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Synthesis of Poly(3-alkylthiophene)-*block*-poly(arylisocyanide): Two Sequential, Mechanistically Distinct Polymerizations Using a Single Catalyst

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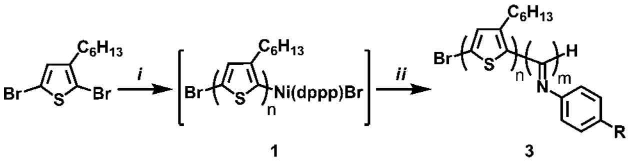
Abstract: Block copolymers of poly(3-hexylthiophene) and a poly(arylisocyanide) were synthesized in a single pot via the addition of 2-bromo-3-hexyl-5-chloromagnesiothiophene followed by *n*-decyl 4-isocyanobenzoate to a solution of Ni(1,3-bis(diphenylphosphino)propane)Cl_2. The respective mechanistically distinct polymerizations proceeded in a controlled fashion and afforded well-defined block copolymers with tunable molecular weights and compositions. The block copolymers exhibited microphase separation characteristics in the solid state.

The self-assembly of semiconducting block copolymers has recently emerged as a promising approach to achieving the hierarchical and morphological control needed for understanding and optimizing the charge separation and shuttling processes inherent to organic photovoltaic (OPV) devices.[1] Block copolymers containing regioregular poly(3-hexylthiophene) (P3HT) are widely studied for such applications due to P3HT's excellent electronic properties and synthetic accessibility[2] as well as the numerous methods available for its modification.[3] The preparation of these block copolymers typically involves either elaborating an end-functionalized polythiophene into an appropriate macroinitiator for the chain extension of a second block via a polymerization process that is mechanistically distinct from that of P3HT[4] or coupling preformed homopolymers with complementary end-functionalities.[5] Such methodologies, however, can be complex and inefficient, frequently resulting in materials that contain inseparable homopolymer impurities. A convenient method that employs a single set of reaction conditions and/or a single catalyst system to grow two mechanistically distinct homopolymers in a sequential fashion[6] would overcome these issues and facilitate access to a broad range of P3HT-containing block copolymers.

Regioregular P3HT is commonly prepared via a Ni-catalyzed Grignard metathesis (GRIM) polymerization of 2,5-dibromo-3-hexylthiophene.[2] In a generally accepted mechanism, the polymerization proceeds via the oxidative addition of a Ni(0) catalyst into a Br-terminated P3HT, followed by transmetalation with a magnesiothiophene monomer and reductive elimination. A reactive Ni(II) species resides at the P3HT terminus in the resting state of this catalytic cycle (**1**, Scheme 1). While treatment of this species with various organomagnesium reagents effectively quenches the polymerization reaction, often with concomitant installation of a functional group,[3] we reasoned that the resulting Ni(II) complex may possess sufficient reactivity to catalyze the polymerization of other monomers, such as isocyanides, which have been reported to polymerize under similar conditions.[7] Moreover, poly(isocyanide)s have been prepared from a large pool of readily available monomers. They may adopt helical architectures,[7b,8] and recent reports have prompted their utility in OPV devices.[9] Hence, block copolymers containing P3HT and poly(isocyanide)s are attractive targets for study in various electronic applications.

Scheme 1. Synthesis of Poly(3-hexylthiophene)-*block*-poly(*n*-decyl 4-isocyanobenzoate) via Sequential Monomer Addition



(***i***) (1) *i*PrMgCl, THF; (2) Ni(dppp)Cl_2. (***ii***) (1) CNPh-*p*-$CO_2C_{10}H_{21}$ (**2**), THF; (2) CH_3OH. R = $CO_2C_{10}H_{21}$

As summarized in Scheme 1, initial efforts focused on exploring the ability to grow a poly(phenylisocyanide) (PPI) from P3HT. Using standard methods,[2] 2-bromo-3-hexyl-5-chloromagnesiothiophene (generated *in situ* from 2,5-dibromo-3-hexylthiophene and *i*PrMgCl) was polymerized in THF using Ni(dppp)Cl_2 ($[\text{monomer}]_0/[\text{Ni}]_0 = 30$) (dppp =1,3-bis(diphenylphosphino)propane) to generate **1**. When no further molecular weight increase was observed by size exclusion chromatography (SEC), an aliquot was removed for further analysis (see below), and *n*-decyl 4-isocyanobenzoate (**2**) ($[\mathbf{2}]_0/[\text{Ni}]_0 = 30$) was added to the reaction vessel. After 1 h, the mixture was poured into excess methanol, and the precipitated solids were collected in 82% isolated yield (over the two polymerization steps) via filtration.

As shown in Figure 1A, SEC analysis revealed that the isolated material was of higher molecular weight and lower polydispersity (M_n = 7.28 kDa; polydispersity index (PDI) = 1.15) than that contained within the aliquot removed after completion of the thiophene polymerization (M_n = 4.19 kDa; PDI = 1.35).[4h] These results were consistent with the chain extension of **1** and, combined with ^{1}H NMR spectroscopy, which revealed signals attributable to both P3HT and PPI, indicated that **3** had formed.

The narrow molecular weight distributions exhibited by the copolymer prepared in our preliminary experiment suggested to us that the polymerization of **2** may have occurred via a controlled chain-growth process. To investigate, a series of chain extension polymerizations were performed by equally dividing a THF solution of macroinitiator **1** (M_n = 2.70 kDa; PDI = 1.31) and adding different quantities of **2** to each fraction. As shown in Figure 1B, a linear correlation between the M_n of the crude reaction polymer products and the feed ratio of **2**/**1** was observed, and each copolymer analyzed exhibited a narrow polydispersity (PDI < 1.35). These results support the established[2] quasi-living nature of GRIM polymerizations and that the polymerization of **2**, as initiated by **1**, also proceeded in a similarly controlled manner.[10]

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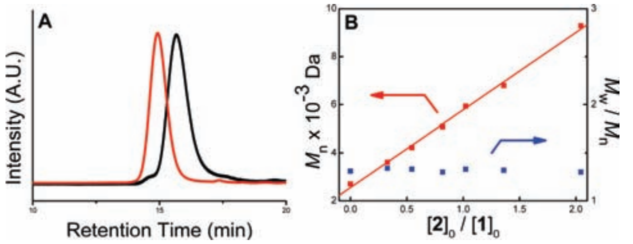

Figure 1. (A) Representative size exclusion chromatograms of homopolymer **1** (black) and its respective block copolymer **3b** (red); see Table 1 for M_n and PDI data. (B) Plot of M_n and M_w/M_n values of **3** measured as a function of the feed ratio of **2** to **1** ($M_n = 2.70$ kDa; PDI = 1.31). M_n and M_w/M_n were determined by SEC (eluent = THF, 25 °C).

As summarized in Table 1, a variety of copolymers with different molecular weights and compositions were synthesized using the aforementioned method by simply varying the initial feed ratio of monomers. In addition, all of the copolymers synthesized were isolated in high yields (81−90%) and exhibited narrow, monomodal distributions by SEC (Figure S2, Supporting Information). Collectively, these results support the successful union of two mechanistically distinct polymerization reactions within a single reaction vessel to obtain well-defined block copolymers containing P3HT.

Table 1. Selected Molecular Weight and Polydispersity Data[a]

3	$[2]_0/[1]_0$[b]	M_n[c] (kDa)	M_w/M_n[c]	P3HT[d] (wt %)	yield[e] (%)
3a	34/1 (2.70)	9.29	1.30	29	90
3b	16/1 (4.19)	7.28	1.15	57	82
3c	25/1 (7.58)	11.6	1.13	65	85
3d	12/1 (5.47)	7.72	1.17	71	85
3e	10/1 (11.6)	13.7	1.17	85	81

[a] Block copolymers **3** were synthesized as shown in Scheme 1 by first preparing macroinitiator **1** of different M_n's, followed by addition of **2**. [b] The M_n of **1** (indicated in parentheses, in kDa) was determined by analysis via SEC of aliquots removed from the respective reaction mixtures prior to the addition of **2**. [c] M_n and M_w/M_n were determined by SEC and are reported as their polystyrene equivalents. [d] Determined by ^{1}H NMR spectroscopy. [e] Isolated yields over the two steps are indicated.

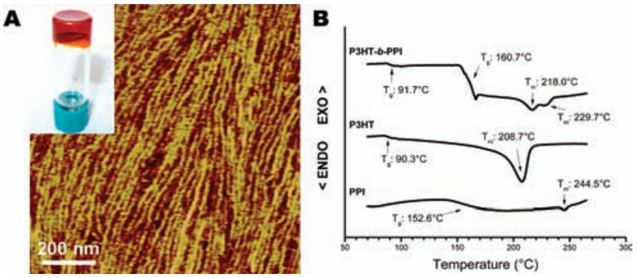

Figure 2. (A) AFM phase image of **3b** drop-casted from $CHCl_3$ ($[\mathbf{3b}]_0 = 10$ mg mL^{-1}) onto a Si wafer (film thickness = 80 nm). Inset: Photograph showing gelation behavior of **3c** in $CHCl_3$ (the critical gelator concentration was determined to be 15 mg mL^{-1} at 25 °C). (B) DSC thermograms of (top) **3c**, (middle) P3HT ($M_n = 8.2$ kDa), and (bottom) a homopolymer of **2** ($M_n = 17$ kDa) (rate = 10 °C min^{-1}).

During the course of our synthesis and characterization studies, **3** was observed to undergo gelation upon dissolution in $CHCl_3$, THF, and chlorobenzene, consistent with the formation of an entangled network of polymer chains in these solvents (Figure 2A, inset). To determine if these block copolymers were capable of assembling into higher order structures in the solid state, a film of **3b** drop-casted from $CHCl_3$ was investigated by tapping-mode atomic force microscopy (AFM). As shown in Figure 2A, the film exhibited a nanofibrillar morphology, consistent with other films of P3HT-containing block copolymers.[4,6] The nanofibrils were unidirectionally aligned and exhibited long-range order with persistent lengths of up to 1 μm (cf. Figure S4, Supporting Information). Differential scanning calorimetry (DSC) of **3c** provided further evidence that these block copolymers were capable of undergoing phase separation, as glass transition (T_g) and melting (T_m) temperatures assignable to both P3HT and PPI phases were observed (Figure 2B).

In conclusion, we have prepared a block copolymer containing regioregular P3HT and a poly(arylisocyanide) in one pot via the sequential addition of monomers that may be further modified. A single Ni complex was used to effect two mechanistically distinct polymerizations, each of which proceeded in a controlled fashion to give well-defined copolymers with low polydispersities and M_n's proportional to the monomer-to-catalyst feed ratios. The copolymers were found to aggregate in solution and exhibited microphase separation in the solid state, features which warrant their study in OPV and other electronic devices.

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Supporting Information Available: Synthetic procedures, spectroscopic and AFM data, and size exclusion chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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