Deposition of Poly(methyl methacrylate) Films by UV Laser Ablation

Graciela B. Blanchet

E. I. du Pont de Nemours and Company, Central Sciences and Engineering, E356/139, Wilmington, Delaware 19898

Received October 24, 1994; Revised Manuscript Received March 22, 1995[⊗]

ABSTRACT: Thin films of poly(methyl methacrylate) (PMMA) were deposited by laser ablation using the fourth harmonic, at 266 nm, of a Nd-YAG laser. The temperature of the glass substrate during deposition was found to be critical in determining the morphology and molecular weight of the ablated films. When the temperature of the glass substrate was maintained below the glass transition, hazy films of low density and molecular weight were obtained. In contrast, above T_g the ablated material coalesced into a clear, denser film of high molecular weight and excellent adhesion to the glass. We suggest that pyrolytic decomposition and subsequent repolymerization are a plausible mechanism to the formation of PMMA films by laser ablation.

Introduction

The thermal degradation of poly(methyl methacrylate) (PMMA) has been studied extensively, and, although the details of the degradation mechanism are still somewhat controversial,[1–4] it is generally accepted that PMMA degrades thermally by chain depolymerization, yielding methyl methacrylate as the only decomposition product. This type of degradation is, in its general character, the reverse of polymerization. It is a chain process characterized by an initiation, propagation, and termination. Early studies[1,2] suggested that degradation occurred via a chain end initiating unzipping; other points of initial attack, such as combinations of chain ends, weak links, and randomly initiated unzipping,[3,4] were later proposed.

We have introduced[5–7] the use of UV laser ablation as a solvent-free deposition technique that allows the direct formation of fluoropolymer coherent films with thicknesses varying from about 100 Å to a few microns. In this study we show that the use of UV laser ablation can be extended to the deposition of PMMA, also known to thermally decompose by chain depolymerization.

The ablative photodecomposition model[8] describes UV ablation of organic materials as a direct bond dissociation process. However, the mere fact that poly(methyl methacrylate) (PMMA) films can be grown via laser ablation is not reconcilable with an unselective bond cleavage as proposed by this model,[8] pointing to the importance of a thermal component in the ablation process.[9] By unselective bond cleavage we mean the random breakup of material with the formation of nonmonomeric molecular fragments in a small volume in the vicinity of the surface. Within a thermal picture, photoabsorption rapidly heats the target materials beyond the onset of their pyrolytic decomposition, and, in polymers such as PMMA, decomposition leads primarily to monomer via a chain depolymerization reaction.[10] Since the specific volume of monomer in the gas phase is larger than that in the solid state, it ejects explosively at high velocities impinging upon the glass substrate where it repolymerizes, forming a film.

Early studies on plume composition[8,11] showed that ablation of PMMA with nanosecond pulses at 193 nm led to monomer formation while ablation at 248 nm did not. The first attempts[12] to deposit PMMA by ablation at 248 nm with nanosecond pulses led to discontinuous films. Difficulties were later circumvented by using femptosecond pulses,[13] an approach that also resulted in clean material removal with an ablation threshold of 50 mJ/cm^2.

The results presented here show that PMMA films can be deposited by ablation of a PMMA target with nanosecond pulses at 266 nm when at low laser fluences and in vacuum or under low pressures of selected gases. The morphology, molecular weight, and properties of the ablated films are discussed in detail. We measured "in situ" MMA formation and an ablation threshold of about 40 mJ/cm^2. The similarities between ablation and pyrolytic mass spectra suggest that PMMA ablation is a thermally driven process. UV absorption initiates radical formation and locally heats the polymer initiating the pyrolytic decomposition of the target via the depolymerization or unzipping of the polymer chains generating monomer that, in turn, can repolymerize on nearby surfaces, forming a film.

Experimental Section

We have utilized a mass spectrometer to identify the species emitted from a PMMA target under laser irradiation. The targets were positioned at the center of a vacuum chamber maintained at a background pressure of 10^{-7} Torr. The targets were ablated using the fourth harmonic (266 nm) of a Spectra-Physics DCR-11 Nd-YAG laser at fluences ranging from 10 mJ/cm^2 to 1 J/cm^2.[10] The pulse width in the Q-switch mode use for the deposition of PMMA was 10 ns and the repetition rate 10 Hz. The beam was directed into the chamber by a pair of plane mirrors and focused onto the target by a 250 mm focal lens place at the entraced of the vacuum chamber. When in the film deposition configuration, the target was rotated by 90° and a substrate/heater assembly was placed 3 cm away with the surface of the substrate parallel to that of the target. Uniform coverage of the glass substrates was ensured by rastering the laser beam over the target with a set of motorized micrometers placed on the last plane mirror. The laser beam, incident at 45° through a quartz window, was focused to a 2 mm^2 spot size onto the surface of a solid pellet. The targets were prepared by melt pressing PMMA to 10 000 psi at 180 °C for 15 min and cooled to ambient temperature under pressure. The plume, viewed normal to its expansion direction, was collected through a 3 mm diameter pinhole located 12 cm away from the center of the chamber into an IQ200 Inficon mass spectrometer. The pyrolytic decomposition spectrum was measured using a commercial Hewlett-Packard 5790A mass spectrometer at 600 °C in a He atmosphere.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

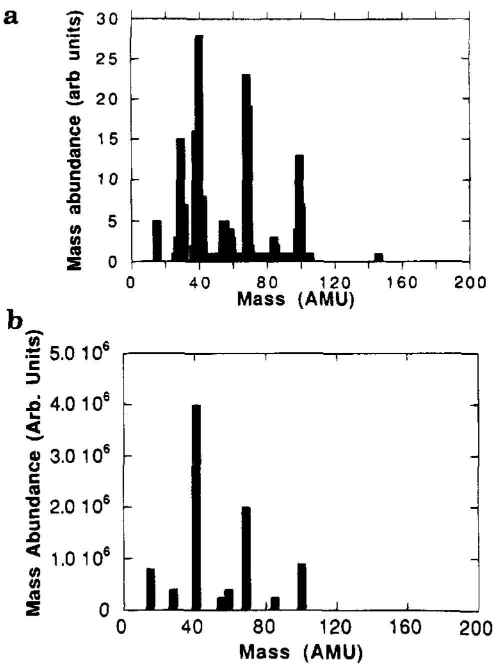

Figure 1. (a) Mass distribution of the spectra generated by laser ablation of PMMA at 266 nm, 0.4 J/cm^2 laser fluence, and 10^{-7} Torr background pressure. (b) Mass distribution of PMMA pyrolyzed at 600 °C in a He atmosphere.

Targets were reconditioned after each deposition by slightly sanding their surface. The laser-ablated PMMA films described here were deposited in an argon atmosphere of 200 mTorr at fluences ranging from 0.2 to 0.5 J/cm^2 in 10 ns pulses. The compositions of the laser-ablated PMMA films appear to be independent of laser fluence when operating in the 40 mJ/cm^2 to 1 J/cm^2 fluence regime and at a repetition rate of 2–10 Hz. Similarly, the morphology of films deposited at ambient temperature shows no dependence on the particular substrate used for the deposition of the film. Typical substrates were quartz, KBr, Si, and CaF_2.

Results

During laser irradiation there is disassociation of bulk material, and the species emitted may range from radicals and volatile molecules to fragmented polymer whose molecular weight is less than that of the parent polymer. Therefore, a study of the composition of the laser plume is perhaps the most direct path toward understanding the ablation mechanism in PMMA.

Figure 1 shows that the products in the PMMA ablation plume are those obtained in the standard pyrolytic decomposition of PMMA. It is generally accepted that the pyrolytic decomposition of PMMA leads to depolymerization and monomer (MMA)[4] formation. The main spectral peaks in the ablative decomposition of PMMA in the 0–200 amu region appeared at 41, 69, and 100. They correspond to monomer ($H_2C{=}C(CH_3)CO_2CH_3$) and the partial or the total removal of the methyl carbonyl side ($H_2C{=}C(CH_3)$ and $H_2C{=}C(CH_3)CO$) due to interactions and collisions within the plasma. The smaller features at 15, 28, 59, and 85 are assigned to CH_3, CO, $COOCH_3$, and $H_2C{=}C(CH_3)CO_2$. The dimer and higher mass components were not observed either in the ablaion plume or as a pyrolysis product.

Figure 2 shows the monomer content in the plume resulting from the ablation of PMMA at 266 nm as a function of laser fluence. In general,[8,13] the ablation threshold is determined by measuring the etch depth of ablated holes as a function of laser fluence using a profilometer. While this method has limited accuracy in the neighborhood of the ablation threshold, "in situ" measurement of the ablation plume allows the detection of monomer of 1 part in 10^5. The PMMA data shows a slow rise at low fluences, perhaps resulting from beam inhomogeneities, followed by a precipitous increase at higher fluences. We estimate a PMMA ablation threshold of 40 mJ/cm^2, a value corresponding to the onset of the rapid rise in the monomer peak intensity. This value is in good agreement with those reported in ref 8 for C2 formation in the fluorescence spectrum and the onsets of monomer formation for nanosecond ablation at 193 nm and picosecond ablation[13] at 248 nm.

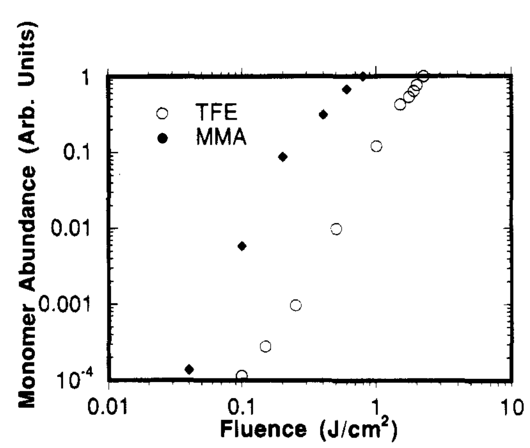

Figure 2. MMA abundance as a function of laser fluence.

The PMMA films were deposited in the configuration described above at fluences ranging between 0.2 and 0.5 J/cm^2. Following deposition the films were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) and gas phase chromatography (GPC).

Figure 3, parts A and B, shows scanning electron micrographs of PMMA films deposited by laser ablation at ambient temperature and 150 °C, respectively. The charging of the film by the incoming electrons was avoided by applying a thin layer of palladium gold prior to imaging. Although beam damage was considerably reduced by limiting the electron beam voltage to 4 kV, beam-induced cracking was apparent at higher magnifications. As shown in the micrographs, film morphology is strongly dependent on the temperature of the glass substrate during deposition. PMMA films deposited at room temperature appeared hazy and adhere poorly to the glass. This sponge-like structure appears to be mainly composed of fairly spherical particles of various sizes forming a loosely packed low-density matrix (Figure 3A). In contrast, films deposited above T_g are dense and clear and show excellent adhesion to the glass (Figure 3B). Curve C (Figure 3) shows film thickness versus deposition temperature for films otherwise prepared under identical conditions. As shown in the figure, the thickness, fairly constant at low temperatures, changes rapidly in the neighborhood of T_g. The large densification (ca. a factor of 7) is in good agreement with the morphology changes observed in the micrographs. Films deposited at low temperatures are cloudy and have low density and poor mechanical properties, while those deposited above T_g are clear with excellent adhesion and mechanical properties.

Figure 4 shows the infrared spectrum of thin PMMA films laser ablated and spin coated onto 13 mm KBr disks at room temperature. The laser-ablated film was deposited at 0.2 J/cm^2 laser power at 10 Hz in an Ar atmosphere of 250 mTorr. Since films ablated onto

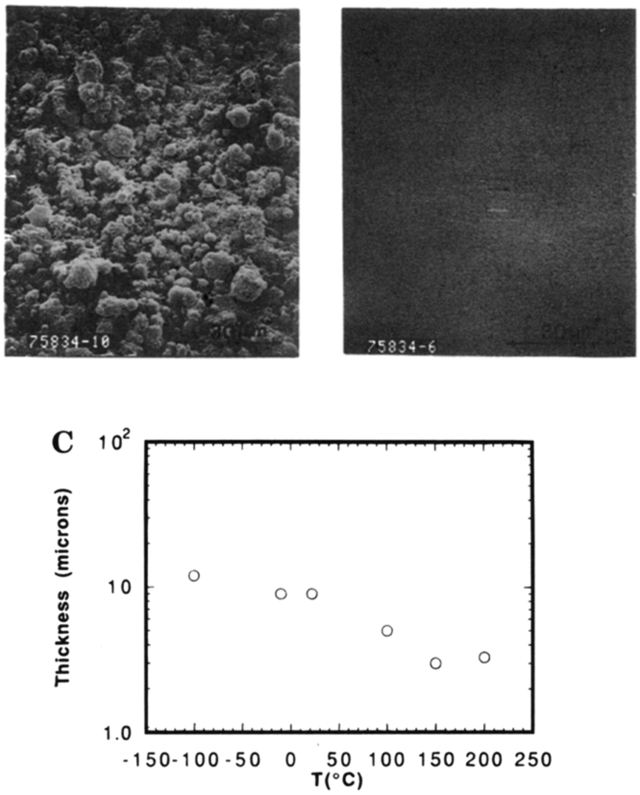

Figure 3. (Top) Scanning electron micrographs of PMMA thin films deposited by laser ablation at 4 kV electron beam voltage and 10^4 magnification: (top left) PMMA deposited at room temperature; (top right) PMMA deposited on a substrate maintained at 150 °C. (Bottom) Thickness of ablated films vs deposition temperature.

substrates maintained at ambient temperature are very hazy, it was necessary to anneal the film in vacuum at 90 °C for 3 min prior to spectrum collection. However, the IR spectrum of this film, which was converted from a hazy film to a clear film by annealing, is indistinguishable from the spectrum of a PMMA film deposited as a clear film by maintaining the glass temperature at 150 °C. These results suggest that although the morphology is different the local conformation is not.

Films were spin coated (bottom) from a 20% by weight solution in methylene chloride at 4000 rpm. The residual solvent was eliminated by heating in a vacuum oven at 60 °C for 5 min. Figure 4 shows that there is a one-to-one correspondence between the peaks in the cast and ablated films.

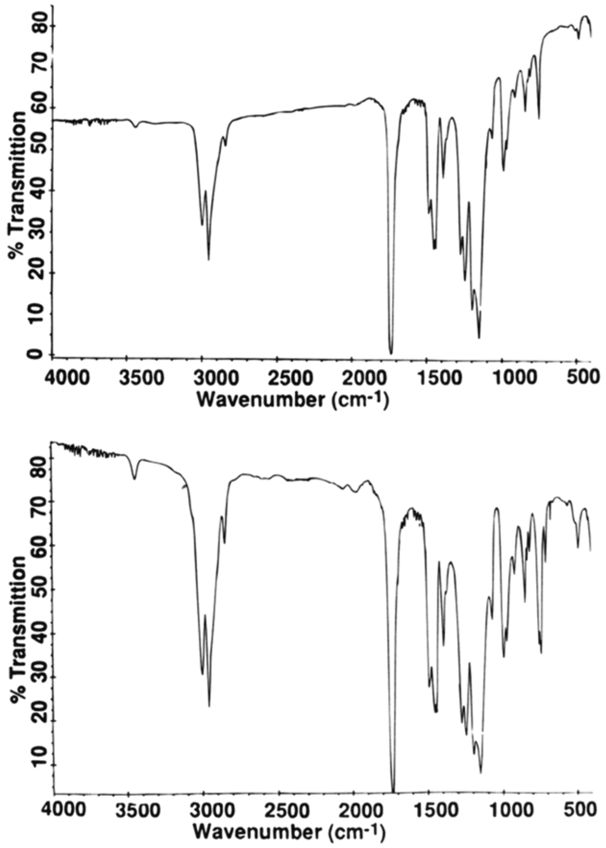

Figure 4. Infrared spectra of a thin PMMA film laser ablated onto a KBr substrate at 0.2 J/cm^2 fluence (top) and spin-coated PMMA film (bottom).

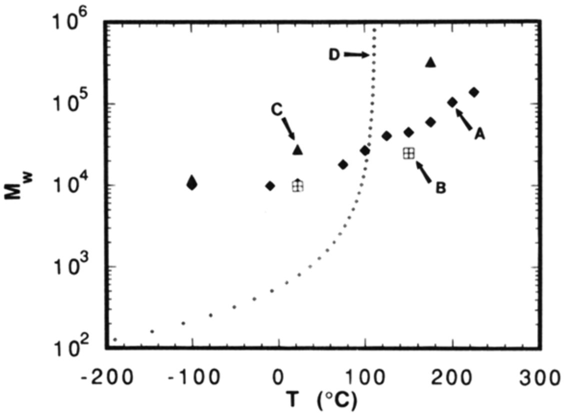

Figure 5. Molecular weight of PMMA films deposited by laser ablation at 266 nm as a function of the deposition temperature: (A) Ar background pressure of 250 mTorr, and M_w(target) = 500 000; (B) Ar background pressure of 250 mTorr and M_w(target) = 5280; (C) Ar background pressure of 10^{-7} Torr and M_w(target) = 500 000; (D) chain length dependence of the glass transition temperature.[14]

The curves in Figure 5 illustrate the dependence of the molecular weight (M_w) of PMMA films on the deposition temperature and background pressure. The molecular weights were determined by gel permeation chromatography (GPC). Films were deposited from targets with molecular weights (M_w) of 500 000 and 5280 at background pressures of 10^{-7} Torr and 250 mTorr of Ar. After deposition and thickness determination using a profilometer, the films were removed from the glass substrate dissolved in 1 mL of tetrahydrofuran and injected into the chromatography column. The curves show two distinct behaviors: at low temperatures M_w is independent of temperature while it increases linearly above T_g. Curves A and B show that the molecular weights of films deposited from targets of 5280 and 500 000 molecular weights under otherwise identical conditions are very similar. M_w's are about 10^4 for temperatures ranging from −196 to +80 °C, increasing linearly to 6×10^4 at 175 °C. In contrast, the temperature dependence of films deposited from the same target under different background pressures is shifted along the x axis by about 100 °C. While the molecular weight of the films deposited in vacuum at 175 °C is 325 000, those deposited in an Ar atmosphere of 250 mTorr have M_w's of about 60 000. Curve D shows T_g as a function of the number-average chain length, M_n.[14]

Discussion

The extraordinary similarities between the mass spectrum of the ablation plume and the pyrolysis products PMMA shown in Figure 1 suggest that, at low fluences, ablation and pyrolysis may proceed by similar mechanisms. It is generally accepted that vacuum pyrolysis of PMMA proceeds via an unzipping or depolymerization reaction initiated by random cleavage followed by a depropagation step[1-4] with the formation of monomer. Since bond energies are generally larger than the photon energy ($h\nu = 266$ nm $= 4.66$ eV), it is unlikely that bond scission results from one photon absorption and one must consider single photon transitions to predissociative states followed by photofragmentation. In a photofragmentation process, the additional energy is released into vibrational modes, leading to the heating of the solid.

Srinivasan[8] first showed under somewhat different experimental conditions that the ablation products of PMMA at 193 nm are CO_2 monomer, and PMMA fragments of 2500 molecular weight, while 248 nm ablation products are CO_2 and PMMA fragments of 3500 molecular weight. Although there are some differences between these earlier studies and the data in Figure 1, they may only reflect differences in experimental configuration since their ablation products were collected in a glass vessel at 200 mTorr and transported into the mass spectrometer for spectral analysis. The time delay between plum formation and spectral analysis could easily lead to fragment recombination and perhaps repolymerization of the highly reactive monomer. Larciprete and Stuke's[11] first reported "in situ" studies of PMMA ablation products in vacuum which showed a multitude of spectral peaks that could not be easily attributed either to monomers or to fragments of the polymer chain. Their spectra cannot be easily reconciled with Srinivasan's or the data present here. Larciprete and Stuke measured a multitude of peaks corresponding to carbon clusters of various sizes, suggesting that they operated at much *higher fluence* outside the regime investigated here. The formation of a graphic-like surface by the ablation of PMMA is known to occur.[15] However, films deposited from a plume of the composition of ref 11 would not lead to PMMA films but to graphic-like and/or diamond-like carbon films[15] instead.

The thermal decomposition of a PMMA chain can be crudely analyzed as follows. For significant pyrolysis to occur via unzipping, the decomposition rate must be comparable to or faster than the thermal relaxation time of PMMA. One can estimate the thermal relaxation time, $1/\tau = \lambda/c_p\alpha^2$, where λ is the thermal conductivity, c_p the specific heat, and α the absorption coefficient, to be about 50 μs for PMMA.[10] Although this result assumes α of about 10^4 cm^{-1}, much higher than values estimated from optical spectroscopy measurements, it is consistent with absorption coefficients obtained by us and others[8,13] from etch rate measurements. The two processes governing the kinetics of PMMA decomposition are (1) initiation followed by (2) chain depolymerization. The depolymerization reaction is a thermally driven process, and its rate constant can be estimated from the thermodynamic values for the depolymerization of PMMA into MMA with the Arrhenius parameters of $A = 10^{13}$ s^{-1} and $E_a = 18$ kcal/mol.[16,17] If we assume that the temperature of the ablated volume would rise to 700 °C throughout the ablation process, 4×10^4 monomer units would unzip in the relaxation time of about 50 μs. Therefore, a thermal depolymerization reaction can clearly account for the ablation products *provided that initiation has occurred*. The initiation step could be either thermally induced or photoinduced. Within a thermal initiation, radicals can be generated either by random scission or at chain ends. The Arhenius parameters for chain end initiation are $A = 4.0 \times 10^7$ s^{-1} and $E = 6.03$ kcal/mol, leading to an estimated time for the generation of a chain end radical of about 1 μs. By contrast, Arrhenius parameters for random scission are $A = 4 \times 10^{16}$ s^{-1} and $E = 62.4$ kcal/mol, indicating a generation time of 1 ms/radical. Since the thermal relaxation time is about 50 μs, initiation at chain ends is feasible while random initiation would appear to be too slow. Therefore, these results suggest that ablation of PMMA is a two-step process: an initiation reaction in which the radical is either photoinduced or thermally generated at a chain end followed by the thermal depolymerization of the polymer chain.

As shown in Figure 4, the IR spectrum of an ablated film is identical to that of a bulk polymer film prepared by nondestructive means. In particular, the IR spectrum shows that there is a one-to-one correspondence in the positions as well as in the widths of the infrared-active modes of cast and ablated films. While the chain morphology remains intact throughout the casting process, upon ablation PMMA thermally depolymerizes into monomer that subsequently repolymerizes on a substrate, forming a film. Then, similarities in width of the IR features between ablated and cast films suggest that the material deposited by ablation is essentially indistinguishable from the starting polymer. This is quite remarkable since chain defects, cross-linking, molecular displacements, or changes in bond length would shift peak positions, increase their width, or introduce new spectral features. By contrast, the differences in morphology and molecular weight (for MW > 2000) are not apparent either in the IR or in the DSC spectra since the short-range order and molecular conformation are identical. The infrared spectra of samples that were deposited at room temperature and annealed afterwared are identical to those of samples deposited at elevated temperatures and not annealed. Deposition fluence, repetition rate, and differences in background pressure or gas also seemed to have no effect on the IR spectrum.

As shown in Figures 3 and 5, the morphology and molecular weight are determined by deposition temperature and background pressure. Films deposited below the glass transition temperature form an open structure while those deposited at elevated temperatures are dense and clear and have higher molecular weight. It is likely that these changes in morphology are associated with changes in radical and/or chain mobility. The latter can be inferred from the observation that the hazy, low-density film deposited at room temperature can be converted into a clear, smooth, and dense film by annealing above T_g. The implication is then that chain mobility, which increases with temperature, plays a role in determining the film morphology. The MMA in the plume approaches the substrate with a high kinetic energy ($v \sim 2000$ m/s), and it is thermalized by repetitive collisions at the film/vacuum interface. That is, MMA reaches the substrate at much higher temperatures, and over some interaction time it will effectively cool to the temperature of the glass. Therefore, MMA must be added to the chain before it has a chance to thermalize and, for low-temperature deposition, even solidify. However, as the temperature of the substrate increases, the mobility of the "in situ" polymerized chain also increases, leading to denser films of higher molecular weight.

To conclude, we have shown that laser ablation can be used as a tool to deposit PMMA films and suggest that ablation of methacrylates is predominantly of a thermal nature. The photon energy initially absorbed as electronic excitation is rapidly converted to vibrational heating of the solid. The intense local heating results in the pyrolytic decomposition of the target, forming, via rapid unzipping of the polymer chains, an ablation plume primarily composed of MMA. The explosively ejected monomers arrive at the substrate where repolymerization occurs. The morphology of the films can be modified by deposition parameters, especially temperature and background pressure. The films deposited slightly above T_g are clear and smooth and have excellent adhesion and high molecular weight. It is our current belief that laser ablation of polymers can provide a solvent-free route to the formation of high-quality thin films.

Acknowledgment. The author is grateful to Dr. Ralph Fuller for the GPC analysis and to Robin Carson and Gail Raty for their excellent technical assistance.

References and Notes

(1) Simha, R.; Wall, L. A. *J. Polym. Sci.* **1950**, *5*, 615.
(2) Grassie, N.; Melville, H. W. *Proc. R. Soc. London*, A **1949**, *199*, 14.
(3) Brockhaus, V. A.; Jenckel, E. *Makromol. Chem.* **1956**, *12*, 263.
(4) Manring, L. E. *Macromolecules* **1991**, *24*, 3304 and references therein.
(5) Blanchet, G. *Appl. Phys. Lett.* **1993**, *62*, 479.
(6) Blanchet, G. B.; Shah, S. I. *Appl. Phys. Lett.* **1993**, *62*, 1026.
(7) Blanchet, G. B.; FIncher, C. R.; Jackson, C.; Shah, S. I.; Gardner, K. H. *Science* **1994**, *262*, 719.
(8) Srinivasan, R.; Mayne-Banton, W. *Appl. Phys. Lett.* **1982**, *41*, 576. Srinivasan, R. *J. Vac. Sci. Technol.* **1983**, *B1*, 923. Srinivasan, R. *Science* **1986**, *234*, 539. Srinivasan, R.; Braren, B. *Chem. Rev.* **1989**, *89*, 1303.
(9) Brannon, J. H.; Lankard, J. R.; Braise, A. I.; Burns, F.; Kaufman, J. *J. Appl. Phys.* **1985**, *58*, 2036.
(10) Blanchet, G. B.; Fincher, C. R. *Appl. Phys. Lett.* **1994**, *65*, 10.
(11) Larciprete, R.; Stuke, S. *Appl. Phys. B* **1987**, *42*, 181.
(12) Hansen, G.; Robitaille, T. E. *Appl. Phys. Lett.* **1988**, *52*, 81.
(13) Kuper, S.; Stuke, S. *Appl. Phys. B* **1987**, *54*, 4.
(14) O'Driscoll, K.; Sanayeu, R. A. *Macromolecules* **1991**, *24*, 4480.
(15) Athwal, I. S.; Ogryzlo, E. A. *Mol. Cryst. Liq. Cryst.* **1992**, *219*, 183.
(16) Odian, G. Principles of Polymerization, 2nd ed.; Wiley: Chichester, 1970, p 258.
(17) Mita, I. *Aspects of Degradation and Stabilization of Polymers*; Viehe, H. G., et al., Eds.; D. Reidel: Dardrecht, 1986; p 123.

MA9462518