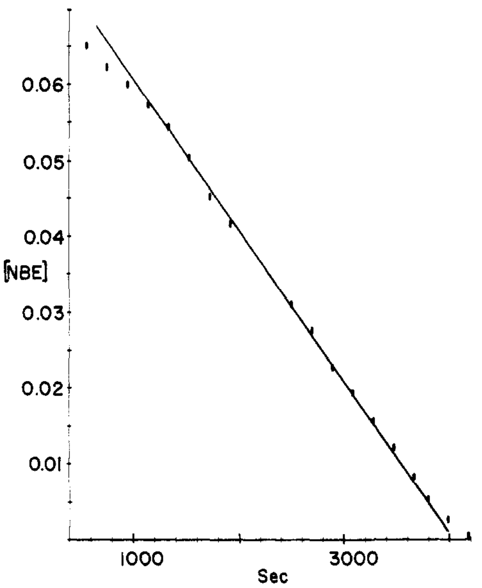

Figure 3. Plot of the consumption of 20 equiv of NBE by **2a** at 50 °C in C_6D_6.

Table II
GPC Analysis of Polynorbornene Prepared at 65 °C Using 2a as the Catalyst[a]

run	equiv of NBE	$\bar{M}_n$(uncor)	$\bar{M}_w/\bar{M}_n$
1	100	22 000	1.63
2	200	48 000	1.66
3	500	127 000	1.73
4	200 (~75% complete)	32 100	1.04[b]

[a] A -30 °C solution of 20 mg of **2a** in toluene was mixed with a -30 °C solution of norbornene in toluene such that the total volume was ~15 mL. The resulting solution was heated in an oil bath and checked by GLC to ensure that norbornene was completely consumed. The reactions were heated for an additional 30 min to 1 h and cooled to 25 °C. Acetone (~1 mL) was added, and the mixture was heated to 65 °C for approximately 15 min. The solvent was removed in vacuo, and the polymer was rinsed with methanol and dried in vacuo. In run 4 the reaction was taken to only ~75% completion. The polynorbornene was analyzed in toluene at 25 °C on a Waters 150C instrument vs. polystyrene standards using three Styragel columns. [b] The polymer with the expected molecular weight made up ~94% of the sample; ~6% of a fraction with a relatively high molecular weight could be resolved as a separate peak in this GPC spectrum.

is not the case), then k_1 is smaller when R = ^{t}Bu than when R is the growing polymer chain. This result is surprising until one considers that the steric congestion probably is greater out near the isopropyl groups of the phenoxide ligands than it is in the region where the *tert*-butyl group is found; i.e., the growing chain exerts a greater steric effect.

Toward the end of the reaction the plot of NBE consumption deviates from linearity. A plot of ln [NBE] vs. time in this region is linear; i.e., the rate depends on [NBE] at low values of [NBE]. Using the steady-state approximation for **3**, one finds that the reactions shown in eq 1 yield the expression $-d[NBE]/dt = k_1k_2[Ta][NBE]/(k_{-1} + k_2[NBE])$, where [Ta] is the catalyst concentration. Evidently $k_2[NBE] > k_{-1}$ until toward the end of the run. From the slope of the ln [NBE] vs. time plot we can show that $k_2/k_{-1} \approx 150\ M^{-1}$ at 57.0 °C.

Analysis of the polynorbornene prepared with **2a** as the catalyst in toluene (Table II) confirms that the molecular weight is directly proportional to the amount of monomer employed. The higher than desired polydispersities can be ascribed to slow secondary metathesis reactions after all norbornene has been consumed. In one case (run 4) the polymerization was stopped at ~75% completion. The polydispersity in that case was what one would expect from an essentially monodispersed polymer. These results suggest that this polymerization is truly living and that the slightly slower initiation step relative to propagation has a negligible adverse effect on polydispersity.

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Registry No. **1a**, 105945-15-1; **2a**, 105945-16-2; NBE, 498-66-8; NBE (homopolymer), 25038-76-0; Ta(CH*t*-Bu)(DMP)$_3$THF, 105969-47-9; Ta(CH*t*-Bu)(DIPP)$_3$THF, 106034-24-6.

References and Notes

(1) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.
(2) For preparation of the DIPP derivative, see: Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2162. The DMP derivative is prepared in an analogous fashion.
(3) Anal. Calcd for $TaC_{48}H_{71}O_3$: C, 65.72; H, 8.18. Found: C, 65.90; H, 8.36.
(4) Ivin, K. J. *Olefin Metathesis*; Academic: New York, 1983.
(5) We have seen no evidence that **2b** loses NBE in the time period of a typical run. Therefore we assume that this step is slow, as one might expect for this highly strained olefin.

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Dopant-Induced Ablation of Poly(methyl methacrylate) by a 308-nm Excimer Laser

Recently, excimer laser ablation of polymeric materials has been the subject of many studies,[1] and some lithographic[2] and medical applications[3] have been reported. Because the ablation is initiated by absorption of laser photons, a necessary condition is that the target materials have an appreciable absorption at the appropriate wavelengths. Some reports have dealt with the effect of absorbance upon ablation, correlating the etched depth with the absorbance of the films.[3-6] However, in these studies both absorbance and wavelength were varied simultaneously so that it is difficult to analyze independently the effects of these two parameters. In the present work, the wavelength remains constant at 308 nm while the absorbance at 308 nm is varied. This is accomplished by varying the concentration of π-electronic chromophores in PMMA films. The dopants used in this work are pyrene and benzophenone; the photophysical data of these dopants are well documented.[7]

PMMA (ultrapure, Eastman Organic Chemicals), pyrene (Aldrich), and benzophenone (Aldrich) were used as received. PMMA and the dopant were dissolved in chlorobenzene and spin-coated on a quartz plate at a thickness of 1.5 μm. A Lambda Physik EMG 201 XeCl excimer laser was used as an exposure source. Its beam was focused into a 1 × 2 mm^2 spot by using a lens with a focal length of 12 in. and an aperture. The laser fluence was measured with a Scientec 362 power meter. A copper mesh mask made photolithographically was used in contact with the polymer films. All ablation experiments were single-shot exposures. Depth profiles were measured by a Tencor Alpha-Step 200. Scanning electron micrographs were recorded with a Philips 500 SEM instrument after argon ion metal sputter deposition.

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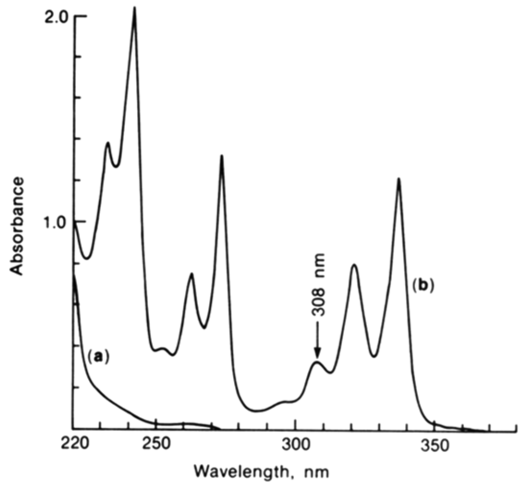

Figure 1. Absorption of PMMA films with thickness of 1.45 μm: (a) neat films; (b) doped with 7.7 × 10^{-3} mol of pyrene per mol of MMA unit.

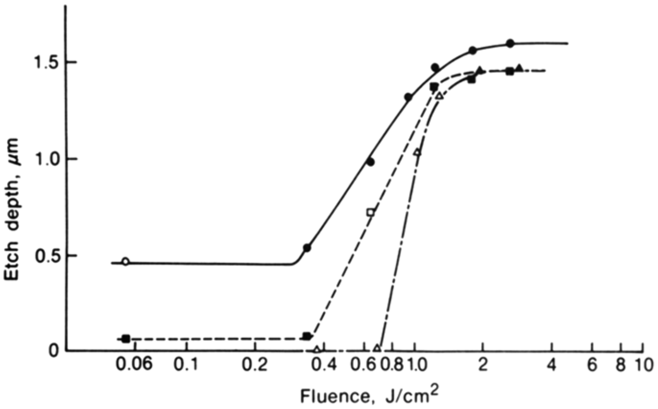

Figure 2. Relation between etch depth and laser fluence of doped PMMA films. Closed and open symbols mean homogeneous and inhomogeneous etching, respectively. Dopants are (a) 7.7 × 10^{-2} mol of pyrene per mol of MMA unit (○, ●); (b) 7.7 × 10^{-3} mol of pyrene per mol of MMA unit (□, ■); (c) 8.5 × 10^{-2} mol of benzophenone per mol of MMA unit (△, ▲). The thickness of the film (a) is 1.55 μm, and that of the other films is 1.45 μm.

Control experiments confirm that for neat PMMA films no optical and morphological changes are caused by laser exposure at 308 nm even for a fluence of 3 J/cm^2. For doping experiments, films with 7.7 × 10^{-2} and 7.7 × 10^{-3} mol of pyrene per mol of MMA unit and 8.5 × 10^{-2} mol of benzophenone per mol of MMA unit were prepared, yielding absorbances at 308 nm of 0.32, 0.2, and ~0.01, respectively. Representative absorption spectra are shown in Figure 1. Etching phenomena were studied in the fluence region from 50 mJ/cm^2 to 2.9 J/cm^2 in a single-shot irradiation. From the depth profile measurements summarized in Figure 2, the following observations were made: (1) above 1.8 J/cm^2 fluence all of the doped films studied are etched completely; (2) a typical relation where etched depth increases in proportion to the logarithm of laser fluence was observed only for the polymer doped with a high concentration of pyrene, (3) in the case of the other films, at a fluence less than 1.8 J/cm^2, efficient etching was induced only in some parts of the exposed areas (conditions that lead to such nonuniform etching are indicated by open symbols in Figure 2)—in other words, homogeneous, uniform etching has a distinct threshold for these systems; and (4) even in the case of the films doped with a high concentration of pyrene, a nonuniformly etched area was observed at laser fluences below 100 mJ/cm^2.

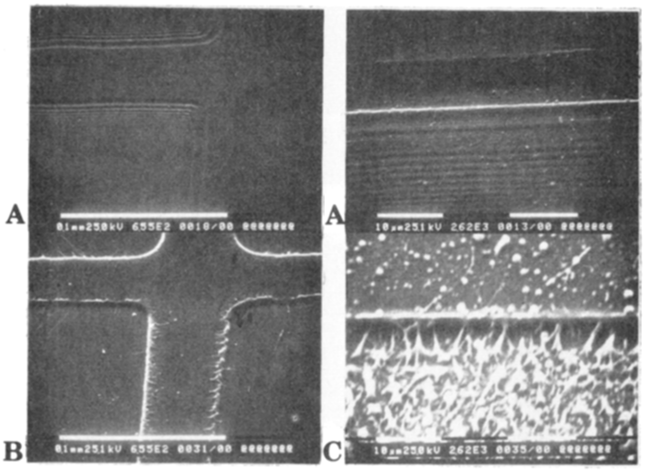

Figure 3. Scanning electron microscope photographs of doped PMMA films: (A) doped with 7.7 × 10^{-2} mol of pyrene per mol of MMA unit, 1.8 J/cm^2 fluence; (B) doped with 7.7 × 10^{-3} mol of pyrene per mol of MMA unit, 1.8 J/cm^2; (C) doped with 7.7 × 10^{-3} mol of pyrene per mol of MMA unit, 650 mJ/cm.^{2}

The present work clearly demonstrates that ablation of nonabsorbing polymers can be induced by the addition of an absorbing dopant species. Doping of PMMA with acridine is reported to lower the energy threshold for etching at 248 nm.[6] Some SEM photographs of our ablated films are shown in Figure 3, where one can see interesting effects of exposure fluence and dopant concentration on the physical and mechanical conditions of the etched surface. After exposure, PMMA films doped with a high concentration of pyrene (7.7 × 10^{-2} mol of pyrene per mol of MMA unit) showed a very clear periodic diffraction pattern that extended from the edge of the mask pattern into the exposed areas (Figure 3A). The periodic images can be ascribed to a diffraction effect caused by passing the laser beams through a grid mask. A similar circular diffraction image was reported previously in the 193-nm excimer laser ablation of PMMA,[8] where multiple-shot laser exposures make the interpretation of the image difficult because of the fluctuating laser intensity. Our experiments were carried out exclusively in a single-shot exposure mode.

This periodic image was observed for all such films ablated with fluences larger than 100 mJ/cm^2. In comparison, for films doped with a low concentration of pyrene (7.7 × 10^{-3} mol of pyrene per mol of MMA unit) no such diffraction patterns were observed. Instead, stringy residuals were formed in the boundary region between exposed and unexposed areas (Figure 3B). At low fluence, this effect is more pronounced, with the production of small curd-like particles inside the exposed region (Figure 3C). The PMMA films doped with benzophenone showed a behavior different from that just described for pyrene-doped films. Neither periodic patterns nor stringy residuals were observed; instead a smooth surface was observed in the etched areas. The benzophenone-doped films required a higher fluence for the ablation, which mich have resulted in a high temperature.

A possible explanation of the different surface conditions obtained after the ablation of the doped PMMA with high and low pyrene concentrations is as follows. For high dopant concentrations, the bond scission of PMMA caused by the energy transfer from the excited pyrene results in far smaller fragmented segments of PMMA than the ones obtained with the films with the low dopant concentration. This is because the greater light absorption of such films results in more efficient energy deposition into the film and thus a higher density of bond scissions during the laser

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pulses. Such a homogeneous scission into smaller units would result in the etched image being a closer representation of the light intensity distribution striking the polymer film, in a manner analogous to the use of finer grain sizes in a photographic film for higher resolution photography. Thus, periodic patterns such as in Figure 3A are observed for films with high pyrene concentrations. This kind of periodic image is not observed with films having the low dopant concentration, because ablated fragments are bulkier in this case (a larger "grain size"), leaving relatively large residues, particularly with smaller laser fluences.

The presence of the periodic images in films heavily doped with pyrene is an indication that the temperature of the film during the ablation was not high enough for the polymer to undergo extensive thermal flow. PMMA is a UV-softened polymer,[9] which flows below its T_g after UV irradiation, different from UV-hardened materials like novolac resins and poly(hydroxystyrene).[10] In contrast, with a low concentration of pyrene dopant, the etched area shows evidence of having been heated to its melting point (Figure 3B). It is interesting to compare these differing surface conditions to those observed in the laser ablation of PMMA at 193 nm and at 248 nm.[5,6,8] In that work, the presence of periodic patterns in the etched image after irradiation at 193 nm is associated with an ablation mechanism believed to be largely photochemical, while the presence of signs of melting in an area etched with 248-nm light is considered evidence that photothermal ablation is dominant. A similar switching between photochemical and photothermal mechanisms depending on optical absorption may be operative in the present work.

The lowest T_1 excited states of benzophenone and pyrene are 69 and 48 kcal/mol, respectively; the excited S_1 state of benzophenone is 74 kcal/mol.[7] Since the C–C bond energy in PMMA is about 85 kcal/mol, single electronic energy transfer from these excited dopants may not be sufficient for main-chain scission of PMMA. The laser ablation induced by the dopant's presence must involve multiphoton excitation of the dopant or annihilation of two dopant excited states. Higher electronic energy transfers made possible in such mechanisms may trigger the primary bond scission. The energy transfer from these higher excited states of PMMA and/or thermal energy attained by fast dissipation of electronic excitation energy from the latter state resulted in bond scissions of PMMA. With benzophenone as a dopant, a Norrish type II process may have contributed to a certain degree. Enhanced ablation through addition of a dopant to PMMA films has been reported for 248-nm excimer laser exposure;[4,6] however, competitive absorptions by the polymer film and dopant at this wavelength complicate the analysis and mechanistic discussion. We will study the mechanism in detail from a photophysical viewpoint in the near future.

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Registry No. PMMA, 9011-14-7; $C_6H_5COC_6H_5$, 119-61-9; pyrene, 129-00-0.

References and Notes

(1) For example: Srinivasan, R.; Mayne-Bantan, V. *Appl. Phys. Lett.* **1982**, *41*, 576. Andrew, J. E.; Dyer P. E.; Forster, D.; Key, P. H. *Appl. Phys. Lett.* **1983**, *43*, 717. Koren, N.; Yen, J. T. C. *Appl. Phys.* **1984**, *56*, 2120. Srinvasan, R.; Braren, B. *J. Polym. Sci., Polym Chem. Ed.* **1984**, *22*, 2601 and papers cited therein.
(2) For example: Linsker, R.; Srinivasan, R.; Wynne, J. J.; Alens, D. R. *Lasers Surg. Med.* **1984**, *4*, 2.
(3) Cole, H. S.; Liu, Y. S.; Phillip, H. R. *Appl. Phys. Lett.* **1986**, *48*, 76.
(4) Toyoda, K. *Zairyo Gijitsu* **1986**, *4*, 40.
(5) Srinivasan, R.; Braren, B.; Seeger, D. E.; Dreyfus, R. W. *Macromolecules* **1986**, *19*, 916.
(6) Srinivasan, R.; Braren, B.; Dreyfus, R. W.; Hadel, L.; Seeger, D. E. *J. Opt. Soc. Am. B* **1986**, *3*, 785.
(7) For example: Turro, N. J. *Modern Molecular Photochemistry*; W. A. Benjamin: Menlo Park, CA, 1978.
(8) Srinivasan, R. *J. Vac. Sci. Technol., B* **1983**, *1*, 923.
(9) Todokoro, Y.; Takasu, Y.; Ohkuma, T. *Proc. SPIE—Int. Soc. Opt. Eng.* **1985**, *537*, 179–187.
(10) Hiraoka, H.; Pacansky, J. *J. Electrochem. Soc.* **1981**, *128*, 2645.
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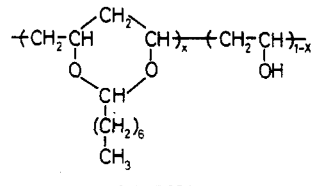
Stepwise Deposition of Oriented Monolayer-Polymer Films by the Langmuir-Blodgett Technique

The Langmuir-Blodgett (LB) technique is an excellent method for obtaining ultrathin films with a well-defined molecular assembly, and there has been much interest in LB films because of this molecular assembly.[1] Studies of LB films have been conducted primarily on amphiphilic molecules, such as long-chain fatty acids and dyestuffs with long alkyl chains. However, there has been little study of LB films consisting of monolayers of synthetic polymers.[2-9] Orientation of synthetic amphiphilic polymers at the air/water interface and transfer of the monolayer films onto substrates are of interest as a route to oriented, ultrathin, synthetic polymer films.

We have demonstrated[10] that poly(vinyl acetals) spread on the air/water interface can be transferred onto various substrates by Y-type deposition and that the one-layer thickness increases with increasing length of the alkyl side chain. We report here that the one-layer thickness of LB films of poly(vinyl octal) is constant at 1.1 nm from one monolayer to 100 layers and that the films have an oriented structure.

Poly(vinyl octal) (OA-PVA) was prepared from commercially available poly(vinyl alcohol) (Wako Pure Chemicals, >98% hydrolyzed, average molecular weight 8.8 × 10^4) and octaldehyde in the presence of hydrochloric acid in chloroform.[10] The mole fraction of acetalized units (x) was 0.7. The OA-PVA was amorphous, with a glass transition temperature of 25 °C.


OA-PVA

A benzene solution of OA-PVA (0.126 g/L) was dropped on the surface of distilled water (10–11 °C) in a Langmuir trough. The solution spread on the surface immediately. After evaporation of the solvent, a surface pressure–area curve was recorded by using a Lauda film balance with a

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