Macromolecules **1992,** *25,* 1582–1587

Laser Ablation of Doped Polymers: Transient Phenomena as the Ablation Threshold Is Approached[1]

Bradley R. Arnold and J. C. Scaiano*,[2]

Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Canada K1A 0R6

Received June 7, 1991; Revised Manuscript Received November 1, 1991

ABSTRACT: The photochemistry of PMMA films doped with 1,1,3,3-tetraphenylacetone (TPA) has been studied using 266-nm laser excitation at energy doses below and above the ablation threshold. One-, two-, and at least three-photon processes are shown to play a key role in the delivery of energy to the polymer. Transient phenomena involving the formation of ground- and excited-state reaction intermediates lead to instantaneous absorbances during the laser pulse that are very different from those recorded under low-intensity conditions. Surprisingly, the ablation threshold is reached in the polymer samples without any dramatic change in the nature or behavior of the reaction intermediates involved in the decomposition of TPA when compared to those observed in solution, other than an increase in light scattering due to bubble formation and fragment ejection from the polymer surface. The comparison of photoprocesses in polymers with the same reactions in solution allows for a qualitative discussion of the possible mechanism underlying the ablation of doped polymers.

Introduction

The report on photoablation of polymer films by Srinivasan and Leigh[3] has generated interest in areas ranging from high technology to the health sciences. Theoretical models have been proposed to understand the ablation phenomena that may be classified as photochemical or photothermal models,[4,5] depending on the type of phenomena on which they are primarily based. Many of the studies on ablation[4] have focused on the material ejected, or that which is left behind, at photon fluxes well above the limit for ablation while spectroscopic studies under ablative conditions have demonstrated that polymer ablation is frequently accompanied by light emission from small fragments, such as diatomics, in the gas phase.[5–7] There is no doubt that the conversion of a high molecular weight polymer (e.g., polystyrene) into gaseous excited diatomics (e.g., C_2*) must be a multiphoton process. Further, most of the chemical and mechanistic information pertaining to ablation will be lost by the time these small fragments are produced. It is therefore not surprising that little is known about the chemical processes that occur at or just below the ablation threshold.

There are several mechanisms by which a laser pulse can create its own absorption. For example, simultaneous multiphoton absorption into a state not accessible by single-photon excitation may account for the photoablation of polymers that do not have significant absorbance at the wavelengths used. Alternatively, the generation and subsequent excitation of one or more intermediates produced during the laser pulse is also possible at the photon fluxes typically used for photoablation, as will be shown in this study.

Several reports during the last few years have demonstrated that "transparent" polymers could be efficiently ablated by incorporating suitable absorbing dopants.[8–12] In this report we concentrate on the transient phenomena observed upon 266-nm laser excitation of poly(methyl methacrylate) (PMMA) doped with 1,1,3,3-tetraphenylacetone (TPA) or 1,1-diphenylacetone (DPA) using laser intensities that varied from well below to just over the ablation threshold. The selection of these specific dopants was based on the extensive solution studies of excited diphenylmethyl radicals by Meisel[13,14] and ourselves[15–18] that make us confident that we can accurately interpret the one-, two-, and to some extent three-photon phenomena that are expected at the high intensities used for ablation. While some experiments have been carried out under ablative conditions, we have placed emphasis on processes occurring in the preablation regime in the hope that an understanding of the processes that occur below the ablation threshold will ultimately lead to a better understanding of the detailed mechanism of ablation. PMMA is essentially transparent at 266 nm, so that over 95% of the initial absorbance is due to the dopants. The laser flux required to ablate the doped PMMA films is approximately one-tenth as high as that required to ablate films of PMMA alone, leading to the expectation that the ablation phenomenon will be dominated by the dopant's photochemistry.

For the purposes of this study we have defined the ablation threshold as the onset of visible damage to the sample. It will be shown below that light scattering due to the damage of the polymer appears to be a very sensitive measure of this threshold.

Experimental Section

The polymer samples were prepared by dissolving 1.0 g of PMMA (Aldrich medium molecular weight, used as received) and 0.050 g of TPA (prepared as reported previously)[15] in 3.0 g of 2-methoxyethyl ether (Aldrich, used as received) to form a viscous solution. This solution was then spread onto a 10 × 10 cm quartz plate using a no. 80 metering rod (Paul N. Gardner Co., Inc.) producing a 200-μm-thick liquid layer. The plate was heated for 1 h in an oven at 70 °C to evaporate the solvent and allow the film to harden. The resulting films were about 50 μm thick, and the optical densities recorded at several different positions on the film were 0.3 and varied by less than 5% over the entire film. The 1,1-diphenylacetone (DPA; Aldrich, recrystallized from hexanes–ethanol) samples were produced in the same way except 0.070 g of DPA was used in place of the TPA, the resulting films also having an optical density of 0.3.

For solution experiments we employed 0.04 M TPA or DPA in ethyl acetate (DBH OmniSolv). This concentration was chosen as a compromise between the high concentrations used in the polymer samples and the small optical density required at the laser wavelength.

The laser flash photolysis apparatus is similar to that which has been described elsewhere[19] and is shown schematically in Figure 1. The polymer or solution samples were irradiated on the front face with 10-ns pulses of 266-nm light from a quadrupled Lumonics HY750 Nd:YAG laser as the excitation source. When

0024-9297/92/2225-1582$03.00/0

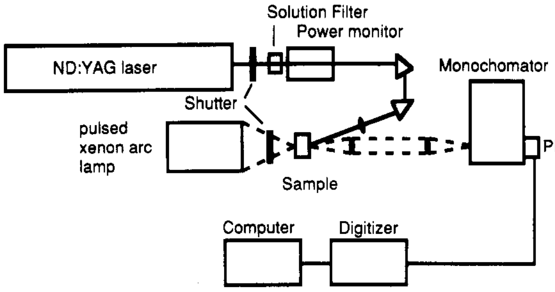

Figure 1. Diagram of the laser flash photolysis apparatus used for the solution and polymer experiments.

high-flux measurements were made the excitation beam was concentrated by focusing the laser from 8 mm down to 2 mm diameter. The high optical density of the solutions used and the geometry of the polymer samples required a front face arrangement for laser irradiation. The angle between the incoming probe beam and the laser beam was close to 165°. The polymer samples where mounted on a computer-controlled motor-driven platform. This made it possible to move the sample between laser pulses, thus allowing each pulse to excite a fresh area of the sample. Note that this contrasts with most ablation work in the literature, where the same area of polymer is irradiated repeatedly. The solution samples were degassed by bubbling with N_2 and a 0.3-cm-path-length flow cell was used for this work.

The laser power was monitored using a home-built diode power monitor that was calibrated using a pyroelectric power meter to measure the incident laser power before and after each experiment. In this way the relative laser power striking the sample could be determined within about ±2% while the absolute value may be determined only to about ±30% of the reported value. The laser power was adjusted using a solution filter containing solutions of $K_2Cr_2O_7$ of different optical density.

A pulsed 75-W xenon arc lamp with a PTI housing and power supply was used as the monitoring beam. The transmitted light was collected, collimated, and refocused into the entrance slit of a Digikrom 240 monochromator. Typically 1.0-mm slit widths were used. A Burle 4840 photomultiplier tube and housing with a six-dynode chain was attached to the exit slit of the monochromator, and the photomultiplier tube was powered by a home-built computer-controlled power supply. The signal from the photomultiplier tube was connected via 93-Ω cable to a back-off circuit and finally to a Tektronics 7912AD digitizer equipped with a 7A16P amplifier and a 7B90P time base. The digitizer is connected to a PDP 11/55 computer via a GPIB interface for data storage and analysis. A Stanford Research Systems digital delay/pulse generator is used to supply the TTL trigger pulses for the lamp, laser, and digitizer while a Scimetric Instruments Labmate instrument is used to control the shutters.

Results and Modeling

Characterization of Intermediates. While TPA has been well studied,[15-18] a description of the absorption properties at the laser wavelength and the kinetic behavior of all of the species involved is necessary for the understanding of the high-flux behavior and has been included here. Two diphenylmethyl radicals are produced from this precursor in a stepwise process. The first is produced along with a diphenylacetyl radical by rapid (<2-ns) cleavage of the triplet state of the ketone. Decarbonylation of the acetyl radical produces the second diphenylmethyl radical with a rate constant of at least 10^8 s^{-1}.[20] Both processes occur, to a large extent, within the duration of the laser pulse (~10 ns). The diphenylmethyl radical is characterized by a sharp intense absorption at 330 nm ($\epsilon_{330} \sim 88\,000$ M^{-1} cm^{-1}) with a slight shoulder at 315 nm ($\epsilon_{315} \sim 40\,000$ M^{-1} cm^{-1}).[21] The absorbance decreases until it is quite weak at 270 nm ($\epsilon_{270} \sim 800$ M^{-1} cm^{-1}).

The UV absorbance difference spectrum of a diphenylmethyl radical is shown in Figure 2. The low free-radical absorbance at the laser wavelength makes the accumulation of significant concentrations of the doublet excited state difficult even at extremely high laser intensities. This is in contrast with results obtained when 308-nm excimer laser excitation was used[15] where the radical has significant absorptivity and is excited readily within the duration of the single pulse. If the 266-nm pulse is followed by a 308-nm pulse, a sharp absorbance at 360 nm and a broad absorbance at 450 nm are observed; these have been assigned to the excited diphenylmethyl radical.[13,15,22] The absorbance difference spectrum of the excited diphenylmethyl radical produced using two laser pulses is also shown in Figure 2. By comparison of the bleaching and recovery data for the ground state and excited radical it is possible to obtain extinction coefficients for the excited species. This treatment assumes that the excited radical does not show significant absorptions where the bleaching is monitored (330 nm). The values obtained for the extinction coefficients of the excited radical are 80 000 and 35 000 M^{-1} cm^{-1} for the 360- and 450-nm maxima, respectively. At 270 nm the extinction coefficient is about 24 000 M^{-1} cm^{-1}. These extinction coefficients as well as those of the radical will be used to convert the observed signals into the absolute concentrations of the intermediates. The excited radical also emits over the 510-540-nm region. Comparison of the emission intensity with the optical density changes at 360 nm allows for the emission signal to be calibrated for the determination of excited radical concentrations, thus allowing these signals to be used even when the absorbance is too weak to be observed.

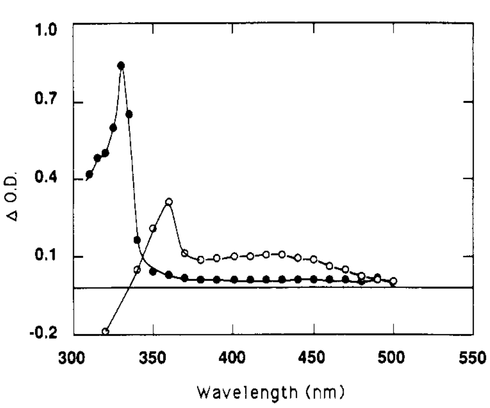

Figure 2. Transient absorption spectra of diphenylmethyl radical (●) and diphenylmethyl radical excited state (○) in ethyl acetate solution. The diphenylmethyl radical was produced by 266-nm irradiation of 1,1,3,3-tetraphenylacetone. Subsequent irradiation with a 308-nm pulse bleaches the diphenylmethyl radical and produces its excited state.

Experiments in Solution. In nitrogen-purged samples of TPA in ethyl acetate the radical decays with second-order kinetics with the first half-life typically around 2 μs under our experimental conditions. The excited radical decay follows first-order kinetics with a lifetime of about 250 ns. This is not the case of DPA samples where the radical decay has an initially rapid region followed by a slower decay and the excited radical decay is strongly flux-dependent. The reasons for the differences in the kinetic behavior of the transients from the two precursors are unclear, and mechanistic analysis of the transients produced from DPA is difficult. For this reason TPA samples were used unless otherwise stated. Figure 3 shows the dependence of the radical concentration on the laser dose incident on the sample. In all cases the transient concentrations were measured 80 ns after the laser pulse and the known lifetimes allowed the calculation of the concentrations of both species during the laser pulse ($t = 0$). When low laser intensities are used, the absorbance due

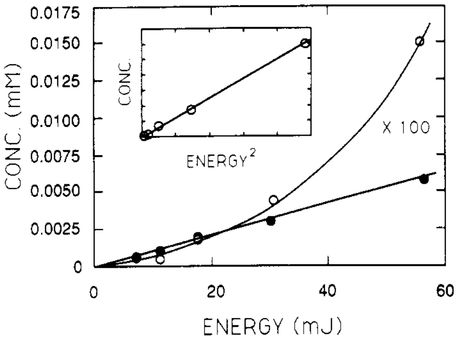

Figure 3. Plot of the concentrations of diphenylmethyl radical (●) and diphenylmethyl radical excited state (○) in ethyl acetate solution as a function of 266-nm laser intensity, at low laser intensities.

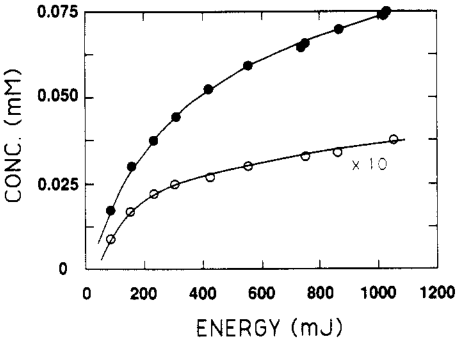

Figure 4. Plot of the concentrations of diphenylmethyl radical (●) and diphenylmethyl radical excited state (○) in ethyl acetate solution as a function of the incident 266-nm laser intensity, at high laser intensities.

to a ground-state diphenylmethyl radical (sometimes monitored at 340 nm or at 300 nm where the extinction coefficients are about one-third and one-tenth of the value at 330 nm, respectively) follows a linear dependence with the laser intensity, supporting the expectation that the radicals result from a one-photon process. The plot of the excited radical concentration is not linear but appears to be approximately parabolic, indicating that these signals are derived from a multiphoton process. The inset in Figure 3 shows a plot of the excited radical concentration versus the square of the laser dose. The linearity of this plot confirms that these signals are derived from a two-photon process.

At very high laser intensities the concentrations of both species no longer follow the low-flux behavior (Figure 4) but deviate in a manner that is characteristic of saturation of the excited states. In order to understand the high-flux behavior a simple model is proposed to account for the correlation between the concentrations of all of the species involved as a function of laser intensity.

Modeling. The proposed model uses a sequence of first-order reactions to describe the photochemistry of TPA and subsequent species, as shown below.

$$\mathrm{TPA} \xrightarrow{h\nu} 2\mathrm{Ph_2CH^{\bullet}} + \mathrm{CO} \quad (1)$$

$$\mathrm{Ph_2CH^{\bullet}} \xrightarrow{h\nu} \mathrm{Ph_2CH^{\bullet *}} \quad (2)$$

$$\mathrm{Ph_2CH^{\bullet *}} \xrightarrow{h\nu} \mathrm{X} \quad (3)$$

The occurrence of the unknown intermediate X as part of the reaction scheme is necessary in order to produce the leveling effect observed for the excited radical concentration. The bleaching of the excited diphenylmethyl radical has been reported previously[14] although the identity of this species is not known. Another possible mechanisms that may be suggested to account for this effect is the bleaching of the diphenylacetyl radical, produced along with the first diphenylmethyl radical, before it is able to decarbonylate. This bleaching would require that neither $\mathrm{Ph_2CH^{\bullet}}$ nor $\mathrm{Ph_2CH^{\bullet *}}$ is produced by photodecomposition of the diphenylacetyl radical. The results obtained when 1,1-diphenylacetone is used, where a diphenylacetyl radical is not formed, also show saturation behavior, allowing this possibility to be discounted. Intermediate X must be stable on the time scale of these experiments (~500 ns) to provide an adequate mechanism for the bleaching of $\mathrm{Ph_2CH^{\bullet}}$ and $\mathrm{Ph_2CH^{\bullet *}}$. This model also assumes that the radical and its excited state are stable on the time scale of the laser pulse duration and that the production of both diphenylmethyl radicals occurs simultaneously. While the first assumption is reasonable, given the ≥2-μs and 200-ns lifetimes for the ground and excited states, the assumption of rapid decarbonylation may be severely optimistic.[20] The fact that the diphenylacetyl radical has a lifetime comparable with the duration of the laser pulse makes the concentration of $\mathrm{Ph_2CH^{\bullet}}$ available for further excitation during the pulse smaller than predicted. This in turn will cause an underestimation of the efficiency of the $\mathrm{Ph_2CH^{\bullet *}}$ production. A further complication of this model is that the optical densities of the samples used and the relative sizes of the excitation beam and observation beam were such that the excitation intensity throughout the observation volume would not be completely homogeneous. The qualitative behavior of the model will not suffer however, and the model is used with the knowledge that the quantitative predictions may be suspect.

Table I
Quantum Yields and Absorption Data for the Species Involved in the Photochemistry of TPA

species	Φ_n[a]	ϵ_s,[b] $M^{-1}\ cm^{-1}$
$\mathrm{Ph_2CHCOCHPh_2}$	0.5	880
$\mathrm{Ph_2CH^{\bullet}}$	1.0	800
$\mathrm{Ph_2CH^{\bullet *}}$	0.5[c]	24 000

[a] Φ_n is the quantum yield for the conversion of species to product for reactions 1–3. [b] ϵ_s is the absorbtivity of the species at 266 nm. [c] Estimated.

The kinetic equations produced from this model reduce to linear first-order differential equations that have well-known solutions.[23-25] Strictly speaking, in order to use this model to make comparisons with the experimental data the absorptivities for each species at the laser wavelength and the quantum yields for each conversion must be known. Using a combination of the experimental data where possible and reasonable estimates when necessary, these values have been collected in Table I. The predicted concentrations of the species involved as a function of laser dose are shown in Figure 5. The agreement between experiment and the model predictions is surprisingly good (compare with Figure 4), especially in lieu of the assumptions made. This lends some confidence in the ability of the model to predict the high laser dose photochemistry of TPA.

Experiments in Polymer Films. Experiments using 50-μm PMMA films containing 5% TPA (w/w) in the low-intensity range show essentially the same phenomena as the solution experiments. That is, the radical concentration, calculated from the optical density at 330 nm is linear with dose while the concentration of the excited radical, calculated from the absorbance at 450 nm and/or

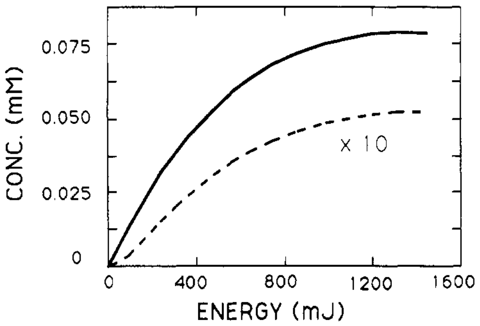

Figure 5. Plot of the concentrations of diphenylmethyl radical (—) and diphenylmethyl radical excited state (- - -) as a function of the incident 266-nm laser intensity, predicted by the assumed model (see text).

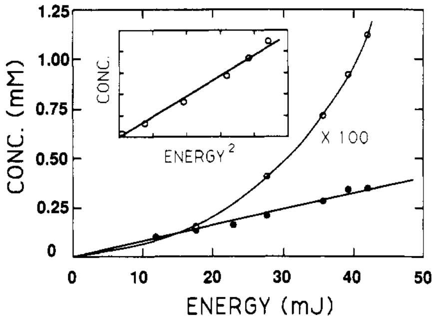

Figure 6. Plot of the concentrations of diphenylmethyl radical (●) and diphenylmethyl radical excited state (○) in 50-μm PMMA films as a function of the incident 266-nm laser intensity, at low laser intensities.

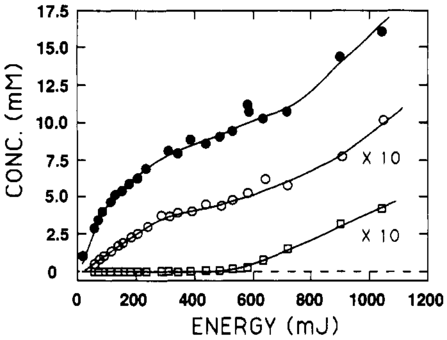

Figure 7. Plot of the concentrations of diphenylmethyl radical (●) and diphenylmethyl radical excited state (○) in 50-μm PMMA film as a function of the incident 266-nm laser intensity, at high laser intensities. Also included is the plot of scattering intensity (□), which was assumed to have an extinction coefficient equivalent to 80 000 M^{-1} cm^{-1} to allow for comparison with the excited radical concentrations.

emission at 520 nm, is not. This is shown in Figure 6. Under these conditions no ablation is detected.

Figure 7 illustrates the high-flux behavior for the polymer samples. Up to moderate flux levels there appears to be simple saturation effects for both the radical and excited radical as already observed in solution. However, at the extreme flux limits there is an observable change in the slopes of the graphs. This rapid increase in absorbance occurs at the same flux as the onset of ablation. The absorbance at 450 nm measured 1.2 μs after the laser pulse should be free from signals due to the radical or excited radical, yet a residual absorbance is observed. This residual signal is adequately described as a single-exponential growth with a rate constant of 2 × 10^{-6} s^{-1}. The transient absorbance spectra recorded at low laser doses before and high doses after the onset of this new growth are identical except that the latter is vertically shifted. This suggests that the absorbance increase observed is due to light scattering from fragments ejected from the polymer surface and bubble formation within the sample. The behavior of this new signal as a function of the laser dose is also included in Figure 7. The absorption increase was measured 1.2 μs after the laser pulse and corrected to the 80-ns value using the rate constant given above. In order to facilitate a comparison of these data with the concentrations of other species, the scattering data presented in Figure 7 have been displayed as if they have a formal extinction coefficient of 80 000 M^{-1} cm^{-1}. If the optical density increase due to scattering is subtracted from the signals observed for both $Ph_2CH^•$ and $Ph_2CH^{•*}$, the curves again appear similar to those observed in solution.

Emissions from excited diatomics such as C_2, reported in the ablation of PMMA itself,[5-7] are not evident in these experiments, either because they are masked by dopant-derived signals or, more likely, because at the lower fluxes used in these experiments these high-energy fragments are not formed. The scattering increase as a function of time for the doped polymers is identical to that recorded for PMMA alone although it is observed at much lower fluences, indicating that while the photochemistry involved in the two cases must be very different the ejection of material and bubble formation occurs with similar characteristics.

Observation of the irradiated polymer under a microscope shows that the first laser pulse does not produce a crater but instead produces a dome at the incident spot with many bubbles observed under the surface. The content of the bubbles is unknown although it is anticipated that carbon monoxide is one of the components. Bubble formation is estimated to occur at depths up to about 20 μm at the highest fluxes used, and two laser pulses in one spot produce a crater about 10 μm deep. Less than eight pulses are necessary to ablate the entire 50 μm thickness.

Discussion

The photochemistry of TPA under conditions of one- and two-photon excitation has been examined in considerable detail here and elsewhere.[13-18] The results given above show that the transient phenomena induced by laser excitation of TPA in solution and in PMMA films have many common features. It is clear—and perhaps surprising—that as the ablation regime is approached and even exceeded the transient phenomena remain rather simple and are not appreciably different in the polymer than what is observed in solution. The only significant difference is a substantial increase in the amount of light scattering above the ablation threshold in the case of the polymer films.

In all of the proposed mechanisms for photoablation, the first step in the delivery of energy is of a photochemical nature. Surely the absorbed photons produce a nonequilibrium condition that results in ablation. It is the nature of this condition with respect to ablation that is the center of the debate. If the absorbed photon produces an excited state that is, in itself, the cause of ablation, the mechanism would then be truly *photochemical*. In TPA-doped PMMA this does not appear to be the case as the photochemistry involved, while multiphotonic in nature, appears to be rather simple. Perhaps the fact that the photochemical decomposition of tetraphenylacetone leads to the formation of three molecules in the space previously occupied by one, one of which is a small stable gas molecule (CO), assists bubble formation and ejection of material. These molecules are confined to a relatively small volume and are presumably rather hot. It is then possible that the internal pressure built up after the laser pulse could cause ablation. If this is the case, it is difficult to explain the occurrence of a sudden threshold for ablation since the concentrations of these fragments are building up slowly within the sample and the efficiency with which they are formed decreases with increasing flux. This, of course, assumes that intermediate X (see reaction 3) is not actually many small fragments derived from the excited diphenylmethyl radical but is instead a rearrangement product[14] and that subsequent absorption by X is either inefficient or does not produce fragments (in a four or more photon process). Information on these points cannot be obtained from our experimental data. However, it seems unlikely that the mechanisms that is the cause of ablation of the films used in this study by purely photochemical in nature.

If the excited state or states are deactivated rapidly and release the absorbed energy as heat, the local heating may ultimately cause ablation. This would be a purely *photothermal* mechanism, where the polymer is decomposed and vaporized by the localized heating. Obviously photochemically derived products would be expected in the effluent since they would be the vehicle by which the heat is delivered to the sample, and these products may be the result of the absorption of many photons in a short period of time. Surely the local heating caused by the absorption of three photons of 266-nm light, in the volume surrounding one tetraphenylacetone molecule, within 10 ns, would be tremendous. This would result in extremely hot centers randomly dispersed in a relatively unperturbed polymer. The amount of heat necessary to decompose and vaporize the polymer is larger than that necessary to vaporize the solvent used in the solution experiments, but we did not observe ablation, as such, in the solution experiments under these conditions. The differences in the concentration of the dopant and the difference in the rates of heat conductance in the polymer and the solutions used may be large enough to account for this observation.

These experiments do clearly indicate that at the fluences used to ablate polymers three or more photons may be absorbed during a single laser pulse. It is also apparent that the buildup of a strongly absorbant species may be accomplished even though the precursors leading to its formation may be weakly absorbing or their photochemistry inefficient. This leads to a dramatic increase in absorption, thus allowing the laser pulse to "create its own absorption". The formation of ca. 20 mM $Ph_2CH^\bullet$ with an extinction coefficient of 88 000 M^{-1} cm^{-1} at 330 nm leads to an absorbance of ca. 9 au over the thickness of the polymer film at this wavelength. In the polymer films intermediate X is produced in considerable concentrations after the absorption of three photons by precursors that are relatively weakly absorbing at the laser wavelength (880 and ~800 M^{-1} cm^{-1} for the extinction coefficients of TPA and $Ph_2CH^\bullet$ at 266 nm) and are present in low concentrations. The effect of the buildup of absorbing species from modest absorbers is to concentrate the absorption near the surface. This is illustrated in Figure 8 where the penetration depth of laser is plotted as a function of fluence. Here penetration depth is defined as the fraction of the sample thickness necessary to absorb 50% of the incident radiation and is calculated on the basis of the extinction coefficients of the species involved and their concentrations obtained using the model to fit the polymer data. The top boundary of the hatched area is the limit if intermediate X is assumed to be transparent at the laser wavelength while the lower boundary occurs if X has an extinction coefficient of 20 000 M^{-1} cm^{-1} at 266 nm. The severe concentrating of the absorbance toward the front surface as the flux increases deposits more photons in an ever-decreasing volume. It is likely that this effect is an important part of the ablation process. It is also plausible that a highly absorbing species may be formed from one or more photons being absorbed by PMMA itself, even though it is weakly absorbing at this wavelength (extinction coefficient of ~0.3 M^{-1} cm^{-1} per monomer unit at 266 nm), resulting in the same type of absorbance concentration. We note that for PMMA the absorption at 266 nm is over an order of magnitude weaker than at 248 nm, a wavelength frequently employed in ablation work. It is little wonder then that the simple expression[26-28] $I_f = 1/a \log (F/F_0)$, which relates the etch depth per pulse (I_f) to the fluence (F), fluence threshold (F_0), and absorptivity (a), fails to produce the ground-state (or low-flux) absorptivity of many polymers since the absorptivities of subsequent reactive intermediates are not considered. The error of not considering the absorbance changes caused by subsequent transients has only recently been realized,[4] and the failure of this model might be an indication that the phenomenon of absorbance concentration is quite general, particularly in the cases of weakly or modestly absorbing polymers.

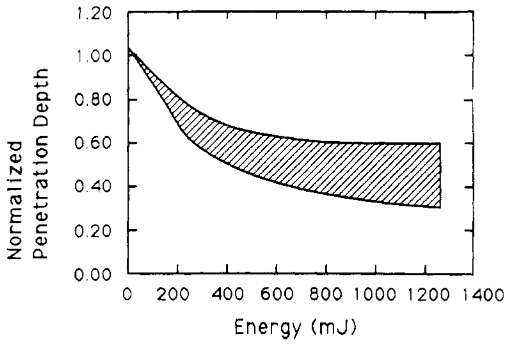

Figure 8. Plot of the laser radiation penetration depth as a function of the incident laser energy. The penetration depth is defined as the fraction of the sample thickness required to absorb 50% of the incident radiation. The hatched area indicates the limits of the expected depth of penetration (see text).

In conclusion, the ablation of doped polymer films has been examined from the perspective of the reaction intermediates generated as the ablation threshold is approached. The results suggest that transient phenomena appear to remain surprisingly simple in spite of the dramatic damage induced by the laser pulse. It is also clear that short-lived reaction intermediates play a key role in controlling the absorption properties of the film during the laser pulse; models that aim at correlating the dependence of physical damage with incident energy must allow for time-dependent variations in optical properties. Finally, the role of intermediate species cannot be ignored, since, whatever the actual mechanism for ablation, the delivery of energy to the film depends upon the absorptive nature of the polymer and any photochemically produced intermediates.

Acknowledgment. Thanks are due to Mr. S. E. Sugamori and Mr. G. Charette for technical assistance.

References and Notes

(1) Issued as NRCC-33266.
(2) Present address: Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5.
(3) Srinivasan, R.; Leigh, W. J. *J. Am. Chem. Soc.* **1982,** *104,* 6784.
(4) Srinivasan, R.; Braren, B. *Chem. Rev.* **1989,** *89,* 1303.
(5) Srinivasan, R. *Science* **1986,** *234,* 559.

(6) Koren, G.; Yeh, J. T. C. *J. Appl. Phys.* **1984**, *56*, 2120.
(7) Koren, G.; Yeh, J. T. C. *Appl. Phys. Lett.* **1984**, *44*, 1112.
(8) Srinivasan, R.; Braren, B.; Dreyfus, R. W.; Hadel, L.; Seeger, D. E. *J. Opt. Soc. Am. (A)* **1986**, *3*, 785.
(9) Masuhara, H.; Hiraoka, H.; Domen, K. *Macromolecules* **1987**, *20*, 450.
(10) Hiraoka, H.; Chuang, T. J.; Masuhara, H. *J. Vac. Sci. Technol.* **1988**, *B6*, 463.
(11) Chuang, T. J.; Hiraoka, H.; Mödl, A. *Appl. Phys. A* **1988**, *45*, 277.
(12) Srinivasan, R.; Braren, B. *Appl. Phys. A* **1988**, *45*, 289.
(13) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1984**, *106*, 3056.
(14) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83.
(15) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.
(16) Weir, D.; Scaiano, J. C. *Chem. Phys. Lett.* **1986**, *128*, 156.
(17) Bohne, C.; Boch, R.; Scaiano, J. C. *J. Org. Chem.* **1990**, *55*, 5414.
(18) Scaiano, J. C.; Shi, J. L. *Chem. Phys. Lett.* **1990**, *173*, 271.
(19) Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430.
(20) Gould, I. R.; Baretz, B. H.; Turro, N. J. *J. Phys. Chem.* **1987**, *91*, 925.
(21) Redmond, R.; Scaiano, J. C., to be published.
(22) Steenken, S.; Warren, C. J.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans.* **1990**, 335.
(23) Lachish, U.; Shafferman, A.; Stein, G. *J. Chem. Phys.* **1976**, *64*, 4205.
(24) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; John Wiley and Sons: New York, 1981.
(25) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; John Wiley and Sons: New York, 1961.
(26) Deutsch, T. F.; Geis, M. W. *J. Appl. Phys.* **1983**, *54*, 7201.
(27) Andrew, J. E.; Dyer, P. E.; Forster, D. *Appl. Phys. Lett.* **1983**, *43*, 717.
(28) Srinivasan, R.; Braren, B. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2601.