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# Photocrosslinked surface relief gratings on azobenzene-containing copolymer films

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## Abstract

An amorphous polymer containing Disperse Red 1 (DR1) and crosslinkable acrylic groups as separate side groups was synthesized. Surface relief gratings were optically inscribed onto films of this polymer. Grating depths of 350 nm were obtained after 40 min of irradiation. The first-order diffraction was monitored during the laser irradiation, and an efficiency of about 22% was achieved. The polymer could be photocrosslinked at 80 °C under UV light. Although some photo-degradation due to UV irradiation of the azo chromophores was observed, the surface relief itself was fixed by the photocrosslinking, as observed by the improved thermal stability of the diffraction efficiency. Even after heating above the glass transition temperature ($T_g$) for 2.0 h, significant diffraction was still present and the grating was still observed. In comparison with the photocrosslinked gratings, a non-crosslinked grating rapidly lost most of its shape when heated above $T_g$. Thus, photocrosslinking is a useful method to improve the thermal stability of the gratings.

*Keywords:* Azobenzene; Surface relief gratings; Photocrosslinking

## 1. Introduction

Photofabrication of surface gratings on azobenzene-containing polymer films using a laser has been widely investigated in recent years. Surface relief gratings can easily be inscribed by a single-step all-optical process, in contrast to other methods such as chemical etching or photoresist processing. In addition, photoinduced multiple surface gratings can be locally inscribed and they are erasable. The gratings inscribed on amorphous azo polymer films are stable below $T_g$ and can be erased either by heating above $T_g$ or with a polarized laser [1]. This grating inscription technique is expected to have many interesting applications in various areas of photonics [2,3] such as optical couplers, filters, holographic image storage or liquid crystal anchoring. Surface relief gratings with an uniform sinusoidal pattern are optically inscribed using a polarization interference pattern obtained using contra-circularly polarized laser beams [4,5]. Large surface modulations are observed by atomic force microscopy (AFM) [6]. Several models were proposed for the mechanism of the surface grating formation, but these are still under discussion [7–12]. All models agree that mass transport is induced by laser irradiation although the origin of the driving force is still in question. Gratings can also be produced in the bulk of the film by laser ablation [13], photo-bleaching [14], or involving liquid crystalline phases [15,16]. In all cases, the photochemical *trans-cis-trans* isomerization of the azo chromophore seems to be a cause of large-scale polymer chain migration that induces the gratings either on the surface or in the bulk.

For optical devices, long-term stability of the optical properties is a pre-requisite. In the case of polymer materials for non-linear optics or reversible optical storage, it has been reported that high $T_g$ polymers, crosslinking or formation of interpenetrating polymer networks (IPNs) improve the thermal stability of the chromophore's orientation. For surface relief gratings, which involve both the chromophore as well as the polymer matrix, grating stability is needed if the grating films are used in optical components. In a previous study [17], high $T_g$ polymers were seen to have

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better thermal stability of the gratings. However, the inscription time was relatively long, the grating depth was shallow and their diffraction efficiency was quite small. In the present report, a crosslinkable amorphous polymer that contains separate azobenzene and acrylic groups in the side-chain is prepared, and an interfering circularly polarized light is used to inscribe surface relief gratings onto the surface. Photocrosslinking with UV light is then performed and its effect on the stability of the gratings is investigated.

## 2. Experimental

### 2.1. Materials

The synthetic route for a crosslinkable copolymer is shown in Scheme 1. 2-[4-(4-nitrophenylazo)-N-ethyl-phenylamino]ethanol Disperse Red 1 (DR1) and 2,2′-azobisisobutyronitrile (AIBN) were recrystalized in ethanol. Tetrahydrofuran (THF), toluene, triethylamine, methacryloyl chloride and acryloyl chloride were distilled before use. Catechol, hydroquinone and 2-methyl-4′-(methylthio)-2-morpholino propiophenone were used without further purification.

### *2.1.1. 4′-[(2-(Methacryloyloxy)ethyl)ethylamino]-4-nitroazobenzene (DR1M)*

DR1M was synthesized according to the method described previously [18].

### *1.1.2. 2-Methacryloyloxy-phenol*

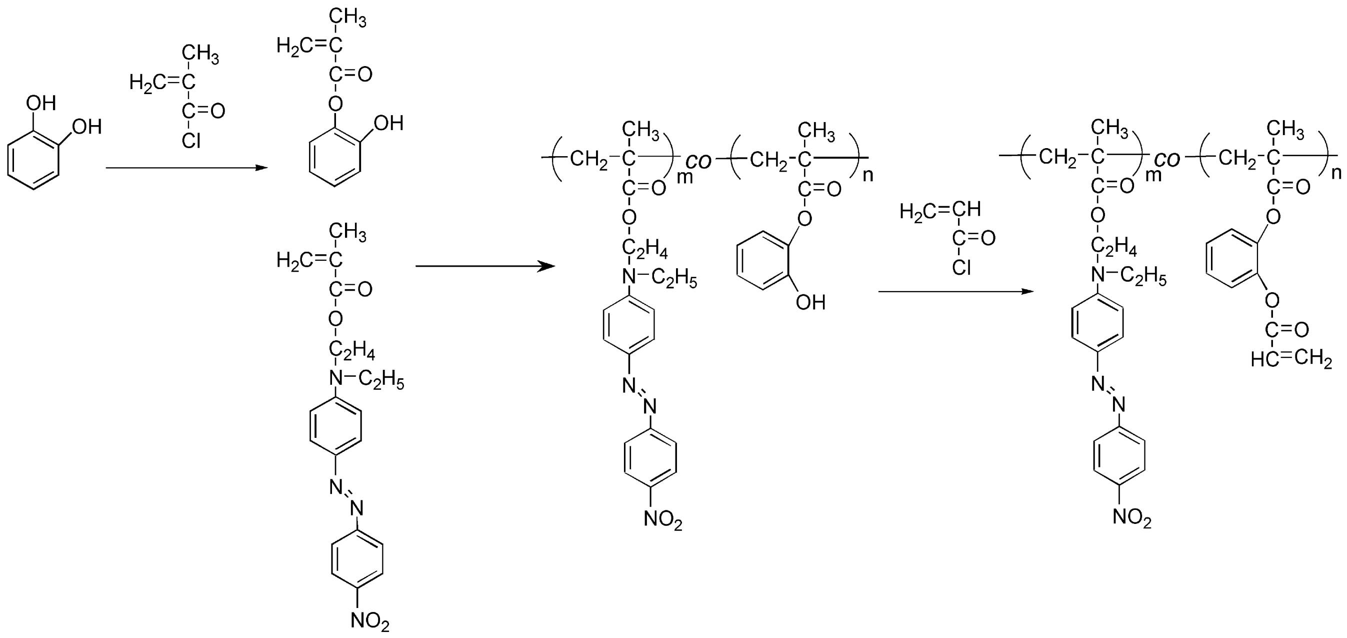
2-methacryloyloxy-phenol was prepared by esterifying Catechol with methacryloyl chloride. After the resultant solution was filtrated, the crude compound was purified on a silica gel column using the mixture of *n*-hexane and ethyl acetate (1:3 by volume) as eluent, and the second fraction was collected. A clear liquid was obtained (72% yield). $^1$H NMR ($CDCl_3$, ppm): $\delta$ 2.11 (s, $CH_3$), 5.57 (s, OH), 5.83 and 6.43 (s, $H_2C{=}C(CH_3)-$), 6.93–7.05 and 7.10–7.18 (m, aromatic protons).

### *1.1.3. Copolymerization procedure*

The copolymerization of DR1M with 2-methacryloyloxy-phenol was carried out by free-radical mechanism in toluene solution at 65 °C for two days. DR1M (0.48 g), 2-methacryloyloxy-phenol (0.22 g), and AIBN (0.07 g) were dissolved in toluene (5 mL) in an ampoule. The solution was degassed by bubbling argon for 20 min, and the ampoule was sealed under argon and placed in an oil bath set at 65 °C. After stirring for two days, the resultant solution was poured into methanol. The precipitate was collected, dissolved in a small amount of THF, and then reprecipitated twice from methanol. The red solid was dried in vacuum at 50 °C overnight. A dark purple powder was obtained (0.63 g, 90% yield).

### *1.1.4. Esterification of copolymer with acryloyl chloride*

The obtained copolymer was esterified with acryloyl chloride in THF. The copolymer (0.45 g) was dissolved with triethylamine (0.53 mL) and hydroquinone (500 ppm) in THF (30 mL). A solution of acryloyl chloride (0.31 mL) in 20 mL of THF was added dropwise under stirring, while the flask was kept in an ice bath. The solution was stirred for 12 h under argon atmosphere at room temperature. The



Scheme 1. Synthetic route of crosslinkable azo polymer.

reaction mixture was poured into water, filtrated and then dissolved in THF. The solution was poured into *n*-hexane, and the precipitate was collected and dried at room temperature under vacuum overnight. A dark purple powder was obtained (0.39 g, 74% yield). The $^1$H NMR spectrum of the polymer is shown in Fig. 1.

The glass transition temperatures of the polymers were measured on a Perkin–Elmer DSC 6 at a scan rate of 10 °C/min. The $^1$H NMR spectra were obtained on a Bruker AC-F 300 NMR spectrometer in deuteriodimethyl sulfoxide solution. The molecular weight of the polymer was estimated by gel permeation chromatography (GPC). A Water Associates liquid chromatograph equipped with a Model R401 differential refractometer was used. The electronic spectrum of the polymer film was recorded on a Shimadzu TR-280 UV-visible spectrometer.

### 2.2. Film preparation and photopolymerization of acrylic groups in the polymer

The polymer was dissolved into THF solution to make the film. For photocrosslinking of the acrylic groups in the polymer, 2-methyl-4′-(methylthio)-2-morpholino propiophenone (10 wt% of the polymer) was added as a photoinitiator into the THF polymer solution. The sample solution was spin-coated onto either a glass slide for grating inscription or a KBr disc for IR measurement and then dried in vacuum. The thickness was about 450 nm in both cases. The film thickness for grating inscription was measured by profilometry and the thickness for IR measurement was estimated from a calibration curve of the corresponding UV absorption.

A 250 W high-pressure mercury lamp was used for photopolymerization of the acrylic groups. The photopolymerization was carried out at 80 °C under blowing nitrogen by irradiating with the UV lamp at an intensity of 20 mW/cm$^2$. The conversion of the acrylic groups was measured on a Nicolet Impact 410 FT-IR spectrometer.

### 2.3. Surface relief gratins inscription

The gratings were optically inscribed onto the films with a single beam split by a mirror and reflected onto the film surface coincident with the other half to form an interference pattern, as reported previously [19]. A 488 nm beam from an argon laser passed through a spatial filter and expanded to a diameter of 10 mm was used as a writing beam. The beam with circular polarization was

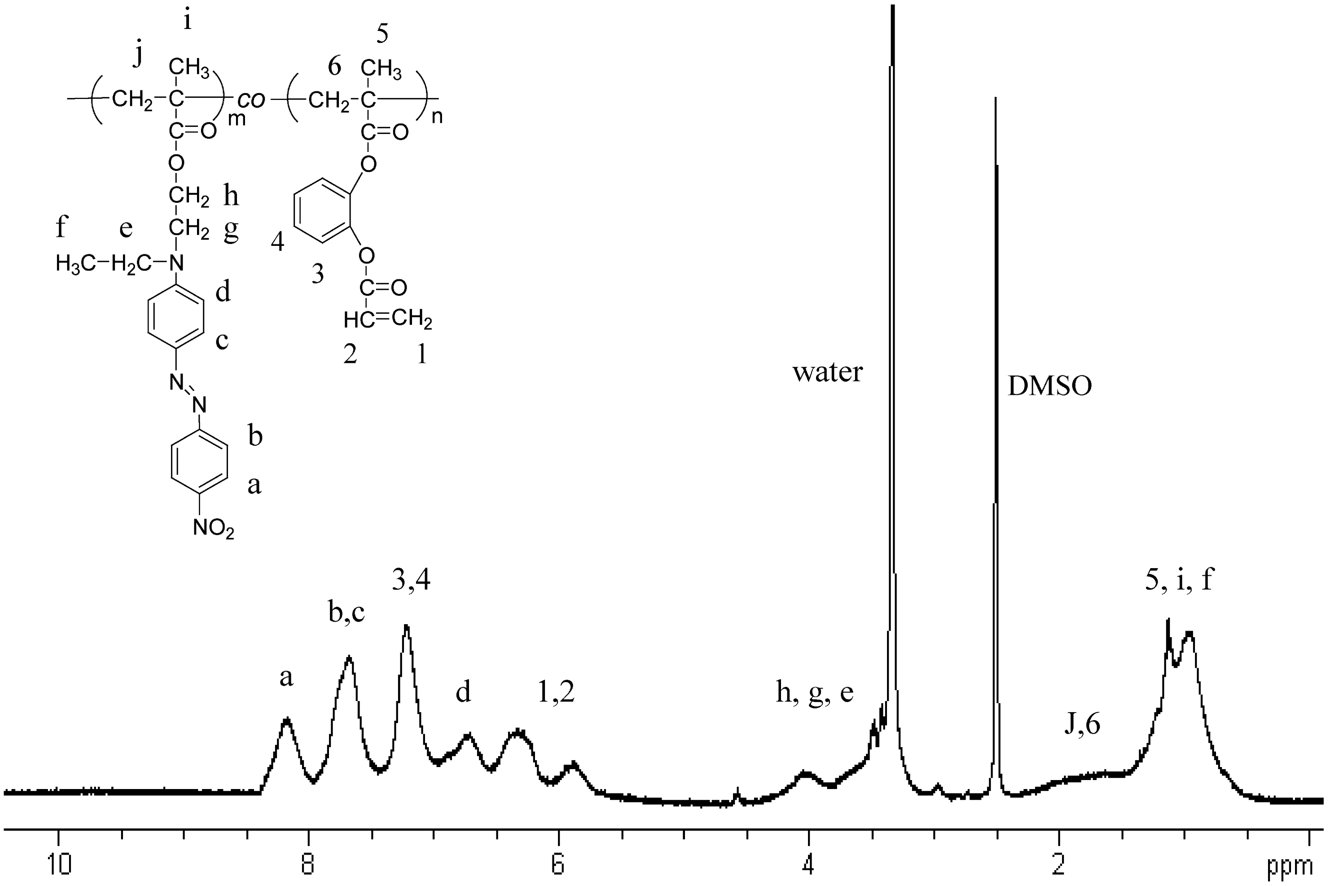


Fig. 1. $^1$H NMR spectrum of the esterified copolymer. The assignments are given on the spectrum. The copolymer composition values *m* and *n* were calculated to be 0.49 and 0.51, respectively.

prepared using a quarter wave plate. The intensity was 140 mW/cm$^2$, low enough to avoid the photo-bleaching of azo chromophore as reported by Kaino's group [14]. The surface profiles of the resulting gratings were recorded by a NanoScope atomic force microscope (AFM) in the tapping mode. The progression of the grating inscription was monitored by measuring the growth of the first-order diffracted beam over time with a 0.1 mW beam from a 670 nm diode laser. After or before grating inscription, photocrosslinking was carried out at 80 °C under nitrogen for 15 min using the UV lamp at 20 mW/cm$^2$.

## 3. Results and discussion

### *3.1. Characterization and photocrosslinking of the polymer*

The copolymer composition was determined from the $^1$H NMR spectrum. According to the ratio of the integrated proton peak areas of aromatic and vinyl groups, the copolymer contained 51 mol% azobenzene and 49 mol% acrylic groups. The hydroxyl groups were completely reacted due to the use of an excess of acryloyl chloride. The molar fraction of DR1M in the polymer is close to the feed fraction, indicating similar reactivities of the two methacrylate monomers. The glass transition temperature of the polymer is 115 °C, and after crosslinking it increases to 152 °C. Adding a benzene group between the polymer main chain and acrylic group resulted in an increase in $T_g$ when compared to the polymer that we had previously reported in Ref. [20]. As a result, the polymer is more stable at high temperature. The number-average molecular weight ($M_n$) is 10,700 and the polydispersity ($M_w/M_n$) is 2.8 by GPC. The polymer is completely amorphous as determined by DSC and polarized microscopy.

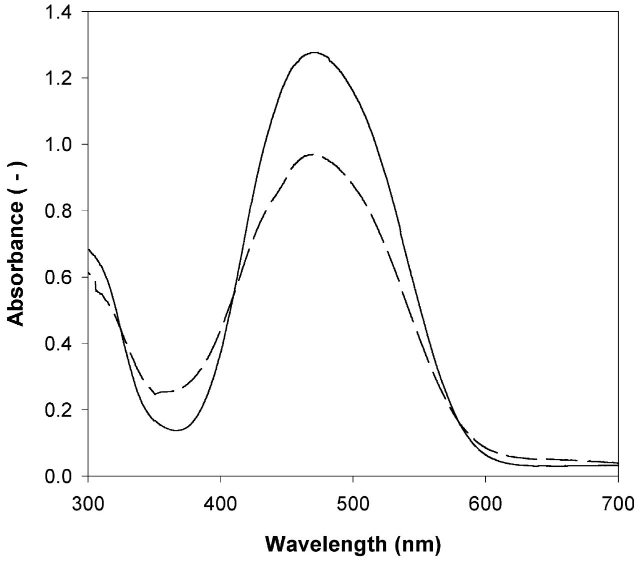


Fig. 2. UV–Vis spectra of the samples before (full line) and after (broken line) UV irradiation.

As shown in Fig. 2, the polymer shows a maximum UV absorption at 468 nm and a relatively low absorbance around 365 nm, which is useful for the photoinitiator cleavage and where the UV lamp emits strongly. Usually, trans-azobenzene has the UV absorption around 360 nm which is caused by $\pi-\pi^*$ transition, so it is difficult to polymerize reactive groups in azo polymeric system via photo-radical polymerization [21]. However, by substituting electron donor and acceptor groups on the para positions of azobenzene, such as the polymer used here, the UV absorption can be shifted to longer wavelengths [22]. The photoinitiator may then absorb the UV energy, decompose in the polymer film, and initiate photopolymerization of the acrylic groups.

Fig. 3 shows the conversion curve of the acrylic groups monitored by FT-IR. The absorbance at 810 cm$^{-1}$, the twisting vibration of H–C(=C), decreases with UV irradiation time, and the conversion is estimated from the ratio of the peaks at 810 and 755 cm$^{-1}$, the bending vibration of aromatic C–H, which stays constant. The conversion reaches about 50% after irradiating with UV light at 80 °C for 20 min. When the molar extinction coefficients of DR1M and the photoinitiator are compared at 365 nm, which is one of the strong emission lines of the UV lamp, they are 2300 and 102 L/mol/cm, respectively. Thus, as the azobenzene in the polymer still absorbs 20 times more UV energy more than the photoinitiator at 365 nm, the photopolymerization rate is still relatively slow. We have found that even if the temperature is increased to 100 °C, still lower than the $T_g$, the photopolymerization conversion does not change significantly. This may be because both the propagating radical and the acrylic groups in the polymer cannot diffuse easily in the glassy state. Nevertheless, after irradiating at 80 °C with UV lamp for 20 min, the film cannot be dissolved in any solvent.

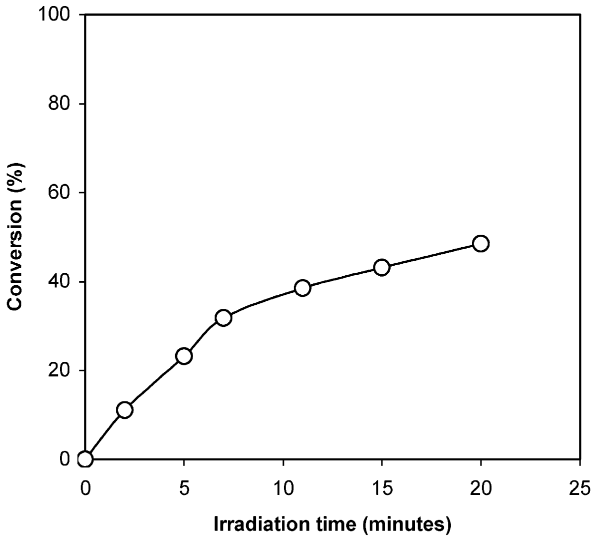


Fig. 3. Conversion curve of acrylic groups in the polymer, measured as the ratio of the IR peaks at 810 and 755 cm$^{-1}$.

### 3.2. Surface relief gratings inscription

Surface relief grating inscription was carried out on the films before and after photo-crosslinking by irradiating with an interference pattern of a circularly polarized laser. The diffraction efficiency of the first order peak is shown in Fig. 4. The efficiency was calculated by dividing the intensity of the first diffracted order by the intensity of the incident probe beam. The diffraction efficiency of the film before photocrosslinking increases with the irradiation time and reaches a plateau after about 35 min. The maximum diffraction efficiency is 22%, which is similar to that of poly 4′-[(2-(acryloyloxy)ethyl) ethylamino]-4-nitroazobenzene (polyDR1A) containing the same azo group, while the azo content here is half of the molar fraction in polyDR1A [4]. The diffraction efficiency or the formation rate of the gratings depends on many factors, such as the azo structure, the molecular weight, the glass transition temperature, and the intensity, the polarization direction or angle of the incident laser [3,7]. The azo content in the polymer may not be the dominant factor although a certain amount of azo chromophore is needed for polymer chain migration. In contrast the diffraction efficiency of the polymer that was photocrosslinked before the grating inscription was much smaller, less than 1%, and may be due to photoinduced birefringence.

The grating on the non-crosslinked polymer film was observed by AFM as shown in Fig. 5. After 40 min of irradiation, surface gratings with a depth and spacing period of 355 nm and 1100 nm, respectively, are uniformly inscribed using a relatively weak laser at an intensity of 140 mW/cm$^2$. On the other hand while surface gratings are also observed on the photocrosslinked film, but their depth is only about 30 nm. Large-scale polymer chain migration which is responsible for the surface gratings is much lower in the crosslinked network [23]. In the photoinduced orientation measurement [20], some azo chromophore could be oriented even in a tightly crosslinked polymer network upon irradiation with polarized laser, and photo-induced birefringence was observed. In contrast, cross-linking limits large-scale polymer chain migration significantly, thus inhibiting surface grating formation, even though micro-scale chromophore re-orientation can still occur.

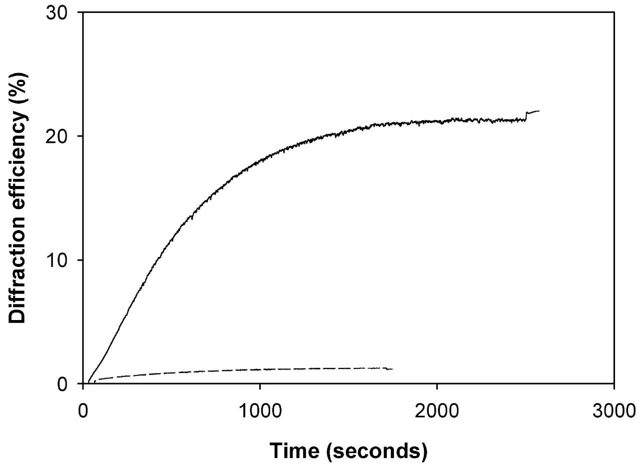


Fig. 4. Diffraction efficiency changes of the samples before (full line) and after (broken line) photocrosslinking.

### 3.3. Photocrosslinking of the film with surface gratings

After the gratings were inscribed on a non-crosslinked film, UV light was shone at 80 °C for 15 min under nitrogen to perform photocrosslinking. Although heating around the $T_g$ is efficient for photopolymerization of acrylic groups [24], 80 °C was chosen because higher temperatures lead to erasure of the gratings. As shown in Fig. 2, UV irradiation causes a decrease in the maximum absorption in the UV–Vis spectrum and a slight shift to shorter wavelength. Some discoloration of the polymer films was observed. We assume that some photo-degradation of the azo chromophore is induced by the UV irradiation, as reported previously [25,26]. An absorption peak corresponding to an N–H bond around 3350 cm$^{-1}$ appeared in the IR spectrum of the film after UV irradiation. This suggests some photodecomposition of the azo groups [27]. At the same time, the diffraction efficiency of the grating decreased (from 22 to 18%). The depth of the grating profile also decreased from 355 to 310 nm, while the grating maintained its shape. The decreases in both the diffraction efficiency and the grating depth might arise from the photodegradation of the azo chromophore in addition to some volume shrinkage during photocrosslinking. Nevertheless, UV irradiation did not cause a significant change in the surface gratings.

### 3.4. Thermal stability of the gratings

In order to investigate the effect of photocrosslinking on the thermal stability of the gratings, the films with gratings were heated at several temperatures, and the diffraction efficiency was measured as a function of the heating time (Fig. 6). The diffraction efficiency is normalized for comparison between the samples, and the initial value before heating is defined as 100%. For the samples with the photocrosslinked gratings (Fig. 6(b)), the value at − 15 min corresponds with the efficiency before photocrosslinking is defined as 100%. The change between − 15 min and zero is caused by the photocrosslinking process. For the samples with the gratings without photocrosslinking (Fig. 6(a)), most of the diffraction efficiency disappears quickly by heating at 120 °C, which is near $T_g$, but over 30% of efficiency still remains after the rapid decrease. Heating at 120 °C for several minutes may cause thermal crosslinking, even without adding a thermal initiator. In fact, when—after the measurement–the sample was soaked into THF, it did not dissolve completely. Another possibility is the formation of density gratings, as previously reported by Pietsch

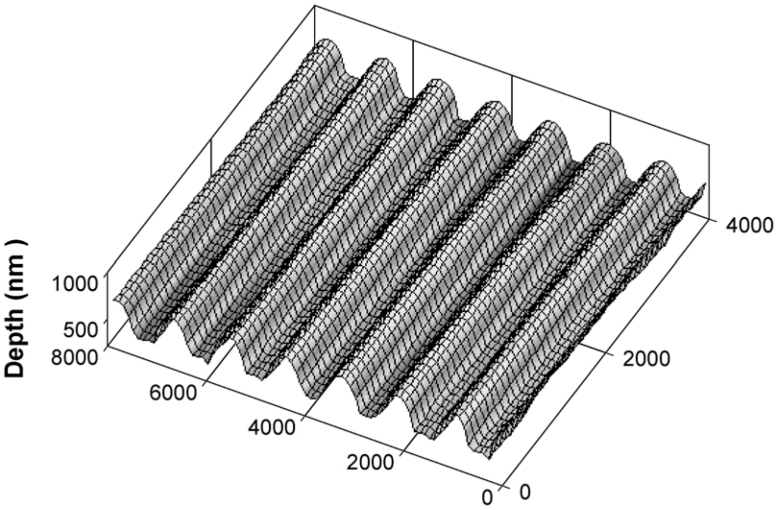


Fig. 5. AFM image of surface grating of the sample before photocrosslnking.

et al. [28]. In that report, the surface grating disappeared completely, and no surface modulation was observed by AFM, but diffraction, dependent on the probe laser intensity, was still observed. In our experiments, a grating with a depth of 207 nm was still observed. At 100 °C, below $T_g$, the efficiency decreases more slowly and at 80 °C, it is more stable.

When photocrosslinking was done after inscription, the thermal stability significantly improved as shown in Fig. 6(b). As in the case above, the efficiency initially decreased during photocrosslinking but was relatively stable even upon heating to 120 °C. The $T_g$ of the crosslinked film was now 152 °C and only a slight decrease was observed during heating at 150 °C. When the sample was heated above $T_g$ (180 or 210 °C), the efficiency decreased gradually, and 33% of the initial diffraction efficiency still remained even after heating at 210 °C for 2 h. Thus, the photocrosslinked gratings do not disappear even after heating above $T_g$.

## 3. Conclusions

An azo copolymer that can be crosslinked by photopolymerization was synthesized by free-radical copolymerization followed by a substitution reaction. Surface relief gratings were inscribed by irradiating onto the film surface with an interference pattern of circularly polarized beams. Photocrosslinking with UV irradiation after inscription fixed the gratings permanently but was accompanied by some photo-degradation of the azo chromophore. The shape was maintained and significant diffraction was still observed even when heating well above $T_g$. For gratings without

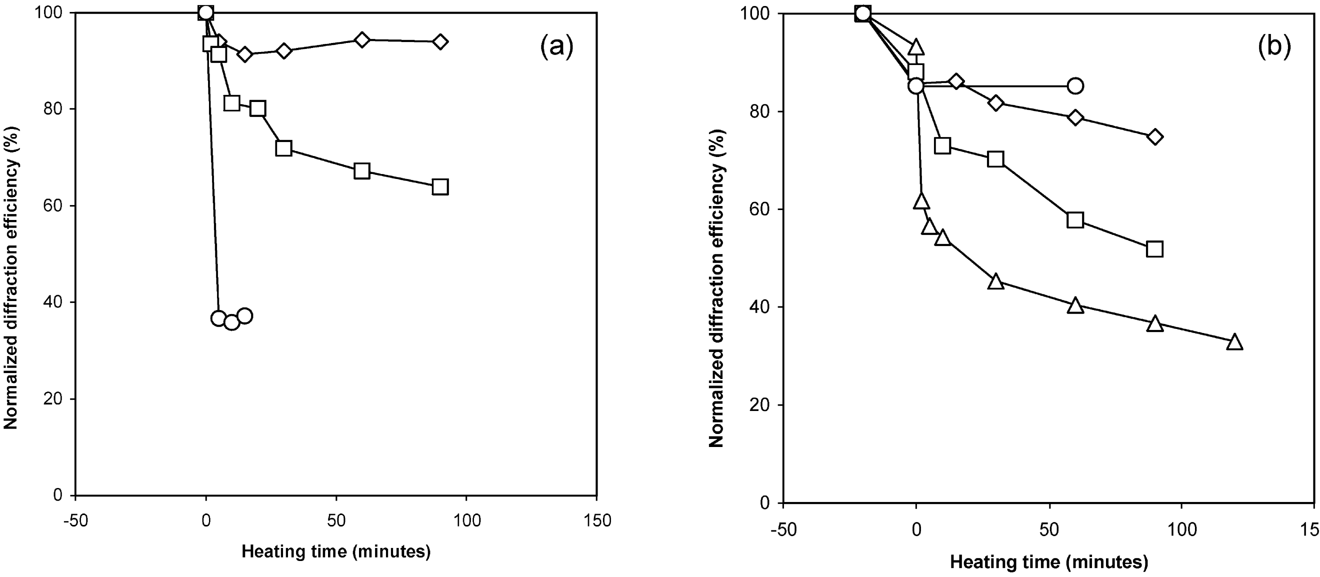


Fig. 6. Thermal stability of normalized surface gratings; (a) samples without crosslinking, (◇) 80 °C: (□) 100 °C: (○) 120 °C, (b) samples photocrosslinked after the grating inscription, (○) 120 °C: (◇) 150 °C: (□) 180 °C: (△) 210 °C.

photocrosslinking, diffraction decreased rapidly upon heating near the $T_g$.

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