified by double recrystallization from n-hexane. 3.29 g of **M12** was obtained as yellowish crystals (yield 78%; m.p. 171.7 °C). ^{1}H NMR (CDCl$_3$, 400 MHz, d): 1.38 (s, H^1, 9H), 7.46–7.48 (m, H^4, 2H), 7.5–7.61 (m, H^{12}, H^{13}, 4H), 7.69–7.72 (m, H^5, 2H), 8.01 (m, H^{14}, 2H), 8.42 (s,H^{16},1H), 8.65 (m,H^{11}, 2H);

^{13}CNMR ($CDCl_3$,100 MHz,d): 31.21(C^1), 34.87 (C^2), 85.71 (C^7), 100.97 (C^8), 117.65 (C^6), 120.6 (C^{10}), 125.51 (C^4), 125.63 (C^{12}), 126.48 (C^{13}), 126.83 (C^{11}), 127.43 (C^{16}), 128.63 (C^{14}), 131.20 (C^9), 131.42 (C^5), 132.55 (C^{15}), 151.83 (C^3); IR (DRIFT, KBr), cm^{-1}: 414 (w), 456 (w), 485 (w), 515 (w), 552 (w), 562 (s), 615 (m), 626 (w), 690 (w),739(s), 784(m),834(s),841(s), 871(w),880(m),927(w), 957(m), 1013 (m), 1040 (w), 1107 (m), 1142 (w), 1155 (w), 1178 (w), 1188 (w), 1199 (w), 1223 (w), 1267 (m), 1361 (m), 1393 (m), 1409 (m), 1440 (m), 1456 (m), 1503 (m), 1518 (m), 1557 (w), 1623 (w), 1670 (w), 1693 (w), 1715 (w), 1759 (w), 1805 (w), 1820 (w), 1828 (w), 1836 (w), 1910 (w), 1931 (w),1954 (w), 2861 (m),2902 (m),2963 (s), 3055 (m),3072 cm^{-1} (w); Anal. calc. for $C_{26}H_{22}$: C 93.37, H 6.63; found: C 93.40, H 6.67.

Polymerizations and copolymerizations of monomers M1, M2, M10-M12

General procedure

Polymerizations were carried out under argon atmosphere in a dry box using the Schlenk flask technique, adopting the procedure described earlier. A suspension of active catalyst species was prepared by dissolving $WOCl_4$ (20 mg, 0.06 mmol) and Ph_4Sn (25 mg, 0.06 mmol) in toluene (2 ml) and stirring the formed solution at 80°C for 15 min. Polymerization was started by adding the argon-bubbled solution of weighed amount(s) (typically about 300 mg for the above catalyst amount) of monomer(s) in toluene (3 ml) to the ripe catalyst system and the formed mixture was allowed to react under mixing at 60°C for 24 hours. The formed viscous polymer solution was then diluted with THF (10 ml) and dropwise added through an S2 sinter into stirred methanol (50 ml) to precipitate the polymer formed. The crude polymer was twice reprecipitated from the THF/methanol system, isolated by filtration, several times washed with methanol and dried in a vacuum oven to the constant weight to determine the isolated polymer yield by gravimetry.

The conditions for the $TaCl_5/Bu_4Sn$ catalyzed polymerizations were identical.

- *Poly(1-phenylhex-1-yne)* ***A0***

Monomer: 1-phenylhex-1-yne, M0, (300 mg, 1.9 mmol). Homopolymer A0 was obtained as a yellowish solid in the isolated yield of 267 mg (89 %). Anal. calculated for $C_{12}H_{14}$ (%): C 91.14, H 8.86; found: C 91.20, H 8.79. (For spectra see Results and Discussion)

- *Poly[1-(4-tert-butylphenyl)-6-chlorohex-1-yne]* ***A4***

Monomer: **M4**, (700 mg, 2.8 mmol). Homopolymer **A4** was obtained as a yellowish solid in the isolated yield of 322 mg (46 %). IR (drift, KBr-diluted, cm^{-1}): 1608 vw and 1506 s, 1363 s, 736 s, 654 m. Anal. calc. for $C_{16}H_{21}Cl$ (%): C 76.80, H 8.40, Cl 14.20, found: C 76.85, H 8.61, Cl 14.22.

- *Poly(M0-co-M1), molar feed ratio 75/25* ***A1***

Monomers: **M0** (567 mg, 3.6 mmol); **M1** (300 mg, 1.2 mmol). Copolymer **A1** was obtained as a yellowish solid in the isolated yield of 790 mg (91 %). Elemental analysis: found (%): C 86.11, H 8.86, Cl 4.56.

- *Poly(M0-co-M1), molar feed ratio 50/50* ***A2***

Monomers: **M0** (189 mg, 1.2 mmol); **M1** (300 mg, 1.2 mmol). Copolymer **A2** was obtained as a yellowish solid in the isolated yield of 342 mg (70 %). Elemental analysis: found (%): C 85.70, H 8.94, Cl 5.22.

- *Poly(M0-co-M1), molar feed ratio 25/75* ***A3***

Monomers: **M0** (63 mg, 0.4 mmol); **M1** (300 mg, 1.2 mmol). Copolymer **A3** was obtained as a yellowish solid in the isolated yield of 268 mg (74 %). Elemental analysis: found (%): C 83.24, H 8.91, Cl 7.77.

- *Poly[1,2-bis(4-tert-butylphenyl)ethyne]* ***P(M10)***

Monomer: **M10** (348 mg, 1.2 mmol). Polymer **P(M10)** was obtained as a yellowish powder in the isolated yield of 247 mg (71%). IR (DRIFT, KBr, cm^{-1}): 490 (w), 560 (w), 575 (s), 609 (w), 743 (w), 825 (vs), 855 (m), 878 (w), 900 (w), 921 (w), 936 (w), 947 (w), 1017 (s), 1066 (m), 1109 (s), 1184 (w), 1202 (m), 1253 (w), 1270 (s), 1362 (s), 1392 (m), 1403 (w), 1461 (m), 1475 (m), 1511 (s), 1609 (s), 1767 (m), 1892 (m), 2866 (m), 2962 (vs), 3029 (w), 3047 (w), 3085 (w); Anal. calc. for C22H26: C 90.98, H 9.02; found: C 81.54, H 9.98.

- ***Poly(2-[(4-tert-butylphenyl)ethynyl]naphthalene) P(M11)***

Monomer: **M11** (341 mg, 1.2 mmol). Polymer **P(M11)** was obtained as a yellowish powder (isolated yield 150 mg, 44%). IR (DRIFT, KBr) cm^{-1}: 473 (vs), 570 (s), 741 (s), 808 (vs), 1016 (vs), 1261 (vs), 1362 (w), 1393 (w), 1507 (m), 1598 (m), 1773 (w), 1891 (m), 1936 (s), 2866 (m), 2903 (m), 2962 (m), 3055c (w); Anal. calcd for $C_{22}H_{20}$: C 92.91,H 7.09; found: C 89.82, H 7.21.

- ***Poly(9-[(4-tert-butylphenyl)ethynyl]anthracene) P(M12)***

Monomer: **M12** (401 mg, 1.2 mmol). Polymer **P(M12)** was obtained as low-molar-mass oligomers contaminated by residual solvent (isolated yield 80 mg, 20%). mmol).

Modification of polymers A1 to A4 by substitution of Cl for N3 groups

General procedure

A weighed amount (tenfold stoichiometric excess with respect to Cl atoms) of NaN_3 was added into a polymer (**A1** to **A4**) solution in DMF (10 ml) and the reaction mixture was kept under stirring at 40°C for 24 hours. Then it was poured to distilled water and precipitated modified polymer (further denoted as B1 to B4, respectively) was then twice reprecipitated using the THF/methanol system, filtered, and dried to the constant weight.

- ***A1** modified by NaN_3- **B1***

Starting polymer: **A1** (400 mg). Modified polymer **B1** was isolated as a yellowish solid in the yield of 320 mg (80 %). Elemental analysis: found (%): C 87.29, H 8.72, N 2.16, Cl 1.79.

- ***A2** modified by NaN_3- **B2***

Starting polymer: **A2** (250 mg). Modified polymer **B2** was isolated as a yellowish solid in the yield of 188 mg (75 %). Elemental analysis: found (%): C 86.19, H 8.69, N 2.56, Cl 2.51.

- ***A3** modified by NaN_3- **B3***

Starting polymer: **A3** (200 mg). Modified polymer **B3** was isolated as a yellowish solid in the yield of yield 148 mg (74 %). Elemental analysis: found (%): C 82.13, H 10.27, N 4.11, Cl 3.46.

- ***A4** modified by NaN_3- **B4***

Starting polymer: **A4** (250 mg). Modified polymer **B4** was isolated as a yellowish solid in the yield of 238 mg (95 %). Elemental analysis: found (%): C 76.08, H 8.39, N 4.59, Cl 10.91.

Modification of B1 to B4 by click reaction N3 groups with PN

General procedure

A weighed amount of a polymer (**B1** to **B4**), **PN** (molar ratio $PN/N_3 = 1:2$) and Cu_2I_2 (5 mole % with respect to **PN**) were dissolved in piperidine (5 ml) in a dry Schlenk flask, a solution formed was several times degassed and flushed with argon and then allowed to react under stirring at 40°C for 4 hours. Then it was through a frit (to remove solid catalyst residues) dropwise added into methanol, the obtained crude polymer was twice reprecipitated from the system THF/methanol, several times washed with methanol and dried in a vacuum oven. The polymer was then dissolved in $CHCl_3$ and its solution was three to five times extracted with aqueous solution of ethylenediaminetetraacetic acid (0.1 M) to remove residual copper ions. The purified polymer solution was five times washed with water, then poured to methanol and the precipitated polymer was isolated in a usual way.

- ***B1** modified by **PN**- **C1***

Starting polymer: **B1** (250 mg), **PN** (48.8 mg). Modified polymer **C1** was isolated as an intensely yellow solid in the yield of 238 mg (82 %). Elemental analysis: found (%): C 85.65, H 8.27, N 3.12, Cl 1.52.

- ***B2** modified by **PN**- **C2***

Starting polymer: **B2** (150 mg), **PN** (34.8 mg). Modified polymer **C2** was isolated as an intensely yellow solid in the yield of 154 mg (86 %). Elemental analysis: found (%): C 89.76, H 8.21, N 3.59, Cl 2.17.

- ***B3** modified by **PN**- **C3***

Starting polymer: **B3** (100 mg), **PN** (37.32 mg). Modified polymer **C3** was isolated as an intensely yellow solid in the yield of 76 mg (58 %). Elemental analysis: found (%): C 80.57, H 7.90, N 5.19, Cl 3.94.

- ***B4** modified by **PN**- **C4***

Starting polymer: **B4** (200 mg), **PN** (82.34 mg). Modified polymer **C4** was isolated as an intensely yellow solid in the yield of 142 mg (53 %). Elemental analysis: found (%): C 75.76, H 7.65, N 5.56, Cl 7.68.

Quaternization modification of Cl-containing PA with N-methylimidazole

Into 50ml glass vial were added polymer **A4**/**A5** (100 mg). 5 ml methanol was injected into the vial to disperse the polymer. N-methylimidazole (420 mg, 0.41 ml) was then added. The resulting dispersion was heated at 60°C for 48 hours. Then THF (2 ml) was added in order to increase the solubility of the polymer in the reaction mixture and the temperature was increased to 65°C. The mixture was heated overall for 4 days till complete dissolving of the polymer. Then the heating was continued for another day. The solvent was evaporated in vacuum, the resulting crude product was purified by washing with THF and hexane and reprecipitation.

Polymerizations and copolymerizations of PN and PN1 with various monosubstituted acetylenes

General procedure

All the polymerizations were catalysed by [Rh(nbd)acac] complex and were performed in CH_2Cl_2. The polymerizations aimed at the preparation of the linear homo- and copolymers were performed at room temperature; the reaction time was either 3 h or 24 h. The initial concentration of catalyst was 7.5 mmol/l, the initial overall concentration of comonomers was 0.15 mol/l. Copolymerization of **PN** with **M3** is described as a typical example: 48 mg (0.15 mmol) of **PN** and 95 mg (0.6 mmol) of **M3** were placed in a screw cap vial and dissolved in 4 ml CH_2Cl_2. Then a solution of 11 mg of [Rh(nbd)acac] (0.0375 mmol) in 1 ml CH_2Cl_2 was added into the solution of the monomers under stirring, which started the copolymerization. The time course of the reaction was monitored by SEC: samples of the volume of 0.01 ml were withdrawn from the reaction mixture at given times. The withdrawn samples were diluted with THF and injected into SEC columns in order to estimate the yield of the copolymer from the resulting SEC chromatograms. After 24 h, the reaction mixture was poured into methanol (40 ml) and the precipitated copolymer was separated, washed repeatedly by methanol and dried in vacuum at room temperature to the constant weight. The yield of the copolymer was determined gravimetrically.

Preparation of PA type networks

The polymerizations aimed at the preparation of the homo- and copolymer networks were performed at 75°C; the reaction time was 72 h. The initial concentrations were: $[\text{Catalyst}]_0$ = 18 mmol/L, the overall concentration of comonomers = 0.6 mol/l. Copolymerization of **PN** with **M9** is described as a typical example: 96 mg (0.3 mmol) of **PN** and 546 mg (2.7 mmol) of **M9** were dissolved in 4 ml CH_2Cl_2 and the solution was transferred into a thick-wall glass ampoule. Then a solution of 26 mg of [Rh(nbd)acac] (0.09 mmol) in 1 ml CH_2Cl_2 was added into the solution of the monomers under stirring. The ampoule with the reaction mixture was flushed with argon, sealed and placed in a laboratory oven at 75 °C for 72 h. Then the ampoule was opened and the formed copolymer monolith was mechanically pulverized and repeatedly washed with CH_2Cl_2 and finally dried in vacuum at room temperature. The yield of the network was determined gravimetrically.

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