WELL-DEFINED POLY(3-HEXYLTHIOPHENE)-*b*-POLY(ACRYLATE) DI-BLOCK COPOLYMERS

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Introduction

Due to their excellent electrical properties, regioregular poly(3-alkylthiophene)s (rr-PAT) constitute one of the most promising class of electrically conductive polymers.[1] However, their wide-spread use in electronic applications has been limited by their relatively poor processability and film forming properties. McCullough et al. reported that diblock and triblock copolymers containing regioregular poly(3-hexylthiophene) (rr-PHT) and amourphous segments have improved mechanical properties while maintaining surprisingly high conductivities.[2] Using copolymers therefore opens up a wide range of possibilities in developing new materials with interesting properties.

The key to synthesizing these block copolymers is to control the end-groups of the conjugated polymers. The end-groups can be transformed into initiators for the polymerization of amorphous polymers.[3-5] We use Atom Transfer Radical Polymerization (ATRP) to incorporate a variety of well-defined amorphous polymer segments into rr-PHT block copolymers. Here, we compare properties of diblock copolymers of rr-PHT containing amorphous segments of various glass transition temperatures. The first amorphous polymers that we chose are poly(methyl acrylate) (T_g 5°C)[6] and poly(*n*-butyl acrylate) (T_g -54°C)[6]. By varying the physical properties of the non-conjugated segment, we hope to fine-tune the physical and electrical properties of the copolymer for various device applications.

Experimental

Synthesis of PHT macroinitiator. The PHT macroinitiator was synthesized as previously described, using a nearly 100% allyl-terminated poly(3-hexylthiophene) as precursor.[3-5,7] The formation of the bromoester was confirmed by ^{1}H NMR.

ATRP of acrylates using PHT macroinitiator. The polymeriations were performed using the CuBr-PMDETA catalyst in trichlorobenzene (33 vol% monomer) at 80°C. The molar ratio for the polymerization of acrylate (methyl acrylate (MA), n-butyl acrylate (BA)) was [M]:[PHT-MI]:[CuBr]:[PMDETA]=500:1:3:3.

Analysis. Gel permeation Chromatography (GPC) was performed using chloroform as the eluent (flow rate 1 mL/min, 30°C) and a Waters 2487 dual λ absorbance UV detector. It was calibrated using polystyrene standards. NMR spectra were collected on a Bruker Avance 500 MHz spectrometer using $CDCl_3$ as the solvent. MALDI-TOF MS was used to evaluate the end-group composition of the allyl-terminated PHT and was performed with a Voyager-DE STR BioSpectrometry workstation by Biosystems.

Results and Discussion

The synthesis of the diblock copolymers is depicted in **Figure 1**. A well-defined bromoester terminated rr-PHT is used as the macroinitiator for the ATRP of acrylates.

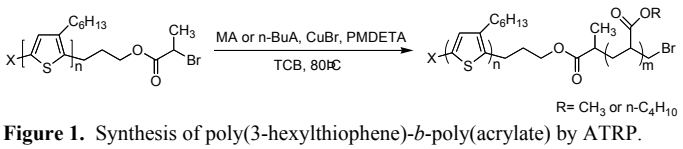

Figure 1. Synthesis of poly(3-hexylthiophene)-*b*-poly(acrylate) by ATRP.

Aliquots were taken at various polymerization times and purified to remove the copper catalyst. The samples were analyzed by GPC for molecular weight distribution and by ^{1}H NMR for composition. Figure 2 shows the evolution of the GPC traces with reaction time. The molecular weight of the copolymer increased with conversion and narrow polydispersity were observed (see Table 1). The composition of the diblock copolymers were analyzed by ^{1}H NMR via integral analysis of the aromatic proton of PHT at 6.98 ppm, the methylene protons of PHT at δ 2.8 ppm and the methoxy proton of PMA at 3.66 ppm.

The resulting diblock copolymers with various amounts of PMA or PBA will be further characterized to compare their electrical, physical, and film forming properties.

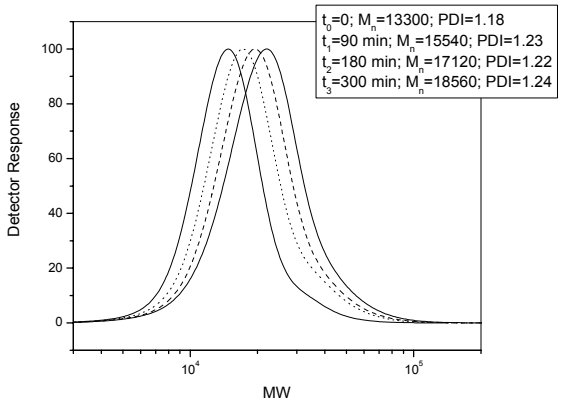

Figure 2. GPC traces showing the incorporation of methyl acrylate during the polymerization of poly(3-hexylthiophene)-*b*-poly(methyl acrylate).

Table 1. Poly(3-hexylthiophene)-*b*-poly(methyl acrylate) composition as a function of polymerization time.

Reaction Time (min)	mol % PHT (NMR)	mol % PMA (NMR)	M_n (GPC)	PDI (GPC)
0	100	0	13300	1.18
30	93	7	13700	1.18
60	81	19	14620	1.21
90	70	30	15540	1.23
180	58	42	17120	1.22
300	49	51	18560	1.24

Conclusions

Well defined diblock copolymers of rr-PHT were synthesized and characterized, and their electrical and physical properties were compared. Changing the amorphous segment in these copolymers should enable us to fine-tune the copolymer properties for various device applications.

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