Highly Efficient Photogeneration of Surface Relief Structure and Its Immobilization in Cross-Linkable Liquid Crystalline Azobenzene Polymers

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ABSTRACT: A new family of azobenzene containing polymer applicable for photoinduced surface relief formation is reported. An azobenzene containing acrylate was copolymerized with methacrylate monomers bearing an oligo(ethylene oxide) chain via free radical copolymerization, yielding soft liquid crystalline polymers. These copolymers displayed a smectic liquid crystal phase at room temperature. After preexposure to ultraviolet light, thin films of the liquid crystalline polymers showed highly sensitive photoinduced material transfer to generate the surface relief structures. The typical exposure dose required for full polymer migration was as low as 50 mJ cm^{-2}. The inscribed surface relief structures could be rapidly and fully erased either upon incoherent nonpolarized ultraviolet light irradiation or by heating close to the clear point of the soft liquid crystalline polymers. On the other hand, the chemical cross-linking, using a mixed vapor of hydrogen chloride and formaldehyde after surface relief inscription, resulted in a drastic improvement of the shape stability, maintaining the structure at high temperatures up to 250 °C. After cross-linking, the trans-to-cis photoisomerization readily proceeded without any modification of the surface morphology and can therefore be applied to the photoswitchable alignment of nematic liquid crystals.

Introduction

Since the discovery in 1995,[1−6] studies on photoinduced surface relief grating (SRG) have been a fascinating research area of azobenzene (Az) polymer chemistry due to the basic phenomenological interests and attractive technological possibilities. Most SRGs were frequently inscribed onto amorphous Az polymer films by exposure to interference argon ion laser (Ar$^+$) beams. Sinusoidal undulations were constructed through a photoinduced lateral movement of polymer chains at micrometer level distances. The periodicity and height of the inscriptions can be actually controlled on demand by the irradiating conditions such as the interference angle, exposure energy, and polarization combinations of the writing beams.

To date, various types of Az containing materials have been employed for SRG studies, including amorphous polymers,[1−6] liquid crystalline polymers,[7−10] host−guest systems,[11] and so forth.[12−14] We have recently reported that a marked rapid mass migration takes place in a liquid crystalline Az polymer hybridized with a low-molecular-mass liquid crystal molecule.[15] The total photon dose required for the full SRG inscriptions can be reduced by a level of approximately 3 orders of magnitude. Without hybridization of the liquid crystal molecule, no appreciable surface undulation was formed. It is probable that addition of the liquid crystal molecule enhanced the fluidity of the material, thereby favoring the effective mass migration. However, this approach suffered from a drawback. In that, the resulting relief structure was unstable at elevated temperatures. Shape stability, in terms of long time storage and durability at higher temperatures, is of great demand in photonic applications such as waveguide couplers and aligning layers for liquid crystals. To solve this issue, some research groups have adopted various amorphous azobenzene polymers with high glass transition temperatures (T_g) such as azocarbazole-based polyimide,[16] polyurethane containing V-shaped bisazo unit,[17] and maleimide-based polymer.[18] However, use of high-T_g polymers leads to significant reductions in the efficiency of the mass transport; the requirement for typical total photon dose reaches a level of few hundred J cm^{-2}.

In the above contexts, we present herein a new family of Az polymers that fulfills both requirements of high sensitivity and shape stability in SRG formation. Our strategy involves two steps: first, rapid SRG inscription, and second, chemical cross-linking in a vapor phase for persistent storage of the relief structure. On the basis of this idea, we have designed a series of soft cross-linkable Az containing copolymers possessing an oligo(ethylene oxide) side chain.[19] In this case, the oligo(ethylene oxide) chain plays two important roles. First, the flexibility of the chain lowers the T_g, which favors efficient mass transport. Second, the terminal hydroxyl group can be utilized for chemical cross-linking after the relief inscription. This paper describes the details of such an investigation and presents the photoswitching of liquid crystal alignment on the fixed SRG films as a typical example for the application of this strategy.

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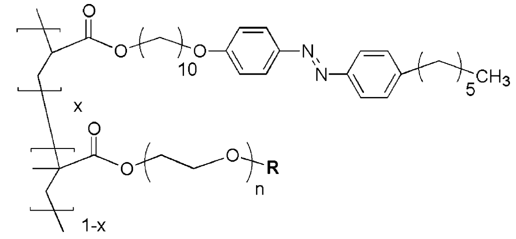
Scheme 1. Chemical Structures of Cross-Linkable Liquid Crystalline Azobenzene Polymers



Experimental Section

Materials. The Az chromophore containing an acrylate monomer, 10-{4-[(4′-hexylephenyl)azo]phenoxy}decyl acrylate, was synthesized according to the published method.[20] Methacrylate monomers possessing an oligo(ethylene oxide) chain were kindly supplied by NOF Corp., Japan. Three types of oligo(ethylene oxide) containing monomers were employed, with various side chains of $(-O-CH_2-CH_2)_nOH$, with $n = 4.5$ (PE4.5, mixture of 4 and 5) and 8 (PE8), and the $(-O-CH_2-CH_2)_nOCH_3$ side chain with $n = 4$ (PME4).

Polymerization. The Az polymers were synthesized via the free radical polymerization of an acrylate monomer bearing the Az moiety and a (meth)acrylate monomer containing the oligo(ethylene oxide) chain (Scheme 1). The resulting copolymers are abbreviated as 6Az10Ac-PE*n*(*x*), where the *n* and *x* indexes denote the unit number of oligo(ethylene oxide) and the content of Az units in mole percent, respectively. The homopolymer of the Az containing acrylate was also synthesized and is abbreviated as p6Az10Ac. Copolymerization was performed in a mixed solvent of benzene and tetrahydrofuran (THF) (4:1 by weight) containing 2,2-azobis(isobutyronitrile) (AIBN) as an initiator. The reaction media was heated under reflux for 6 h, cooled to room temperature, and then poured into vigorously stirred ethanol. The resulting copolymer was collected by centrifugalization. The orange viscous solid obtained was dried in vacuo. The reaction yields were approximately 70%.

Polymer Characterization. The weight-average molecular weight (M_w) was determined by gel permeation chromatography (GPC) calibrated with polystyrene standards (JASCO: 875-UV, column: Shodex K800P and K-805L, eluent: THF). The content of Az unit in the resulting copolymers were estimated by ultraviolet−visible absorption spectroscopy (UV−vis, Hewlett-Packard: 8452A diode array spectrometer) using the molar extinction coefficient of Az at 352 nm ($\lambda_{352} = 30\ 000$ M^{-1} cm^{-1}). The thermotropic behavior and liquid crystalline phase analysis were examined on a differential scanning calorimeter (DSC, Seiko Instruments: DSC-200) and polarizing optical microscope (POM, Olympus: BH-2) equipped with a temperature-controlled hot stage (Mettler: FP-80).

Methods. a. Holographic Irradiation. Polymer thin films were prepared by spin-coating on a cleaned quartz substrate from a 3 wt % THF solution at 2000 rpm for 30 s. The films were dried at 60 °C for 10 min under vacuum conditions. The thickness of the films was typically 100 nm as evaluated by surface profilometory (Sloan/ULVAC: Dektak^{3}ST). Preirradiation with ultraviolet (UV) light at 365 nm was achieved with a high-pressure mercury lamp (San-ei Electric MFG: Supercure-203S) equipped with an appropriate set of optical filters (Toshiba glass: UV-D36A and UV-35). Surface relief gratings were inscribed on the films at room temperature using s-polarized interfering beams. Details regarding the optical setup used have been previously reported.[15] The intensity of the recording beam from an argon ion (Ar^+) laser (Omnichrom 543R-AP-A01), after passing through the collimating lens, was 2 mW cm^{-2}. The angle between the two writing beams was 7°, providing a grating periodicity Λ of 4 μm. The formation of the SRG was monitored from the change in the first-order diffraction intensity of a helium−neon (He−Ne) laser beam on the transmission side using a photodetector. The relief structures were visualized by atomic force microscope (AFM) in a cyclic contact mode (Seiko Instruments: SPA300/SPI3700).

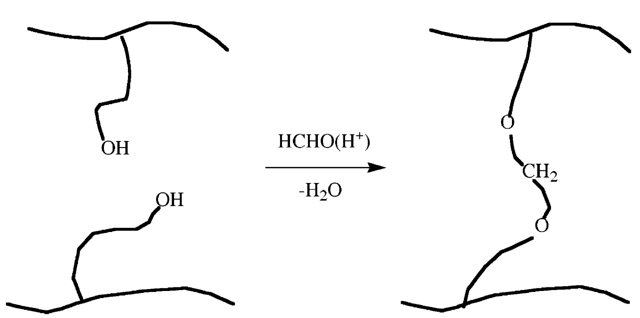


Figure 1. Scheme of the acetal reaction of two hydroxyl groups located at the terminus of an oligo(ethylene oxide) side chain.

Table 1. Characterizations of the Polymers

polymer[a]	*n*	R	M_w/ $\times 10^4$	*x*/ mol %[b]	phase transition behavior/°C
p6Az10Ac	4.5	H	0.8	100	T_g 45 Sm 95 I
p6Az10Ac-PE4.5(30)	4.5	H	1.9	30	T_g 8 Sm 85 I
p6Az10Ac-PE4.5(50)	4.5	H	1.0	50	T_g 16 Sm 85 I
p6Az10Ac-PE4.5(80)	4.5	H	2.0	80	T_g 20 Sm 85 I
p6Az10Ac-PE48(50)	8.0	H	1.5	50	T_g 20 Sm 80 I
p6Az10Ac-PME4(30)	4.0	CH_3	2.6	30	T_g 4 Sm 45 I

[a] The index "4.5" means mixture of 4 and 5. [b] Mole percent of azobenzene containing unit as determined by UV−vis spectroscopy measurements.

b. Postfixation. The chemical cross-linking for the relief-inscribed film was carried out via acetal reaction between two hydroxyl groups located at the terminus of the oligo(ethylene oxide) side chain in the vapor phase (Figure 1).[21] Two flat containers, filled with a 6 N hydrochloric acid aqueous solution and a formaldehyde (30 wt %) aqueous solution, were placed together with the relief-inscribed film within a sealed vessel. After a 6 h period of storage at room temperature, the vessel was opened. The film was washed with pure water (Millipore grade) and then insufflated with dry nitrogen gas for drying purposes. The stability of the resulting relief structure was evaluated by monitoring the changes in the first-order diffraction efficiency of the He−Ne laser beam during a heating process. The heating rate was 2.0 °C s^{-1} from room temperature.

c. X-ray Measurement. X-ray diffraction analysis was performed (Philips, X'Pert PW 1711) for a spin-coated 200 nm thick film of p6Az10Ac-PE4.5(50) using Cu Kα radiation with a wavelength of 1.54 Å and operated in the range of 2θ between 1° and 30°.

d. Fabrication of a Liquid Crystal Cell. A vacant cell was assembled using a pair of fused silica plates. One of the plates was covered with a cross-linked SRG film and the other with a self-assembled layer of *n*-octadecyltriethoxysilane (ODS, Chisso Corp.). ODS treatment of the substrate was achieved according to the literature.[22] The cell gap was adjusted by using silica particle spacer (12 μm). The cell was then filled with a nematic liquid crystal material, NPC-02 (Rodic Co. Ltd.). This hybrid cell was exposed to nonpolarized light with normal incidence at 365 or 436 nm. The orientation of the liquid crystal molecules was evaluated by POM observation.

Results and Discussion

Characterizations of the Polymers. The copolymers containing different Az contents were successfully synthesized by free radical polymerization. Most of the polymers were obtained as an orange viscous solid. The results of characterization performed on the synthesized polymers are summarized in Table 1. Molecular weights (M_w) were in the range (0.8−2.6) × 10^4. The resulting

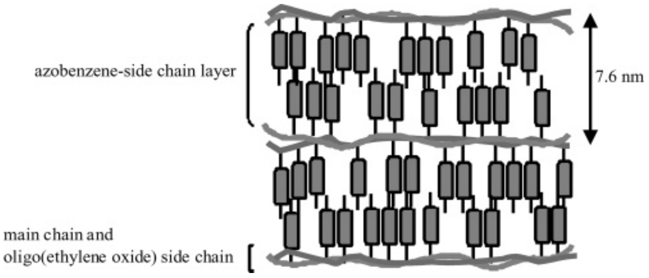


Figure 2. Schematic illustration of a possible microstructure formed in the p6Az10Ac-PE4.5(50) film at room temperature.

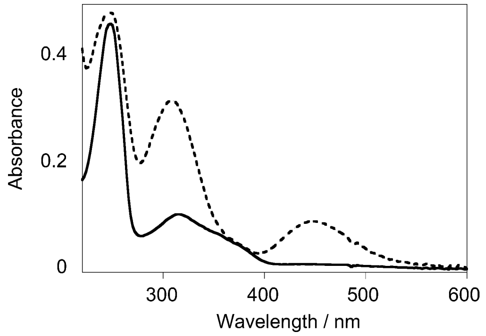


Figure 3. UV−vis absorption spectral changes of p6Az10Ac-PE4.5(50) film before (solid) and after illumination with 365 nm light (dotted) at the photostationary state.

Az contents were almost in agreement with that expected from the feed ratio.

The DSC analysis and POM observations revealed that all of the polymers display transitions from a glassy state, smectic liquid crystal phase, and isotropic liquid state on heating. With respect to thermal properties in relation to chemical structure, the followings issues can be extracted: (i) All copolymers revealed lower T_g than the homopolymer (p6Az10Ac). This can be ascribed to the introduction of the flexible soft segment in the polymer. (ii) The increase in the Az content for the series of PE4.5 (30, 50, and 80%) revealed a slightly raised T_g, which is also explained by the reason given in (i). (iii) The unit length of ethylene oxide in PE ($n = 4.5$ or 8) did not affect the transition behavior. (iv) Substitution to a methyl group for hydrogen at the terminus (R in Scheme 1) resulted in significant decreases of both T_g and the isotropization temperature, suggesting that a hydrogen-bonding network is formed via the hydroxyl terminal polymers. It should be noted that the all copolymers in the trans state of Az revealed the semctic phase (Sm) at room temperature when the experiments were performed.

The X-ray diffraction profile for a p6Az10Ac-PE4.5(50) film at room temperature displayed a defined peak at $2\theta = 1.2°$, which corresponds to a layer spacing of 7.6 nm. This spacing corresponds to a long-range ordering of approximately twice the length of the fully extended Az side chain. From this evidence, it seems that a hydrogen-bonding network is effectively formed in the bilayered state where the Az side chains and oligo(ethylene oxide) chains are phase separated at the nanometer level, as shown in Figure 2. Interestingly, the layer spacing was retained with some shifts also above the isotropization temperature. This result indicates that such nanophase separation is maintained even above the optical clearing point. Therefore, the present polymer shows an isotropic state at higher temperatures, which in terms of the optical property does not indicate a complete randomization at the molecular level. This structural feature may be attributed to the strongly exclusive characteristic between the hydrophobic Az side chain and the hydrophilic oligo(ethylene oxide) chain containing a comparable volume.

Photoisomerization Behavior in Spin-Cast Film. The copolymers used in this study exhibited a low ordered smectic liquid crystal phase at room temperature. Figure 3 shows typical changes of ultraviolet−visible (UV−vis) absorption spectra of p6Az10Ac-PE4.5(50) film before and after UV light irradiation. The absorption maximum ($\lambda_{\max}$) for the $\pi-\pi^*$ band of trans Az for the copolymers in THF was positioned around 352 nm, whereas that of the spin-coated film showed a large hypsochromic shift to 316 nm with significant broadening (solid line). This could be explained as the consequence of partial H-aggregation of Az units. The spectrum was measured with normal incidence, so that the significantly small absorbance of the $\pi-\pi^*$ band indicates an upright orientation of the Az chromophore with respect to the film plane. Irradiation with UV light enhanced the $n-\pi^*$ transition band for the cis form at approximately 440 nm (dotted line). This result indicates that the H-aggregation was disorganized to give a cis-rich state via efficient photoisomerization. It is well-known that trans to cis photoisomerization of the azobenzene moiety in a nematic[23] or smectic[24] liquid crystalline polymer can lead to a melt with an ordered phase structure. Subsequent irradiation at 436 nm results in the absorption spectrum almost reverting back to its original features. Such recovery of H-aggregation and upright orientation is evidential of dynamic self-organization behavior, which is characteristic for the process of photochemical phase transition from an isotropic to a smectic phase in the side chain Az polymer films.[25−27]

Photoinduced Surface Relief Gratings. a. Surface Relief Formation. Surface relief gratings were directly inscribed onto the films using the interference pattern of an Ar^+ laser. Figure 4a shows the changes in the first-order diffraction intensity as a function of irradiation time for the UV-treated film (open circle) and as-cast film (closed circle) for p6Az10Ac-PE4.5(50) as typical examples. A sharp increase in diffraction intensity was observed for the UV-treated film after an induction time of approximately 1 s, and the intensity became saturated at 7 s. In contrast, without preexposure treatment, there was no diffracting beam observed at low-intensity exposure.

Figure 4b shows the topological AFM image of the film after exposure to the interference Ar^+ laser beam for 10 s at 2 mW cm^{-2}. The surface topology features exhibited a sinusoidal shape with a modulation depth of approximately 200 nm with a grating spacing of approximately 4 μm, as evident in the figure,. The height difference was approximately double thickness of the initial flat film (approximately 100 nm), indicating that mass migration was almost fully achieved during such a short exposure period. This light sensitivity was very similar to that observed in the Az polymer−liquid crystal hybrid materials.[15] The efficiency of the photoinscribed surface relief grating is enhanced by approximately 1000 those of other hitherto reported Az polymer systems.[1−14] All copolymers under investigation displayed essentially the same behavior when the UV preirradiation was applied. Without preexposure treatment, no appreciable SRG was formed when the identical irradiation procedures were applied.

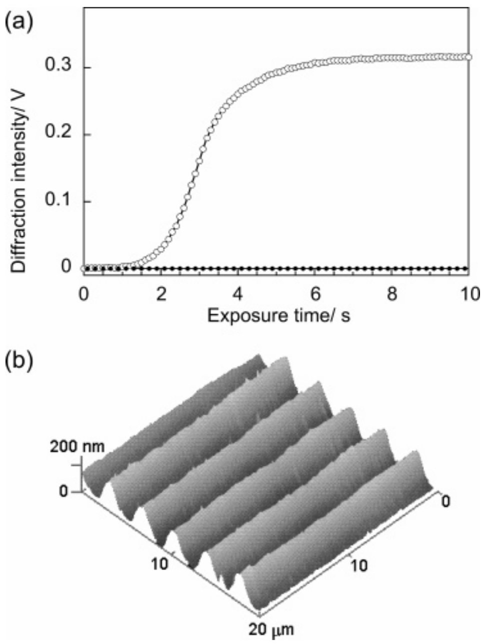


Figure 4. (a) Growth of the first-order diffraction intensity as a function of irradiation time for the UV-treated film (open circle) and as cast one (closed circle) for p6Az10Ac-PE4.5(50) as typical examples. (b) The corresponding AFM scan of the surface topography.

In sharp contrast with the copolymers, there was virtually no enhancement of the diffraction intensity observed for the homopolymer. The first-order diffraction efficiency reached only 0.05% even after a large exposure of 1000 mJ cm^{-2}. This is most probably because the homopolymer is in the glassy state at room temperature and does not possess sufficient fluidity for lateral migration at micrometer levels. Thus, rapid SRG formation should fulfill two requirements; namely, (i) the holographic illumination should be applied onto a film in the cis-rich state, and (ii) in the reverted trans Az form, the polymer should adopt the Sm state at the ambient temperature of the experiment. These features are exactly consistent with those of the Az polymer/liquid crystal hybrid materials.[15]

We have recently reported the unconventional polarization characteristics of the rapid SRG formation in these materials.[28] The rapid SRG formation is promoted only by intensity holographic conditions, and the polarization modulation of the irradiating light does not induce the mass transfer. The lack of any polarization character obviously indicates that rapid SRG formation in the present systems is triggered by a spatially patterned distribution of the trans and cis Az isomers. The actual mass transfer can be the consequences of secondary elemental processes such as local dewetting of the polymer film, the self-organizing motion of the liquid crystalline polymer, and translational diffusion in the trans/cis Az patterned film.

b. Repeatability. Natansohn and Rochon[6] described in their review that the inscriptions on Az-based amorphous polymer films could not be fully erased by light irradiation, whereas a full erasure could be achieved by heating the film slightly above the T_g of the polymer. In the present systems, the inscribed relief structure was retained for a year as long as it was kept at room temperature, and the relief could be erased by both heating and irradiation procedures. In both cases, complete erasure could be performed as described below.

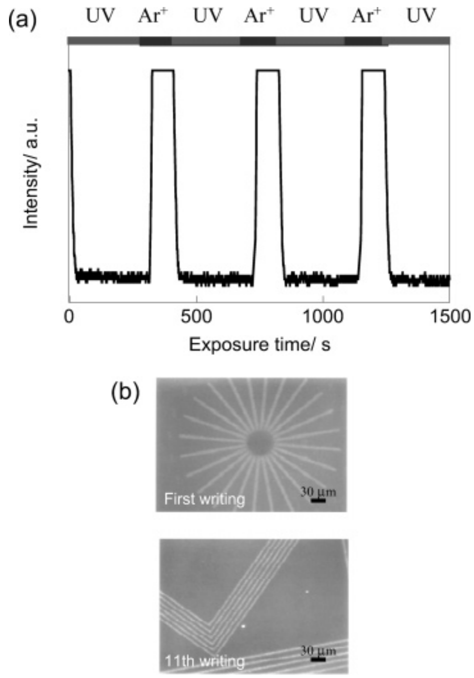


Figure 5. Rewritable behavior of the rapid SRG formation in all optical processes. (a) The changes in the diffracted beam intensity of the He−Ne laser upon irradiation with 365 nm light (erasing) and subsequent holographic Ar$^+$ laser beam (writing). (b) Microphotographs of the resulting films after the first (upper) and eleventh inscription (lower) using differently patterned photomasks.

Figure 5a displays the repeated erasure/rewriting behavior of a p6Az10Ac-PE4.5(50) film. Incoherent nonpolarized UV (365 nm) light and an interference Ar$^+$ laser beam irradiation were used for erasure and rewriting, respectively. The first-order diffraction intensity of the monitoring He−Ne laser beam decayed immediately upon irradiation to the film inscribed SRG with 365 nm for 25 s at 4 mW cm^{-2}. This decay in the diffraction intensity was accompanied by the disappearance of the SRG. Upon UV light irradiation, the film changed to the isotropic state, and thus the flat film was regenerated due to the action of surface tension. When the holographic irradiation with an Ar$^+$ laser beam was subsequently applied, the diffraction intensity recovered exactly to the original level. No damage was evident, even after more than 10 treatment cycles were applied.

Surface relief structures could be inscribed on the copolymer films by exposure to patterned incoherent blue light passed through a photomask instead of using an interference Ar$^+$ laser beam.[28] Figure 5b shows an optical microscopic image of the resulting films after the first (upper) and eleventh inscription (lower) using differently patterned photomasks. The eleventh inscription exactly traced the pattern of photomask, and no cross-talk (memory effect) was observed.

Postfixation. a. Stability Improvement of the Relief Structure. There are basically two strategies for improved stability of the inscribed relief structure, that is, use of high-T_g polymers and post-cross-linking. It has been recognized that the shape stability of the relief structure is strongly associated with the rigidity of the polymer main chain.[16−18] Some research groups have shown that use of high-T_g polymers is effective in improving the shape stability. Kimura et al.[29] and Takase et al.[30] have independently proposed photo-cross-linkable Az polymers as another strategy for shape

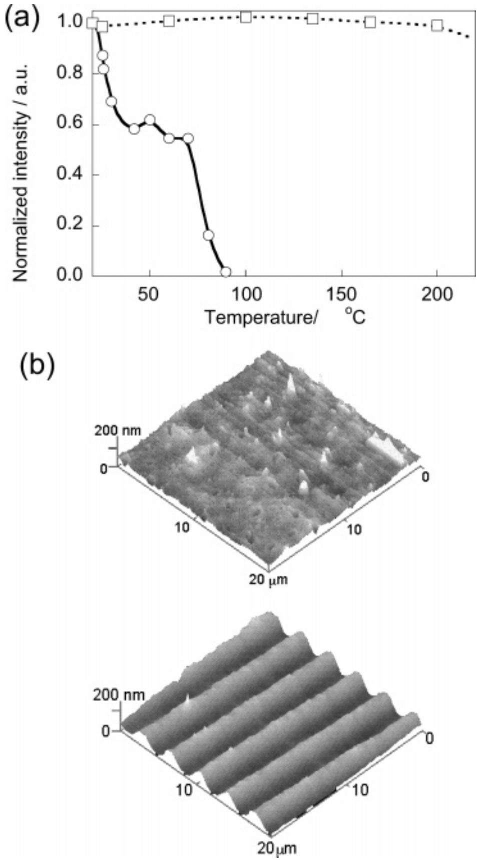


Figure 6. Examination of thermal stability of the SRGs. (a) The changes in normalized diffraction efficiency with increasing temperature for a p6Az10Ac-PE4.5(50) film before (circle) and after chemical cross-linking (square). (b) The topological AFM images of a nontreated, inscribed film after heating to 100 °C (upper) and cross-linked inscribed film after heating to 250 °C (bottom).

stability. The thermal stability was also considerably enhanced with this method. However, the above two approaches pose additional disadvantages. High-T_g polymers require exposure to vast amounts of energy to promote the mass migration, and photo-cross-linking of the polymer film leads to photobleaching of the functional Az units.

We propose a chemical postfixation process for persistent storage of the SRG under mild conditions. For this purpose, the inscribed film was exposed to a mixed vapor of formaldehyde and hydrogen chloride for 6 h at room temperature. The acetal reaction should link the two hydroxyl groups located at the terminus of the oligo(ethylene oxide) chain to yield a cross-linked polymer network. Effects of this chemical treatment were obvious. Figure 6a displays the changes in normalized diffraction efficiency with increasing temperature for a p6Az10Ac-PE4.5(50) film. Without cross-linking treatment, the diffraction efficiency was drastically reduced to around 80 °C, which is in exact accord with the clear point of this liquid crystalline polymer. In sharp contrast, the treated SRG film retained diffraction efficiency up to 250 °C without appreciable reduction. Figure 6b depicts the AFM images of the SRG inscribed films after heating: Before exposure to the mixed vapor (upper), the relief structure was completely destroyed after heating at 100 °C. In contrast, after the vapor treatment (lower), the exact relief structure was retained without damage, even after heating at 250 °C for 3 h. Unfortunately, we could not obtain direct evidence for the chemical cross-linking formed between the two hydroxyl groups by infrared spectroscopy. Nevertheless, the process of cross-linking is strongly supported by the following facts. (i) The film became completely insoluble in THF or chloroform—good solvents for the initial polymer film. (ii) The homologous polymer that possesses an oligo(ethylene oxide) with a methoxy terminus (p6Az10Ac-PME4.5(30)) instead of a hydroxyl group did not show any fixation effect after the same procedure.

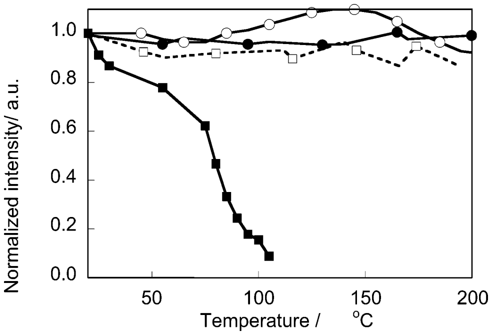


Figure 7. Effect of polymer structure on the SRG fixation. The changes in diffraction intensity of He−Ne laser from the cross-linked SRG films in the four types of copolymers: p6Az10Ac-PE4.5(30) (open circle), p6Az10Ac-PE4.5(50) (closed circle), p6Az10Ac-PE4.5(80) (open square), p6Az10Ac-PE*8*(50) (closed square).

b. Effects of Polymer Structure. The postfixation effects were further examined for other soft cross-linkable polymers, p6Az10Ac-PE4.5(30), p6Az10Ac-PE4.5(80), and p6Az10Ac-PE8(50). The former two polymers differ in the copolymerization ratio and the latter in the length of the ethylene oxide unit. All the copolymers became practically insoluble in THF and chloroform after the vapor treatment, as was observed for p6Az10Ac-PE4.5(50). This suggests that the effective cross-linking proceeds in the same way for these films.

Figure 7 displays the results of the change in intensity for the first-order diffraction of the monitoring He−Ne laser beam for the cross-linked SRG films. For the three polymers, possessing an ethylene oxide unit of 4.5 (n = 4.5) the diffraction efficiency was maintained up to 200 °C without appreciable reduction and essentially no difference in heat durability. Thus, the variation of Az content, from 30 to 80%, did not alter the fixation effect. Interestingly, only a 20% content of the ethylene oxide chain (p6Az10Ac-PE4.5(80)) was sufficient for the postfixation.

The fixation behavior was drastically affected by the difference in the length of oligo(ethylene oxide). The relief structure on the film of p6Az10Ac-PE8(50), with $n = 8$ and $x = 50$, indicated only a slight improvement in thermal stability, however, and did not survive above 100 °C. In the above manner, the postfixation via chemical cross-linking of the PE4.5 series is not affected by the copolymerization ratio but is very sensitive to the length of the oligo(ethylene oxide) chain. It appears that too much conformational flexibility is allowed for the PE8 copolymer to be fixed effectively.

c. Photoisomerization of Az and Possible Application. Figure 8a shows the change in the UV−vis spectra of the inscribed p6Az10Ac-PE4.5(50) film after cross-linking. As shown, the absorption maximum of the $\pi-\pi^*$ band in the trans form of Az was positioned at 356 nm. This shows a marked difference with that before cross-linking (316 nm, see Figure 2) and implies

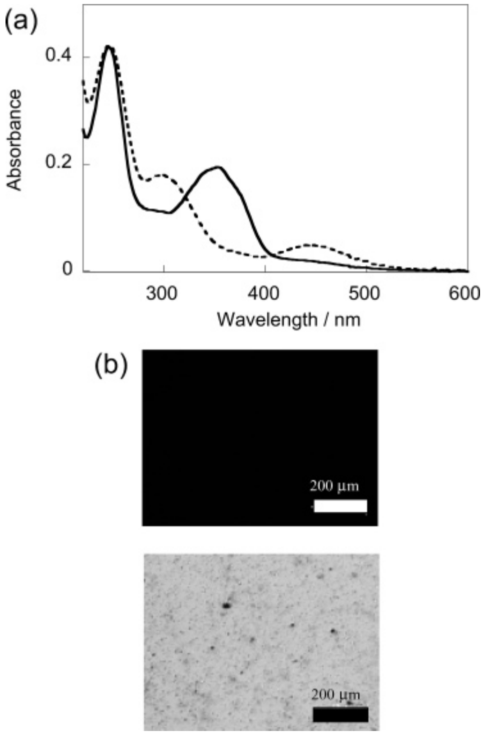


Figure 8. (a) Change in the UV−vis spectra of the fixed SRG film in p6Az10Ac-PE4.5(50), before (solid) and after (dotted) 365 nm UV light. (b) Polarized micrographs of a nematic liquid crystal hybrid cell before (top) and after (bottom) 365 nm UV light.

the dissociation of the H-aggregate in the cross-linked polymer network. It seems that the three-dimensional cross-linking can disrupt the two-dimensional array of the H-aggregated Az layer structure in the film. UV light exposure gave rise to an absorbance enhancement at 440 nm, corresponding to the n−π* transition band of the cis formed Az. Subsequent visible light irradiation restored the UV−vis absorption spectra to its initial state. It should be stressed here that such trans-to-cis photoisomerization occurred readily, without changing the relief structure. This shows a marked contrast with the behavior before cross-linking in which the relief structure is fully erased upon UV light illumination. Thus, reversible mass transfer and full erasure can be readily achieved before cross-linking, and local photoisomerization only occurs in the cross-linked film without deformation of the inscribed relief structure.

Following the above results, photoswitchable optical modulations were performed in the cross-linked relief film. The following demonstrates one practical application for the photoswitching of the nematic liquid crystal alignment. Figure 8b indicates the polarized optical microphotographs of a nematic liquid crystal cell (LC cell) before (upper) and after (lower) nonpolarized UV light irradiation. No transmitted light was observed in the initial LC-cell, indicating that the nematic LC was oriented homeotropically. The trans 6Az10 side chain in the copolymer can act as a homeotropic aligning reagent. The LC cell resulted in a homogeneous texture upon irradiation with nonpolarized UV light in normal incidence. The direction of the nematic LC was perpendicular to the grating vector, namely parallel to the undulations. For flat photoalignment films, the homogeneous alignment of nematic liquid crystals is generally attained by using linearly polarized light.[31−33] In this case, the chemically fixed topological surface undulations provide the homogeneous alignment. Subsequent visible light irradiation restored the initial homeotropic alignment, and thus this photoprocess was reversible. Therefore, the chemically fixed SRG films are able to behave as another type of command surface[31−33] for liquid crystal alignment.

Conclusion

New cross-linkable liquid crystalline Az polymers have been proposed that can be applied for photoinduced surface relief formation, where two difficult requirements, rapid formation of the relief structure by low-intensity illumination and improvement of stability at high temperature, are both fulfilled. The copolymerized component of an oligo(ethylene oxide) chain (soft segment) with a hydroxyl group at the end (cross-linking unit) plays an essential role for attainment of the above properties. The light energy required for full migration is approximately 10^3-fold lower than that for widely reported amorphous polymers. After postfixation via chemical cross-linking, the exact relief structure can be retained at 250 °C. Before cross-linking, full erasure with illumination of UV light and reinscription with an interference Ar^+ laser beam can be repeated many times. Once the film is cross-linked, the Az moiety in the fixed relief structures undergoes an efficient reversible trans-to-cis photoisomerization without affecting the relief structure. This behavior can be applied to the photoswitching of liquid crystal alignment as another type of command surface system. The original properties of these polymers described here may lead to new opportunities for photonic applications.

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References and Notes

(1) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136−138.
(2) Kim, D.; Tripathy, K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166−1168.
(3) Viswanathan, N.; Kim, D.; Bian, S.; Williams, J.; Liu, W.; Li, L.; Samuelson, L.; Kumar, J.; Tripathy, S. *J. Mater. Chem.* **1999**, *9*, 1941−1955.
(4) Natansohn, A.; Rochon, P. *Adv. Mater.* **1999**, *11*, 1387−1391.
(5) Yager, K.; Barrett, C. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 487−494.
(6) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139−4176.
(7) Ramanujam, P.; Holme, N.; Hvilsted, S. *Appl. Phys. Lett.* **1996**, *68*, 1329−1331.
(8) Hvilsted, S.; Ramanujam, P. *Monatsh. Chem.* **2001**, *132*, 43−51.
(9) Gaididei, Y.; Christiansen, P.; Ramanujam, P. *Appl. Phys. B: Laser Opt.* **2002**, *74*, 139−146.
(10) Yamamoto, T.; Hasegawa, M.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Phys. Chem. B* **1999**, *103*, 9873−9878.
(11) Fiorini, C.; Prudhomme, N.; Veyrac, G.; Maurin, I.; Raimond, P.; Nunji, J. *Synth. Met.* **2000**, *115*, 127−131.
(12) Nakano, H.; Takahashi, T.; Kadota, T.; Shirota, Y. *Adv. Mater.* **2002**, *14*, 1157−1160.
(13) Frey, J.; Darrcq, B.; Chaput, F.; Lahlil, K.; Jonathan, J.; Roosen, G.; Boilot, J.; Levy, Y. *Opt. Commun.* **2000**, *173*, 11−16.

(14) He, J.; Bian, S.; Li, L.; Tripathy, S.; Samuelson, L. *Appl. Phys. Lett.* **2000**, *76*, 3233−3235.
(15) Ubukata, T.; Seki, T.; Ichimura, K. *Adv. Mater.* **2000**, *12*, 1675−1678.
(16) Lee, T.; Kim, D.; Jiang, X. L.; Li, L.; Kumar, J.; Tripathy, S. *J. Polym. Sci., Part A* **1998**, *36*, 283−289.
(17) Wu, Y.; Natansohn, A.; Rochon, P. *Macromolecules* **2001**, *34*, 7822−7828.
(18) Fukuda, T.; Matsuda, H.; Shiraga, T.; Kimura, T.; Kato, M.; Viswanathan, N.; Kumar, J.; Tripathy, S. K. *Macromolecules* **2000**, *33*, 4220−4225.
(19) Preliminary results have been already reported as communication: Zettsu, N.; Ubukata, T.; Seki, T.; Ichimura, K. *Adv. Mater.* **2001**, *13*, 1693−1697.
(20) Angeloni, A.; Caretti, D.; Carlini, C.; Chiellini, F.; Galli, G.; Alcomare, A.; Solaro, R.; Laus, M. *Liq. Cryst.* **1989**, *4*, 513−527.
(21) Kani, R.; Nakano, Y.; Hayase, S. *Macromolecules* **1995**, *28*, 1773−1777.
(22) Moon, J. H.; Shin, J. W.; Kim, S. Y.; Park, J. W. *Langmuir* **1996**, *12*, 4621−4624.
(23) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873−1875.
(24) Li, M.-H.; Auroy, P.; Keller, P. *Liq. Cryst.* **2000**, *27*, 1497−1502.
(25) Rochon, P.; Gosselin, J.; Natansohn, A.; Xia, S. *Appl. Phys. Lett.* **1992**, *60*, 4−5.
(26) Geue, Th.; Ziegler, A.; Stumpe, J. *Macromolecules* **1997**, *30*, 5729−5738.
(27) Han, M.; Morino, S.; Ichimura, K. *Macromolecules* **2000**, *33*, 6360−6371.
(28) Zettsu, N.; Fukuda, T.; Matsuda, H.; Seki, T. *Appl. Phys. Lett.* **2003**, *83*, 4960−4962.
(29) Kimura, T.; Kim, J. Y.; Fukuda, T.; Matsuda, H. *Macromol. Chem. Phys.* **2002**, *203*, 2344−2350.
(30) Takase, H.; Natansohn, A.; Rochon, P. *Polymer* **2003**, *44*, 7345−7351.
(31) Ichimura, K.; Suzuki, Y.; Seki, T.; Hosaki, A.; Aoki, K. *Langmuir* **1988**, *4*, 1214−1216.
(32) Ichimura, K. *Supramol. Sci.* **1996**, *3*, 67−82.
(33) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847−1873.

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