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Time-resolved Absorption Spectral Measurement of Polymer Films during Laser Ablation

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Transient absorption spectra of p-terphenyl doped poly(methyl methacrylate) (PMMA) film upon laser ablation shows that no other transient species than the excited singlet and triplet states is involved. Fragmented particles were observed from 50 ns after excitation, while all morphological changes were completed in sub-ms time range.

Excitation of aromatic molecules doped in solid films with an intense laser pulse results in characteristic behavior; multi-photon ionization, S_1-S_1 annihilation, T_1-T_1 annihilation, and so on. Further increase of excitation intensity brings about bond scission, decomposition, melting, vaporization of solid film, leaving a hole. This behavior is called laser ablation and has received much attention as a novel photochemical behavior characteristic of intense laser excitation and also as a new technique for microfabrication.1) Since the first demonstration was given for doped film,2) a lot of works have been reported;3) however, transient absorption spectral measurement during ablation has been rarely given as far as we know.4)

It is probable that ionic species of doped aromatic molecules, which may be formed by multiphoton ionization and/or S_1 - S_1 annihilation, trigger decomposition of PMMA, followed by unzipping reactions. Actually, an important role of S_1-S_1 annihilation in laser ablation was experimentally confirmed for poly(N-vinylcarbazole) film.5) It is expected

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that molecular mechanism of laser ablation will be elucidated in detail by measuring directly ionic states and/or relevant intermediates with laser photolysis method. In the present paper we study p-terphenyl in PMMA film upon laser ablation.

PMMA (gifted as pellets from Kuraray Co. Ltd.) was reprecipitated three times from benzene-methanol and dried under freezing. p-Terphenyl (Tokyo Kasei, Scintillation grade) was purified by a home-made zone-refiner (100 steps). Chlorobenzene (Wako, Special grade) was stirred with H_2SO_4 and $CaCl_2$ to remove impurity and water, respectively, and distilled. Chlorobenzene solution of 15 wt% polymer and a small amount of p-terphenyl was spin-coated on a quartz substarate, and the prepared film was dried under vacuum for longer than 3 h. The film thickness was 25 μm, and the concentration of p-terphenyl was 1.4×10^{-2} mol/mol MMA unit.

Time-resolved absorption spectra were measured by a laser photolysis system using a streak camera (Hamamatsu C2830) as a detector. For absorption rise and decay curves a storage scope (Iwatsu TS-8123) was used. A 248 nm excimer laser and a pulsed 150 W Xe lamp were used as excitation and monitoring light sources, respectively. Only the ablated area was interrogated in transmitance mode by adjusting the monitored area (1.5 mm diameter) smaller than the excited one. The angle between the monitoring beam and the film was 60^o. All the data were measured only for fresh surface and not averaged over several measurements. The delay time was given by defining the time, when the laser light attaines the maximum intensity, to zero.

An absorbance at 248 nm was 0.06 and 0.29 for the neat and doped PMMA films, respectively. Ablation threshold for neat and doped films was 400 and 160 mJ/cm^2, respectively. This means that an excitation of doped p-terphenyl induces more efficient ablation, so that its excited states have a key role in ablation processes.

Time-resolved absorption spectra of p-terphenyl in PMMA at 90 mJ/cm^2 are given in Fig.1(A). Although S/N is poor because of a single shot measurement, it is safely concluded that the band is due to T_n-T_1 transition.6) Above the threshold (Fig.1(B)), the spectrum at an early stage can be ascribed to the triplet state, while an intense absorption descending from the short to long wavelength was observed at a few tens of ns after excitation. It is worth noting that neither bands of ionic species such as cation, anion, nor those of decomposed radicals of p-terphenyl were observed. A similar flat band was also measured independently upon the delay time for laser ablation of the neat film. This means that the band is not related to p-terphenyl but due to PMMA or

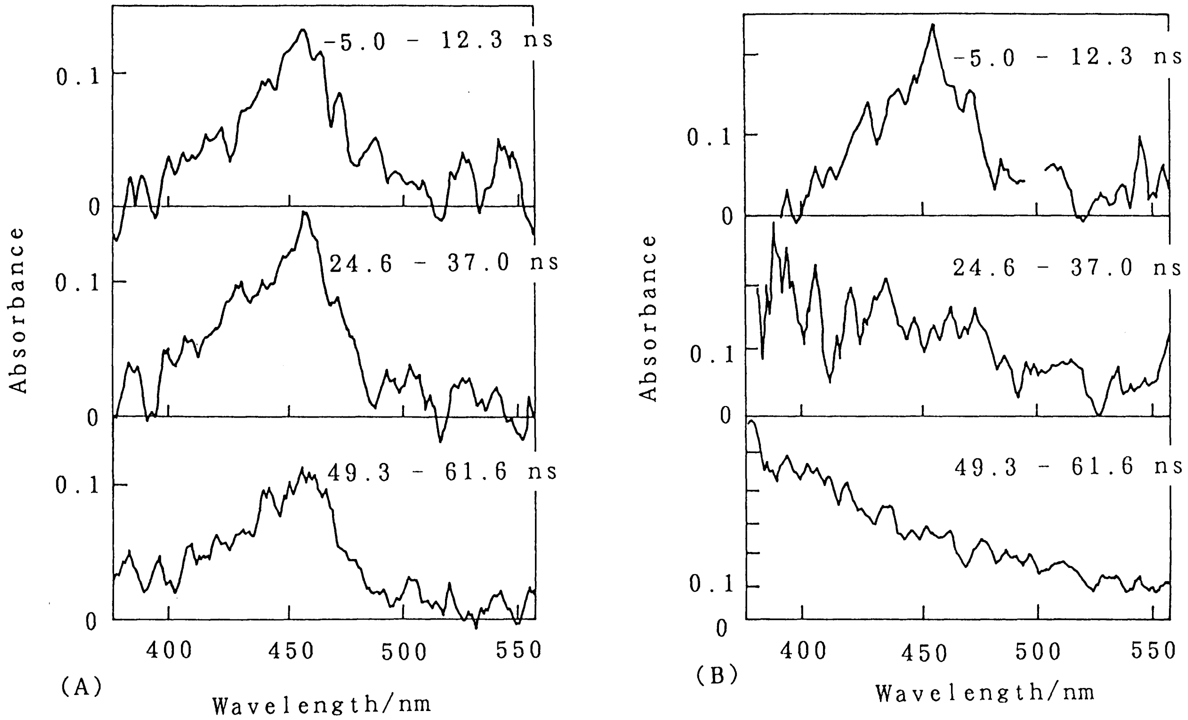

Fig.1. Time-resolved absorption spectra of PMMA film doped with p-terphenyl. Laser intensity is (A) 90 mJ/cm^2 and (B) 360 mJ/cm^2.

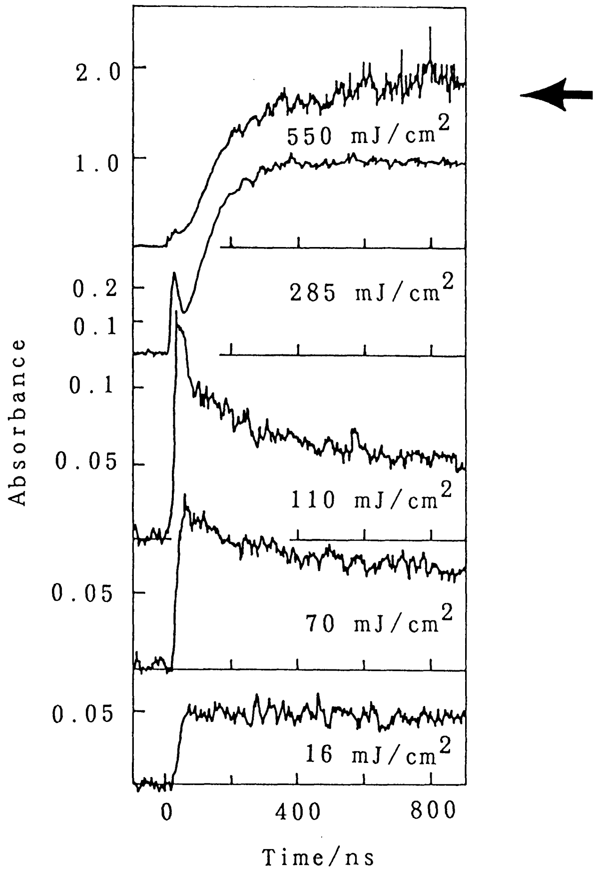

Fig.2. Absorption rise and decay curves at 455 nm of PMMA film doped with p-terphenyl. Laser intensity is given in the figure.

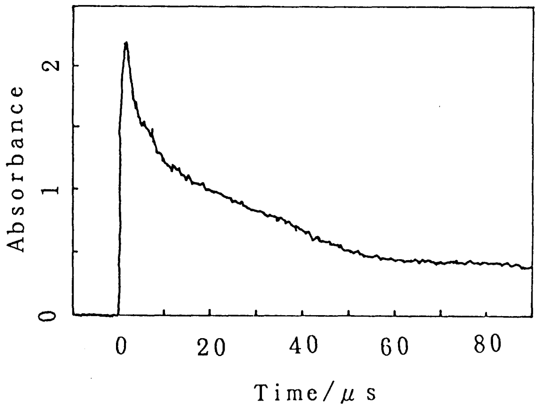

Fig.3. Absorption decay curve at 455 nm of PMMA film doped with p-terphenyl. Laser intensity is 530 mJ/cm^2.

some common optical phenomena.

Absorption rise and decay curves at 455 nm (the maximum wavelength of the triplet p-terphenyl) were shown in Fig.2. At 16 mJ/cm^2 excitation, no appreciable decay was observed in the sub-μs, while a fast decay component was superimposed as the excitation intensity was increased. This behavior was greatly changed when the excitation intensity was increased to be larger than its ablation threshold. The triplet absorption decayed rapidly, and this was followed by a slow and intense absorption rise. The latter rise component was also observed for the neat film.

We consider that the flat band can be ascribed to a scattering of monitoring light by fragmented particles which are ejected from the film. The idea that the band is due to dissociated intermediates decomposed from PMMA is rejected, because the absorption band was observed only upon ablation. Refractive index change of the film is not responsible to the present result, since its change should be induced even below the threshold. The scattering was strongest at a few μs after excitation, and showed a slow decay up to 100μs as in Fig. 3. It may correspond to a disappearance of fragmented particles.

Thus, dynamic and molecular aspects of laser ablation have been elucidated by transient absorption spectroscopy for the first time. Since no other transient besides the excited singlet and triplet states of p-terphenyl was observed in the doped PMMA systems, absorbed laser energy should be transferred to PMMA as a thermal one via S_1-S_1 and T_1-T_1 annihilation processes. Fragment ejection reaches the maximum in sub-μs, and the ablation is completed in sub-ms. To confirm that the present behavior is common to various films doped with aromatic molecules, a systematic study on laser ablation of doped polymer film is in progress.

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