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Donor–Acceptor Block Copolymers

Crystalline–Crystalline Donor–Acceptor Block Copolymers**

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One of the challenging issues in designing new materials for organic electronics, such as photovoltaics or field-effect transistors, is that film-forming properties must be combined with functional and well-defined nanostructured morphologies to fulfill the complex requirements of light absorption, charge separation, and charge transport in confined geometries.[1,2] Morphological control on the nanoscale is also required to tune the interface between the functional domains and to ensure long-term stability of such devices. Block copolymers can meet these requirements, as they undergo phase segregation into versatile equilibrium microdomains such as cylinders, gyroids, or lamellae,[3] thus offering the possibility to control the type, size, and orientation of microstructure in the device. We have demonstrated the chain of control on all length scales—from molecular through mesoscopic to macroscopic—using the principle of self-assembly of donor–acceptor block copolymers for photovoltaic (PV) applications.[4–6] A polymerizable perylene bisimide derivative was used as electron acceptor and crystalline microdomains in an amorphous poly(triaryl amine) matrix (donor) were observed as a result of strong π–π interactions between adjacent perylene bisimide moieties.[7] Block copolymers that contain conjugated donor segments and electron-acceptor segments have also been presented,[8–11] but microphase separation was not reported.

The design of the Grignard metathesis polymerization (GRIM) of poly(3-hexylthiophene), P3HT,[12,13] and the in situ introduction of defined end groups[14] has stimulated the synthesis of P3HT block copolymers.[15–18] Recently, nitroxide-mediated radical polymerization (NMRP)[20] starting from P3HT macroinitiators was demonstrated.[11,19]

Herein we report on the first synthesis of crystalline–crystalline donor–acceptor block copolymers with P3HT as donor block and poly(perylene bisimide acrylate) (PPerAcr) as acceptor block (Figure 1). The crystallinity of both blocks not only can give rise to rich phase behavior in the bulk of these materials, but is also advantageous for charge-carrier mobility in the domains. We show that all important prerequisites for PV applications such as a high optical density, photoluminescence quenching in film, and microphase separation can be achieved in one molecule at the same time.

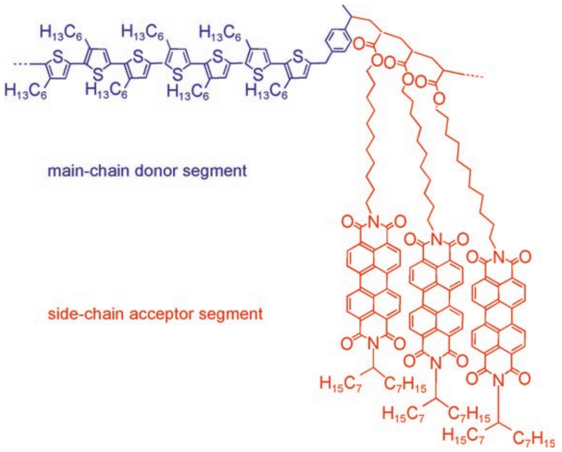

Figure 1. Poly(3-hexylthiophene)-*block*-poly(perylene bisimide acrylate), P3HT-*block*-PPerAcr. The first block consists of a rigid-rod poly(3-hexylthiophene) (blue); the second segment is built up of a flexible polyacrylate backbone with pendant side chains of crystalline perylene bisimides (red).

A set of donor–acceptor block copolymers poly(3-hexylthiophene)-*block*-poly(perylene bisimide acrylate) (P3HT-*block*-PPerAcr) was prepared in only two steps (Scheme 1). In the first step, we used a modified procedure of Yokozawa et al. starting from the thiophene derivative **1**.[21] In the last stage of polymerization, quenching of the active P3HT chain end in situ with **2** yields well-defined and narrowly distributed macroinitiator P3HT-I (**3**; polydispersity index (PDI) ≈ 1.1, $M_{n,SEC} = 8900\ g\,mol^{-1}$). The introduction of **2** at the end of the P3HT block was verified by ^1H NMR spectroscopy, which showed 84 % of the chains to be functionalized. However, this is outweighed by the simple and straightforward one-pot procedure for **3**. Nonfunctionalized P3HT and the resulting block copolymers with perylene bisimide acrylate can be separated in a later purification process which is necessary anyway. In the second step, **3** was used to polymerize perylene bisimide acrylate (PerAcr, **4**). To obtain a series of block copolymers with different segment lengths of **4**, the reaction time and [**3**]/[**4**] ratio were varied. All other reaction parameters, including the solvent, 0.2 equivalents TIPNO (**5**), and 5 mol % styrene (with respect to **4**), were kept constant. Similar reaction conditions were already applied in earlier polymerizations of PerAcr.[22] Addition of a small amount of styrene as comonomer[23] results in improved control of the polymerization of PerAcr, whereby self-initiation of styrene leading to possible homopolymerization of PerAcr **4** is not observed. Also, incorporation of a few styrene units into the chain does not affect the charge-transport properties of PPerAcr negatively.[24] In this manner,

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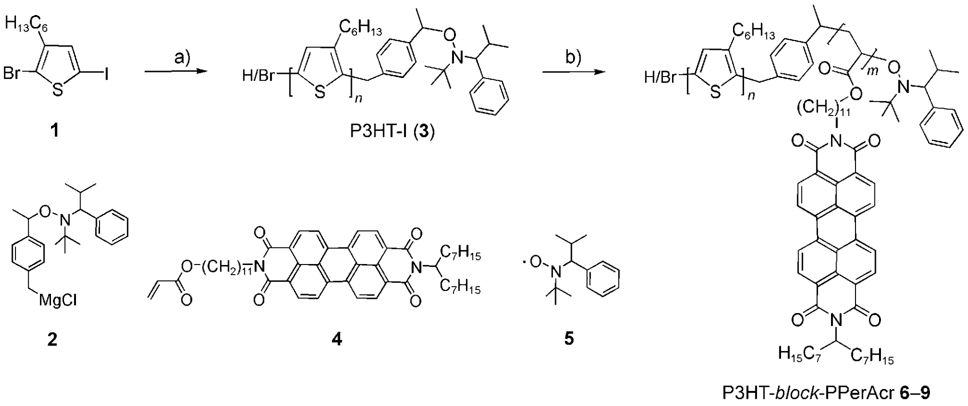

Scheme 1. Synthesis of poly(3-hexylthiophene) macroinitiator P3HT-I (**3**) and poly(3-hexylthiophene)-*block*-poly(perylene bisimide acrylate) block copolymers **6**–**9**. a) 1. THF, 0 °C, *i*PrMgCl, 90 min; 2. [Ni(dppp)Cl$_2$], 60 min; 3. **2**, 30 min; 4. HCl, MeOH; b) **4**, styrene, 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO), 1,2-dichlorobenzene, 125 °C, 10–24 h. Since the styrene comonomer fraction is too small for determination by ^{1}H NMR spectroscopy, it is not depicted in the chemical structure of the PPerAcr block. dppp = 1,3-bis(diphenylphosphino)propane.

four P3HT-*block*-PPerAcr block copolymers **6**–**9** with different block lengths of PPerAcr were synthesized. PerAcr monomer and unconverted P3HT were removed by Soxhlet extraction of the block copolymers. The size exclusion chromatography (SEC) curves of the macroinitiator and the purified block copolymers are shown in Figure 2 a. The peaks of the block copolymers shift towards smaller elution volumes. The number-average molecular weights M_n of **6**, **7**, **8**, and **9** are 16.1, 16.9, 20.6, and 24.8 kg mol^{-1}, respectively (Table 1), while the polydispersity indices, which are exceptionally low for fully functionalized block copolymers,[4,6] range between 1.24 and 1.53. The PPerAcr weight fractions (determined by ^{1}H NMR spectroscopy) for **6**, **7**, **8,** and **9** are 53.2, 59.7, 73.7 and 81.4 %, respectively, and thus a set of polymers is available in which the acceptor content is systematically varied.

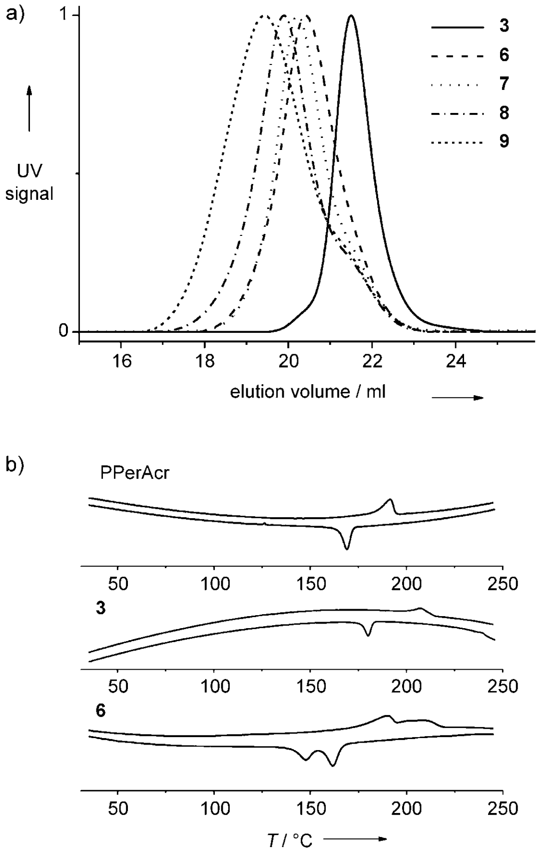

Figure 2. a) SEC traces of macroinitiator **3** and P3HT-*block*-PPerAcr block copolymers **6**–**9** measured in THF containing 0.25 wt % tetrabutylammonium bromide at a flow rate of 0.5 mL min^{-1}. b) DSC traces of macroinitiator **3**, PPerAcr homopolymer, and P3HT-*block*-PPerAcr **6**. The second heating and cooling traces are presented; curves were measured under nitrogen at 10 K min^{-1}.

Table 1: Molecular weights M_n, polydispersities (PDI), composition, and thermal properties of P3HT-I macroinitiator **3** and P3HT-*block*-PPerAcr block copolymers **6**–**9**.

Polymer	M_n [g mol^{-1}][a]	PDI[a]	PPerAcr[b] [wt %]	T_{m1} [°C][c]	T_{m2} [°C][c]	T_{on} [°C][d]
3	8900	1.12	0	208	–	308
6	16 100	1.25	53.2	190	211	327
7	16 900	1.24	59.7	191	211	327
8	20 600	1.31	73.7	202	–	341
9	24 800	1.53	81.4	206	–	348

[a] By SEC. [b] By ^{1}H NMR spectroscopy. [c] By differential scanning calorimetry (DSC). [d] By thermogravimetric analysis (TGA).

We investigated the thermal properties of the block copolymers (Table 1) using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermogravimetric analysis was conducted between 30 and 650 °C and showed very high thermal stability of the block copolymers, with onset temperatures T_{on} between 327 and 348 °C. The DSC trace of P3HT-I (**3**) showed a melting temperature T_m of 208 °C (Figure 2 b). Homopolymer PPerAcr melts at 192 °C. These two transitions are also observed in block copolymer **6**, for which two melting peaks T_{m1} and T_{m2} emerge at 190 and 211 °C. The first melting point at 190 °C arises from PPerAcr segments, and the second corresponds to the melting point of **3**. Block copolymer **7** with a slightly higher PPerAcr weight fraction exhibits the same behavior. The observation of two melting points in a block copolymer with melting temperatures close to those of the respective homopolymers strongly suggests that in **6** and **7** two different types of domains are present, indicative of microphase separation. By contrast, block copolymers **8** and **9** with perylene weight fractions of 73.7 and 81.4, respectively, exhibit only one melting point that lies between the transitions of the two homopolymers. The increased block lengths of PPerAcr in **8** and **9** might be responsible for this behavior, by causing an increased melting point of the second segment. As a result, the T_m of both blocks shift closer together and finally appear as one single melting point.

The optical properties of the block copolymers also confirm that perylene bisimide moieties are attached to the P3HT block. UV/Vis and photoluminescence (PL) data from THF solution are presented in Figure 3. The data of PPerAcr is included in order to identify the contribution of the two segments to the spectra. The UV/Vis spectrum of macroinitiator **3** exhibits one broad absorption band with λ_{max} at 445 nm, and PPerAcr shows three vibronic bands of the S_0–S_1 transition at 470, 490, and 525 nm (Figure 3a).[4] Unlike P3HT absorption, which is characteristic for diluted P3HT chains, the PPerAcr spectrum corresponds to highly aggregated perylene bisimide moieties. This is not surprising, since a short distance between adjacent chromophores is already achieved in a single PPerAcr chain. The absorbance spectra of all block copolymers show a superposition of P3HT and PPerAcr absorption, with contributions of the two segments in accordance with their respective weight fractions. The color of the solutions shifts from orange to red for increasing degrees of polymerization of PPerAcr. The PL behavior under the same conditions (0.02 mg mL^{-1} THF) was investigated on excitation at 400 and at 530 nm, where the absorption of P3HT and PPerAcr, respectively, is very high, to selectively excite each block. On excitation at 400 nm, P3HT (**3**) shows bright yellow fluorescence at 565 nm, and PPerAcr homopolymer emits only weak red light at 620 nm (Figure 3b). Accordingly, the PL of the block copolymers mainly consists of P3HT emission at 565 nm, which decreases for lower P3HT contents. Excitation at 530 nm causes bright emission from PPerAcr, which is now more intense than that from P3HT (Figure 3c). The PL intensity of the block copolymers therefore increases for increasing degrees of polymerization of PPerAcr. These results clearly show that both types of chromophores, namely, P3HT and PPerAcr, are incorporated into the block copolymers. The complete quenching of the PL of the block copolymers in film, however, indicates electron transfer from P3HT to PPerAcr (not shown).

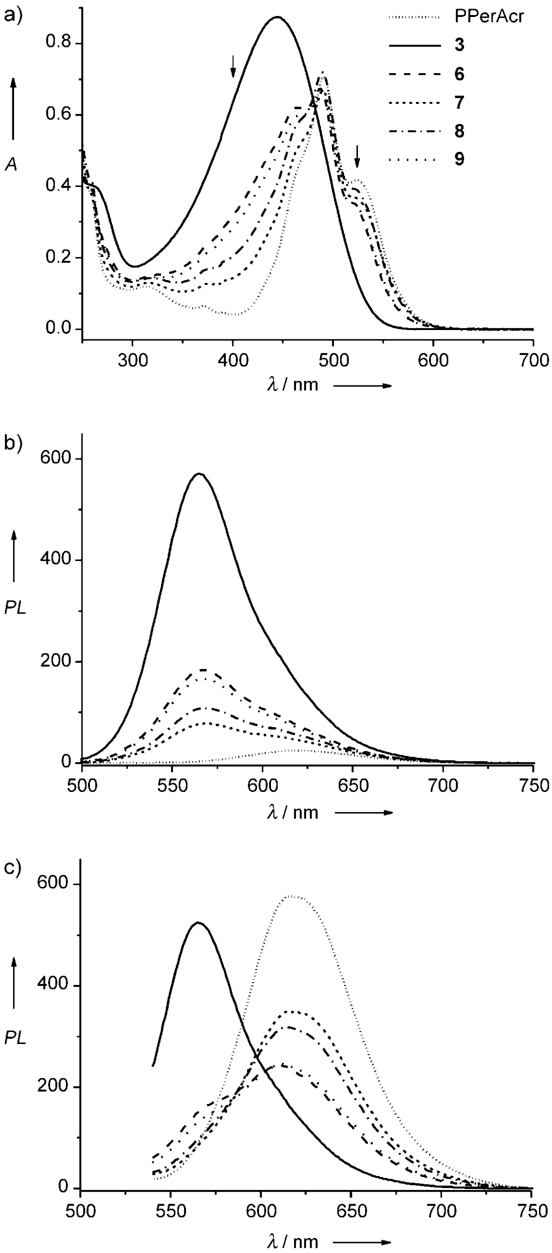

Figure 3. Absorption and emission spectra of macroinitiator **3** and P3HT-*block*-PPerAcr block copolymers **6**–**9** in solution (THF, 0.02 mg mL^{-1}). The code (dashes and dots) is the same for (a), (b), and (c). The data of a perylene bisimide homopolymer PPerAcr are also shown for comparison. a) Absorbance spectra and photoluminescence spectra on excitation at b) 400 and c) 530 nm. The arrows in (a) indicate the wavelength of excitation.

To provide evidence for microphase separation, we performed scanning electron microscopy (SEM) on a bulk sample of **6** (Figure 4). Micrometer-long bright domains of PPerAcr are observed, which most probably are due to a cylindrical microstructure of PPerAcr in a P3HT matrix. The orientation of the cylinders is random, and dotlike and elongated structures suggest vertically and horizontally oriented cylinders. This is in contrast to fibrillar structures

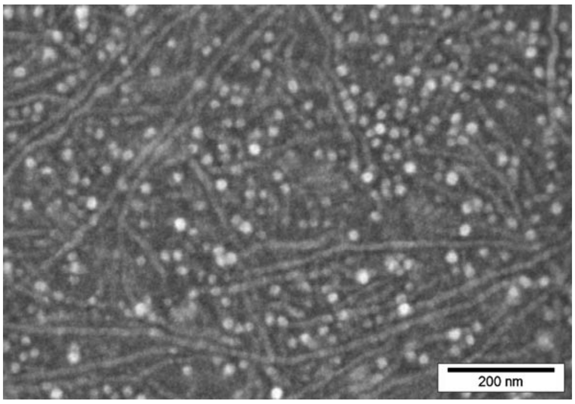

Figure 4. Scanning electron micrograph of the surface of a bulk sample of block copolymer **6** after annealing in chloroform vapor for four days. Bright and dark regions correspond to PPerAcr and P3HT domains, respectively.

commonly observed in films of P3HT and P3HT block copolymers.[25] Here, the bright domains are due to aggregation of perylene bisimide. No structural changes were observed for longer annealing times; this suggests the presence of an equilibrium morphology. Thus, we have demonstrated for the first time that microphase separation is observed in a fully functionalized block copolymer consisting of two crystalline blocks. This finding unambiguously shows that defined charge-transport pathways of both holes and electrons in separate domains can be provided in a single material.

In conclusion, we have presented the first crystalline–crystalline donor–acceptor block copolymers with poly(3-hexylthiophene) as donor block and poly(perylene bisimide acrylate) as acceptor block. We show that the various complex issues in photovoltaic devices or ambipolar field-effect transistors such as light absorption, the presence of a donor-acceptor heterojunction, photoluminescence quenching, crystallinity, and microphase separation can thus be addressed by the tailor-made synthesis of a block copolymer. The observation of microphase-separated domains in the bulk is encouraging, especially when considering that both blocks are crystalline. This finding may also solve morphological problems encountered in organic solar cells from blends of P3HT and low molecular weight perylene bisimides, for which external quantum efficiencies of 19 % were already demonstrated.[26,27] Therefore, we not only expect the novel block copolymers to outperform these simple blend devices, but we also envision additional applications in ambipolar field-effect transistors.

Experimental Section

All synthetic details are given in the Supporting Information.

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Keywords: block copolymers · donor–acceptor systems · microphase separation · polymerization

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