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RELAXATION DYNAMICS OF PHOTOINDUCED EXCITON BLEACHING IN POLYMERS

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Presented in this paper are systematic studies of photoinduced exciton bleaching dynamics in the polymers with nondegenerate ground state, such as polydiacetylene, polythiophene and polyaniline. From a three-level model, the photoexcitation and relaxation of the exciton bleaching in the polymers are simulated. The results show that the exciton bleaching decay is composed of two components, the fast component and the slow component. For the fast component, the speed of exciton bleaching decay depends on the way in which the excitons relax. When the relaxation of the exciton to the ground state is dominant, the polymers exhibit an ultrafast initial bleaching relaxation; when the relaxation of the exciton to the self-trapped exciton state is dominant, the polymers exhibit a slower initial bleaching relaxation than that in the former case. For the slow component, the exciton bleaching decay is due to the relaxation of the self-trapped excitons to the ground state. Using femtosecond time-resolved pump-probe technology, we measured the relaxation dynamics of the photoinduced exciton bleaching in the emeraldine base form of polyaniline. Fitting the experimental data to the theoretical model indicates that the fast component arises from the relaxation of excitons to the ground state ($\sim$ 100 fs) and the slow component arises from the relaxation of self-trapped excitons to the ground state ($\sim$ 30 ps).

PACC: 4270; 4280W; 4265G

I. INTRODUCTION

Polymers with large nonlinear optical response have attracted considerable attention in recent years.[1-3] A great deal of photoinduced absorption experiments have been performed. The results indicate that femtosecond relaxation processes occur in the materials[4,5] and that the defect states play an important role in the photoexcitation and relaxation in the polymers. The in-gap defects, originated from the electron-phonon interactions, generally have much longer lifetimes than purely electronic excitation. For the polymers with nondegenerate ground state, such as polydiacetylene (PDA), polythiophene (PT) and polyaniline (PAn), defects are polarons and bipolarons. The former results from the interchain excitation and the latter from the intrachain excitation. The photoinduced absorptions in PDA, PT and PAn have been investigated by Huxley *et al.*[4], Kobayashi *et al.*[5], Epstein *et al.*[6] and Kanner *et al.*[7] All their experiments showed that as the photon energy of the fundamental femtosecond pulse for the pump-probe experiment is close to the exciton peak, the

polymers exhibit photoinduced exciton bleaching, which is composed of two components: the initial fast component and the following slow component, which is due to the relaxation of self-trapped excitons to the ground state. In terms of the origin of the fast component, there are different explanations. Huxley *et al.* proposed that the initial fast component is due to the relaxation of the exciton to the self-trapped exciton state, based on their study on PDA. While Epstein *et al.*, on the basis of their study on PAn, suggested that the origin of the fast component is due to the relaxation of the exciton state to the ground state because this process does not involve the lattice relaxation, hence it may be fast. In addition, Kanner *et al.* have studied the exciton bleaching in PT and found that the theoretical model assuming the route of exciton bleaching decay to be the following: the exciton state→ the self-trapped exciton state→ the ground state does not fit well to the fast component observed. On the basis of the above discussion, in order to understand the origin of the fast component exactly and the effects on exciton bleaching in polymers with nondegenerate ground state, it is necessary to carry out systematic theoretical studies. In this paper, we present the detailed, systematic studies of photoinduced exciton bleaching dynamics in polymers with nondegenerate ground state. From a three-level model, the excitation and relaxation of exciton bleaching are simulated. In order to test the theoretical model, we measured the photoinduced exciton bleaching process in the emeraldine base (EB) form of polyaniline. The experimental data are in good agreement with the theoretical results.

II. THEORY

For the polymers with nondegenerate ground state, the localized photoexcitation can induce in-gap excitons. As soon as the excitation occurs, the binding electron will be strongly coupled with the lattice (phonon). As a result, distortions in the polymer backbone structure take place, and excitons may relax to the self-trapped exciton state (neutral bipolarons).[8]

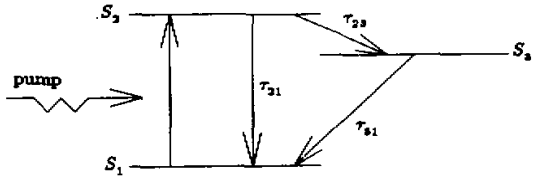

Fig. 1. A three-level system used to simulate the photoexcitation and relaxation in polymers.

This relaxation process is usually very fast (on femtosecond time scale).[9] But, the relaxation of the self-trapped excitons to the ground states is likely to involve the lattice relaxation, hence it may be very slow (up to millisecond time scale).[4,10] The excitation and relaxation process of excitons can be described by a three-level model, as shown in Fig. 1.

Pump laser excites the electrons from the ground state (S_1) to the exciton state (S_2). The excitons decay in two ways. One is from the exciton state directly back to the ground state and the other is from the exciton state to the self-trapped exciton state (S_3), then back to the ground state. The above dynamic process can be described by the following rate equations:

$$\frac{dN_1}{dt} = -\frac{I_p\sigma_g}{h\nu_p}(N_1 - N_2) + \frac{N_2}{\tau_{21}} + \frac{N_3}{\tau_{31}}, \tag{1}$$

$$\frac{dN_2}{dt} = \frac{I_p\sigma_g}{h\nu_p}(N_1 - N_2) - \frac{N_2}{\tau_{21}} - \frac{N_2}{\tau_{23}}, \tag{2}$$

$$\frac{dN_3}{dt} = \frac{N_2}{\tau_{23}} - \frac{N_3}{\tau_{31}}, \tag{3}$$

$$\frac{\partial I_p(Z,t)}{\partial Z} = -I_p(Z,t)[\sigma_g(N_1 - N_2) + \sigma_s N_2 + \sigma_{s'} N_3], \tag{4}$$

where N_1, N_2 and N_3 are the densities of the ground state, the exciton state and the self-trapped exciton state, respectively; τ_{21}, τ_{23} and τ_{31}, represent the time constants for the relaxations from S_2 to S_1, S_2 to S_3 and S_3 to S_1, respectively; σ_g, σ_s and $\sigma_{s'}$ represent the cross-sections of the ground state, the exciton state and the self-trapped exciton state, respectively; $h\nu_p$ is the pump photon energy. $I_p(Z,t)$ is the temporal intensity of the pump laser. The probe laser intensity $I_{Pr}(Z, t'-t)$, regarded as a function of position within the absorbing medium, is described by

$$\frac{\partial I_{pr}(Z,t-t')}{\partial Z} = -I_{pr}(Z,t'-t)[\sigma_g(N_1(t') - N_2(t') + \sigma_s N_2(t') + \sigma_{s'} N_3(t')]. \tag{5}$$

The transmission of the probe beam delayed with respect to the pump beam is

$$T(t) = \frac{\int_{-\infty}^{\infty} I_{pr}(Z=L, t'-t)dt'}{\int_{-\infty}^{\infty} I_{pr}(Z=0, t'-t)dt'}, \tag{6}$$

with the initial conditions

$$N_1(Z, t=-\infty) = N, \quad N_2(Z, t=-\infty) = N_3(Z, t=-\infty) = 0,$$
$$I_p(Z=0,t) = I_p^0 f(t), \quad I_{pr}(Z=0,t) = I_{pr}^0 f(t),$$

where $f(t)$ is the pulse shape described by $f(t) = \exp[-c(t/\tau_L)^2]$ with c being a constant, τ_L the pulse width. I_p^0 and I_{pr}^0 are the peak intensities of pump laser and probe laser, respectively. We can determine the resonant excitation dynamics in a sample with a thickness of L by solving the above equation system Eqs. (1)–(6) numerically with a microcomputer.

When the pump laser and the probe laser have the same wavelength, the polymer will exhibit photoinduced bleaching, and the condition $(\sigma_s, \sigma_{s'}) \ll \sigma_g$ must be satisfied. Under this condition, the exciton bleaching (saturable absorption) occurs between the ground state and the exciton state.

Since the exciton absorption in PDA, PT, and PAn are all near to 2 eV, we can select the following parameters:

$$h\nu_{\rm p} = h\nu_{\rm pr} = 2\,{\rm eV}\ , \quad \tau_{\rm L} = 150\,{\rm fs}\ ,$$
$$I_{\rm p} : I_{\rm pr} = 4:1\ , \quad \sigma_{\rm g} \approx 10^{-16}\,{\rm cm}^2\ .$$

The temporally relative transmission of the probe beam through sample can be calculated for various delay times τ_{21}, τ_{23}, and τ_{31}, and the calculated results are shown in Figs. 2, 3 and 4, respectively.

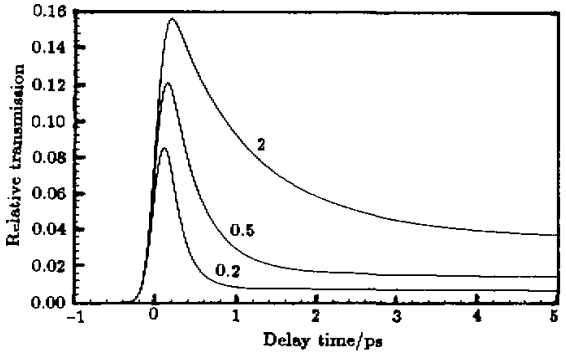

Fig. 2. The photoinduced exciton bleaching and decay in polymers with $\tau_{23} = 2\,{\rm ps}$, $\tau_{31} = 30\,{\rm ps}$ and $\tau_{21} = 2, 0.5, 0.2\,{\rm ps}$, respectively.

Figure 2 shows the excitation and relaxation process of exciton bleaching for $\tau_{23} = 2\,{\rm ps}$, $\tau_{31} = 30\,{\rm ps}$ and $\tau_{21} = 2, 0.5, 0.2\,{\rm ps}$, respectively. As shown in Fig. 2, when τ_{21} decreases, the decay curve, following the initial rise, becomes sharper and the peak drops down, which indicates that the relaxation for the fast component is faster. However, the change in τ_{21} does not affect the relaxation for the slow component. From Fig. 2, we can see that more excitons relax directly back to the ground state as τ_{21} decreases. When $\tau_{21} = 0.2\,{\rm ps}$, almost all excitons decay to the ground state in 600 fs.

Figure 3 shows the excitation and relaxation process of exciton bleaching for $\tau_{21} = 20\,{\rm ps}$, $\tau_{31} = 2\,{\rm ps}$ and $\tau_{23} = 0.2, 0.1, 0.01\,{\rm ps}$, respectively. As shown in Fig. 3, when τ_{23} decreases, the relaxation for the fast component becomes slower and the bleaching peak drops down. The relaxation from exciton state to the self-trapped exciton state leads to the depopulation of the exciton state, and more transitions from the ground state to the exciton state. As a result, the magnitude of the exciton bleaching decreases. Compared with Fig. 2, it is clear that the effect of changing τ_{21} on the exciton bleaching decay is substantially different from that of changing τ_{23}. As is shown in Fig. 3, no significant change of the slow component is caused by the variation of τ_{23}.

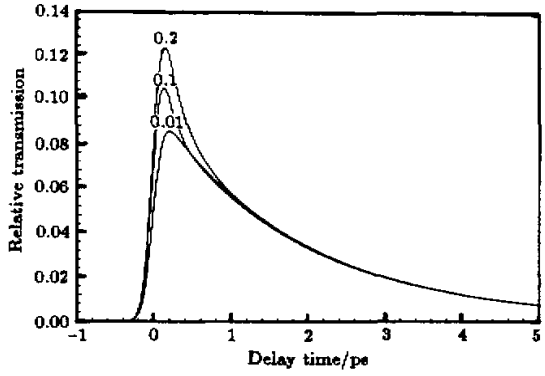

Fig. 3. The photoinduced exciton bleaching and decay in polymers for $\tau_{21} = 20\,\text{ps}$, $\tau_{31} = 2\,\text{ps}$ and $\tau_{23} = 0.2, 0.1, 0.01\,\text{ps}$, respectively.

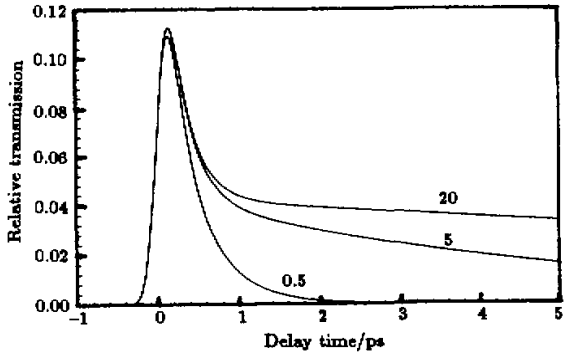

Fig. 4. The photoinduced exciton bleaching and decay in polymers for $\tau_{21} = 0.5\,\text{ps}$, $\tau_{23} = 0.5\,\text{ps}$ and $\tau_{31} = 20, 5, 0.5\,\text{ps}$, respectively.

Figure 4 shows the excitation and relaxation process of exciton bleaching for $\tau_{21} = 0.5\,\text{ps}$, $\tau_{23} = 0.5\,\text{ps}$ and $\tau_{31} = 20, 5, 0.5\,\text{ps}$, respectively. As τ_{31} decreases, the relaxation for the slow component becomes faster. As $\tau_{31} = 0.5\,\text{ps}$, all excitons finish the recombination within 2.5 ps, Accordingly, in order to shorten the switch time in polymers, it is necessary to shorten the lifetimes of the self-trapped excitons except for the requirement of very short decay time (τ_{21}, τ_{23}). In addition, comparison of Figs. 2, 3 and 4 indicates that the change in τ_{31} does not result in significant change of the fast component.

III. EXPERIMENT

Using femtosecond time-resolved pump-probe technology, we measured the photoexcita-

tion and the relaxation processes in the EB form of polyaniline. In our experiment, the light source was a colliding pulse mode-locked (CPM) dye laser with a repetition of 110 MHz, pulse width of 50 fs, average power of 16 mW, and at a wavelength of 630 nm ($\sim$ 2 eV). The laser beam derived from the laser system was split into pump beam and probe beam with a ratio of 4:1. The polarizations of the pump and the probe pulses were parallel to each other. The relaxation dynamic process of photoinduced exciton bleaching was measured by detecting the relative transmission ($\Delta T/T$) of the probe beam delayed with respect to the pump beam. The probe pulses through the sample were monitored by a photomultiplier tube, equipped with a lock-in amplifier and a micro-computer.

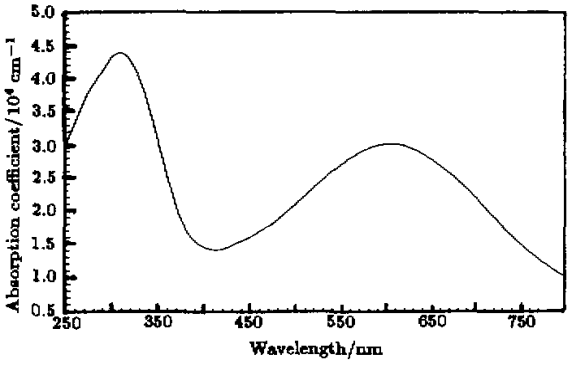

Fig. 5. The linear absorption spectrum of EB.

The EB film was prepared by the following procedure: EB powder was dissolved in N-methylpyrrolidinone (NMP) first. Then, by spin-casting the solution onto glass substrates, thin and optically transparent EB film was obtained. The thickness of the EB film is 1.56 μm. Figure 5 shows the linear absorption spectrum of EB. The optical absorption of EB is characterized by a strong absorption band in the UV at 320 nm (similar to other polymers with nondegenerate ground state) and another broad excitation absorption at about 630 nm ($\sim$ 2 eV), which is attributed to the transition from a benzenoid-ring-based energy level to a quinoid-based energy level.[11]

Figure 6 shows the result of the pump-probe experiment on EB. As shown in Fig. 6, the initial rise of $\Delta T/T$ is followed by a rapid decay and then by a much slower decay. With the fitting parameters of τ_{21} = 100 fs, τ_{23} = 200 fs and τ_{31} = 30 ps, the curve shape from theoretical simulation is found to fit well to our experimental data. On the basis of the results, the fast component in EB is due primarily to the combination of the excitons by relaxing back to the ground state ($\sim$ 100 fs), and the slow component is originated from the relaxation of the self-trapped excitons to the ground state ($\sim$ 30 ps), which is in accord with the analysis by Epstein and Roe *et al.*[6,11] In their experiment, the laser pulse width is

about 8 ps, so that the fast component in EB cannot be observed although it was expected to be shorter than 40 ps.

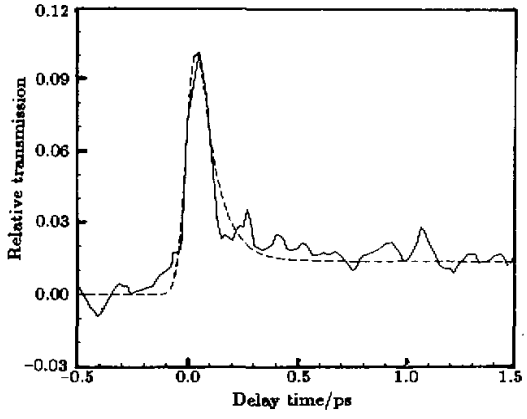

Fig. 6. The photoexcitation and relaxation of the exciton bleaching in EB at 2 eV. The dashed line is the theoretical result.

IV. DISCUSSION

Based on our theoretical and experimental studies, the speed of the photoinduced exciton bleaching decay in the polymers with nondegenerate ground state is affected strongly by both the lifetime of the excitons and the time for formation and relaxation of the self-trapped excitons, which depend on polymer backbone structure. For EB, a molecular structure of alternate benzenoid rings and the quinoid rings exists, and the formation and relaxation of the defects are related with the quinoid ring rotations with respect to adjacent benzenoid ring. Hence, the defects have long lifetimes ($\sim$ 30 ps). For PDA, however, the backbone has a planar, fully conjugated structure.[12] The formation and the relaxation of photoinduced defects only involve the lattice vibration, hence, they have shorter lifetimes ($\sim$ 1.5 ps)[11], compared with those in EB. Since the exciton recombination undergoing directly form the exciton state to the ground state in EB is much faster than that in PDA, there is a relation of $\tau_{21} < \tau_{23} < \tau_{31}$ for EB. As a result, the fast component in EB is due primarily to the relaxation directly from the exciton state to the ground state. According to the above theoretical and experimental studies, this process is very fast ($\sim$ 100 fs). Meanwhile, a fast relaxation of the exciton bleaching in the polymer appears. For PDA, there is $\tau_{21} > \tau_{31} > \tau_{23}$, hence, the fast component is due primarily to the relaxation from the exciton state to the self-trapped exciton state. Although this process is very fast ($\sim$ 150 fs), the polymers do not exhibit fast initial bleaching relaxation process.

V. CONCLUSION

We have studied the excitation and relaxation of the photoinduced exciton bleaching in the polymers with nondegenerate ground state. The conclusions derived from the study are:

A. The relaxation of the photoinduced exciton bleaching in the polymers with nondegenerate ground state is composed of a fast component and a slow component. The fast component consists of contributions from the relaxations of the excitons to both the ground state and the self-trapped exciton state. The slow component is derived from the relaxation of the self-trapped excitons to the ground state.

B. In order to shorten the relaxation time of the photoinduced exciton bleaching, following conditions must be satisfied:

(a) The decay time from the exciton state to the ground state τ_{21} must be shorter than that from the exciton state to the self-trapped exciton state τ_{23}, as the ultrafast formation of self-trapped excitons cannot lead to the ultrafast relaxation of the exciton bleaching in the polymers.

(b) The relaxation from the self-trapped exciton state to the ground state must be rapid.

C. Our theoretical model established for describing the relaxation of photoinduced exciton bleaching can account for the excitation dynamics in the polymers more accurately than earlier theories.[4]

In summary, the theoretical and the experimental studies of the photoinduced exciton bleaching in the polymers with nondegenerate ground state are helpful in understanding the transformations of electronic structures and their relaxation with the optical response in the polymers. Furthermore, the ultrafast relaxation in the polymers may be used in high-speed optoelectronics and information processing.

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