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Photoresponsive behavior of two well-defined azo polymers with different electron-withdrawing groups on *push-pull* azo chromophores

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Abstract

Two well-defined methacrylate-based azo polymers bearing strong push-pull azo chromophores were synthesized by RAFT polymerization. The polymers contain cyano and carboxyl as electron-withdrawing groups at 4-positions of the azo chromophores. The polymers exhibited significantly different photoresponsive properties on all light-driven motion levels. When irradiated with a linearly polarized laser beam at 532 nm, the cyanoazobenzene-containing polymer showed rapid birefringence growth relative to that of the carboxylazobenzene-containing polymer. When the light was switched off, a much lower orientation decay was observed for the carboxylazobenzene-containing polymer compared with its counterpart. Upon irradiation with the interfering laser beams at these two wavelengths, surface-relief-grating amplitude formed on the film of the cyanoazobenzene-containing polymer was substantially larger than that for the other. When the polymer films were irradiated with a homogenous laser beam at 488 and 532 nm, self-structured surface pattern was only detected for the cyanoazobenzene-containing polymer with the 532 nm light irradiation.

Key Words: Azobenzene, RAFT, Hydrogen-bonding, Photoinduced birefringence, Surface-relief-grating, Self-structured surface pattern.

1. Introduction

Polymers containing aromatic azo chromophores (azo polymers for short) have attracted considerable attention in recent years for their unique photoresponsive properties and potential applications [1-7]. Those properties that have been extensively explored include photoinduced phase transition [8], photoinduced dichroism and birefringence [9], surface-relief-grating (SRG) formation [10, 11], photo-mechanical thin film contraction and bending [12-14], spontaneous surface pattern formation [15], and photoinduced colloidal deformation among others [16, 17]. Azo polymers are expected to be applied in areas such as optical data-storage, photo-switching, holography, photomechanical devices, sensors and actuators. The above-mentioned interesting properties are closely related with the *trans-cis* photoisomerization of the azo chromophores. According to the spectral feature and isomerization behavior, azo chromophores have been classified into azobenzene type, aminoazobenzene type, and pseudo-stilbene type [18]. The pseudostilbene type azo chromophores usually contain strong electron donating and withdrawing substituents at 4 and 4' positions on the aromatic rings. The push-pull type azo chromophores possess strong absorption bands in visible light region caused by $\pi \rightarrow \pi^*$ electronic transition. Different from azobenzene type compounds, the ${}^{1}(\pi, \pi^{*})$ state might have lower energy than that for ${}^{1}(n, \pi^{*})$ state, i.e. the levels of ${}^{1}(n, \pi^{*})$ and ${}^{1}(\pi, \pi^{*})$ states are reversed on the state energy diagram [18]. This type of azo chromophores shows fast *trans*-to-*cis* isomerization and thermal relaxation. The polymers containing push-pull type azo chromophores can show a variety of photoresponsive functions [1-4, 9-11, 15-17].

Light-driven motions at different levels are the most important photoresponsive properties that have been intensively investigated in recent years [2]. At the molecular level, repeated cycles of trans-cis-trans isomerization will force the azo chromophores of the polymers to take preferential orientation in a direction perpendicular to the light polarization. The orientation can also cause some correlative alignments of adjacent groups or segments in the azo polymers. The irradiation-driven orientation will result in the photoinduced anisotropy (PIA) of solid thin films, such as optical dichroism and birefringence. The photoisomerization can induce massive motion of azo polymers at the micrometer level [2, 10, 11, 15-17]. Upon irradiation with interfering laser beams, surface-relief-gratings (SRGs) will be formed on the azo polymer films [10, 11]. SRGs are usually formed at a temperature well below the glass transition temperature (T_{α}) of the polymers and can be erased by heating sample to a temperature above its T_{g} . More recently, another interesting photoinduced effect occurring on azo polymer film surfaces has been observed, which is known as spontaneous surface pattern formation through light irradiation [15]. It is characterized by the self-structured surface patterns such as submicrometer hexagonal pillar arrays formed on the azo polymer films after irradiation with a uniform single laser beam at normal incidence. To understand the structureproperty relationship and optimize those useful properties, azo polymers with different structures have been prepared and studied by different methods [1-7, 19-22]. The influence of experimental parameters, such as polarization of the laser beam, irradiation time and intensity, has been investigated [1-3]. In comparison with the extensive exploration of the PIA and SRG formation, there are relatively few studies devoted to the photoinduced self-structured pattern formation.

It has been known for years that electron-withdrawing groups on azo chromophores can significantly influence the absorption band position and molar extinction coefficient of azo dyes and pigments [23, 24]. In recent years, effects of the electron-withdrawing groups on photoresponsive properties of azo polymers have been investigated, which include their influences on the SRG formation [25, 26], dichroism and birefringence [2, 27] and self-structured surface pattern formation [28]. The studies show that there exists a close correlation between the electron-withdrawing groups on the push-pull azo chromophores and the photoresponsive behavior of azo polymers. However, most of the studies were carried out by using azo polymers obtained from the common radical polymerization or polycondensation, which was difficult to control the molecular weight and usually resulted in a broad molecular weight distribution. Moreover, the studies were mainly concentrated on one or two of the photoresponsive properties, which could not give a unified picture of the effect of the electron-withdrawing groups.

In this study, two azo polymers with narrow molecular weight distributions are used to study a series of the photoresponsive properties including photoisomerization, photoinduced birefringence and dichroism, self-structured surface pattern formation and SRG formation. One of the azo polymers, poly(6-(*N*-methyl-*N*-(4-(4'-carboxylphenylazo) phenyl)amino)hexyl methacrylate) (PAzoCA-6), was synthesized in this study. For another azo polymer, poly(6-(*N*-methyl-*N*-(4-(4'-carboxylphenylazo)phenyl)amino)hexyl methacrylate) (PAzoCA-6), its synthesis has been reported by us previously [29]. This polymer is used here to study the properties for the comparison. The two azo polymers were synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization to possess narrow molecular weight distributions. The structural difference of the polymers only exists in the electron-withdrawing substituents at the 4-

position of the azo chromophores. The photoresponsive properties of the azo polymers were investigated to understand their correlation with the electron-withdrawing substituents on the azo chromophores.

2. Experimental Section

2.1 Materials

Anisole and THF were distilled from sodium prior to use and the other solvents were flash distilled before use. All other reagents and chemicals were purchased from commercial sources and used as received without further purification. The synthetic route to obtain the monomers is shown in Scheme 1. The synthetic route to synthesize the two azo polymers is shown in Scheme 2. The synthetic detail of poly(6-(*N*-methyl-*N*-(4-(4'-cyanophenylazo)phenyl)amino)hexyl methacrylate) (PAzoCN-6) has been given in our previous report [29]. The chain transfer agent 2-(2-cyanopropyl)dithiobenzoate (CPDB) and the intermediate products to obtain the monomer 6-(*N*-methyl-*N*-(4-(4'-carboxylphenylazo)phenyl)amino)hexyl methacrylate (AzoCA-6) were synthesized according to the literature method [30, 31]. ¹H NMR of the intermediate products and the monomers are given in the Supporting Information.

2.2 Syntheses

6-(*N*-Methyl-*N*-(4-(4'-carboxylphenylazo)phenyl)amino)hexyl methacrylate) (AzoCA-6). 4-Aminobenzoic acid (6.85 g, 0.05 mol) was dissolved in a mixture of HCl (15 mL) and deionized water (30 mL). An aqueous solution (20 mL) of NaNO₂ (4.14 g, 0.06 mol) was slowly dripped into the mixture cooled with an ice bath. The reaction

mixture was stirred at 0 °C for 5 min and then filtrated to obtain the solution of the diazonium salt. The solution of 6-(*N*-methyl-*N*-phenylamino)hexyl methacrylate (11.01 g, 0.04 mmol) in DMF (50 mL) was added into a reaction flask and cooled with an ice bath for 30 min. The diazonium salt solution was added dropwise into the DMF solution while the temperature was controlled to be below 5 °C. After stirring for 3 h, the solution was poured into an excess of deionized water. The precipitate was collected by filtration and washed with plenty of water. After drying, the product was purified by recrystallization from ethanol and dried under vacuum. Yield: 89%. ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.20 (d, *J* = 6.9 Hz, 2H), 7.91-7.86 (overlap, 4H), 6.73 (d, *J* = 9.3 Hz, 2H), 6.09 (s, 1H), 5.55(s, 1H), 4.15 (t, *J* = 6.5 Hz, 2H), 3.43 (t, *J* = 7.4 Hz, 2H), 3.07 (s, 3H), 1.94 (s, 3H), 1.74-1.64 (m, 4H), 1.48-1.37 (m, 4H). FT-IR (KBr, v, cm⁻¹): 2935, 2654, 2542, 1716, 1684, 1635, 1599, 1516, 1421, 1379, 1290, 1246, 1136. MS (MALDI-TOF): calcd. for C₂₄H₃₀N₃O₄ [M + H]⁺: *m/z* = 424.22; found: 424.22.

Poly(6-(N-methyl-N-(4-(4'-carboxylphenylazo)phenyl)amino)hexyl methacrylate) (**PAzoCA-6**). AzoCA-6 (0.846 g, 2 mmol), 2,2'-azobis(2,4-dimethyl) valeronitrile (ABVN, 2.5 mg, 0.01 mmol), and CPDB (11.1 mg, 0.05 mmol) were added into a 50 mL Schlenk flask, followed by the addition of THF (3 mL). The mixture was degassed by three freeze-pump-thaw cycles and sealed under Argon. The flask was then placed in an oil bath of 55 °C. After reaction for 20 h, the flask was immersed in ice water to terminate the reaction. The reaction solution (100 μ L) was extracted for ¹H NMR measurement to determine the conversion of the monomer. The reaction solution was then diluted with THF and precipitated in a large amount of hexane to obtain the crude product. The purification procedure was repeated three times and the polymer was dried in a vacuum oven for 24 h. The conversion of the monomers was calculated by Eq. 1 on

the basis of the integration areas of the ¹H NMR peaks at 6.09 *ppm* ($I_{6.09}$) and 6.55 *ppm* ($I_{6.55}$), which represents the vinyl proton of the methacrylate of the remaining monomer and the two protons of the phenyl at the *ortho*-position to the amino group.

$$conv(\%) = (1 - 2 \times I_{6.09} / I_{6.55}) \times 100\%$$

Conversion of the monomer was estimated to be 95 mol % obtained from the ¹H NMR analysis. M_n (GPC) =13,000, M_w/M_n (GPC) = 1.21. ¹H NMR (300 MHz, DMSO- d_6): δ (ppm): 8.11-7.95 (m), 7.84-7.59 (m), 6.79-6.37 (m), 4.09-2.55 (m), 1.52-0.48 (m). FT-IR (KBr, v, cm⁻¹): 2935, 2858, 2659, 2542, 1720, 1686, 1601, 1516, 1419, 1381, 1290, 1248, 1138.

2.3 Characterization

The molecular weights and molecular weight distributions were measured using gel permeation chromatography (GPC) equipped with a PLgel 5 μ m mixed-D column and a refractive index (RI) detector (Wyatt Optilab rEX). The measurements were carried out at 35 °C and the molecular weights were calibrated with polystyrene standards. THF was used as the eluent and the flow rate was 1.0 mL/min. ¹H NMR spectra were recorded on a JEOL JNM-ECA300 spectrometer (300 MHz for proton) by using CDCl₃ and DMSO-*d*₆ as the solvent and tetramethylsilane as the internal standard. Fourier transform infrared spectroscopic (FT-IR) measurements were carried out on a Nicolet 560-IR spectrophotometer by incorporating the samples in the KBr tablets. UV-vis spectra were measured on an Agilent 8453 UV-vis spectrophotometer. Thermal properties of the polymers were tested by using TA Instrument DSC 2920 with a heating rate of 10 °C/min in the nitrogen atmosphere.

(1)

2.4 Sample preparation

Solid thin films of the azo polymers were prepared by spin-coating and used for the following experiments. To obtain solutions for spin-coating, PAzoCN-6 was dissolved in chloroform and PAzoCA-6 was dissolved in DMF with weight fractions ranging from 1.0 -2.5 %. The homogeneous solutions were filtered through 0.45 μ m syringe filters and spin-coated on clean substrates (quartz and glass slides) at a speed of 1500 rpm. The films obtained from the spin-coating were first dried under the ambient condition for 12 h and then annealed at 100 °C under vacuum for 24 h. The film thicknesses were estimated by scratching the films with a razor blade and measuring the step heights by the scanning probe microscopy (Nanoscope– \Box A) in the tapping mode.

2.5 Photoresponsive property measurements

Photoinduced *trans-cis* isomerization was measured by irradiating the solid films on quartz slides at 25 °C for different time periods. The irradiation was conducted by using Asahi Spectra model MAX-302 xenon light source (300 W), which was equipped with band pass filters (Asahi Spectra) to obtain the light of $\lambda = 500 \pm 2$ nm. The spectroscopic variations caused by the irradiation were recorded using a UV-vis spectrophotometer (Agilent 8453).

The photoinduced birefringence of the azo polymers was measured *in-situ* using an optical setup similar to those reported before [32, 33]. Both a diode-pumped frequency-doubled solid-state laser at 532 nm and an Ar^+ laser at 488 nm were used as the light source. The polymer films spin-coated on glass slides were irradiated with the linearly *p*-

polarized laser beam at these two wavelengths. The intensity of the laser beam was adjusted to be 25 mW/cm². The laser beam was expanded through a spatial filter and collimated to provide a homogeneous intensity profile over the irradiated area on the films. The photoinduced change in the refractive index was probed using an unpolarized beam from a He-Ne laser (632.8 nm, 2.3 mW/cm²). The intensity of the probe beam that transmitted through the sample set between a pair of crossed polarizers was recorded by a photodiode. The polarization directions of the polarizers were set at $\pm 45^{\circ}$ angle to the polarization of the excitation beam. When the intensity variation of the probe beam was saturated, the excitation beam was switched off to investigate the relaxation process. Photoinduced dichroism of the azo polymer films was evaluated using polarized FT-IR spectroscopy. Films spin-coated on CaF₂ plates were used for the polarized FT-IR measurements, respectively. The light irradiation condition was the same as those described above for the photoinduced birefringence experiments.

SRG and self-structured surface pattern were inscribed using the polymer films spincoated on glass slides. A linearly polarized laser beam at 488 nm or 532 nm was used as the light source. The experimental set-up for inscribing SRGs was similar to those reported before [10, 11]. The laser beam was spatially filtered, expanded and collimated to provide homogeneous intensity profile. Half of the laser beam was incident on the films directly and the other half of the beam was reflected onto the films from a mirror. The space periods of the SRGs were controlled by selecting the proper incident angle. The time evolution of the gratings was monitored using a He-Ne laser (633 nm) as the probe beam and the first-order diffraction efficiency was recorded in a real time manner. Self-structured surface patterns on the azo polymer films were induced by irradiation with linearly polarized and circularly polarized laser beams at the normal incidence for both

wavelengths. The surface patterns formed on the films after light irradiation were probed using a Nanoscope-III A scanning probe microscope in the tapping mode.

3. Results and Discussion

3.1 Synthesis and characterization

The two azo polymers poly(6-(*N*-methyl-*N*-(4-(4'-cyanophenylazo)phenyl)amino)hexyl methacrylate) (PAzoCN-6), and poly(6-(*N*-methyl-*N*-(4-(4'-carboxylphenylazo) phenyl)amino)hexyl methacrylate) (PAzoCA-6), were synthesized by RAFT polymerization. The synthetic routes of the monomers and polymers are given in the Scheme 1 and 2. The polymerizations needed to be carried out in good solvents for the azo polymers, which were different for these two polymers. AzoCN-6 was polymerized by using anisole as the solvent at 75 °C and AIBN was used as the initiator. As PAzoCA-6 is almost insoluble in a low-polar solvent, the polymerization of AzoCA-6 was carried out in THF at 55 °C. Owing to the lower polymerization temperature, which was determined by the low boiling point of THF, 2,2'-azobis(2,4-dimethyl) valeronitrile (ABVN) with a lower T_d compared to AIBN was selected as the initiator.

GPC analysis indicates that PAzoCN-6 and PAzoCA-6 with narrow molecular weight distributions were obtained under the conditions (Figure 1). The number average molecular weights obtained from the GPC measurements are 13,000 and 15,400 for PAzoCA-6 and PAzoCN-6 with the polydispersities of 1.21 and 1.18, respectively. It shows that the azo polymers with narrow molecular weight distributions can be obtained from the RAFT polymerization. On the other hand, the conversions of the two monomers are obviously different under the conditions. Compared with the low conversion of 45%

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for AzoCN-6, the conversion of the AzoCA-6 can nearly reach 100%. By adjusting the polymerization condition, such as increasing the polymerization time and using similar polymerization condition to PAzoCA-6, the conversion of AzoCN-6 cannot be obviously improved. The foregoing result indicates that AzoCA-6 is a monomer suitable for the RAFT polymerization. Moreover, as the carboxylic groups are ionizable functional groups, PAzoCA-6 might show advantages to be used as polyelectrolytes or in hydrophilic materials.

Figure 2 shows the ¹H NMR spectra of PAzoCN-6 and PAzoCA-6 in CDCl₃ and DMSO- d_6 , respectively. The resonance signals of the spectra can be readily assigned to the protons of the polymers. The resonances in the low magnetic field range are the contribution from the push-pull azo chromophores. The obvious difference can be seen for the resonances of the protons on the aromatic rings, which is related to the different electron-withdrawing groups on the azo chromophores. Optical microscopic observation shows that the polymers functionalized with the strong push-pull azo chromophores do not form a liquid crystalline phase. Figure 3 gives DSC curves of the two azo polymers from the second heating and cooling scans under N₂ protection. PAzoCN-6 shows a thermal phase transition behavior of an amorphous polymer and has a glass transition temperature (T_g) of 58 °C. No obvious glass transition or crystalline transition can be identified for PAzoCA-6, which is attributed to the intermolecular hydrogen-bonding formed between the carboxyl groups.

3.2 Spectral characteristics and photoisomerization

Figure 4 gives the UV-vis spectra of the solid films of the two azo polymers before and after the light irradiation. PAzoCN-6 and PAzoCA-6 possess similar absorption

spectra before the light irradiation. The strong absorption bands with the maxima around 460 nm can be seen for both polymers. The absorption bands in the visible light range are attributed to the π - π * electronic transition of the azo chromophores. The weak n- π * transition band is overlapped with the π - π * band, which cannot be identified in the spectra. The spectra exhibit typical characteristics of the pseudo-stilbene type azo chromophores [18]. The two electron-withdrawing substituents at 4-positions of the azo chromophores do not cause discernible variance in their UV-vis spectra.

Upon light irradiation ($\lambda = 500$ nm, I = 5 mW/cm²), both azo polymers show the spectral changes related to the *trans-cis* photoisomerization. When the irradiation light is turned off, the electronic absorption spectra show reversal changes and recover the original features. Figure 4 shows the UV-vis spectra of the two azo polymers after the light irradiation for 1 min. For PAzoCN-6, the absorbance band at 460 nm decreases significantly and a new absorption band ($\lambda_{max} = 383$ nm), corresponding to π - π * transition of the *cis* isomer, appears at the same time. The spectral variation evidences the significant *trans-cis* isomerization occurring for the polymer. On the other hand, PAzoCA-6 shows a much lower decrease for the absorbance band at 460 nm after the irradiation. It indicates that although both azo polymers can reach the photo-stationary states quickly upon the irradiation, the ratios between the *cis* and *trans* isomers are obviously different at the steady-states for the polymers. The quantum yields of the two isomerization processes (Φ_{tc} and Φ_{ct}) could not be obtained because of the ultrafast photoisomerization and fast thermal relaxation of push-pull substituted azobenzenes [18, 34, 35]. The much lower *cis* content for PAzoCA-6 at the photo-stationary state can be attributed to the low Φ_{tc} , high Φ_{ct} , and rapid thermal relaxation. The relative significance

of these factors to cause this result is unclear at this stage. The hydrogen-bonding between the carboxyl groups, especially for the solid film, may also play an important role.

3.3 Photoinduced birefringence and dichroism

Photoinduced birefringence of the two polymers was investigated in a real-time manner by irradiating the solid thin films of the polymers with linearly polarized laser beams (25 mW/cm²) at 488 nm and 532 nm as described in the experiment section. The photoinduced birefringence was calculated from the detected transmittance of the probing laser by Equation 3, where I_T is the intensity of the transmitted probe beam when the sample film is irradiated with the writing beam, I_0 is the intensity of the probe beam that transmitted through the first polarizer, λ is the wavelength of the probing beam (632.8 nm), d is the film thickness, and Δn is the birefringence.

$$\Delta n = \frac{\lambda}{\pi d} \sin^{-1} \sqrt{\frac{I_T}{I_0}}$$
⁽²⁾

Figure 5(a) shows a typical writing-relaxing-erasing sequence for the film of PAzoCN-6 observed in a real-time manner. Before the excitation laser was switched on, no transmittance of the probing laser beam could be detected by the photodiode, because the sample placed between the crossed polarizers was isotropic. When the writing laser beam was switched on (point A), the intensity of the transmitted probing laser beam increased rapidly and then gradually reached the saturated value after a certain period of time. When the incident laser beam was turned off (point B), Δn slowly decayed and maintained about 67% of the saturated value after the relaxation. When the film was then

irradiated with a circularly polarized laser beam at the same wavelength (point C), the photoinduced anisotropy was completely erased. The photoinduced birefringence is a result of the repeated cycles of *trans-cis-trans* isomerization caused by the light irradiation, which forces the azo chromophores of the polymer to orientate preferentially in a direction perpendicular to the electric vector of the light.

The photoinduced birefringence is closely related to the wavelengths of the excitation Figure 5(b) compares the birefringence growth and light and polymer structures. relaxation profiles of PAzoCN-6 and PAzoCA-6, when the polymer films were irradiated with the 488 nm and 532 nm laser beams (25 mW/cm^2) for 125 s and then the excitation laser was switched off. The correlation with the excitation wavelength can be seen by comparing the birefringence growth profiles of the polymers under the irradiation of different wavelengths. For PAzoCN-6, upon irradiation with a 532 nm laser, a typical birefringence growth curve can be obtained with a saturated Δn of 0.036. However, the photoinduced birefringence instantaneously jumps upon irradiation with a 488 nm laser and then stabilizes at a Δn value about 0.0055. When PAzoCA-6 films were irradiated with laser beams at these two wavelengths, the birefringence growth rates are much slower compared to those of PAzoCN-6. For irradiation with these two wavelengths, no obvious difference can be observed for the photoinduced birefringence growth behavior. The result indicates that although the absorption spectra of these two polymers are similar, their photo-responsive orientation behavior is quite different.

Another important point that can be seen from the figure is the significantly different relaxation behavior of these two polymers. After switching off the excitation laser beam, the residual birefringence after relaxation appears to be much higher for PAzoCA-6 (91%) compared to PAzoCN-6 (67%). The disparity of the birefringence decay between

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PAzoCA-6 and PAzoCN-6 can be attributed to the hydrogen-bonding formed between the carboxyl groups on the side chains of PAzoCA-6. The above observation related to the hydrogen-bonding effect is consistent with results reported for epoxy-based azo polymers [27]. The effect of the hydrogen-bonding can prohibit the relaxation after switching off the irradiation light, which will be further discussed in Section 3.6.

The birefringence growth curve can be fitted by the biexponential relationship (Eq. 3),

$$\Delta n = A \cdot \{1 - \exp(-k_a t)\} + B \cdot \{1 - \exp(-k_b t)\}$$
(3)

where Δn is the birefringence measured at time t, k_a and k_b are the rate constants for birefringence growth, and A and B are two constants [32, 33]. The sum of A and B represents the maximum induced birefringence and the proportions of A and B to the sum represent the relative contribution of each term to the induced birefringence. The k_a and $k_{\rm b}$ represent the characteristic rate constants for the slow and fast growth processes. The fast process is linked to orientations of the chromophores and the slow process is related to the motion of the backbone, which are both caused by the repeated trans-cis-trans isomerization cycles [32]. The fitting parameters for the birefringence growth are listed in Table 1, except the aberrant result for PAzoCN-6 irradiated with 488 nm laser, which cannot be fit by the equation. Table 1 shows that the slow process plays the predominant role for PAzoCA-6, whilst the fast process is dominated for PAzoCN-6. The birefringence values (Δn_{max}) of these two polymer films after an irradiating period of 120s are given in the same table, which are almost the same for the two polymers when irradiated with 532 nm light and show no obvious difference when irradiated at the two wavelengths for PAzoCA-6.

The photoinduced dichroisms of the PAzoCA-6 and PAzoCN-6 films were characterized using polarized FTIR spectra. Figure 5(c) gives the polar plots of the

relative infrared absorption intensities of stretching vibration bands of the N=N bond (1379 cm⁻¹) of the two polymer films. The polymer films were irradiated using linearly polarized laser beam (532 nm) till saturation and then measured with a polarized FTIR spectrophotometer. PAzoCA-6 shows a much higher dichroic ratio than PAzoCN-6, which can be rationalized by the small relaxation of PAzoCA-6 after switching off the light. The orientation order parameter (S) was calculated by the following equation

$$\mathbf{S} = (\mathbf{A}_{\square} - \mathbf{A}_{\parallel})/(\mathbf{A}_{\square} + 2 \mathbf{A}_{\parallel}) \tag{4}$$

where A_{\perp} and A_{\parallel} are the absorbance perpendicular and parallel to the polarization direction of the laser beam. The orientation order parameters derived from the angular-dependent absorption are 0.023 and 0.044 for PAzoCN-6 and PAzoCA-6, respectively.

3.4 Photoinduced SRG formation

The surface relief gratings (SRGs) were obtained by exposing spin-coated films of the azo polymers to the interference patterns formed by the two *p*-polarized laser beams. The laser beams with the wavelengths of 488 and 532 nm and an intensity of 150 mW/cm² were used as the excitation light. Under the conditions, SRG formation was observed on films of both azo polymers, whilst the SRGs on the films of the two polymers showed different modulation amplitudes under the same condition. Figure 6 shows typical AFM images of the SRGs formed on the films of PAzoCA-6 and PAzoCN-6 after the films were irradiated using interfering laser beams with the wavelength of 488 nm for 1 h. The sinusoidal surface patterns with a period of about 1 μ m can be seen from the images. The average amplitude of the SRG inscribed on the surface of the PAzoCN-6 film can reach 400 nm, whilst the amplitude of SRG on the PAzoCA-6 film is only 40 nm.

The first order diffraction efficiency of the SRGs was measured in the real-time manner to characterize the grating growth rate. Figure 7 presents the first order diffraction efficiency as a function of the irradiation time in the process of SRG formation on the films of PAzoCN-6 and PAzoCA-6. Although the absorption maxima of the two polymers approximately appear at the same wavelength, PAzoCN-6 and PAzoCA-6 exhibit different dependences of the grating growth rates on the excitation wavelengths. For PAzoCN-6 film, the 1st order diffraction efficiency shows an obviously higher growth rate when irradiated at 532 nm than that obtained by the irradiation at 488 nm with the same light intensity (Figure 7A). This wavelength dependence is similar with those observed for the photo-induced birefringence (Figure 5(b)). On the contrary, for PAzoCA-6 film, this sequence of the wavelength dependence is reversed, where the irradiation with 488 nm light can more efficiently induce the SRG formation (Figure 7B). The first order diffraction efficiency of the SRG on PAzoCN-6 is much higher than that for PAzoCA-6, which is consistent with the AFM observation. After being exposed to the interfering laser beams at 532 nm for 1600 s, the first order diffraction efficiency of the SRG on PAzoCN-6 film can reach as high as 22%, whilst the value is only 0.41% for PAzoCA-6. The low efficiency for the SRG formation can also be attributed to the hydrogen-bonding formed between the carboxyl groups for PAzoCA-6. As the SRG formation needs a larger scale motion compared with photoinduced orientation [2], the restraint caused by the hydrogen-bonding appears more severe in this case.

3.5 Self-structured surface pattern formation

The ability of these two polymers to form self-structured surface pattern was investigated by the irradiation with a uniform laser beam. For comparison, the azo

polymer films were irradiated with a homogeneous normal-incident laser beam (200 mW/cm²) at different wavelengths (488 nm and 532 nm) for 30 min. The self-structured surface patterns can only be observed on PAzoCN-6 films when irradiated with the 532 nm laser as the incident beam. No discernible well-ordered surface pattern can be formed on the PAzoCA-6 films when irradiated using laser beams of these two wavelengths, neither can PAzoCN-6 films when irradiated using 488 nm laser. Figure 8 shows typical AFM images and their two-dimensional Fourier transform (2D-FT) images of the photoinduced surface patterns on the PAzoCN-6 film after irradiation at 532 nm for 30 min. The surface patterns are composed of regularly spaced pillar-like structures with certain localized hexagonal arrangements. The periodic orders of the surface structures on a large scale can be witnessed from the 2D-FT images. The surface patterns obtained after irradiation using linearly and circularly polarized laser beam are different in the arrangement of the self-structured pillar-like structures. In the case of irradiation with the linearly polarized laser beam, the relief structures are observed to be elongated with their elongation axis aligning along $\pm 60^{\circ}$ with respect to the polarization direction of the excitation beam, which can be seen from the two dimensional Fourier transform image. On the contrary, no such correlation is observed for the irradiation with circularly polarized light. The above observations on the self-structured pattern formation are consistent with the previous report [15, 36]. In contrast to the well-organized surface pattern formation, irradiating PAzoCA-6 films with a homogeneous beam with the same light intensity (200 mW/cm²) can only result in the bleaching of the irradiated area. The bleaching is caused by the chromophore orientation along the direction perpendicular to the film surface [2]. AFM height image of the irradiated area indicates that the surface of the films is smooth within the detect limit (see supporting information). The observation

further indicates that due to the restraint of the hydrogen-bonding, only small scale motion can be induced by the light irradiation.

3.6 Effect of hydrogen-bonding

Above results indicate that the hydrogen-bonding in PAzoCA-6 could play a significant role to cause the differences observed for these two polymers. To further confirm this point, we prepared another azo polymer PAzoCE-6, which is a polymer of 6-(*N*-Methyl-*N*-(4-(4'-ethoxycarbonylphenylazo)phenyl)amino)hexyl methacrylate). The synthesis of this polymer was suggested by the referees during the paper reviewing process. The synthetic route, structure and analytical results of this polymer are given in the Supporting Information (Scheme S1, Figure S2 and S3). The main difference between PAzoCA-6 and PAzoCE-6 is that the carboxyl group of PAzoCA-6 is replaced by ethoxycarbonyl group, which can avoid the hydrogen-bonding formation in PAzoCA-6.

The UV-vis spectrum of PAzoCE-6 before and after UV light irradiation is given in Figure S4 (in the Supporting information). The spectral profile of this polymer is similar to those of PAzoCN-6 and PAzoCA-6. Distinct from PAzoCA-6, PAzoCE-6 shows a more significant spectral change caused by *trans-cis* isomerization upon light irradiation. Figure 9 compares the photoinduced birefringence growth and relaxation behavior of these three azo polymers. The birefringence (Δn) was induced by the irradiation with a linearly polarized laser beam at 532 nm (25 mW/cm²) for 120 s and the relaxation was recorded after switching off the light. The photoinduced Δn growth of PAzoCE-6 shows an obviously slower rate compared with PAzoCN-6, but is similar to PAzoCA-6. On the other hand, after switching off the light, the relaxation decay of PAzoCA-6 is much smaller compared with those of the other two polymers.

The surface-relief-grating formation behavior of PAzoCE-6 was also studied and compared with the other two azo polymers under the same conditions. The experimental details can be seen in the Experimental Section and Supporting Information. After the irradiation with the interfering laser beams at 532 nm (150 mW/cm²) for 1 h, the 1st order diffraction efficiency of the SRG formed on PAzoCE-6 film can reach 5.1 %, whilst that for PAzoCA-6 is only c.a. 0.4 %. The AFM height images of the SRGs on the films of these two polymers are given in Figure 10. The average amplitude of the grating on PAzoCE-6 film can reach 150 nm in comparison to 20 nm on PAzoCA-6 film.

Above results indicate that both electronic interaction and hydrogen-bonding ability of the electron-withdrawing groups can play an important role in the photoresponsive processes. The difference between PAzoCE-6 and PAzoCN-6 can be attributed to the different electronic interaction of the substituents. This effect on the photoinduced orientation can be seen from the results given in Figure 5(b) and Figure 9. On the other hand, the PAzoCA-6 show significant differences in the orientation decay and SRG formation behavior compared with the other two polymers. These differences can be attributed to the effect of hydrogen-bonding. It means that the hydrogen-bonding can most significantly affect the orientation relaxation after light irradiation and SRG formation that is related to the large-scale mass-transfer.

4. Conclusion

The two azo polymers (PAzoCN-6 and PAzoCA-6) synthesized by RAFT polymerization show significant difference in their photoresponsive properties and photomechanical properties, which is related to the electron-withdrawing groups on the

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azo chromophores. Compared with PAzoCA-6, PAzoCN-6 shows a rapid growth rate for photoinduced birefringence, much higher efficiency for the SRG formation, and ability to form self-structured surface pattern when irradiated with the laser beam of the appropriate wavelength. On the other hand, much lower orientation decay is observed for PAzoCA-6 compared with its counterpart after switching off the irradiation light. The difference in the orientation decay and SRG formation can be attributed to the hydrogen-bonding between the carboxyl groups in PAzoCA-6. The hydrogen-bonding can restrain the large-scale motion of the azo chromophore and associated groups. Although these two polymers possess similar UV-vis spectra, their responses to the irradiation at these two wavelengths are different. To understand the mechanism of the wavelength effect, further theoretical and experimental investigations are required.

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Supporting Information Available: More characterization results are given there. This information is available free of charge via the Internet at <u>http://www.sciencedirect.com.</u>

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Captions of Tables, Schemes and Figures

- **Table 1.**Parameters obtained from curve-fitting of the photoinduced birefringencekinetics for PAzoCN-6 and PAzoCA-6.
- Scheme 1. Synthetic route for the monomers AzoCN-6 and AzoCA-6.
- Scheme 2. Synthetic route for the azo polymers PAzoCN-6 and PAzoCA-6.
- Figure 1. GPC curves of PAzoCN-6 and PAzoCA-6.
- Figure 2. ¹H NMR spectra of PAzoCN-6 in CDCl₃ (A) and PAzoCA-6 in DMSO-*d*₆ (B).
- **Figure 3.** DSC curves of the PAzoCN-6 and PAzoCA-6 on the second heating scan and second cooling scan with a heating/cooling rate of 10 °C/min.
- Figure 4. UV-vis spectra of PAzoCN-6 (A) and PAzoCA-6 (B) films before and upon irradiation at 500 nm ($I = 5 \text{ mW/cm}^2$).
- Figure 5. (a) Typical writing, relaxing and erasing sequence for the film of PAzoCN-6 irradiated with incident laser beam (25 mW/cm²) at 532 nm. Point A: The linearly polarized writing beam is switched on; Point B: The writing beam is switched off; Point C: The circularly polarized beam as the erasing beam is switched on. (b) Photoinduced growth and relaxation of birefringence as a function of time for the films of PAzoCN-6 and PAzoCA-6 under irradiation of laser at 488 nm and 532 nm. (c) Polar plots of the infrared absorbance at 1379 cm⁻¹ due to N=N stretching vibration for the films of PAzoCN-6 and PAzoCN-6 and PAzoCA-6

10°. The arrow denotes the direction of electric vector of the writing laser beam.

- Figure 6. AFM images (10 μ m × 10 μ m) of the surface relief grating (SRG) formed on the films of PAzoCA-6 (a, b) and PAzoCN-6 (c, d) with irradiation at 488 nm.
- Figure 7. The first order diffraction efficiency of the SRGs as a function of time in the course of the SRG formation on the films of PAzoCN-6 (A) and PAzoCA-6 (B) with excitation laser beam at 488 nm and 532 nm.
- Figure 8. Typical AFM images (10 μm × 10 μm) and 2D-FT images of the photoinduced surface patterns formed on the films of PAzoCN-6 after irradiation at 532 nm with different polarizations: (a) linearly polarized, 2D-view; (b) linearly polarized, 3D-view; (c) linearly polarized, 2D-FT image; (d) circularly polarized, 2D-view; (e) circularly polarized, 3D-view; (f) circularly polarized, 2D-FT image.
- **Figure 9.** Photoinduced growth and relaxation of birefringence as a function of time for the films of PAzoCA-6, PAzoCN-6 and PAzoCE-6 under irradiation of laser at 532 nm.
- Figure 10. AFM images ($10 \ \mu m \times 10 \ \mu m$) of the surface relief grating (SRG) formed on the films of PAzoCA-6 (a, b) and PAzoCE-6 (c, d) with irradiation of laser at 532 nm.

	PAzoCN-6	PAzoCA-6	
	532 nm	488 nm	532 nm
$k_{\rm a}(10^{-2}{\rm s}^{-1})$	2.62±0.23	1.85±0.13	1.23±0.06
$k_{\rm b} (10^{-1} {\rm s}^{-1})$	2.13±0.67	2.32±0.20	3.01±0.23
A (10 ⁻²)	0.995 ± 0.042	2.58±0.04	3.46±0.06
<i>B</i> (10 ⁻²)	2.68±0.04	1.28±0.06	1.10±0.03
$A_n^{\ a}$	0.271 ± 0.012	0.668 ± 0.015	0.759±0.016
$B_n^{\ a}$	0.729 ± 0.012	0.332±0.015	0.241±0.016
Correl. Coeff.	0.9988	0.9998	0.9991
$\Delta n_{max} (10^{-2})$	3.6	3.6	3.8

Table 1.

^a $A_n = A/(A+B), B_n = B/(A+B)$

Title: Photoresponsive behavior of two well-defined azo polymers with different electron-withdrawing groups on push-pull azo chromophores

Authors: Yu Zhu, Yuqi Zhou, Xiaogong Wang

Highlights

- Two well-defined azo polymers were synthesized by RAFT polymerization.
- The polymers were functionalized with strong push-pull azo chromophores.
- The polymers exhibited different photoresponsive properties on all motion levels.
- Photoinduced motion at large scales was severely restrained by hydrogen bonding.
- Birefringence decay can be reduced with the existence of the hydrogen bonding.



Retention Time (min)

















CHR HAN















Photoresponsive behavior of two well-defined azo polymers with

different electron-withdrawing groups on *push-pull* azo

chromophores

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Supporting Information

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1. Polymer synthesis and characterization

The ¹H NMR spectra of the intermediate products and the monomers, AzoCN-6 and AzoCA-6, are shown in Figure S1.

The monomer 6-(*N*-Methyl-*N*-(4-(4'-ethoxycarbonylphenylazo)phenyl) -amino)hexyl methacrylate) (AzoCE-6) was synthesized by using similar method as these for AzoCA-6 and AzoCN-6 syntheses. PAzoCE-6 was obtained by RAFT polymerization using cumyl dithiobenzoate (CDB) as chain transfer agent (Scheme S1). The ¹H NMR spectra of AzoCE-6 and PAzoCE-6 are shown in Figure S2. The GPC curve of the polymer PAzoCE-6 is shown in Figure S3. M_w/M_n =1.28, M_n (GPC) = 25 000.



Scheme S1. Synthetic route of PAzoCE-6







2. Photoisomerization

Figure S4 shows the UV-vis spectra of spin-coated film of PAzoCE-6. Upon irradiation at 500 nm, the change of the absorption can be witnessed by the spectral variation. It indicates that a certain amount of the azobenzene moieties in the polymer undergoes *trans-cis* isomerization.



Figure S4. UV-vis spectra of thin films of PAzoCE-6 (a) before irradiation (b) after irradiation at 500 nm.

3. Photoinduced birefringence and surface modulation

The photoinduced birefringence change of PAzoCE-6 was studied by method similar to those for PAzoCN-6 and PAzoCA-6 investigation. The spin-coated film of the polymer was irradiated with a linearly polarized laser beam at 532 nm (25 mW/cm²) and birefringence change was recorded in a real time manner. After irradiated for 120 s, the laser beam was switched off and the relaxation of orientation of the azobenzene groups in PAzoCE-6 was detected.

For surface-relief-grating inscription, spin-coated film of PAzoCE-6 was irradiated with interfering laser beams at a wavelength of 532 nm (150 mW/cm²) for 1 h. The experimental setup was the same as that described in the article, and the film thickness PAzoCE-6 was measured to be around 200 nm.

The film of PAzoCE-6 was also irradiated using a homogeneous linearly polarized beam at 532 nm. The experimental condition was the same as that given in the article. The AFM height image of the resultant surface was shown in Figure S5. Only irregular surface roughness (1-2 nm) can be seen from the image. Figure S6 shows AFM height images of the PAzoCA-6 films before and after irradiation



Figure S5. AFM height image of surface of PAzoCE-6 after light irradiation.



