

Femtosecond transient absorption dynamics in low bandgap polymer solar cell materials including poly(thienylenevinylene) derivative and benzothiadiazole moiety



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ABSTRACT

We report dynamics of photo-generated charge carriers in (E)-poly[2,2'-(1,2-ethenediyl)bisthiophene-*alt*-4,7-(2,1,3-benzothiadiazole)] (PEBTBT) donor/acceptor copolymer, and in PEBTBT:fullerene bulk heterojunctions (BHJs) blended with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and with [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₀BM) by using femtosecond transient absorption (TA) spectroscopy. The TA decay dynamics appeared that both photo-induced bleaching and absorption of the PEBTBT/fullerene BHJs exhibited slower lifetimes compared to the decay of the pristine copolymer. This can be an evidence of photo induced charge separation at PEBTBT/fullerene interface. When the pump fluence exceeded over the threshold for exciton-carrier (and exciton-exciton) annihilation, within short time delays, the PEBTBT:PC₇₀BM BHJ exhibited a bit faster decay by bimolecular process than the PEBTBT:PCBM BHJ. With regard to the decay property of interfacial charge transfer states, slower geminate recombination was expected in the PC₇₀BM blended film compared with PCBM blended film.

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1. Introduction

Polymer solar cells (PSCs) are attracting attention on account of their competitive properties such as high absorption coefficient, simple structure, and low manufacturing cost by solution process. Since the advent of the bulk heterojunction (BHJ) solar cells based on polymer as a donor and fullerene (or polymer) as an acceptor in 1990s [1,2], the steady improvement in PSCs has been accomplished [3]. For further progress, a bandgap of solar cell must be minimized for effective absorption of large range of solar spectrum to create more excitons which are associated with a high short circuit current density (J_{SC}). In recent years, several kinds of low bandgap polymers have been proposed in order to extend an absorption spectrum more than the absorption range of conventional poly(3-hexylthiophene-2,5-diyl) (P3HT) based polymers. Typically, a concept of alternatively arranged donor and acceptor moieties is applied to reduce the bandgap of polymers [4–7].

We have previously developed donor/acceptor (D/A) alternating low bandgap copolymer (E)-poly[2,2'-(1,2-ethenediyl)bisthiophene-*alt*-4,7-(2,1,3-benzothiadiazole)] (PEBTBT), which contains both poly(thienylenevinylene) (PTV) derivative segments and benzothiadiazole moieties. In addition, we have synthesized the BHJ film by blending PEBTBT as an electron donor and PC₇₀BM as an electron acceptor, and studied the device performances of the BHJ solar cell. The bandgap of the PEBTBT was 1.37 eV and the power conversion efficiency of PEBTBT:PC₇₀BM was 1.07% with J_{SC} of 4.16 mA/cm², open circuit voltage (V_{OC}) of 0.45 V, and fill factor of 57% [8]. But the femtosecond (or picosecond) carrier dynamics of these D/A copolymers has not been studied yet. In this paper, we report the photo-induced charge carrier generation and recombination dynamics in the PEBTBT copolymer and the PEBTBT:PC₇₀BM BHJ by using a femtosecond transient absorption spectroscopy.

Both [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and PC₇₀BM are well-known electron acceptors as soluble fullerenes for BHJ solar cells. Compared to the PC₇₀BM, the PCBM has an edge in price competitiveness and higher electron mobility, but shows considerably lower absorption in the visible range. However, the PC₇₀BM typifies relatively aspheric structure and big molecular size compared with PCBM, so the device with the PC₇₀BM induces relatively low fill factor. Leaving aside the question of the cost,

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these pros and cons of the PCBM and of PC₇₀BM work differently in different polymer:fullerene BHJ blends, i.e., the high photovoltaic performance is not assured by only one specific fullerene [9–11]. Therefore, we also introduce the blend between the PEBTBT and the PCBM to investigate influences of fullerene type on the charge carrier dynamics in the blended film fabricated with the PEBTBT copolymer.

2. Experimental

Synthetic procedure of pristine PEBTBT copolymer, PEBTBT:PCBM BHJ, and PEBTBT:PC₇₀BM BHJ films conforms with the method described in the previous report [8]. All films were spin-coated on a glass substrate, and the thicknesses of films were ~30 nm. The blending ratio of polymer:fullerene was 1:2. The steady state absorption measurement was achieved by using a spectrometer (V-570, JASCO). The time-resolved measurements were measured with a home-built femtosecond transient absorption (TA) spectrometer applying second harmonic of main beam (800 nm, 45 fs, 1 kHz) as pump and a white light continuum as probe, and a methodological explanation is specified elsewhere [12]. The polarizations of pump and probe were tuned to be a magic angle (54.7°). The TA time-resolved measurements were performed under vacuum (<10⁻³ torr) and room temperature conditions.

3. Results and discussion

3.1. Steady state absorption

The steady state absorption was measured for an initial characterization, and the resulting spectra of pristine PEBTBT copolymer, PEBTBT:PCBM BHJ, and PEBTBT:PC₇₀BM BHJ are depicted in Fig. 1. The absorption range of the pristine PEBTBT copolymer is shown from UV to near-IR (~900 nm). From the long wavelength absorption edge (900 nm), the bandgap of PEBTBT film is approximated to ~1.37 eV. Two distinct absorption bands are shown at ~432 nm and ~664 nm. These two large absorption bands in D/A copolymer are ascribed to π - π^* transition of the main polymer chain and intramolecular donor-acceptor interaction [13–15]. In case of the blend films, the absorption valley of the copolymer is compensated by a superposition with fullerenes absorption. Notably, the PEBTBT:PC₇₀BM BHJ film shows higher absorption in the visible

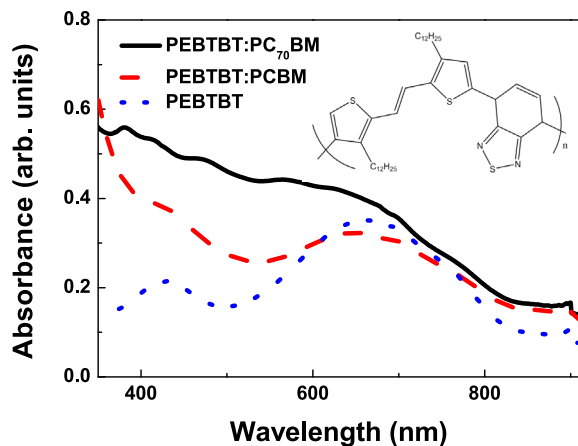


Fig. 1. Steady state absorption spectra of PEBTBT copolymer (blue dotted line), PEBTBT:PCBM BHJ (red dashed line), and PEBTBT:PC₇₀BM BHJ films (black line). Molecular structure of the PEBTBT is also shown in the inset. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

wavelength region than the PEBTBT:PCBM BHJ film, because the absorption of pure PC₇₀BM film is stronger than that of the PCBM film in the region [9]. But these results on steady state absorption were insufficient for explaining the charge carrier performance, so the femtosecond transient absorption (TA) spectroscopy was employed.

3.2. Femtosecond transient absorption

Fig. 2 shows TA spectra of pristine PEBTBT copolymer, PEBTBT:PCBM BHJ, and PEBTBT:PC₇₀BM BHJ after 400 nm excitation at intensity of 23 $\mu\text{J}/\text{cm}^2$. In the TA spectra of PEBTBT copolymer, the positive differential transmission (DT, $\Delta T/T$) band is observed from 525 nm to ~780 nm (Fig. 2(a)). This positive DT band is ascribed to photo-induced bleaching (PB) originated from ground state depletion since the range is matched well with the extent of its steady state absorption. An absorption shoulder around 750 nm in the steady state absorption is reflected into TA spectra as a small peak. The negative DT band is observed above 780 nm and this negative DT band is attributed to photo-induced absorption (PIA) of excited states. Almost none of PIA signal was measured for wavelengths above 780 nm at long time delay time (1.2 ns), and this signifies that recombination in excited states are completed within several hundred picoseconds. Thus, triplet states can be excluded as the main origin of this PIA range because of this fast-decaying feature.

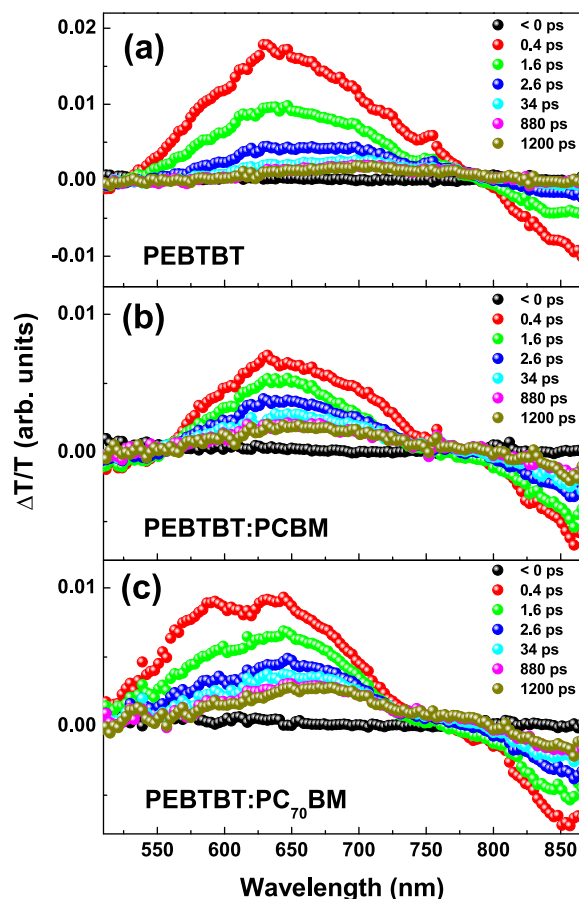


Fig. 2. TA spectra of (a) PEBTBT copolymer, (b) PEBTBT:PCBM BHJ, and (c) PEBTBT:PC₇₀BM BHJ films measured at several time delays from <0 ps to 1200 ps. Every film was excited by 400 nm pump with 23 $\mu\text{J}/\text{cm}^2$.

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