

PHOTOPRIMARY PROCESSES AND NANOMETER-NANOSECOND MORPHOLOGICAL DYNAMICS OF POLYMER FILMS STUDIED BY PUMP AND PROBE MEASUREMENT

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Abstract – Intense excimer laser irradiation of polymer films results in expansion and the following contraction, recovering the initial flat surface. The morphological dynamics is measured directly by nanosecond time-resolved interferometry for polystyrene (PS), polyurethane, and polyimide films. The expansion proceeds with a speed of a few nm/ns, while the contraction depends upon the polymer; very slow contraction for PS, rapid 2 component shrinking for polyurethane, and rapid monotonous decay for polyimide. These characteristic behaviors are considered from viewpoints of interpenetrating structures of polymers, glass-rubber phase transition, thermal diffusion, and photothermal mechanism.

INTRODUCTION

Photophysics and photochemistry of molecular systems excited by an intense excimer laser irradiation has received much attention, as many unique dynamic behaviors are expected. High density excited states are formed, undergoing efficient mutual annihilation, and multiphoton ionization is frequently induced. Eventually these processes result in temperature elevation, where photothermal mechanism is an interesting subject to be clarified. In the case of excimer laser irradiation of molecular materials, the excited area shows decomposition, melting, vaporization, fragmentation, and ejection of debris. This is called laser ablation/etching, which is an important process as one of modern fabrication techniques. As a fundamental study it is extremely important and interesting to reveal how densely absorbed energy is converted to heat and brings about morphological changes. From this viewpoint we have conducted systematic studies by applying fluorescence spectroscopy,¹⁻⁴ transient absorption spectroscopy,²⁻⁸ nanosecond shadowgraphy,^{2,3,5,6,9,10} time-resolved interferometry¹¹⁻¹⁷ in addition to conventional etching profile and photoacoustic measurements, and SEM observation.

In our studies examined polymers are classified into two groups. One is for neat polymers which undergo decomposition upon excimer laser irradiation. A triazenopolymer shows sudden decomposition from its excited state during excimer laser excitation, leaving no debris on the etched surface.¹¹ At the present stage of investigation it is considered that the polymer film is a representative example showing

photochemical ablation mechanism. A nitrocellulose film undergoes exothermal degradation triggered by excimer laser and its decomposition rate was obtained to be ~ 1 nm/ns.¹² Their ablation dynamics was discussed in relation to combustion, detonation, and shock wave propagation.^{11,12,18,19}

The other group consists of conventional polymers such as poly(methyl methacrylate) (abbreviated as PMMA) and polystyrene (abbreviated as PS) films doped with aromatic molecules.^{3,4,8,20,21} As photophysical and photochemical processes of dopants are well known, studies on these systems are expected to clarify primary processes in laser ablation by spectroscopic methods. It is necessary and important to identify the excited states and transient chemical species which are responsible to laser ablation. We have shown that no new transient species are formed besides excited states and radicals. Thus, we have proposed a laser ablation mechanism where transient states and species similar to those under weak excitation operate as efficient photothermal energy converters.²² This is called cyclic multiphotonic absorption mechanism which is now being recognized in the relevant research fields.

During these studies, we have found that some polymer films undergo transient expansion and contraction even when laser fluence is below ablation threshold and that the polymer surface comes back to the original position without permanent changes.¹³⁻¹⁵ This is a novel phenomenon which has never been reported before our studies. The transient photothermal morphological dynamics is now considered to be a quite general behavior upon intense pulse excitation and needs systematic study. In the present work, neat PS, polyurethane, and polyimide films without dopant molecules are chosen, and their expansion and contraction behaviors are measured directly by time-resolved interferometry. It is noticeable that for all the films nm morphological dynamics takes place in the ns time domains, and the results

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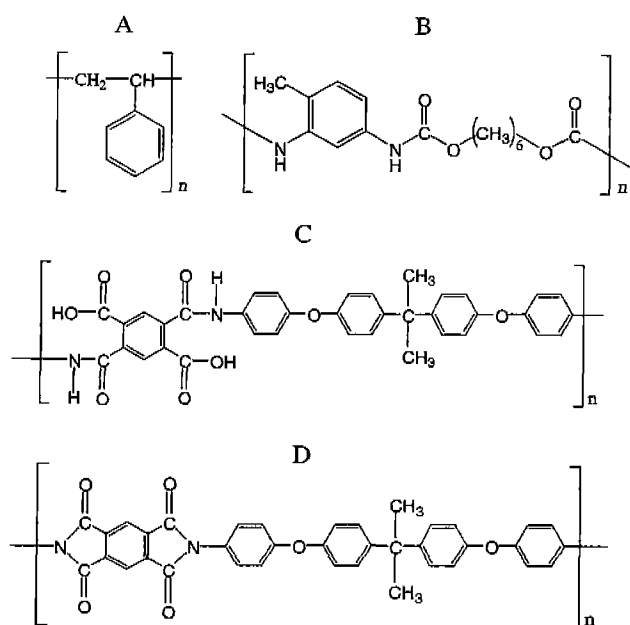
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are discussed in terms of photothermal conversion mechanism.

MATERIALS AND METHODS

Two types of PS (Fluka) whose molecular weights were 3.0×10^3 and 1.0×10^6 were dissolved into chlorobenzene (Wako Pure Chemicals, 99.0 % purity) and their concentration was adjusted to 22 wt% and 5 wt%, respectively. After spin-coating them on quartz substrates, PS films of 3.0×10^3 and 1.0×10^6 molecular weights were dried at room temperature for 8 h and at 358 K for 10 h under vacuum, respectively. The film thickness of the lower molecular weight was about $1.8 \mu\text{m}$ and that of the higher molecular weight was about $2.1 \mu\text{m}$. Their absorption coefficients were 0.32 and $0.31 \mu\text{m}^{-1}$ at 248 nm, respectively.

Polyurethane supplied by Drs. N. Hayashi and K. Suzuki (Hitachi Ltd., Electron Tube Devices Division) and phenol resin as a binder was dissolved in chlorobenzene, whose polymer concentration was adjusted to be 15 wt%. The film was prepared by spin-coating and dried for 2 h at 373 K under vac-



Scheme 1. Chemical Structure of polymers. A; PS, B; polyurethane, C; a precursor of polyimide, D; polyimide. C changes to D by heating at 523K for 1 h.

uum. The film thickness was about $1 \mu\text{m}$, and its absorption coefficient at 248 nm was estimated to be $12.2 \mu\text{m}^{-1}$.

Polyimide film was prepared by spin-coating from a N-methyl-2-pyrrolidone solution of the precursor polymer (Nissan Chemical Ltd.). For inducing polymerization the film was heated for 1 h at 523 K. The film thickness obtained was about $1.5 \mu\text{m}$. Absorption coefficient of the film is $3.72 \mu\text{m}^{-1}$ at 248 nm. Chemical structures of polymers used here are summarized in Scheme 1.

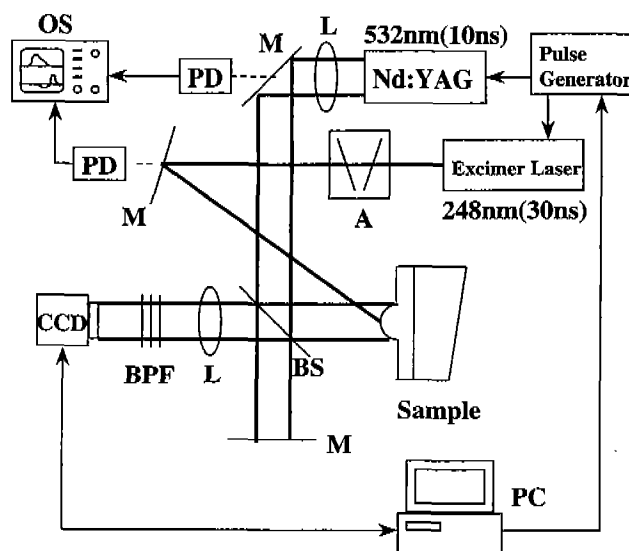


Figure 1. Time-resolved interferometry system to examine the expansion and/or contraction of sample films. A 248 nm excimer laser pulse (30 ns FWHM) as an excitation light and a 532 nm pulse (10 ns FWHM) as a probe light are incident on a sample film. Abbreviations are PD, photodiode, OS: oscilloscope, BS: beam splitter, PG: pulse generator; A: attenuator, L: lens, M: mirror, BPF: band pass filter.

The time-resolved interferometry system is schematically shown in Fig. 1. A 248 nm pulse (~ 30 ns FWHM) from excimer laser (Lambda Physik, LEXTRA 200) was used as an excitation light source, while the second harmonic pulse (532 nm, 10 ns FWHM) of a Q-switched Nd³⁺:YAG laser (Continuum, Sure-lite I) was used as a probe light for the Michelson-Type interferometer. The central area of the latter pulse where the homogeneous intensity is available was used after enlarging the beam diameter by 4 with lenses of $f = 30$ mm and $f = 120$ mm. Time-resolved measurement was carried out by controlling a delay time (Δt) between excitation and probe laser pulses with a digital delay/pulse generator (Stanford Research System, DG535). The delay time was monitored shot by shot by a digital oscilloscope, and $\Delta t = 0$ is defined to be the time when two pulse peaks coincide with each other. Interference fringe patterns were acquired by a CCD camera before which a band pass filter (Toshiba, G54, central wavelength 540 nm) was set to remove

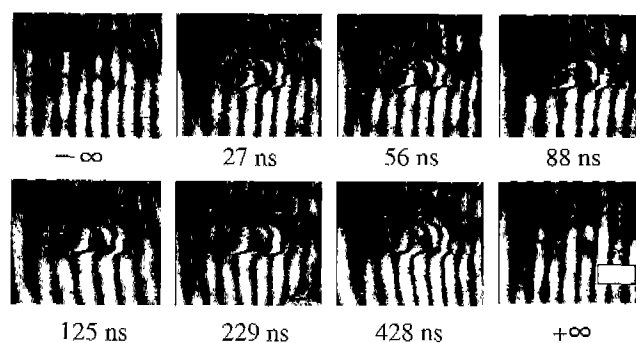


Figure 2. Time-resolved interferometric images of PS film of 3.0×10^3 molecular weight at the fluence of $270 \text{ mJ}/\text{cm}^2$. Here fringe shift to right means expansion. White bar equals to 2 mm.

emission from the films. All data were obtained by one-shot measurement to avoid effects due to excitation of photoproducts formed by the previous irradiation. In the experiment a movement of the fringe to the one side represents an expansion of polymer film, which was confirmed by adjusting the optical condition. A shift of one fringe spacing corresponds to 266 nm expansion, a half-wavelength of the probe pulse. Some representative interference patterns of PS film on the quartz substrate are shown in Fig. 2. Deformation of fringe pattern can be recognized in the central area, although laser fluence is rather low. It is clearly seen that the initial shift showing expansion is followed by coming back to the original position.

Surface morphology was observed with a depth profiler (Sloan Technology, Dektak³) and AFM (Digital Instruments, Nanoscope IIIa).

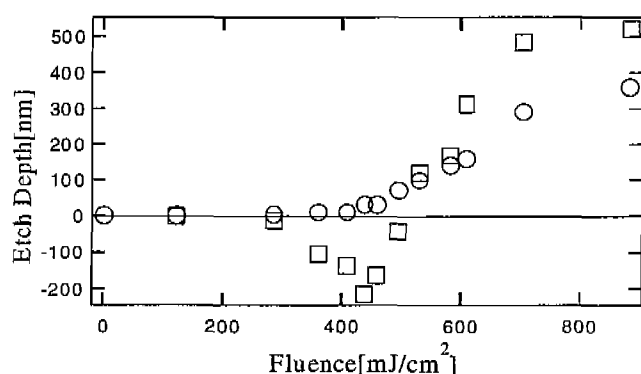


Figure 3. Fluence dependence of laser etching and swelling of PS film. Circle and square show molecular weight of 1.0×10^6 and 3.0×10^3 PS, respectively.

RESULTS AND DISCUSSION

Ablation threshold of PS film. Etch depth obtained by one shot excitation is plotted against laser fluence in Fig. 3, where high and low molecular weight polymers were examined. It is noticeable that a film of the low molecular weight PS shows at first permanent expansion and then etching by increasing laser fluence. Swelling and ablation thresholds above which protuberance and etching are confirmed by a surface depth profiler, were determined to be about 300 and 500 mJ/cm^2 , respectively. On the other hand, a conventional etching behavior was observed for the high molecular weight PS; nothing was detected below ablation threshold of 420 mJ/cm^2 , while clean etching above the threshold. As absorbance at the excitation wavelength, film thickness, and refractive index are considered to be similar between two PS films, the interesting difference of etching behavior between them may be ascribed to characteristic interpenetration structures of polymer chains.

Upon excitation polymer chains undergo rigorous motion, and interpenetrating polymer chains are stressed and pulled from each other. Before chemical decomposition is involved, slip movements between chains are induced, leading to

expansion. When the sample film is contracted in ms~s time domains, original interpenetrating structures should be recovered in the case of the high molecular weight polymer. Namely, many polymer chains are caught by each other at many crossing points, so that permanent shift from the initial interpenetration structure should be difficult. Higher laser fluence leads to higher local energy and consequently more rigorous motion, and eventually chemical bond cleavage may be brought about, leading to ablation. The low molecular weight polymer can undergo mutual slipping of chains before bond scissions are induced, as its polymer chain is shorter by 3 orders of magnitude. The discussion may be related to free volume distribution, and more systematic study on molecular weight dependence is necessary and now being conducted in our laboratory.

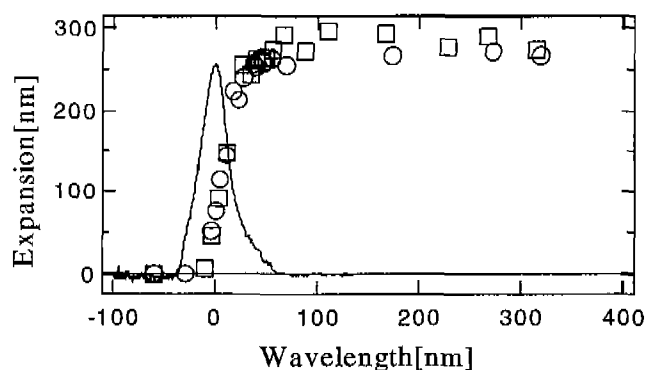


Figure 4. Expansion dynamics of PS film. Circle and square show molecular weight of 1.0×10^6 and 3.0×10^3 , respectively. Solid line shows the excimer laser pulse.

Expansion dynamics of PS film. By analyzing the fringe patterns in Fig. 2, we can estimate the surface displacement as a function of delay time, which is shown in Fig. 4. The surface expands during irradiation and reaches a plateau value when the laser excitation ends. The expansion of 270 nm (about 13~15 % of the original thickness) is attained in a few tens ns. It is interesting that laser induced expansion proceeds with a rate of a few nm/ns.

No additional energy is injected into film after the excimer pulse ends, so that further expansion stops but the rapid decay was not observed in a few hundreds ns time region. Thermal dissipation in PS film is not fast, which is similar to doped PMMA film where contraction takes place in ms on a quartz plate.¹³ It was considered that contraction time is determined by thermal energy transport to the substrate.

One of the different physical properties between these two PS films is glass-rubber transition temperature (T_g). According to the literature,²³ high and low molecular weight polymers have T_g of 373 K and 340 K, respectively. Upon 270 mJ/cm^2 irradiation, it is calculated that temperature elevation is 50 K by using the following equation,²⁴ $T = T_0 + F \alpha / \gamma C$, where T is a film temperature, T_0 is a room temperature (293 K), F is a fluence (270 mJ/cm^2), α is an absorption coefficient, γ and C are density and specific heat whose

values are 1.06 g/cm^3 and 1.25 J/gK , respectively, for both PS films. Here, it is assumed that Lambert-Beer equation holds even for high intensity excitation and absorbed energy is entirely converted into heat. Furthermore, the present film thickness is shorter than α^{-1} , so that α^{-1} is replaced here by the film thickness. Therefore, phase transition from glass to rubber might be induced for the low molecular weight polymer. However, no clear difference was observed in the expansion amplitude and curve. In the case of doped PMMA films it was demonstrated that the transition takes 10–20 ns and expansion coefficient of the rubber is larger than that of the glass.^{13,14} Also the expansion just as glass or rubber is enough fast and expansion coincides with a time-integrated function of the excimer laser pulse. When the fluence was increased a little above 270 mJ/cm^2 , permanent swelling was observed. Thus we consider that the phase transition is not involved in a PS film of 3×10^3 molecular weight. The transition should be closely related to the permanent swelling; once the rubber state is realized, recovery to the original surface position is not attained.

Expansion dynamics of polyurethane film. Etch profile measurements gives 40 mJ/cm^2 as laser ablation threshold, and no permanent swelling was observed by changing the

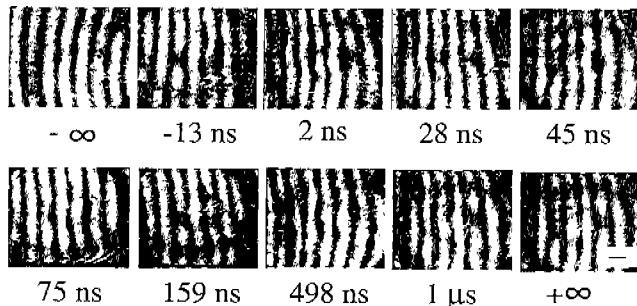


Figure 5. Time-resolved interferometric images of polyurethane film at the fluence of 20 mJ/cm^2 . Fringe shift to left side means expansion. The flatness of the original surface is worse compared to PS film, so that the interference image shows position dependent pattern. Note that transient expansion and contraction are analyzed by comparing the same area before and after excimer laser irradiation. White bar equals to 1 μm .

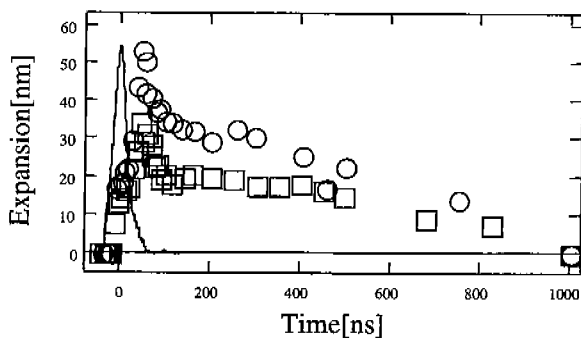


Figure 6. Expansion and contraction dynamics of polyurethane film below the ablation threshold. Circle and square show fluence of 20 mJ/cm^2 and 12 mJ/cm^2 , respectively. Solid line shows excimer laser pulse.

laser fluence. Above the threshold the film undergoes efficient and rapid etching. Here expansion behavior is examined at the laser fluence of 20 mJ/cm^2 , and a series of time-resolved fringe patterns are shown in Fig. 5. Absolute displacement in the fringe pattern is small, but we can say that the maximum shift was attained at 45 ns and then followed by quick contraction. It is worth noting that a back shift to original fringe was attained at 1 μs . In Fig. 6, the expansion and contraction dynamics at 12 and 20 mJ/cm^2 is shown. Indeed the film starts to expand during the laser pulse and reaches the maximum displacement at 45 ns. Then contraction starts, while it consists of two processes with time constants of a few tens ns and a few hundreds ns. Such fast contraction was not observed for the above PS film of the high and low molecular weights and doped PMMA film,¹³ so that this should be characteristic point.

AFM observation of polyurethane film surface. Analysis of expansion and contraction behavior is based on time-resolved interferometry, while permanent etching or swelling is confirmed by using a depth profiler. The latter height resolution is worse than the former, and the lateral resolution

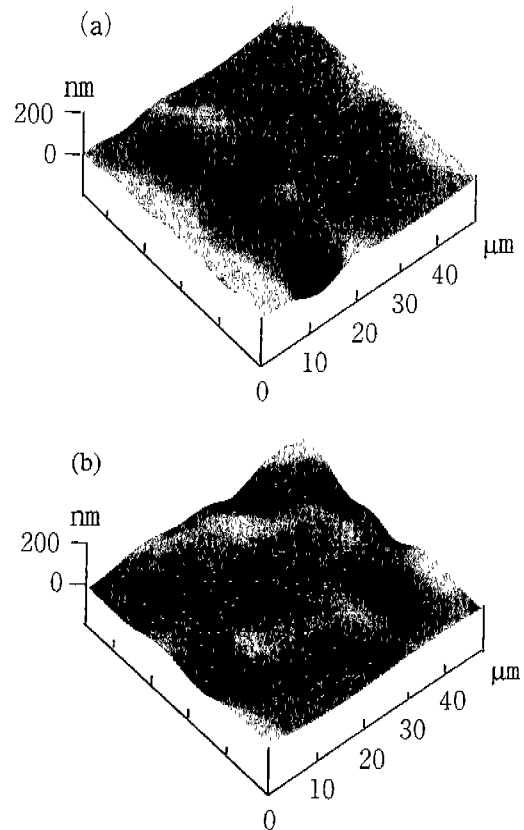


Figure 7. AFM images of the polyurethane films. (a) and (b) images are taken before and after irradiation, respectively. There is no noticeable difference between them.

concerning the flatness is not high. Furthermore, no information about fine structures such as small holes, protrusives, and lines is available. Small gas molecules formed by decomposition may be ejected,^{25,26} which suggests formation of hole

or bit. Furthermore we have recently reported that surface roughness with order of a few tens nm is produced by fs irradiation of amorphous organic films (Y. Hosokawa, unpublished) and neat liquids¹⁹ by using time-resolved surface light scattering imaging. Here we observe surface morphology of the polyurethane film by AFM before and after irradiation, which is given in Fig. 7. Even before the excitation the surface has a small slope over a few tens μm range, but fine structures of protrusive or hole are not observed. After one shot irradiation of 20 mJ/cm^2 , under whose condition Figs. 5 and 6 are obtained, AFM image was not modified so much. We cannot find any clear difference of surface morphology between before and after irradiation, hence it is considered that the surface is recovered well after expansion and contraction.

Expansion and contraction dynamics of polyimide film. The film, whose surface is originally flat within 20 nm, was irradiated, and depth profile measurement was done by changing laser fluence. No permanent swelling was confirmed, and the ablation threshold was estimated between 20–30

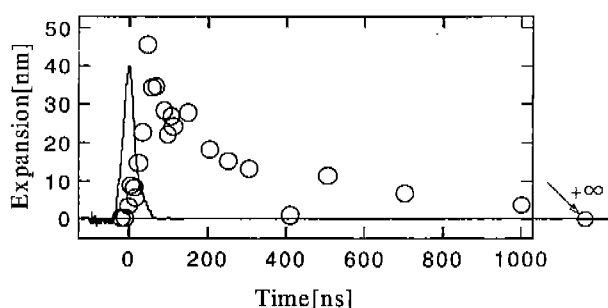


Figure 8. Transient expansion dynamics of polyimide film. Solid line shows an excimer laser pulse.

mJ/cm^2 . In the case of 20 mJ/cm^2 excitation, expansion starts around 0 ns and reaches the maximum value at 40 ns as shown in Fig. 8. The contraction follows monotonously the expansion and its time constant is about 200 ns, while expansion is a little left at 1 μs . The initial surface position is completely recovered at a few s after excitation.

Comparison of nanometer-nanosecond morphological dynamics of neat films. The present three polymer films show characteristic expansion and the following contraction processes: rapid expansion followed by very slow contraction for PS, rapid expansion followed by fast 2 component shrinking for polyurethane, and rapid expansion with a monotonous, fast decay for polyimide. One possible interpretation will be that the behaviors are due to different decomposition mechanisms; photothermal and photochemical. We have already studied laser ablation mechanism of PS film and concluded that rapid photothermal heating is most probable.²⁷ Thus, polyurethane and polyimide films are possibly ablated by photochemical mechanism, but we consider this is not true. Once photochemical processes are involved, complete recovery of the flat surface is difficult, as photochemical reaction is irreversible. More detailed examinations are necessary for concluding the mechanism, which pho-

tothermal heating is probable.

Second interpretation is concerned with the thickness of the excited surface layer. Although the film thickness is about 1–2 μm , the excited layer is quite different for three films as absorption coefficient at 248 nm is scattered. In the case of PS film of the high molecular weight, about 48 % of 270 mJ/cm^2 fluence is absorbed by 2.1 μm film and the film is excited as a whole. Then the whole film undergoes expansion, giving large expansion amplitude of 270 nm. This corresponds to 15 and 12 % of the thickness for the low and high molecular weight polymers, respectively. The surface layer of about 80 nm and 270 nm of polyurethane and polyimide films are excited and shows 50 and 40 nm transient maximum expansion at 20 mJ/cm^2 , respectively. In the case of polyimide film the expansion is about 15 %, while it is surprising that 60 % thickness expansion is induced for polyurethane film. It is considered that the latter large expansion results in large constrain and mechanical recovering becomes different from those of PS and polyimide films.

The third interpretation is based on heat transport time. As the thickness of the excited layer changes from film to film, the contraction dynamics which is of course due to cooling depends on the thickness. PS film is heated almost homogeneously, so that thermal dissipation is determined by heat transfer to quartz substrate. This needs ms, which is consistent with the present results as mentioned above. In the case of polyurethane film only 80 nm is excited, so that the thermal transport over $\sim 100 \text{ nm}$ may give fast, non exponential decay. For polyimide film the penetration depth is not so thin as polyurethane, but still small compared to the whole thickness, which may be responsible to the contraction behavior different from PS.

At the present stage of investigation we do not know which interpretation is probable. Separately we are studying polyurethane and polyimide films more systematically by changing the laser fluence widely.

Photothermal mechanism. In the present work expansion and contraction dynamics of three polymer films are considered to be due to rapid heating effect by excimer laser irradiation. How absorbed energy is rapidly converted to heat, leading to temperature elevation, depends upon photophysical processes of polymers. It is difficult to say definitely in general, but high density excitation of thin surface layer may induce mutual interaction between excited states such as S_1 - S_1 annihilation, leading to local heating. Also it is considered in general that multiphoton ionization should be induced, and geminate and homogeneous recombinations emit excess energy as heat. As the excimer laser has a pulse width of about 30 ns, even one chromophore whose fluorescence lifetime is a few ns can absorb several photons,^{20,21} which means the film can absorb photons more than the number of the chromophore. This is sequential photon absorption which may be responsible to efficient rapid photothermal heating.

The other mechanism we have proposed for polymers doped with aromatic molecules is cyclic multiphotonic absorption, where excited states and transient species have

important roles. At early stage of the excimer laser pulse, those states and species are formed enough densely and absorb excitation photons competitively with the ground state chromophores. Usually the higher excited states and excited state of transient species like cation, anion, and neutral radicals have very short lifetime, so that the original excited state and transient species are recovered in a few ps. This timescale is far short compared to the excitation pulse width, namely, these states and species are never depleted. On the other hand the ground state is brought up to the excited state and its recovering time is usually ns. Therefore, excited states and transient species work as very efficient photon-to-heat energy converters, and it is reasonable to consider that this cyclic multiphotonic absorption is the origin of the present transient expansion and contraction behavior. The cyclic multiphotonic absorption mechanism was supported by fluorescence, and transient absorption spectroscopy,²⁸ and time-of flight mass spectrometry,²⁹ which was proved for PMMA and PS films doped with aromatic molecules. The present PS, polyurethane, and polyimide films have not been examined by such spectroscopic methods, but we consider that cyclic multiphotonic absorption process is responsible to the present morphological dynamics.

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