Syntheses of Gradient π-Conjugated Copolymers of Thiophene
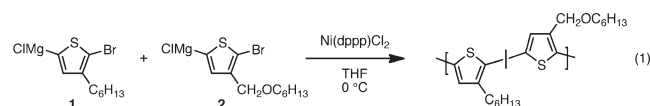
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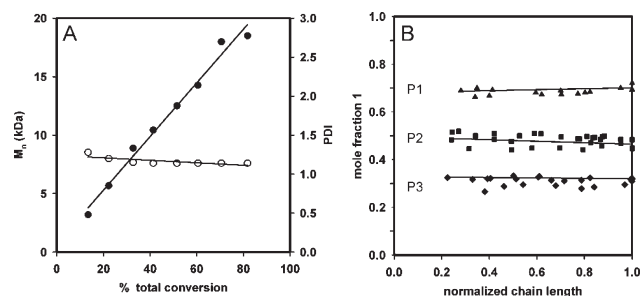Organic π-conjugated polymers are an increasingly important class of materials because of their widespread application in electronic devices.[1] Although there have been extensive studies aimed at controlling their physical and optoelectronic properties through synthetic modifications,[2] processing conditions,[3] and device designs,[4] little is known about the effect of copolymer sequence because these materials have been synthetically inaccessible. Now π-conjugated copolymers with varying sequences can be prepared through the newly discovered Ni-catalyzed chain-growth polymerization.[5−7] The ability to tailor properties by simply altering the copolymer sequence should provide a powerful new design strategy for preparing the next generation of tunable organic materials. We targeted *gradient* π-conjugated copolymers, which exhibit continuously changing composition along the polymer chain, because their anticipated phase-compatibilizing abilities may solve a long-standing problem in polymer-based solar cells by providing access to stable, nano-structured polymer blends.[8] Herein we report the first syntheses and characterization of gradient π-conjugated copolymers.

Figure 1. (A) Plot of M_n (●) and PDI (○) versus conversion for a batch copolymerization of **1** and **2** in THF at 0 °C ([**1**] = [**2**] = 0.04 M; [Ni(dppp)Cl₂] = 0.002 M). (B) Plot of the cumulative mole fraction of **1** in the copolymer versus the normalized chain length for the batch copolymerizations (**1**:**2** = 67:33 (**P1**, ▲); 50:50 (**P2**, ■); 33:67 (**P3**, ◆)).

Thiophene-based monomers were chosen because they have been successfully used to prepare block copolymers,[6] which suggests that cross-propagation can readily occur between these monomers.[9] Moreover, polythiophenes are one of the most widely studied and utilized π-conjugated polymers because of their good hole mobility and long wavelength absorption.[10] We began by evaluating whether the Ni-catalyzed copolymerization of monomers **1**[5a] and **2**[11] followed a chain-growth mechanism (eq 1). Both monomers were prepared in situ by magnesium−halogen exchange[12] using a mixed halogen precursor (I/Br) to regioselectively generate the Grignard reagents (Supporting Information). All copolymerizations were run at 0 °C to prevent monomer decomposition via reaction with *i*-PrI generated in the metathesis reaction.[13] When Ni(dppe)Cl₂ and Ni(dppp)Cl₂ were used as initiators, a linear increase in the number-average molecular weight (M_n) as a function of conversion was observed, consistent with a chain-growth mechanism (Figure 1A).[14] Other commercially available Ni catalysts, such as Ni(dppf)Cl₂ and Ni(PPh₃)₂Cl₂, did not exhibit chain-growth behavior in the copolymerizations (Supporting Information). Given that Ni-(dppp)Cl₂ produced copolymers with the lowest polydispersity (PDI), it was selected for the gradient copolymer syntheses.

A series of batch polymerizations were performed, wherein the initial molar ratio of **1**:**2** was varied, forming copolymers with different final compositions (**P1**−**P3**, Figure 1B). During these experiments it became apparent that there was little difference in the relative reactivity of **1** and **2**, which is not surprising given their similar steric and electronic properties.[9] To quantify these differences, the monomer reactivity ratios were determined through a series of experiments wherein the initial concentrations of **1** and **2** were varied, and the rates of monomer consumption were followed for the first 10% conversion (Supporting Information). These data were then fit to the copolymerization equation via least-squares regression.[15] In total, 17 experiments at different initial concentrations were simultaneously fit to determine the reactivity ratios. Consistent with our qualitative observations, monomer **1** gave a reactivity ratio (r_1) of 1.12 ± 0.04 while monomer **2** gave a reactivity ratio (r_2) of 1.09 ± 0.02. These values indicate that the growing polymer chain has little preference for either monomer. Thus, the copolymers synthesized using this batch method have a random sequence.

Because r_1 and r_2 are approximately equal to 1, the semibatch method is required to synthesize gradient copolymers. In semibatch copolymerizations, one monomer is gradually added to the reaction over time via syringe pump. One advantage of this technique is that gradient copolymers with varying composition profiles can be prepared by using different rates of monomer addition. Herein, monomer **1** was added to the reaction at varying rates to generate gradient copolymers **P4**−**P8** (Figure 2A).[16] Ni(dppp)Cl₂ was used to prepare gradient copolymers **P4**−**P7**. Given that propagation was recently shown to occur at both chain ends in the Ni(dppe)Cl₂-catalyzed synthesis of poly(3-hexylthiophene),[17] gradient copolymer **P8** was synthesized using a functionalized Ni(dppe)ArBr initiator, which can only propagate from one chain end (see Supporting Information). To elucidate the copolymer sequence, aliquots were taken during polymerization and analyzed by ¹H NMR spectroscopy and GPC to determine the mole fraction incorporation of each monomer as a function of chain length. Representative data are shown in Figure 2A, where the rate of monomer addition determines its mole fraction distribution along the copolymer chain.[18]

The influence of copolymer sequence on the optical and physical properties was investigated. For comparison, the results for the block, random, and gradient copolymers with the same molar composition (1:1) are presented in Table 1 along with the homopolymer data. The spectroscopic studies revealed similar spectra for all three copolymers in solution. The emission maxima resemble those of P3HT, suggesting efficient energy transfer to oligothiophene moieties within the polymer chains. In contrast,

$$ \text{(1)} $$

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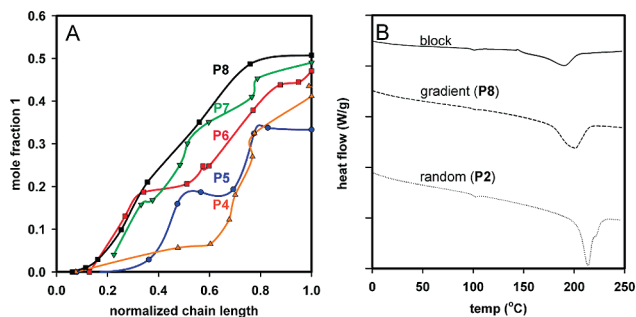
Figure 2. (A) Plot of the cumulative mole fraction of **1** in the copolymer versus the normalized chain length for the semibatch copolymerizations (**1** addition rates (mmol/min) = 0.12 (**P4**, ▲), 0.20 (**P5**, ●), 0.28 (**P6**, ■), 0.40 (**P7**, ▼), and 0.48 (**P8**, ■)). (B) DSC data for selected copolymers.

Table 1. Copolymer Characterization Data

	M_n (kDa)	PDI	T_c (°C)	T_m (°C)	soln (CHCl$_3$) abs λ_{max} (nm)	em λ_{max} (nm)
P3HT	18.5	1.1		240	445	568
P3HOMT	16.5	1.1	240		425	556
block	22.1	1.1		190	451	572
random (**P2**)	16.0	1.3		213	449	574
gradient (**P8**)	10.3	1.1		200	445	568

thin-film spectroscopic studies revealed some differences among the copolymers (Supporting Information). In addition, each co-polymer exhibited a unique thermal transition (Figure 2B and Supporting Information). These results indicate that there are sequence-dependent changes in the solid-state organization, which is reflected in the different thin film optical and physical properties. As a result, these gradient copolymers might be useful not only for their potential phase-compatibilizing abilities but also for tailoring solid-state properties.

In summary, we prepared the first gradient π-conjugated copolymers via Ni-catalyzed chain-growth copolymerization of 3-hexylthiophene and 3-((hexyloxy)methyl)thiophene. Because rate studies indicated little difference in monomer reactivities, one monomer was gradually added to the polymerization over time to form gradient copolymers. Now that controlled sequence π-conjugated copolymers can be synthesized, the next goal is to identify their unique properties, including phase-compatibilizing abilities in homopolymer blends. Preliminary data reported herein suggest that the solid-state optical and physical properties are influenced by the copolymer sequence. Finally, although the Ni-catalyzed copolymerizations are chain growth under the conditions reported herein, our preliminary attempts to expand the substrate scope by examining the copolymerization of mono-mers with varying steric and electronic properties has high-lighted[9] a need for developing improved catalysts.

Supporting Information Available: Experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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