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Communication

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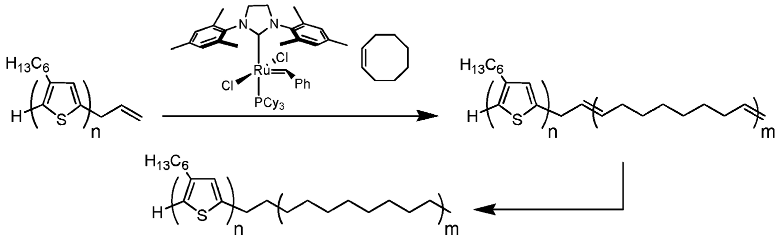

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Crystalline−Crystalline Block Copolymers of Regioregular Poly(3-hexylthiophene) and Polyethylene by Ring-Opening Metathesis Polymerization

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The established route to semiconducting block copolymers typically combines a crystalline or amorphous conjugated polymer block with an amorphous, random-coil polymer that provides solubility and facilitates processing.[1] These block copolymers permit access to a range of nanoscale morphologies (e.g., spheres, rods, co-continuous and lamellar structures) depending on the volume fractions of its components. We are interested in combining regioregular poly(3-hexylthiophene) (P3HT) with polyethylene (PE) to obtain block copolymers comprising *two* crystalline parts. Crystalline−crystalline block copolymers are new to the field of semiconducting polymers and also represent a less explored area of polymer research.[2,3] P3HT is currently the most widely used semiconducting polymer for electronic applications.[4] Semicrystalline P3HT can self-organize into thin films, displaying high charge-carrier mobilities as result of close chain packing.[4a] Linear PE, a superb insulator, is a highly crystalline commodity polymer, conveniently processible at elevated temperatures from the melt and solution. The novel P3HT−PE block copolymers would allow exploration of new functional morphologies and expand the processing and structural toolbox for conjugated materials.

Here, we describe an efficient synthetic route to the first high molecular weight P3HT−PE block copolymer using ruthenium-catalyzed ring-opening metathesis polymerization (ROMP).[5] ROMP is efficient because of the high activity, stability, and low catalyst loadings required to achieve high molecular weight materials. Highly linear, defect-free PE via ROMP has been reported previously.[6] Our synthesis of P3HT−PE is based on a scheme recently described for polyacetylene block copolymers[7] and utilizes an allyl-functionalized P3HT as chain transfer agent during the ROMP of cyclooctene. Subsequent hydrogenation leads to the P3HT−PE block copolymer (Figure 1).

The regioregular P3HT ($M_n = 15$ kg·mol^{-1}) chain transfer agent was prepared by the Grignard metathesis polymerization of 2,5-dibromo-3-hexylthiophene, followed by quenching with allylmagnesiumbromide.[8] ROMP of cyclooctene was performed in the presence of allyl-endcapped P3HT. After 24 h of reaction time, the soluble precursor block copolymer was isolated and characterized by NMR and GPC. The unsaturated polycyclooctene (PCO) block of the P3HT−PCO copolymer was then hydrogenated using *p*-toluenesulfonhydrazide as a mild reagent.[9] Complete hydrogenation was confirmed by FT-IR (Figure S2, Supporting Information) and NMR. The ratio of cyclooctene to P3HT was used to prepare copolymers (**1**−**3**) with different P3HT:PE ratios. Soxhlet extractions in THF and chloroform allowed removal of unreacted P3HT and low molecular weight P3HT−PE copolymers, leaving the high molecular weight fractions. At temperatures less than 70 °C, the copolymers are resistant to solvents, such as THF and chloroform; however, they dissolve at more elevated temperatures in, for instance, xylenes and chlorobenzenes.

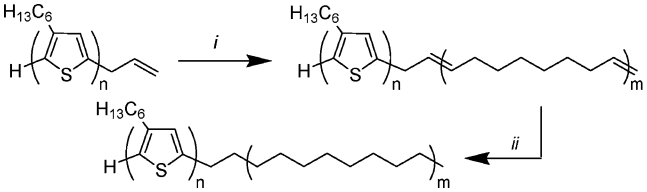

Figure 1. Synthesis of P3HT−PE block copolymers. (*i*) Cyclooctene, Ru(H_2IMes)Cl_2PCy_3(=CHPh), chlorobenzene, 55 °C, 24 h. (*ii*) *p*-Toluenesulfonhydrazide, *p*-xylene, 130 °C, 8 h.

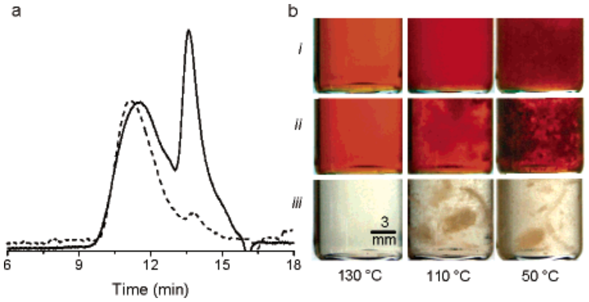

Figure 2. (a) GPC traces of P3HT−PCO in THF with refractive index detection (- - -) ($M_n = 153$ kg·mol^{-1}, $M_w = 266$ kg·mol^{-1}) and UV/vis detection (—) (470 nm). (b) Photographs of 0.1 wt % cyclohexanone solutions of (*i*) the P3HT−PE copolymer (11 wt % P3HT), (*ii*) a corresponding P3HT/PE blend, and (*iii*) a PE reference sample during cooling from 130 to 50 °C.

GPC of the unsaturated precursor block copolymer allowed us to monitor the molecular weight distribution using both refractive index (RI) and UV/visible detection at 470 nm (Figure 2a). The broader peak in the UV/vis-detected GPC trace corresponds to higher molecular weight material, whereas the sharp peak at later elution time corresponds to unreacted P3HT. Comparison of the UV/vis and RI-detected traces suggests that unreacted P3HT is a minor component in the crude mixture. The similarity of the high molecular weight region in both traces indicates that the PCO formed contains the 470 nm absorbing P3HT block. The solid materials exhibited the characteristic purple color and UV/vis spectrum of aggregated P3HT, even at low P3HT weight percent-

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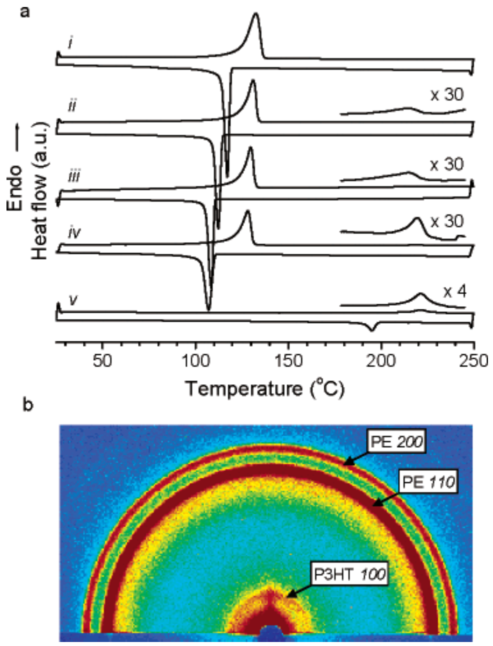

Figure 3. (a) Differential scanning calorimetry (DSC) of (*i*) PE; (*ii*) P3HT−PE (11 wt %); (*iii*) P3HT−PE (14 wt %); (*iv*) P3HT−PE (22 wt %); (*v*) P3HT. (b) WAXS image of P3HT−PE. PE *110* and *200* having $Q = 1.53$ and 1.70 Å^{-1}, respectively. The small inner circle is the *100* reflection of P3HT, $Q = 0.38$ Å^{-1}.

ages of 11% w/w (Figure S3, Supporting Information). Visual evidence of the copolymeric nature of the present material was obtained when homogeneous cyclohexanone solutions of the copolymer and of a P3HT/PE blend were cooled to room temperature (Figure 2b). The images show that crystallization of the copolymer from this solvent proceeds in a homogeneous fashion, as opposed to that of the blend and reference PE, which is preceded by liquid/liquid phase separation and occurs at more elevated temperatures.

High-temperature ^{1}H NMR spectroscopy was used to observe both P3HT and PE resonances (Figure S4, Supporting Information). Using the molecular weight of the initial P3HT, careful integration of the P3HT resonances compared to the PE resonance allowed us to determine the molecular weight of the PE block and the block copolymer. On the basis of this integration, the weight percentage of the P3HT and overall molecular weight (M_n) were determined to be **1**: 11%, 142 kg·mol^{-1}; **2**: 14%, 109 kg·mol^{-1}; **3**: 22%, 71 kg·mol^{-1}, in agreement with estimates from GPC of the precursor P3HT−PCO.

The onset of thermal decomposition of **1**−**3** as determined by TGA in air occurred at temperatures exceeding 300 °C. The melting transitions of **1**−**3** (Figure 3a) determined by DSC are consistent with high molecular weight PE and P3HT blocks, as they occur close to the melting transitions of the neat homopolymers: at 132 °C (100 kg·mol^{-1} for PE) and 221 °C (14 kg·mol^{-1} for P3HT). The thermal stability determined from TGA indicates that P3HT−PE can be processed from the melt without comprising its structural integrity. The copolymers exhibit weak endotherms for P3HT, due to the low content. Since branched and lower molecular weight PE's are known to exhibit lower melting endotherms,[10] DSC confirms the linearity and high molecular weight of our block copolymers.[6c,11] A significant decrease in the onset of PE crystallization from 118 to 107 °C accompanied by broadening of the exotherms was observed with increasing amount of P3HT in the copolymers. This can be explained by the covalently bonded P3HT block hindering the efficient crystallization of the PE moieties.

Grazing incidence wide-angle X-ray scattering (WAXS) of drop-cast films of P3HT−PE confirmed that the material formed separate domains of crystalline PE and P3HT. Characteristic *110* and *200* reflections of PE and a less intense P3HT *100* reflection were observed (Figure 3b).[12] The P3HT π-stacking *010* reflection is masked by the intense PE reflections. There are essentially no intensity variations along the Debye−Scherrer rings of PE (Figure 3b), suggesting that the PE crystallites have a random orientation in the present films.

P3HT−PE is the first example of a crystalline−crystalline semiconducting block copolymer and combines the most widely used semiconductor and insulator polymers into a single material. A systematic investigation of the morphology and self-assembly of P3HT−PE with respect to composition, solution or melt processing, and polydispersity will allow us to understand the interplay between the semiconducting and mechanical properties of this new class of materials.

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Supporting Information Available: Experimental conditions, synthesis, and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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