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Conducting Block Copolymer Nanowires Containing Regioregular Poly(3-Hexylthiophene) and Polystyrene

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Grignard Metathesis polymerization (GRIM) for the synthesis of regioregular poly(3-alkylthiophenes) proceeds via a "living" chain growth mechanism. Due to the "living" nature of this polymerization regioregular poly(3-alkylthiophenes) with predetermined molecular weight, narrow molecular weight distributions and desired chain end functionality are now readily available. Allyl terminated poly(3-hexylthiophene) was successfully used as a precursor for the synthesis of di-block copolymers containing polystyrene. The addition of "living" poly(styryl)lithium to the allyl terminated regioregular poly(3-hexylthiophene) generated the di-block copolymer. Poly(3-hexylthiophene)-b-polystyrene was also synthesized by atom transfer radical polymerization. Integration of poly(3-hexylthiophene) in di-block copolymers with polystyrene leads to the formation of nanowire morphology and self-ordered conducting nanostructured materials.

Keywords conjugated polymers, regioregular poly(3-hexylthiophene), block-copolymers, anionic polymerization, atom transfer radical polymerization

Introduction

Poly(3-alkylthiophenes) represent a class of conducting polymers that have good solubility in organic solvents and environmental stability (1, 2). The synthesis of regioregular poly(3-alkylthiophenes), first discovered by McCullough et al., resulted in the generation of structurally homogeneous head-to-tail coupled poly(3-alkylthiophenes). These regioregular polymers have greatly improved electronic and photonic properties over their regiorandom analogues (3–8). The discovery of the Grignard Metathesis (GRIM) method allowed the polymerization to occur at room temperature or at reflux, hence leading to a quick and cost effective technique for the large scale synthesis of regioregular poly(3-alkylthiophenes) (9, 10). We reported recently that the nickel-initiated cross-coupling polymerizations (McCullough and GRIM methods) are quasi-"living" chain growth reactions and the molecular weight of regioregular poly(3-alkylthiophenes) can be predicted by the molar ratio of monomer to nickel initiator (11, 12). *In situ* addition of

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various Grignard reagents to the nickel terminated poly(3-alkylthiophene) results in the formation of chain end functionalized polymers (13, 14). These end functionalized polymers can be used as precursors for the synthesis of various block-copolymer structures. Mechanical and processing properties of regioregular poly(3-alkylthiophenes) can be tuned by integrating them in copolymer structures with various conventional polymer blocks. In addition, optical and electrical properties of these block-copolymers can be adjusted by changing the ratio between the conducting and non-conducting segments. Preparation of such well-defined block-copolymers requires the use of "living" polymerization techniques, such as, anionic polymerization or controlled radical polymerization (CRP) (15, 16). Our group developed two alternative pathways to the synthesis of di- and tri-block copolymers containing regioregular poly(3-hexylthiophene) (17, 18). We are reporting here two alternative methods for the synthesis of poly(3-hexylthiophene)-*b*-polystyrene. The first approach is based on the addition of "living" poly(styryl)lithium to the allyl terminated poly(3-hexylthiophene) resulting in the formation of a di-block copolymer. The second method utilizes a bromoester terminated poly(3-hexylthiophene) as a macroinitiator for atom transfer radical polymerization (ATRP) of styrene. The incorporation of regioregular poly(3-hexylthiophene) in block copolymers is expected to answer the need for advanced electronic materials with improved processibility and tunable electrical and optical properties.

Experimental

Materials

All reactions were conducted under prepurified nitrogen or argon, using oven-dried glassware. All glassware was assembled while hot and cooled under nitrogen or argon. Commercial chemicals, purchased from Aldrich Chemical Co., Inc., were used without further purification unless noted otherwise. All solvents were freshly distilled under nitrogen atmosphere prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Titration of the Grignard reagents was performed following the procedure described by Love (19). Styrene was purified according to a procedure described elsewhere (20). Cyclohexane was distilled from sodium potassium alloy.

Analyses

Size exclusion chromatography (SEC) measurements of poly(3-hexylthiophene)-*b*-polystyrene were performed on a Waters 2690 separations module apparatus and a Waters 2487 dual λ absorbance detector with chloroform as the eluent (flow rate 1 mL/min, 35 °C, $\lambda = 450$ nm) with a series of three Styragel columns (10^4, 500, 100 Å; Polymer Standard Services). Calibration based on polystyrene standards was applied for determination of molecular weights and toluene was used as an internal standard. ^{1}H-NMR spectra of the polymer solutions in $CDCl_3$ were collected on a Bruker Avance 500 MHz spectrometer. MALDI-TOF MS analysis was performed using a Voyager-DE STR Bio-Spectrometry workstation by Biosystems. Electrical conductivity measurements were conducted on thin polymer films by the standard spring-loaded pressure-contact four-point probe method at ambient conditions. The polymer solutions in anhydrous toluene (5 mg mL^{-1}) were filtered through PTFE 0.45 μm filter and drop cast onto 22 mm sq cover glass. The cover slips were covered with a glass dish to prevent rapid evaporation of the solvent. The films were oxidized by exposure to iodine vapors for 1 h. At least 5 times of repeating measurement were taken for a selected, most uniform film area. The film thickness (cross-section) was measured by profilometry and the conductivity σ [S cm^{-1}] calculated according to the following equation:

$$\sigma = 1 \div 4.53 * R * l$$

where R is the resistance ($R = V/I$) [Ω] and l is the film thickness [cm].

Synthesis of Allyl Terminated PHT

Allyl terminated poly(3-hexylthiophene) was synthesized by *in situ* addition of allyl magnesium bromide to nickel terminated polymer, as previously described (13, 14).

Synthesis of Polystyryl Lithium

The polystyrene segment was prepared by "living" anionic polymerization in moisture and oxygen free cyclohexane, according to the previously described method (21).

Coupling of Living Polystyryl Lithium with Allyl Terminated PHT

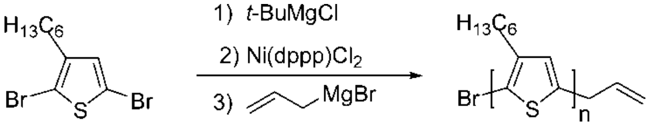
Poly(3-hexylthiophene)-*b*-polystyrene di-block copolymer was synthesized by reacting poly(3-hexylthiophene) (M_n(GPC) = 17600; DP_n(NMR) = 60) as a solution in dry THF (5 mL) and *living* polystyryl lithium (M_n(GPC) = 8200; DP_n(NMR) = 80) in cyclohexane. The coupling reaction was allowed to proceed for 20 min at 40°C. The coupling reaction was performed in a glove box under nitrogen atmosphere. The copolymer was precipitated in methanol and washed with cold cyclohexane to remove the polystyrene homopolymer.

Synthesis of Hydroxypropyl Terminated Poly(3-Hexylthiophene)

Allyl terminated PHT (3 g, 0.45 mmol, DPn (NMR) = 40) was dissolved in anhydrous THF (100 mL) under nitrogen. To this reaction mixture, a 0.5 M solution of 9-BBN (4 mL, 2 mmol) in anhydrous THF was added via a syringe. The reaction mixture was stirred for 24 h at 40°C, at which point a 6 M solution of NaOH (2 mL) was added to the reaction flask. The reaction mixture was stirred for another 15 min (at which point the oil bath was removed). The reaction mixture was allowed to cool down to room temperature followed by addition of a 33% aqueous solution of hydrogen peroxide (2 mL), and the reaction was allowed to proceed for additional 12 h at 40°C. The hydroxypropyl terminated PHT was isolated by precipitation in a methanol-water mixture. The polymer was filtered and purified by a Soxhlet extraction with methanol.

General Procedure for Synthesis of Bromoester Terminated Poly (3-Hexylthiophene) (ATRP Macroinitiator)

Hydroxypropyl terminated PHT (1 g, 0.15 mmol) was dissolved in anhydrous THF (100 mL) under nitrogen. The reaction mixture was stirred for 15 min at 40°C followed by addition of triethylamine (3 mL, 22 mmol) and a drop-wise addition of 2-bromoisobutyryl bromide (2.5 mL, 20 mmol). The reaction mixture was stirred for 8 h at 40°C. The



Scheme 1. Synthesis of allyl terminated poly(3-hexylthiophene).

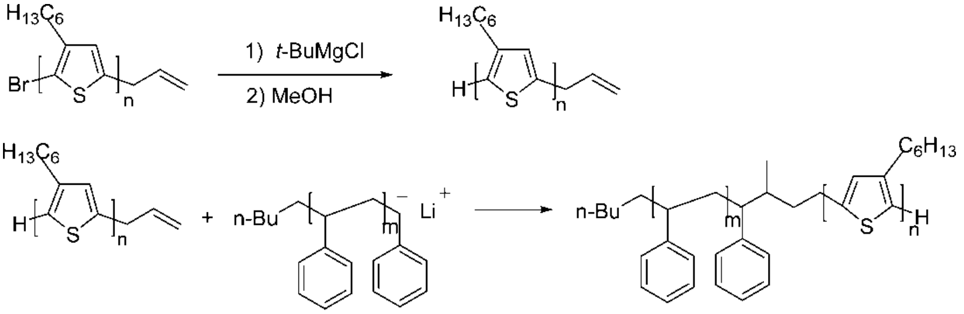
resulting PHT macroinitiator was precipitated in methanol and washed with cold methanol (300 mL), followed by drying under vacuum for 24 h.

Atom Transfer Radical Polymerization (ATRP) of Styrene Using Bromoester Terminated Poly(3-Hexylthiophene) as Macroinitiator

ATRP of styrene was performed using CuBr-PMDETA, in toluene as solvent (33 vol% monomer), at 90°C. The molar ratio was $[\mathrm{Sty}]_0$:$[\mathrm{PHT\text{-}MI}]_0$:$[\mathrm{CuBr}]_0$:$[\mathrm{PMDETA}]_0$ = 300 : 1:1:1. A dry Schlenk flask was charged with PHT macroinitiator (0.5 g, 0.075 mmol), styrene (2.6 mL, 22.5 mmol), toluene (4.6 mL), 0.1 g *p*-dimethoxy benzene (GC internal standard) and CuBr (11 mg, 0.075 mmol). After three freeze-pump-thaw cycles the reaction mixture was immersed in a thermostated oil bath at 80°C. Then, PMDETA (20 μL, 0.075 mmol) was added to the reaction mixture via a deoxygenated syringe and an initial sample was removed. Samples were periodically withdrawn from the reaction mixture to follow conversion and the molecular weight.

Results and Discussion

Incorporation of polystyrene block into copolymer structures with regioregular poly (3-hexylthiophene) should result in improved processibility and film forming ability. We developed a new method for the synthesis of poly(3-hexylthiophene)-*b*-polystyrene copolymers. This method is based on the addition reaction of "living" poly(styryl)lithium to allyl terminated poly(3-hexylthiophene). This approach was inspired by a previous report which indicated that poly(styryl)lithium adds to ethylene, generating the mono-addition product (22). Addition of allyl magnesium bromide to the GRIM polymerization generates polymer with bromine and allyl end-groups as shown in Scheme 1. Prior to the coupling reaction the bromine end-group was reduced by magnesium halogen exchange generating



Scheme 2. Synthesis of poly(3-hexylthiophene)-*b*-polystyrene by coupling of "living" polystyryl lithium with allyl terminated poly(3-hexylthiophene).

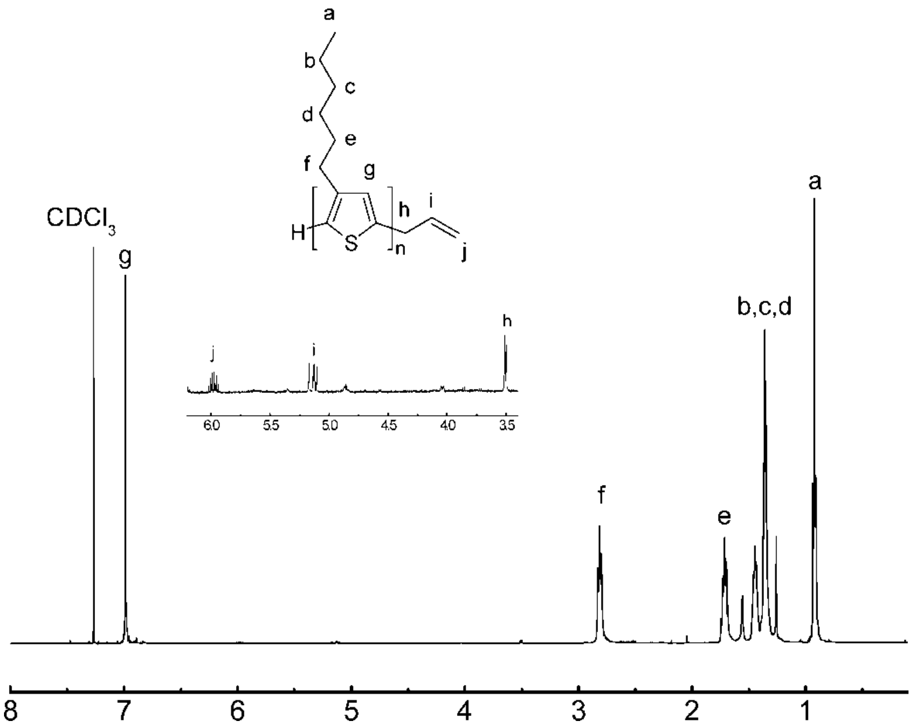


Figure 1. ^{1}H-NMR spectrum of allyl terminated poly(3-hexylthiophene) (DP$_n$ = 60).

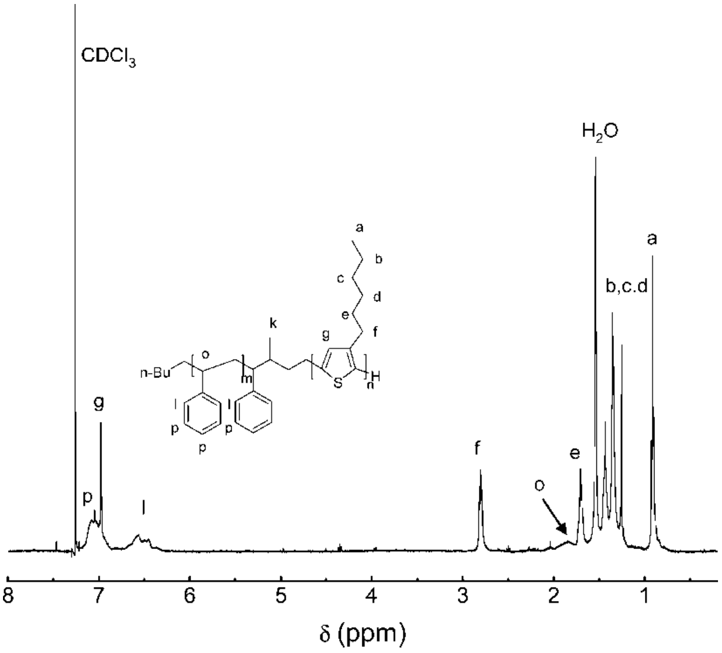


Figure 2. ^{1}H-NMR spectrum of poly(3-hexylthiophene)-*b*-polystyrene.

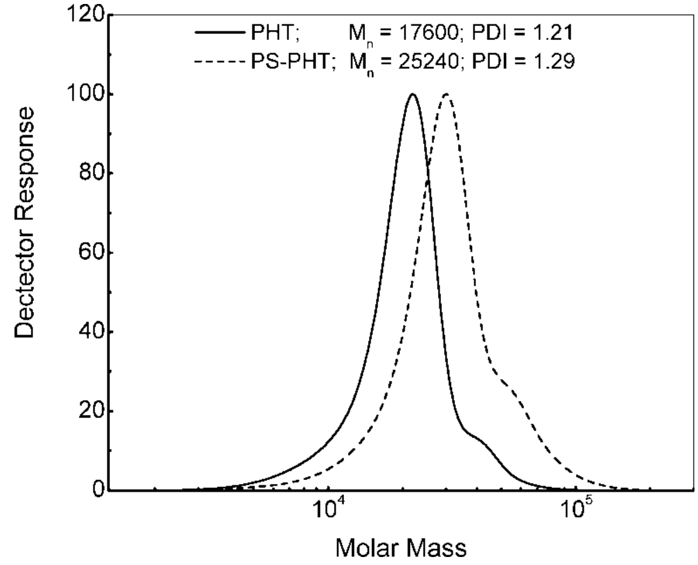
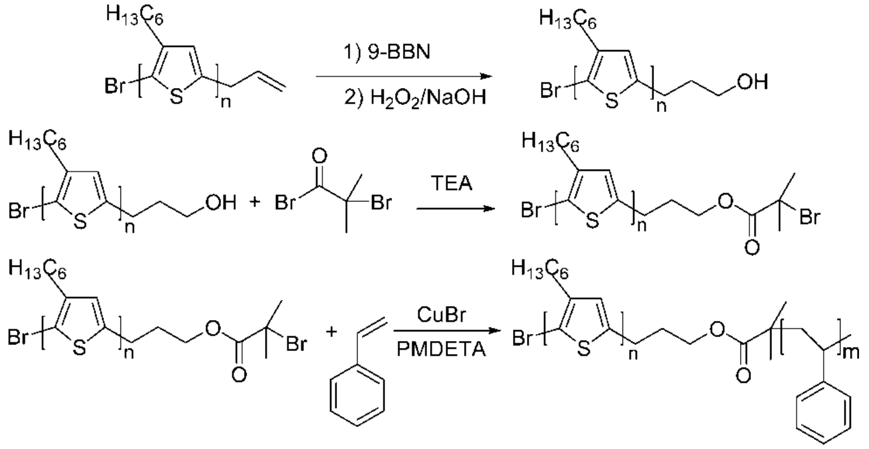


Figure 3. GPC traces of allyl terminated poly(3-hexylthiophene) precursor (PHT) and poly(3-hexylthiophene)-*b*-polystyrene copolymer (PS-PHT).

H/allyl polymer (Scheme 2). This step was necessary in order to avoid a possible side reaction of lithium bromine exchange during the coupling process. Formation of allyl terminated poly(3-hexylthiophene) was confirmed by ^{1}H-NMR and MALDI-TOF MS. End-capping of poly(3-hexylthiophene) resulted in ~90% allyl end groups as indicated by MALDI-TOF MS analysis (13, 14). The conversion of Br/allyl to H/allyl end groups was also confirmed by MALDI-TOF-MS. ^{1}H NMR spectrum of allyl terminated PHT shows the presence of allyl protons as indicated in Figure 1. Molecular weight of allyl terminated PHT was estimated by integrating **f** protons *vs.* **h** protons ($DP_n = 60$).



Scheme 3. Synthesis of poly(3-hexylthiophene)-*b*-polystyrene by atom transfer radical polymerization.

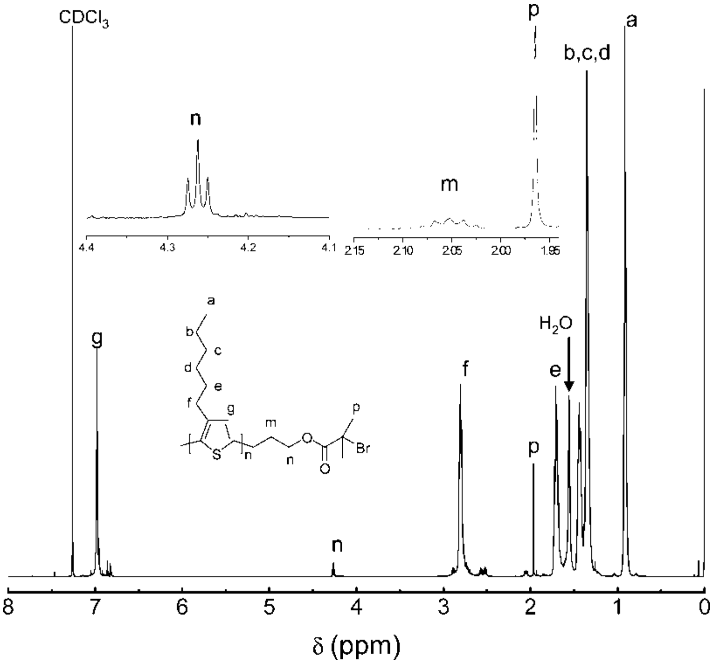


Figure 4. ^{1}H-NMR spectrum of bromoester terminated poly(3-hexylthiophene).

"Living" poly(styryl)lithium was prepared in cyclohexane under nitrogen atmosphere, as previously described (21). A solution of H/allyl poly(3-hexylthiophene) in tetrahydrofuran was added to the solution of poly(styryl)lithium in cyclohexane. ^{1}H-NMR spectrum of poly(3-hexylthiophene)-*b*-polystyrene (Figure 2) showed the complete disappearance of the allyl protons and the formation of the di-block copolymer. The molar composition of the copolymer was estimated from the integration of **l** protons *vs* **f** protons. HSQC-DEPT NMR spectrum of poly(3-hexylthiophene)-*b*-polystyrene) showed that the methyl protons **k** resonate at 0.95 ppm and the corresponding methyl carbon resonate at 23 ppm. The formation of the di-block copolymer was also indicated by the shift in the GPC traces, as shown in Figure 3.

We have previously reported the synthesis of di-block copolymers containing poly (3-hexylthiophene) and polyacrylates by ATRP (18). We show here the synthesis of poly (3-hexylthiophene)-*b*-polystyrene using our previously reported method

Table 1
Composition of poly(3-hexylthiophene)-*b*-polystyrene di-block copolymers synthesized by ATRP

Time (min)	Mol% PHT	M_n(GPC)	PDI
0	100	10000	1.26
60	90	11500	1.27
250	60	14600	1.43
400	48	16800	1.50

Table 2
Conductivities of poly(3-hexylthiophene) and poly(3-hexylthiophene)-*b*-polystyrene

Sample	M_n(GPC)	Mol% PHT	Conductivity (σ, S/cm)	Film thickness (μm)
PHT-allyl	17600	100	27.0	3.3
PHT-PS (anionic)	25240	50	2.9	0.6
PHT-bromoester	10000	100	16.0	2.8
PHT-PS (ATRP)	16800	48	1.5	1.4

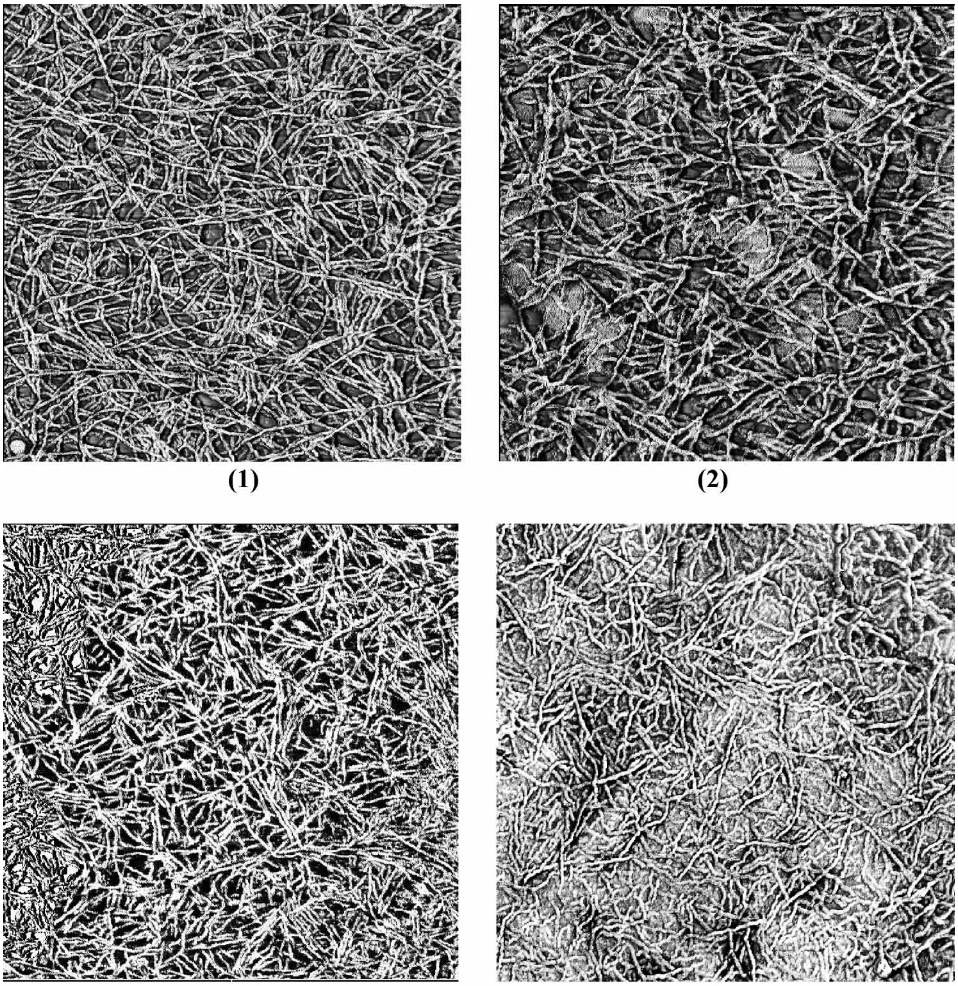

(1) (2)
(3) (4)

Figure 5. AFM phase images (scale: 2 μm): **(1)** allyl terminated poly(3-hexylthiophene), **(2)** poly(3-hexylthiophene)-*b*-polystyrene synthesized by coupling of "living" polystyrene with allyl terminated poly(3-hexylthiophene), **(3)** bromoester terminated poly(3-hexylthiophene) and, **(4)** poly(3-hexylthiophene)-*b*-polystyrene synthesized by ATRP.

(Scheme 3). The allyl end group was readily converted to hydroxypropyl end group, which was subsequently reacted with 2-bromoisobutyryl bromide to give bromoester terminated poly(3-hexylthiophene). The latter was used as macroinitiator for ATRP of styrene. Formation of the bromoester terminated poly(3-hexylthiophene) was confirmed by ^{1}H-NMR (Figure 4). Composition of poly(3-hexylthiophene)-*b*-polystyrene copolymer synthesized by ATRP was estimated from the ^{1}H NMR spectra. The obtained results are shown in Table 1.

The increase in the polydispersity index with the conversion of styrene indicates the presence of termination and chain transfer reactions. Chain transfer to polymer can take place through radical attack on the α methylene groups of the hexyl side chains. When one compares the two proposed pathways to poly(3-hexylthiophene)-*b*-polystyrene di-block copolymers it is easy to notice that anionic coupling procedure results in better structural control.

As expected, conductivities of the poly(3-hexylthiophene) precursors are higher than those of the di-block copolymers (Table 2). However, relatively high conductivities were observed for the di-block copolymers. The resulting copolymers were very soluble in many organic solvents and possessed excellent film forming properties. Solid state morphology of these materials was investigated by AFM (Figure 5).

We have observed that the regioregular poly(3-hexylthiophene) precursors and the di-block copolymers show the formation of nanowire morphology (Figure 5) (17, 23). The nanowire morphology was observed for thin films of the polymers prepared by drop-casting from toluene solutions followed by free evaporation of the solvent. The dilution of the nanowires observed for the di-block copolymers it is most probably due to presence of the polystyrene block (Figure 5).

Conclusions

Allyl terminated poly(3-hexylthiophene) was used as a starting material for the synthesis of di-block copolymers containing polystyrene. The addition of “living” poly(styryl)-lithium to the allyl terminated regioregular poly(3-hexylthiophene) generated the di-block copolymer. Poly(3-hexylthiophene)-*b*-polystyrene was also synthesized by atom transfer radical polymerization. Integration of poly(3-hexylthiophene) in di-block copolymers with polystyrene leads to the formation of nanowire morphology and self-ordered conducting nanostructured materials.

Acknowledgment

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