bility may not have been achieved in the experiments reported here, this is thought to be a limitation of the maximum strains allowed by the equipment used rather than refutation of the flow-induced mixing argument. Future experiments will employ a rotary shear device in order to overcome the strain limitations of our present equipment.

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References and Notes

(1) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979.
(2) Snyder, H. L.; Meakin, P.; Reich, S. *Macromolecules* **1983**, *16*, 757.
(3) Hashimoto, T.; Kumati, J.; Kawai, H. *Macromolecules* **1983**, *16*, 641.
(4) Hill, R. G.; Tomlins, P. E.; Higgins, J. S. *Macromolecules* **1985**, *18*, 2555.
(5) Fruitwala, H.; Higgins, J. S.; Tomlins, P. E., submitted for publication in *Br. Polym. J.*
(6) Rangel-Nafaile, C.; Metzner, A. B.; Wissbrun, K. F. *Macromolecules* **1984**, *17*, 1187.
(7) Kramer, H.; Wolf, B. A. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 21.
(8) Mazich, K. A.; Carr, S. H. *J. Appl. Phys.* **1983**, *54*, 5511.
(9) Katsaros, J. D.; Malone, M. F.; Winter, H. H. *Polym. Bull.* **1986**, *16*, 83.
(10) Lyngaae-Jorgensen, J.; Sondergaard, K. *Polym. Eng. Sci.* **1987**, *27*, 344.
(11) Lyngaae-Jorgensen, J.; Sondergaard, K. *Polym. Eng. Sci.* **1987**, *27*, 351.
(12) Pistoor, N.; Binder, K., contributed paper, Tagung der Deutschen Physikalischen Gesellschaft, Fachausschuss Polymerphysik, Berlin, 1987.
(13) Cheikh Larbi, F. B.; Malone, M. F.; Winter, H. H.; Halary, J. L.; Leviet, M. H.; Monnerie, L. *Macromolecules* **1988**, *21*, 3532.
(14) Katsaros, J. D.; Malone, M. F.; Winter, H. H., submitted for publication in *Polym. Eng. Sci.*
(15) The phase diagram of this mixture exhibits lower critical solution temperature (LCST).
(16) Bird, R. R.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids*; Wiley: New York, 1977.

Notes

Characterization of Polymer Surfaces after KrF Laser Ablation by Infrared Spectroscopy

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Introduction

Pulsed ultraviolet laser radiation can lead to clean and precise material removal at the irradiated site of polymer surfaces. This phenomenon was discovered in the early 1980s using an excimer laser[1,2] and was termed ablative photodecomposition.[2] It has been reported that the absorption of laser light in polymers is governed by Beer's law and that the etch depth exhibits a logarithmic dependence on the incident laser fluence above a threshold value.[3-6] The penetration depth of ultraviolet laser light is usually greater than the etch depth, so that the surface left behind after ablation has been exposed to laser light. So far, the properties of only a few polymer surfaces after ablation have been studied by means of X-ray photoelectron spectroscopy (XPS) and wet chemical techniques.[7-9] In the case of two polymers, poly(ethylene terephthalate) (PET) and polyimide (PI), the oxygen-to-carbon atomic ratio at the surfaces after 193-nm laser ablation was found to decrease significantly.[7] A further study on PET suggested that the fresh surface created after ablation consisted of some oligomer.[8] In this note we report the results of attenuated total reflection infrared (ATR-IR) spectroscopy studies on modified PET and PI surfaces remaining after 248-nm laser ablation. The characterization of modified surfaces is performed with the spectral subtraction method.

Experimental Section

PET films (Toray Industries Inc., Lumirror, 70 μm thick) and PI films (Ube Industries Ltd., Upilex-S, 20 μm thick) were used as received. Laser pulses (248 nm, 20-ns fwhm) were produced from Lambda-Physik EMG 160 excimer laser at 1 Hz. The energy of the pulses was measured with a Gentec ED-200 joulemeter. On the basis of the threshold fluence for the ablation at 248 nm of PET (130 mJ/cm^2)[4] and of PI (27 mJ/cm^2 or 80 mJ/cm^2),[4,5] both polymer films were irradiated at a fluence of 145 mJ/cm^2 to obtain the fresh surfaces after ablation, using a quartz lens and a metal mask of 1.0-cm^2 area. Laser irradiation was carried out with a single laser pulse in air.

The IR spectra were recorded on a Digilab FTS-40 Fourier transform infrared spectrometer by an ATR attachment using a KRS-5 internal reflection element (IRE) at a nominal 45° angle of incidence. A total of 64 spectral scans were averaged at a resolution of 4 cm^{-1}.

Results and Discussion

The IR spectrum of an original PET film is shown in Figure 1a. The main absorption bands[10,11] associated with C=O (502 and 1716 cm^{-1}), C–O (1099 and 1245 cm^{-1}), and the aromatic ring (725, 872, and 1331 cm^{-1}) appear in the spectrum. The IR spectrum of a laser-irradiated PET film is shown in Figure 1b. The same absorption bands are observed in this spectrum; however, the relative intensity of an absorption band at 725 cm^{-1} is greater than that for the original PET film.

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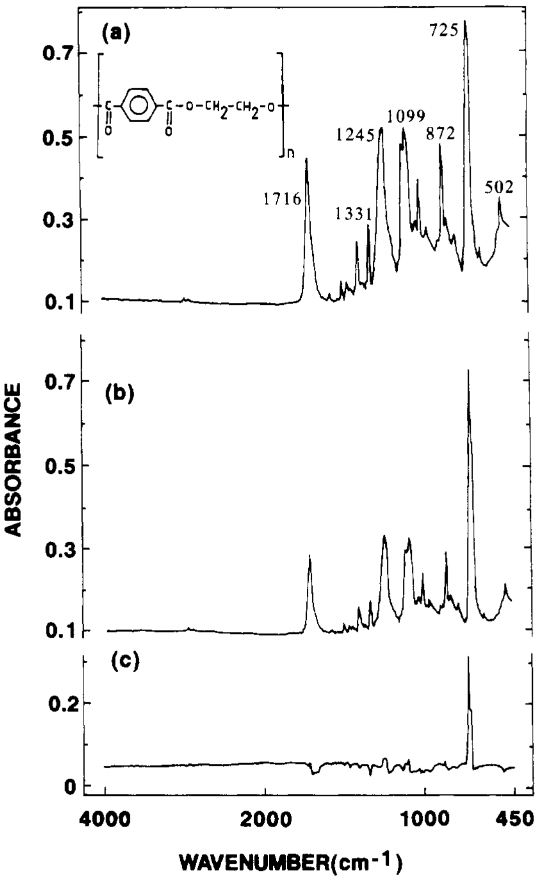

Figure 1. (a) IR spectrum of an original PET film. The chemical formula of PET is also presented. (b) IR spectrum of a PET film irradiated by a KrF laser at the incident laser fluence of 145 mJ/cm^2. (c) The difference spectrum of the spectrum of a PET film irradiated by a KrF laser minus the spectrum of an original PET film with a scale factor of 0.52.

As PET strongly absorbs 248-nm photons (absorption coefficient of 10^5 cm^{-1}),[12] the penetration depth (99% absorption) of 248-nm laser light in PET surface is limited to 200 nm, as is that of 193-nm laser light.[2] Some part of the PET surface exposed to laser light is etched away by ablation. On the other hand, the penetration depth, d_p, of the monitoring IR beam of wavelength λ in the ATR technique is given by the equation[13]

$$d_p = (\lambda/2\pi n_1)[\sin^2\theta - (n_2/n_1)]^{-1/2} \qquad (1)$$

where n_1 and n_2 are the refractive indices of the IRE and the sample, respectively, and θ is the incidence angle of the IR beam on the IRE–sample interface. In the present experimental arrangement, in which $n_1 = 2.38$ (for KRS-5), $n_2 = 1.64$ (for PET), and $\theta = 45°$, d_p is calculated to be 1.4–9.4 μm in the wavenumber region of 450–3000 cm^{-1}. Therefore, most of the absorbance in the spectrum of an irradiated PET film is attributed to the PET layer not exposed to laser light.

The characterization of the surface layer exposed to laser light has been performed with the following spectral subtraction method. At a wavenumber of ATR-IR spectra, the absorbance due to the surface layer exposed to laser light, A_s, can be evaluated from the relation[14]

$$A_s = A_i - fA_0 \qquad (2)$$

where A_i and A_0 are absorbances measured for a laser-irradiated film and for an original PET film, respectively, and f is a wavenumber-dependent scale factor due to exponential decay of the evanescent wave on penetration. Although simple subtraction using a constant f value in eq 2 does not provide quantitative absorbances for all spectral regions,[15] some characteristic bands for the surface layer exposed to laser light can be identified qualitatively.

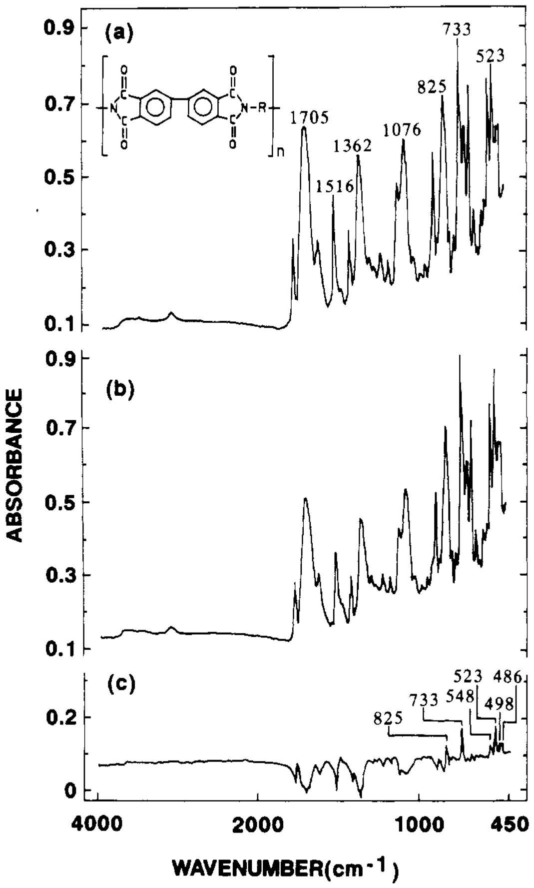

Figure 2. (a) IR spectrum of an original PI film. The chemical formula of PI (Upilex-S) is also presented. R indicates an oxydianiline derivative; the detailed chemical structure of the oxydianiline derivative is unknown. (b) IR spectrum of a PI film irradiated by a KrF laser at 145 mJ/cm^2. (c) The difference spectrum of the spectrum of a PI film irradiated by a KrF laser minus the spectrum of an original PI with a scale factor of 0.82.

An example of a difference spectrum obtained with a scale factor of 0.52 is shown in Figure 1c. The absorption band at 725 cm^{-1} (C–H out-of-plane bending vibration of aromatic ring) appears clearly above the base line, while most of the absorption bands appear near the base line. Therefore, the absorption band at 725 cm^{-1} can be identified as a band peculiar to the fresh surface after ablation. This absorption band suggests that the surface after ablation is mainly composed of aromatic rings. We have also confirmed the presence of a carbon-rich surface after 248-nm excimer laser ablation by XPS as well as the ablation with a 193-nm excimer laser.[16] The complementary results obtained from IR and XPS suggest the etching process is due to primary bond breakings between an aromatic ring and carbonyl groups in the PET molecule, followed by the ejection of carbon oxides. From the difference spectrum, only the absorption band associated with C–H out-of-plane bending vibration of the aromatic ring is identified for the surface layer exposed to laser light. This may result from the formation of new C–H bonds and other rearrangement reactions after bond breakings. The surface structure of PET after ablation is completely different from that after continuous irradiation of weak ultraviolet light, which results in the formation of carboxylic acid end groups.[17]

The IR spectra of PI films are also presented in Figure 2. The same absorption bands are observed in the spectra of an original PI film and of a laser-irradiated PI film. The main absorption bands[18-20] associated with C=O (1705 cm^{-1}), C–N (1362 cm^{-1}), C–O (1076 cm^{-1}), and aromatic rings (733 and 1516 cm^{-1}) appear in the spectra. The penetration depth of 248-nm laser light in a PI surface is limited to about 200 nm due to strong absorption of PI.[21,22] Also, the penetration depth of the IR monitoring beam in a PI film seems to be of the same order as that in a PET film.

An example of a PI difference spectrum obtained by subtraction method mentioned above with a scale factor of 0.82 is shown in Figure 2c. In the region of 900–4000 cm^{-1}, the absorption bands similar to those of PET are seen under the base line due to using a large scale factor, and there is no characteristic band of the modified surface. However, in the region of 450–900 cm^{-1}, several absorption bands are seen above the base line and can be identified as characteristic bands of the modified PI surface layer. From the molecular structure of PI, at least two distinct absorption bands associated with C–H out-of-plane bending vibration of aromatic rings could appear in the spectrum. The absorption band at 825 cm^{-1} can be assigned to a band associated with C–H vibration of aromatic rings directly bonded to carbonyl groups (1,2,4-substituted benzene ring).[23] In addition, similar to an absorption band at 725 cm^{-1} in the PET spectrum, the absorption band at 733 cm^{-1} can be assigned to a C–H vibration of oxydianiline derivative (probably 1,4-substituted benzene). According to the difference in IR absorption spectra of maleimide and phthalimide,[24] absorption bands at 486, 498, 523, and 548 cm^{-1} seem to be associated with other vibrations of aromatic rings of PI. As a result, it is suggested that the modified PI surface after ablation is mainly composed of aromatic rings. From the XPS studies, we have found a significant decrease in the atomic ratios (both oxygen to carbon and nitrogen to carbon) of PI surfaces remaining after 248-nm laser ablation.[16] As suggested by Yeh[25] from the etch product analysis for the ablation of PI, the primary cleavage reaction induced by laser irradiation is believed to be the rupture of imide rings.

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Registry No. Lumirror, 25038-59-9; Upilex-S, 32197-39-0.

References and Notes

(1) Kawamura, T.; Toyoda, S.; Namba, S. *Appl. Phys. Lett.* **1982**, *40*, 374.
(2) Srinivasan, R.; Mayne-Banton, V. *Appl. Phys. Lett.* **1982**, *41*, 576. Srinivasan, R.; Leigh, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 6784.
(3) Andrew, J. E.; Dyer, P. E.; Forster, D.; Key, P. H. *Appl. Phys. Lett.* **1983**, *43*, 717.
(4) Srinivasan, R.; Braren, B. *J. Polym. Sci.* **1984**, *22*, 2601.
(5) Brannon, J. H.; Lankard, J. R.; Baise, A. I.; Burns, F.; Kaufman, J. *J. Appl. Phys.* **1985**, *58*, 2036.
(6) Dyer, P. E.; Sidhu, J. *J. Appl. Phys.* **1985**, *57*, 1420.
(7) Lazare, S.; Hoh, P. D.; Baker, J. M.; Srinivasan, R. *J. Am. Chem. Soc.* **1984**, *106*, 4288.
(8) Lazare, S.; Srinivasan, R. *J. Phys. Chem.* **1986**, *90*, 2124.
(9) Burrell, M. C.; Liu, Y. S.; Cole, H. S. *J. Vac. Sci. Technol.* **1986**, *A4*, 2459.
(10) Miller, R. G.; Willis, H. A. *Trans. Faraday Soc.* **1953**, *49*, 433.
(11) Liang, C. Y.; Krimm, S. *J. Mol. Spectrosc.* **1959**, *3*, 554.
(12) Lazare, S.; Soulignac, J.; Fragnaud, P. *Appl. Phys. Lett.* **1987**, *50*, 624.
(13) Harrick, N. J. *Internal Reflection Spectroscopy*; Interscience: New York, 1967.
(14) Iwamoto, R.; Ohta, K. *Appl. Spectrosc.* **1984**, *38*, 359. Ohta, K.; Iwamoto, R. *Anal. Chem.* **1985**, *57*, 2491.
(15) The influence due to the difference of IR beam wavelength on the scale factor can be estimated by evaluating $\exp(-2z/d_p)$ at the two wavelengths,[14] where z is the thickness of the layer exposed to KrF laser light. According to the data by Srinivasan and Braren,[4] the etch depth per pulse at the influence of 145 mJ/cm^2 is about 100 nm. Consequently, assuming 100 nm as the thickness of the layer exposed to laser light, the values of $\exp(-2z/d_p)$ are 0.92 at 1700 cm^{-1} ($d_p = 2.5\ \mu$m) and 0.98 at 450 cm^{-1} ($d_p = 9.4\ \mu$m). The difference in scale factors to be used in the region of 450–1700 cm^{-1} is 7%.
(16) Kokai, F.; Saito, H.; Fujioka, T., unpublished results.
(17) Day, M.; Wiles, D. M. *J. Appl. Polym. Sci.* **1972**, *16*, 175.
(18) Ehlers, G. F.; Fisch, K. R.; Powell, W. R. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 3511.
(19) Salem, J. R.; Sequeda, F. O.; Lee, W. Y.; Yang, R. M. *J. Vac. Sci. Technol.* **1986**, *A4*, 369.
(20) Snyder, R. W.; Sheen, C. W.; Painter, P. C. *Appl. Spectrosc.* **1988**, *42*, 503.
(21) Koren, G.; Yeh, J. T. C. *J. Appl. Phys.* **1984**, *56*, 2120.
(22) Philipp, H. R.; Cole, H. S.; Liu, Y. S.; Sitnik, T. A. *Appl. Phys. Lett.* **1986**, *48*, 192.
(23) Shimanouchi, T.; Kakiuti, U.; Gamo, I. *J. Chem. Phys.* **1956**, *25*, 1245.
(24) For example: Simons, W. W., Ed. *The Sadtler Handbook of Infrared Spectra*; Sadtler Research Laboratories, Inc.: Philadelphia, PA, 1978.
(25) Yeh, J. T. C. *J. Vac. Sci. Technol.* **1986**, *A4*, 653.

Molecular Modeling of Polymers. 7. Ab Initio Demonstration of Torsional Angle Cooperativity in Linear Chains by Molecular Dynamics

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Cooperativity is a concept often invoked to explain physicochemical processes in macromolecular systems. Most notably, transition processes of macromolecules have been described in terms of cooperative behavior among the degrees of freedom of the macromolecules. The success of the Ising model[1] in characterizing helix–coil transitions illustrates the utility of the concept of cooperativity in polymer science. Still, the ab initio demonstration that cooperative behavior is intrinsic to high molecular weight linear molecules has remained elusive. We believe that we may have come upon evidence of cooperative behavior as part of a molecular dynamics (MD) simulation of the β-orthorhombic (β_o) to α-hexagonal (α_h) transition in the C_{21} n-alkane crystals.[2]

The full details of the MD simulation will be given later, but a brief description follows. A total of 12 21-carbon chains were placed in each of two layers of the β_o

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