SYNTHESIS AND CHARACTERIZATION OF POLY(3-HEXYLTHIOPHENE)-*b*-POLYSTYRENE DI-BLOCK COPOLYMERS

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Introduction

Polythiophenes constitute a particularly important class of conjugated polymers, which has been extensively studied. While unsubstituted polythiophene is an intractable material, the substituted polythiophenes are soluble and fusible. Substituted polythiophenes are also chemically and thermally stable, which make them very attractive materials. [1-3]

The synthesis of regioregular PATs, first discovered by McCullough *et al*.[4-5], resulted in the formation of defect-free, head-to-tail coupled PATs with greatly improved electronic and photonic properties over regiorandom analogues.[6-8] Latter, the Grignard Metathesis Method (GRIM) has been reported as a simpler alternative to successfully synthesize regioregular PATs as well.[9,10]

The incorporation of PATs in block copolymers is expected to answer the need for novel materials, which self-assemble in a variety of new morphologies. Incorporation of PATs in block copolymer structures with other polymers is expected to generate various materials with tunable properties, function of the composition of the copolymers. Additionally the block copolymers are expected to have better mechanical and processing properties than PATs.

In 2002 our group reported a method for the synthesis of PATs di- and tri-block copolymers,[11] followed recently by an alternative, simpler method, for generating di-block copolymers.[12] *In situ* end functionalization of PATs allows the synthesis of vinyl and allyl terminated polymer in high yield (>90 %).[13] It has been shown that end functionalization with vinyl or allyl moieties, generates mono-capped PATs.[13] The success of the end-capping technique developed in our group, opened new directions for the synthesis of PATs block copolymers.

We report here a new method for the synthesis of poly(3-hexylthiophene)-*b*-polystyrene di-block copolymers which employs the coupling of allyl terminated poly(3-hexylthiophene) with the *living* polystyryl lithium.

Experimental

Synthesis of allyl terminated PHT. 2,5-dibromo-3-hexylthiophene (4.9 g, 15 mmol) was dissolved in 150 mL dry THF. A solution of *t*-butyl magnesium chloride 2M in diethyl ether (7.5 mL; 15 mmol) was added via syringe under nitrogen and the reaction mixture was refluxed for 90 min. The reaction mixture was cooled to room temperature and $Ni(dppp)Cl_2$ (0.15 g ; 0.27 mmol) catalyst was added. The mixture was stirred for additional 10 min at room temperature, followed by the addition of a solution of allyl magnesium bromide 1M (3 mL; 3 mmole). After 5 min. the reaction mixture was poured into methanol and the polymer precipitated. The polymer was extracted in sequence with methanol, hexane and chloroform. Poly(3-hexylthiophene) with Br/allyl and H/allyl end groups was isolated from the chloroform fraction. The Br/allyl end groups were converted to H/allyl *via* magnesium halogen exchange, using *t*-butyl magnesium chloride.

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.[14]

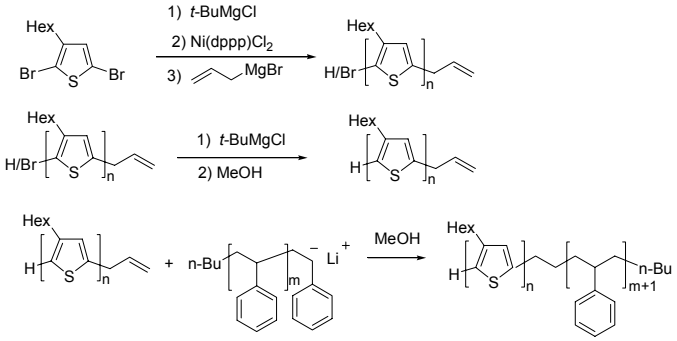
Coupling of living polystyryl lithium with allyl terminated PHT. Poly(3-hexylthiophene)-*b*-polystyrene di-block copolymer was synthesized by reacting poly(3-hexylthiophene) (M_n(GPC)=17600; M_n(NMR)=9000) as a solution in dry THF (5 mL) and *living* polystyryl lithium (M_n(GPC)=10720) in cyclohexane (a slightly excess of polystyryl lithium can be used). The coupling reaction was allowed to proceed for 10 min at 40^0C. The copolymer was precipitated in methanol and washed with cold cyclohexane to remove the polystyrene homopolymer.

Analyses. Size exclusion chromatography (SEC) measurements 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 ºC, λ=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. ^{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 BioSpectrometry workstation by Biosystems.

Results and Discussion

Living anionic polymerization is the most powerful synthetic tool for the preparation of polymers with well-defined molecular weights, narrow molecular weight distributions, controlled composition and architectures.[15] Owing to the reactivity of carbanions toward oxygen, moisture and carbon dioxide, anionic polymerization requires inert atmosphere and sometimes the use of high vacuum technique. In general, substituents that stabilize negative charge by anionic charge delocalization are substituents that make vinyl monomers polymerizable by an anionic mechanism. Such substituents include aromatic rings, double bonds, carbonyl, ester, cyano, sulfoxide and nitro groups. The range of monomers which can be anionically polymerized in *living* (no termination and chain transfer) fashion includes styrenes, dienes, methacrylates, epoxides, episulfides, cyclic siloxanes and lactones.[15]

The ability to mono-cap poly(3-hexylthiophene) (PHT) with allyl or vinyl end groups it is extremely important since it opens new routes for the synthesis of di-block copolymers. The new method developed for the synthesis of poly(3-hexylthiophene)-*b*-polystyrene copolymers consists in the coupling reaction of *living* polystyryl lithium with the allyl terminated PHT (Scheme 1). The coupling reaction shown in Scheme 1 takes place *via* the addition of *living* polystyryl lithium to the allyl double bond.



Scheme 1. Synthetic protocol for the synthesis of poly(3-hexylthiophene)-*b*-polystyrene

End-capping of PHT results in ~ 90 % allyl end groups as indicated by MALDI-TOF MS. MALDI-TOF MS spectrum of allyll mono-capped PHT show two major peaks corresponding to Br/allyl and H/allyl end groups . The conversion of Br/allyl to H/allyl end groups was also confirmed by MALDI-TOF-MS.

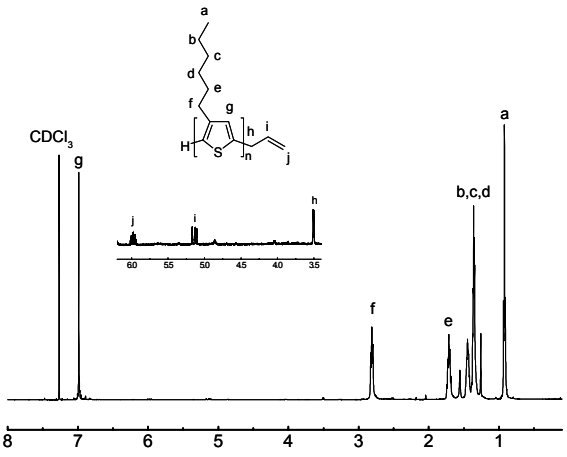


Figure 1. ^{1}H NMR spectrum of allyl terminated poly(3-hexylthiophene)

^{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.

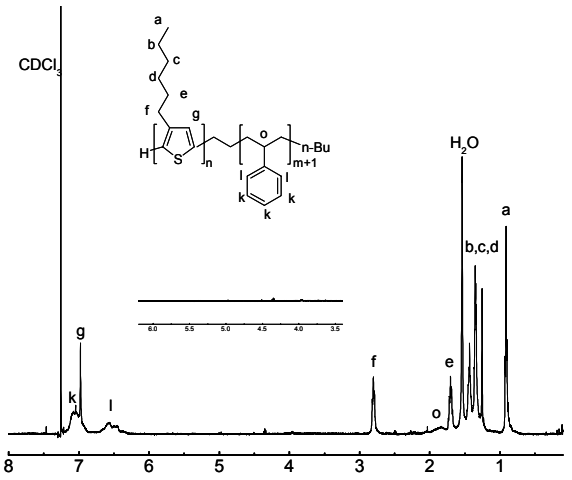


Figure 2. ^{1}H NMR spectrum of poly(3-hexylthiophene)-*b*-polystyrene

^{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 copolymers was estimated from the integration of **l** protons *vs* **f** protons.

The formation of the di-block copolymer was also indicated by the shift in the GPC traces, as shown in Figure 3.

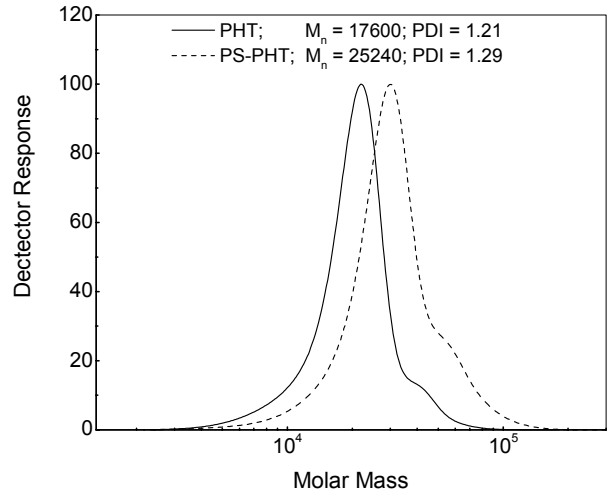


Figure 3. GPC traces of allyl terminated poly(3-hexylthiophene) precursor and poly(3-hexylthiophene)-*b*-polystyrene copolymer.

Conductivities (Table 1) were measured for films of the polymers oxidized with I_2, using the 4-point probe method.

Conclusions

A new simple method for the synthesis of poly(3-hexylthiophene)-*b*-polystyrene di-block copolymers was developed using allyl terminated poly(3-hexylthiophene) as precursor.

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Table 1. Conductivities of Poly(3-hexylthiophene) and Poly(3-hexylthiophene)-*b*-polystyrene

Sample	M_n(GPC)	wt % PHT	wt % PS	Conductivity (σ, S/cm)	Film thickness (μm)
PHT	17600	100	0	26.8	3.27
PHT-PS	25240	60	40	2.9	0.64

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