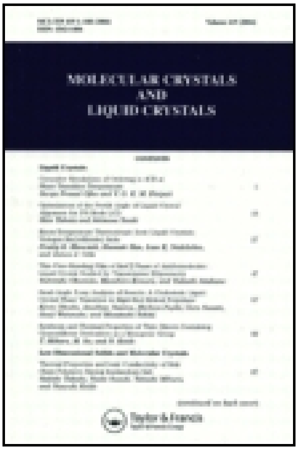

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic Field Effect on Laser Ablation of Organic Polymer Films as Revealed by Atomic Force Microscopy

Yasuyuki Tsuboi [a] & Akira Itaya [a]

[a] Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto, 606, Japan E-mail:

Version of record first published: 04 Oct 2006

Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 291–296
Reprints available directly from the publisher
Photocopying permitted by license only

Magnetic Field Effect on Laser Ablation of Organic Polymer Films as Revealed by Atomic Force Microscopy

YASUYUKI TSUBOI and AKIRA ITAYA
Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606, Japan.
e-mail: twoboys@ipc.kit.ac.jp or itaya@ipc.kit.ac.jp

A magnetic field effects on 308 nm excimer laser ablation of poly(N-vinylcarbazole) (PVCz) films was investigated by means of atomic force microscopy. The morphology of ablated surface exhibited characteristic modification by applying a magnetic field. An orientation pattern was observed on the polymer surface ablated in a horizontal magnetic field. PVCz films prepared by the cast-method in a magnetic filed were not oriented. A novel technique combining laser light and a magnetic field was developed for sub-micron surface patterning.

Keywords: laser ablation; atomic force microscopy; magnetic orientation; thin film; surface morphology; poly(N-vinyl carbazole)

INTRODUCTION

Recently laser ablation has been a subject of considerable interest[1], partly because of numerous technological applications with implication in surface patterning, modification, surgery, and so on. The innovation of atomic force microscope (AFM) which enables us to observe the surface morphology *softly* has accelerated such studies during past a few years. It has been revealed that the surface morphology was quite sensitive to the irradiation condition. Various methods have been developed to optimize the surface fabrication, a great part of which was focused mainly on laser parameters such as fluence, shot number, wavelength, pulse width, and polarization[2]. Further approach to modify and control the surface morphology is to employ an external physical perturbation in addition to laser light, however, such study has hitherto been limited. The external field may result in a novel mesoscopic structure and makes it possible to regulate the morphology more rigorously by adjusting two parameters of laser light and the perturbation independently.

Using a strong magnetic field as an external perturbation, quite recently we succeeded in forming a characteristic oriented pattern on polymer surfaces ablated with a nanosecond laser pulse, the essentials of which are presented in this paper. Past numerous studies have revealed that some organic compounds such as liquid crystalline polymers could be oriented regularly by applying an magnetic field[3]. The target material in the present work is poly(N-vinylcarbazol) (PVCz), a photoconductive polymer, of which photochemical and photophysical properties have been well examined. The mechanism of UV laser ablation of PVCz has been studied in detail by Masuhara et al.[4,5].

EXPERIMENTAL

PVCz was prepared by cationic polymerization and purified by repetitive reprecipitations. Cyclohexanone solution of PVCz obtained was coated onto a quartz substrate by a spinner, the prepared films were dried in a vacuum oven. The experimental setup is quite simple. A 308 nm excimer laser (Lumonics EX500, FWHM~15 ns) was used as an excitation light source. The sample plates were interposed horizontally between the poles of an electric magnet in such a way that the polymer surface was parallel to the direction of magnetic vector. The excitation pulse was irradiated vertically to the sample plate. The strength of a magnetic field was measured with a Gauss meter and fixed to 1.3 T. The irradiated surfaces were analyzed employing an atomic force microscope (Digital Instruments, Nanoscope III) in the tapping mode. All the experiments were performed in atmosphere and at room temperature.

RESULTS AND DISCUSSION

By analyzing laser fluence dependence of etch depth, the ablation threshold was evaluated to be ~30 mJ/cm^2, which was invariant by introducing a magnetic field. In the fluence region from 100 to 350 mJ/cm^2, the etch depth tended to slightly (~10 %) reduce by applying a magnetic field. AFM images of the surface morphology altered with a single pulse of 800 mJ/cm^2 are shown in Fig. 1. A striking feature which distinguishes the surface morphology modified in the presence of magnetic field (Fig. 1 (a)) from that in the absence of the field (Fig. 1 (b)) is that dot-structures are drawn up in rows with micron ~ sub-micron dimensions by a external magnetic field. The direction of the rows (orientation pattern) is perpendicular to that of a magnetic field. The perpendicular alignment was confirmed also for the surface ablated with a fluence of 300 mJ/cm^2.

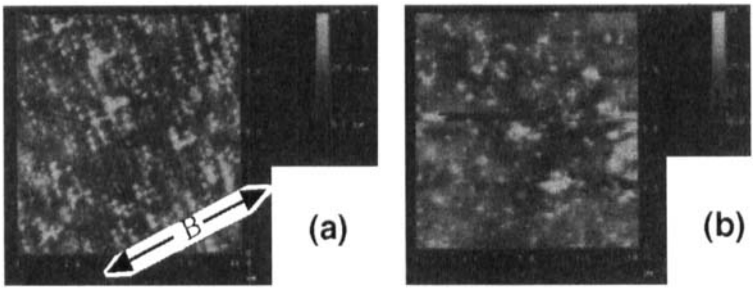

FIGURE 1 AFM images of PVCz surface ablated with a laser pulse of 800 mJ/cm^2 (10 μm(x) x 10 μm(y) x 50 nm (z)). (a) in the presence of a magnetic field (1.3 T). (b) in the absence of a magnetic field.

Thus, we have revealed that the morphology of irradiated surfaces are quite sensitive to an external magnetic field. Here we briefly discuss the mechanism responsible for the *laser-magnetic field induced surface orientation* (alignment). Note that such *linear* orientation pattern has never been achieved in the past related studies in which the external physical perturbation introduced was only laser light. Several orientation patterns in ablation have been reported so far, however, the origin of which has been the interference effect between the incident laser light and the scattered one by the material surface. Obviously, this is not for the present case because the orientation patterns were not obtained in the absence of a magnetic field. Since the energy of the present magnetic field is considered to be quite small compared to the thermal energy (kT), we should take various factors into account to elucidate the mechanism. It has been clarified that UV laser ablation of PVCz proceeds photothermally[4,5]. In addition, by analyzing birefringence, it has been once reported that PVCz could be oriented by applying an external magnetic field during cast process due to the anisotropy of magnetic susceptibility[6]. Hence, linear arrangement above the ablation threshold is explained tentatively as follows; the intense irradiation results in considerable temperature rise and melting, and then the polymer chain can be rearranged by a magnetic field. We also applied a magnetic field to the cast process of PVCz, and observed the cast film with a polarization microscope. In our experiment, however, no evidence for the orientation was obtained. Therefore, a simple model described above hardly holds for the present orientation in ablation. It is well known that radicals are densely ganerated in ablation by intense laser irradiation. Presumably, various organic radicals with large magnetic moments play a key role in the orientation. It is noteworthy here that the perpendicular orientation to a magnetic vector was recently observed also for crystal growth of organic molecules[7,8].

In summary, although the fundamental mechanism is not clear at present, we have demonstrated that an external magnetic field combined with laser ablation has a high potential to control and modify the polymer surfaces.

Acknowledgment

The present work was partly supported by the Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture of Japan (06239107 Priority-Area-Research "Photoreaction Dynamics" and

09740521)

References

[1.] R. Srinivasan and B. Braren, *Chem. Rev.*,**89**, 1303 (1989).
[2.] J. Heitz, E. Arenholz, D. Bauerle, R. Sauerbrey, and H. M. Phillips, *Appl. Phys. A*, **59**, 289 (1994).
[3.] W. R. Krigbaum, in *Polymer Liquid Crystal*, edited by A. Ciferri, W. R. krigbaum, and R. B. Meyer (Academic Press, London, 1982), Chap. 10.
[4.] H. Masuhara, S. Eura, H. Fukumura, and A. Itaya, *Chem. Phys. Lett.*, **156**, 446 (1989).
[5.] H. Fukumura, H. Hamano, and H. Masuhara, *J. Phys. Chem.*, **97**, 12110 (1993).
[6.] M. Nagao and A. M. Hermann, *J. Polym. Sci. Polym. Lett. Edn.*, **12**, 69 (1974).
[7.] A. Katsuki, R. Tokunaga, S-I. Watanabe, and Y. Tanimoto, *Chem Lett.*, 607 (1996).
[8.] Y. Tsuboi, H. Akita, K. Yamada, and A. Itaya, *Jpn. J. Appl. Phys.*, **36**, L1048 (1997).