Influence of molecular weight on the solar cell performance of double-crystalline donor-acceptor block copolymers

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We investigate the influence of the molecular weight of double-crystalline donor-acceptor block copolymers comprised of poly(3-hexylthiophene) as donor and poly(perylene bisimide acrylate) as acceptor segments on the device performance of polymer solar cells. Two block copolymers 1 and 2 exhibiting different molecular weights but the same composition are compared. Block copolymer 2 with the higher molecular weight shows an improvement in the hole carrier mobility μ_{OFET} of more than two orders of magnitude, and an improvement in the external quantum efficiency of one order of magnitude reaching 31%, which is the highest reported value for a block copolymer system. © 2009 American Institute of Physics. [doi:10.1063/1.3257367]

Substantial research progress has been made in the field of solution-processed organic photovoltaic cells (OPVs) over the past decade.^{1,2} In such devices, the active layer morphology has been shown to be crucial to the device performance.^{3–5} State-of-the-art OPVs mostly employ blends of conjugated polymers as donor and fullerene derivatives as acceptor materials, which have already attained high power conversion efficiencies of $\sim 4\% - 6\%$.⁶⁻⁹ Perylene bisimides (PBI) are promising acceptor materials due to their absorption in the visible region and their tendency to crystallize.^{10,11} In general, a phase separation of the donor and acceptor material on a nanoscale is needed to separate charges efficiently, thereby addressing the conflict of the relatively large optical absorption length (~ 100 nm) and the short exciton diffusion length (~10 nm). Polymer blends comprised of low molecular weight PBIs and conjugated polymers such as poly(3hexylthiophene) (P3HT) give rise to uncontrolled crystallization of PBI, and hence lead to a reduction in the interfacial area, hindered charge transport, and moderate device performance.¹² One possible approach to solve this is the use of polymers with PBI units in the main chain.¹³ Yet, macrophase separation generally occurring in polymer-polymer blends is a drawback in terms of controlling the size and shape of the interfacial area. Block copolymers (BCPs) microphase separate into well-defined periodic nanostructures due to the interplay of covalent connectivity and demixing of the two polymer segments,¹⁴ and therefore are expected to guarantee distinct charge transport pathways for both holes and electrons.¹⁵ Indeed, the concept of fully functionalized BCPs comprised of amorphous donor blocks and side-chain crystalline perylene bisimide acceptor segments has demonstrated that co-continuous morphologies with domain sizes commensurate to the exciton diffusion length can be obtained while PBI crystallization is confined to microdomains.^{16–18} This approach has recently been extended to double-crystalline BCPs comprised of P3HT and

side chain crystalline PBI blocks by our group and others. $^{19\mathchar`21}$

Here, we report on the photovoltaic properties of these double-crystalline BCP systems. Two BCPs P3HT-*b*-poly(perylene bisimide acrylate) (P3HT-*b*-PPerAcr 1 and 2), which possess the same composition but differ in molecular weight by a factor of 2, are compared in single component single layer solar cells (Fig. 1).

The synthesis of P3HT-*b*-PPerAcr 1 was reported recently.¹⁹ A batch of the high molecular weight BCP 2 with exactly the same composition was synthesized analogously for this comparative study here. 1 and 2 exhibit molecular weights of 16.1 and 29.5 kg/mol [determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF) using polystyrene standards], and very low polydispersities of 1.25 and 1.15, respectively. The molecular weights of the P3HT segments in 1 and 2 are 8.9 and 17.0 kg/mol, respectively. The content of PPerAcr (determined by ¹H-NMR) is maintained at 55 wt % in both BCPs. Since the charge carrier mobility of P3HT films depends on the molecular weight considerably, we assumed such a dependence to be of importance here as well.^{22,23} The absorption profiles of 1 and 2 in films spun from chlorobenzene are depicted in Fig. 2(a).

The common characteristic P3HT homopolymer absorption at 610 nm arising from interchain exciton



FIG. 1. (a) Chemical structure of poly(3-hexylthiophene)-b-poly(perylene bisimide acrylate) P3HT-b-PPerAcr 1 and 2. (b) SEC curves showing the difference in molecular weights. The composition is maintained at 55 wt% of PerAcr for both 1 and 2.

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FIG. 2. Optical and electrical properties of 1 and 2. (a) Optical densities of thin films spin cast from chlorobenzene. (b) External quantum efficiency (EQE). (c) *J*-*V*-curves measured in the dark and under AM 1.5G conditions (at 100 mW/cm²). (d) OFET transfer characteristics of 1 and 2 in bottom-gate bottom-contact devices with gold electrodes (prepared by spin coating from chloroform).

delocalization²⁴ is visible in both BCPs, however the intensity at 610 nm is higher for 2, which indicates a higher degree of P3HT crystallinity.²⁵ Apart from this difference, the similar UV-visible profiles of both BCPs guarantee that the same amount of light is absorbed in the devices. Solar cells were fabricated using the device structure indium tin oxide/PEDOT:PSS/active layer/Al. The best devices were obtained by spin coating solutions of 15 mg BCP in 1 ml chlorobenzene at 700 r/min, giving a film thickness of ~ 60 nm. Using these parameters, a maximum external quantum efficiency (EQE) of 31% at 495 nm was obtained for 2. The average values measured from 16 solar cells resulted in an EQE_{max}=25%, J_{SC} =1.14 mA/cm², V_{OC} =0.40 V, fill factor=27.6%, and η =0.10%. Additional post production treatments of devices made from 2 such as chloroform vapor annealing²⁶ or thermal annealing did not lead to further improvements in the EQE. Devices with 1 as the active layer yielded EQE peak values of 3% only [Fig. 2(b)]. The corresponding J-V characteristics are shown in Fig. 2(c). P3HT-b-PPerAcr 1 with a molecular weight of 16.1 kg/mol gave very low short circuit currents $J_{\rm SC}$ around 0.08 mA/cm² and open circuit voltages $V_{\rm OC}$ of 0.51 V, resulting in poor power conversion efficiencies η of 0.007%. BCP 2 with a molecular weight of 29.5 kg/mol again shows a drastic improvement; a J_{SC} of 1.5 mA/cm² and a power conversion efficiency η of 0.2% are observed. The fill factor also increases from 0.17 to 0.25, and the open circuit voltage V_{OC} was 0.44 V. Organic field effect transistors (OFETs) with a bottom-gate bottom-contact configuration and gold electrodes using 1 and 2 as active layers both show p-channel behavior [Fig. 2(d)]. The hole carrier mobility $\mu_{\rm h}$ of 2 after spin coating is 5×10^{-3} cm²/V s, while the OFET device made of BCP 1 only shows a mobility of 3 $\times 10^{-5}$ cm²/V s. Thus, BCP 2 with the higher molecular weight exhibits an improvement of the EQE by one order of magnitude in solar cells, and an improvement of the hole carrier mobility by more than two orders of magnitude compared to BCP 1.



FIG. 3. Crystallinity of P3HT-*b*-PPerAcr 1 and 2. (a) Differential scanning calorimetry at 10 K/min under nitrogen. The second heating (solid lines) and second cooling curves (dashes-dots) are shown. The inset enlarges the recrystallization peak of 2. (b) X-ray scattering of 1, 2, P3HT macroinitiator, and PPerAcr homopolymer. Curves are offset in y-direction.

Differential scanning calorimetry (DSC) and x-ray scattering (XRD) experiments are used to investigate the phase behavior and to explain the huge difference in the device parameters of 1 and 2. The DSC curve of 1 shows two endotherms at 190 and 211 °C that are ascribed to the melting of PPerAcr and P3HT, respectively [Fig. 3(a)].

On cooling, PPerAcr crystallizes first at 162 °C followed by P3HT at 148 °C. This is evidenced by the crystallization peak at 162 °C, intensity increasing with increasing PPerAcr weight fraction. In the heating curve of 2, two endotherms are observed at 204 and 244 °C, corresponding to PPerAcr and P3HT, respectively. Note that the difference in the melting temperatures of 2 is larger than of 1. The single peak in the cooling curve of 2 at 178 °C entails the crystallization of both, P3HT and PPerAcr. The magnification of this peak reveals a small shoulder at 176 °C [see inset of Fig. 3(a)], arising from PPerAcr. Hence, crystallization of P3HT and PPerAcr occurs almost simultaneously in BCP 2. The larger distance between the two melting points and the coincidence of the two crystallizations in 2 are caused by the strong dependence of the melting and crystallization temperature of P3HT on its molecular weight.²⁷ Note that the thermal behavior of P3HT causes a fundamental difference in the thermal properties of 1 and 2: On cooling from the melt, PPerAcr crystallizes first in 1, while simultaneous crystallization of the two blocks occurs in 2. The different block lengths of P3HT in 1 and 2, together with the varying behavior of crystallization, finally give rise to different degrees of P3HT crystallinity, as can be tracked by the melting enthalpies $\Delta H_{\rm m}$. $\Delta H_{\rm m}$ (P3HT) is 15.4 J/mol for 2, but only 10.3 J/mol for 1. Qualitatively, the lower degree of P3HT crystallinity in 1 is also visible from the different optical densities at 610 nm [Fig. 2(a)].²⁵ In addition, the higher melting point of 244 °C of the P3HT segment in 2 depicts larger P3HT domains compared to those in 1, which melt at 211 °C. A larger domain size in turn should favor charge percolation and obviously is responsible for the improved hole transport in BCP 2. Indeed, a similar dependence has been observed in amorphous-crystalline BCPs, in which improvements of the OPV device performance with molecular weight were ascribed to better charge percolation due to microphase separation.²⁸

Further investigation of the crystalline nature of P3HT-*b*-PPerAcr is accomplished using XRD of thermally annealed powders [Fig. 3(b)]. Both P3HT macroinitiators exhibited very similar diffraction patterns. As a typical example, the XRD pattern of 1 is shown in Fig. 3(b). The known (100), (200), and (002) reflections of lamellar stacks

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of P3HT are observed at 2θ values of 5.3°, 10.6°, 16.1°, and 23.4°, respectively, in agreement with reported values.^{29,30} In the PPerAcr homopolymer two strong Bragg reflections appear at 2θ values of 3.0° and 4.8° , respectively. These result from a two-dimensional lattice formed by stacks of the PBI units of PPerAcr where the individual stacks are separated by the alkyl groups. An additional reflection at 2θ =25.6° indicates the π - π distance of 0.35 nm between two PBI moieties within one stack. The two BCPs 1 and 2 feature the reflections of the individual homopolymers and hence, stacks of P3HT and PPerAcr coexist here. A comparison of the intensities $100_{P3HT}/d(2\theta=3.0^{\circ})_{PPerAcr}$ and $002_{P3HT}/d(2\theta$ =25.6°)_{PPerAcr} yields higher values for 2, which is indicative of a higher degree of P3HT crystallinity. These results are in accordance with the higher degree of P3HT crystallinity of 2 observed in the absorption spectrum [Fig. 2(a)] and in the DSC curves [Fig. 3(a)].

In conclusion, we have shown that the molecular weight of double-crystalline donor acceptor BCPs P3HT-*b*-PPerAcr is influencing their solar cell performance to a large extent. A higher molecular weight of P3HT-*b*-PPerAcr (and thus a larger block length of P3HT) leads to a larger degree of P3HT crystallinity and to larger P3HT crystals, which again favor charge percolation, increase the EQE and finally the short circuit current. The reported EQE value of over 25% up to 31% exceeds those of blend cells comprised of P3HT and low molecular weight PBIs.^{11,21,31} Current research is concerned with light intensity-dependent measurements and the improvement of the fill factor, which limit the overall device efficiency.

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