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Controlling Phase Separation and Optical Properties in Conjugated Polymers through Selenophene–Thiophene Copolymerization

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Conjugated polymers are important because of their rich opto-electronic properties and potential use in low-cost electronic devices.[1] While morphological and optical properties are of paramount importance, controlling these properties is a major challenge. Approaches to meeting this challenge include controlling polymer regioregularity, annealing, patterning, and processing with additives.[2] Controlling phase separation is perhaps the most attractive approach because it is a spontaneous process that offers significant control over nanoscale structure and can be effected in a rational chemical manner. From a device standpoint, nanoscale phase separation achieves morphologies that facilitate charge transfer and charge transport.[1,2] In general, polymers can be designed to undergo phase separation by synthesizing copolymers that contain blocks with distinct functional groups.[3] While this strategy has been demonstrated for a variety of nonconjugated polymers, there are far fewer ways to design and synthesize distinct block structures and hence control phase separation in conjugated polymers. Conjugated/nonconjugated block copolymers can be prepared, but they require the incorporation of insulating segments into the polymer system.[4] Fully conjugated block polythiophenes in which each block contains a unique alkyl side chain have been synthesized.[5] Side chains mainly control intermolecular interactions, which influence optical properties; however, this is primarily an indirect way to control properties that is often difficult to predict.

Herein we report the synthesis and characterization of novel selenophene–thiophene block copolymers and the discovery that blocks of distinct heterocycles can control phase separation. Polythiophene is well-studied and known to organize into ordered domains.[6] Polyselenophene is a new conjugated polymer with a narrower HOMO–LUMO gap than in polythiophene.[7] Both polymers can be synthesized under quasi-living conditions,[8] which allows for the synthesis of distinct block copolymers.

For this study, thiophene and selenophene monomers with identical side chains were prepared. The thiophene monomers (2,5-dibromo-3-hexylthiophene) were synthesized according to previously reported procedures.[6] The selenophene monomers (2,5-dibromo-3-hexylselenophene) were synthesized by an initial alkylation of 3-iodoselenophene with *n*-hexylmagnesium bromide under Kumada-type coupling conditions followed by isolation and di-bromination using *N*-bromosuccinimide [see the Supporting Information (SI)]. To prepare the block copolymers, the selenophene monomers were activated with *n*-butylmagnesium chloride and treated with [1,3-bis(diphenylphosphino)propane]nickel(II) chloride [Ni(dppp)Cl₂] to initiate polymerization (Scheme 1). In a second vessel, the thiophene monomers were activated and added to the polymerization reaction after the selenophene monomers were consumed (10 h). The selenophene:thiophene molar ratio was 1:1, and the catalyst:total monomer molar ratio was 1:100. For control experiments, statistical copolymers and homopolymers [poly(3-hexylthiophene), P3HT, and poly(3-hexylselenophene), P3HS] were prepared under similar conditions (see the SI).

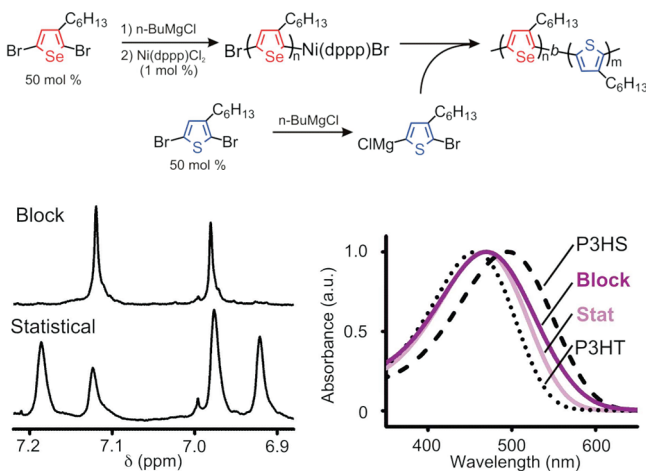**Scheme 1.** Synthesis of Block Copolymers

Figure 1. Comparison of (left) ¹H NMR spectra and (right) solution absorption spectra of block and statistical copolymers. In the right panel, homopolymer spectra are also shown.

The thiophene and selenophene repeat units have distinct ¹H NMR resonances (6.98 and 7.12 ppm, respectively), and thus, NMR spectroscopy was initially used to determine the structure of the polymers and quantify the monomer incorporation of block and statistical copolymers. Accordingly, the selenophene:thiophene ratios are found to be 57:43 and 45:55 for the block and statistical copolymers, respectively (Figure 1). In the statistical copolymer, the aromatic resonances of thiophene and selenophene appear at different chemical shifts when the alternate heterocycle is present at the 5-position. The spectrum of the statistical copolymer was therefore particularly useful for quantifying each combination of units along the backbone. The thiophene–thiophene:thiophene–selenophene:selenophene–selenophene distribution is 29:50:21, confirming the statistical distribution of monomers in the chain. In the block copolymer, the resonance that corresponds to the single selenophene–thiophene linkage was difficult to quantify above the noise in the spectra for this molecular weight range (M_n = 7.4 kg/mol; see the SI for ¹H NMR data for oligomers).

To further determine structure, optical studies in chlorobenzene were carried out. The absorption edge of the block copolymer and P3HS are identical (620 nm), confirming the presence of the long polyselenophene chromophore in the block structure (Figure 1). The absorption edge of the statistical copolymer (600 nm) is positioned between those of P3HT and P3HS, indicating that a combination of thiophene and selenophene constitute the chro-mophore. The full width at half-maximum of the absorption band of the block copolymer (145 nm) is greater than those of the statistical copolymer (130 nm) and the two homopolymers (P3HT = 123 nm; P3HS = 140 nm). This is consistent with a structure in
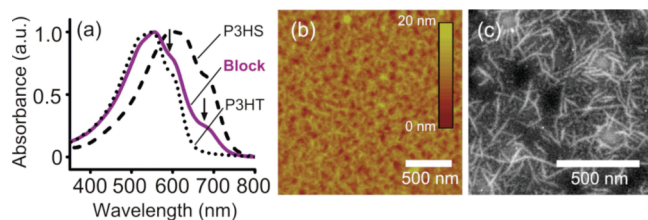
Figure 2. (a) Absorbance spectrum, (b) AFM height image, and (c) dark-field STEM image of poly(3-hexylselenophene-*block*-3-hexylthiophene) films. In (c), electron-dense regions appear brighter.

which the block copolymer contains intact polythiophene and polyselenophene chromophores.

The solution fluorescence spectra are also indicative of structure. For reference, P3HT and P3HS emit at 578 and 623 nm, respectively (see the SI). The block copolymer emission spectrum is dominated by emission from the thiophene block because of this block's greater fluorescence intensity. On the other hand, the statistical copolymer emits weakly at 598 nm, a frequency positioned between the P3HT and P3HS emissions. Taken together, the ^{1}H NMR and solution optical measurements are consistent with the proposed structures of the polymers.

We next designed experiments to examine the solid-state properties of the block copolymer. Films were prepared by spin-casting followed by annealing (150 °C, 1 h), and the absorbance properties were measured. Interestingly, the absorption profile of the block copolymer possesses shoulders (marked by arrows in Figure 2) that coincide with the π-stacking bands of both P3HT and P3HS. These features indicate association and organization of blocks with corresponding blocks in adjacent chains. This observation stands in contrast to that for the statistical copolymer, which has a nearly featureless absorption profile. The film morphology of the block copolymer was also investigated using atomic force microscopy (AFM). Distinct domains are present in the film (Figure 2). This morphology is striking when compared with the statistical copolymer film, which has much smaller domains with a smoother morphology, or when compared with blends of the two pure polymers, which appear unstructured at the nanoscale (see the SI). Taken together, the absorption and AFM data demonstrate that the block copolymer undergoes a significant degree of phase separation in the solid state.

More detailed information was available from dark-field scanning transmission electron microscopy (STEM) measurements. In these unstained images (Figure 2c), bright cylindrical features similar in size to those observed using AFM can be seen. These features represent domains with a high electron scattering ability and are most likely due to selenophene-rich phases. Topographic elemental mapping lends support to this hypothesis, showing that the bright regions are rich in selenium and deficient in sulfur. Conversely, the darker regions are rich in sulfur and deficient in selenium (see the SI), confirming that the features arise from blocks of distinct heterocycles that preferentially associate in the film. This preference is quite surprising in view of the fact that selenophene and thiophene are so structurally similar.

In conclusion, poly(3-hexylselenophene-*block*-3-hexylthiophene)s are an important new class of copolymer because they have broad optical absorption properties, with an onset that is red-shifted by 80 nm relative to that of P3HT, and the ability to undergo phase separation in the solid state. Until the present work, phase separation

in conjugated polymers has been effected with nonconjugated blocks or pendant groups. We have discovered that phase separation as well as the optical properties can be controlled by the heterocycle in the polymer chain. This represents a distinct type of phase separation that is driven by elemental composition and simultaneously offers a direct means for controlling the optical properties. Because of this remarkable ability and resultant properties, poly(3-hexylselenophene-*block*-3-hexylthiophene)s should find utility in fundamental studies, such as testing the limits of phase separation, as well as in optoelectronic applications.

Supporting Information Available: Experimental procedures and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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