

## (Hetero) Arylene Polymers Having Polystyrene Chains as Branches

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**Summary:** Four monomers; 1,4-bis(1-naphthyl) benzene (**5** and **7**) and 1,4-bis(2-thienyl)benzene (**6** and **8**) containing one or two polystyrene short chains substituted in 2 or 2, 5 positions of central phenylene ring were synthesized by Suzuki coupling reaction of two polystyrene based macromonomers (**3** and **4**) with 1-naphthalene- and 2-thiophene boronic acid, respectively. By chemical oxidative polymerization using FeCl<sub>3</sub> as oxidant, copolymers containing alternating phenylene and binaphthyl (**9**, **11**) or phenylene and bithienyl groups (**10**, **12**) and polystyrene as side chains have obtained. The exact control of polystyrene branch length was performed by atom transfer radical polymerization of styrene using as initiators 1,4 dibromo-2-(bromomethyl)benzene (**1**) and 1,4-dibromo-2,5 di(bromomethyl)benzene (**2**). Polymers were characterized by FT-IR, <sup>1</sup>H-NMR, UV and fluorescence spectroscopy and thermal methods.

**Keywords:** branched copolymers; hairy-rod copolymers; (hetero)arylene copolymers; naphthalene and thiophene monomers; oxidative polymerisation

### Introduction

There is a long interest to prepare soluble conjugated polymers so that polymerization, purification, characterization and processability to be carried out in solution, polymers to be free defects, with a known structure and to form thin films.<sup>[1]</sup> Owing to their intrinsic chemical structure, conjugated polymers are insoluble in most organic solvents and improving their solubility and processability has been become an important objective that focused many research efforts. From the chemistry viewpoint this disadvantage could be surpassed by design of adequate monomers and introduction of solubilizing side chains onto the conjugated backbone is a very used and

efficient method for solubility improving. However, the side substituents used until now are short alkyl chains or other functional substituents for introduction of other supplementary properties; liquid crystallinity, optical activity, ionic groups, etc. There are some reports about synthesis of soluble graft copolymers of polyacetylene by polymerization of ethylene oxide and methyl methacrylate initiated by electron transfer from sodium doped-polyacetylene<sup>[2,3]</sup> or by Ziegler-Natta polymerization of acetylene initiated by polybutadiene-based catalyst<sup>[4]</sup> and also by attaching oligophenylenevinylene segments to polystyrene or polymethylmethacrylate backbone.<sup>[5,6]</sup> The attaching of usual polymer short chains with a well defined length; i.e., polystyrene, polytetrahydrofuran, polylactone and poly-N-acetyl ethylenimine chains, onto polyphenylenes and polythiophenes and properties of branched copolymers have reported.<sup>[7–10]</sup> The purpose of this communication is to present synthesis and characterization of some monomers containing naphthalene

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or thiophene rings as active groups in the chemical oxidative polymerization, i.e., 1,4-*bis*(1-naphthyl) benzene and 1,4-*bis*(2-thienyl)benzene, where one or two polystyrene grafts on every monomer unit are present. The polystyrene grafts have a well defined length (approximately 16–17 monomer units in every branch) and are obtained by a controlled radical polymerization of styrene using as initiators 1,4-dibromo benzene mono-**(1)** and *bis*-substituted **(2)** with bromomethyl groups, copper (I) bromide/ 2,2'-bipyridine complex as catalyst, in bulk and 110 °C. The synthesized branched copolymers are hairy-rod materials with an electrical conducting core based on  $\pi$ -conjugated polybinaphthylene or polythiophene jacketed by an insulated materials formed from polystyrene side chains.

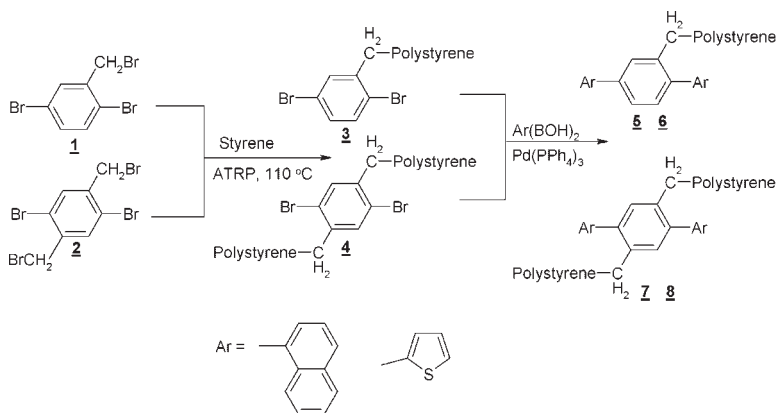
## Experimental Part

Tetrahydrofuran (THF) was dried over potassium hydroxide, distilled over sodium wire and finally distilled over sodium/benzophenone ketyl prior to use. Other solvents were purified and dried by usual methods. 2-Thiophene boronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub> (both Aldrich) and FeCl<sub>3</sub> anhydrous (Fluka) were used as received. The synthesis of 1-naphthalene boronic acid was previously presented.<sup>[11]</sup> Styrene (St) was

purified by usual methods, and distilled *in vacuo* from CaH<sub>2</sub> just before use. 1,4-Dibromo-2-(bromomethyl)benzene (**1**) and 1,4-dibromo-2,5 bis(bromomethyl)benzene (**2**) were prepared by bromination of toluene and p-xylene in 2,5-positions with Br<sub>2</sub>, followed by bromination of methyl groups using N-bromosuccinimide.<sup>[9,12]</sup> Macromonomers **3** and **4** were prepared by controlled radical polymerization of styrene using **1** and **2** as initiators and their detailed synthesis was previously presented.<sup>[9,12]</sup> Four naphthalene- and thiophene-based monomers (**5–8**) have synthesized by Suzuki coupling reaction of macromonomers **3** and **4** with boronic acid derivatives<sup>[10,11]</sup> and reactions are resumed in Scheme 1.

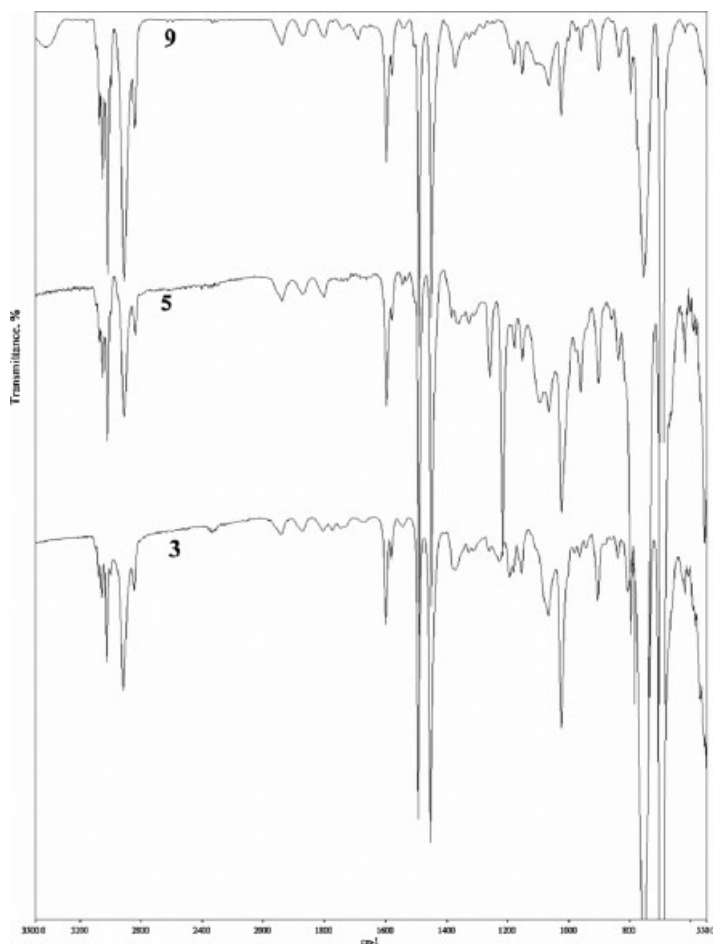
### General Procedure for Chemical Oxidative Polymerization in the Presence of anhydrous FeCl<sub>3</sub> of Functionalized Monomers

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 and 7 ml CHCl<sub>3</sub> and 0.08 g (0.492 mmol) FeCl<sub>3</sub> were introduced under inert atmosphere. 0.35 g of polystyrene with naphthyl groups **7** in 2 ml CHCl<sub>3</sub> was added dropwise



**Scheme 1.**

Synthesis of naphthyl- and thienyl- functionalized polystyrene monomers.



**Figure 1.**

FT-IR (KBr pellet) spectra of macromonomer **3**, monomer **5** and polymer **9**.

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. Polymer (**11**) was redissolved in  $\text{CHCl}_3$  and reprecipitated in methanol. Conversion = 94%.

### Characterization

$^1\text{H-NMR}$  spectra were recorded on a Bruker 250 MHz spectrometer with  $\text{CDCl}_3$  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 ultrastaygel columns with porosities 104, 500 and 100 Å, respectively. THF was used as the eluent at a flow rate of 1 ml/min 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 and fluorescence spectra were registered on a Perkin Elmer LS 55 apparatus. DSC analyses were performed on a Perkin Elmer Differential Scanning Calorimeter DSC-6, in the range 20–200°C, under nitrogen, with a scan rate of 10°C/min. The glass transition temperature ( $T_g$ ) is taken as the mid-point in the heat capacity change.

**Table 1.**

Molecular weights of the macromonomers (**3** and **4**), functionalized monomers (**5–8**) and polymers (**9–12**) calculated from  $^1\text{H-NMR}$  and GPC data.

| Compound  | Mn, ( $^1\text{H-NMR}$ ) <sup>a)</sup> | Mn(GPC) <sup>b)</sup> | P.D. <sup>c)</sup> |
|-----------|----------------------------------------|-----------------------|--------------------|
| <b>3</b>  | 1970                                   | 2025                  | 1.24               |
| <b>4</b>  | 4000                                   | 4260                  | 1.22               |
| <b>5</b>  | 2470                                   | 2700                  | 1.38               |
| <b>6</b>  | 2300                                   | 2480                  | 1.44               |
| <b>7</b>  | 4660                                   | 4890                  | 1.46               |
| <b>8</b>  | 4200                                   | 4400                  | 1.22               |
| <b>9</b>  | –                                      | 19200                 | 2.30               |
| <b>10</b> | –                                      | 35000                 | 2.45               |
| <b>11</b> | –                                      | 28400                 | 1.70               |
| <b>12</b> | –                                      | 21500                 | 2.32               |

<sup>a)</sup> calculated from  $^1\text{H-NMR}$  spectrum;

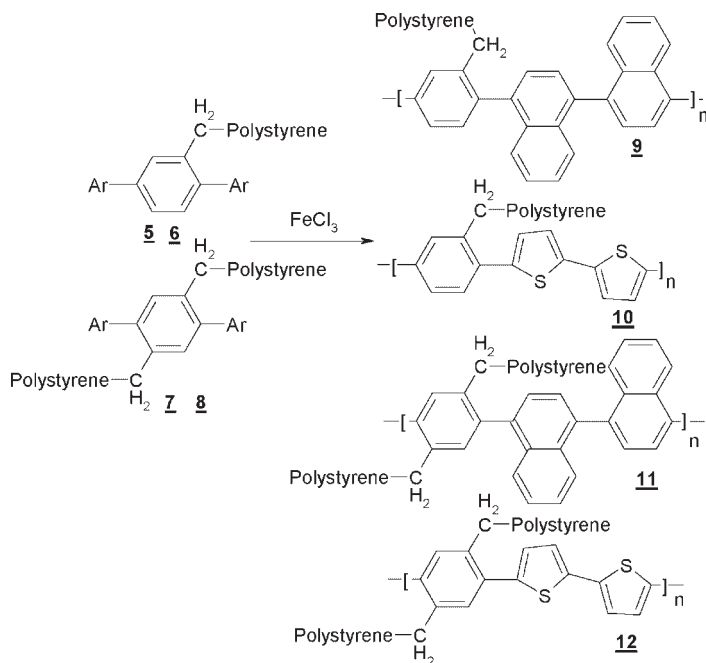
<sup>b)</sup> determined by GPC;

<sup>c)</sup> polydispersity degree.

## Results and Discussion

Synthesis of naphthyl- and thienyl- functionalized polystyrene monomers was carried out according to Scheme 1. Macromonomers **3** and **4** were synthesized by atom transfer radical polymerization of styrene using 1,4-dibromo-2-(bromomethyl)benzene (**1**) and 1,4-dibromo-2,5 di(bromomethyl)-

benzene (**2**) as initiators, CuBr/2,2'-bipyridine complex, in bulk and  $110^\circ\text{C}$ .<sup>[9,12]</sup> Monomers **5–8** were prepared by a palladium catalyzed Suzuki coupling reaction<sup>[13]</sup> of macromonomers **3** and **4** with 1-naphthyl boronic acid and 2-thiophene boronic acid, respectively. Their molecular weight was calculated from  $^1\text{H-NMR}$  spectra using integral ratio of the end groups signals and those of the main polymer chain and also determined by GPC using polystyrene standards and a close agreement between the set of values was observed (Table 1). A slight increase of the molecular weights of the monomers, as comparing to the starting dibrominated macromonomers took place. This fact can be a result of the effect of the new introduced naphthalene and thiophene moieties but also to a partial fractionation of the products during the reprecipitation processes. Monomers **5–8** contain two aromatic groups, naphthyl and thienyl, having positions 4 and respectively 5 accessible for encatennation by chemical oxidative polymerization (Scheme 2).

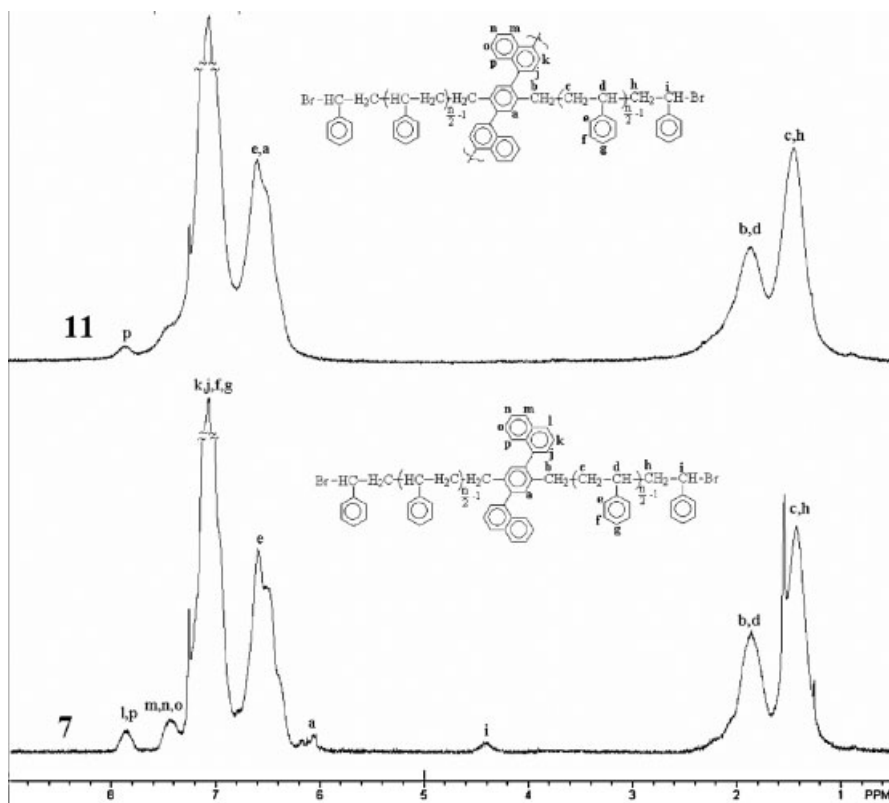
**Scheme 2.**

Synthesis of poly(hetero)arylenes with polystyrene branches by chemical oxidative polymerisation.

### FT-IR Analysis

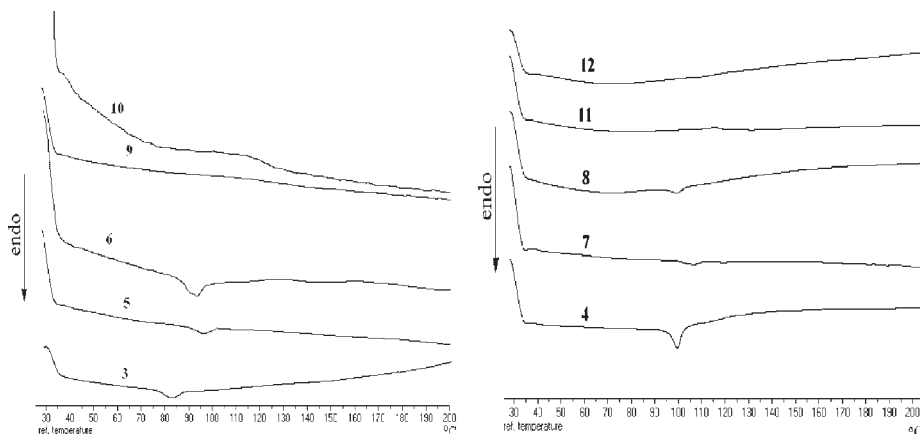
Polystyrene side chains show absorptions situated at 3058 and 3025  $\text{cm}^{-1}$  (aromatic C–H stretching), 2970, 2851 and 2848  $\text{cm}^{-1}$  (aliphatic C–H stretching), 1937, 1867, 1798, 1665 and 760  $\text{cm}^{-1}$  (out-of-plane C–H deformation), 1598, 1489 and 1446  $\text{cm}^{-1}$  (in plane-bend-stretching vibrations of phenyl ring), 758 and 697  $\text{cm}^{-1}$  (out-of-plane hydrogen deformation) and these peaks are present in spectra of all macromonomers, functionalized-monomers and polymers. The absorptions due to benzene 1,2,4-trisubstituted and 1,2,4,5-tetrasubstituted are very slight and difficult to be assigned because are in low concentration. The thiophene monomers show an absorption at 1260  $\text{cm}^{-1}$  that can be assigned to  $\gamma$  ring vibration of thiophene moieties while the slight peak at  $\sim 800 \text{ cm}^{-1}$  in correspond-

ing polymer spectra can be assigned to the C–H out-of-plane vibration of the 2,5-disubstituted thiophene rings. In the case of naphthalene-functionalized monomers and polymers we notice a new peak centered at 774  $\text{cm}^{-1}$  ( $\gamma$  CH of *ortho*-disubstituted benzene ring from naphthalene group) present in the spectrum of **5** and **7**. The absorption from 800  $\text{cm}^{-1}$  in the spectrum of **3** has an increased intensity in the case of **5** and **7** ( $\gamma$  CH of 1,2,3-trisubstituted benzene ring from naphthalene moiety). Other new or with increased intensity signals, from 969  $\text{cm}^{-1}$ , 1024  $\text{cm}^{-1}$  ( $\beta$  CH), or 1259  $\text{cm}^{-1}$  ( $\delta$  CH) are also due to the 1-naphthyl specific absorptions. In the spectra of polymers it can be noticed the disappearance of peaks from the region 850–950  $\text{cm}^{-1}$  due to the changes in the naphthalene rings substitution. A new



**Figure 2.**

$^1\text{H}$ -NMR spectra (250 MHz,  $\text{CDCl}_3$ ) of monomer (**7**) and polymer (**11**).



**Figure 3.**

DSC traces of macromonomers, monomers and polymers.

shoulder at about  $816\text{ cm}^{-1}$  is attributed to  $\gamma\text{ CH}$  of 1,2,3,4-tetrasubstituted benzene rings from the 1,4-naphthalene groups.

### <sup>1</sup>H-NMR Analysis

The <sup>1</sup>H-NMR spectra of the polynaphthalenes (polymers **9**, **11**) and polythiophenes (polymers **10**, **12**) are very similar with those of the corresponding monomers and Figure 2 shows typical spectra for a naphthalene functionalized monomer and its polymer with signals assignments. In the case of polymers there is not possible an estimation of the molecular weight by <sup>1</sup>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 loosing of two protons for every repeating unit in the oxidative polymerization. Moreover, by recalculating the molecular weights of the repeating units, taking in account the new number of protons for the naphthalene moieties, similar values with those of the starting monomers are found. This result shows both that the polyarylenes are formed and no degradation of PSt side chains took place durring oxidative polymerization.

### DSC Analysis

Both macromonomers **3** and **4** show endothermic peaks situated at about  $80^\circ\text{C}$  and  $98^\circ\text{C}$  that can be assigned to the enthalpic relaxation at the glass transition temperature of the short polystyrene branches (Figure 3). In the case of monomers, substitution of bromine atoms with two 1-naphthyl or 2-thienyl moieties has as effect an increase of  $T_g$  both due to the slight increase of molecular weight and also to the influence of the conjugated sequences on the mobility of PSt chains and this tendency is observed also for polymers (Table 2).

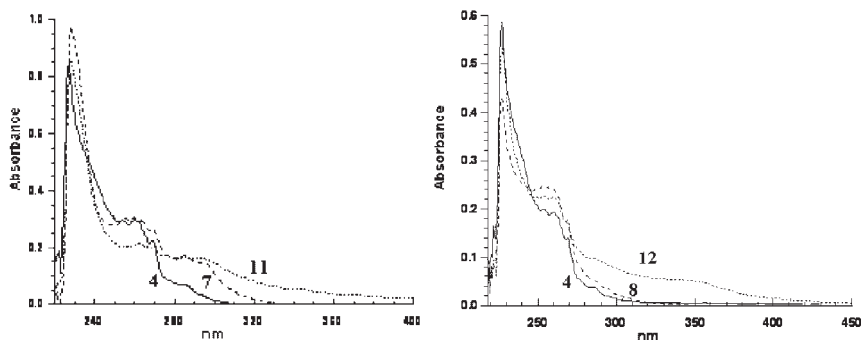
### Optical Properties

The absorption and emission spectra of all compounds were investigated in  $\text{CHCl}_3$  solution and some typical absorption and

**Table 2.**

Glass transition temperatures of macromonomers, monomers and polymers.

| Macromo-<br>nomer,<br>$T_g$ ( $^\circ\text{C}$ ) | Monomer,<br>$T_g$ ( $^\circ\text{C}$ ) | Polymer,<br>$T_g$ ( $^\circ\text{C}$ ) |
|--------------------------------------------------|----------------------------------------|----------------------------------------|
| <b>3</b> 80                                      | <b>5</b> 94                            | <b>9</b> 125                           |
|                                                  | <b>6</b> 89                            | <b>10</b> –                            |
| <b>4</b> 98                                      | <b>7</b> 105                           | <b>11</b> 118                          |
|                                                  | <b>8</b> 96                            | <b>12</b> 105                          |



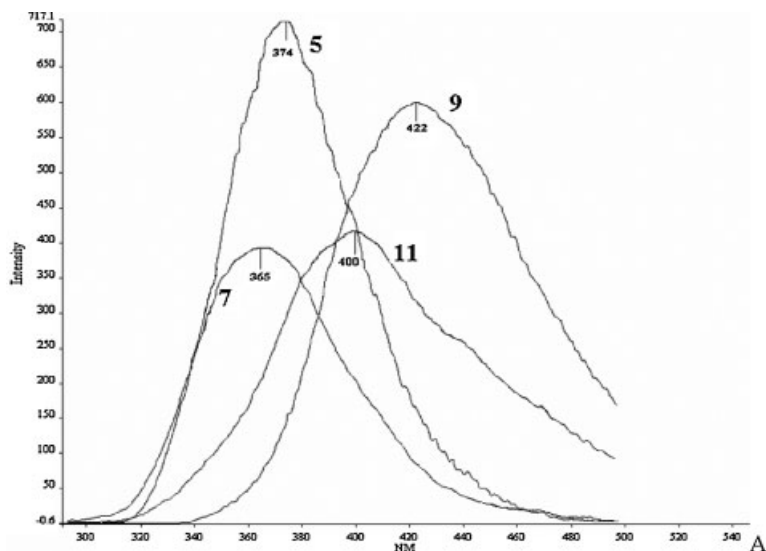
**Figure 4.**

UV spectra of macromonomer and naphthalene- and thiophene-monomers and polymers.

emission spectra are presented in Figures 4 and 5 and all data are collected in Table 3.

Dibrominated macromonomers **3** and **4** show UV absorptions situated between 225–270 nm with long tails until 280–

320 nm assigned to  $\pi-\pi^*$  transition in phenyl rings of polystyrene. The presence of 1-naphthyl or 2-thienyl moieties in the functionalized monomers **5–8** determines a bathochromic shifting of the absorption



**Figure 5.**

Emission spectra of **5** ( $\lambda_{\text{exc.}} = 240$  nm), **7** ( $\lambda_{\text{exc.}} = 230$  nm), **9** ( $\lambda_{\text{exc.}} = 240$  nm), **11** ( $\lambda_{\text{exc.}} = 230$  nm).

**Table 3.**

Optical properties of the macromonomers, monomers and polymers.

| Macromonomer |                                         | Monomer  |                                         |                                       | Polymer   |                                         |                                       |
|--------------|-----------------------------------------|----------|-----------------------------------------|---------------------------------------|-----------|-----------------------------------------|---------------------------------------|
| Code         | $\lambda_{\text{max}}$<br>absorption nm | Code     | $\lambda_{\text{max}}$<br>absorption nm | $\lambda_{\text{max}}$<br>emission nm | Code      | $\lambda_{\text{max}}$<br>absorption nm | $\lambda_{\text{max}}$<br>emission nm |
| <b>3</b>     | 260, 270                                | <b>5</b> | 233, 260, 294                           | 374                                   | <b>9</b>  | 233, 262, 301                           | 422                                   |
| <b>4</b>     | 260, 270                                | <b>7</b> | 229, 260, 285                           | 365                                   | <b>11</b> | 230, 262, 294                           | 400                                   |
| <b>3</b>     | 260, 270                                | <b>6</b> | 260, 270                                | 368                                   | <b>10</b> | 260, 270, 320                           | 509                                   |
| <b>4</b>     | 260, 270                                | <b>8</b> | 255, 270, 290                           | 385                                   | <b>12</b> | 260, 270, 325                           | 448                                   |

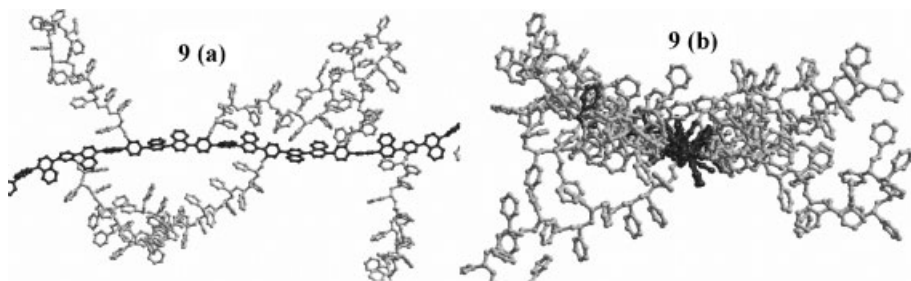


Figure 6.

Three dimensional ball-and stick models of polyarylene **9**: up (a) and frontal (b) images.

spectra due to extension of conjugated sequence of type: 1,4-*bis* (1-naphthyl) phenylene and 1,4-*bis* (2-thienyl) phenylene. However, naphthalene monomer with two polystyrene branches (**7**) has absorption at lower wavelength comparing with (**5**), probably due to sterical hindrances between naphthyl rings and polystyrene pendants. It would be expected that the conjugation lengths in the corresponding polymers to increase substantially and consequently the maximum of absorption to be more clear red shifted. Despite this, there is only a limited increase of the wavelength of the maximum of absorptions in the poly(hetero)arylenes **9–12** as compared to their corresponding monomers. This fact can be explained only by the minor modification of the effective conjugation length in the main chain. Due to the bulky macromolecular substituents (polystyrene chains) the torsion angles between the naphthylene and thienylene groups in the 4,4'-binaphthyl and 5,5-dithienyl moieties is increased and the effective conjugation length in such kind of polymers is limited to several aromatic units that are arranged in a conformation close to planarity. So, the difference between functionalized monomers and their polymers are limited from this point of view. This aspect is more evident in the case of monomer **7** and polyarylene **11**, that have two PSt chains at every repeating unit, as comparing with the other studied polymers. In this case the sterical influences are higher and the maximum of absorption appear at lower wavelengths. The same behavior is

observed for emission spectra of monomers and polymers when a bathochromic shift of the  $\lambda_{\text{max}}$  emission is observed for all polymers with respect to monomers due to the partially extending of the conjugation length.

The maximum values for emission are lower that in similar polymers having thiophene moieties instead of naphthalene ones and the reason can be a sterical one as discussed above. However Figure 5 shows clear different spectra for polyarylenes as comparing to their starting monomers.

All synthesized copolymers can be considered as hairy-rod polymers with a rigid conjugated backbone having a pronounced tendency to self-organize forming nano-scale structures in bulk and in solution.<sup>[14]</sup> Model molecules for polymer fragments were obtained by molecular mechanics (MM+) and the three dimensional ball-and stick models obtained after energy minimization for polymer **9** are shown in Figure 6. It can be observed that polystyrene grafts have an encapsulating role of the conjugated polymer chain and all macromolecular system can be considered as a conducting molecular wire (core) insulated by polystyrene grafts as shell, similar with conducting polymers with rotaxane architecture.<sup>[15]</sup>

## Conclusion

Macromonomers containing a well determined molecular weight with narrow molecular weight distribution and having



aromatic bromine atoms can be functionalized by Suzuki coupling reaction with naphthalene and thiophene boronic acids. Their chemical oxidative polymerization was carried out in solution using  $\text{FeCl}_3$  as oxidant and copolymers with alternating phenylene and binaphthyl or dithienyl units in the main chain and polystyrene as side chains are obtained. The structures of the monomers and polymers were analyzed by spectral methods and GPC measurements. DSC measurements show an increase of  $T_g$  from monomer to polymer. Optical properties of the polymers were followed by UV and fluorescence spectroscopy. By comparing the UV spectra of the starting macro-monomers, monomers and polymers clear differences can be noticed, due to the introduction of the new groups and the increasing of conjugation length. However, a limited increase of the conjugation length is noticed when comparing the functionalized monomers with the corresponding polymers, probably due to the rotation of the two aromatic rings in the 1, 1' binaphthyl and 2,2'-bithienyl moieties that breaks the planarity and the conjugation system. Despite this, the emission spectra of the polymers show a bathochromic shift

of the  $\lambda_{\text{max}}$  emission in all the cases with respect to the monomers.

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