Photoinduced surface relief structures formed on polymer films doped with photochromic spiropyrans

Takashi Ubukata,* Koji Takahashi and Yasushi Yokoyama

Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, Japan

ABSTRACT: Poly(methyl methacrylate) (PMMA) films containing photochromic spiropyran (SP) derivatives with an alkyl chain produced surface relief structures upon photoirradiation. The material moved from the dark to the irradiated part by the light longer than 350 nm from a high-pressure mercury lamp. This is the first example that the surface relief structures are formed on a polymer film containing a photochromic compound that is not an azobenzene-related compound. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: spiropyran; photoinduced surface relief

INTRODUCTION

A large dynamic motion amplified by photoisomerization has been receiving a great deal of attention in view of academic interests and potential technological applications.[1] In particular, optical microstructure patterning induced by the material migration over micrometer distances has received much attention since the pioneering two reports in 1995.[2,3] These structures, often called photoinduced surface relief gratings (SRGs),[4] are formed on various azobenzene-containing films composed of amorphous polymers,[2–4] liquid crystalline polymers,[5,6] sol–gel matrices,[7] and amorphous molecular materials.[8] Recently it has been reported that SRGs are formed even on a crystal.[9]

There are several publications devoted to easy fabrication of SRGs using the materials that are not containing azobenzene units.[10–17] Majority of them were composed of photocrosslinkable polymers[10,11] or photopolymerizable monomers,[12–14] in which the formation mechanism of SRGs is considered to be molecular diffusion from unilluminated parts to illuminated ones. Naturally, reversible SRG formation cannot be anticipated in this case. A few research groups have recently reported on fabrication of SRGs using the materials which have possibility of reversible SRG formation.[15–17] However, there are as yet no reports on examples of the reversible SRG formation, which is one of the most

advantageous properties of SRG, except for the azobenzene-containing materials. When the reversible SRG formation on the films containing a photochromic compound other than azobenzene becomes possible, a number of ways of application will be expected, in addition to obtaining the important knowledge as to the SRGs formation mechanisms. Therefore, we have started the research to find the novel agents that can induce SRGs.

In the beginning, we employed spiropyran (SP) derivatives because they represent thermally reversible photochromic compounds like azobenzenes.[18–21] SP derivatives show a large structural change upon photoirradiation; an approximately 90° rotation of one half of the molecule occurs during the ring-opening and closing reactions between the spiro and the merocyanine forms (Fig. 1). Among the SP derivatives known to date, we chose **1**, which shows the negative photochromism; the ring-opened colored merocyanine form (MC form) is more stable than the ring-closed spiro-form (SP form). Therefore, **1** has a strong and broad absorption band in the visible region and exhibits bright red–purple color both in solution and polymer films. Recently, we have reported that Langmuir–Blodgett films of **1** changed its topography upon photoirradiation, indicating that the change in the molecular structure induced the macroscopic shape.[22] This means that **1** has the advantageous nature that the change in the molecular structure can be transferred to the bulk environmental shape with amplification to a certain extent. We here report the formation of the photoinduced surface relief structures using **1** and other SP derivatives (Fig. 1).

Correspondence to: T. Ubukata, Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, Japan.
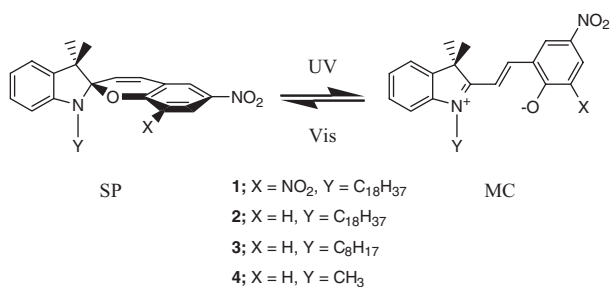E-mail: ubukata@ynu.ac.jp

Figure 1. Interconversion of merocyanine (MC) and spiropyran (SP) isomers of **1–4**

RESULTS AND DISCUSSION

Photochromism of **1**

SP **1** exhibited negative photochromism either in solution or in polymer films upon irradiation with 505-nm light. Figure 2 shows the change in absorption spectra of decoloration of **1** in a poly(methyl methacrylate) (PMMA) film during 505-nm light irradiation. The absorbance at the absorption maximum (544 nm) decreased to 1% of the original at the photostationary state, where the back-and-forth rates of isomerization are the same. The backward ring-opening coloration reaction took place thermally.

Surface relief formed on **1**-doped film

Figure 3 shows the surface relief structure produced by the patterned light irradiation through a photomask. When the light was shaded completely, only a flat surface was observed as shown on the left-hand side of Fig. 3a. On the other hand, when the film was irradiated with patterned light, regular surface modulation was produced, and its spatial period was coincident with that of the photomask as shown on the right-hand side of Fig. 3a. When we examined the cross-sectional topography, we found that the top of the convex is higher than
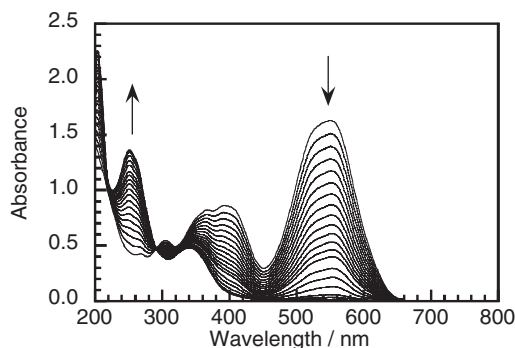

Figure 2. Changes in the UV–vis absorption spectra of a **1**-doped PMMA film upon irradiation with 505-nm light. Irradiation periods are 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 15, 17, 20, 25, 30, and 60 min
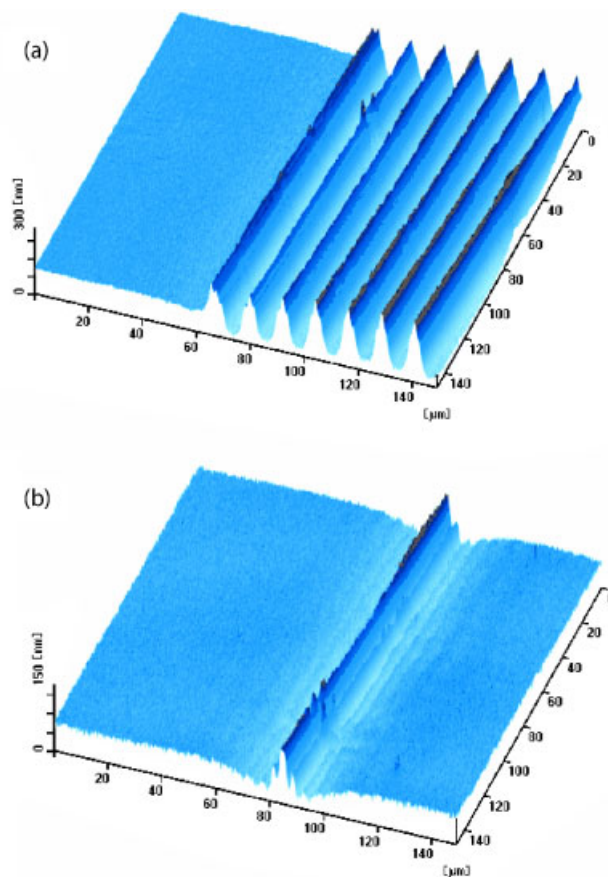

Figure 3. Atomic force microscopy image of a **1**-doped PMMA film (60 wt% of **1**) after exposure to high-pressure mercury lamp (>350 nm) with 100 mW cm^{-2} for 2 h through a photomask. The photomask was composed of stripes with the same widths (6.25 μm) of the transparent and opaque lines (a), and of one slit line with 6.25-μm width (b). This figure is available online at www.interscience.wiley.com/journal/poc

the initial surface level and base of depression is lower than the initial level. This result clearly shows that the lateral material motion occurred at the film surface.

In order to investigate the direction of material migration, an irradiation experiment through a photomask possessing one slit line with 6.25-μm width was performed (Fig. 3b). In the case of a **1**-doped PMMA film, irradiation produced a significant topographic maximum, indicating that polymer migration occurred from the shaded areas to the exposed areas. The direction of migration was the same for all of our experiments, irrespective of the materials used (see below).

To induce surface relief structures, we have to irradiate with a light of proper wavelength. Long wavelength light, such as g-line (436 nm) that only MC form absorbs, did not induce the surface relief structures on the film. Shorter wavelength lights with higher photon energy such as i-line (366 nm) and h-line (405 nm) were adequate to induce SRGs. This criterion coincides with the absorption band of SP form as shown in Fig. 2. It means that the back-and-forth photoisomerization between MC and SP

forms is inevitable to form SRGs. In azo-polymers, it is believed that the *trans–cis–trans* isomerization cycles to induce the decrease in the viscosity of the film[23] have played an important role in the formation of SRGs. Therefore, as for the case of **1**, increase in the photoinduced flexibility of the film caused by the large motion of the **1** molecules during the iterative photo-isomerization must be one of the requirements to induce the material transfer.

It was reported that while the low-molecular-mass azobenzene-dye-doped systems exhibited rather small ability to form SRG (a few ten nm), the covalently bonded azobenzene polymer systems usually showed several hundred nanometer height differences.[24,25] On the other hand, we observed SRGs with large surface modulation in SP dye-doped polymer systems. This difference was probably due to the high solubility of **1** to the polymer matrix, showing no dye–polymer segregation even at a relatively high concentration. Differential scanning calorimetry revealed that the mixture of **1** and PMMA (60/40 wt%) gave obscure glass transition temperature (T_g) at 38 °C, which was 66 °C lower than that of the pure PMMA. Although the irradiation through the photomask was carried out under room temperature, the temperature at the irradiated part became 50–60 °C. It should be concerned with the smooth material migration observed in the **1**-doped PMMA film that the photoirradiation was carried out at higher temperature than T_g.

In order to know the limit of concentration of **1** in PMMA film, SRG formation experiments were done at different concentrations. Figure 4 displays the surface modulation depth of the PMMA films doped with **1** after UV light treatment for 2 h at various dye concentrations. Height differences of surface relief increased with the increase in the concentration of **1** when it was more than 50 wt%. However, when it came to exceed 75 wt%, the SRG formed on the film was not so distinct. It should be due to the formation of aggregation of **1**. In other words, the ability for SRG formation was excellent when the concentration of **1** was as high as possible so far as a uniform film was maintained. This result is similar to the
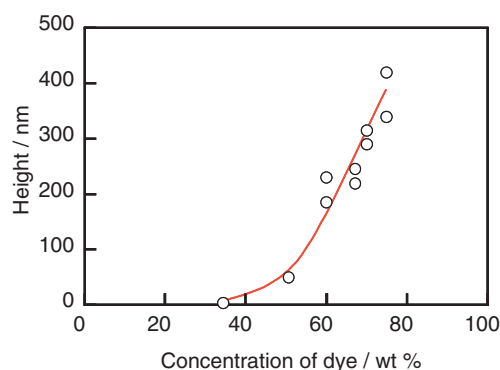
azobenzene-functionalized polymer systems.[26] This result may have relations with the decline of viscosity caused by the increase in the frequency of the cycle of photoisomerization per unit volume and time. This hypothesis was supported by the result that the formation speed of SRG was increased by the increase in the light power for inscription. In a practical sense, data in Fig. 4 further indicate that the SRG formation efficiency is readily tunable simply by changing the ratio of compounds, which would eliminate the tedious task of the chemical modifications of polymer structures.

Surface relief formation of SP derivatives

Grating formation experiments on the PMMA films doped with mononitro **2**–**4** were also investigated as listed in Table 1. The ratios of the SP derivatives were set to 60 wt% for all the mixture films. Regularly spaced SRGs were obtained on the films of **2**–**4** as well, similar to the case of **1**. However, the modulation depth was shallower than that of **1** under the same conditions.

SP **1**, possessing two electron-withdrawing nitro groups on the chromophore to stabilize the colored zwitterionic open-ring form, shows negative photochromism. On the contrary, **2** shows the positive photochromism because the colored form is less stable than the colorless form. These differences may have affected the photoreactivity and the ability of SRG formation. More importantly, long alkyl chain on the nitrogen atom plays the decisive role to improve the ability of SRG formation, by comparing the modulation depth obtained from electronically equivalent **2**–**4**. This result indicates, by taking the results of the SRG formation in the azobenzene dye systems into account, that the large structural change during the photoisomerization is the essential factor. Entwining of the polymer chain with the long alkyl chain of SP dyes may be important because of the host–guest system in our case.

Unfortunately, reversibility was not recognized in the SRGs formed in the films composed of SPs. It should be ascribed to low durability of the SPs against the UV light. Reversible SRG formation is anticipated using the other photochromic compounds with high durability against UV light, and will be the subject of our future investigation.

Figure 4. Effect of dye concentration on surface modulation depth of the samples after irradiation through a photomask. This figure is available online at www.interscience.wiley. com/journal/poc

Table 1. Modulation depth and shape of surface relief in SP-doped PMMA films

Spiropyran	Type of photochromism	Approximate height (nm)	Shape
1	Negative	200	Convex
2	Positive	80	Convex
3	Positive	30	Convex
4	Positive	10	Complex[a]

[a] Basically, convex shape was observed, though the head was sunk.

In conclusion, permanent SRGs with a few hundred nanometer depths are recorded on the surface of a PMMA film doped with SP derivatives. As far as we know, this is the first SRG formation using a photochromic compound other than the azobenzene derivatives.

EXPERIMENTAL

Materials

A series of SPs was synthesized by the condensation of a nitrosalicylaldehyde with an N-alkylindolenium bromide, as described in the previous report.[22] Matrix polymer, PMMA, $(C_5H_8O_2)_n$ $(n = 1000–1500)$, was purchased from Wako Pure Chemical Industries, Ltd. Chloroform for film preparation was of spectroscopic grade (Junsei Chemical).

Film preparation

The spin-coated films were prepared from the chloroform solutions of each SP derivative and PMMA on a cleaned glass substrate. The thickness of films was measured using a DEKTAK3 (Sloan Co.). The thickness ranged from 0.2 to 0.6 μm depending on the concentration of SP derivatives. Typically, the film was composed of 60% of SP and 40% of PMMA in weight, with 0.3-μm thickness.

Photoirradiation

Patterned light irradiation to form surface relief structures was performed through a custom-made photomask (Toppan Printing Co.) attached to the film.[27] The light was collimated to obtain a homogeneous light intensity (100 mW cm^{-2}) over the entire area to be exposed. The wavelength of the light for irradiation longer than 350 nm was taken out from a high-pressure mercury lamp (USHIO electric, SX-UI 500HQ) by a long pass filter UV35 and a 5 cm water filter. The emission line of 505 nm for photochromism was separated by filters (a 5 cm water filter, a Y-47 glass filter, a KL-50 interference filter, and an IRA-25S glass filter).

Physical measurements

UV–vis spectra were recorded on a JASCO V-550 UV–vis spectrometer or a Shimadzu Multispec-1500 UV–vis spectrometer. The surface relief structures were observed through a differential interference microscope (Olympus, BX50) and an AFM using an SII SPA300 module with an SPI3800N probe station in the cyclic contact mode. Thermal properties were studied by differential scanning calorimetry (SII, DSC6100) with a scanning rate of 10 $°$C min^{-1}.

REFERENCES

1. Yu YL, Nakano M, Ikeda T. *Nature* 2003; **425**: 145.
2. Rochon P, Batalla E, Natansohn A. *Appl. Phys. Lett.* 1995; **66**: 136–138.
3. Kim DY, Tripathy SK, Li L, Kumar J. *Appl. Phys. Lett.* 1995; **66**: 1166–1168.
4. Viswanathan NK, Kim DY, Bian S, Williams J, Liu W, Li L, Samuelson L, Kumar J, Tripathy S K. *J. Mater. Chem.* 1999; **9**: 1941–1955.
5. Pedersen M, Hvilsted S, Holme NCR, Ramanujam PS. *Macromol. Symp.* 1999; **137**: 115–127.
6. Zettsu N, Ubukata T, Seki T, Ichimura K. *Adv. Mater.* 2001; **13**: 1693–1697.
7. Darracq B, Chaput F, Lahlil K, Lévy Y, Boilot JP. *Adv. Mater.* 1998; **10**: 1133–1136.
8. Nakano H, Takahashi T, Kadota T, Shirota Y. *Adv. Mater.* 2002; **14**: 1157–1160.
9. Nakano H, Tanino T, Shirota Y. *Appl. Phys. Lett.* 2005; **87**: 061910.
10. Yamaki S, Nakagawa M, Morino S, Ichimura K. *Appl. Phys. Lett.* 2000; **76**: 2520–2522.
11. Ono H, Emoto A, Kawatsuki N, Hasegawa T. *Appl. Phys. Lett.* 2003; **82**: 1359–1361.
12. Park JH, Yoon TY, Lee WJ, Lee SD. *Mol. Cryst. Liq. Cryst.* 2002; **375**: 433–440.
13. Zhou J, Sun C, Xiong B, Wang J, Luom Y. *Appl. Phys. Lett.* 2004; **84**: 3019–3021.
14. Ramanujam PS, Berg RH. *Appl. Phys. Lett.* 2004; **85**: 1665–1667.
15. Baldus O, Leopold A, Hagen R, Bieringer T, Zilker SJ. *J. Chem. Phys.* 2001; **114**: 1344–1349.
16. Krebs FC, Ramanujam PS. *Opt. Mater.* 2006; **28**: 350–354.
17. Taguenang JM, Kassu A, Govindarajalu G, Dokhanian M, Sharma A, Ruffin PB, Brantley C. *Appl. Opt.* 2006; **45**: 6903–6909.
18. Berkovic G, Krongauz V, Weiss V. *Chem. Rev.* 2000; **100**: 1741–1753.
19. Minkin VI. *Chem. Rev.* 2004; **104**: 2751–2776.
20. Schaudel B, Guermeur C, Sanchez C, Nakatani K, Delaire JA. *J. Mater. Chem.* 1997; **7**: 61–65.
21. Raymo FM, Giordani S, White AJP, Williams DJ. *J. Org. Chem.* 2003; **68**: 4158–4169.
22. Yokoyama Y, Hara W, Inoue T, Ubukata T, Sakomura M, Tukada H. *Chem. Lett.* 2005; **34**: 1622–1623.
23. Srikhirin T, Laschitsch A, Neher D, Johannsmann D. *Appl. Phys. Lett.* 2000; **77**: 963–965.
24. Fiorini C, Prudhomme N, Veyrac G, Maurin I, Raimond P, Nunzi JM. *Synth. Met.* 2000; **115**: 121–125.
25. Labarthet FL, Buffeteau T, Sourisseau CJ. *J. Phys. Chem. B* 1998; **10**: 2654–2662.
26. Fukuda T, Matsuda H, Shiraga T, Kimura T, Kato M, Viswanathan NK, Kumar J, Tripathy SK. *Macromolecules* 2000; **33**: 4220–4225.
27. Ubukata T, Higuchi T, Zettsu N, Seki T, Hara M. *Colloids Surf. A* 2005; **257–258**: 123–126.