

Stabilization of the nanomorphology of polymer–fullerene “bulk heterojunction” blends using a novel polymerizable fullerene derivative

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The morphological stabilization of donor–acceptor blends for bulk heterojunction solar cells can be achieved by cross-linking of the small molecular phase in the polymer matrix using a polymerizable fullerene derivative. In a comparative study the morphology of polymer–fullerene blend films was investigated using poly(3-hexylthiophene) (P3HT) as the polymer and C₆₁-butyric acid methyl ester (PCBM) or the newly synthesized polymerizable fullerene derivative, C₆₁-butyric acid glycidol ester, PCBG, as the acceptor molecule, respectively. Changes in the nanomorphology due to heat treatment of the films were studied by means of atomic force microscopy (AFM), transmission electron microscopy (TEM) and photoluminescence (PL) studies. The polymerization process was monitored with infrared absorption studies. As demonstrated by these comparative studies this newly synthesized fullerene gives considerable stabilization of the solid state morphology in these blends. Such prevention of the long term, high temperature instability of bulk heterojunction morphology displays an important route to increase the operational stability of plastic solar cells in future applications.

Introduction

Organic photovoltaic devices have been studied intensively for more than three decades due to their potential for low-cost, light-weight, flexible solar cells.^{1,2} Many of the investigated organic semiconductors were based on small molecules vacuum evaporated into thin films.³ The bilayer configuration used in many of the solar cell device architectures is based on the idea of exciton dissociation at donor–acceptor interfaces. As such there is an electron transfer from the donor phase onto the acceptor phase with consecutive transport of the charges to the respective electrodes. A major breakthrough in the field of donor–acceptor based systems for photovoltaic applications was the discovery of an ultrafast charge transfer from conjugated polymers to the fullerene C₆₀.⁴ In blends of conjugated, semiconducting polymers with fullerenes the forward electron transfer takes place within approximately 45 femtoseconds.⁵ This charge transfer is the basis for efficient photoinduced charge separation at the donor–acceptor interfaces that is needed in photovoltaic devices. Several approaches towards efficient organic solar cells have been investigated including polymer–fullerene blends,^{6–8} polymer–polymer blends,^{9–11} and evaporated small molecules^{3,12,13} as the active layer.

The polymer–fullerene bulk heterojunction concept is based on an active layer formed from a blend of an electron donor polymer and an acceptor fullerene material.¹⁴ The active layer can be produced in an easy fashion by casting films from a blend solution. In such a solid state blend the intimate mixing of the two phases enables an interface within a couple of nanometres everywhere within the bulk, thus “bulk heterojunction”. Excitons created in either phase will encounter within their lifetime an interface to the opposite phase and dissociate there, resulting in charge carriers. Thus, the length scale of the phase separation of the two components within the bulk heterojunction shall be less than the exciton diffusion length within the organic semiconductors, *i.e.* *ca* 10–20 nm. Solar cell (AM1.5) power conversion efficiencies exceeding 3% have been demonstrated using this approach.¹⁵

An important parameter for the solar conversion efficiency of these blend devices is the nanomorphology of the active layer.⁷ Close proximity of the phase boundary to the origin of excitation on the polymer is detrimental,^{16,17} phase separation into domains larger than the exciton diffusion length of *ca* 10–20 nm has to be prevented. To obtain such intimate mixing different solvents and post-production treatments were reported earlier.^{7,15} Once the nanomorphology is optimized there is also a challenge to preserve the nanostructure of this. For market implementation of organic solar cells the stability of the morphology is therefore a critical issue. Especially diffusion of the low-molecular-weight components at elevated temperatures leading to phase separation needs to be prevented. Here the fullerene molecules are the more critical component in such bulk heterojunctions. Studies show that fullerene molecules diffuse into large aggregates under elevated temperatures leading to a demixing of the active layer.^{18,19}

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Several approaches have been made to stabilize the morphology of donor–acceptor blends for photovoltaic application. In the so-called double-cable approach donor and acceptor are covalently bound together.^{20,21} Also, fullerene-containing polyester was used as a polymer acceptor in polymer–polymer blends.²²

Here we present a novel approach to stabilize the morphology of conjugated polymer–fullerene blend films by introducing the polymerizable fullerene C₆₁-butyric acid glycidol ester (hereafter referred to as PCBG) as the fullerene acceptor material. The polymerization reaction can be induced by an initiator material (tris(pentafluorophenyl)borane) or by heat, leading to a network of fullerene molecules throughout the bulk of the active layer that prevents further diffusion of fullerene molecules. The novelty of this approach is that the PCBG molecule is very similar to the well-established C₆₁-butyric acid methyl ester (PCBM) and therefore all methods to improve the morphology of polymer–fullerene blends can be used. After optimum morphology realization it can be fixed by polymerization of the PCBG molecules.

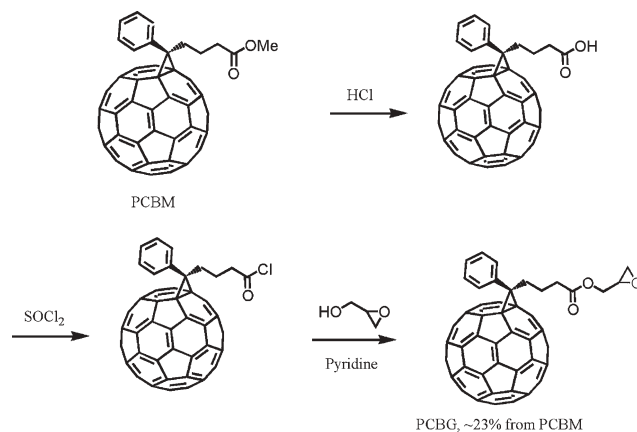
In a comparative study the morphology of polymer–fullerene blend films was investigated using poly(3-hexylthiophene) (P3HT) as the polymer and PCBM or the newly synthesized PCBG as the acceptor molecule, respectively. Changes in the nanomorphology due to heat treatment of the films were studied by means of atomic force microscopy (AFM), transmission electron microscopy (TEM) and photoluminescence (PL) studies. The results clearly demonstrate the stabilization of the nanomorphology preventing diffusion of the fullerene component. Fourier transform infrared spectroscopy (FTIR) was used to study the polymerization of PCBG in films. In addition photovoltaic devices were fabricated and compared in device performance using either PCBM or PCBG as the electron acceptor.

Experimental

Synthesis

All solvents were spectral grade unless otherwise noted. Silica gel was obtained from VWR International. Anhydrous 1,2-dichlorobenzene, acetic acid, hydrochloric acid, carbon disulfide, thionyl chloride, toluene, pyridine, glycidol, hexanes and dichloromethane were purchased from Aldrich Chemical Co., Inc.

The route to PCBG is outlined in Scheme 1. First C₆₁-butyric acid methyl ester (PCBM) was synthesized according to literature procedure.²³ PCBM (1.00 g, 1.1 mmol) was dissolved in 1,2-dichlorobenzene and to this solution was added acetic acid (100 mL) and concentrated aqueous hydrochloric acid (40 mL). The mixture was heated to reflux for 20 h. The solvents were removed *in vacuo* and residue was suspended in methanol. The precipitates were collected by filtration and dried in vacuum to afford the corresponding carboxylic acid (0.94 g, 95%). The carboxylic acid was then suspended in dry carbon disulfide (300 mL) under nitrogen and thionyl chloride (300 mL) was added. The reaction was heated to reflux for 18 h and the volatile components were removed on a rotary evaporator. To the residue was added dry toluene (100 mL), pyridine (4 mL) and then glycidol (200 mg).



Scheme 1 Synthesis of C₆₁-butyrac acid glycidol ester (PCBG).

The reaction was stirred at room temperature for 20 h and the solvents were removed. The residue was purified by flash chromatography (dichloromethane–hexanes, 1 : 4 ramping up to 4 : 1) to give the pure PCBG (203 mg, 25% from the carboxylic acid, 23% from PCBM): ¹H NMR (CDCl₃, 250 MHz): 7.94 (m, 2H), 7.60 (m, 3H), 4.47 (dd, 13.3, 3.0 Hz, 1H), 3.93 (dd, 12.3, 6.4 Hz, 1H), 3.22 (m, 1H), 2.91 (m, 3H), 2.67 (m, 3H), 2.22 (m, 2H); Exact mass calcd for C₇₄H₁₆O₃Na (M + Na): 975.0992, found: 975.0979.

Polymerization of PCBG

The polymerization of glycidyl ester can be initiated by the addition of Lewis acid such as Et₂O·BF₃ (boron trifluoride diethyl etherate).²⁴ However, this causes PCBG to precipitate from solution almost immediately making the solution unusable for film coating. Thus a sterically more hindered, organic-solvent-soluble Lewis acid tris(pentafluorophenyl)borane was used as a mild initiator. The polymerization procedure of PCBG in solution was carried out using the following procedure: PCBG (7 mg) was dissolved in dry chloroform (500 mg) in a Schlenk tube. To this solution was added tris(pentafluorophenyl)borane (0.07 mg in 0.5 mL dry dichloromethane). The tube was sealed and the solution was heated to 120 °C for 5 min resulting in brown precipitation of the polymer or oligomer of the ring-opened product of PCBG. Thin layer chromatography (TLC) of the solution showed only traces of starting materials. The addition of mild acid initiator or no acid initiator allows the polymerization to occur very slowly in solution so that homogeneous films can be coated. Further polymerization of PCBG in solid film can be realized by heating. However, significant amount of PCBG remained reacted even after the films were annealed at 120 °C for 5 min.

Morphology studies

Regioregular P3HT was purchased from American Dye Source (regio regularity >96%, molecular weight ~36 000 g mol⁻¹, polydispersity 1.9). Blend films were prepared by spin casting films from a 3% wt/vol P3HT–fullerene (1 : 2 by weight) solution from dichlorobenzene onto glass substrates. The surface morphology was then analysed with a Dimension 3100 AFM system (Digital Instruments, Santa Barbara, CA)

in tapping mode. TEM specimen were prepared by spin casting films onto glass substrates that were covered with a thin layer of sodium metaphosphate (Victawet, SPI supplies, Westchester, PA). Afterwards films were released from the substrate by submerging the substrate in deionized water and floating off the spincoat polymer–fullerene layer. Films were then lifted onto the TEM grids and dried in an N₂ flow box before measurements with a JEOL 2011 FasTEM high resolution TEM in bright field mode. PL spectra were obtained at room temperature under vacuum using a monochromator in combination with a photodetector and an Ar-ion laser as excitation source (476 nm, 40 mW). The heat treatment of the films was done on a hot plate inside of an Argon glovebox.

FTIR studies

Attenuated total reflection infrared spectroscopy (ATR-FTIR) was used to study the polymerization of PCBG in films. Samples were prepared by dropcasting 1% wt/vol fullerene or 1% wt/vol polymer–fullerene–initiator (1 : 1 : 2.5 × 10⁻⁴) blend solutions from chloroform onto the Ge elements. For the blend solutions the initiator was added 10 min before dropcasting the films. Films were dried in vacuum for 1 h before measurement. Annealing of the films was done on a hot plate inside of an argon glovebox.

Device preparation

Plastic solar cells were prepared as described elsewhere.¹⁵ In the work presented here the photoactive materials P3HT and PCBG or P3HT and PCBM were dissolved in chloroform (3% wt/vol) in a concentration 1 : 2 by weight. The cross linking of PCBG molecules in the active layer was induced by adding small amounts of initiator tris(pentafluorophenyl)borane or by simply storing the sample for up to 1 h at about 140 °C. At this temperature P3HT–PCBM devices show a strong morphology change while P3HT–PCBG films remain clear indicating that a cross-linking takes place at this temperature. Different metal electrodes were evaporated as cathode including LiF/Al, Ca, Ca/Al. Devices were post treated similar to the procedures in ref. 15 by annealing devices with the metal top electrode on a hot plate in an Ar glovebox for 4 min at 140 °C. Longer annealing times exceeding the optimum post treatment time were chosen to study the influence of elevated temperatures on the device performance.

Results

A. AFM and TEM studies

AFM is a powerful tool to study the nanomorphology of organic blends in thin films. The surface topography usually gives a good insight into the film formation ability and the tendency of the components to phase separate. Fig. 1 shows a series of AFM images of the P3HT–fullerene blend films. The unheated blend films are both very flat and do not show any coarse separation into different phases. Upon heating to 140 °C for 4 min the surface roughness of both films increases. The film containing PCBG is slightly rougher than the film containing PCBM. When the heating time is extended to 1 h the PCBM containing film shows large aggregates of several

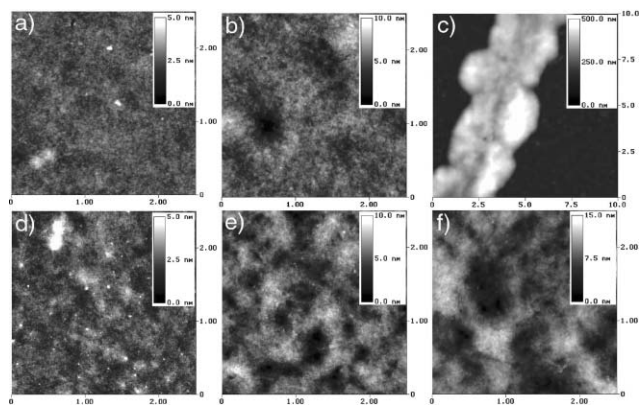


Fig. 1 AFM images of P3HT–PCBM (a–c) and P3HT–PCBG (d–f) blend films spin cast on glass. The images show unheated films (a and d), films annealed for 4 min at 140 °C (b and e), and films annealed for 1 h at 140 °C (c and f).

micrometres in diameter. In contrast to that the PCBG containing film barely shows any increase in surface roughness compared to initial heating periods.

The AFM studies are complemented by TEM studies of the films. While AFM can only give an image of the surface topography of a film, TEM allows one to look into the bulk of the film. In addition, selected areas can immediately be tested for crystallinity by checking the diffraction image of the electron beam. The aggregate formation already observed in the AFM images of the long-heated P3HT–PCBM films can also be seen in TEM images shown in Fig. 2. The dark square-shaped borders in the images are from the Cu grid, which was chosen to have a small grid-size for good support of the films. The P3HT–PCBM blend film annealed at 140 °C for 1 h shows large dendrite-like aggregates that have formed during the heating process. They are several micrometres in diameter and several tens of micrometres long. On the other hand the P3HT–PCBG film heated under the same conditions doesn't show any observable aggregation. Electron scattering experiments on the aggregates in the heated P3HT–PCBM films show a diffraction pattern with distinct reflexes indicating crystallinity of the aggregates. The P3HT–PCBG films don't show any such signs of crystallinity even after long heating periods.

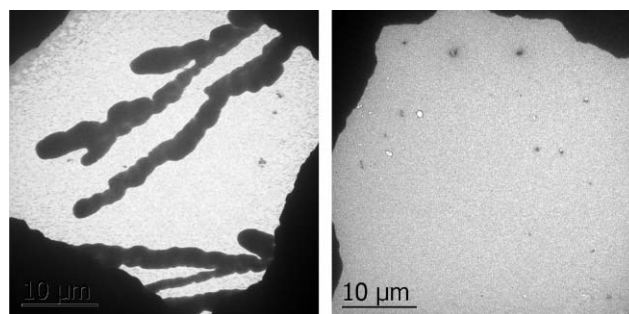


Fig. 2 TEM images of a P3HT–PCBM film (left) and a P3HT–PCBG film (right), both annealed at 140 °C for 1 h. While the PCBM has phase separated into large crystals, the PCBG does not show any large scale phase separation.

B. Photoluminescence measurements

The photoluminescence of blend films, which has to be quenched by photoinduced electron transfer upon intimate mixing of the donor and acceptor phases, can be used to study the stability of the nanomorphology of donor–acceptor blends. If there is (or will be) a large scale phase separation which goes beyond the exciton diffusion length scale of 10–20 nm, the luminescence will be recovered again as compared to the intimate mixture. Fig. 3 shows that upon introducing PCBM or PCBG as the acceptor in the films the PL is quenched by two orders of magnitude compared to pristine polymer film. Once these films are heat treated, the PL increases for both PCBM and PCBG by an order of magnitude.

In addition to the magnitude also the shape of the PL spectra changes. This can be seen in the normalized PL spectra in Fig. 4. The pristine polymer film shows its maximum PL at 720 nm and a smaller peak at 665 nm. In contrast to this the unheated blend films have their maximum PL at 640 nm and a second, weaker peak at 700 nm.

Heat treatment of the P3HT–PCBM film results in a redshift of the PL spectrum (compare Fig. 4a). Also the intensity of the lower wavelength peak gets weaker than the second peak. While the film heated for 4 min shows an intermediate state of shifting from the unheated blend film PL to the pristine polymer film PL, the film heated for 1 h exhibits a normalized PL spectrum that closely matches the spectrum of the pristine polymer film.

The PL spectra of the P3HT–PCBG blend films change in a different way (compare Fig. 4b). First of all the change in the shape of the spectrum is independent of the heating time. The normalized spectrum of the film heated for 4 min closely matches the one heated for 1 h. Also the lower wavelength

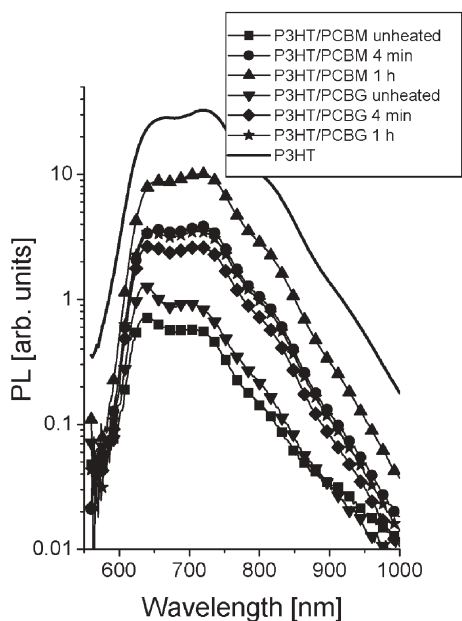


Fig. 3 Photoluminescence spectra of unheated and heated P3HT–PCBM and P3HT–PCBG blend films. In the unheated blend films the PL is quenched by two orders of magnitude compared to the pristine polymer. In the heated films the PL increases slightly compared to the unheated films.

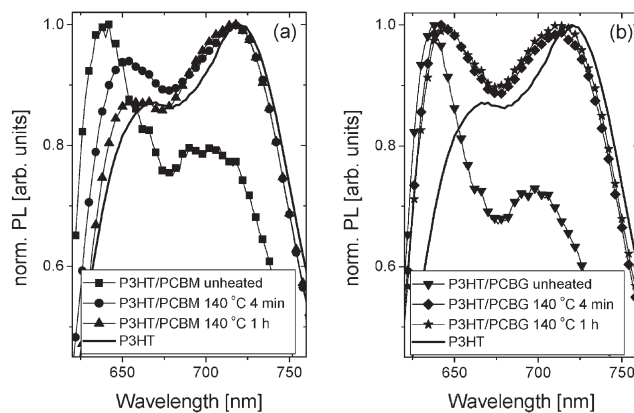


Fig. 4 Normalized PL spectra of unheated and heated P3HT–PCBM (a) and P3HT–PCBG (b) films. While the unheated blend films show their maximum PL around 640 nm and a second peak at 700 nm, the pristine polymer has its maximum PL at 720 nm and a smaller peak around 667 nm. The heated P3HT–PCBM films show PL peaks that shift with longer heating times from the unheated to the pristine polymer peak positions. The heated P3HT–PCBG films show two peaks of about the same magnitude, one of them close the maximum PL of the unheated blends and one close to the maximum of the pristine polymer film. The heating time does not influence the shape of the PL in the case of P3HT–PCBG films.

peak barely shifts compared to the unheated film. The second peak redshifts to 710 nm and therefore is close to the position of the stronger peak of the pristine polymer film. Both peaks of the heated P3HT–PCBG spectra have the same intensity.

C. FTIR studies on the cross-linking

FTIR can be used to study the molecular structure of materials. Epoxy rings typically have absorption features in the region of 800 to 1000 wavenumbers where PCBM does not show any strong features. These features should disappear during the ring-opening polymerization. To demonstrate this, a PCBG film dropcast from chloroform was measured using ATR-FTIR technique. Afterwards the film was polymerized by dropcasting a 0.05% wt/vol tris(pentafluorophenyl)borane solution in chloroform on top of the fullerene film and then remeasured. As reference a PCBM film was measured and treated the same way. Fig. 5 shows the IR absorption spectra of the fullerene films before addition of the initiator and of a pristine initiator film (drop cast from a 0.05% wt/vol solution in chloroform). In addition Fig. 5 shows the absorption difference spectra of the fullerene films before and after the addition of the initiator. The absorption difference spectrum of the PCBG film shows two negative peaks at 910 and around 850 cm^{-1} whereas the PCBM does not show any changes. This shows that the epoxy ring can be detected in PCBG. Also its disappearing during the polymerization reaction is observable. The positive signal at 975 cm^{-1} in the absorption difference spectra stem from the initiator that was added in between measurements. In addition it should be mentioned that the polymerized PCBG film was completely insoluble whereas the PCBM film was easily dissolved after the initiator treatment.

In a next step P3HT–PCBG–initiator blend films were prepared with very low concentration of initiator (see

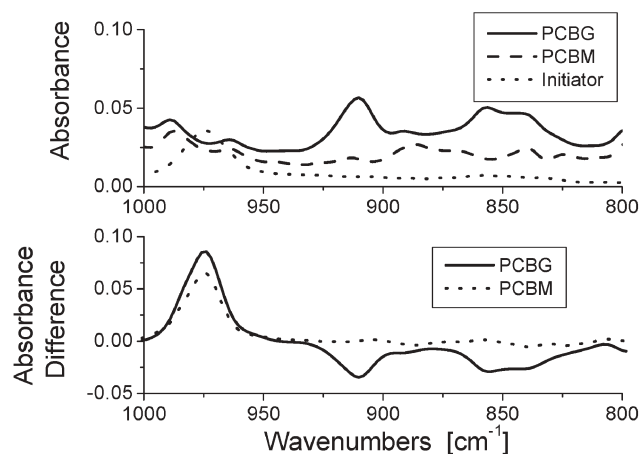


Fig. 5 IR absorption spectrum of a PCBG, a PCBM and a tris(pentafluorophenyl)borane film (top) and IR absorption difference spectra of PCBG and PCBM before and after addition of the initiator (bottom).

experimental section for details). Higher initiator concentrations lead to doping of the photoactive layer and are therefore not suitable for photovoltaic device application. Films were measured before and after 1 h annealing at 140 °C. For comparison a pristine P3HT film was measured. Results are shown in Fig. 6. While the epoxy ring feature at 850 cm^{-1} is overlapped by an absorption of the P3HT, the absorption at 910 cm^{-1} is clearly observable. The peak intensity of the epoxy ring absorption is slightly reduced after heating of the film.

D. Devices

P3HT-PCBG devices with efficiencies $>2\%$ (80 mW cm^{-2} , AM1.5 simulated) can be prepared. Devices using PCBG have not been optimized. When heating devices to 140 °C for several minutes (exceeding the post treatment annealing) the active layer of the device showed no change in the film morphology. However a strong degradation of the current voltage curve is observed (Fig. 7). While the short circuit

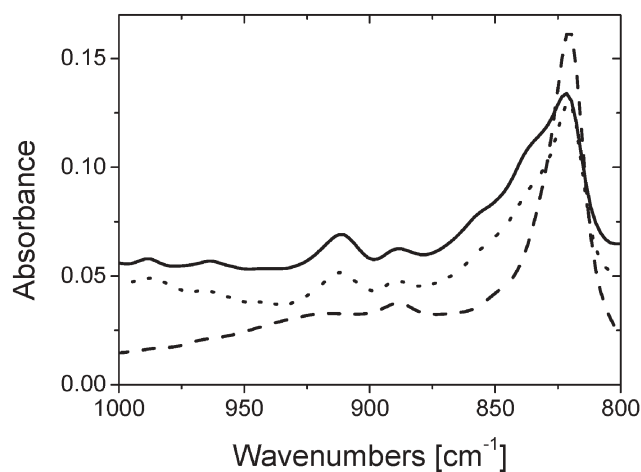


Fig. 6 IR absorption spectra of a P3HT-PCBG-initiator film before (solid) and after (dotted) heating at 140 °C for 1 h. For reference a pristine P3HT film is shown (dashed).

current (5.2 mA cm^{-2}) and the open circuit voltage (530 mV) remain unchanged the FF is reduced from 0.621 to 0.3. P3HT-PCBM devices that were prepared as references showed a completely different degradation behaviour. The shape of the current-voltage curve under illumination did not change. Only the short circuit current decreased due to the demixing of P3HT and PCBM.

Discussion

The AFM and the TEM studies both clearly show that the blend films containing PCBG do not phase separate under the prolonged heating. While the PCBM can easily diffuse when the films are annealed at 140 °C and forms aggregates at the surface of the film, this diffusion is not observed for PCBG. Both studies show that PCBG stabilizes the morphology of the blend films preventing phase separation of the polymer and fullerene content.

It should be noted here that the annealing for AFM and TEM studies was done without the metal top electrode. It has been shown that confinement of the active layer by a metal electrode can reduce the process of phase separation.²⁵ Nevertheless the reduction in short circuit current in our P3HT-PCBM devices clearly shows that the demixing of polymer and fullerene also occurs with the metal electrode in place.

The PL studies show about the same PL quenching in blends with PCBG and PCBM compared to a pristine polymer film. This shows the modification of PCBM to PCBG does not influence the molecule's ability as an electron acceptor. Also even though the PL quenching in all heated films is weaker than in the unheated films, Fig. 3 indicates that the PL quenching is less influenced by long heating periods when PCBG is used as the acceptor. Since the PL should increase when polymer and fullerene separate into different phases the lack of increase in the PL signal after 1 h heating compared to the 4 min again shows the stability of the morphology.

There is a difference in the PL spectrum shape of a pristine P3HT film as compared to the unheated blend film. This is due

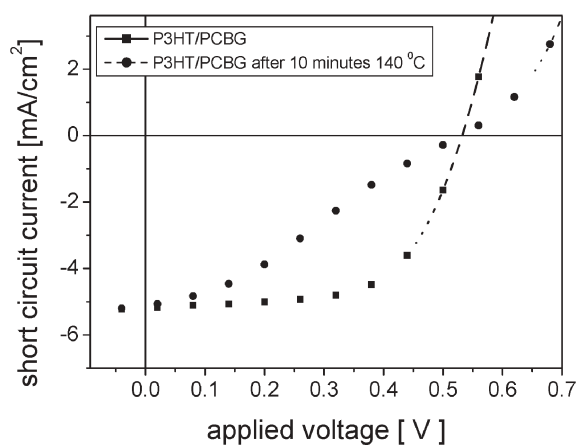


Fig. 7 Current-voltage curves measured under illumination (AM 1.5 simulated, 80 mW cm^{-2}). Squares, P3HT-PCBG device after production and post treatment, circles, P3HT-PCBG device after an additional thermal treatment (10 min, 140 °C).

to the fact that the regioregular P3HT chains can organize themselves into ordered structures in the pristine film.²⁶ This lamellar order is interrupted by the presence of the fullerene molecules. In the case of PCBM, where the fullerene molecules can easily move in the film at elevated temperatures, the polymer chains can rearrange into their ordered structure and the shape of the PL spectra shifts with longer heating periods more and more from the disordered mixture PL in the unheated films to the spectrum of pristine, ordered P3HT films.

In contrast to this the PL spectra of the P3HT-PCBG films do not change shape with long heating periods. The normalized PL of the film heated for 1 h exactly matches the short-heated film. This shows that the PCBG fixes the morphology of the film rapidly and does not allow any further rearrangements in the film.

The IR studies show that PCBG can be polymerized with significant amounts of initiator that are not suitable for photovoltaic device operation. The epoxy ring absorption features fully disappear showing the ring-opening polymerization. Unfortunately the polymerization of PCBG is much less efficient using small amounts of initiator and annealing. The IR absorption spectra show significant amounts of epoxy rings remaining even after 1 h of heat treatment at 140 °C.

Even though AFM, TEM and PL studies show that the morphology of P3HT-PCBG blend films is very stable, the IR absorption studies show that the PCBG molecules do not all polymerize into a network. A significant amount of epoxy rings still remains in the film. It is likely that during heat treatment small amounts of PCBG polymerize to very short oligomer chains but these short chains are already enough to suppress diffusion, therefore explaining the discrepancy between stable morphology and remaining epoxy rings.

While the morphology of the P3HT-PCBG blend films is stabilized by the polymerization reaction, the electrical characteristics of the solar cells built from this blend show an unusual degradation during the heat treatment. The origin of this degradation process is not known. It could be related to the incomplete polymerization of PCBG molecules. The shape of the current-voltage curve is typical for a barrier blocking the charge transport which is usually formed near the electron accepting electrode. It is interesting to note that the short circuit current and the open circuit voltage remain unchanged after the thermal treatment. This indicates that the active layer is not degraded and the film morphology does not change. Most likely the epoxy groups may react with the evaporated metal atoms forming an insulating layer at the metal-active layer interface.

Conclusions

The morphological stabilization of the bulk heterojunction solar cells can be achieved by cross linking of the small molecular phase using a polymerizable fullerene derivative. As demonstrated by comparative nanomorphology studies using combined AFM, TEM and photoluminescence experiments this approach gives considerable stabilization of the solid state morphology. Such prevention of the long term, high temperature instability of bulk heterojunction morphology displays an important route to increase the operational stability of plastic

solar cell in future applications. The electrical stability of these devices has to be achieved by improving the method of crosslinking to minimize the incomplete reaction.

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