Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 6501–6509
polymer
www.elsevier.com/locate/polymer

# Synthesis and characteristics of polymacromonomers composed of alternating binaphthalene–phenylene main chain and polystyrene side chains

I. Cianga [a,b], V.M. Mercore [a,b], M. Grigoras [a], Y. Yagci [b,*]

[a] "P. Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica Voda Alley, Iasi 700487, Romania
[b] Istanbul Technical University, Department of Chemistry, Maslak 34469, Istanbul, Turkey

Received 7 June 2007; received in revised form 31 August 2007; accepted 1 September 2007
Available online 5 September 2007

## Abstract

Well-defined polystyrene (PSt) based polymers containing middle- or end-chain 2,5- or 3,5-dibromobenzene moieties, prepared by Atom Transfer Radical Polymerization (ATRP) were implied in Suzuki type couplings with 1-naphthalene boronic acid. The resulting polymers, containing a conjugated sequence with 1-naphthyl groups at the extremities, were used as macromonomers in chemical oxidative polymerization in the presence of anhydrous $FeCl_3$. Polyarylenes, with a hairy-rod structure, having binaphthyl groups in the main chain and the respective PSt chains as lateral substituents, were obtained.

All the starting, intermediate or final polymers were structurally analyzed by spectral methods ($^1$H NMR, IR) and GPC measurements. Thermal behavior of the macromonomers and final polymers was investigated by Differential Scanning Calorimetry (DSC) analyses. Optical properties of the polymers were followed by UV and fluorescence spectroscopies. The absorption spectra of the polymers indicate only a limited extend of conjugation as compared to the naphthalene functionalized polystyrenes. However, in the emission spectra of the polymers, a bathochromic shift with respect to the monomers was observed in all cases.

*Keywords:* Macromonomers; Suzuki coupling; Polyarylenes

## 1. Introduction

Semiconducting polymers have been shown to be attractive candidates in plastic electronic devices because of their compatibility with high-throughput, low-cost processing techniques and their capability to be precisely functionalized through the techniques of organic synthesis to afford desired performance attributes [1,2]. Considerable research efforts have been directed toward the preparation of well-defined conjugated polymers with improved solubility, processability and stability characteristics by incorporating relatively long and flexible side chains onto the polymers backbone [3,4]. As a solution for this challenge the combination between living/controlled polymerization methods (ATRP, ROP) [5] with different organometallic polycondensations specific in synthesis of conjugated polymers was employed [6,7].

In our earlier studies, we reported the synthesis of poly(phenylenes) (PPs) with polystyrene (PSt) side chains starting from designed ATRP initiators [8–12]. The synthesis of poly(tetrahydrofuran) PTHF based macromonomers by cation ring opening polymerization (CROP) and PPs with PTHF or with PTHF/PSt alternating side chains which were synthesized by Suzuki or Yamamoto methods [13] was reported as well. Poly(ε-caprolactone) or poly(2-methyloxazoline)s substituted polyarylenes were also obtained by combining ring opening polymerization with transition metal catalyzed polymerization methods [14,15]. Other macromonomers and the corresponding PPs were also designed [6,7]. Starting from well-defined

---

* Corresponding author.
*E-mail address:* yusuf@itu.edu.tr (Y. Yagci).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.09.002

macromonomers having an end- or middle-chain conjugated sequence with oxidable moieties at the ends, comb-like copolymers with a rigid coil and flexible macromolecular substituents were synthesized by cation-radical polymerization [16–20].

Conjugated polymers containing naphthalene nucleus compose a unique class of electrically active materials [21]. Polybinaphthalenes are helical polymers if they are appropriately designed and show excellent thermal, chemical and photochemical stabilities [22]. The angle between the rings ranges from 60° to 120° and therefore conjugation between the two naphthalene units is minimal [23]. They can be optically active conjugated polymers if their synthesis starts from chiral 1,1′-binaphthyl derivatives [22–25]. On the other hand, naphthyl-substituted derivatives yield optically inactive polybinaphthalenes. Therefore, 1-bromonaphthalene was used in Ullman [26] or Williamson [27] condensation with various counterparts and in palladium-catalyzed *N*-arylation reaction with *p*-anisidine [28]. Other derivatives of naphthalene were employed for synthesis of a bis-ethynyl-bis naphthyl monomer that was polymerized in the presence of Rh or Pd complexes [21]. 1-Naphthyl amine, 1-naphthyl aldehyde [29] and 2-hydroxy-1-naphthaldehyde [30] were used to synthesize monomers containing Schiff base functionality between naphthyl moieties. 1-Naphthyl boronic acid was condensed with dibromine [31] or ditriflate aromatic derivatives [26].

In the present work, 1-naphthyl boronic acid was used for the synthesis of well-defined polystyrene (PSt) macromonomers containing a conjugated sequence with 1-naphthyl groups at the extremities. Their oxidative polymerization for obtaining polyarylenes with 1,1′-binaphthyl moieties in the main chain and having the respective PSt fragments as lateral substituents is also reported.

## 2. Experimental

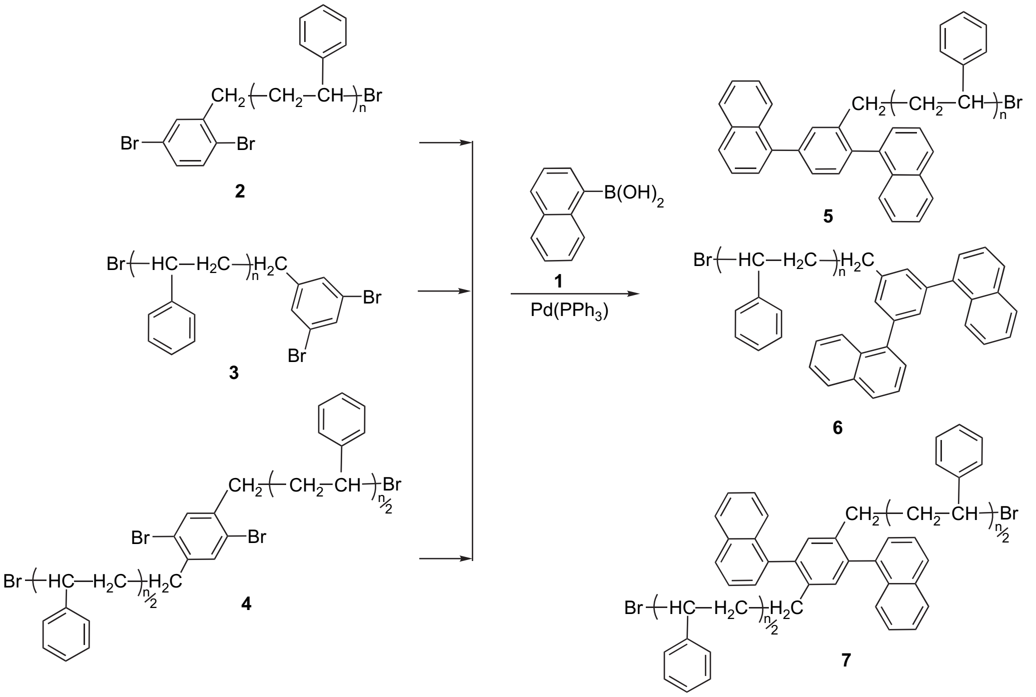
### 2.1. Materials

All solvents were purified and dried by usual methods. Anhydrous $FeCl_3$ (Fluka) was used as received. 1-Naphthyl boronic acid (**1**, Scheme 1) was synthesized starting from 1-bromonaphthalene and trimethyl borate using a previously reported procedure [16,26]. M.p. 109–110 °C; $^1H$ NMR (acetone-$d_6$) (*δ*, ppm): 8.63–8.25 (m, 1H, naphthyl-4 poz.), 7.92–7.52 (m, 4H, OH, naphthyl-5 and 8 poz.), 7.52–7.12 (m, 4H, naphthyl-2, 3, 7 and 7 poz.); IR ($cm^{-1}$): (3300, OH), 1360, 1230 (B–O).

The synthesis of the starting PSt based macromonomers (**2–4**, Scheme 1) was performed by ATRP of styrene in the presence of 1,4-dibromo-2-(bromomethyl)benzene, 1,3-dibromo-5-(bromomethyl)benzene, or 1,4-dibromo-2,5-di(bromomethyl)benzene as initiator and the procedures were previously reported [8,10].

### 2.2. General procedure for the synthesis of naphthalene functionalized macromonomers by Suzuki coupling

An 100-mL three necked round bottom flask equipped with a condenser, a rubber septum, nitrogen inlet–outlet and magnetic stirrer was charged with 10 mL, 1 N $NaHCO_3$ aqueous solution and 15 mL THF. Solvents were previously desaerated by bubbling nitrogen over a period of 30 min and the mixture was refluxed under nitrogen for 3 h. A 20-mL three necked round bottom flask equipped in the same way as the previous one was charged under inert atmosphere with 0.208 mmol of **2**, **3** or **4** (Scheme 1), 0.143 g (0.833 mmol), 1-naphthyl



Scheme 1. Synthesis of PSt type macromonomers with naphthyl groups in the conjugated sequence.

Table 1
Molecular weights of the polymers calculated from $^1$H NMR and GPC data

| Bromo-macromonomer | | | Naphthyl-macromonomer | | | Polyarylene | |
|---|---|---|---|---|---|---|---|
| Code | $M_{n,\ ^1H\ NMR}$ | $M_{n,\ GPC}$; P.D. | Code | $M_{n,\ ^1H\ NMR}$ | $M_{n,\ GPC}$; P.D. | Code | $M_{n,\ GPC}$; P.D. |
| **2** | 1970 | 2025; 1.24 | **5** | 2470 | 2700; 1.38 | **5P** | 19200; 2.30 |
| **3** | 2030 | 2020; 1.28 | **6** | 2680 | 2720; 1.43 | **6P** | 17800; 1.92 |
| **4** | 4200 | 4000; 1.35 | **7** | 4660 | 4890; 1.46 | **7P** | 28400; 1.71 |

boronic acid (**1**) and 0.01 g (0.008 mmol) Pd(PPh$_3$)$_4$. The mixture of solvents was introduced with a syringe through the septum. The reaction was maintained under vigorous stirring and with the exclusion of oxygen and light. The naphthyl functionalized polymers (**5**, **6** or **7**) were separated by precipitation in methanol, filtrated, washed several times with water to remove the inorganic salts and dried. The PSt based macromonomers functionalized with naphthyl groups were purified by passing through a silicagel column using THF as eluent and reprecipitating into methanol. Some characteristics are presented in Table 1.

### *2.3. General procedure for chemical oxidative polymerization in the presence of anhydrous FeCl$_3$ of naphthyl functionalized macromonomers*

A typical procedure for oxidative polymerization of naphthyl functionalized polystyrene is as follows:

A 25-mL round bottom flask equipped with magnetic stirrer and a lateral neck with a dropping funnel was used. The system was vacuumed and back-filled with dry nitrogen several times. CHCl$_3$ (7 mL) and 0.08 g (0.492 mmol) FeCl$_3$ were introduced under inert atmosphere. A solution of 0.07 mmol polystyrene with naphthyl groups (**5**, **6** or **7**) in 2 mL CHCl$_3$ was added dropwise during 20 min. The reaction mixture was stirred at room temperature for 4 days. After that time the polymer was separated by precipitation in methanol and dried. Polyarylenes (**5P**, **6P** or **7P**, Scheme 2) were redissolved in CHCl$_3$ and reprecipitated in methanol.

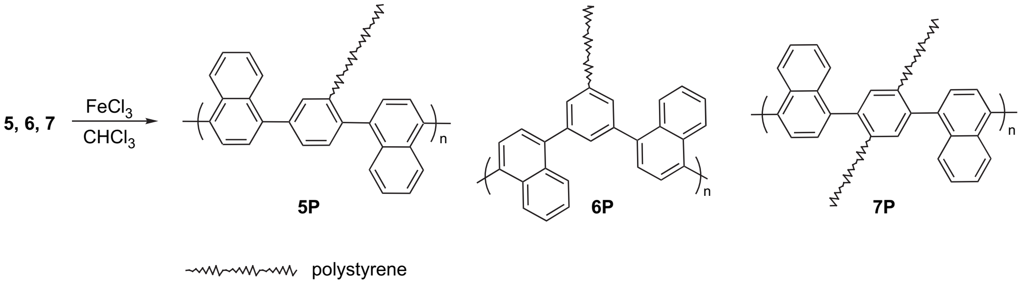
### *2.4. Analysis*

$^1$H NMR spectra were recorded on a Bruker 250 MHz spectrometer with CDCl$_3$ or acetone-$d_6$ as solvent and TMS as the internal reference. Infrared spectra were registered on KBr pellets using a Specord M80 spectrometer. GPC analyses were performed with a set-up consisting of a Waters Pump (model 600E) and three ultrastyragel columns with porosities 104 Å, 500 Å and 100 Å, respectively. THF was used as the eluent at a flow rate of 1 mL min$^{-1}$ and the detection was achieved with a Waters Differential Refractometer (model 410). Molecular weights were calculated using polystyrene standards. Ultraviolet measurements were performed on a Specord M42 spectrophotometer from CHCl$_3$ solutions with the same concentration (0.0428 g L$^{-1}$). DSC analyses were performed on a Perkin Elmer Differential Scanning Calorimeter DSC-6, in the range 20–300 °C, under nitrogen, with a scan rate of 10 °C min$^{-1}$. Fluorescence measurements were performed using the model LS-55 spectrometer of Perkin and Elmer.

## 3. Results and discussion

We showed in our previous works [8–11] that by using proper initiators, well-defined phenyldibromo functional polymers can be obtained by ATRP of styrene (**2**–**4** from Scheme 1). They have low molecular weights and polydispersities (listed in Table 1) and could be used directly as macromonomers in Suzuki or Yamamoto type polycondensation reactions for the synthesis of conjugated polymers with macromolecular side chains. Moreover, they could also be modified by reacting with low molecular weight 2-thiophene boronic acid in Suzuki type couplings and macromonomers having conjugated sequences ended with oxidable thienyl moieties were obtained, as precursors for poly(thienyl arylene)s with macromolecular side chains [16,17]. In the present work, for the synthesis of naphthalene functionalized PSt type macromonomers, precursor polymers **2**–**4** were reacted with 1-naphthyl boronic acid as depicted in Scheme 1.

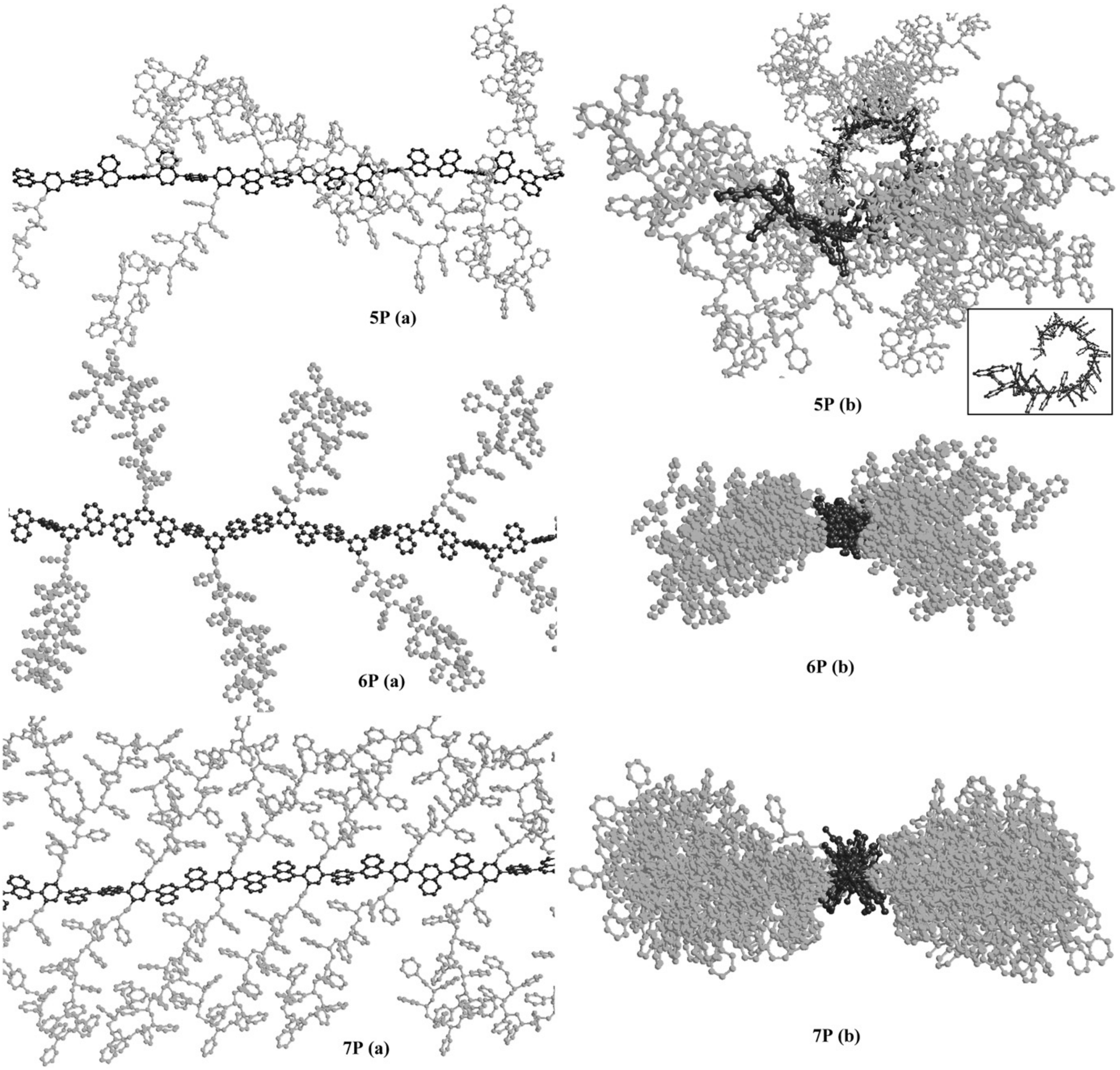
The reaction between aryl halides and aryl boronic acids (Suzuki coupling) [32] is one of the most convenient method for C–C coupling. The reaction is quite simple and insensitive



Scheme 2. Synthesis of polyarylenes with PSt side chains by chemical oxidative polymerization.

to moisture. Furthermore, this coupling reaction can be applied to monomers carrying functional groups [33]. In this case, three PSt macromonomers containing a middle- or end chain conjugated sequence (1-naphthyl-1,4-(or 1,3)-phenylene-1-naphthyl) (**5**, **6**, or **7** in Scheme 1) could be prepared by reacting **2**, **3** or **4** with 1-naphthyl boronic acid in a Pd catalyzed coupling. The reaction conditions (high excess of boronic acid and long reaction times) were chosen to assure complete functionalization. As can be seen from Table 1, a slight increase of the molecular weights of the polymers, as compared to the starting dibrominated compounds took place. This fact can not only be attributed to the effect of the newly introduced naphthalene moieties but also to a partial fractionation of the polymers during the reprecipitation processes. As the conjugated sequences contain naphthalene oxidable groups at both the ends, these compounds are chosen as candidates for the synthesis of conjugated polymers with macromolecular side chains by oxidative polymerization (chemical or electrochemical). Using anhydrous $FeCl_3$ as the chemical oxidant, polyarylenes containing naphthalene moieties in the main chain were synthesized as depicted in Scheme 2. Some characteristics are shown in Table 1.

The molecular weights measured by GPC based on PSt standards, should be taken as the minimum estimation because of the highly branched or comb-like structure of the obtained structures. The polymers have similar solubilities in usual organic solvents and processability properties with those of the starting macromonomers.



5P (a)

5P (b)

6P (a)

6P (b)

7P (a)

7P (b)

Fig. 1. Three dimensional ball and stick models of polyarylenes: up (a) and frontal (b) images.

Polymacromonomers, graft polymers and branched polymers exhibit unique properties which are generally not observed in their linear counterparts. In a particular case, homopolymerization of macromonomers provides comb polymers or polymer brushes [4]. In our case, due to the rigidity of the main chain, the synthesized polymers belong to the class of “hairy-rod molecules” [34], a concept that in fact merges with that of cylindrical polymer brushes [7]. By comparing with conventional polymers, the importance of such cylindrical objects consists in that their diameter is in the order of a few nanometers rather than few angstroms. As a consequence, the rigidity is so high that the persistence length of an individual chain is not in the order of 10 nm, but may instead exceed 50 nm. Such cylindrical rods, due to their high bending moduli, could potentially be used for constructions in the nanometer scale [7]. On the other side, introduction of branches onto a polymer chain facilitates control over the processability and rheological properties and moreover such copolymers show different morphologies due to the microscopic phase separation in the solid state and selective solvation in solution. Model molecules for polymer fragments were obtained by molecular mechanics (MM+). The three dimensional ball and stick models are shown in Fig. 1, obtained after energy minimization. From Fig. 1 it becomes clear that the fact that the position of the polymeric side chain substituents in rapport with both phenylene ring and binaphthalene sequences influence the main chain conformation. Thus, polymers **6P** and **7P** have a pronounced cylindrical symmetry, slightly modified due to the steric repulsion between densely grafted side chains [7]. In the case of **5P**, the model shows a helicoidal conformation of the main chain. This difference, as compared to **6P** and **7P**, could be due to the presence of PSt side chains at the 2 position of phenylene ring, namely due to an unsymmetrical manner of the substitution.

### 3.1. $^{1}$H NMR analysis

In the $^{1}$H NMR spectra of polystyrene starting macromonomers **2–4**, obtained by ATRP, the peak from about 4.5 ppm corresponding to the last CH proton, directly linked to the final bromine atom, was used for calculating molecular weights. The results are presented in Table 1 and are close to those obtained from GPC measurements (PSt standards). In the $^{1}$H NMR spectra of PSt polymers with naphthalene moieties (**5–7**), the peaks corresponding to the newly introduced groups appear outside the region 7.4–6.2 ppm specific to the PSt aromatic protons (Figs. 2 and 3), clearly indicate the completion of functionalization. In the mean time, the peaks could be used for recalculating the molecular weights of the polymers by comparing the integrals of the protons from naphthalene groups with those of PSt. The results are again close to those obtained by GPC measurements (Table 1).

The $^{1}$H NMR spectra of the polyarylenes (polymers **5P**, **6P** and **7P**) are similar with those of the corresponding macromonomers (Fig. 2, **5P**). In this case it is not possible to estimate the molecular weight of the polymers by $^{1}$H NMR calculations. Despite this, the ratio between the two groups of protons of the naphthalene moieties is slightly changed (the integral of the group of protons from higher ppm becomes lower) due to the loss of two protons for every repeating unit in the oxidative polymerization. Moreover, by recalculating the molecular weights of the repeating units, taking into account the new number of protons for the naphthalene moieties, similar values with those of the starting macromonomers are found. This result shows both that the polyarylenes are formed and no degradation of PSt side chains took place.

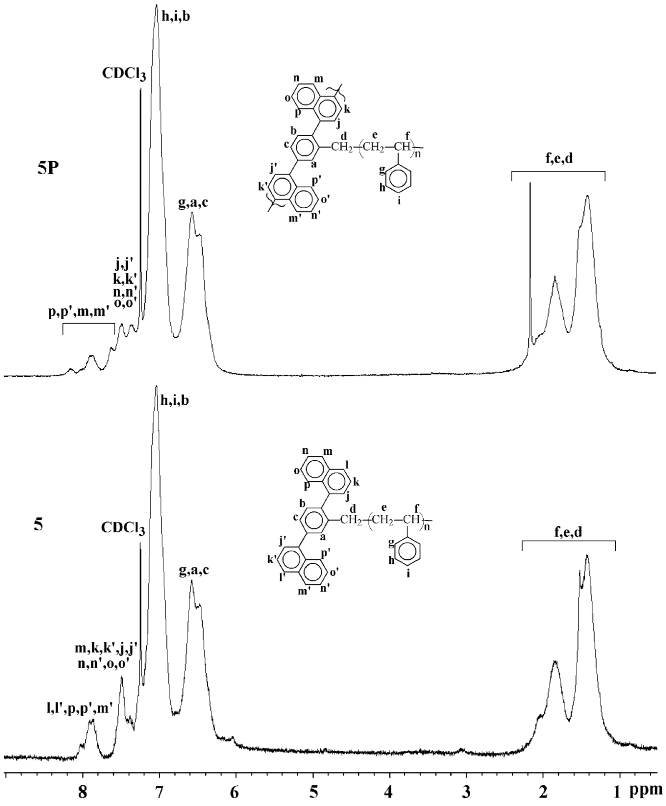


Fig. 2. $^{1}$H NMR spectra of naphthyl functionalized macromonomer **5** and the corresponding polyarylene **5P**.

### 3.2. IR analysis

The IR spectra of all the polymers display usual PSt strong absorptions at 3058 cm$^{-1}$, 3025 cm$^{-1}$ (aromatic CH stretching), 2970 cm$^{-1}$, 2851 cm$^{-1}$, 2848 cm$^{-1}$ (aliphatic CH stretching), 1937 cm$^{-1}$, 1867 cm$^{-1}$, 1798 cm$^{-1}$, 1665 cm$^{-1}$ and 760 cm$^{-1}$ (out-of-plane hydrogen deformation), 1598 cm$^{-1}$, 1489 cm$^{-1}$, 1446 cm$^{-1}$ (in-plane-bend-stretching vibrations of phenyl ring), 758 cm$^{-1}$ and 697 cm$^{-1}$ (out-of-plane hydrogen deformation). In the case of naphthalene functionalized macromonomers (**5–7**), due to the presence of naphthalene groups some changes were noticed. Fig. 4 presents the IR spectra of polymers **3**, **6** and **6P**.

Typical changes can be seen when the spectra of **3** and **6** were compared. A new peak centered at 774 cm$^{-1}$ ($\gamma$ CH of *ortho*-disubstituted benzene ring from naphthalene) group is present in the spectrum of **6**. The absorption from 800 cm$^{-1}$

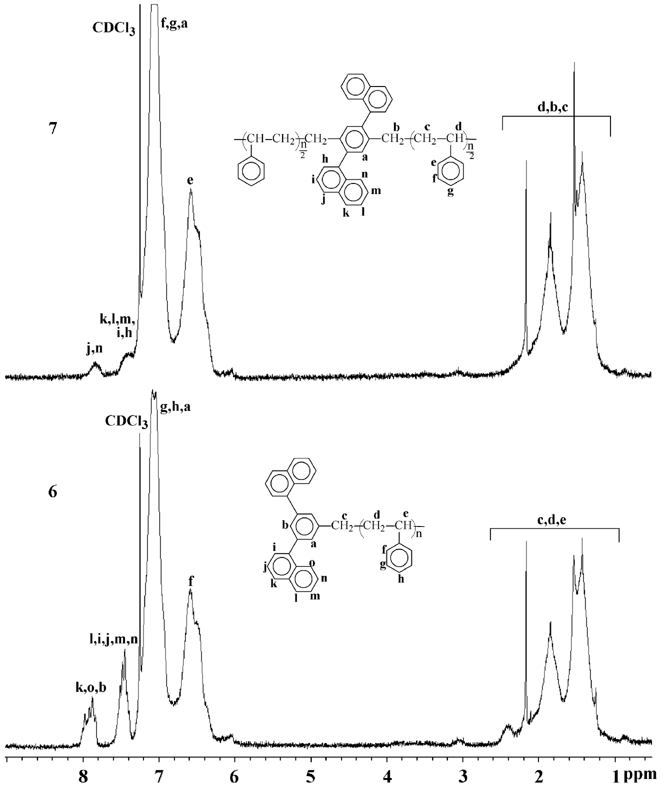


Fig. 3. $^1$H NMR spectra of naphthyl functionalized macromonomers **6** and **7**.

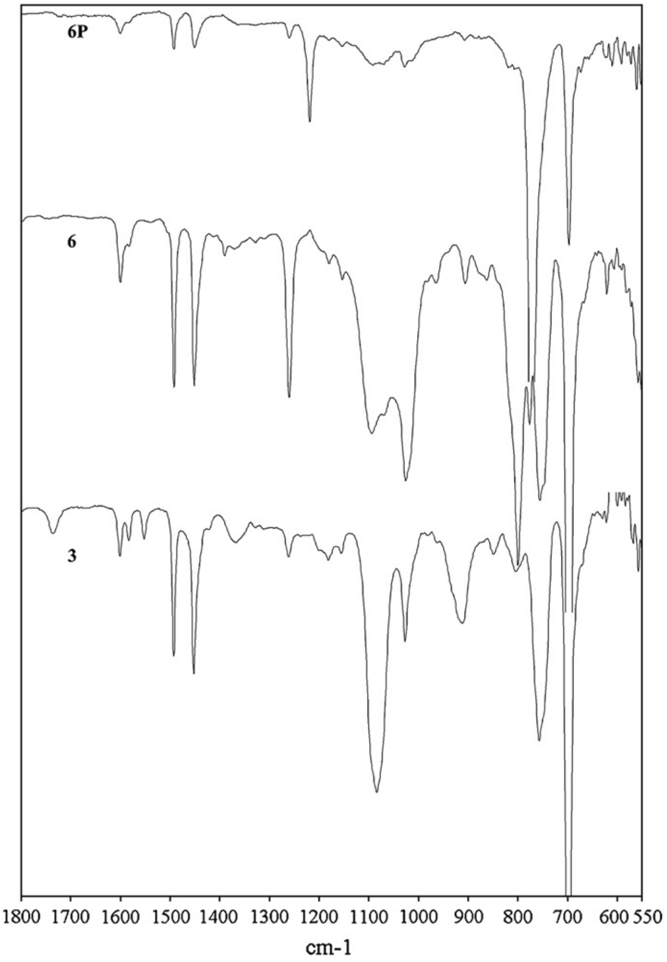


Fig. 4. IR spectra of polymers **3**, **6** and **6P**.

in the spectrum of **3** has an increased intensity in the case of **6** (γ CH of 1,2,3-trisubstituted benzene ring from naphthalene moiety). Other new or with increased intensity peaks, from 969 cm$^{-1}$, 1024 cm$^{-1}$ (β CH), or 1259 cm$^{-1}$ ($\delta$ CH) are also due to the 1-naphthyl specific absorptions. From the spectrum of **6P** it can be noticed that the disappearance of peaks from the region 850–950 cm$^{-1}$ is due to the changes in the naphthalene rings' substitution. A new shoulder at about 816 cm$^{-1}$ is attributed to γ CH of 1,2,3,4-tetrasubstituted benzene rings form the 1,4-naphthalene groups.

Similar observations were made also in the case of the other macromonomers and corresponding polymers.

### *3.3. DSC analysis*

The thermal behavior of the synthesized polymers was investigated using Differential Scanning Calorimetry (DSC), under nitrogen, the heating rate being 10 °C min$^{-1}$.

In the case of dibrominated polymers **2**–**4**, the endothermic peaks found at 80 °C, 82 °C and 98 °C, respectively, are attributed to the glass transition characteristic of polystyrene. The last value is higher due to the increased molecular weight of **4** as comparing with **2** and **3**.

The DSC traces of **5**–**7** show that the glass transition of the polymers increases significantly (94 °C, 96 °C and 105 °C, respectively) due to the effect of the conjugated sequences on the mobility of PSt chains. This effect is more visible in the corresponding polyarylenes, where the $T_g$ is less evident due to the limitation of the PSt chains mobility linked to a rigid backbone and appears at higher values (124 °C for **6P** and 118 °C for **7P**). In the case of **5P**, the transition temperature is missing and can be due to the increased length of the main chain as compared with the other two polymers. In the case of **6P**, the conjugation length can be affected by 1,3-linkage at the benzene ring originating from the rest of ATRP initiator as comparing with 1,4-linkage in **5P**. In the case of **7P**, the more dense substitution with PSt chains can determine an increased rotation angle between the aromatic rings due to the steric hindrances. As a consequence it results in a decrease in the conjugation length of the main chain.

### *3.4. Optical properties*

The absorption and emission spectra of the compounds were investigated in CHCl$_3$ solutions (Fig. 6). Some data are given in Table 2.

Dibrominated macromonomers **2**–**4** show UV absorptions situated between 225–260 nm with tails until 280–320 nm. Generally, a substituted group affects the electronic and optical properties of a polymer by its electronic nature and its size (sterical hindrances). In our case, macromonomers are of short chain styrene type and contain a monosubstituted or disubstituted 1,4-dibromobenzene or monosubstituted 1,3-

Table 2
Optical properties of the macromonomers and polymers in $CHCl_3$ solutions (0.0428 g $L^{-1}$)

| Bromo-macromonomer | | Naphthyl-macromonomer | | | Polyarylene | | |
|---|---|---|---|---|---|---|---|
| Code | $\lambda_{max}$ abs. (nm) | Code | $\lambda_{max}$ abs. (nm) | $\lambda_{max}$ emis. (nm) | Code | $\lambda_{max}$ abs. (nm) | $\lambda_{max}$ emis. (nm) |
| **2** | 225, 258 | **5** | 233, 260, 294 | 374 | **5P** | 233, 262, 301 | 422 |
| **3** | 228, 258 | **6** | 229, 260, 295 | 367 | **6P** | 230, 269, 305 | 407 |
| **4** | 228, 260 | **7** | 229, 260, 285 | 365 | **7P** | 230, 262, 294 | 400 |

dibromobenzene ring as a terminal group. Therefore, the observed UV absorptions are mainly assigned to π–π* transitions in phenyl rings from polystyrene and from terminal groups. The last absorptions are red-shifted due to methylene and bromine substituents and are dependent on position and number of the substituents (Fig. 5).

The addition of 1-naphthyl moieties in the polymers **5–7** causes an appearance of a new maximum of absorbance between 285–294 nm. This is due to the newly introduced aromatic rings and the resulting conjugated sequence is 1,4-naphthalene-1,4 (or 1,3) phenylene-1,4-naphthalene. It would be expected that the conjugation lengths in the corresponding polymers increase substantially and consequently the maximum of absorption is more clearly red-shifted. Despite this, there is only a limited increase of the wavelength of the maximum of absorptions in the polyarylenes **5P**, **6P** and **7P** as compared to their corresponding macromonomers. This fact can be explained by the effective conjugation length of the main chain. Due to the bulky macromolecular substituents (PSt chains) the torsion angles between the 1,4-naphthalene groups in the 4,4′-binaphthyl moieties (Fig. 1) are increased and the effective conjugation length in such kind of polymers is restricted to several aromatic units that are arranged in a conformation close to planarity. Therefore, the difference between naphthalene macromonomers and their polymers is limited. This aspect is more evident in the case of macromonomer **7** and polyarylene **7P** that have two PSt chains at every repeating unit, as compared with the other studied polymers. In this case, the sterical influences are higher and the

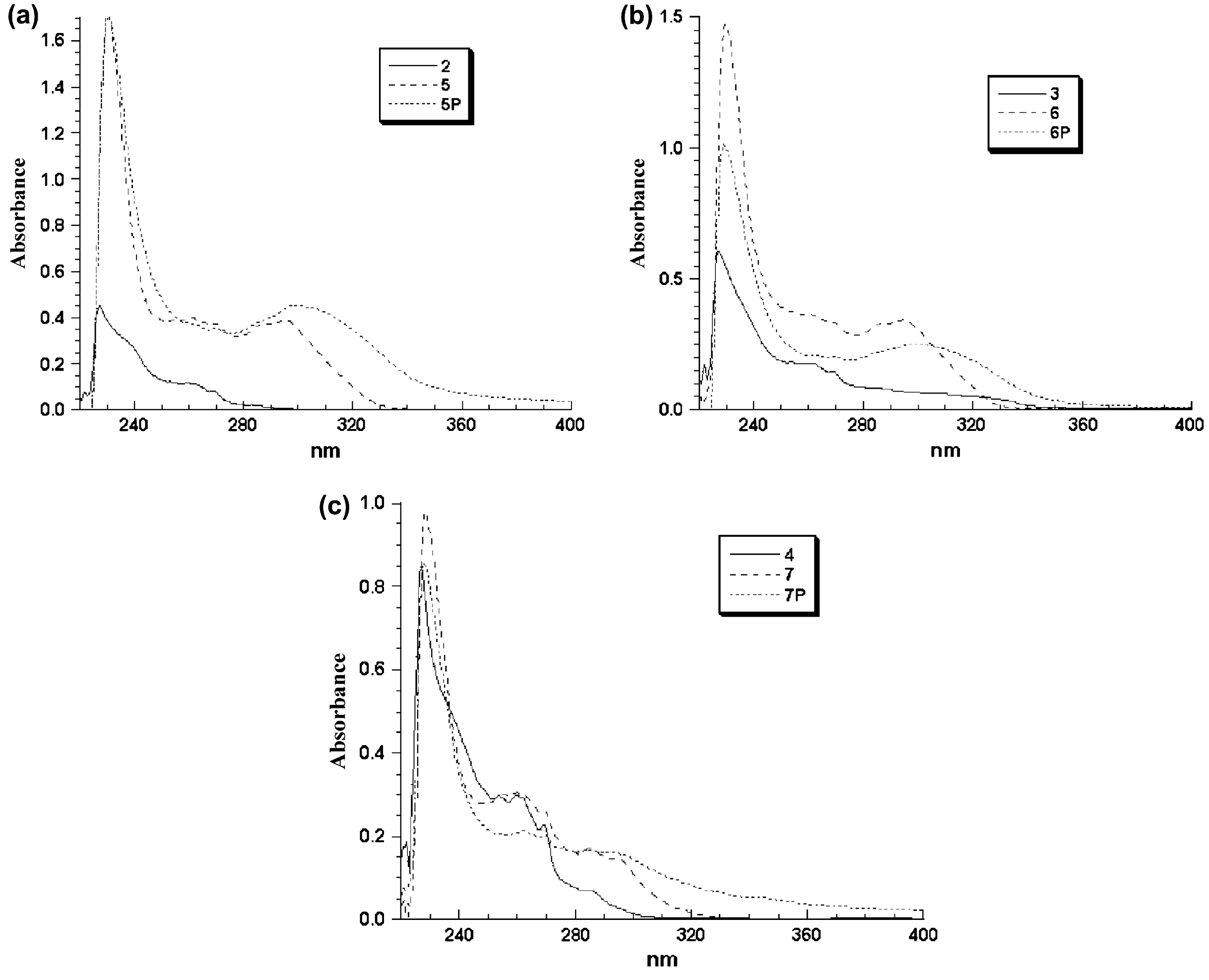


Fig. 5. UV spectra of polymers **2**, **5** and **5P** (a), **3**, **6** and **6P** (b), **4**, **7** and **7P** (c).

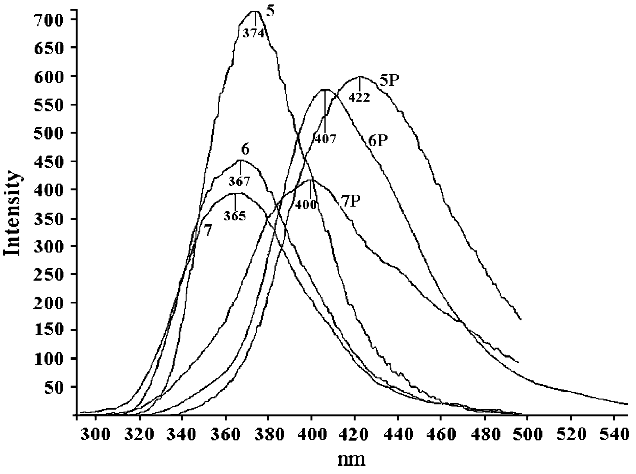


Fig. 6. Emission spectra of **5** ($\lambda_{exc.} = 240$ nm), **6** ($\lambda_{exc.} = 230$ nm), **7** ($\lambda_{exc.} = 230$ nm), **5P** ($\lambda_{exc.} = 240$ nm), **6P** ($\lambda_{exc.} = 298$ nm), **7P** ($\lambda_{exc.} = 230$ nm).

maximum of absorption appears at lower wavelengths. It would also be expected that the 1,3-linkage at the phenylene ring in **6** and **6P** also decreases the conjugation length compared to **5** and **5P** that have a more favorable 1,4-connection. The results show that the differences between the maximum of absorptions are minimal, proving that the induced sterical effects of the PSt substituents have higher influence on the effective conjugation length.

Data regarding the emission spectra of the polymers measured in $CHCl_3$ solutions are presented in Table 2. The PL spectra of the polymers are shown in Fig. 6.

A bathochromic shift of the $\lambda_{max}$ emission is observed for all polymers with respect to monomers due to the partial extending of the conjugation length. The maximum values for emission are lower than that in similar polymers having thiophene moieties instead of naphthalene ones [17] and the reason can be a sterical one as discussed above. However, Fig. 6 shows a clear difference in the spectra for polyarylenes as comparing to their starting macromonomers. In the case of the emission spectra of the polymers, the introduction of 1,3-disubstituted phenylene ring in the main chain that breaks the delocalization pathway, led to appearance of the maximum of emission for **6P** at lower wavelength as comparing with **5P**. The increased density of PSt chains in the case of **7P** determines also a hypsochromic shift of the maximum of emission as comparing to the other two studied polymers.

## 4. Conclusions

Polymeric precursors that possess designed molecular weights with narrow molecular weight distributions, prepared by ATRP were modified in Suzuki type coupling with 1-naphthalene boronic acid. In this way, macromonomers containing a conjugated sequence with 1-naphthyl groups at the extremities were obtained. Polyarylenes having PSt chains as lateral substituents were synthesized by oxidative chemical polymerization in the presence of anhydrous $FeCl_3$ from the respective macromonomers.

The structures of the new macromonomers and polymers were analyzed by spectral methods and GPC measurements. DSC of the PSt based polymers shows an increase of $T_g$ from macromonomer to polymer. Optical properties of the polymers were followed by UV and fluorescence spectroscopies. By comparing the UV spectra of the starting phenyl-bromine polymers with those of naphthyl containing, clear differences can be noticed, due to the introduction of the new groups and the increase of conjugation length. A limited increase of the conjugation length is noticed when comparing the naphthyl functionalized macromonomers with the corresponding polyarylenes, probably due to the rotation of the two naphthalene rings in the 1,1′ binaphthyl moieties that break the planarity and the conjugation system. Despite this, the emission spectra of the polymers show a bathochromic shift of the $\lambda_{max}$ emission in all the cases with respect to the monomers.

## Acknowledgment

Viorela-Mihaela Mercore and Ioan Cianga would like to thank Tubitak for financial support.

## References

[1] Kelley TW, Baude PF, Gerlach C, Ender DE, Muyres D, Haase MA, et al. Chem Mater 2004;16:4413.
[2] Reichmanis E, Katz H, Kloc C, Maliakal A. Bell Labs Tech J 2005;10:87.
[3] Zhang W, Shiotsuki M, Masuda T, Kumaki J, Yashima E. Macromolecules 2007;40:178.
[4] Zhang W, Shiotsuki M, Masuda T. Macromolecules 2007;40:1421.
[5] Matyjaszewski K. Prog Polym Sci 2005;30:858.
[6] Cianga I, Yagci Y. Prog Polym Sci 2004;29:387.
[7] Cianga I, Ciang L, Yagci Y. New applications of living/controlled polymerization methods for synthesis of copolymers with designed architectures and properties. In: Dragan ES, editor. New trends in nonionic (co)polymers and hybrids. NY: Nova Science Publishers; 2006. p. 1.
[8] Cianga I, Yagci Y. Eur Polym J 2002;38:695.
[9] Cianga I, Yagci Y. Polym Bull 2001;47:17.
[10] Yurteri S, Cianga I, Demirel AL, Yagci Y. J Polym Sci Part A Polym Chem 2005;43:879.
[11] Yurteri S, Cianga I, Yagci Y. Designed Monom Polym 2005;8:61.
[12] Yurteri S, Cianga I, Degirmenci M, Yagci Y. Polym Int 2004;53:1219.
[13] Cianga I, Hepuzer Y, Yagci Y. Polymer 2002;43:2141.
[14] Demirel AL, Yurteri S, Cianga I, Yagci Y. Macromolecules 2005;38:6402.
[15] Demirel AL, Yurteri S, Cianga I, Yagci Y. J Polym Sci Part A Polym Chem 2007;45:2091.
[16] Mercore VM, Cianga I, Grigoras M, Yagci Y. Rev Roum Chim 2004;49(7):607.
[17] Cianga I, Mercore VM, Grigoras M, Yagci Y. J Polym Sci Part A Polym Chem 2007;45:848.
[18] Sahin E, Camurlu P, Toppare L, Mercore VM, Cianga I, Yagci Y. J Electroanal Chem 2005;579:189.
[19] Sahin E, Camurlu P, Toppare L, Mercore VM, Cianga I, Yagci Y. Polym Int 2005;54:1599.
[20] Colak D, Cianga I, Muftuoglu AE, Yagci Y. J Polym Sci Part A Polym Chem 2006;44:727.
[21] Rodriguez JG, Tejedor JL. J Polym Sci Part A Polym Chem 2007;45:2038.

[22] Koeckelberghs G, Verbiest T, Vangheluwe M, Groof LD, Asselberghs I, Picard I, et al. Chem Mater 2005;17:118.
[23] Gomez R, Segura JL, Martin N. J Org Chem 2000;65:7501.
[24] Cheng Y, Chen L, Zou X, Song J, Zhiliu W. Polymer 2006;47:435.
[25] Cheng Y, Zou X, Zhu D, Zhu T, Liu Y, Zhang S, et al. J Polym Sci Part A Polym Chem 2007;45:650.
[26] Percec V, Wang JH, Okita S. J Polym Sci Part A Polym Chem Ed 1992; 30:429.
[27] Tsuchiya K, Shibasaki Y, Aoyagi M, Ueda M. Macromolecules 2006;39: 3964.
[28] Lin HY, Liou GS, Lee WY, Chen WC. J Polym Sci Part A Polym Chem 2007;45:1727.
[29] Grigoras M, Cianga I, Farcas A, Nastase G, Ivanoiu M. Rev Roum Chim 2000;45:703.
[30] Kaya I, Bilici A. J Appl Polym Sci 2007;105:1356.
[31] Percec V, Okita S. J Polym Sci Part A Polym Chem Ed 1992;30: 1037.
[32] Myaura N, Suzuki A. Chem Rev 1995;95:2457.
[33] Schluter AD. J Polym Sci Part A Polym Chem 2001;39:1533.
[34] Wegner G. Macromol Chem Phys 2003;204:347.