EXCITED STATE ENERGY DYNAMICS OF POLY(2,5-DIETHYNYLTHIOPHENE) COPOLYMERS WITH DIFFERENT EFFECTIVE CONJUGATION LENGTHS

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Abstract—The relaxation dynamics of photoexcitation of poly(2,5-diethynylthiophene) copolymers (PDETs) with different repeating unit numbers ($n = 12, 16, 18$) were investigated by steady-state fluorescence spectroscopy and picosecond time-resolved fluorescence decay measurements. All three copolymers presented two peaks in a fluorescence spectrum; however, the position and the intensity of each peak changed, depending upon polymer size. These two peaks were assigned as radiative relaxations from a self-trapped (polaronic) exciton state and a conformational kink state, in comparison with the results of polydiacetylenes and polythiophenes. A bathochromic shift in the fluorescence spectra occurred between the PDET with $n = 12$ and the PDET with $n = 16$, but it was negligible for the PDET's with n between 16 and 18. The ratio of the populational relaxation at the conformational kink state to the relaxation at the self-trapped (polaronic) exciton state is larger in the PDET with $n = 12$ than in PDETs with $n = 16$ or $n = 18$. From the results of iterative least-squares fitting of time-resolved fluorescence decay data at different emission wavelengths, we obtained the relaxation lifetimes of 139 ± 5 psec and 205 ± 3 psec for each state and fluorescence build-up times of 18 ± 2 psec and 51 ± 5 psec, depending on the size of the copolymers; values which are attributed to charge carrier recombination times. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Conjugated organic polymers have been intensively investigated in the past few years because of their unusual electrical and optical properties. Of special interests are electroluminescence, photoconductivity [1–3], photovoltaic effects, and the electrical conductivity of oxidized or reduced polymers [4, 5]. Moreover, because of their often large non-linear optical susceptibilities and their roles as model compounds for quasi-one-dimensional semiconductors, considerable interest has been directed towards studies of electrical and optical properties with long conjugated chain polymers such as polyacetylenes (PAs) [6, 7], polydiacetylenes (PDAs) [8, 9], polythiophenes (PTs) [10–12], polypyrroles, polyphenylenes and polyphenylenevinylenes [13]. To understand the electrical conductivities of π-conjugated polymers as well as their promising optical and non-linear optical properties, charge carrier generation and transport behaviours in these polymers have become subjects of interest. Since the charge carrier dynamics occur over very rapid time ranges, generally from femtoseconds to milliseconds, pulsed laser spectroscopy has been utilized to investigate the mechanisms of charge carrier generation and transport.

The poly(2,5-diethynylthiophene) copolymers (PDETs) which were investigated in this study had

both diacetylene and thiophene as monomeric units. And, even though polydiacetylene or polythiophene polymers have been extensively studied to understand their chemical and physical properties, particularly in terms of charge carrier generation/relaxation and transport mechanisms, the properties of copolymers consisting of these two monomeric units have not been studied since they were synthesized in 1988 by Callstrom *et al.* [14]. Therefore it seems of interest to understand the charge carrier dynamics of PDETs in comparison with those of PDAs or PTs. To perform spectroscopic studies of polymers in the solution phase, the main problem arises from the solubilities of the polymers, which was the case for PDET synthesized by Callstrom *et al.* [14]. Generally, polymers are likely to be non-soluble, particularly when they possess a large number of repeating units [15]. However, in this study, we have synthesized three soluble PDET copolymers of different chain lengths ($n = 12, 16, 18$) without any long alkyl chains, and carried out spectroscopic experiments with liquid solution samples. Throughout the study, we have investigated the excited state charge carrier dynamics using steady-state fluorescence properties and picosecond fluorescence decay dynamics. From the steady-state fluorescence experiments, we obtained two peaks in the spectra and were able to assign them by comparing their characteristics with those of PDAs and PTs. The first sharp fluorescence band at 470–480 nm was assigned as the relaxation of the

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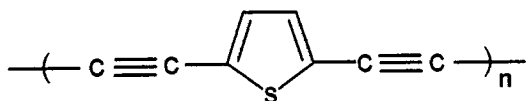*To whom all correspondence should be addressed.

Fig. 1. Structure of poly(2,5-diethynylthiophene)s ($n = 12$, 16, 18).

self-trapped (polaronic) exciton state and the second broad band at about 520 nm was assigned as that of the conformational kink state which was reported to be caused by an increase in entropy associated with the many degrees of freedom in coil-like conformations [16]. Time-resolved fluorescence experiments resulted in fluorescence decay constants for the three polymers in the fluorescence wavelength range (456–536 nm). From triple exponential fitting procedures of the decay data, we could obtain the lifetimes (139 ± 5 psec and 205 ± 3 psec) and their corresponding amplitudes, which were interpreted as the relaxation dynamics of the self-trapped (polaronic) exciton state and the conformational kink state. We also obtained lifetimes with negative amplitudes, which were faster than the fluorescence lifetimes of the self-trapped (polaronic) exciton state and the conformational kink state, and we have discussed these rising times in terms of the charge carrier mobilities on the excited potential surfaces of the PDETs.

EXPERIMENTAL

Soluble PDET copolymers of different chain lengths were prepared by oxidative polymerization of 2,5-diethynylthiophenes with the solvent ratio acetone/pyridine = 10:1 [17]. The repeating unit numbers of the copolymers were determined by degree of polymerization, n, which was calculated by the molecular weight averaging method from GPC data. The degree of polymerization, n, for each PDET

copolymer was 12, 16 and 18. The solution samples were prepared in THF solvent (Aldrich) for steady-state and time-resolved fluorescence experiments. The PDET copolymer with $n = 12$ was dissolved completely, whereas the $n = 16$ and $n = 18$ polymers were not completely dissolved in THF solvent. Thus, in the case of the $n = 16$ and 18 copolymers, filtered solutions were prepared for the measurements. The concentration of the $n = 12$ PDET was 1.1×10^{-5} M and the concentrations of the other PDET copolymers ($n = 16$ and 18) were expected to be less than that of the $n = 12$ PDET. All experiments were performed at room temperature. Steady-state fluorescence spectra of the samples were obtained using a spectrofluorimeter (Hitachi F-2000) and, for time-resolved fluorescence experiments, a picosecond time-correlated single photon counting system was employed. The TCSPC laser system utilized in this study consisted of a cavity dumped dye laser that was synchronously pumped by a mode-locked argon ion laser. The temporal pulse width of the excitation beam was 2–3 psec and the excitation wavelength was 285 nm. More detailed information on this TCSPC system has been given in a previous publication [18]. The exponential fittings were done with iterative least-squares fitting procedures. The fluorescence lifetimes were measured at several fixed emission wavelengths on the fluorescence spectrum.

RESULTS AND DISCUSSION

PDET copolymers consist of diacetylene and thiophene monomeric units, which are alternatively connected, as shown in Fig. 1. Due to such structural characteristics, the energetic coupling between these two units can be an important factor in determining the physical and chemical properties of these copolymers.

As shown in Fig. 2, the fluorescence spectra of PDETs appeared in the wavelength range 470–520 nm. The fluorescence bands of PDETs are positioned at somewhat higher energy compared to those (620–690 nm) of PDAs or PTs [5, 19]. This implies that the effective conjugation length of
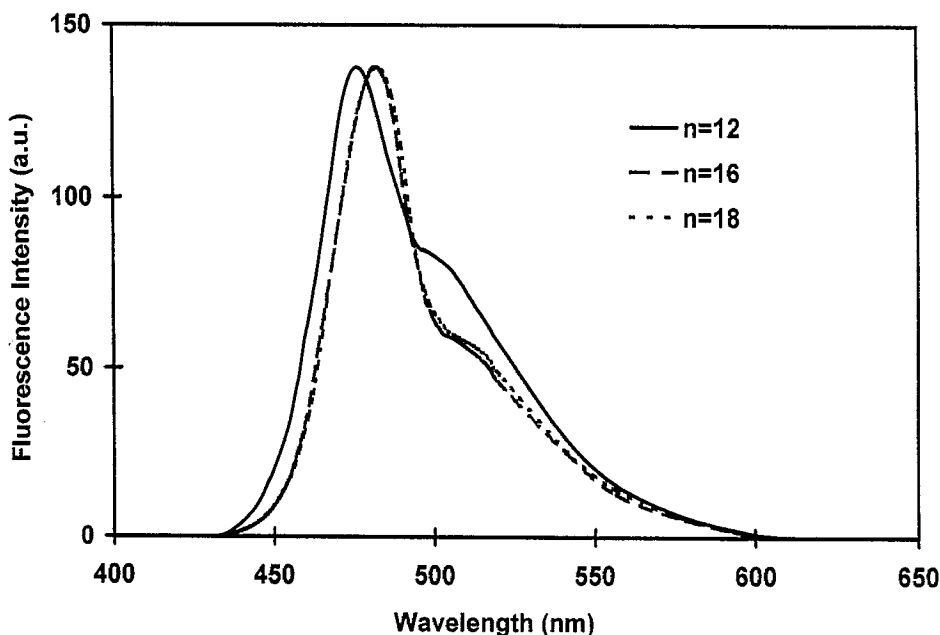

Fig. 2. Steady-state fluorescence spectra of poly(2,5-diethynylthiophene)s ($n = 12$, 16, 18).
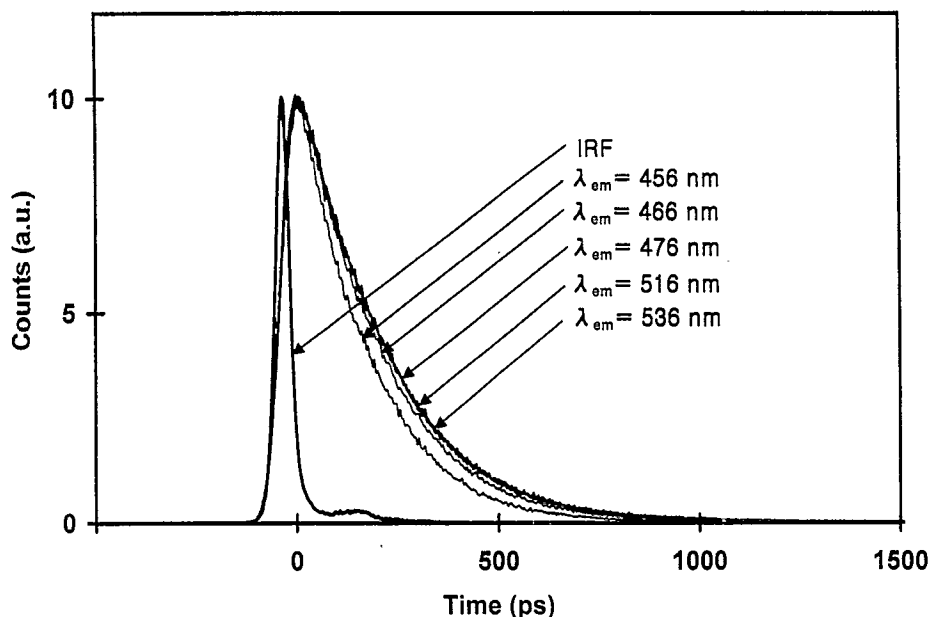
Fig. 3. Fluorescence decay data of poly(2,5-diethynylthiophene) with $n = 12$. IRF is the instrument response function of the excitation pulse. The excitation wavelength is 285 nm.

PDETs could be shorter than that of PDAs or PTs due to weaker energetic couplings between diacetylene and thiophene units in PDET than the couplings among the monomeric units in PDAs or PTs [20].

According to many ultrafast relaxation studies of conjugated polymers, it is well known that free excitons and self-trapped (polaronic) excitons and conformational kink states (or trapped states) can exist in excited states of PDAs and PTs, and that the relaxation of free excitons is in the time-scale of a few hundred femtoseconds and self-trapped (polaronic) excitons have a radiative lifetime of several hundred picoseconds [19, 21]. In the case of conformational kink states, where the effective conjugation is broken by the dynamic motion of the polymer chain and steady structural changes, such as from rod-like to coil-like structures, they usually have longer lifetimes and lower energies than self-trapped (polaronic) excitons [16, 19, 21, 22]. It is also reported that the fluorescence phenomena in PDAs or PTs occur due to the self-trapped (polaronic) exciton states and the

conformational kink states [21]. Therefore the fluorescence spectra shown in Fig. 2 are also considered to occur due to the self-trapped (polaronic) exciton state and the conformational kink state in PDET copolymers because of the structural similarities [14, 20]. From all these considerations, it is suggested that the first fluorescence band at 470–480 nm is due to the relaxation of self-trapped (polaronic) excitons and the second band located at about 520 nm is due to that from a conformational kink state. These results are supported, in terms of lifetime scales, by the picosecond fluorescence lifetime studies shown in Fig. 3 and Table 1.

As shown in Fig. 3, we measured the picosecond time-resolved fluorescence decays across the fluorescence wavelength range 456–536 nm for all three different sized PDETs ($n = 12$, 16, 18). The fluorescence decay curves were not fitted by single or double exponentials, but were fitted well by triple exponentials including one rising component. Non-single exponential decays of PDAs have been reported by Wong et al. [23]. From the fitted values

Table 1. Iterative least-squares fitting results of decay data of poly(2,5-diethynylthiophene)s with $n = 12$, 16, 18

Size	λ_{em} (nm)	A_1	τ_1 (psec)	A_2	τ_2 (psec)	A_3	τ_3 (psec)	A_3/A_2	χ^2
$n = 12$	456	− 0.21	17	0.120	129	0.019	207	0.16	1.10
	466	− 0.23	20	0.099	139	0.043	205	0.43	1.26
	476	− 0.21	20	0.075	143	0.063	204	0.84	1.28
	516	− 0.22	17	0.061	139	0.072	205	1.18	1.10
	536	− 0.23	16	0.053	134	0.076	207	1.43	1.34
$n = 16$	472	− 0.0020	53	0.016	142	0.019	204	1.19	0.95
	482	− 0.0046	50	0.015	142	0.020	202	1.33	1.11
	533	− 0.0027	45	0.009	141	0.013	204	1.49	1.15
$n = 18$	473	− 0.0043	58	0.039	141	0.045	204	1.15	1.48
	483	− 0.0089	47	0.037	142	0.049	203	1.32	1.22
	533	− 0.0100	55	0.035	133	0.054	214	1.54	1.40

$I(t) = A_1 e^{-t/\tau_1 F} + A_2 e^{-t/\tau_2 F} + A_3 e^{-t/\tau_3 F}$; $I(t)$, n, λ_{em}, A and τ are the time-dependent fluorescence intensity, degree of polymerization, detection wavelength of emission, amplitude and lifetime (psec), respectively. The excitation wavelength for all decays was 285 nm.

in Table 1, it is realized that there are two decaying time constants of 139 ± 5 psec (τ_2) and 205 ± 3 psec (τ_3) for all repeating unit lengths, and one rising time constant which is about 18 ± 2 psec for the PDET with $n = 12$ and 51 ± 5 psec for the PDETs with $n = 16$ and 18. The amplitude ratios of A_3/A_2 in Table 1 indicate that the first fluorescence band at 470–480 nm has a lifetime of 139 ± 5 psec and the second band at around 520 nm has a lifetime of 205 ± 3 psec. The afore-mentioned results of PDAs or PTs imply that the first band is due to the relaxation of self-trapped (polaronic) excitons and the second one is contributed to from the relaxation at the conformational kink state.

The steady-state fluorescence spectra show the size-dependent properties of PDETs. As shown in Fig. 2, a bathochromic shift is observed as the polymer size increases from $n = 12$ to $n = 16$; however, it is not significant from $n = 16$ to $n = 18$. This suggests that the effective conjugation length of PDET would be between $n = 12$ and $n = 16$. Also, the shape of the spectrum changes more as the polymer size increases from $n = 12$ to $n = 16$ than it does from $n = 16$ to $n = 18$. In particular, the relative intensity of the conformational kink state band to the self-trapped (polaronic) exciton band is larger in $n = 12$ PDET than in the $n = 16$ or $n = 18$ PDETs. Also, the first band (470–480 nm) is bathochromically shifted, but the second band (about 520 nm) is not shifted as the polymer size increases from $n = 12$ to $n = 16$. These behaviour patterns in the spectra result in the characteristics of the self-trapped (polaronic) exciton state and the conformational kink state. The energy level of the self-trapped (polaronic) exciton state should be affected by the conjugation length of the polymers when this is shorter than the effective conjugation length; however, as the size of the polymer becomes larger than the effective conjugation length, it should not depend on the conjugation length any more. On the other hand, the conformational kink state should not show such spectral changes, since the effective conjugation has been broken in this case; instead, the band intensity of the conformational kink state would be lower in the polymer which has repeating units longer than the effective conjugation length, since the differences in relative band intensities of the PDETs with $n = 12$ and $n = 16, 18$ should be caused by the heights of the potential barriers between the self-trapped (polaronic) exciton states and the conformational kink states in PDETs. Since the PDET with $n = 12$ has the peak of the higher fluorescence band at about 470 nm shifted by about 10 nm to higher energy in comparison with the PDETs with $n = 16$ and 18, whereas the peak of the second band at around 520 nm does not show any significant changes in energy for all three copolymers, the energy gap between the two energy states is larger in the $n = 12$ PDET than in the $n = 16$ or 18 PDETs; thus the potential barrier between the two states is larger in the $n = 16$ or 18 PDETs than in the $n = 12$ PDET [24]. Therefore the conformational kink state band intensity relative to the self-trapped (polaronic) exciton state band will be larger in the $n = 12$ PDET than in the $n = 16$ or 18 PDET copolymers.

Finally, the fitted fluorescence decay data also show that there is one fast lifetime (τ_1) with negative amplitude, which corresponds to the rise-time component for building up the fluorescence intensity. A rise-time of 18 ± 2 psec is observed in the PDET copolymer with $n = 12$ at all detection wavelengths, while the PDET copolymers with $n = 16$ and 18 both show the longer fluorescence build-up time of 51 ± 5 psec. It is plausible to consider that the rise-time originates from the lag-time for free excitons to become self-trapped (polaronic) excitons, since the lag-time is shorter in the PDET with $n = 12$ where the conjugation length is shorter than the effective conjugation length, and the PDET copolymers with $n = 16$ and 18 both show the same lag-time of 51 ± 5 psec due to the same effective conjugation length. Such an interpretation for the rise-times can be supported by studies of ultrafast relaxation dynamics in PDAs or PTs. It has been reported that processes such as self-trapping, phonon emission, thermalization, and cooling could occur in the transition from the free exciton state to the self-trapped (polaronic) exciton state of PDAs, and such dynamics have been known to progress within a few tens of picoseconds [21].

CONCLUSION

We have obtained the following results from steady-state and time-resolved fluorescence studies of PDETs ($n = 12, 16, 18$). The steady-state fluorescence spectra of PDETs show two peaks, which have somewhat higher energies in comparison with those of PDAs or PTs, and these two peaks are assigned as relaxations from the self-trapped (polaronic) exciton state and the conformational kink state, by comparison with the results of PDAs and PTs. In terms of the size-dependent properties of PDETs, the effective conjugation length of PDET is observed to be between $n = 12$ and $n = 16$ from the bathochromic shift of the fluorescence band for the self-trapped (polaronic) exciton state. From the dependence of the relative fluorescence band intensities of the self-trapped (polaronic) exciton and the conformational kink states on the PDET copolymer sizes ($n = 12, 16, 18$), the height of the potential barrier of the self-trapped (polaronic) exciton state moving to the conformational kink state is higher in the $n = 16$ or 18 PDET copolymers than in the $n = 12$ PDET. The time-resolved fluorescence decay studies indicate that the self-trapped (polaronic) exciton state in PDET has a lifetime of 139 ± 5 psec and the conformational kink state in PDET has a lifetime of 205 ± 3 psec, and that the rise-times of the fluorescences in PDETs, which are the lag-times of free-excitons changing to self-trapped (polaronic) excitons, are 20–50 psec, depending on the conjugation lengths of the PDET copolymers.

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