

Self-trapped exciton dynamics in highly ordered and disordered films of polythiophene derivative

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We measured the time-resolved photoluminescence of highly ordered and disordered films of a polythiophene derivative, poly(3-[2-((S)-2-methylbutoxy)ethyl]thiophene). The formation of self-trapped excitons (STE's) within 10 ps after photoexcitation and the subsequent migration of the STE's are common behavior in both films. The spectral narrowing of the phonon sidebands within 10 ps after photoexcitation is associated with the formation process of STE's and the spectral changes on a few hundred ps time scale are explained by the STE migration and the dependence of the electron-phonon coupling on the effective conjugation length.

π conjugated polymers have received considerable attention as a model system for understanding the optical characteristics in one-dimensional (1D) materials, where excitons play an important role in optical properties and electron-phonon coupling is also essential.¹⁻⁴ In the 1D system, it is known that there is no potential barrier from a free exciton state to a self-trapped state, and that most of photogenerated excitons relax to self-trapped excitons (STE's) within extremely short time.⁵ Since luminescence observed in π conjugated polymers is mainly radiation from the STE, time-resolved photoluminescence spectroscopy gives us information about the self-trapping process and the relaxation process of the STE.

Studies of luminescence dynamics have been extensively performed on poly(*p*-phenylenvinylene) and its derivatives (PPV's).⁶⁻¹⁰ A short-lived luminescence tail on the high-energy side and a slow redshift of luminescence peaks have been observed in PPV's. Both observations have been explained by an exciton migration to lower-energy segments.^{7,8} This migration model has also explained the luminescence spectrum narrower than the absorption spectrum. However, luminescence spectra of PPV's show large inhomogeneous broadening, and it is difficult to analyze experimental results in detail. Inhomogeneous broadening in optical properties is an inevitable feature of π conjugated polymers because of the following reason: In π conjugated polymers, the π electron is localized due to the torsion of the main chain. Microscopic optical properties are strongly dependent on the localization length, which is called the effective conjugation length. In most cases, samples consist of various effective conjugation lengths. Therefore the optical properties of π conjugated polymers show large inhomogeneous broadening.

Polythiophene derivatives (PT's) can be obtained in the form of high quality thin film, whose absorption and luminescence spectra show clear vibronic structure.¹¹⁻¹³ At the same time, these films have enough luminescence quantum efficiency to allow the investigation of their STE dynamics. Moreover, by a recent advance on the synthesis of polymers, it has become possible to control the distribution of the ef-

fective conjugation length.¹¹⁻¹³ Therefore it is possible to study the structural dependence of the STE dynamics.

In this paper, we report on the time-resolved photoluminescence experiments on films of a polythiophene derivative with long and short average lengths of the effective conjugation to reveal the STE dynamics and the structural dependence of the STE behavior in PT's.

We used poly(3-[2-((S)-2-methylbutoxy)ethyl]thiophene), whose chemical structure is depicted in the inset of Fig. 1. This polymer has an advantage of the ability to control the average length of the effective conjugation over a wide range by the synthesis and/or fabrication method.^{12,13} The regular polymer, which is hereafter abbreviated as HT-P(S)MBET, contains exclusively head-to-tail (HT) coupling of thiophene rings, while the regiorandom one, which is abbreviated as R-P(S)MBET, contains TT and HH coupling as well, where the side chains collide with each other and the π conjugation is limited. We can fabricate a high quality Langmuir-Blodgett (LB) film of HT-P(S)MBET because of its high HT ratio and hydrophilicity of oxygen atoms in its side chains. This film has a large $\chi^{(3)}$ and a large length of

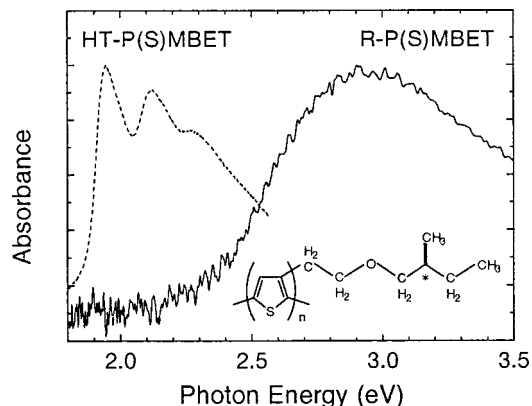


FIG. 1. Absorption spectra of LB film of HT-P(S)MBET and spin-coated film of R-P(S)MBET at 10 K. Inset: Chemical structure of P(S)MBET.

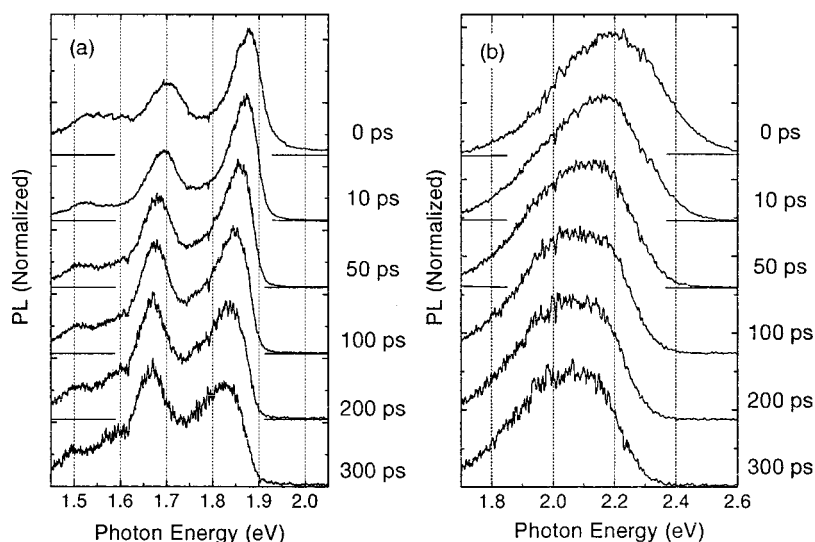


FIG. 2. Photoluminescence spectra of (a) HT-P(S)MBET excited at 2.4 eV and (b) R-P(S)MBET excited at 3.1 eV at various times after photoexcitation. The spectra are normalized at the maximum of each spectrum and the time zero is taken to be the time when the luminescence takes its maximum intensity.

the effective conjugation.^{14,15} The average length of the effective conjugation in HT-P(S)MBET was estimated to be 21 thiophene rings from the absorption and $|\chi^{(3)}|$ spectra at 10 K.¹⁵ On the other hand, R-P(S)MBET was obtained in the form of a spin-coated film. The average effective conjugation length in R-P(S)MBET is estimated to be a few thiophene rings from the HT ratio of 56% and the assumption that π conjugation is interrupted in the TT and HH couplings.

The absorption spectra of these films at 10 K are shown in Fig. 1. The absorption spectrum of HT-P(S)MBET shows a clear vibronic structure, which consists of the exciton transition (1.94 eV) and its phonon sidebands (2.12 and 2.29 eV) associated with the C=C stretching mode. In R-P(S)MBET, although the vibronic structure is not seen because of its large inhomogeneity, we believe that the broad spectrum actually consists of the 0-0 transition and its sidebands.

A HT-P(S)MBET solution shows thermochromism, which is a dramatic color change dependent on its temperature due to the phase transition of side chains between trans and gauche forms.^{16,17} The gauche-type side chains disrupt the regularity of the main chain and decrease the effective conjugation length. The structure of the main chain in HT-P(S)MBET and R-P(S)MBET films correspond to the ordered (trans) and disordered (gauche) phases, respectively.

Time-resolved photoluminescence measurements were performed using a monochromator and a streak camera with a 7-ps time resolution. The samples were kept in a cryostat that was maintained at a pressure of 10^{-5} torr to prevent chemical changes, and all measurements were made at 10 K. An optical parametric amplifier seeded by an amplified mode-locked Ti:sapphire laser was utilized to produce excitation pulses at an energy of 2.4 eV. These pulses were spectrally filtered by a grating pair and a slit to obtain pulses with a spectral width of about 0.02 eV. Pulses from the mode-locked Ti:sapphire laser were frequency doubled in a nonlinear optical crystal of beta-barium borate (BBO) to produce excitation pulses at an energy of 3.1 eV. The duration of these excitation pulses was a few hundreds fs, which is one order of magnitude shorter than the time resolution of the streak camera.

The photoluminescence spectra of HT-P(S)MBET at various times after photoexcitation at 2.4 eV are shown in Fig.

2(a). The broad luminescence tails are observed at 0 ps on the low-energy (near 1.5 eV) as well as high-energy (near 2.0 eV) sides, but disappeared within 10 ps. The spectral narrowing of the phonon sideband around 1.7 eV also occurs on the same time scale after photoexcitation. These short-term features show evidence for the formation process of STE. In fact, some ultrafast measurements indicate that the formation of STE's occurs within a few hundred fs,^{5,7,18} which is much shorter than the time resolution of our apparatus. A relaxation process of free excitons is illustrated in Fig. 3(a). After photoexcitation, a free exciton immediately induces lattice motion to form hot STE's. The dissipation of the kinetic energy of atoms takes place within a few hundred fs in PT's (Ref. 5) and then a new stable configuration, thermalized STE, is formed. From this picture, the observed short-lived luminescence tails on the both energy sides are assigned to radiation from the hot STE. During the thermalization process, the distance between carbon atoms varies continuously, and the energy of the C=C stretching mode, which determines the interval energy of the phonon side bands, is modulated. This modulation causes the broadening of the sideband around 1.7 eV at 0 ps. After the hot STE thermalizes, the spectrum of the phonon sidebands narrows.

The hot STE can decay not only radiatively but also nonradiatively through potential crossing and/or tunneling between two potential curves of the STE and the ground state [the broken arrow in Fig. 3(a)].⁵ The nonradiative decay channel decreases the luminescence quantum efficiency.

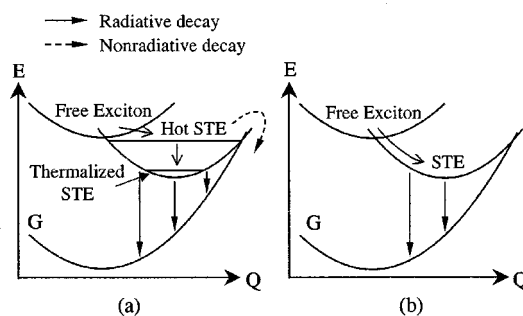


FIG. 3. Adiabatic potential-energy curves in the configuration space for (a) HT-P(S)MBET and (b) R-P(S)MBET.

A slow redshift of the luminescence peak occurs exponentially with a time constant of 180 ps. The shift energy is about 60 meV. The redshift is due to the migration of STE's to segments with longer effective conjugation, i.e., low-energy segments.^{7,8} It was recently reported that, in poly(2-methoxy, 5-(2-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV), the migration between chains takes place in a few ps and that the migration along the main chain occurs on a time scale of a few hundred ps.¹⁹ Therefore the energy shift seen in Fig. 2(a) has been assigned to the intrachain migration.

The low-energy tail of the 0-0 transition grows on the time scale of a few hundred ps, although the side bands remain sharp. This is explained by the following reason: The sample contains a few segments with extremely long effective conjugation, and radiation from them appears at the low-energy side of the 0-0 transition. The STE in these segments no longer migrates, and has to decay with a radiative decay time, which is longer than the migration time constant. The 0-0 transition from these segments does not have its phonon side bands, because the segment with longer effective conjugation has smaller electron-phonon coupling. Therefore, as time evolves, the low-energy tail of the 0-0 transition grows, while its phonon sidebands remain sharp.

The photoluminescence spectra of R-P(S)MBET excited at 3.1 eV are shown in Fig. 2(b). The broad luminescence tail is observed only on the high-energy side. The formation process of STE in R-P(S)MBET is illustrated in Fig. 3(b). In the LB film of HT-P(S)MBET, the side chains are almost crystallized and all main chains are fixed to each other through the side chains. After photoexcitation, all atoms in crystallized area will have to be reorganized to form thermalized STE. Thus it takes a few ps to form the thermalized STE in HT-P(S)MBET. On the other hand, the spin-coated film of R-P(S)MBET has low crystallinity, and the side chains are relatively free. Only local deformation is required to form STE. Therefore the thermalization process in R-P(S)MBET takes a shorter time than in HT-P(S)MBET. As a result, the free excitons relax to the minimum of the STE potential along the potential curve without overshooting [Fig. 3(b)], which leads to the observation of a short-lived tail only on the high-energy side. The fast thermalization indicates that STE in R-P(S)MBET has a low probability to decay to the ground state through potential crossing and/or tunneling. This must be a reason why the luminescence quantum efficiency is higher for the disordered phase than for the ordered one in PT's.²⁰

The redshift of the luminescence peak due to the migration of STE's is also observed in R-P(S)MBET. The shift energy is 190 meV. This larger shift is due to shorter conjugation than that in HT-P(S)MBET.

Figure 4(a) shows the time-integrated photoluminescence spectra of R-P(S)MBET excited at 3.1 and 2.4 eV. The dependence of luminescence spectrum on the excitation photon energy is explained by site selective fluorescence:²¹ segments with the resonance energy are selectively excited. Figures 4(b) and (c) show the photoluminescence spectra at 0 and 500 ps, respectively. STE's migrate to the segment with longer conjugation until they cannot find lower segments. Finally, the STE's reach segments with the same conjugation length at 500 ps in both cases of excitation at 3.1 and 2.4 eV.

On the other hand, independence of luminescence spectrum on the excitation photon energy was observed in HT-

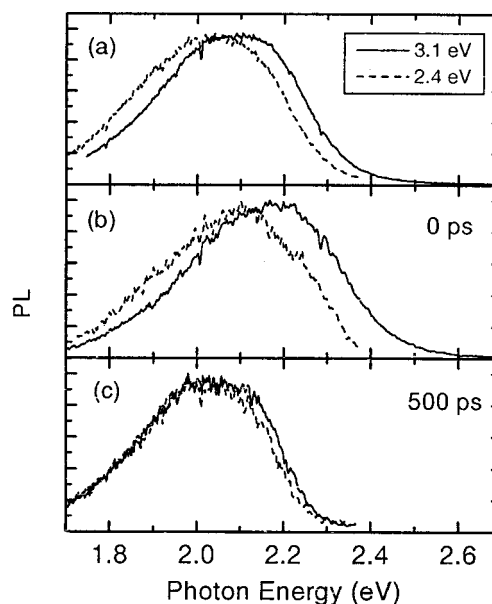


FIG. 4. (a) Time-integrated photoluminescence spectra of R-P(S)MBET excited at energy of 3.1 eV (solid line) and 2.4 eV (broken line). Photoluminescence spectra at (b) 0 ps and (c) 500 ps after photoexcitation.

P(S)MBET (not shown here). This independence suggests another ultrafast relaxation process that occurs before STE's are thermalized. This process might be the interchain migration because, in highly ordered films, the polymer chains are closely packed and the interchain interaction is enhanced by the small stacking distance of the thiophene rings. Recent advances¹⁹ in nanoscale control of polymer morphologies should enable us to investigate the relaxation dynamics where the STE formation and the interchain migration coexist.

In conclusion, we measured the time-resolved photoluminescence on highly ordered and disordered films of a polythiophene derivative, P(S)MBET, and found that the formation of self-trapped exciton (STE) within 10 ps and the intrachain migration of the STE to segments with longer effective conjugation is a common behavior in both films. It is interesting that the STE is formed in even disordered film where an average length of the effective conjugation is only a few thiophene rings. In the disordered film, the thermalization of the STE occurs within a very short time. On the other hand, a longer time is required to thermalize the hot STE in the ordered film, and this causes the lower luminescence quantum efficiency in the ordered film than in the disordered film. From the experiments on the highly ordered film where the vibronic structure of the luminescence is clear, the narrowing of the phonon sidebands within 10 ps and broadening of the 0-0 transition on a few hundred ps time scale are observed. The narrowing is explained by the thermalization process of STE, and the broadening by the STE migration and the dependence of the electron-phonon coupling on the effective conjugation length.

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