

Femtosecond transient photophysics of polyfluorene copolymers tuned by carbazole side group

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ABSTRACT

Ultrafast dynamics of newly synthesized low band gap polymers polyfluorene–thiophene–benzothiadiazole are studied. Additional carbazole groups are added to the side chain to modify its morphological and electronic characters. In solution, ultrafast interband excitation energy transfer is found to be faster in polymer without carbazole side group. In film form, fast quenching happens for exciton–exciton annihilation and charge recombination. The existence of carbazole group dramatically affects the excitation behavior of the film. The polaron–pair recombination was resolved dominant with carbazole group present in side chain.

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1. Introduction

Conjugated polymers are core materials for organic photovoltaic (OPV) devices [1–6]. Polyfluorene based electron donor–acceptor copolymers show broad absorption in visible region and are potentially suitable for polymer solar cells (PSC) [7–12]. Their photon conversion efficiency in bulk hetero junction (BHJ) solar cell varies from 1% to 5% [13–15]. Studies on the photophysics of alternating polyfluorene copolymers of low band gap, such as F8BT and DiO–PFDTBT, uncover the primary processes following optical excitation [16–18]. Exciton dissociation mechanisms of polyfluorene derivatives in solid state have been reported [19–21]. Polaron–pair generation and exciton–exciton annihilation were introduced to explain the emissive behaviors and other excited state properties for copolymers in film condition [19–26].

In this work, we report our ultrafast study on the photophysics of two low band gap copolymers, polyfluorene–thiophene–benzothiadiazole. Electron donating unit thiophene/fluorene and electron accepting unit benzothiadiazole were copolymerized onto the backbone of the copolymers, as shown in Figure 1. Sample P2 differs from P1 by adding a carbazole moiety on the side chain at fluorene part. Transient absorption spectroscopy with sub-picosecond resolution is applied to samples in solution and thin film. We also compared and explained the side chain influence on emission spectral behaviors.

2. Experimental section

Polymer samples were synthesized by Liang of Northeast Normal University by the same protocol as in [28]. Samples were

dissolved in chlorobenzene with concentration of 400 μM for all time-resolved measurements and $\sim 5 \mu\text{M}$ for the steady-state measurement. Film samples were made by drop casting the 400 μM solutions onto quartz substrate slides.

Ultraviolet–Visible (UV–VIS) absorption and static emission spectra were recorded with regular setup [29]. Picosecond time-resolved emission spectra (TRES) measurements of solution samples were conducted through our streak camera system [29]. Femtosecond transient absorption (TA) measurements were performed using a pump–probe setup with time resolution of 300 fs [30]. In brief, the samples are pumped at 415 nm, 1 kHz, while probed by white light continuum generated through flowing water cell. The energy density of pump pulse was attenuated to $\sim 150 \mu\text{J}/\text{cm}^2$ before entering the sample cell.

3. Results and discussion

3.1. Solution phase

Figure 1 shows the stationary absorption and emission spectra of the samples in solution. The absorption spectra exhibit a similar profile for the two samples, suggesting that the conjugation structures of these copolymers are closely approximate in solution. Two characteristic absorption bands can be observed for both samples, with almost the same peak wavelengths (~ 438 and ~ 543 nm). These results are similar to the quantum-chemical calculation and experimental studies on F8BT and DiO–PFDTBT [16,17], where the peaks centered at 384 and 540 nm for DiO–PFDTBT. Considering the structural similarity, we conclude that these two bands have the same origins as DiO–PFDTBT that the red side band corresponds to the absorption from ground state to the first excited state S_1 which has charge-transfer (CT) character with negative charge localized on benzothiadiazole unit, while the blue transition

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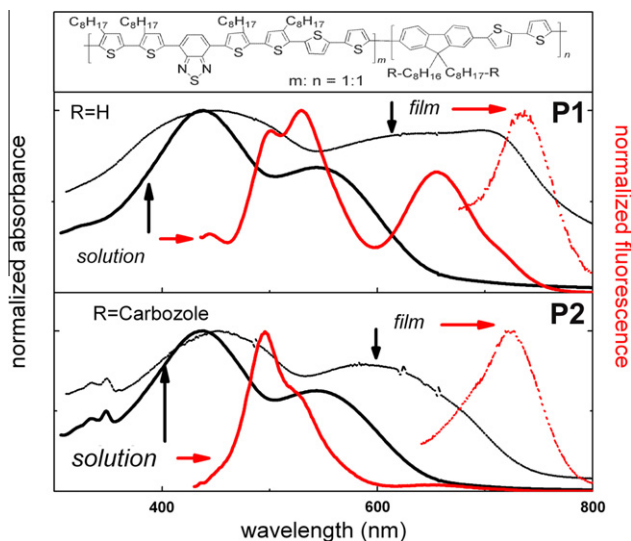


Figure 1. Steady-state absorption and emission spectra of sample P1 and P2 in chlorobenzene and in film form.

band corresponds to a π - π^* transition to the second strongly transition-allowed state S_2 , which is delocalized over the whole chain [17]. The static emission spectra also show two distinct bands, corresponding to fluorescence from those two characteristic states. The band at blue side shows a peak at ~ 495 nm and a shoulder at 530 nm. The red emission band shows a peak at ~ 655 nm with shoulder at 720 nm.

TRES were recorded only for samples in condensed phase with 'blue' (415 nm) excitation. For the red side band corresponding to emission from S_1 , the TRES shows wavelength-dependent characters that there is a fast decay (~ 7 ps) for shorter wavelengths, while a slower decay or an initial fast rise can be resolved for longer wavelengths. This is a typical feature of intraband energy relaxation (transfer) to the lowest energy level of S_1 . With 'red excitation' of Dio-PFDTBT, Jespersen also reported a similar dynamics decay of 7 ps by transient absorption method and assigned it to energy transfer (exciton hopping) within S_1 [18]. Transients of blue side band show a very fast decay component shorter than the instrument response time (~ 5 ps). This decay is wavelength-independent, which usually indicates a quenching pathway from S_2 to another species. With 'blue excitation', Jespersen observed an ultrafast decay around 200 fs. He attributed this component to internal conversion (IC) and faster excitation energy transfer (EET) from S_2 to S_1 [18]. It is also true in our samples since excitation in S_2 absorption lead to the emission from S_1 state, especially in P1.

Figure 2 shows the TA spectra for solution samples taken at several discrete time delays. Four distinct bands were featured for both samples. The first two bands around 440 and 550 nm coincide with the region of ground state absorption, and are attributed to photo-bleaching (PB) signal. The third band with smaller negative ΔOD value around 692 nm overlaps with S_1 emission, and is therefore assigned to stimulated emission (SE) signal of S_1 . Similar to Dio-PFDTBT at 'blue excitation' [18], a fast rise can be resolved from the time-resolved spectra between 0.5 and 4 ps, representing the formation of S_1 . As time goes, the SE signal is red shifted, which is consistent with the TRES at this range and stands for intraband energy relaxation from S_1 to its stabilized lower-energy level. The 692 nm positive signal at long decay time comes from photo-induced absorption (PIA) of the excited state. PIA dominates the fourth band at infrared region (804 nm). Similar to Dio-PFDTBT, the ultrafast decay at 804 nm also represents IC and EET from S_2 to S_1 .

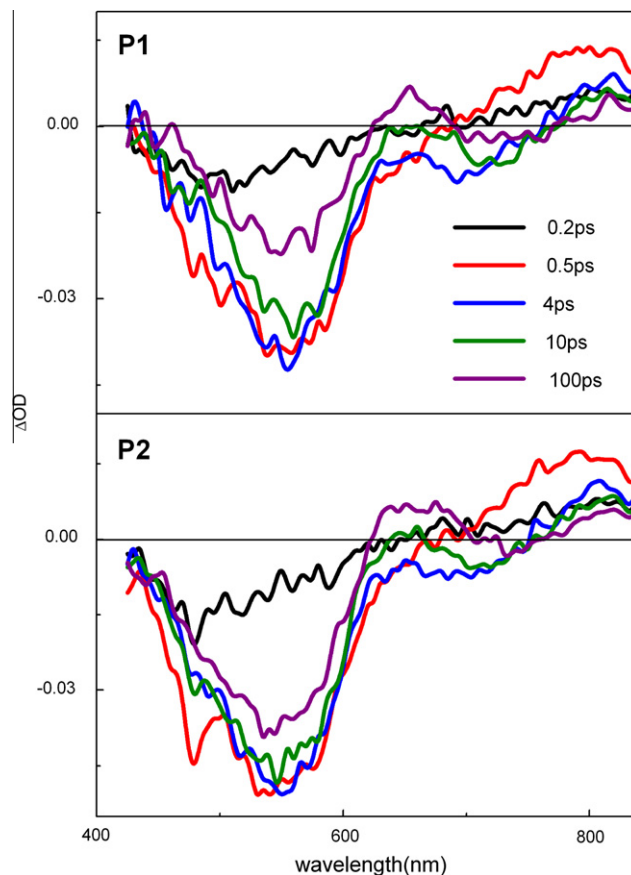


Figure 2. Transient absorption spectra for samples P1 and P2 in chlorobenzene.

Compared to P2, P1 shows a much stronger emission peak for the red side band of stationary emission spectra. This emission intensity discrepancy indicates the different rates and efficiency of the EET process from S_2 to fluorescent state S_1 . We also measured transient traces at several typical wavelengths of TRES and TA. At 529 nm (TRES), P1 shows a faster decay (4.6 ps) with drastically larger amplitude (73%) than P2 (7.5 ps, 28%). At 804 nm (TA), P2 shows a relatively slower initial decay (1.78 ps) with less weight (41%), while P1 exhibits a faster initial decay (1.49 ps) with larger weight (56%). The ultrafast rise at 692 nm (TA) also show similar trend (data not shown). Together, these results indicate that the EET process is easier and more efficient for P1 than P2. From this evolution, we speculate that the larger side chain group of P2 (two carbazole groups compared with P1) may bring a larger steric hindrance for the copolymer structure. This will lead to more conformational defects along the polymer backbone and have a remarkable influence on the rate and efficiency of EET. These defects may also bring fluorescence quenching.

3.2. Film form

For films, a new absorption band appears due to aggregation enhanced intermolecular charge-transfer in solid state. As shown in Figure 1, P1 has a wider absorption with a tail extending to 800 nm, while the absorption of P2 cuts off at ~ 700 nm. The more twisted spatial structure caused by the carbazole group on side chain is speculated to result in this narrowed spectrum. The emission spectra of samples in solid state are much weaker compared to condensed phase. The emission peak is 735 nm for P1 and 722 nm for P2. No shoulder was resolved from the profile.

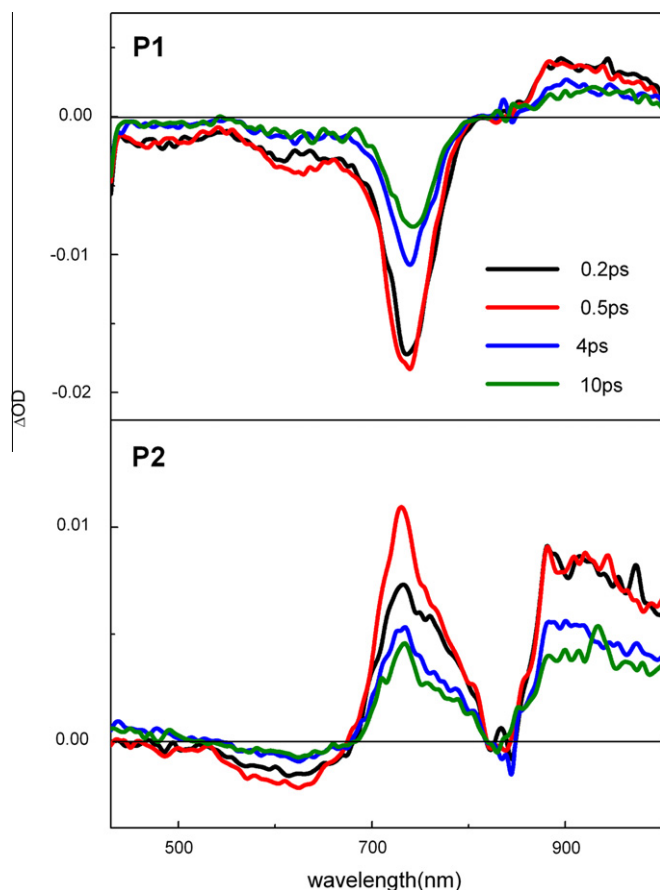


Figure 3. Transient absorption spectra for samples P1 and P2 in film.

Figure 3 shows the transient absorption spectra for the film samples. Four featured bands can be resolved as well. The first two with negative ΔOD around 480 and 625 nm still derive from PB of the two characteristic steady-state absorption bands. The third band at 730 nm is assigned to SE (negative) for P1 and PIA (positive) for P2. The last band with positive value around 900 nm represents the PIA signal.

The transients of several typical wavelengths are shown in Figure 4 and summarized in Table 1. Firstly, the near-IR PIA at 890 nm (1.39 eV) and the PB at 480 nm (2.58 eV) both show sub-picosecond decay with similar values and amplitudes. In accordance with studies on related copolymers [19–23], singlet excitons dominate these two bands. Similar to F8BT [20], the sub-picosecond decay becomes faster and stronger with higher pump intensity (data not shown), and is therefore attributed to exciton–exciton annihilation which depopulates the singlet excitons. This kind of exciton dissociation was discussed to follow the Förster energy transfer mechanism [20], whose strength depends on the extent of the overlap between exciton emission and absorption spectra. This explains the faster time constant and larger amplitude for the initial decay of P1 than P2.

Secondly, we focus on the bands of 625 and 730 nm. It was proposed that polarons would arise from exciton–exciton annihilation and sequential excitation [20]. Cadly and co-workers demonstrated polaron absorption of poly(9,9-dioctyl fluorene) peaked at 2 eV by quasi-steady-state photo-induced absorption [24]. Similar results have been reported for other polyfluorene derivatives [20,25]. Therefore, we expect that PIA from polarons contributes to these visible bands. At long decay time, the recovery of negative ΔOD increases from 480 to 625 nm for P2, indicating the incoming

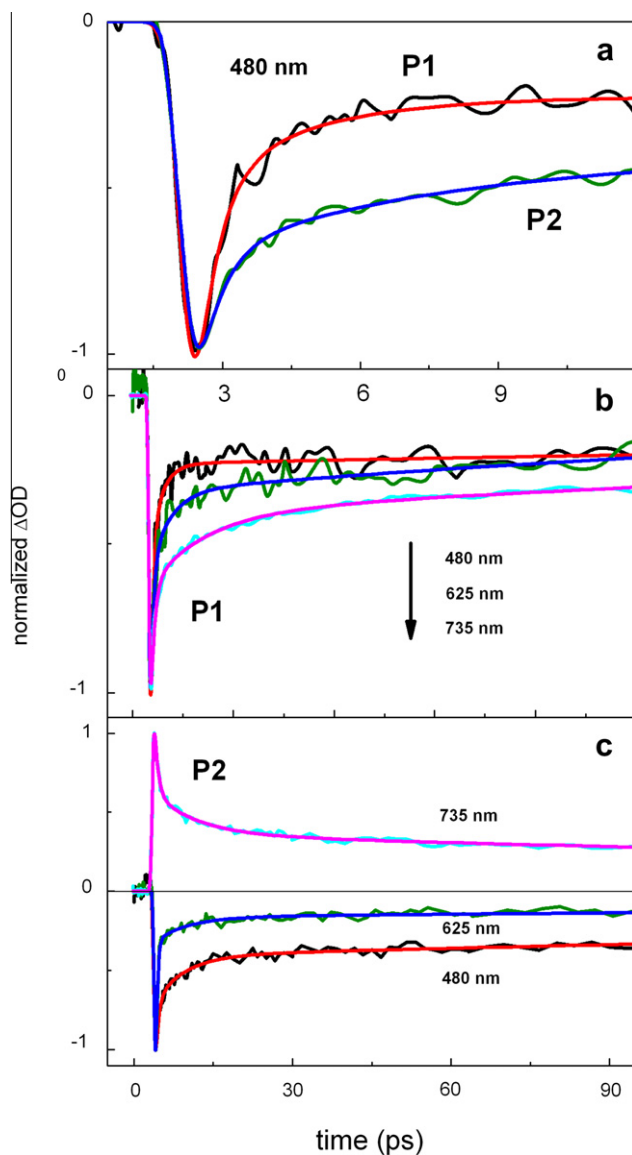


Figure 4. Transients decay for samples P1 and P2 at 480 nm in film (a). Longer time decay of P1 (b) and P2 (c) at 480, 625 and 735 nm.

Table 1
Fitting parameters of several featured wavelengths.

	480 nm	625 nm	735 nm	890 nm
P1	0.44 ps (70%)	0.51 ps (61%)	0.56 ps (53%)	0.41 ps (60%)
	2.3 ps (17%)	4.0 ps (18%)	5.5 ps (22%)	7.4 ps (17%)
	690 ps (13%)	222 ps (21%)	182 ps (25%)	674 ps (23%)
P2	0.52 ps (51%)	0.29 ps (86%)	0.69 ps (56%)	0.72 ps (48%)
	5.6 ps (21%)	6.3 ps (7%)	8.2 ps (19%)	9.7 ps (20%)
	455 ps (28%)	484 ps (7%)	358 ps (25%)	435 ps (32%)

PIA contribution of polarons at visible range (~ 2 eV). For P2, the initial sub-picosecond decay at 735 nm is independent of pump intensity (data not shown), which is typical for interchain polarons recombination [26,27]. Moreover, for PIA from polarons, the weight of polaron contribution became larger as probe wavelength goes shorter [19]. We consequently conclude the positive ΔOD at 735 nm for P2 is mostly due to polaron-pair absorption with absence of PB. In contrast, for P1 at 625 and 730 nm, the corresponding bleaching and SE signal dominate the dynamics, while PIA from polarons contributes little.

It is suggested that polarons can be formed from two different mechanisms, exciton–exciton annihilation and sequential excitation [20]. In our case for P1, exciton–exciton annihilation operates through Förster mechanism, which is facilitated by the large overlap between exciton emission and absorption spectra. This indicates that the exciton–exciton annihilation is a non-local effect, which prefers better conjugation in film. Similar to F8BT, P1 also shows little polarons absorption in the visible range. The PIA from polarons only accounts for the long lifetime 674 ps of P1 in near-IR range (890 nm). For P2, exciton migration is weakened due to weaker aggregation in film and larger steric hindrance caused by bulky carbazole. In this case, exciton–exciton annihilation is weaker, while sequential excitation may take place. This leads to direct local polaron formation during the pump pulse (strong initial PIA in visible range). The local polaron pair then takes fast recombination, displaying as the ultrafast decay at 735 nm. Compared to F8 in Ref. [20], although the charge donor–acceptor groups are organized on the main chain for P2, its behaviors are similar. This may lead to a suppose that the polaron formation by sequential excitation is correlated to the reduced charge separation ability, i.e. F8 films are pure polyfluorene without charge push–pull group, while weak conjugations are found for P2. Therefore, aggregation in film plays a critical role to the excited-state charge formation. By attaching proper side groups, the aggregation and charge formation process can be tuned.

4. Conclusion

In conclusion, we have investigated here the photophysics of thiophene, fluorene and benzothiadiazole based copolymers with different side chains. Steady-state spectra and transient absorption spectra were studied in both condensed phase and solid state as well as time-resolved emission spectra for condensed phase. The conjugation strength was found to be similar for the two samples in solution, but it was weaker for sample P2 than P1 in film form. This was assigned to a more twisted side chain conformation brought by carbazole group that weakens the aggregation. The ultrafast EET process between the second strongly allowed excited state and the first excited state was well resolved for samples in solution. Energy transfer became slower in P2, which indicates larger groups on side chain will bring larger steric hindrance for the structure and lead to more conformation defects along the polymer backbone. Sub-picosecond exciton–exciton annihilation and inter-chain polaron pairs recombination have been detected from transient absorption profiles of film samples. The former mechanism is stronger for P1 due to larger overlap between exciton emission

and absorption. For P2, polarons were formed immediately during sequential excitation and subsequent ultrafast polaron recombination took place.

Acknowledgements

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