Donor−Acceptor Poly(thiophene-*block*-perylene diimide) Copolymers: Synthesis and Solar Cell Fabrication

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ABSTRACT: Donor−acceptor diblock copolymers, composed of regioregular poly(3-hexylthiophene) (*rr*P3HT) as the electron donor block and poly(perylene diimide acrylate) (PPDA) as the electron acceptor block, were prepared and used to fabricate a solar cell. Vinyl-terminated *rr*P3HT was synthesized by Grignard metathesis polymerization and converted to an alkoxyamine macroinitiator. This polythiophene macroinitiator was used in controlled free radical polymerization of a perylene diimide-containing acrylate. The targeted donor−acceptor diblock copolymers were prepared with low-to-moderate polydispersity indices (1.2−1.4) and molecular weights sufficiently high for producing films by spin-coating. These copolymers showed efficient photoluminescence quenching in the solid state, indicative of charge separation, and were used to produce a solar cell with power conversion efficiency of 0.49%.

Introduction

The efficient utilization of renewable and sustainable energy sources grows in urgency with increasingly rapid fossil fuel consumption. Solar energy is abundant, but the production of solar cells based on silicon and other inorganics remains expensive despite optimization.[1,2] Conjugated polymers represent more easily processable and cost-effective alternative materials for producing solar cells, as they can function as light-harvesting plastics in applications where inorganic materials are not well-suited.[3]

Most conjugated polymers are hole transporters (electron donors).[4] In the heterojunction photovoltaic design, an electron-transporting (electron-accepting) material is combined with the hole transporter to form a bicontinuous morphology.[5] Upon photoexcitation, the generated excitons diffuse to the donor−acceptor interface and dissociate, whereupon charges diffuse to their respective electrodes, producing current. Considering an exciton diffusion length of ~10 nm or less,[6] the donor and acceptor phases should be of this order to minimize recombination. Blends of two different homopolymers (i.e., an electron transporter and hole transporter) that are initially phase separated on the micron scale eventually coarsen into large domains. More efficient morphologies for charge separation and transport would be those associated with microphase-separated block copolymers, in which the sizes of the microdomains are comparable to the exciton diffusion length. Block copolymers microphase separate into a variety of nanoscale morphologies, depending on the volume fraction of the blocks, the rigidity of the chains comprising the blocks, and the magnitude of the Flory−Huggins segmental interaction parameter.[7,8] Control over the orientation and ordering of the microdomains can afford viable potential routes toward efficient, all-polymer-based photovoltaic devices.

Donor−acceptor block copolymers have been prepared with the objective of obtaining nanoscale domains of the electronically active blocks.[9−13] Hadziioannou and co-workers prepared PPV- and polythiophene-based diblock copolymers by nitroxide-mediated polymerization from suitable macroinitiators.[9] Thelakkat and co-workers[10−13] described diblock copolymers containing a poly(4-vinyltriphenylamine) (electron donor) block and a perylene bisimide acrylate (electron acceptor) block. The reported power conversion efficiencies in devices constructed from these diblock copolymers were as high as 0.35%, and continued optimization of the fabrication process should improve the efficiency.

An attractive electron donor for polymer-based photovoltaics is regioregular poly(3-hexylthiophene) (*rr*P3HT). Integration of *rr*P3HT into block copolymers can be accomplished by terminating the P3HT chain with functionality useful for initiating polymerization. When such P3HT macroinitiators are used to grow electron-accepting blocks, the desired donor−acceptor diblock materials can be obtained. Recent advances in *rr*P3HT synthesis, as described for example by McCullough and co-workers, have enabled the preparation of *rr*P3HT with narrow polydispersity and well-defined chain ends.[14,15] As an electron-accepting material, 3,4,9,10-perylene tetracarboxyl diimide (abbreviated perylene diimide) is appealing for its high electron mobility due to π-stacking of the perylene units.[16,17] Fabricated devices based on blends of P3HT and perylene diimide gave calculated power conversion efficiencies of ~0.4% when excited at 540 nm[16] and power conversion efficiencies of 0.18% under AM 1.5G solar simulation.[18] Here we report the synthesis of a donor−acceptor diblock copolymer in which the donor block is *rr*P3HT and the acceptor block is a polyacrylate with pendent perylene diimide groups. Generating this structure hinges on a smooth synthetic transition from the initially prepared polythiophene block to the perylene-containing block. With this diblock copolymer in hand, we were able to fabricate solar cells and evaluate devices containing this diblock copolymer as the active layer using AM 1.5G solar simulation.

Results and Discussion

We first considered the preparation of a *rr*P3HT macroinitiator from which a perylene-containing acrylate could be polymerized. While there is a reported route to P3HT macroinitiators for nitroxide-mediated polymerization,[19] we encountered difficulties with this procedure, and thus designed the method shown in Scheme 1, which proved simpler in our hands. First, 2,5-dibromo-3-hexylthiophene (**2**) was polymerized by the Grignard metathesis (GRIM) method to give *rr*P3HT **3** with a bromothiophene chain end.[15] The thiophenyl bromide chain end of **3** was converted to olefin **4** by palladium-catalyzed Stille coupling with tri-*n*-butylvinyltin.[20] Heck coupling of the vinyl-

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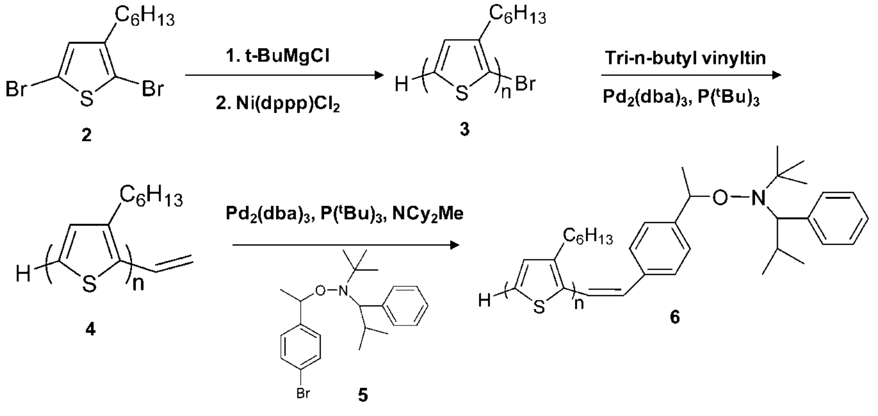
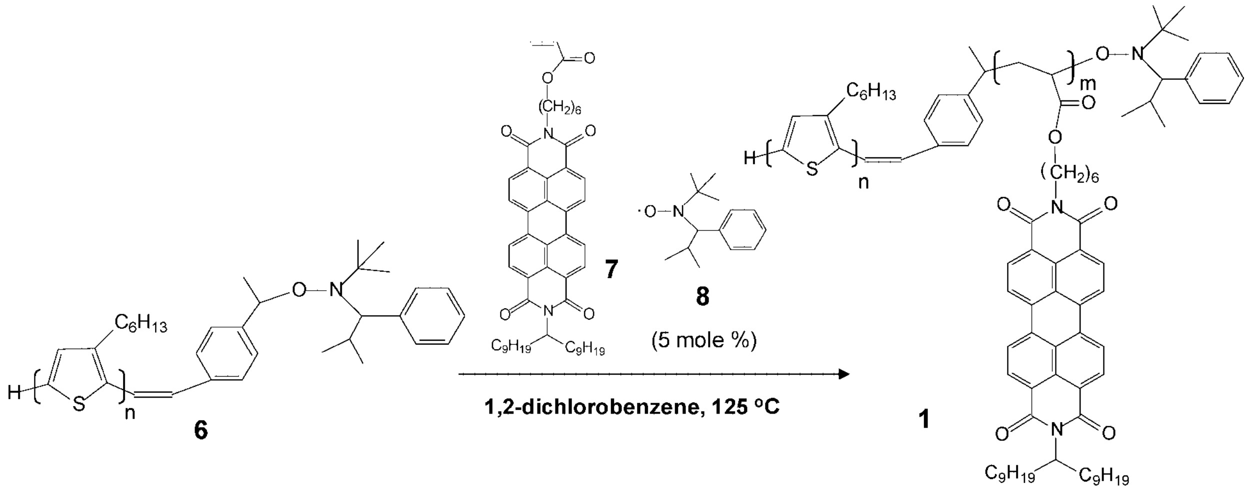
Scheme 1



Scheme 2



terminated *rr*P3HT **4** with phenyl bromide-functionalized alkoxyamine **5**[21,22] gave the desired *rr*P3HT macroinitiator **6**, which was used for the controlled free radical polymerization of perylene diimide acrylate (**7**).

The synthesis of perylene-containing acrylate monomer **7**, similar to that used by Thelakkat et al.,[10] is described in the Supporting Information. Following successful control experiments for nitroxide-mediated homopolymerization of **7**, the desired *rr*P3HT-*b*-poly(perylene diimide acrylate) copolymer **1** was prepared. Nitroxide-mediated polymerization of acrylate **7** from *rr*P3HT macroinitiator **6** was best conducted at 125 °C in 1,2-dichlorobenzene for 24 h under a nitrogen atmosphere, in the presence of a small excess (5 mol % based on **5**) of nitroxide **8** (Scheme 2).

A *rr*P3HT macroinitiator **6** with M_n 5500 and PDI 1.2 was used for the synthesis of diblock copolymers of type **1** with number-average molecular weights (M_n) of ~10 000 and ~16 000 g/mol and PDI values between 1.2 and 1.4. Following the polymerization, the reaction mixture was diluted with THF and precipitated into acetone, which removes (by dissolution) any residual unreacted monomer **7**. The molecular weights of copolymer **1** were controlled by the molar ratio of acrylate **7** to macroinitiator **6**. Figure 1 shows representative GPC traces of macroinitiator **6** (showing the expected narrow molecular weight distribution) and two examples of diblock copolymers of different estimated molecular weights (11 400 and 15 500 g/mol by GPC). The ^{1}H NMR spectrum of diblock copolymer **1** showed characteristic chemical shifts from the P3HT block (a singlet at 6.97 ppm for the thiophene CH and a triplet at 2.80 ppm for the methylene of the *n*-hexyl group nearest the thiophene) as well as the perylene diimide block (seen as a broad signal from 8.50 to 7.00 ppm for the aromatic protons and a signal at 5.0 ppm for the methine group). Integrating the aromatic thiophene protons against the methine protons of the perylene block gives the relative block lengths of the copolymer. Adjusting the feed ratio of macroinitiator **6** and perylene **7** allowed for adjustment of block lengths to give samples with a 3:1 and 1:1 ratio of thiophene and acrylate monomer units within the respective blocks.

In contrast to the intense photoluminescence of thin films of PPDA homopolymers, irradiation of thin films of block copolymer **1** with a hand-held UV lamp gave no apparent photoluminescence (complete quenching). Figure 2 compares solid-state fluorescence spectra of *rr*P3HT and PPDA homopolymer films to films of the *rr*P3HT−PPDA diblock copolymers. The fluorescence quenching observed for this block copolymer is the expected consequence of efficient charge transfer between

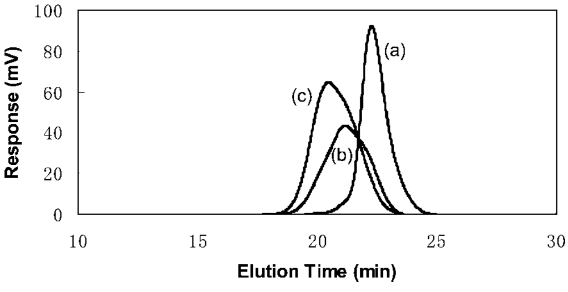


Figure 1. GPC traces (refractive index detection) of (a) P3HT macroinitiator **6**, (b) block copolymer with M_n 11 400 g/mol and PDI 1.4, and (c) block copolymer with M_n 15 500 g/mol and PDI 1.4.

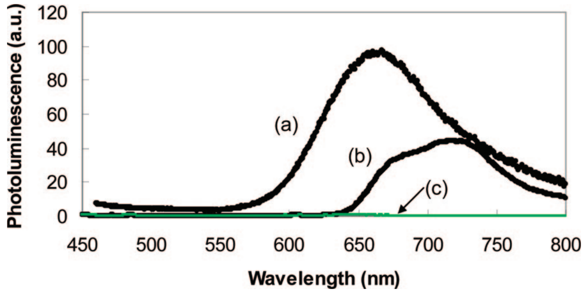


Figure 2. Photoluminescence spectra of (a) poly(perylene diimide acrylate), (b) poly(3-hexylthiophene) (P3HT), and (c) block copolymer **1**.

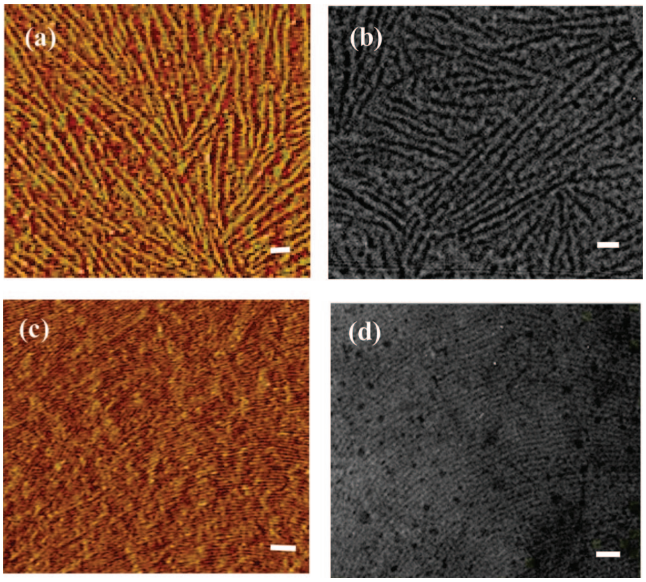


Figure 3. (a) SFM phase image and (b) TEM image of block copolymer thin film (from a 1 wt % toluene solution at 2500 rpm) after annealing for 2 h in toluene/chloroform vapor. (c) SFM phase image and (d) TEM image of drop-cast block copolymer film from 0.1 wt % toluene solution on Si substrate. Each scale bar = 100 nm.

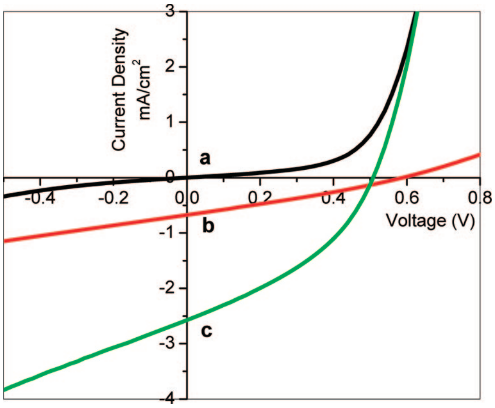


Figure 4. *J*−*V* characteristics (AM 1.5G, 100 mW cm^{-2}) of the P3HT-*block*-poly(perylene diimide acrylate)-based devices, using polymer **1** with molecular weight 13.6K: (a) under dark; (b) as-fabricated device; (c) following annealing at 150 °C for 20 min.

Table 1. Performance of ITO/PEDOT:PSS/1/LiF/Al Bulk Heterojunction Photovoltaic Devices under a Simulated Photovoltaic Light with 100 mW cm^{-2} Illumination (AM 1.5G)[a]

devices	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
pristine	0.67	0.59	0.28	0.11
annealed	2.57	0.51	0.37	0.49

[a] Solar mismatch factors were not applied in this study. J_{sc} = short-circuit current; V_{oc} = open-circuit voltage; FF = fill factor; PCE = power conversion efficiency.

the two electronically active polymers. As this initial and qualitative characterization suggested that these donor−acceptor diblock copolymers might be useful in solar cell fabrication, we initiated studies in that direction as described below.

Figure 3 shows scanning force microscopy (SFM) and transmission electron microscopy (TEM) images of diblock copolymer **1** (M_n 13.6K). In Figure 3a,b, the samples were prepared by spin-coating thin films of block copolymer **1**, followed by solvent annealing from a toluene/chloroform (50:50, v/v) mixture. The as-spun or "pristine" films (i.e., before solvent annealing) were smooth and used for solar cell fabrication (described later). We note that this solvent vapor annealing procedure, when performed on thin films of the diblock copolymer, led to a fibrillar morphology. The fibrils were ~25 nm in diameter and microns in length, typical of P3HT-containing block copolymers when the P3HT block is of substantial molecular weight.[19,23−25] In Figure 3c,d, the samples were prepared by solution-casting from toluene, followed by solvent evaporation over 1 day in a glass Petri dish. As seen in the figure, a fibrillar morphology was also obtained by this sample preparation.

Photovoltaic measurements were performed on solar cell devices fabricated with the following architecture: ITO/PEDOT:PSS/copolymer **1**/LiF/Al. To evaluate the efficiency of these devices, an AM 1.5G solar simulator was used, with an intensity of 100 mW/cm^2. All of the device fabrication, annealing, and characterization steps were performed in a $N_{2(g)}$-filled glovebox. Current−voltage (*J*−*V*) characteristics of the diblock copolymer-based devices are shown in Figure 4, both in the dark and under AM 1.5G illumination. The key characteristics of a device prepared using *rr*P3HT−PPDA diblock copolymers in the active layer are given in Table 1, including open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), and power conversion efficiency (η).

In fabricated solar cells containing the as-spun or pristine films in the active layer, the observed power conversion efficiency (PCE) was about 0.11%. Attempts to improve the efficiency by solvent annealing (to potentially take advantage of the fibrillar morphology) were ineffective due to dewetting of the film from the ITO/PEDOT-PSS support. Thus, thermal annealing was used subsequent to fabrication of the complete device, typically performed at 150 °C for 20 min. As shown in Table 1, the PCE of these solar cells improved significantly following thermal annealing. This postannealing increase in PCE arises from the increased short-circuit current and only slight decrease in the open-circuit voltage. The increased short-circuit current may arise from a reorientation and enhanced ordering of the copolymer during annealing, which would facilitate charge transport. Both AFM and TEM images of pristine and annealed block copolymer **1** films on ITO/PEDOT-PSS provide evidence that annealing enhanced the microphase separation of the diblock copolymer, while X-ray diffraction measurements showed an improved ordering (Supporting Information). In the dark current measurement, continuous injection of charges below 400 mV is attributed to impurities or defects (i.e., traps or pinholes).

The higher power conversion efficiency in these devices relative to triphenylamine-based copolymer systems[12] can be ascribed to the high carrier mobility and broad absorption (400−650 nm) of P3HT. Moreover, the nanostructured nature of the *rr*P3HT-*block*-PPDA copolymer appears to be advantageous over blended homopolymer systems. Annealed devices fabricated from polymer **1** under AM 1.5G solar simulation gave a higher measured PCE (0.49%) than blends of P3HT and *N,N′*-

bis(1-ethylproprcyl)-3,4,9,10-perylene bis(tetracarboxyl diimide) (EP-PTC) (0.4%), in which the calculated efficiencies derive from excitation at 540 nm rather than using solar simulation.[16] Integrating P3HT and the perylene units into a block copolymer structure limits the phase separation between the donor and acceptor blocks to the nanometer scale, closer to the exciton diffusion length. This phase separation may also be responsible for higher PCE relative to blends in which solar simulation was used.[17] Future optimization of the morphology of these donor−acceptor diblock copolymers, and improving control over domain orientation, will improve solar cell performance in these all-polymer active layer structures.

Experimental Section

3-Bromothiophene was purchased from TCI America and all other reagents from Aldrich. Tetrahydrofuran (THF) was dried and distilled over sodium/benzophenone ketyl. All reactions were run under an inert atmosphere of nitrogen or argon. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with an ATR accessory. HRMS data were acquired on a JEOL JMS 700 spectrometer. Solution NMR spectra were recorded on a Brüker DPX 300 MHz spectrometer. Chemical shifts are expressed in parts per million (δ) using residual solvent resonances for calibration. Gel permeation chromatography (GPC) was performed in THF (35 °C at a flow rate of 1.0 mL/min) using a Knauer K-501 pump with a K-2301 refractive index detector and K-2600 UV detector and a column bank consisting of two Polymer Laboratories PLGel Mixed D columns and one PLGel 50 Å column (1.5 × 30 cm). Molecular weights are reported relative to polystyrene calibration standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Brüker Reflex III spectrometer. MALDI-TOF samples were prepared by drop-casting a THF solution of polymer with terthiophene as a matrix. Fluorescence spectra were recorded on a Perkin-Elmer LS-55 fluorimeter. For solar cell fabrication, indium tin oxide (ITO)-coated glass substrates (20 Ω cm^{-2}), purchased from Thin Film Devices, Inc., were cleaned with detergent, ultrasonicated in deionized water, acetone, and isopropanol, then oven-dried at 100 °C for 1 h, and finally treated with oxygen plasma. Device production and current/voltage property measurements were conducted in a nitrogen-filled glovebox system (MBraun) (moisture <0.1 ppm; oxygen <0.1 ppm). An aqueous PEDOT:PSS (Baytron PH 500, HC Starck Inc.) solution was passed through a 0.45 μm filter and then spin-coated from aqueous solution at 5000 rpm. The substrate was dried for 10 min at 150 °C on a hot plate. A layer of copolymer **1** was deposited on top of the PEDOT:PSS layer by spin-coating (1200 rpm) from an anhydrous chlorobenzene (25 mg/mL) solution. A lithium fluoride (LiF, 6 Å) and aluminum layer (100 nm) was deposited on the polymer films by thermal evaporation at $\sim 2 \times 10^{-6}$ mbar. The active area of all devices was 6 mm^2. Thermal annealing was done by directly placing the completed devices on a digitally controlled hot plate at various temperatures, inside the glovebox filled with nitrogen gas. After annealing, the devices were placed on a metal plate and cooled to room temperature prior to conducting measurements. All current−voltage ($I-V$) characteristics of the devices were measured using a Keithley 2400 sourcemeter under AM 1.5G-filtered irradiation (100 mW cm^{-2}) from a 1 kW Oriel solar simulator. The light intensity was measured with an Oriel radiant power meter.

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Supporting Information Available: Syntheses of monomer **7** and block copolymer **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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