Synthesis and Molecular Characterization of Polythiophene Block Co-, Ter-Polymers and Four-Arm Star Homopolymer

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Abstract: We report the synthesis of polythiophene (PT) block copolymers with polystyrene (PS) or polyisoprene of increased 3,4 microstructure ($PI_{3,4}$) and tri-block terpolymer of the PS-b-PI-b-PT type. Tetrathienylsilane ($C_{16}H_{12}S_4Si$) was also prepared in order to react with thiophene and eventually synthesize a four-arm star PT homopolymer. The preparation of the functional precursors and intermediate products (PS, PI, PS-b-$PI_{3,4}$, and $C_{16}H_{12}S_4Si$) was achieved through high vacuum techniques, and PT was synthesized under ambient conditions via the corresponding chemical oxidative polymerization reaction. The final polymers and the intermediate precursors were molecularly characterized by size exclusion chromatography (SEC), membrane osmometry (MO), proton nuclear magnetic resonance (^{1}H-NMR), and carbon nuclear magnetic resonance (^{13}C-NMR) spectroscopies.

Keywords: Block copolymers-terpolymer; Oxidation-anionic polymerization; Polythiophene; Star homopolymer

INTRODUCTION

During the past few decades, conducting polymers, such as polyaniline, polyacetylene, polypyrrole, and polythiophene, have received considerable attention due to their remarkable conductive and electroactive properties. More specifically, since their electrical and optical properties are precisely controlled via oxidation and/or reduction, their applicable state can be also altered. Some examples of their applications are: polymer rechargeable batteries,[1] microtweezers, microvalves, actuators for micromechanical sorting, and nanowires.[2] Polythiophene (PT) could be used as a microvalve in membrane pores and therefore alter their state by using electrical charge, which will eventually modify the polymer's oxidation state. A range of volatile compounds with concentrations of 10 ppm or less can be detected by PT sensors,[3] therefore they can be used in environmental chemistry for the increased absorption and removal of various types of pollutants.

Several applications of conducting polymers have been reported, but their solubility and processability remains an important challenge. Synthesis of more soluble substituted polythiophene derivatives seems to be promising but it is considered that their electrical properties are degraded.[4] François and Olinga[5] have reported that ''an alternative way to maintain doped conducting polymer sequences in solution is the synthesis of copolymers in which these sequences are chemically bonded to soluble sequences of 'classical' polymer such as polystyrene.'' We have adopted their basic synthetic route and we have synthesized polythiophene (PT) block copolymers with polystyrene (PS), polyisoprene of increased 3,4 microstructure ($PI_{3,4}$) approximately equal to 60%, and tri-block copolymers consisting of PS-b-PI-b-PT. At this point, we must indicate that François and Olinga[5] synthesized PS-b-PT copolymers in order to obtain pure PT films through thermal treatment, whereas we have examined the copolymer films without any treatment in order to discover new properties and applications.

The synthesis of tetrathienylsilane is reported in the literature to be the precursor of highly conducting polythiophene via electropolymerization.[6] We report the synthesis of a four-arm star homopolymer of thiophene through a different synthesis approach using tetrathienylsilane via oxidative polymerization.

EXPERIMENTAL SECTION

Purification of Materials

The living polymeric chains were prepared by anionic polymerization using high vacuum techniques in evacuated, *n*-butyllithium

(n-BuLi)-washed and benzene-rinsed glass vessels. Analytical information on the high vacuum technique as well as the purification procedures for the monomers (styrene (St), isoprene (Is)), solvents (benzene, tetrahydrofuran (THF), methanol), and initiator (sec-butyllithium (sec-BuLi)) to the standards required for anionic polymerization are well known and established.[7] Thiophene (Fluka, 98%), N, N, N′, N′-tetramethylethylenediamine (TMEDA, Fluka, 99%), and tetrachlorosilane (SiCl$_4$, Acros, 99.8%) were stirred overnight with calcium hydride (CaH$_2$) and distilled into calibrated ampules. Chloroform (Lab-Scan, 99.8%), diethyl ether (Riedel de Haën, 99.8%), and cyclohexane (Lab-Scan, 99%) were purified by stirring overnight with CaH$_2$ and were finally distilled into ampules. 2-Bromothiophene (2-BrT, Fluka, 95%) was injected through a septum into an ampule, degassed through the vacuum line, and the necessary amount of this reagent was collected into an evacuated ampule and diluted in THF. Iron trichloride (FeCl$_3$, anhydrous, $\geq$98%, Riedel de Haën) and n-butyllithium (Fluka, 1.6 M in hexane) were used without any further purification.

Instrumentation

The polydispersity index (I) and the number-average molecular weights ($\overline{M}_n$) of the precursors and the final products were measured via size exclusion chromatography (SEC) and membrane osmometry (MO) respectively.

SEC, equipped with an isocratic pump (SpectraSystem P100), column oven (LabAlliance) heated to 30°C, three columns in serial connection (PLgel 5 μm Mixed-C, 300 × 7.5 mm), refractive index (RI, Shodex RI-101), and ultraviolet absorbance (UV, SpectraSystem UV1000) detectors and THF as the eluent solvent (flow rate: 1 mL/min), was calibrated with eight PS standards (Mp: 4,300 to 3,000,000 g/mol). In many cases, the concentration of the polymer solution used varies according to the molecular weight. For usual molecular weight, varying from 10,000 to 100,000 g/mol, the concentration used was approximately 0.1 g/100 mL. In every case, prior to calculating the polydispersity indices of the unknown materials a series of standard PS solutions were tested in order to examine the calibration accuracy of the instrumentation. Finally, it should be mentioned that the volume of the injection loop was 100 μL.

Membrane osmometry (MO) experiments were carried out with a Gonotec Osmomat 090 membrane osmometer at 30°C. THF, dried over CaH$_2$ and sodium wires, was the measuring solvent. The concentrations of the polymer solutions were approximately the same for all samples and equal to: 2 g/100 mL, 4 g/100 mL, 6 g/100 mL, 8 g/100 mL, and 10 g/100 mL.

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained in order to determine the composition and the microstructure of the PI$_{3,4}$-b-PT copolymer and the PS-b-PI-b-PT terpolymer. Measurements were carried out in CDCl$_3$ at 30°C using a Bruker AVANCE II spectrometer. Data were processed using UXNMR (Bruker) software.

Carbon nuclear magnetic resonance (^{13}C-NMR) spectra were obtained at 62.895 MHz with Bruker AVANCE II instrument at 298 K from d-chloroform (CDCl$_3$) solutions. The NMR system was controlled by TopSpin 1.3 software (Bruker, Germany). The 24 K data points were recorded with a sweep width of 15,723 Hz.
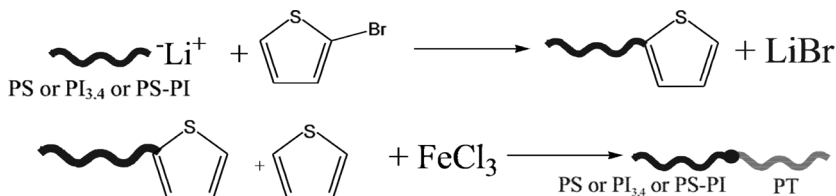
Synthesis of the PT Copolymers

The synthesis of a PS-b-PT copolymer (sample PS-PT_1, according to Table I) is described and the apparatus used is shown in Scheme 1.

First, a living polystyrene chain (PS$^-$Li$^+$) is synthesized in a nonpolar solvent (benzene) via anionic polymerization and well-known procedures (43.5 mmol St, 0.151 mmol sec-BuLi).[7] Then, it reacts with a solution consisting of a polar solvent (tetrahydrofuran) and the halogenated thiophene derivative (2-BrT, 52.2 mmol) in order to prepare a new functionalized polymer with thiophene end groups. Actually, bromothiophene monomeric units react with the polystyrene's living ends. Two hours later, the reaction mixture is transferred in another section of the apparatus (S2) and the solvent mixture (benzene and THF) is removed via distillation in the first section (S1). The end-functionalized polymer is then dissolved in chloroform, and a small amount of methanol is added in order to terminate the living polymer chain ends that have not been functionalized. The solution is transferred into a beaker, where under ambient conditions it reacts with the appropriate quantity of thiophene monomeric units (53.8 mmol) and iron trichloride (FeCl$_3$, 215.3 mmol). Four hours later, the reaction is completed and the copolymer is finally synthesized (Scheme 2).

A distinct dark solution is obtained, with a black precipitate in most cases due to the excess of the FeCl$_3$. The solution is filtered through a Büchner funnel, and the filtration product is then precipated in methanol excess. The precipitated material is purified through continuous rinsing with methanol until the filtration product becomes clear (no color indicated) since the excess of FeCl$_3$ is removed. Actually, the filter retains both the unreacted initial living chain and the copolymer. By controlled fractionation of this product, using THF and methanol as a solvent and non-solvent pair respectively, it is possible to obtain the pure PS-b-PT copolymer.
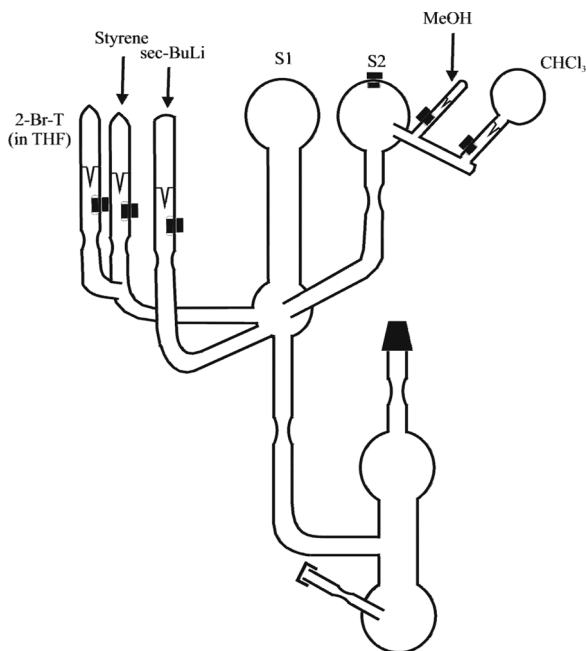
Scheme 1. Apparatus used for the synthesis of PS-b-PT copolymer.

Scheme 2. Synthesis reactions of the end-functionalized polymer and the final copolymer.

Synthesis of the PT Terpolymer

The apparatus used for the synthesis of PS-b-PI-b-PT terpolymer is similar to the one used for the synthesis of PS-b-PT copolymer, shown in Scheme 1. First, in a similar manner to the previous synthesis, a living polystyrene-b-polyisoprene chain (PS-b-PI$^-$Li$^+$) is synthesized in benzene via anionic polymerization and well-known procedures (40 mmol St, 42 mmol Is, 0.139 mmol sec-BuLi).[7] The mixture reacts with a solution consisting of a polar solvent (THF) and the halogenated thiophene derivative (2-BrT, 56 mmol) in order to prepare a new functionalized

polymer with thiophene end groups. Twenty hours later the reaction is completed and the solvent mixture (benzene and THF) is removed via distillation, similar to the synthesis procedure of PS-b-PT copolymer. The end-functionalized polymer is then dissolved in chloroform, and a small amount of methanol is added in order to terminate the living polymer chain ends that have not been functionalized. The solution is transferred into a beaker, where under ambient conditions it reacts with the appropriate quantity of thiophene monomeric units (23.7 mmol) and iron trichloride ($FeCl_3$, 94.8 mmol). Four hours later, the reaction is considered complete and the terpolymer synthesized.

Synthesis of Four-Arm Star PT Homopolymer

Initially, thiophene (13 mmol) reacts under vacuum with n-butyllithium (13 mmol) in diethyl ether and in the presence of TMEDA (13 mmol), which behaves as a catalyst, according to the literature.[8] Lithiation of thiophene is followed by the reaction of 2-thienyllithium with tetrachloro-silane (71.40 mmol) in THF and by recrystallization in cyclohexane in order to synthesize the wanted tetrathienylsilane (T_4Si).[6] Then T_4Si reacts in chloroform with thiophene (7.58 mmol) and $FeCl_3$ (30.32 mmol), producing a four-arm star homopolymer of thiophene (Scheme 3).
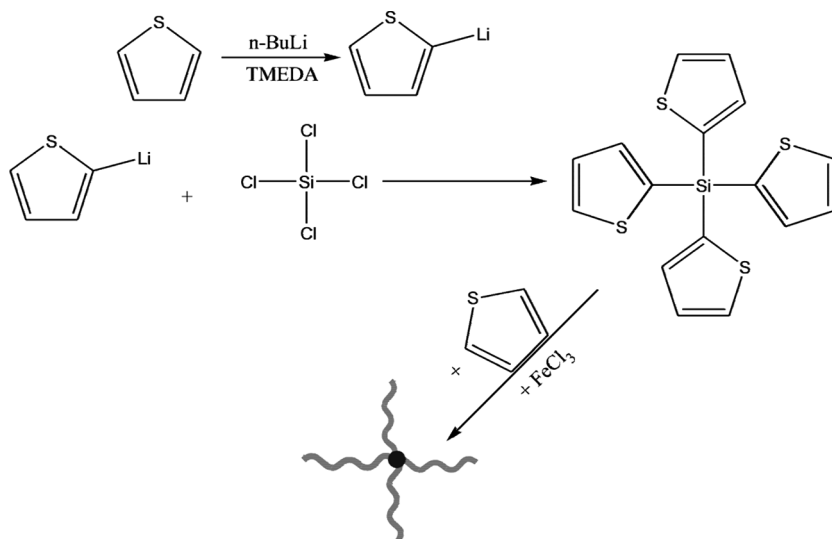
Scheme 3. Synthesis reactions of the 2-thienyllithium, tetrathienylsilane (T_4Si), and the final four-arm star homopolymer of thiophene.

Finally, the PT homopolymer is precipitated in methanol excess, filtered through a Büchner funnel, and rinsed with methanol until the filtration product becomes clear, indicating that $FeCl_3$ is completely removed. The filter retains both the four-arm star PT homopolymer and the PT homopolymer itself.

RESULTS AND DISCUSSION

The chemical oxidative polymerization reaction of thiophene is better manipulated, as reported in the literature, under ambient conditions. Since in our laboratory we have the capability to synthesize polymer materials under high vacuum, we thought it would be challenging to attempt the synthesis procedure of PT under high vacuum conditions, but the results were not promising enough, since the dispersion of $FeCl_3$ was minor and has proven very difficult to handle by such an approach.

Additionally, the quantity of iron trichloride used was tested in order to produce the PT block, and it was found that the best approach was to use a four times excess of this reagent per thiophene quantity (mmol), as already reported to the literature.[5]

In Figure 1 the ^{13}C-NMR spectra of a representative PS-b-PT copolymer is presented (sample PS-PT_1). The characteristic chemical shifts

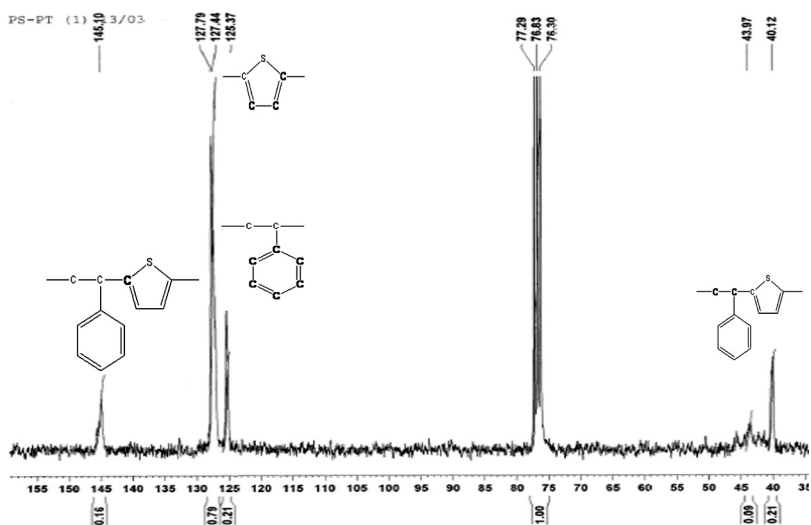**Figure 1.** ^{13}C-NMR spectra of a representative diblock PS-b-PT_1 copolymer. The characteristic chemical shifts are observed and their corresponding carbon bonds are indicated through bold letters in the molecular formulas.

Table 1. Results from membrane osmometry and size exclusion chromatography – molecular characterization for the PT block copolymers and the star homopolymer

Sample	1st block		Copolymer		Terpolymer	
PS-PT_1	$\overline{M}_{nPS}^a = 23{,}000$	$I^b = 1.02$	$\overline{M}_{nPS-PT}^a = 58{,}000$	$I^b = 1.01$		
PS-PT_2	$\overline{M}_{nPS}^a = 49{,}000$	$I^b = 1.02$	$\overline{M}_{nPS-PT}^a = 93{,}000$	$I^b = 1.01$		
PS-PT_3	$\overline{M}_{nPS}^a = 22{,}000$	$I^b = 1.02$	$\overline{M}_{nPS-PT}^a = 44{,}000$	$I^b = 1.02$		
PI_{3,4}-PT	$\overline{M}_{nPI_{3,4}}^a = 16{,}000$	$I^b = 1.06$	$\overline{M}_{nPI_{3,4}-PT}^a = 50{,}000$	$I^b = 1.06$		
PS-PI-PT	$\overline{M}_{nPS}^a = 40{,}000$	$I^b = 1.02$	$\overline{M}_{nPS-PI}^a = 89{,}000$	$I^b = 1.01$	$\overline{M}_{nPS-PI-PT}^a = 150{,}000$	$I^b = 1.08$
(PT)_4	$\overline{M}_{n(PT)_4}^a = 54{,}000$	$I^b = 1.02$				

[a]: Membrane Osmometry in THF at 30°C.
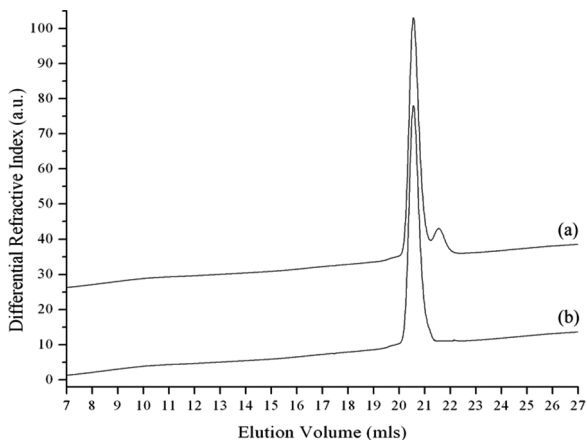[b]: Size Exclusion Chromatography in THF at 30°C.

Figure 2. SEC chromatograph of the sample PS-b-PT_1: (a) unfractionated where two peaks are indicative and (b) fractionated final copolymer.

are observed and more specifically the shift at 145 ppm corresponding to the thiophene carbon atoms bonded directly to the PS chains, at 125–128 ppm to the six-member aromatic ring carbons as well as to the
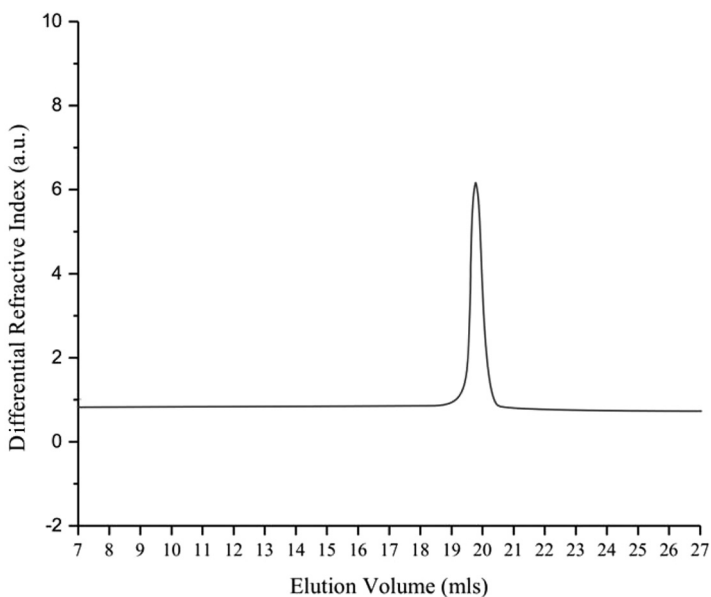

Figure 3. SEC chromatograph of the PT four-arm homopolymer (PT)$_4$.

five-member thiophene ring carbons, and finally at 40–43 ppm, which was assigned to the carbon atoms of the PS chains vinyl parts. In order to make these observations sufficiently clear, the corresponding carbon bonds are indicated with bold letters in the molecular formulas at the ^{13}C-NMR spectra.

^{1}H-NMR spectra indicated that in the case of polyisoprene segments, since a small quantity of a polar solvent (THF, < 1 mL) is added, the isomeric microstructures of the specific block are altered. Specifically, in the case of the PI-b-PT type diblock copolymer the PI microstructures observed were different from those obtained during the usual anionic polymerization of isoprene in benzene ($\sim$90 wt.%-1,4 and 10 wt.% mixture of -1,2 and -3,4 respectively) and was finally calculated to be approximately $\sim$60 wt.% -3,4, 20 wt.% -1,2, and 30 wt.% -1,4.

Moreover, concerning the PS-b-PI-b-PT linear triblock terpolymer, the polymerization of isoprene was accomplished in a nonpolar environment (benzene), and therefore the geometrical isomerisms were identical with those mentioned above for the usual anionic polymerization procedure.

The PT block copolymers-terpolymer and the PT four-arm homopolymer exhibit molecular homogeneity ($I = \overline{M}_w/\overline{M}_n < 1.1$), as indicated from their molecular characteristics shown in Table I. In the literature, no such molecular characterization is reported. The average number molecular weights ($\overline{M}_n$) of the PT chain and the PT homopolymer, provided from SEC, correspond to the PS standards calibration of the instrumentation due to the lack of calibration with PT homopolymers, and therefore they are not trustworthy. Actually it was found that the $\overline{M}_n$ values given from SEC are different from those calculated from MO by a factor of 1.15. This means that the SEC values were approximately 1.15 times larger than those calculated from MO.

Figure 2 shows the SEC chromatogram of the PS-PT_1 sample. Figure 2, curve a, corresponds to the PS-b-PT (left peak)/PS (right peak) mixture prior to fractionation, and Figure 2, curve b, to the PS-b-PT fractionated copolymer. The fractionation procedure was used to remove the residual first block due to uncontrolled termination reactions occurring during the capping reaction with 2-BrT.

In Figure 3, the SEC chromatogram of the four-arm star PT homopolymer is presented. Despite the low solubility of PT in most solvents it is considered that through our synthesis approach we managed to increase the PT solubility in various organic solvents (toluene, benzene, cyclohexane, tetrahydrofuran) at low concentrations (approximately 0.01–0.02 g/mL). Thus, the four-arm star homopolymer exhibits a low peak in the chromatogram due to the low concentration of the solution of the final $(PT)_4$/THF mixture. This disadvantage limited the molecular characterization of the homopolymer only via SEC and MO, since the

solubility in deuterated solvents (e.g., CDCl$_3$) was very limited, making the measurement with NMR spectroscopy impossible.

CONCLUSIONS

The polythiophene copolymers and the four-arm star PT homopolymer exhibit molecular homogeneity (I < 1.1), which was never reported in the past. With this synthetic approach, not only PS-b-PT copolymers but also PI-b-PT copolymer and a PS-b-PI-b-PT terpolymer were synthesized, materials that have not been reported previously in the literature. It is indicated that it is possible to synthesize quite soluble conducting polythiophene via the oxidative polymerization technique using tetrathienylsilane as a precursor. The four-arm star PT homopolymer is believed to be more soluble than the corresponding linear PT homopolymer.

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