

# Laser-Induced Nanometer–Nanosecond Expansion and Contraction Dynamics of Poly(methyl methacrylate) Film Studied by Time-Resolved Interferometry

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Received: July 18, 2000; In Final Form: December 5, 2000

The expansion and contraction behavior of a neat poly(methyl methacrylate) film is induced by 248 nm excimer laser excitation and directly measured by nanosecond interferometry. Above the ablation threshold (1400 mJ/cm<sup>2</sup>), the film expands during the excitation laser pulse, and after 25% expansion of the thickness, it undergoes fragmentation. Below the threshold, the expansion rate is still high (a few nm/ns), and permanent swelling is observed after transient expansion and succeeding contraction. By decreasing the laser fluence below 800 mJ/cm<sup>2</sup>, permanent swelling was not observed, and at a few tens of mJ/cm<sup>2</sup>, novel oscillatory expansion and contraction behavior was successfully detected. The expansion amplitude as a function of laser fluence indicates that the polymer film undergoes phase transition from glass to rubber upon excitation with a fluence higher than 450 mJ/cm<sup>2</sup>. In the glass state, the interpenetrating structure of the polymer film and associated free volume distribution may be changed upon irradiation, and photochemical degradation should be involved. A dynamic view of these polymer properties explains well the unique expansion and contraction behavior. Furthermore, these laser-induced morphological changes are compared with those of polymer films doped with aromatic molecules and considered in general.

## Introduction

Studies on intense pulsed laser excitation of organic materials are now recognized to be indispensable for developing micro-fabrication techniques and receive much attention as an interesting interdisciplinary research.<sup>1–4</sup> In nanosecond excimer laser irradiation experiments, high-density excited states are formed in the surface layer of materials,<sup>5–9</sup> leading to efficient annihilation between excited states,<sup>7,8</sup> multiphoton ionization,<sup>9</sup> and cyclic multiphotonic absorption.<sup>10</sup> Photothermal conversion takes place very efficiently, so laser-induced thermal processes are observed in general.<sup>6,8,10,11</sup> All the processes are considered to be nonlinear photophysical and photochemical behavior and lead to morphological changes such as expansion, melting, etching, and so on.<sup>12–20</sup> Laser ablation is a representative laser-induced dynamics of polymer films and has been studied in detail since Namba et al.<sup>12</sup> and Srinivasan et al.<sup>13–15</sup> reported it in 1981. We have focused our attention to clarify photoprocesses in laser ablation and related phenomena by applying fluorescence spectroscopy,<sup>5–9</sup> transient absorption spectroscopy,<sup>6,21–25</sup> nanosecond shadowgraphy,<sup>26–29</sup> time-resolved interferometry,<sup>17–20</sup> and so on.

In our systematic studies the polymers examined are classified into two groups, where mechanistic viewpoints of photophysical and/or photochemical processes are emphasized. One is neat polymer which itself decomposes upon laser irradiation. A triazenopolymer film undergoes sudden ablation without leaving any detectable debris, which was discussed as a representative photodecomposition reaction.<sup>19</sup> The ablation occurs only during the excitation laser pulse. A nitrocellulose film shows thermal

degradation, and its ablation continues a few hundreds of nanoseconds after excimer laser irradiation.<sup>20</sup> The dynamics was considered in relation to combustion, detonation, and shock wave propagation. Now the spectroscopic and interferometric studies are being extended to more photochemically interesting and practically important polymeric materials such as polyimides and polyurethanes.

The second class of polymer films consists of poly(methyl methacrylate) (PMMA) and polystyrene films doped with aromatic molecules whose photophysical properties are well-known. We have planned and conducted studies on these films for clarifying primary processes in laser ablation by spectroscopic methods.<sup>6,8,10</sup> It is necessary and important to identify the excited states and transient chemical species which are responsible for laser ablation and to understand how photoprocesses evolve to induce morphological changes. We have confirmed that the laser ablation mechanism of the doped polymer films is photothermal and proposed a cyclic multiphotonic absorption process.<sup>10</sup> The excited states and transient radical species of doped aromatic molecules, formed at the early stage of the excimer laser pulse, absorb excitation photons during the laser pulse, competing with absorption by the ground state. The key point to understand the cyclic multiphotonic absorption is that the higher excited states of aromatic molecules and the excited states of radicals have very short lifetimes compared to the decay times of the lowest excited states and ground-state radicals.<sup>30</sup> The respective relaxations to the lowest excited states and the radicals are quite rapid, so they can absorb the photons repeatedly during the excimer laser pulse, leading to local heating of the polymer. This is quite efficient compared to normal heating by relaxation from the lowest excited state to the ground state. The energy dissipation process is rather slow and the transient temperature elevation is attained, so polymer films undergo thermal decomposition and eventually result in laser ablation.

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The photothermal ablation suggests that transient expansion should be induced before laser ablation takes place, and indeed this expectation was confirmed directly for the above doped polymer films by our time-resolved interferometric measurement.<sup>17–20</sup> Most of the polymers show transient expansion just before ablation, and under the ablation threshold the expansion and the following slow contraction were observed. The time-resolved interferometric analysis is now being recognized as a useful approach to understand the morphological dynamics of polymer films.

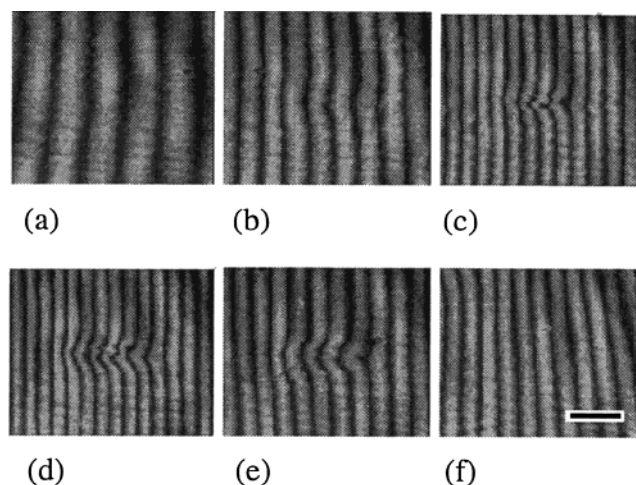
To establish the laser-induced expansion and contraction dynamics as a general process, neat film is chosen as an example in the present work, which has never been examined. The expansion and contraction behavior of a neat PMMA film upon excimer laser irradiation has been measured as a function of the laser fluence directly by time-resolved interferometry. Above the ablation threshold, the neat film expands during the excitation laser pulse, and after 25% expansion, it undergoes fragmentation. Below the threshold, the polymer film shows rapid expansion, slow contraction, and sometimes permanent swelling, depending upon the fluence. Interesting oscillatory expansion and contraction behavior was observed for the first time at rather low laser fluence. It is noticeable that the nanometer expansion occurs in the nanosecond time domains. The results are quite new as fundamental morphological processes and discussed in terms of polymer properties, glass–rubber transition, and photothermal processes.

## Experimental Section

**Sample.** PMMA (Kuraray Co. Ltd.) with a weight-averaged molecular weight of 102 600 was used without further purification. Sample films were prepared by spin-coating a 15 wt % chlorobenzene solution of PMMA on wedged quartz substrates. The film was baked for 2 h at 80 °C to remove the residual solvent, giving a film thickness of ca. 2  $\mu\text{m}$ . Its absorbance at 248 nm was 0.015, and no appreciable absorption band of chlorobenzene was detected.

**Ablation Experiment.** A KrF excimer laser (Lambda Physik Lextra 200, 248 nm, 30 ns fwhm) was used as an excitation pulse for inducing expansion/contraction and ablation. The fluence was adjusted with partially transmitting laser mirrors. A central area of the excimer laser pattern with a homogeneous intensity distribution was chosen with an appropriate aperture and then focused onto the sample surface by using a quartz lens ( $f = 200$  mm). Laser fluence was monitored by a joulemeter (Gentec, ED-200) with an oscilloscope (Hewlett-Packard, HP 54522A). A fresh surface of the sample film was set for shot-by-shot excitation in every measurement so the contribution of photoproducts formed by the preceding excitation is not involved. The etch depth was measured by a surface depth profiler (Sloan, Dektak 3), whose measurement scatter was about  $\pm 50$  nm and is written as an error bar in Figure 2.

**Nanosecond Time-Resolved Interferometry.** The nanosecond time-resolved interferometry applied here is the same as reported before.<sup>17</sup> Briefly, the second harmonic of a Q-switched Nd<sup>3+</sup>:YAG laser (Continuum Surelite I, 532 nm, 10 ns fwhm) was used as a probe light source of the Michelson-type interferometer to measure the excimer-laser-induced morphological change of the present film. Interference patterns were acquired by a CCD camera. In the experiment, a shift of one fringe spacing to the left or right corresponds to an expansion or etching of 266 nm, a half-wavelength of the probe laser beam. Time-resolved measurement was carried out by controlling the delay time ( $\Delta t$ ) between excitation and probe laser pulses with



**Figure 1.** Nanosecond time-resolved interferometric images of a PMMA film on a wedged quartz substrate at a fluence of 540 mJ/cm<sup>2</sup> below the ablation threshold ( $\sim 1400$  mJ/cm<sup>2</sup>). All these images are taken at the different areas of one sample film; namely, the fresh surface is always measured by changing the optical configuration for each measurement. In this case, a fringe shift to the left represents an expansion. The delay time after excitation is (a)  $-\infty$  (before irradiation), (b) 29 ns, (c) 71 ns, (e) 5  $\mu\text{s}$ , and (f)  $+\infty$  (at least a few tens of seconds after irradiation). The black bar in (f) indicates 1 mm in the image.

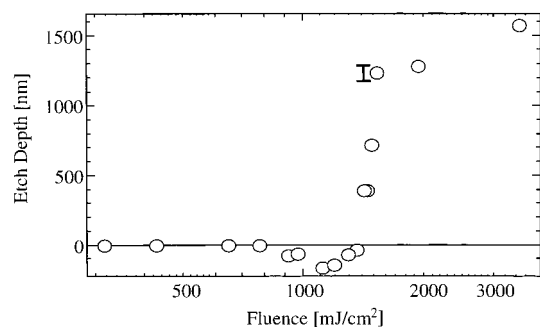
a digital delay/pulse generator (Stanford Research System, DG 535). The delay time was monitored shot-by-shot by a digital oscilloscope. Here we define  $\Delta t = 0$  when the peaks of both laser pulses coincide with each other. All data here were also obtained by one-shot measurement of a fresh surface except in the multiple excitation experiment. The scatter in expansion amplitude, obtained by analyzing the fringe shift, is  $\pm 10\%$  of the amplitude when ablation and swelling are involved (Figures 3 and 4), while it is  $\pm 5\%$  in other cases (Figures 5 and 7). The scatter of  $\pm 10$  nm is the minimum for small expansion (Figures 6, 9, and 10). Marks showing these scatters are included in the corresponding figures.

Some representative interference patterns of the PMMA film on the quartz substrate are shown in Figure 1. Deformation of the fringe pattern can be recognized, which shows transient surface displacement of the PMMA film below the ablation threshold. A fringe shift to the left side is observed and ascribed to an expansion of the film, examining a relation between the shift and optical condition.<sup>17,18</sup>

**Transient Absorbance of the PMMA Film at 248 nm Excitation Wavelength.** The transmittance change of the PMMA film at 248 nm during the excimer laser irradiation was measured similarly to that reported before.<sup>31</sup> The excimer laser light was separated into two beams by a quartz plate, a weak one as a reference beam and another intense one for exciting the polymer film. The reference light and the transmitted light after excitation were measured by two photodiodes. Their signals were monitored shot-by-shot by a digital oscilloscope and compared with each other, and transient absorbance of the PMMA film at 248 nm during the excitation was calculated.

## Results and Discussion

**Etch Depth.** Upon excimer laser irradiation with high fluence, polymer films undergo permanent morphology changes, etching and swelling. The fluence dependence of the morphology change of the PMMA film is given in Figure 2, where no change was observed below 800 mJ/cm<sup>2</sup>, etching was left above 1400 mJ/cm<sup>2</sup>, and permanent swelling was observed between these



**Figure 2.** Etch depth profile of a PMMA film obtained with 248 nm excimer laser irradiation. The negative etch depth observed in the fluence range of 900–1400 mJ/cm<sup>2</sup> means permanent swelling.

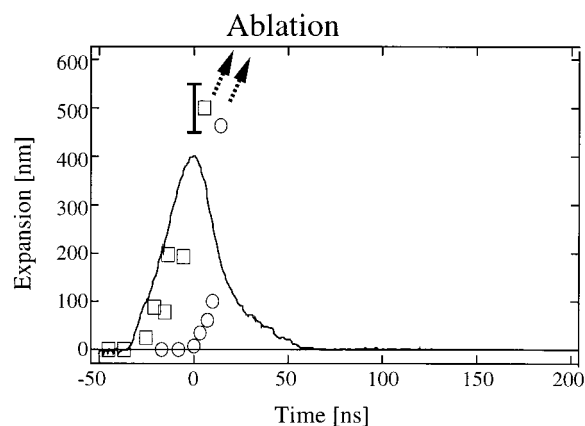
fluences. Therefore, the ablation and the swelling thresholds were determined to be about 1400 and 800 mJ/cm<sup>2</sup>, respectively.

The ablation threshold of PMMA is examined in detail by Sutcliffe and Srinivasan.<sup>32</sup> For 248 nm excitation wavelength, the threshold estimated from a relation between averaged etch depth per pulse and fluence was 0.5 mJ/cm<sup>2</sup>, while it was shown that even five pulses with 1500 mJ/cm<sup>2</sup> are necessary to initiate the etching. It might be considered that contained solvent molecules enhance ablation due to their photothermal rapid evaporation and/or decomposition. The possibility, however, can be examined by measuring absorption spectra of the prepared film. In our case chlorobenzene was used as a solvent, and actually its absorption was detected in the film when the drying was not enough. For the present films it was confirmed that absorption by chlorobenzene is negligible compared to that of PMMA.

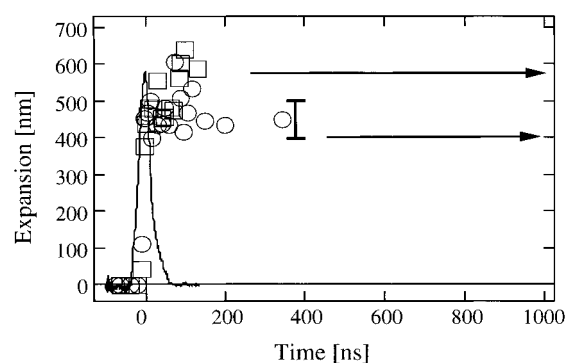
Here rather thin PMMA films with 2  $\mu$ m thickness are applied, while a thick one or a block is usually used. This is one possible reason our threshold is different from the literature values. It is pointed out that the polymer structure of the thin film is in general affected by the interface and surface, which was proved by us by measuring the picosecond fluorescence spectra and dynamics of surface and interface layers under total internal reflection conditions.<sup>33–35</sup> The surface and interface layers with 100 nm thickness in a PMMA film with a thickness of 1–2  $\mu$ m were confirmed to have different structures and properties. Now the thickness dependence of the ablation threshold is being studied for PMMA and polystyrene in our laboratory.

It is worth noting that permanent swelling is clearly observed, as no such behavior was observed for biphenyl- or pyrene-doped PMMA films, which are introduced above. The fluence dependence of the etch profile of the neat PMMA film is classified into three regions, for which we have conducted time-resolved interferometric measurements in detail.

**Expansion Dynamics above the Ablation Threshold.** At fluences of 2000 and 1600 mJ/cm<sup>2</sup>, above the ablation threshold, expansion dynamics induced by the excimer laser irradiation was observed by nanosecond time-resolved interferometry before the fragmentation was initiated. The results are analyzed and summarized in Figure 3. The expansion of several hundreds of nanometers started during the excimer laser pulse, and the starting time became earlier with the higher fluence. It is noticeable that the expansion rate is extremely high (a few tens of nm/ns). We could not get a clear fringe pattern of the interference images of the irradiated area at the stages later than 9 and 25 ns for fluences of 2000 and 1600 mJ/cm<sup>2</sup>, respectively. This is because interference images became dark, which is eventually ascribed to ablated fragments.<sup>17</sup> It is directly con-



**Figure 3.** Expansion dynamics of a PMMA film at fluences of 2000 mJ/cm<sup>2</sup> ( $\square$ ) and 1600 mJ/cm<sup>2</sup> ( $\circ$ ) above the ablation threshold. A solid curve represents an excimer laser pulse. Arrows indicate that the interferometric measurement becomes difficult after those delay times because fragments ejected by ablation scatter the probe light.



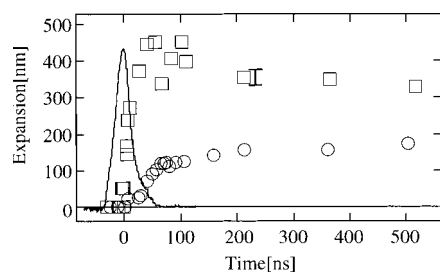
**Figure 4.** Expansion dynamics of a PMMA film at fluences of 1100 mJ/cm<sup>2</sup> ( $\square$ ) and 870 mJ/cm<sup>2</sup> ( $\circ$ ) between the swelling and ablation thresholds. Arrows indicate the time range where the fringe pattern of interference images of the irradiated area cannot be observed by the darkening (see the text). A solid curve represents the excimer laser pulse.

firmed here that ablation is induced during the laser pulse, following rapid transient expansion.

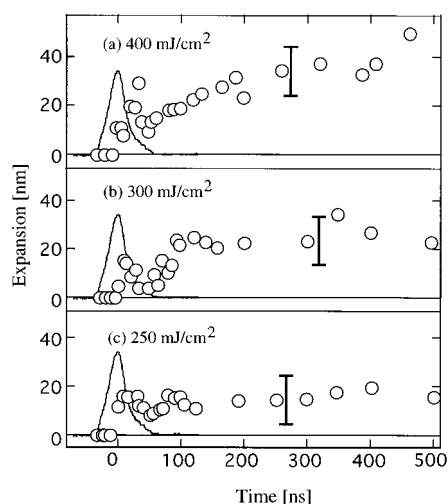
**Expansion and Contraction Dynamics between the Swelling and Ablation Thresholds.** In Figure 4, transient expansion and contraction dynamics is given at fluences of 1100 and 870 mJ/cm<sup>2</sup>, below the ablation threshold. Transient expansion started during the excimer laser irradiation, and its rate is still high (a few nm/ns), which is similar to the behavior above the ablation threshold. At a fluence of 870 mJ/cm<sup>2</sup>, a bump around 100 ns was observed. Then, the film underwent contraction, but the original surface position was not recovered completely. Permanent swelling was left after the transient expansion and contraction, and their amplitudes were 220 and 30 nm at fluences of 1100 and 870 mJ/cm<sup>2</sup>, respectively. The swelling amplitudes by interferometry are just identical to those observed by a depth profiler, which means that our interferometric measurement is precise and reliable.

Though we could measure the fringe pattern of interference images of the area irradiated by the excimer laser during and after excitation, the darkening prevented our observation at the stages later than 130 and 350 ns for fluences of 1100 and 870 mJ/cm<sup>2</sup>, respectively. This may be due to the fact that surface flatness is not maintained during the whole delay time. It is interesting to note that the delay time, when the darkening becomes appreciable, is also dependent on the laser fluence,





**Figure 5.** Expansion and contraction dynamics of a PMMA film at fluences of 700 mJ/cm<sup>2</sup> (□) and 540 mJ/cm<sup>2</sup> (○) below the swelling threshold. A solid curve represents the excimer laser pulse.



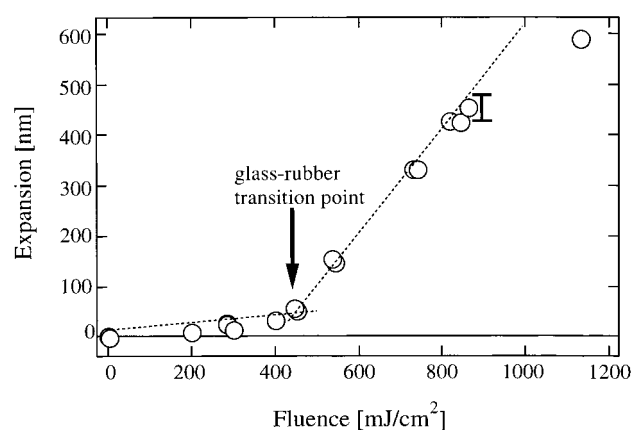
**Figure 6.** Expansion and contraction dynamics of a PMMA film at fluences of (a) 400 mJ/cm<sup>2</sup>, (b) 300 mJ/cm<sup>2</sup>, and (c) 250 mJ/cm<sup>2</sup> below the fluence of 450 mJ/cm<sup>2</sup> at which the glass-rubber transition of PMMA is brought about. A solid curve represents the excimer laser pulse.

and is about 130 and 350 ns for fluences of 1100 and 870 mJ/cm<sup>2</sup>, respectively.

**Expansion and Contraction Dynamics below the Swelling Threshold.** In Figure 5, transient expansion and contraction dynamics was given at fluences of 700 and 540 mJ/cm<sup>2</sup>. The irradiated film began to expand at the late stage of the excimer laser pulse, and the expansion disappeared completely via slow contraction. Namely, the original flat surface was perfectly recovered, and we cannot discriminate the original and recovered surfaces by our interferometry. It is worth noting that transient expansion and rapid contraction gave a bump around ~100 ns at a fluence of 700 mJ/cm<sup>2</sup>, while it was not observed at a fluence of 540 mJ/cm<sup>2</sup>. Such a behavior was never observed in transient expansion and contraction dynamics of a PMMA film doped with an aromatic molecule.<sup>17,18</sup>

Similar interferometric measurements were performed at fluences of 400, 300, and 250 mJ/cm<sup>2</sup> and are summarized in Figure 6. At fluences of 300 and 250 mJ/cm<sup>2</sup>, the film surface showed repetitive expansion and contraction of several tens of nanometers, reached a plateau value, and then recovered to the original flat surface. At a fluence of 400 mJ/cm<sup>2</sup>, the expansion amplitude and the oscillatory period of the film seemed to increase. It is important to point out that expansion and contraction show oscillatory behavior only far below the ablation threshold.

**Possible Expansion Mechanisms.** It is well-known that PMMA decomposes into a monomer, CO<sub>2</sub>, and so on upon excitation, so these gaseous molecules may cause expansion. Concerning ablation of PMMA, Garrison and Srinivasan



**Figure 7.** Fluence dependence of the expansion at 1  $\mu$ s after the excimer laser irradiation of a PMMA film.

reported that gaseous monomer products from PMMA result in a volume increase of 30% under a certain condition,<sup>36</sup> which seems consistent with the present result. Some SEM observations of the ablated polymer surface show that various holes are left,<sup>37,38</sup> which was interpreted as formed gas molecules leak to air, leaving holes. In the present interferometric images, however, the flat surface was completely recovered even when permanent swelling was involved. If a lot of holes are formed by ejection of gaseous molecules upon contraction, clear and bright images should not be observed after the recovery. Thus, we consider that the volume change by gaseous molecules may not have a major role in the present expansion and contraction.

Another possible mechanism is evaporation of solvent chlorobenzene upon excitation. If an appreciable amount of solvent molecules are left in the film, they evaporate and result in a volume increase of the film. Also photodissociation of chlorobenzene to Cl atom and counter radicals may involve formation of gaseous molecules. However, as mentioned above, it is confirmed directly by UV absorption spectral measurements that chlorobenzene absorption is negligible compared to that of PMMA. Hence, we consider that photothermal processes are responsible for the present expansion phenomena.

**Photothermal Mechanism and Glass-Rubber Transition of the PMMA Film.** To understand the nature of the photothermal expansion and contraction behavior of the PMMA film, it is important to correlate the transient dynamics to thermal properties. Here, we measured the fluence dependence of the expansion of the PMMA film at a delay time of 1  $\mu$ s after the bump and oscillatory behaviors were finished. It is clear in Figure 7 that the expansion of the PMMA film consists of two components having different slopes. Around a fluence of 450 mJ/cm<sup>2</sup>, a knick point was observed and the slope increased by a factor of about 8.6. This suggests that the physical and chemical nature attained at a delay time of 1  $\mu$ s is different between two regions. We consider that the area irradiated by the excimer laser was rapidly heated through efficient photothermal conversion processes. This is well consistent with photothermal temperature elevation of the doped PMMA film where nanosecond heating during the pulse was directly confirmed by fluorescence spectral broadening in a few tens of nanoseconds.<sup>6,8</sup> The temperature elevation should result in changes of the physical properties of polymer films, and the temperature of the PMMA film is estimated at a critical fluence of 450 mJ/cm<sup>2</sup>. Assuming that multiphoton absorption and saturation in absorption are excluded and absorbed energy is converted to heat with unit quantum yield, and considering errors in small absorbance at 248 nm, it is concluded that the

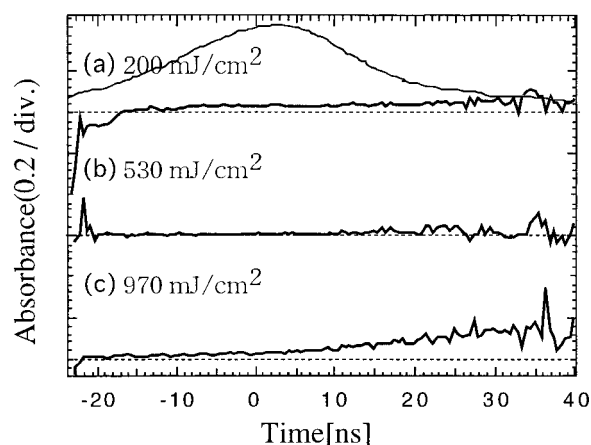
temperature attained at 450 mJ/cm<sup>2</sup> is roughly the same as  $T_g$  of PMMA<sup>39</sup> (378 K). Therefore, it is concluded that the different expansion amplitudes below and above 450 mJ/cm<sup>2</sup> are the resultant behaviors of glass and rubber states of the PMMA film, respectively.

If effective absorbance and photothermal conversion efficiency are independent of the fluence, absorbed energy should be proportional to the latter. Consequently, the slopes can be discussed simply in terms of the thermal expansion coefficient of polymer films. The coefficients of rubber and glass states,  $\alpha_g$  and  $\alpha_r$ , below and above the glass–rubber transition temperature ( $T_g$ ) of PMMA are  $(2.5\text{--}2.7) \times 10^{-4}$  and  $(5.6\text{--}5.8) \times 10^{-4}$  K<sup>-1</sup>, respectively.<sup>39</sup> We consider that the one-dimensional expansion is induced along the perpendicular direction to the film, since the polymer film outside the area irradiated by the excimer laser is still hard. Then, it is assumed that  $(\alpha_r/\alpha_g)^3$  corresponds to the change in the slope below or above the knick point. Indeed,  $(\alpha_r/\alpha_g)^3$  is in agreement with the slope ratio. Not only the thermal expansion coefficient but also the specific heat, elastic modulus, and so on are much influenced by the glass–rubber transition.<sup>40–45</sup> This may raise a difficulty in quantitative analysis, while the present explanation seems quite reasonable.

The present result reminds us that the different expansion behaviors between doped PMMA and poly(methyl acrylate) (PMA) films are explained in relation to the glass–rubber transition.<sup>18</sup> The former and latter films are in glass and rubber states at room temperature, and give smaller and larger expansion coefficients. Also, it was proved that expansion of a pyrene-doped PMMA film in the glass state is faster compared to that involving the glass–rubber transition at a higher fluence.<sup>18</sup> The results were interpreted in terms of phase transition dynamics and efficient photothermal conversion processes of pyrene under high excitation conditions. The present result on the dynamics of a neat PMMA film can be explained also as photothermal expansion and contraction, which shows a new aspect of dynamic morphological properties of polymers.

Assuming that temperature elevation is proportional to absorbed energy, the temperature rise attained around a fluence of 800 mJ/cm<sup>2</sup> is estimated roughly to be 200 K (100 K in the glass state and the following 100 K in the rubber state). The thermal expansion coefficients of glass and rubber PMMA are  $2.6 \times 10^{-4}$  and  $5.7 \times 10^{-4}$  K<sup>-1</sup>, so the expansion amplitude is calculated to be  $(2.6 \times 10^{-4} \times 100 + 5.7 \times 10^{-4} \times 100) \times 2 \times 10^3$  nm = 36 nm. This is too small compared to the observed volume of 400 nm. However, the present expansion is in principle one-dimensional as discussed above, so the temperature difference multiplied by  $2.6 \times 10^{-4}$  K<sup>-1</sup> and that multiplied by  $5.7 \times 10^{-4}$  K<sup>-1</sup> should be cubed. Then, the calculated value comes to on the order of 100 nm, which is not so bad. Additionally, a sudden temperature rise may result in some shock as frequently pointed out by Dlott et al.<sup>21–23</sup> The bump due to some overshooting expansion may be ascribed to this effect. The peak delay time when the bump reaches a maximum shifts to earlier as the fluence is lower. This may be due to the fact that a high fluence greatly involves changes in interpenetrating polymer structures.

**Transient Absorbance of the PMMA Film at 248 nm upon Irradiation.** In the above discussion on the photothermal mechanism, it is assumed that absorbance at 248 nm is constant upon excitation. This sometimes does not hold under high-intensity excitation,<sup>31</sup> which is examined here. Figure 8 shows the transient absorbance of a neat PMMA film at the excitation



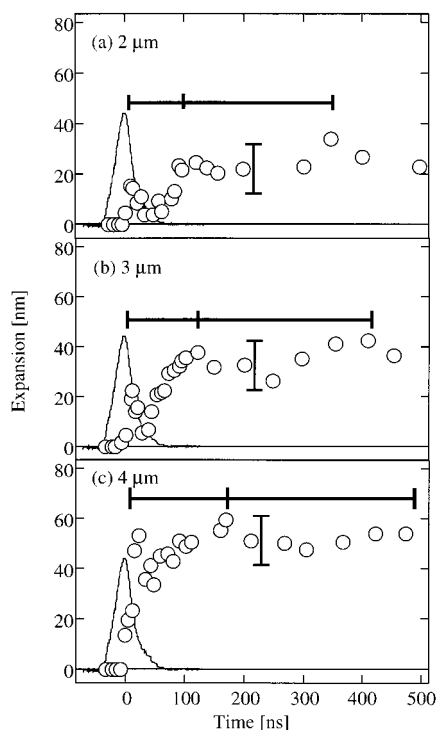
**Figure 8.** Transient absorbance change of a PMA film at 248 nm during 248 nm excimer laser irradiation. The laser fluence is given in the figure. The solid curve in (a) represents the excimer laser pulse.

wavelength itself upon the 248 nm excimer laser irradiation. When the fluence was relatively low (200 and 530 mJ/cm<sup>2</sup>), the absorbance during the excimer laser pulse was confirmed to be almost constant in the present time range. This indicates that light absorption by PMMA is a one-photon process of the ground state, the latter state is not depleted, and excited states do not undergo multiphoton processes at low fluence. Thus, it is reasonable to consider that the temperature elevation of the film estimated by assuming unit quantum yield of photothermal conversion is in proportion to the laser fluence.

On the other hand, the 248 nm absorbance at a fluence of 970 mJ/cm<sup>2</sup> changed from time to time, so a simple relation between the fluence and the temperature does not hold and some nonlinear absorption processes should be involved. Indeed, the expansion at higher fluence in Figure 7 deviates from the linear relation between the expansion value and the fluence. Thus, transient absorbance measurements support well the present interpretation of the fluence dependence of the expansion. Also it is emphasized that the interesting oscillatory expansion and contraction processes of the polymer film are surely due to rapid thermal heating.

**Thickness Dependence of Oscillatory Expansion and Contraction Dynamics of PMMA.** To elucidate the origin of the novel behavior, we have tried to find a new temporal response of the PMMA film. As an example, the thickness dependence of expansion and contraction dynamics was examined at a fluence of 300 mJ/cm<sup>2</sup>. The expansion amplitude and the oscillatory period of the film increased as the thickness of the film did, as shown in Figure 9. As the PMMA film has weak absorbance at 248 nm and is homogeneously excited along the depth, not only the surface layer but also the whole depth is involved in the transient morphological dynamics. It is considered that the film irradiated by the excimer laser elastically oscillates along the perpendicular direction to the film. Thus, a thicker film expands more largely and the oscillation takes a longer time, which seems quite reasonable. It is interesting to note that the second period of the oscillation of the film was much longer than the first. This suggests that the elastic coefficient of PMMA became smaller gradually during the oscillatory expansion and contraction, which may be ascribed to structural relaxation of the polymer chains in the film.

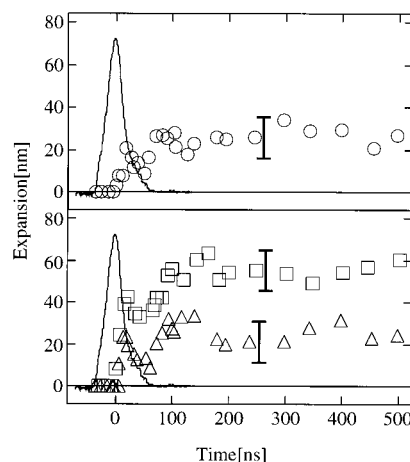
**Absorption Spectra of the PMMA Film after Multiple Excimer Laser Irradiation.** In addition to relaxation of interpenetrating structures of the polymer film, changes in the conformation of polymer chains, and free volume distribution, and so on, photothermal decomposition reactions may be



**Figure 9.** Thickness dependence of the expansion and contraction dynamics of a PMMA film at a fluence of 300 mJ/cm<sup>2</sup>. The thickness of the PMMA film is given in the figure. A solid curve represents an excimer laser pulse.

involved. To confirm this possibility, absorption spectra of the PMMA film were measured after multiple excimer laser irradiation. The absorbance of the film increased at 248 nm, and the absorption around 214 nm was greatly modified, after 10 shots of laser excitation. The absorption at 214 nm can be assigned to the absorption of the carboxyl group of PMMA,<sup>46,47</sup> hence, it is considered that decomposition of the group is induced as an unzipping reaction, leading to the photoproduct at 248 nm. Main chains of PMMA may be cleaved, and radicals are generated inside the film.<sup>48,49</sup> The molecular weight of PMMA becomes smaller, so the elastic coefficient of PMMA decreases gradually as the decomposition of the main chains of PMMA proceeds.

**Expansion and Contraction Dynamics of the PMMA Film by Double-Shot Irradiation.** Similarly the same expansion and contraction dynamics of the PMMA film was not observed upon the second irradiation as shown in Figure 10. Here the second pulse was introduced a few minutes after the first excitation. When the area irradiated by the first excimer laser irradiation of 300 mJ/cm<sup>2</sup> was excited again at the same fluence of 300 mJ/cm<sup>2</sup>, the expansion amplitude and the oscillatory period increased compared to those of the first irradiation. This is consistent with the above explanation that the elastic coefficient of PMMA becomes smaller during and after the excimer laser pulse. Radicals generated inside the film upon the first irradiation, leading to polymer degradation, conformation relaxation, associated free volume redistribution, and so on, should be reflected in the elastic behaviors. Furthermore, an absorbance increase at 248 nm indicates that the second laser pulse is absorbed more efficiently, which also leads to a larger expansion. When the fluence of the second irradiation was turned to 200 mJ/cm<sup>2</sup>, the expansion amplitude of the PMMA film upon the second irradiation was almost the same as that upon the first irradiation of 300 mJ/cm<sup>2</sup>. Extra light absorbance by photoproducts may be suppressed, while the elastic coefficient



**Figure 10.** Expansion and contraction dynamics of a PMMA film by multiple laser irradiation. The areas irradiated by the excimer laser at a fluence of 300 mJ/cm<sup>2</sup> were again excited after a few minutes. Shown are the dynamics upon the second irradiation at 300 mJ/cm<sup>2</sup> (□) and 200 mJ/cm<sup>2</sup> (△) after the first irradiation at 300 mJ/cm<sup>2</sup> (○). A solid curve represents an excimer laser pulse.

of PMMA should be increased. These two effects may compensate each other.

As shown in Figure 10, the first and second periods of the oscillatory expansion upon the first irradiation (300 mJ/cm<sup>2</sup>) were about 100 and 200 ns, respectively. Upon the second irradiation (200 mJ/cm<sup>2</sup>), they were about 150 and 250 ns, respectively. The first period is always shorter than the second one. Furthermore, it is clearly shown that the period of the oscillatory behavior upon the second irradiation is longer than that upon the first one. These results mean that the elastic coefficient of the PMMA film still decreases during the second irradiation.

**Laser-Induced Dynamics and Properties of Polymer Films.** The present experiments on oscillatory expansion and contraction dynamics by changing the excitation fluence, film thickness, and number of excitation shots support a microscopic mechanism that structural relaxation of interpenetrating polymer chains, associated free volume redistribution, and photochemical degradation lead to a smaller elastic coefficient. Double-shot irradiation demonstrates that the film shows a larger expansion amplitude upon the second excitation compared to the first one. The change in chemical and structural properties takes place in a few hundreds of nanoseconds, as the oscillatory expansion shows the repetition period becomes longer.

The change in polymer properties is coupled with the glass–rubber phase transition when the film is excited up to the transition point. At a fluence of 700 mJ/cm<sup>2</sup>, the expansion showed a bump, as in Figure 5. In 50 ns the film expanded by 450 nm, which is an extremely large expansion rate of ~10 nm/ns. This may result in an overshooting and accompany the transition from glass to rubber. At a fluence of 540 mJ/cm<sup>2</sup>, which is a little higher than the glass–rubber transition point, the overshooting is small, a rather mild transition proceeds, and no bump is observed. Only when the fluence is lower than the transition point is an interesting oscillatory behavior observed. In the fluence range the polymer film does not undergo the transition, so the bumping structural change was clearly observed.

It should be pointed out that the bump and oscillatory behavior were not observed for the same PMMA films but for those doped with pyrene and biphenyl.<sup>17–20</sup> We consider that the film layer undergoing expansion and contraction is thin as



doped aromatic molecules have a larger absorption coefficient than neat PMMA. The expansion amplitude was so large compared to the thickness itself that the original structures were lost and the bump should not be clearly detected by the nanosecond interferometry. Therefore, the difference of the laser-induced dynamics between neat and doped PMMA is not important, and the present experimental condition is confirmed to be best to demonstrate the novel behavior.

## Summary

The surface morphological behavior of a neat PMMA film induced by 248 nm excimer laser irradiation above, below, and far below the ablation threshold has been revealed by applying nanosecond time-resolved interferometry. The transient expansion and contraction dynamics of neat PMMA has been made clear for the first time, and its mechanism is considered.

Above the ablation threshold, the irradiated film first underwent rapid expansion during the excimer laser pulse, and then ablation of the film surface was initiated. Below the ablation threshold, expansion of the film started during the excitation laser pulse, and then the film was contracted. However, the original flat surface was not recovered; namely, swelling remained. Far below the ablation threshold, transient expansion and the following contraction were observed, leading to complete recovery of the flat surface. All these are well interpreted in terms of a photothermal process.

Furthermore, below the glass-rubber transition of PMMA, we found the new phenomenon that the film surface showed repetitive expansion and contraction of several tens of nanometers by the excimer laser irradiation, and then the original flat surface was recovered. It is considered that the elastic coefficient of PMMA gradually became small by cleavage of the main chains of PMMA during the expansion. Through the direct experiment of nanosecond time-resolved interferometry, we have revealed for the first time that the excimer laser irradiation of a neat PMMA film induces unique morphological changes.

**Acknowledgment.** We thank the reviewers for their kind and stimulating discussion and comments. The present work was partly supported by a Grant-in-Aid for Scientific Research on Priority Area (B) "Laser Chemistry of Single Nanometer Organic Particles" from the Ministry of Education, Science, Sports, and Culture of Japan (No. 10207204).

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