

Ultrafast Charge Separation and Recombination Dynamics in a Nanometer Thin Film of Polyimide Observed by Femtosecond Transient Absorption Spectroscopy

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Femtosecond transient absorption spectroscopy was used to study how polyimide (PI) interacts with light in a nanometer-thick PI thin film. The PI containing pyromellitic diimide (PMDI) shows absorption by PMDI anions around 710 nm. Its decay occurs on two time scales: one is on the order of 10 ps and the other is on the order of a nanosecond. Each decay time is independent of the excitation wavelength and energy density, indicating that a geminate recombination would be dominant in a PI film. Under excitation by 390 nm light, the faster decay process shows one-photon absorption, but the slower decay process shows a two photon-absorption process.

Introduction

Polyimide (PI) materials are noted for their high thermal stability, excellent insulating integrity, and superior electrical and mechanical properties.^{1–3} PI has been widely adopted as a substance or insulating dielectric material in modern electronics. For example, PI is frequently employed as a dielectric layer in the multilevel structures of very large scale integrated devices. Because of its good insulating and mechanical properties, PI is also used as a material for packaging semiconductor devices.

Many spectroscopic and electrochemical approaches have been used to characterize the physical properties of PI.^{4–7} X-ray photoemission spectroscopy has yielded the electronic properties of PI backbone structures.⁴ Ultraviolet photoemission spectroscopy has been used to measure the intrinsic valence electronic structure of PI.^{5,6} Theoretical calculations to explain the ultraviolet absorption spectra have also been carried out.⁷

Recently, the interaction of PI with light has been a hot issue from the standpoint not only of fundamental science but also of applications. Thin PI layers are widely known to work as orientational layers for liquid crystal (LC) alignment in LC devices. More surprisingly, LCs can be aligned by the exposure of a PI surface to polarized light.^{8–13} The polarized light is believed to induce anisotropy in the PI backbones or side chains. However, the detailed mechanisms have not yet been clarified because of difficulties in detecting intrinsic changes at the PI surface. There has been little discussion of photophysical processes or PI dynamics, in contrast to the orientation and anisotropy of PI backbones or side chains. However, it is quite important to understand the photophysical properties and dynamics when PI is irradiated by light.

The mechanism of PI photoconductivity has also been of great interest.^{14–20} Photogenerated intra- or intermolecular charge transfer by the absorption of radiation contributes to the photoconductivity of a polymer.^{21–24} Using Kapton PI, the

chromophores responsible for photoconduction were identified as radical anions.^{23,24} The photoconduction is believed to follow the hopping of charge between the adjacent pyromellitic imide (PMDI) units by the assistance of an electric field. The initial photophysical process of the interaction of PI with light was studied mainly by Freilich and Lee.^{23,25} Freilich showed that the addition of a small number of electron donors to PI results in an increase in the photocurrent.²³ The increase in photoconductivity was reported to be due to the formation of a charge-transfer complex between the donor and the imide portion of the polymer backbone. Freilich also reported the results of picosecond transient absorption spectroscopy of donor-loaded Kapton PI and observed imide radical anions.²³ However, Freilich did not report the results of transient spectroscopy of undoped Kapton PI. Recently, picosecond-pulse radiolysis by Lee et al. has revealed that the main active species in the photoconductivity of PI are the PMDI anions.²⁵

In this paper, we report on charge separation and recombination in PI by means of femtosecond transient absorption spectroscopy. Our principal purpose is to understand the ultrafast photophysical processes in a PI thin film. We can compare these results with those of PMDI anions in solutions and crystals. We also expect to observe high-density excitation of PI thin films by femtosecond laser spectroscopy. In particular, we focus on PI with PMDI. Data over a range of several picoseconds has not been reported in sufficient detail to yield an understanding of faster processes of the photogenerated species. We have investigated the dependence of femtosecond transient absorption spectra on the excitation wavelength and the excitation energy density. Although Lee et al. reported the transient spectra of PI with PMDI by using pulse radiolysis, the consequences of laser excitation of PI are different from those of pulse radiolysis because the excitation energy is lower than that in pulse radiolysis. Indeed, we observe different behavior of the PMDI anions compared to the results of pulse radiolysis.

Experimental Section

Materials and Preparations. The PIs used in this study were PMDA/BAPP, which consists of pyromellitic dianhydride and

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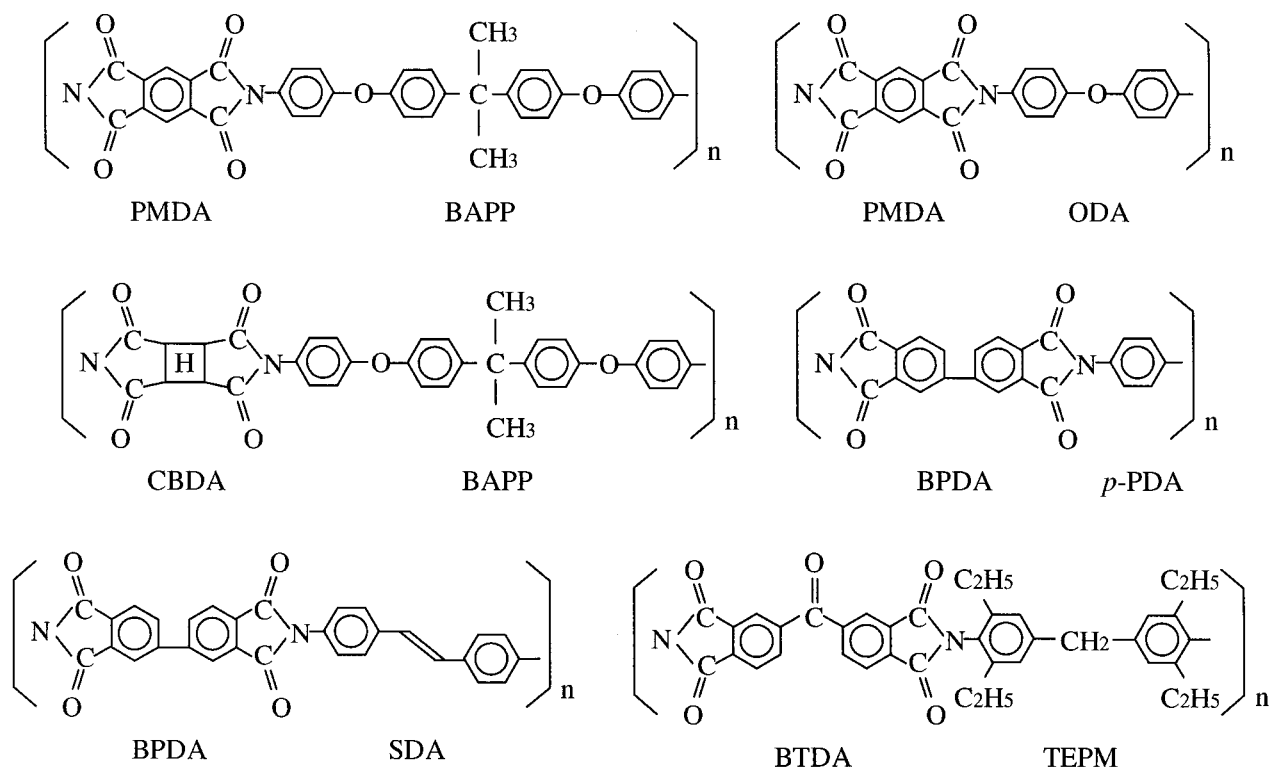


Figure 1. Chemical structures of the PIs used in this study.

2,2-bis[4-(4-aminophenoxy)phenyl]propane; PMDA/ODA, which is made up of pyromellitic dianhydride and oxidianiline; CBDA/BAPP, which is formed from 1,2,3,4-cyclobutanetetracarboxylic dianhydride and 2,2-bis[4-(4-aminophenoxy)phenyl]propane; BTDA/TEPM, which is made up of benzophenonetetracarboxylic dianhydride and diaminotetraethyldiphenylmethane; BPDA/*p*-PDA, which consists of biphenyl tetracarboxylic dianhydride and *p*-phenylene diamine; and BPDA/SDA, which is made up of biphenyltetracarboxylic dianhydride and stilbene diamine. The chemical structures of these PIs are shown in Figure 1.

Each PI thin film was prepared by curing the polyamic acid corresponding to the desired PI film. The polyamic acid that dissolved in 1-methyl-2-pyrrolidone was spin coated on the fused silica substrates. The spin-coated polyamic acid was imidized at 230 °C for 20 min. The film thickness was controlled by the concentration of the polyamic acid solutions.

Measurements. The femtosecond laser system has already been described in detail.²⁶ In brief, we used a CW self-mode-locked Ti/sapphire laser (Mira900 Basic, Coherent) pumped by an Ar⁺ laser (Innova310, Coherent) and a Ti/sapphire regenerative amplifier system (TR70, Continuum) pumped by a Q-switched Nd/YAG laser (Surelight, Continuum). To obtain the 266 and 390 nm excitation wavelengths, the fundamental light (780 nm, 170 fs fwhm, 3–4 mJ/pulse, 10 Hz) was frequency tripled and doubled, respectively. The laser fluence was varied from 1 to 20 mJ/cm² depending on the desired excitation energy density. The fundamental light was also used to produce a white-light continuum, which was generated by H₂O in a quartz cell. The white-light continuum was divided into two beams: a probe beam, which irradiated the samples and was collected by a multichannel spectrometer (HH4-0913, Otsuka Electronics), and a reference beam. A stepper motor controlled an optical delay line that determined the time delay between the pump and the probe beams. We corrected the obtained spectra for chirp.

Results and Discussion

Shown in Figure 2 are femtosecond transient absorption spectra of the different PI films that were excited by 260 and 390 nm light. The broad absorption and weak uniform signal over the entire region can most likely be attributed to various transient species including radical anions, radical cations, and other excited states. However, distinct absorption peaks are observable for PMDA/ODA, PMDA/BAPP, BPDA/*p*-PDA, and BPDA/SDA, but, in the cases of CBDA/BAPP (not shown) and BTDA/TEPM (not shown), the absorption cannot be resolved over the whole region of detection. In the spectra of both PMDA/ODA and PMDA/BAPP, a peak around 710 nm is clearly resolvable. This peak can be assigned to the absorption of the PMDI anions. PMDI is known to be a good electron acceptor, and the absorption spectra of PMDI anions in solutions, crystals, and polymers have already been reported.^{23,25–28} On the basis of the similarities observed in the model systems investigated in solutions, Lee²⁵ assigned the absorption around 720 nm to the PMDI anions in the pulse radiolysis. The shoulder around 660 nm in Figure 2a and b is also similar to that reported by Lee. Our assignment is also supported by Freilich's assignment to the PMDI radical anions by time-resolved laser spectroscopy.²³ Therefore, we conclude that the absorption in our spectra originate from PMDI anions. In our observations, the excitation energy corresponds to the excitation of the PMDI itself or to the $\pi-\pi^*$ transition of benzene for 260 nm excitation.²⁹ These facts tell us that the direct excitation to the first excitation state is also followed by a rapid inter- or intramolecular charge transfer, as in the case of pulse radiolysis. The donor moiety can be a phenyl group or a biphenyl ether. The formation of an imide structure is required to observe PMDI anions, as seen in Figure 3, indicating that the energy level of the lowest unoccupied molecular orbital of an amide group would, most probably, be higher than that of an imide group. The rapid charge-separation process can create PMDI radical anions immediately after the excitation.

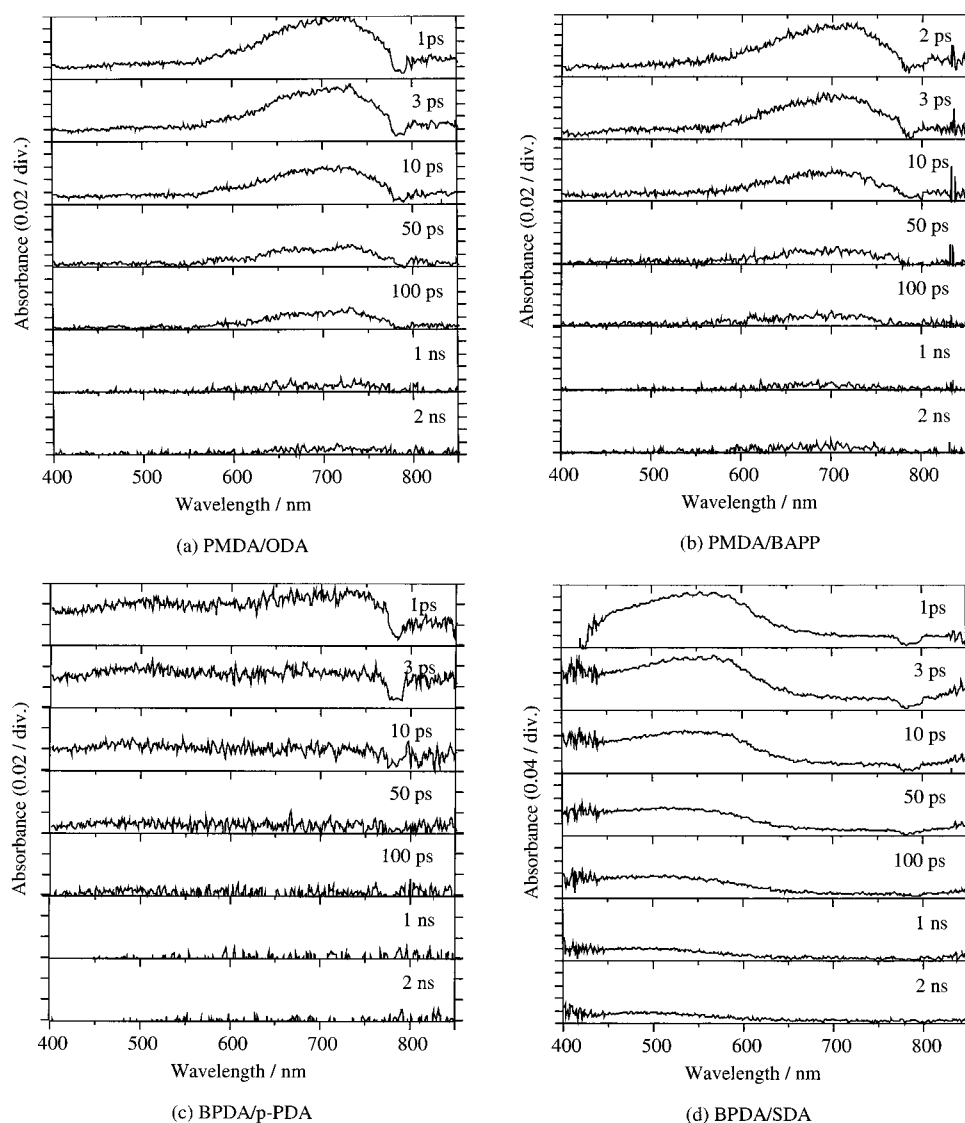


Figure 2. Time-resolved absorption spectra of a series of PI thin films. (a)–(c) Excitation at 260 nm (d) Excitation at 390 nm.

Because of the distinctive absorption due to PMDI anions, we focus on a PMDA/ODA film. Because of femtosecond laser output that has a narrow pulse width and much greater peak power than do picosecond and nanosecond laser pulses, ablation or damage can occur when shining a laser onto the PI surface. To check the change of absorption due to ablation or damage, we measured the transient absorption by changing the delay time from a short to a long delay and vice versa. Figure 4 compares the PMDI anion absorption at 710 nm between the forward and backward adjustment of the optical delay when the excitation is 260 nm. The discrepancy between the data indicates that a permanent change of the PI film is induced during spectral measurement. However, the spectra observed are relatively clear, and the shape is the same irrespective of the direction of the adjustment of the optical delay. Therefore, the damage must be limited to the PI surface, which implies that the damage in this case possibly corresponds to ablation of the PI by the femtosecond laser pulses.

Figure 5 shows the relaxation of the absorption of 710 nm light at different film thicknesses. According to measurements of the UV spectra, the optical density at 260 nm is 0.74 with an 80-nm film thickness. From these values, the absorption length of the 260-nm beam can be estimated to be around 94 nm. In the case of the thinner film in Figure 5, the whole region

of the PMDA/ODA from the air/PI surface to the PI/substrate interface can be excited. On the other hand, the thickness of the thicker film is much larger than the absorption length. These results suggest that there are no differences between the relaxation processes of films of different thicknesses, which implies that we cannot consider the inhomogeneous distribution of mutual association and orientation of PMDI and donor moieties along the direction normal to the substrate plane. However, the relaxation occurs on two time scales. One is a few 10s of picoseconds; the other is a few nanoseconds. The latter would be the same as that observed in pulse radiolysis because the lifetimes are similar. It is the former that can be obtained by laser excitation but not by pulse radiolysis.

Figure 6 presents the excitation energy dependence of the absorption spectra at 710 and 480 nm. The slope of the absorbance to the energy density is less than 1 and is most likely close to the saturation level. When the absorption sites (i.e., benzene or PMDI moieties) for the incoming beam are sufficiently dense despite the fact that the absorption sites are initially in the ground state or relax to the ground state by rapid recombination, the absorption of the photons can approach the saturation level, that is, the excited sites can be considered to be generated densely in the PI film because of the large absorption coefficient at 260 nm. In such a dense population of

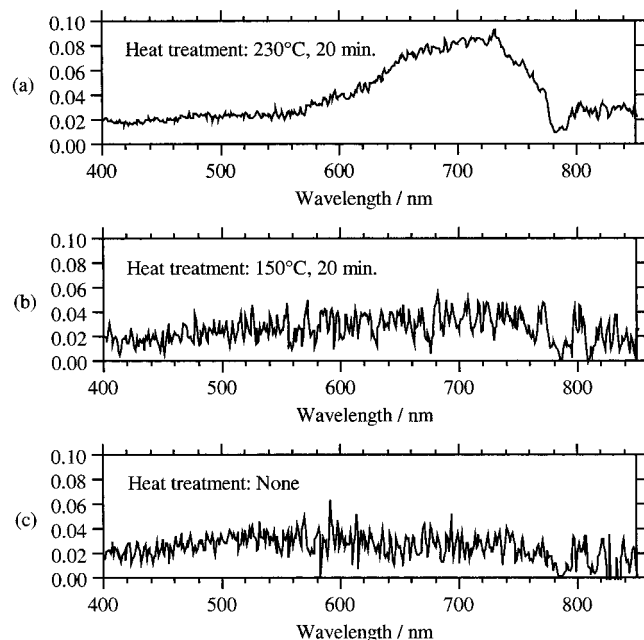


Figure 3. Effect of thermal treatment in the imidization reaction for a PMDA/ODA film. (a) 230 °C/20 min. (b) 150 °C/20 min. (c) No heat applied.

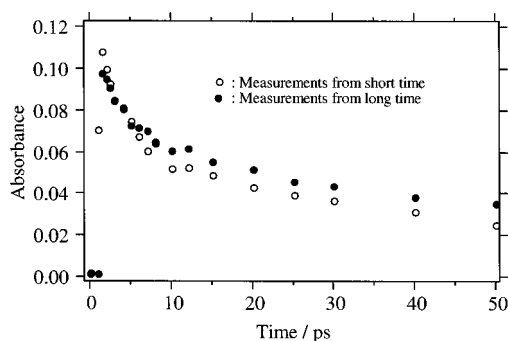


Figure 4. Absorbance of a PMDA/ODA film at 710 nm with respect to delay after excitation at 260 nm.

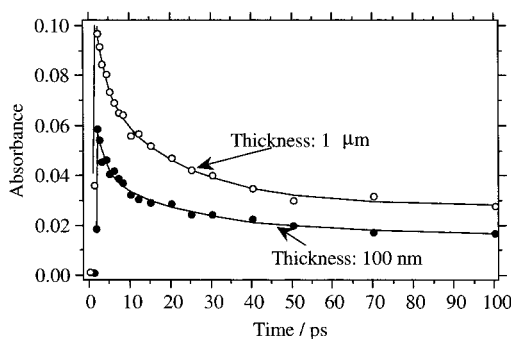


Figure 5. Film thickness-dependent absorbance of a PMDA/ODA film by excitation at 260 nm.

cations and anions, recombination may occur immediately among neighboring cations and anions if random migration is involved in the recombination.

To reduce the density of the generated PMDI anions, we measured the transient absorption spectra of the PMDA/ODA film by 390 nm excitation. We expect that the slower relaxation process would be dominant if random migration is involved because the density of the PMDI anions should be lower. Figure 7 shows the femtosecond transient absorption spectra of the PMDA/ODA film under excitation by 390-nm light. The

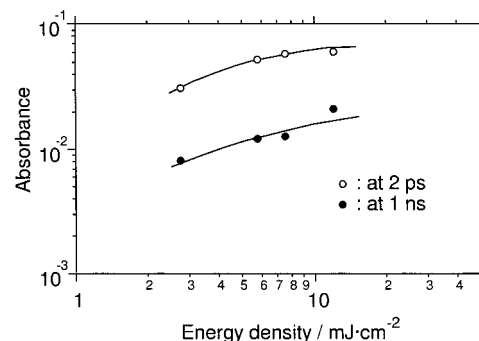


Figure 6. Excitation energy density-dependent absorbance of a PMDA/ODA film at 710 and 480 nm after excitation at 260 nm.

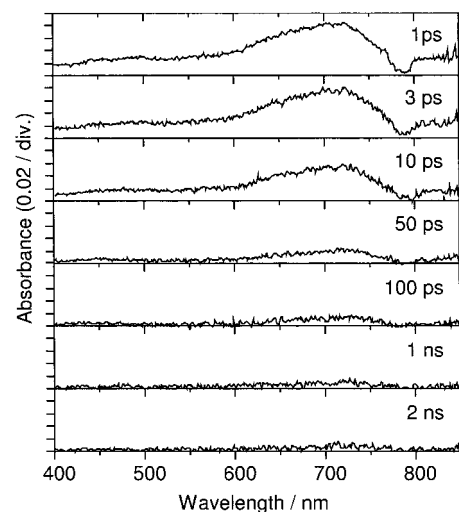


Figure 7. Time-resolved absorption spectra of a PMDA/ODA film after excitation at 390 nm.

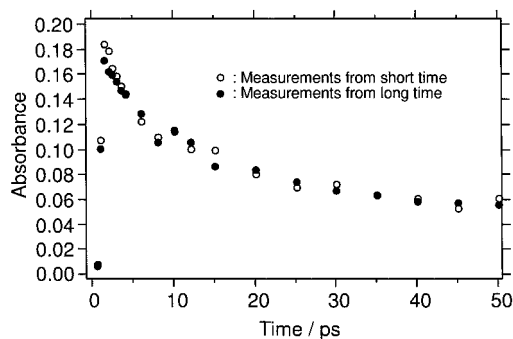


Figure 8. Absorbance of a PMDA/ODA film at 710 nm as a function of delay after excitation at 390 nm.

intrinsic difference between the 390 and the 260-nm excitations lies in the difference in the excited states. The 390-nm excitation corresponds to the direct excitation of a charge-transfer state. The series of spectra obtained using 390-nm excitation are quite similar to those obtained using 260-nm excitation. This fact supports our assertion that there is a charge transfer in PI when exciting the PMDA/ODA film with 260-nm light. The PMDI or benzene moieties are locally excited by 260-nm light, but they are expected to relax immediately to the charge-transfer state. Figure 8 shows the PMDI anion absorption at 710 nm for both forward and backward adjustments of the optical delay under excitation by 390-nm light. The good agreement between these measurements indicates that the spectra can be obtained without ablation or damage of the films, in contrast to the case of excitation at 260 nm. The comparison between the excitation at 260 and 390 nm allowed us to estimate a threshold for

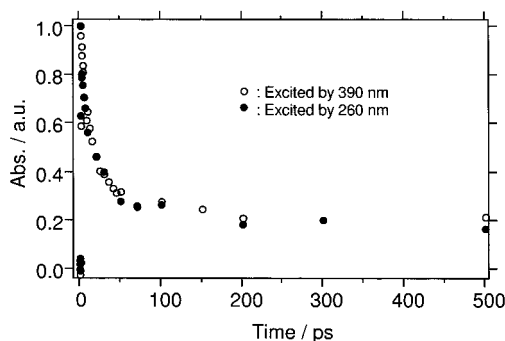


Figure 9. Relaxation behavior of PMDI anions by excitation of a PMDA/ODA film at 260 and 390 nm.

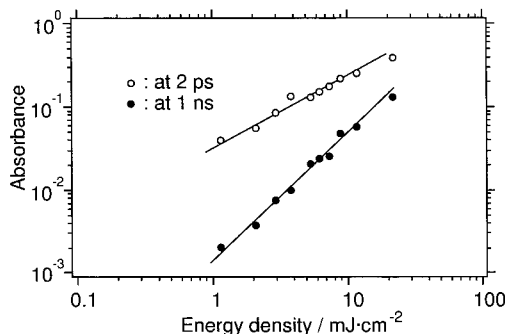


Figure 10. Excitation energy density-dependent absorbance at 710 nm for the 2-ps and 1-ns process in a PMDA/ODA film excited at 390 nm.

ablation or damage by the femtosecond laser in the range of $\sim 1\text{--}7\text{ mJ/cm}^2$. Figure 9 compares the relaxation behavior of the PMDI anions between excitation by 260- and 390-nm light. We would expect that the slower relaxation process would be dominant or that the decay time would be changed when the dynamic recombination corresponds to the shorter relaxation time. As seen in Figure 9, however, the results show no differences in the relaxation behavior between the samples excited by 260- and 390-nm light.

The photogenerated PMDI anions must be produced much less densely by the excitation at 390 nm compared to the density produced by the excitation at 260 nm because of the smaller absorption coefficient. The absorption length at 390 nm is about 890 nm. We measured the excitation energy dependence of absorbance as shown in Figure 10 using two types of photo-generated PMDI anions. To compare the decay behavior of those two species, we measured the dependence of the absorbance on the excitation energy density at 2 and 1 ns, respectively. As expected, the slope of the absorbance versus the excitation energy density increases in comparison to that of the 260-nm excitation. The slope of the rapid decay at 2 ps is almost 1, whereas the slope of the slow decay at 1 ns is nearly 2. These results suggest that the rapid decay is due to charge-transfer band excitation. However, the slow decay that would correspond to the decay of the PMDI anions generated by pulse radiolysis may be due to direct ionization by a two-photon absorption process. The geminate recombinations must be dominant, and random migration is not involved in these decays because they are independent of the excitation wavelength and energy density.

In conclusion, we have used femtosecond transient absorption spectroscopy to study PI thin films. It was found that ultrafast

charge transfer and recombination occur in nanometer PI thin films. As far as the PMDI anion is concerned, the recombination process consists of decay times that last from a few picoseconds to a few nanoseconds. The recombination rates are independent of the excitation wavelength and its energy density, indicating that a geminate recombination is most likely dominant. The only difference in the absorption behavior of the PMDI anion in these two processes is its dependence on the excitation energy density. The faster decay is consistent with a one-photon absorption process, whereas the slower decay possibility occurs by a two-photon absorption process.

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References and Notes

- (1) *Polymer Materials for Electronic Applications*; Feit, E. D., Wilkins, C. W., Eds.; ACS Symposium Series 184; American Chemical Society: Washington, DC, 1982.
- (2) *Polyimides: Synthesis, Characterization, and Applications*; Mittal, K. L., Ed.; Plenum Press: New York, 1984.
- (3) *Recent Advances in Polyimide Science and Technology*, Proceedings of the Second International Conference on Polyimides—Chemistry, Characterization, and Applications, Ellenville, N.Y., 1985; Weber, W. D., Gupta, M. R., Eds.; Mid-Hudson Section, Society of Plastics Engineers: Poughkeepsie, N.Y., 1987.
- (4) Silverman, B. D.; Sanda, P. N.; Ho, P. S.; Rossi, A. R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2857.
- (5) Hahn, P. O.; Rubloff, G. W.; Ho, P. S. *J. Vac. Sci. Technol., A* **1984**, *2*, 756.
- (6) Bredas, J. L.; Clarke, T. C. *J. Chem. Phys.* **1987**, *86*, 253.
- (7) LaFemina, J. P.; Arjavalingam, G.; Hougham, G. *J. Chem. Phys.* **1989**, *90*, 5154.
- (8) Gibbons, G. W.; Shannon, P.; Sun, S.; Swetlin, B. *Nature (London)* **1991**, *351*, 49.
- (9) Hasegawa, M.; Taira, Y. Proceedings the 14th International Display Research Conference, Society for Information Display, Monterey, CA, 1994; p 213.
- (10) Hasegawa, M.; Taira, Y. *J. Photopolym. Sci. Technol.* **1995**, *8*, 241.
- (11) Jang, Y. K.; Yu, H. S.; Yu, S. H.; Song, B. H.; Chae, B. H.; Han, K. Y. *Dig. Technol. Pap.*, 1997; Society for Information Display International Symposium; Boston, 1997; p 703.
- (12) Endo, E.; Shinozaki, T.; Fukuro, H.; Iimura, Y.; Kobayashi, S. *Proc. AM-LCD '96* **1996**, 341.
- (13) Kim, J.-H.; Kumar, S. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1998**, *57*, 5644.
- (14) Weingart, R. C.; Bartlett, R. H.; Lee, R. S.; Hofer, W. *IEEE Trans. Nucl. Sci.* **1979**, *NS-19*, 15.
- (15) Bartlett, R. H.; Fulk, G. A.; Lee, R. S.; Weingart, R. C. *IEEE Trans. Nucl. Sci.* **1979**, *NS-19*, 2273.
- (16) Pillai, P. K. C.; Sharma, B. L. *Polymer* **1979**, *20*, 1431.
- (17) Sharma, B. L.; Pillai, P. K. C. *Phys. Status Solidi A* **1982**, *71*, 583.
- (18) Rashmi; Takai, Y.; Mizutani, T.; Ieda, M. *Jpn. J. Appl. Phys.* **1983**, *22*, 1388.
- (19) Iida, K.; Waki, M.; Nakamura, S.; Ieda, M.; Sawa, G. *Jpn. J. Appl. Phys.* **1984**, *23*, 1573.
- (20) Takimoto, A.; Wakemoto, H.; Ogawa, H. *J. Appl. Phys.* **1991**, *70*, 2799.
- (21) Hoegl, H. J. *J. Phys. Chem.* **1965**, *69*, 755.
- (22) Penwell, R. C.; Ganguly, B. N.; Smith, T. W. *J. Polym. Sci., Part D: Macromol. Rev.* **1978**, *13*, 63.
- (23) Freilich, S. C. *Macromolecules* **1987**, *20*, 973.
- (24) LaFemina, J. P. *Chem. Phys. Lett.* **1989**, *159*, 307.
- (25) Lee, S. A.; Yamashita, T.; Horie, K.; Kozawa, T. *J. Phys. Chem. B* **1997**, *101*, 4520.
- (26) Asahi, T.; Matsuo, Y.; Masuhara, H. *Chem. Phys. Lett.* **1996**, 256, 525.
- (27) Kobayashi, T.; Matsumoto, S.; Nagakura, S. *Chem. Lett.* **1974**, 235.
- (28) Shida, T.; Iwata, S.; Imamura, M. *J. Phys. Chem.* **1974**, *78*, 741.
- (29) Ishida, H.; Wellinghoff, S. T.; Baer, E.; Koenig, J. L. *Macromolecules* **1980**, *13*, 826.