Macromolecules **2008**, *41*, 9505−9507

Communications to the Editor

Facile Synthesis of ABA Triblock Copolymer Containing Regioregular Poly(3-hexylthiophene) and Polystyrene Segments via Linking Reaction of Poly(styryl)lithium

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Received October 5, 2008
Revised Manuscript Received October 29, 2008

There has been growing attention paid to poly(3-alkylthiophene)s in the field of polymer electronic devices such as organic field-effect transistors[1] and plastic solar cells.[2] Since McCullough et al. discovered the quasi-living Grignard metathesis (GRIM) polymerization system for regioregular poly(3-hexylthiophene) (P3HT),[3] followed by the improvement by Yokozawa et al.,[4] various block copolymers with low polydispersity indices (PDIs) have been synthesized.

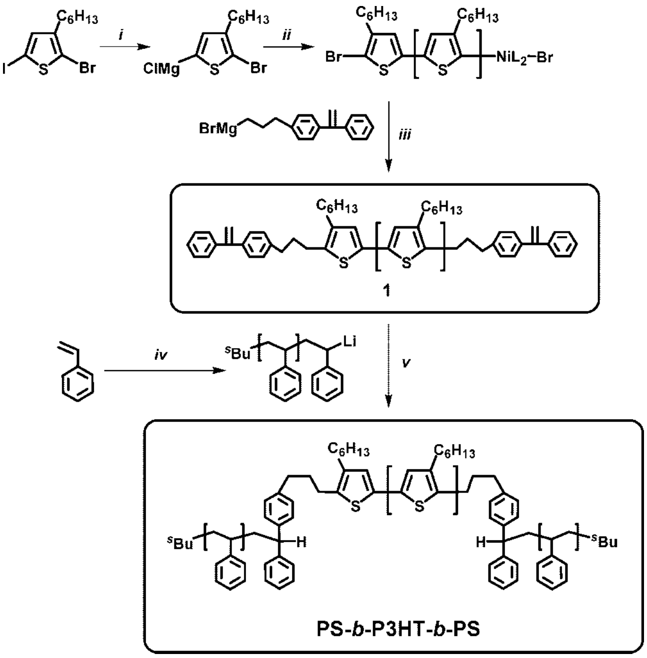
To synthesize rod−coil block copolymers containing P3HT segments, multistep and complex site transformation reactions have been required because different polymerization systems must, in general, be used for P3HT and coil segments. This difficulty limits the number of synthetic examples of well-defined block copolymers containing P3HT segments. Indeed, only a few examples of AB diblock copolymers, P3HT-*b*-poly(alkyl acrylate),[5] P3HT-*b*-polystyrene (PS),[6] P3HT-*b*-polyisoprene,[6] poly(alkylthiophene)-*b*-polylactide,[7] and P3HT-*b*-poly(2-vinylpyridine),[8] have been synthesized so far by the combination of GRIM and controlled radical or living anionic polymerization. The employed methods always involve three or four steps starting from an ω-vinyl monofunctionalized P3HT, which is obtained by the cross coupling reaction of a P3HT−nickel complex with a vinyl-containing Grignard reagent, followed by transformation reactions of the vinyl group to an initiating site and the polymerization of a second monomer. The PDIs of the resulting block copolymers are relatively large (>1.3) in most cases, probably because of multistep reactions, except for P3HT-*b*-poly(2-vinylpyridine)[8] with relatively low PDIs (1.18 to 1.28). In addition, structural variation is restricted to only the AB diblock type because the P3HT−nickel complex reacts with the vinyl-containing Grignard reagent selectively at the ω chain end to form the monofunctionalized P3HT, which is used as the starting material.[9] Therefore, the synthesis of more complex multisegmented blocks and even the ABA type is very difficult by current methodologies.

Herein we describe the facile synthesis of a coil−rod−coil ABA triblock copolymer containing regioregular P3HT and PS segments (PS-*b*-P3HT-*b*-PS) based on a novel approach involving only two steps, an in situ introduction of 1,1-diphenylethylene (DPE) moieties at the α,ω ends of P3HT and a linking reaction with a living anionic polymer of styrene. The extra steps of the transformation reactions are unnecessary. Because the structure of the ABA type containing a regioregular P3HT segment is quite rare, the proposed methodology extends the variation of its self-assembled structures.

The synthesis routes for PS-*b*-P3HT-*b*-PS are shown in Scheme 1. The key step is the in situ introduction of DPE moieties at the α,ω ends of P3HT, which readily and quantitatively link with living PS without oligomerization of DPE units due to its steric hindrance.[10] Advantageously, the proposed polymer−polymer linking method provides more reliable molecular weights and compositions of block copolymers than do conventional macroinitiator methods because both segments can be separately characterized.

The polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene initiated with $Ni(dppp)Cl_2$ (dppp is 1,3-bis(diphenylphosphino)propane) was carried out by the quasi-living GRIM method.[3,4] After the monomer conversion reached 95%, the intermediate P3HT complex was reacted in situ with the Grignard reagent, 1-[4-(3-bromomagnesiopropyl)-phenyl]-1-phenylethylene, in THF at room temperature for 30 min. From matrix-assisted laser desorption ionization time-of-flight (MALDI-

Scheme 1. Synthesis Routes for Polystyrene-*b*-poly(3-hexylthiophene)-*b*-polystyrene[a]



[a] (i) Isopropylmagnesium chloride, LiCl, THF, 0 °C, 30 min; (ii) $Ni(dppp)Cl_2$, rt, 10 min; (iii) 1-hexene as an additive, rt, 30 min; (iv) *sec*-butyllithium, benzene, rt, 2 h; (v) benzene, rt, 24 h, quenched with methanol.

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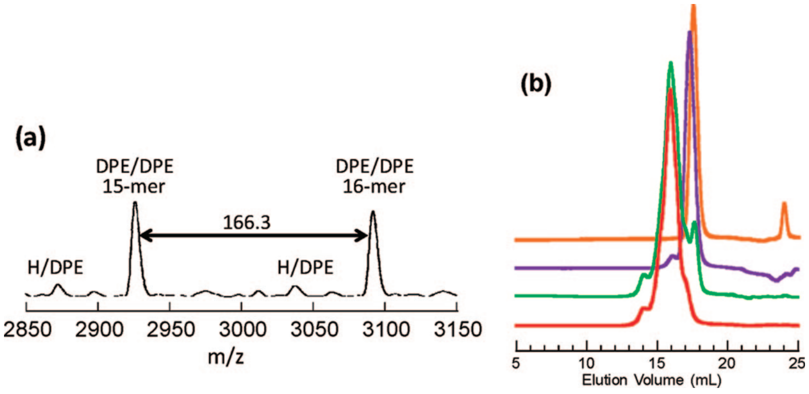

Figure 1. (a) MALDI-TOF MS spectrum of the α,ω-ends DPE-functionalized P3HT (**1**) and (b) GPC traces of homo PS (orange), **1** (purple), the crude product after the linking reaction (green), and the isolated PS-*b*-P3HT-*b*-PS (red).

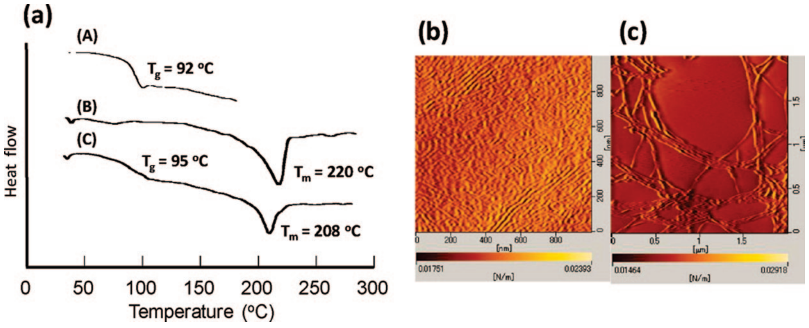

Figure 2. (a) DSC thermograms of (A) PS, (B) P3HT, and (C) PS-*b*-P3HT-*b*-PS and AFM phase images of PS-*b*-P3HT-*b*-PS thin films cast from (b) a toluene solution and (c) a 1,2-dichlorobenzene solution.

TOF) mass spectroscopy, the major disubstituted product, that is, the α,ω-ends DPE-functionalized P3HT (**1**), was found to be obtained in more than 90% yield together with the minor monosubstituted one.[11](See Figure 1a.) This is a surprisingly selective functionalization because the use of alkylmagnesium halide as an end-capping reagent generally provides a disubstituted product in ~70% yield.[9] We mention that such selectivity dominates the structural homogeneity of the block copolymer synthesized afterward. The molecular weight and PDI of **1** are 7 000 and 1.18, respectively, confirmed by gel permeation chromatography (GPC). The ^{1}H NMR spectrum of **1** clearly shows the characteristic signal at 5.43 ppm, which is assignable to the two vinyl protons of the DPE moieties (Figure S1a in the Supporting Information).

Next, **1** was reacted with a two-fold excess of poly(styryl)-lithium (PSLi, M_n = 5 900, PDI = 1.04) toward the DPE moiety in benzene at 40 °C for 24 h. As shown in Figure 1b, the peak top (purple, 17.5 mL) for **1** obviously shifts to a higher molecular weight region (green, 15.9 mL) after the reaction. The excess homo PS was successfully eliminated by fractional precipitation using cyclohexane/hexane. The isolated PS-*b*-P3HT-*b*-PS (red) possesses a major sharp peak with a minor shoulder for a lower molecular weight product that probably corresponds to an AB diblock copolymer (<6%) and with a small peak (<2%) at a higher molecular weight product that cannot be identified. Both M_n values of PS-*b*-P3HT-*b*-PS, which were determined by GPC calibrated using PS standards (18 000) and by GPC right-angle laser light scattering (RALLS) (18 900), are in good agreement with the calculated value (18 860). The PDI corresponding to the main peak determined by GPC is low (1.15). In addition, ^{1}H NMR spectroscopy of PS-*b*-P3HT-*b*-PS confirms the absence of the signal for the vinyl protons of DPE moieties at 5.43 ppm as well as a reasonable composition of two segments being almost consistent with that targeted (Figure S1b in the Supporting Information). Thus, the expected PS-*b*-P3HT-*b*-PS (5 900−7 000−5 900) could be successfully synthesized. Not only the ABA type but also many other multisegmented blocks, for example, ABCBA pentablock and (AB)$_n$ multiblock copolymers, can be synthesized by extending our proposed methodology, which exploits the selective functionalization at the α,ω ends of P3HT.

The thermal property of the polymer was investigated by differential scanning calorimetry (DSC), exhibiting T_g at 95 °C and T_m at 208 °C, which corresponded to the PS and P3HT segments, respectively. (See Figure 2a.) This result supports the phase segregation of PS-*b*-P3HT-*b*-PS.

The optical properties of PS-*b*-P3HT-*b*-PS were studied by ultraviolet−visible (UV−vis) spectroscopy. The solution-state UV−vis spectra of homo P3HT and PS-*b*-P3HT-*b*-PS in chloroform show maximum absorptions (λ_{max}) at ~445 nm (Figure S2a in the Supporting Information). In the film state, the λ_{max} of the two polymers are bathochromically shifted to ~560 nm compared with those in the solution state (Figure S2b in the Supporting Information). Both polymers show a shoulder at ~610 nm that is related to vibronic absorption, indicating a high degree of ordering in the polymer films even when PS is covalently linked to P3HT.

To gain insight into the morphology, we prepared thin films of PS-*b*-P3HT-*b*-PS by drop casting from a toluene or 1,2-dichlorobenzene solution at room temperature, followed by annealing at 120 °C for 24 h. The surface morphology of the thin films was observed by atomic force microscopy (AFM). Continuous nanofibril structures with 10−15 nm widths were observed for the toluene cast film, where the bright and dark areas represent the P3HT and PS domains, respectively (Figures 2b and S3a in the Supporting Information). This observation must be due to the microphase separation derived from flexible PS segments. Interestingly, nanowire networks of 20−25 nm in diameter and a few micrometers in length were clearly observed for the cast film from a 1,2-dichlorobenzene solution (Figures 2c and S3b and S4c in the Supporting Information). The formation of the nanowire structures should be dictated by the immiscibility of PS and P3HT segments, as reported in the literature describing the nanowire structures of P3HT-*b*-PS diblock copolymer,[12] although the reason in which the different solvents resulted in two different morphologies is not clear at the present time. We expect potential applications of such morphologies to plastic solar cells because efficient nanowire-based bulk-heterojunction solar cells have been recently reported.[13]

In conclusion, the synthesis of a well-defined coil−rod−coil ABA triblock copolymer containing flexible coil PS and stiff rod regioregular P3HT segments, respectively, has been demonstrated for the first time by the combination of quasi-living GRIM and living anionic polymerization based on DPE chemistry. The ABA triblock copolymer was characterized by GPC, GPC-RALLS, ^{1}H NMR, DSC, and UV−vis spectroscopy. AFM images of thin films of the block copolymer clearly showed nanofibril and nanowire structures depending on the casting solvents.

Supporting Information Available: Experimental, ^{1}H NMR, and UV−vis spectra and AFM images of PS-*b*-P3HT-*b*-PS. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA802227R