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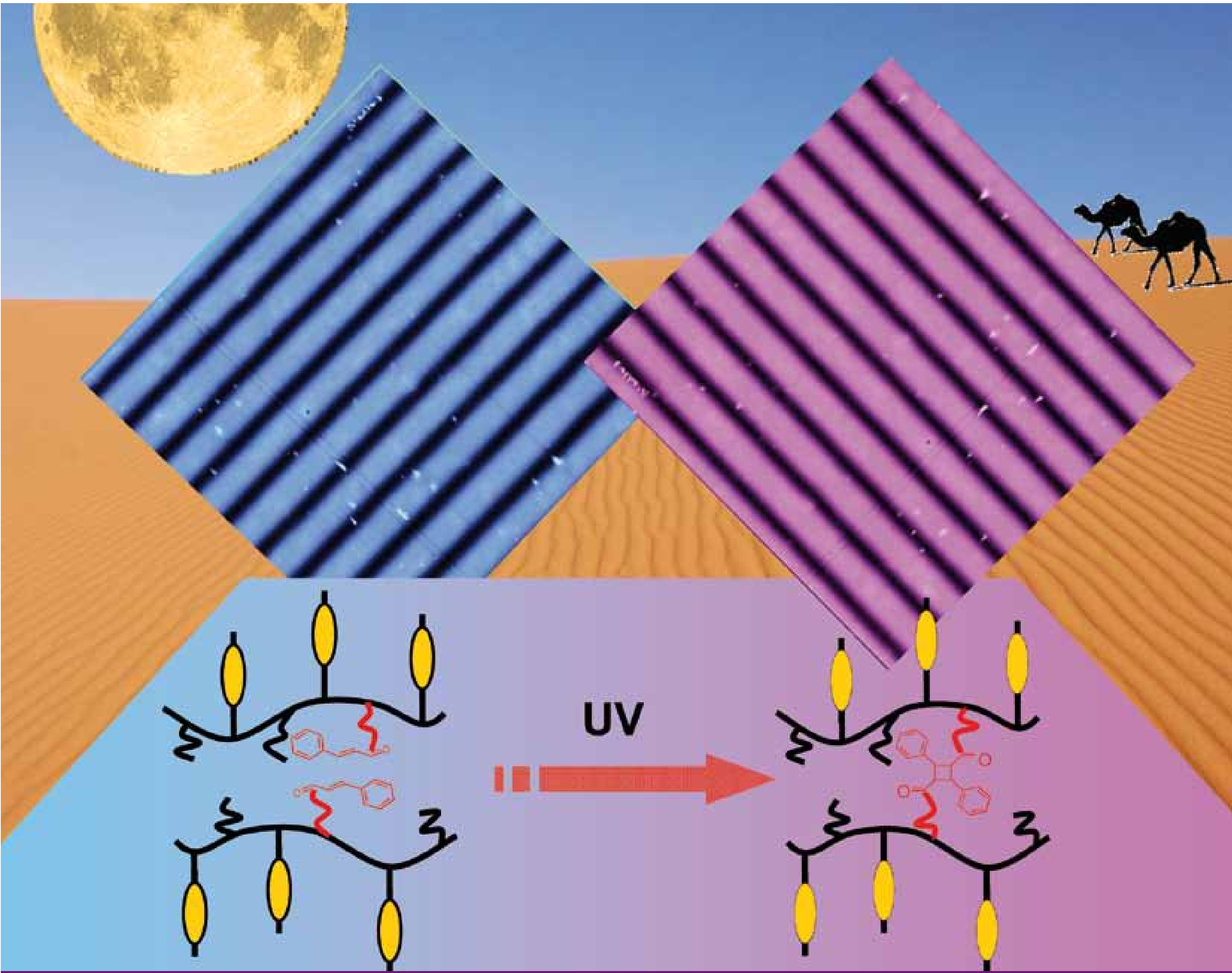

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PAPER
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Photo-crosslinkable liquid-crystalline azo-polymer for surface relief gratings and persistent fixation

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Photo-crosslinkable liquid-crystalline azo-polymer for surface relief gratings and persistent fixation

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Highly efficient migration has been observed for soft liquid-crystalline azobenzene-containing polymer films to form surface relief gratings (SRGs). The efficient migration is probably driven by the interfacial instability at boundaries between the smectic liquid-crystalline phase and photo-induced isotropic one. However, this migration system suffers from long-term and heat stability. This work proposes a new post-fixation method by utilizing the [2 + 2] photo-dimerization reaction of a cinnamoyl unit introduced into the polymer. The polymer synthesis, the properties of SRG formation, and drastic improvement of the stability towards heating and solvent exposure are described.

Introduction

The research groups of Rochon and Natansohn,[1] and Tripathy,[2] followed by Ramanujam and Hvilsted[3] first showed that interference irradiation to an azobenzene (Az)-containing polymer film produces surface relief gratings (SRGs) which is attributed to a mass migration of polymer chains over micrometer distances.[4,5] Since then, a number of researchers have been exploring such phenomena for basic interests and applications.[6–11] From the standpoint of potential applications, holographic optical recording, waveguide formation, and liquid-crystal alignment *etc.* can be proposed.[5] However, conventional amorphous systems require a high light energy dose for the relief formation.

We have recently developed a family of soft liquid-crystalline Az polymers applicable for SRG formation.[12–18] The use of soft liquid-crystalline Az polymer allowed marked enhancement in the SRG formation upon patterned irradiation. The photon dose for the completion of migration is approximately 10^{-3} fold lower than that of widely reported amorphous and liquid-crystalline polymers. From the knowledge obtained by our previous investigations, the mechanism of the SRG formation in this system could be assumed as follows. The patterned visible irradiation gives rise to spatial distributions of *trans*-rich and *cis*-rich regions. The film material starts to move from the *trans*-rich smectic liquid-crystalline regions to *cis*-rich isotropic ones, which is possibly initiated by the disparities of the viscosity and sharp gradient of surface tension at the boundary regions.[7,18]

An important requirement for SRGs is the shape stability in terms of long-term storage and durability at higher temperatures. The stability can be improved when one employs anamorphous polymer with a high T_g (glass transition temperature) or a liquid-crystalline polymer with a high T_i (liquid to isotropic transition (isotropization) temperature). Still, these strategies may lead to great difficulties in material design. Furthermore, polymers with a high T_g or T_i lack the fluidity necessary for the mass migration. The inscribing rate may be enhanced with a highly fluid film, but this choice consequently leads to poor stability for SRG structures.

To overcome this problem, we had earlier proposed a post-crosslinking strategy after the SRG formation *via* a formalization reaction (acetal formation between two hydroxyl groups by formaldehyde) in the vapor phase.[15,17] This strategy, however, sometimes suffers from damage of the relief structure and lacks reproducibility. Also, in view of health safety, use of hazardous formaldehyde should be avoided. Furthermore, procedures totally consisting of photo-processes will be more favorable for the actual fabrication process.

In the above contexts, we propose herein a newly designed polymer material, a cinnamate-containing photo-crosslinkable Az polymer. With this polymer, the [2 + 2] photo-dimerization exerted by exposure to suitable UV light is expected to immobilize the SRG inscription. The process involves two steps: rapid SRG inscription *via* light exposure, followed by on-demand post-fixation for persistent storage. The latter step plays a role in enhancing both thermal stability and insolubility of the polymer. Without fixation, the SRG structure may be erased and regenerated many times. The chemical structure of the polymer is indicated in Fig. 1, and this polymer is abbreviated as p5Az10Me-PE4.5-Ci. Kimura *et al.*[19] formerly proposed a series of amorphous UV-curable Az polymers containing a cinnamate moiety, however, the stabilization after UV irradiation was not effective. They reported that heating above 200 °C, corresponding to T_g, destroyed the SRG structure even for the UV-cured film. Furthermore, their process required a high light dose (>100 J cm^{-2}) to inscribe SRG structures. We report herein a new system in which efficient mass migration occurs at moderate irradiation conditions, and the photo-crosslinking significantly improves stability towards heat and solvent exposure.

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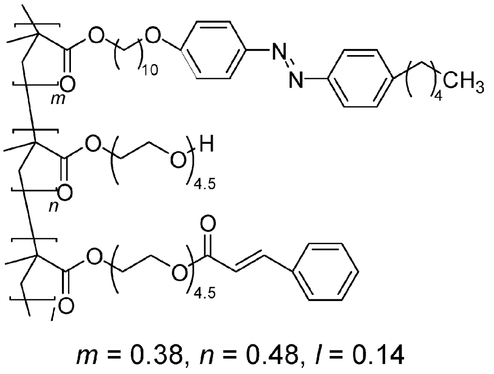

Fig. 1 Chemical structure of photo-crosslinkable Az-containing polymer, p5Az10Me-PE4.5-Ci, in this study.

Experimental

Materials

The methacrylate monomer possessing an oligo (EO) unit (PE4.5) was kindly supplied by NOF Corp. All other reagents were purchased commercially and used without further purification. The detailed information on synthetic procedures is described below.

Synthesis

4-[(4′-Pentyl)azo]phenol (5Az-OH) was synthesized by diazo-coupling of 4-pentylaniline with phenol according to a conventional procedure. 4-Pentylaniline (30 mmol) was dissolved in a mixture of concentrated hydrochloric acid and water. After cooling, the aniline was diazotized by adding dropwise a solution of NaNO$_2$ (60 mmol) in water at 0–5 °C. Addition of the diazotized solution to a solution of phenol (60 mmol), NaOH, Na$_2$CO$_3$ in water led to the diazo-coupling reaction. After neutralization and subsequent filtration, the precipitate was recrystallized from hexane. Recrystallization gave pure 6AzOH as a yellow powder in 87% yield; mp 72–73 °C. ^{1}H NMR (δ[ppm], 270 MHz, CDCl$_3$): 0.89 (3H, t, J = 6 Hz, –CH$_3$), 1.32–1.68 (6H, m, –CH$_2$–), 2.67 (2H, d, J = 8 Hz ArCH_2–), 5.31 (1H, m, Ar–OH), 6.93 (2H, d, J = 9 Hz, Ar-H), 7.30 (2H, d, J = 9 Hz, Ar-H), 7.79 (2H, d, J = 8 Hz, Ar-H), 7.86 (2H, d, J = 9 Hz, Ar-H).

4-[(4′-Pentyl)azo]phenol (5Az-OH) was converted to 4-(10-hydroxydecyl)-4′-pentylazobenzene (5Az10-OH) by a Williamson esterification reaction. To a stirred dried acetone solution (20 ml) of 5AzOH (30 mmol) were added powdered potassium carbonate (8 mmol), potassium iodide (as a catalyst) and a dried acetone solution of 10-bromodecanol (6 mmol). The mixture was stirred at refluxing temperature for 20 h. After removing the precipitate, the filtrate was concentrated to give a solid residue, which was purified by recrystallization from hexane at least twice to give a yellow powder in a yield of 91%; mp 81–82 °C. ^{1}H NMR (δ[ppm], 270 MHz, CDCl$_3$): 0.89 (3H, t, J = 7 Hz, CH$_3$–), 1.21–1.83 (22H, m, –CH$_2$–), 2.67 (2H, t, J = 8 Hz, CH$_2$), 3.65 (2H, t, J = 6 Hz, –OCH$_2$–), 4.04 (2H, t, J = 7 Hz, –OCH$_2$–) 7.00 (2H, d, J = 9 Hz, Ar-H), 7.29 (2H, d, J = 9 Hz, Ar-H), 7.80 (2H, d, J = 9 Hz, Ar-H), 7.90 (2H, d, J = 9 Hz, Ar-H).

A mixture of 5Az10-OH (5 mmol) and triethylamine (10 mmol) in dried tetrahydrofuran (THF) was added to a solution of acryloyl chloride (10 mmol) in THF under a nitrogen atmosphere, and was stirred at room temperature for 5 h. The resulting raw product was washed in water several times and dried over magnesium sulfate. After removing the solvent, the solid residue was recrystallized twice from methanol to give pure 4-(10-methacryloyloxydecyloxy)-4′-pentylazobenzene (5Az10Me) as a yellow powder in 87% yield; mp 75–76 °C. ^{1}H NMR (δ[ppm], 270 MHz, CDCl$_3$): 0.89 (3H, t, CH$_3$–), 1.32–1.94 (25H, m, –CH$_2$–, –CH$_3$), 2.67 (2H, t, J = 8 Hz, –CH_2Ar), 4.03 (2H, t, J = 7 Hz, –OCH$_2$–), 4.14 (2H, t, J = 7 Hz, –CH$_2$O–), 5.54, 6.09 (2H, s, CH$_2$═), 7.00 (2H, d, J = 9 Hz, Ar-H), 7.28 (2H, d, J = 9 Hz, Ar-H), 7.80 (2H, d, J = 8 Hz, Ar-H), 7.90 (2H, d, J = 9 Hz, Ar-H).

The azo-containing polymer p5Az10Me-PE4.5 was synthesized by free radical polymerization in dry THF (5 ml) solution under nitrogen, using AIBN (0.0392 mmol) as an initiator *via* free radical polymerization of the 5Az10Me monomer (0.245 mmol) and PE200 (0.49 mmol), another methacrylate monomer containing an oligo (ethylene oxide unit) chain. The reaction medium was heated at 70 °C for 6 h, cooled to room temperature, and then poured in to a vigorously stirred hexane for reprecipitation. The resulting polymer was collected by centrifugation. The orange solid product was dried in vacuum. The reaction yield was 70%.

Finally, using p5Az10Me-PE4.5 (0.223 mmol) and cinnamoyl chloride (0.116 mmol) as reactants in dry THF (4 ml) as solvent a polymer containing both azobenzene and cinnamate as side chains was synthesized by stirring the mixture at room temperature for 5 h. Reprecipitation was carried out in a mixture solvent of 98.5% hexane and 1.5% chloroform. After being dried in vacuum, the product was observed as a sticky orange solid in a yield of 80%. This product was abbreviated as p5Az10Me-PE4.5-Ci, and the copolymerization ratio ($m : n : l$ in Fig. 1) was determined by ^{1}H NMR as described in the Results and discussion.

Measurements

^{1}H NMR data were measured on a 400 MHz NMR A-400 (JEOL). Molecular mass data for the polymer was obtained by gel permeation chromatography (GPC, Shodex Technology). UV-vis absorption spectra were taken on an Agilent 8453 spectrophotometer (Agilent Technology). Polarized optical microscopic (POM) observations were made using a BX51 (Olympus Technology). Film thickness was determined by atomic force microscopy (Nanoscope 2100, Seiko Instruments), after scratching the film with a micro-spatula. An Hg–Xe lamp (Sanei-200S) was used for both SRG inscription and photo-crosslinking. UV light at 350–380 nm was filtered out for the pre-irradiation of films. To inscribe the SRG structure, visible light at 430–500 nm was irradiated to the film through a photo-mask, which was placed with the support of a cover glass with a thickness of 0.15 mm as the spacer. For photo-crosslinking, a combination of a D33S optical filter (Toshiba Technology) and one glass slide were used to screen out the light of wavelength 300–400 nm. The microphotographs of SRGs were taken by a microscope (Keyence, VHX-500) at different temperatures, 25, 55 and 62 °C. Differential scanning calorimetry (DSC) was undertaken with a DSC 6200 (Seiko Instruments Inc.). Unless stated otherwise, all measurements were conducted at room temperature.

Quartz substrates were formerly cleaned by sequential ultrasonic treatments for 15 min immersing in the following fluids, THF, saturated KOH–methanol, deionized water.

Results and discussion

Characterizations of the ternary copolymer

We observed ^{1}H NMR spectra for the determination of the copolymerization ratio for both p5Az10Me-PE4.5 (before introduction of cinnamoyl groups) and p5Az10Me-PE4.5-Ci (after introduction of cinnamoyl groups). The integral intensities of the two peaks at 6.50–6.55 ppm corresponding to the proton of the cinnamate double bond were compared with those at 7.8–7.9 ppm assignable to the benzene ring of the azobenzene side chain. The side-chain content ratios was found to be $m = 0.38$, $n = 0.48$ and $l = 0.14$ (see Fig. 1).

According to the GPC measurements, the final product showed an weight-average molecular weight (M_w) of 1.51×10^4 and a number average molecular weight (M_n) of 1.18×10^4 ($M_w/M_n = 1.45$).

The thermophysical properties of this ternary copolymer was evaluated by DSC at a heating rate of 10 °C min^{-1} and a polarized optical microscope (POM). The results are shown in Fig. 2. A small dip in the curve at 59 °C and an endothermic peak at 66 °C are observed in the DSC profile in the heating process. A POM image at 63 °C clearly exhibited a birefringence, indicating the liquid-crystalline phase. On the other hand, the birefringence disappeared at the endothermal transition, and the POM image became fully dark at 73 °C. The above data indicate that the two characteristic transitions at 59 and 66 °C correspond to T_g and T_i, respectively. According to our former data of a similar series of copolymers, the liquid-crystalline phase below T_i corresponds to a smectic A phase.[17,18]

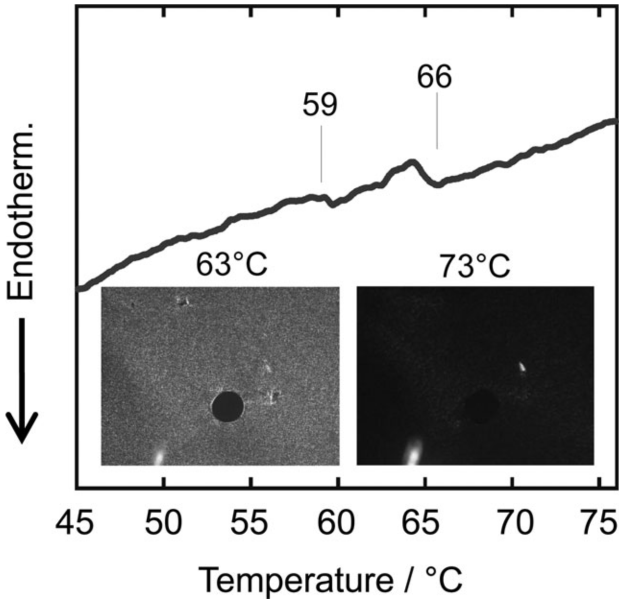

Fig. 2 Thermal analysis of polymer p5Az10Me-PE4.5-Ci as measured by DSC and POM (500 × 900 μm).

SRG inscription

The SRGs were formed on the surface of polymer thin films prepared by spin-coating on a cleaned quartz substrate from a 2% (by weight) THF solution at 2000 rpm for 30 s. The films were kept in the air for 30 min before use. The initial film thickness was *ca.* 70 nm as evaluated by AFM. To inscribe the SRG pattern, the films are first exposed to UV at 365 nm, and then irradiated at 436 nm through a photo-mask having a 10 μm line-and-space pattern at 50 °C. This temperature was selected just below T_g, which ensures the polymer film soft enough to inscribe relief with a low energy dose, but yet rigid enough to maintain the gratings once inscribed. In our earlier work, the irradiation was performed at room temperature since the former polymer had a lower T_g.[15,17] Energy data needed for the SRG formation, including the irradiation power and irradiation time, were optimized by repeating the irradiating processes at different conditions and comparing the SRG structures. It was confirmed that optimized irradiation conditions for the SRG formation were as follows; pre-irradiation with 365 nm light: 10 mW cm^{-2} exposure for 200 s (2 J cm^{-2}) at room temperature, and subsequent patterned irradiation at 436 nm: 5 mW cm^{-2} for 200 s (1 J cm^{-2}) at 50 °C. Both energy doses are much lower than those required for the UV-curable polymer previously reported.[19] This inscribed SRG pattern after these procedures observed by AFM is shown in Fig. 3. The surface profile exhibited a regular undulated shape with a grating depth of 130 nm and a grating period of 20 μm. The top-to-top distance exactly corresponded to the mask patterns. Thus, the highest regions reached approximately twice the initial film thickness, indicating that full mass transfer occurred during the optimized procedures.

Changes in the UV absorption spectrum during the above process are indicated in Fig. 4. The initial film in the *trans*-Az state (solid line) showed the π–π* absorption maximum at 347 nm. The absorption band around 280 nm is ascribed to the π–π* absorption of the cinnamoyl unit. By irradiation with

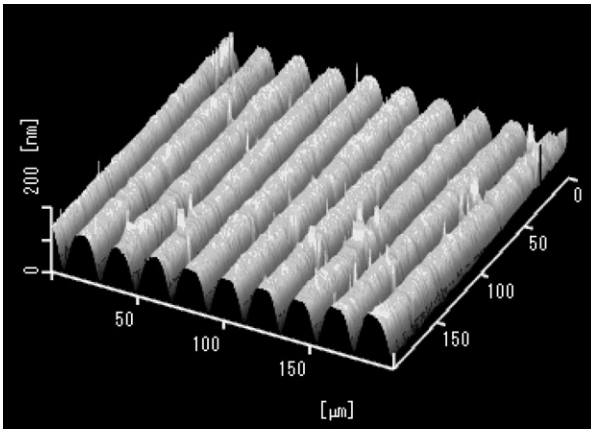

Fig. 3 AFM image of inscribed relief gratings on a p5Az10Me-PE4.5-Ci film surface.

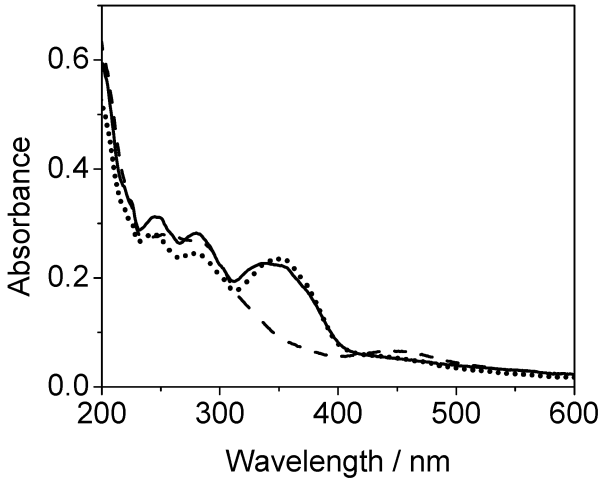

Fig. 4 UV-Vis absorption of a sample film during the SRG inscription process. The solid line is for the original film, the dashed line is for the film irradiated with 365 nm UV and the dotted line is for the film subsequently exposed to 436 nm light.

365 nm light the Az unit was efficiently isomerized to the *cis* form (dashed line). After subsequent irradiation with 436 nm light, the Az unit was mostly reverted to the *trans* form (dotted line), but in this case the band peak of the π–π* absorption was shifted to 361 nm, indicating the disruption of partial H aggregation in the initial film.

Thermal stability of SRG before crosslinking

During heating the SRG inscribed film from 25 to 70 °C at 2 °C min^{-1}, optical microscope observations were made, as shown in Fig. 5. Upon gradual heating, the SRG pattern started to collapse from 55 °C, and almost disappeared at 62 °C. This result was in accord with the data of the thermal analysis taken by DSC and POM (Fig. 2). Thus, the SRG inscription was readily erased by heating above T_i of p5Az10Me-PE4.5-Ci. This observation also coincides with our previous results obtained without the cinnamoyl group.[5]

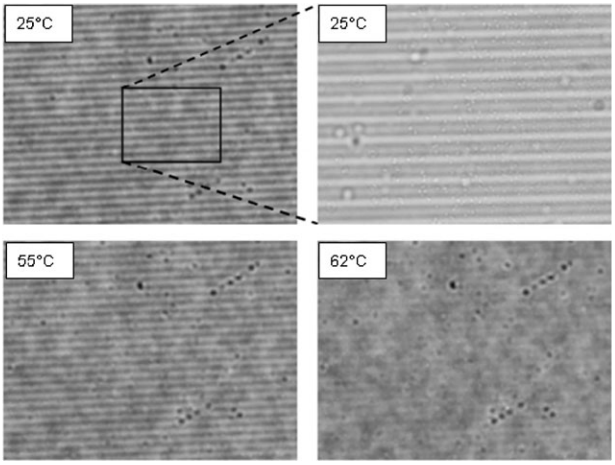

Fig. 5 Optical microscope images taken while heating an SRG inscribed film from 25 to 70 °C at a rate of 2 °C min^{-1}. The top-right image displays a magnified region for the box in the top-left image.

[2 + 2] Photo-dimerization (photo-crosslinking)

Next, the exposure to UV light to induce the [2 + 2] photo-dimerization of cinnamoyl groups in the p5Az10Me-PE4.5-Ci film was performed. At room temperature, an SRG inscribed film was irradiated with UV light at a wavelength in the range 300–400 nm changing the time from 1 to 40 min at room temperature (Fig. 6). As indicated, during the irradiation, the absorption band of the cinnamoyl group at 280 nm was gradually reduced; this should be due to the [2 + 2] cycloaddition photo-dimerization reaction leading to the formation of a cyclobutane ring.[20–22] A sudden upward shift in the spectrum particularly in the UV region was observed at an early stage (within 1 min) of the photo-crosslinking which can be ascribed to light scattering due to an evolution of inhomogeneous domain formation in the polymer film.

The efficiency of crosslinking was confirmed by dissolving behavior in THF, a good dissolving solvent for the original p5Az10Me-PE4.5-Ci. Fig. 7 shows the absorption spectra obtained after subsequently rinsing in THF films which were exposed to UV light at various periods. These data indicate that UV exposure for 15 min leads to insolubility for THF. Essentially the same results were obtained when chloroform was employed as the rinsing solvent.

The microstructures of SRGs under different irradiation energies for the crosslinking were further evaluated by AFM. By comparing them, it was found that for the photo-crosslinking, the best irradiation intensity and time were found to be 50 mW cm^{-2} at 313 nm and 15 min, respectively. The grating pattern picture taken after photo-crosslinking at the above conditions showed almost no change at any scale. The grating depth was also unchanged at 130 nm, which remained the same level as observed before the photo-crosslinking. This irradiation also leads to the *trans*-to-*cis* isomerization of the Az unit, however, this did not influence the SRG structure since the irradiation was performed at room temperature, namely below T_g.

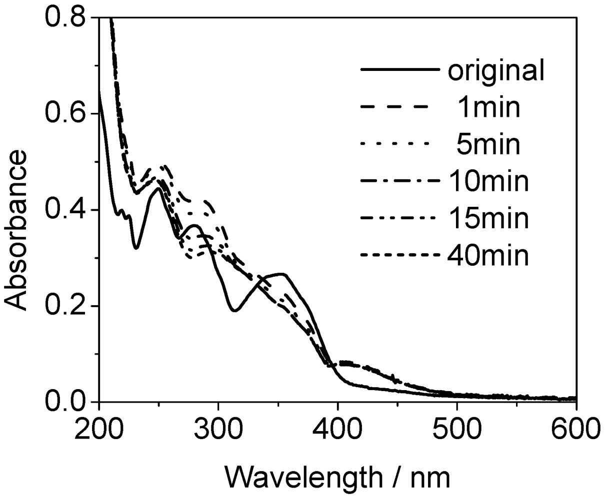

Fig. 6 UV-Vis absorption spectra of the copolymer film irradiated with UV light at wavelength 300–400 nm at room temperature while changing the irradiation time from 1 to 40 min.

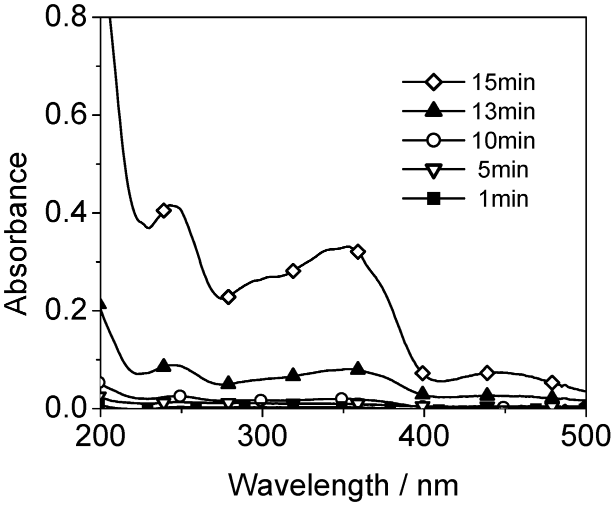

Fig. 7 UV-Vis absorption spectra of five series of films subjected to photo-crosslinking for 1, 5, 10, 13 and 15 min and subsequently rinsed in THF.

Thermal stability of the SRG after crosslinking

Fig. 8 displays the AFM image of the photo-crosslinked SRG structure after the treatment in THF and chloroform, and subsequently heated at 300 °C for 5 min. This SRG pattern showed no significant change compared with that of the as-prepared SRG film as shown in Fig. 3. In sharp contrast, the SRG inscribed film without photo-crosslinking could retain its pattern only up to 55 °C which is just below the T_i. After photo-crosslinking, on the other hand, the SRG pattern was still maintained at 300 °C without any reduction in its grating depth. Thus the high temperature stability was substantially improved as well as the resistance to solvent exposure.

Kimura *et al.*[19] reported that a poly(phenylmaleimide)-based random copolymer containing Az and cinnamate side-chain groups (cinnamate content of 18 mol%) showed only little stability improvement. The SRG structure scarcely endured above T_g around 200 °C. It is worth noting here that significant stability improvement was found in the present system even though the content of the crosslinkable unit is less (14 mol%). This fact suggests more efficient photo-dimerization in the present p5Az10Me-PE4.5-Ci film. It seems likely that the hydrophobic cinnamoyl groups are efficiently aggregated in the nano-segregated layer of hydrophilic oligo(ethylene oxide) side-chain layer regions.

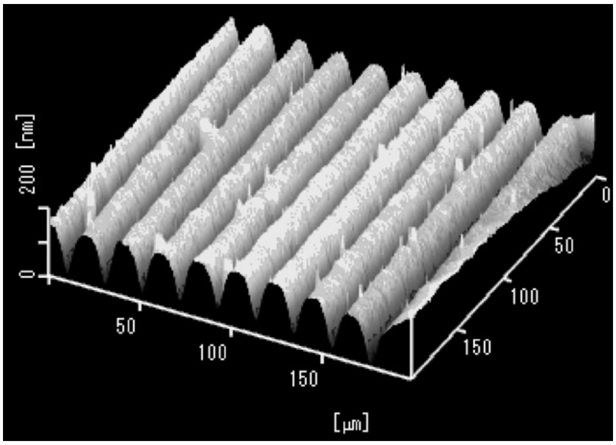

Fig. 8 AFM image of a photo-crosslinked SRG film after immersing in THF and chloroform, and subsequent heating at 300 °C for 5 min.

Conclusions

A photo-crosslinkable ternary Az copolymer was newly developed, in which a cinnamoyl group was introduced in the liquid-crystalline Az side-chain polymer. The polymer showed a favorable property of liquid-crystalline nature to exert the mass transport. After pre-irradiation of 365 nm UV light followed by patterned visible light at 436 nm at 50 °C, the SRG structure was readily formed with a grating depth of 130 nm, which corresponds to nearly twice the level of the initial thickness. This SRG pattern was able to be erased when heated above the isotropization temperature. Without crosslinking, the film was readily dissolved in chloroform or THF. After subsequent photo-crosslinking at room temperature, the SRG patterns remained essentially unchanged after rinsing with the above solvents. The thermal stability was improved drastically, *i.e.*, the SRG structure was not influenced after heating to 300 °C for 5 min. We expect that this new type of photo-crosslinkable polymer will provide wider opportunities for the application of SRG structures.

Acknowledgements

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