

SURFACE-RELIEF-GRATING FORMATION BEHAVIOR OF TWO HYPERBRANCHED AZO POLYMERS

Peng-chao Che, Ya-ning He and Xiao-gong Wang*

Laboratory for Advanced Materials, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract In this work, surface-relief-grating formation behavior was studied by using two hyperbranched azo polymers. The hyperbranched polymers containing pseudo-stilbene type azo chromophores throughout the hyperbranched structure were synthesized by step-growth polycondensation of AB₂ type monomers. The AB₂ monomer, 4-(4'-(bis(2-chloroethyl)amino)-phenylazo)benzoic acid (BAA), was prepared through azo-coupling reaction between *N,N'*-bis(2-chloroethyl)aniline and 4-aminobenzoic acid. The another AB₂ monomer, 4-(4'-(bis(2-chloroethyl)amino)phenylazo)-3-nitro-benzoic acid (BANA), was prepared through azo-coupling reaction between *N,N'*-bis(2-chloroethyl)aniline and 3-nitro-4-aminobenzoic acid. The hyperbranched polymers (PBAA and PBANA) were prepared through nucleophilic substitution reaction of BAA and BANA, respectively. The polymers synthesized were characterized by using spectroscopic methods and thermal analysis. The photoinduced dichroism and photo-induced surface-relief-grating (SRG) formation of the hyperbranched polymers were investigated upon irradiation with Ar⁺ laser at 488 nm. PBAA shows typical photoinduced dichroism SRG formation behavior. On the contrary, PBANA does not show the photoresponsive properties. The results indicate that the nitro at the ortho position of azo group of PBANA shows the effect of inhibiting the photoinduced variations. The effect can be attributed to the blockage of the *trans-cis* isomerization of the azobenzene moieties by the steric hindrance.

Keywords: Hyperbranched azo polymer; Dichroism; Surface-relief-gratings; Isomerization.

INTRODUCTION

Polymers containing azobenzene and its derivatives (azo polymers for short) have been extensively investigated for potential applications in optical data-storage, actuator and photonic devices. The photoinduced isomerization of the azobenzene moieties in the polymers can cause a variety of photoinduced bulk and surface variations, such as phase transition, molecule orientation, surface-relief-grating (SRG) formation and photo-mechanical deformation of thin films among others^[1–3]. Photoinduced orientation and SRG formation are two of the most interesting properties of azo polymers. Photoinduced orientation is caused by repeated *trans-cis-trans* isomerization of azo chromophores, which forces the chromophores and adjacent groups to align perpendicular to the polarization direction of the light^[4, 5]. Photoinduced orientation in azo polymer films can be characterized by the birefringence and dichroism. SRG formation is generally referred to the appearance of sinusoidal surface patterns on azo polymer films induced by irradiation with interfering laser beams^[6, 7]. The surface patterns are inscribed at a temperature well below the glass transition temperature (*T_g*) of the azo polymers and can be erased by heating the films to a temperature above the *T_g*^[3, 6, 7]. This transport of azo polymers induced by the light irradiation has been attributed to the isomerization-driven free volume expansion in bulk, the force based on the dipolar interaction with the optically induced electric field gradient, a translational wormlike diffusion caused by the photoisomerization of the azobenzene chromophores, a mean-field force caused by the molecule alignment

* Corresponding author: Xiao-gong Wang (王晓工), E-mail: wxg-dce@mail.tsinghua.edu.cn

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and a photomechanical effect occurring in thin films^[8–11]. Although some recent research has indicated possible correlation between the photoinduced chromophore orientation and the surface pattern formation, a general understanding of this issue is still in a developing process.

Dendritic polymers (including dendrimers and hyperbranched polymers), having highly branched structures and a large number of terminal groups, have received more and more attentions over the last decade^[12–20]. Due to the structural characteristics, dendritic polymers show a lot of appealing properties such as the feasibility to be functionalized through the peripheral groups, better solubility, lower melt and solution viscosity compared to their linear analogues. Dendrimers, having a well-controlled size and shape, are prepared by multi-step reactions through a divergent or convergent scheme that requires tedious isolation and purification procedures. The time-consuming stepwise synthetic schemes required for the preparation of dendrimers limit their broad-range applications. Hyperbranched polymers possess less regular structures and broader molecular weight distributions compared to dendrimers. On the other hand, they can be prepared by some relatively simple methods, such as one-step self-polycondensation of AB_x type monomers (where *x* is generally 2 or 3). So they are more attractive for large-scale manufactures and industrial utilizations and are considered to be a more economical replacement of dendrimers for various applications^[19–24].

Hyperbranched azo polymers can be a new type material with dendritic structure and SRG-forming properties^[25–29]. As a comparable system to the linear polymers, studying on structure-property relation of hyperbranched polymers can shed new light on the SRG-forming mechanism. However, to our knowledge, the study on the SRG properties of hyperbranched azo polymers (or even other dendritic azo polymers) has scarcely been reported, which is partially due to the lack of a straightforward way to prepare hyperbranched azo polymers under mild conditions.

In this article, we report the synthesis of two kinds of azobenzene-containing hyperbranched polymers through nucleophilic substitution reactions of two new AB₂ monomers. Their SRG formation properties, dichroism properties and their relationship with the structure are also discussed in some detail.

EXPERIMENTAL

Materials and Measurements

N,N-bisethanolaniline and 4-amino-3-nitro-benzoic acid were purchased as commercial products from Acros. All other reagents and solvents such as dimethyl sulphoxide (DMSO) and *N,N*-dimethylformamide (DMF) were used as received without further purification.

¹H-NMR data were obtained on a JOEL JNM-ECA600 NMR spectrometer. The glass transition temperatures (*T*_gs) of the polymers were tested with a TA Instrument DSC 2910 at a heating rate of 10 K/min. The molecular weights and their distributions of the polymers were determined by gel permeation chromatography (GPC) utilizing a Waters model 515 pump and a model 2410 differential refractometer with 3 styragel columns HT₂, HT₃ and HT₄ connected in a serial fashion. THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards with dispersity of 1.08–1.12 obtained from Waters were employed to calibrate the instrument. Infrared spectra were measured using a Nicolet 560-IR spectrometer by incorporating the sample in a KBr disk. UV-Vis spectra of the azo polymers in solutions and as spin-coated films were recorded on a Perkin-Elmer Lambda Bio-40 spectrometer. Surface images of the surface-relief-gratings were monitored using atomic force microscopy (AFM) (Nanoscope IIIa, tapping mode).

Monomer and Polymer Syntheses

N,N'-bis(chloroethyl)aniline (BCA)

N,N-bisethanolaniline (10 g, 0.055 mol) was slowly added into a round bottom flask containing phosphorus oxychloride (10.2 mL, 0.11 mol) with ice bath cooling. After the addition was completed, the mixture was heated to 110°C and reaction was carried out at this temperature for one hour under a nitrogen atmosphere protection. Then, the mixture was poured into benzene (50 mL). A proper amount of water (about 50 mL) was mixed with the benzene solution to extract the water-soluble impurities. The aqueous layer was washed with

benzene (5 mL) three times to extract the remaining product. The benzene solutions were mixed and dried with anhydrous magnesium sulfate. Oily product obtained by removal of the benzene through vacuum evaporation was cooled and stirred to get the solid product. Yield: 82%. IR (KBr): 2970 (s; C—H), 1600 1500 (s; benz. ring), 1340 (s; C—N) and 720 (s; C—Cl) cm^{-1} . $^1\text{H-NMR}$ DMSO- d_6 : δ = 3.72 (m, N—CH₂CH₂Cl, 8H), 6.74 (m, Ar—H, 3H, ortho and para to N), 7.19 (t, Ar—H, 2H, meso to N). Mp: 43°C.

4-{4'-[Bis(2-chloroethyl)amino] phenylazo}-benzoic acid (BAA)

4-{4'-[Bis(2-chloroethyl)amino] phenylazo}-benzoic acid was prepared by azo coupling reaction between *N,N'*-bis(2-chloroethyl)aniline and 4-aminobenzoic acid. 4-Aminobenzoic acid (0.856 g, 6.25 mmol) was dissolved in a homogeneous mixture of glacial acetic acid (10 mL) and sulfuric acid (1 mL). Aqueous solution of sodium nitride (0.500 g, 7.25 mmol) in 1.5 mL water was added dropwise into the 4-aminobenzoic acid solution at 0°C and the solution was kept at this temperature for 5 min. The clear diazonium salt solution was then added dropwise into a solution of BCA (1.09 g, 5 mmol) in 50 mL DMF with ice bath cooling. After the reaction was carried out at 0°C for 7 h, the mixture was poured into an excess amount of water. The precipitate collected by filtration was washed with water repeatedly and dried in a vacuum oven at 70°C for 48 h. Yield: 84%; $^1\text{H-NMR}$ DMSO- d_6 , δ = 3.95 (m, N—CH₂CH₂Cl, 8H), 7.00 (d, 2H, ortho to N), 7.89 (d, 2H, meso to N), 7.97 (d, 2H, meso to COOH), 8.38 (d, 2H, ortho to COOH).

4-{4'-[Bis(2-chloroethyl)amino] phenylazo}-3-nitro-benzoic acid (BANA)

BANA was synthesized and purified *via* a procedure similar to that described above for the BAA preparation. In the reaction, the diazonium salt of 3-nitro-4-aminobenzoic acid (6.25 mmol) was reacted with BCA (1.09 g, 5 mmol) to obtain BANA. Yield: 81%; $^1\text{H-NMR}$ DMSO- d_6 , δ = 3.85 (m, N—CH₂CH₂Cl, 8H), 7.00 (d, 2H, ortho to N), 7.78 (m, 2H, meso to N, 1H, meso to COOH and NO₂), 8.25 (d, 1H, ortho to COOH and para to NO₂), 8.44 (s, 1H, ortho to COOH and NO₂).

Hyperbranched polymer PBAA

Hyperbranched polymer PBAA was prepared by the nucleophilic substitution reaction of BAA. BAA (0.732 g, 2 mmol) was dissolved in DMSO (50 mL) in a 100 mL round bottom flask. Potassium carbonate (0.5 g) and potassium iodide (0.1 g) were added into the DMSO solution. The reaction was carried out at 110°C for 12 h with stirring and then the mixture was poured into an excessive amount of water. The precipitated PBAA was collected by filtration and washed with water repeatedly. After being dried, the product was dissolved in DMF (20 mL) and then dropped into an excess amount of ethanol slowly with stirring. The precipitate was collected by filtration, washed with ethanol and then dried in a vacuum oven at 70°C for 48 h. Yield: 72%. $^1\text{H-NMR}$ DMSO- d_6 , δ = 7.90–8.15 (2H), 7.30–7.90 (4H), 6.60–7.15 (2H), 4.70–4.40 (2H), 4.20–3.80 (6H). T_g : 161°C. T_d : 287°C. IR (KBr, cm^{-1}): 1709 (C=O, s), 1600 1510 1450 (benz. ring, s), 1240 (C—O, s), 750 (C—Cl, s).

Hyperbranched polymer PBANA

Hyperbranched polymer PBANA was prepared and purified *via* a procedure similar to that described above for PBAA. Yield: 70%. $^1\text{H-NMR}$ DMSO- d_6 , δ = 7.90–8.25 (2H), 7.40–7.90 (3H), 6.60–7.40 (2H), 4.70–4.40 (2H), 4.20–3.80 (6H). T_g : 163°C. T_d : 244°C. IR (KBr, cm^{-1}): 1716 (C=O, s), 1600 1510 1450 (benz. ring, s), 1356 (N—O, s), 1230 (C—O, s), 760 (C—Cl, s).

Preparation of Polymer Films

Suitable amounts of the polymer samples were dissolved in DMF to obtain solutions with concentrations about 0.1 g/mL. The solutions were filtered through 0.45 μm membranes. The films were obtained by spin-coating the solutions onto glass slides. The spinning-speed was adjusted to control the thickness of the films to be around 1.0 μm . The films were then dried in a vacuum oven at 70°C for 48 h. Thinner films were obtained by spin-coating the diluted polymer solutions for photoinduced dichroism study.

Photoinduced Dichroism and SRGs

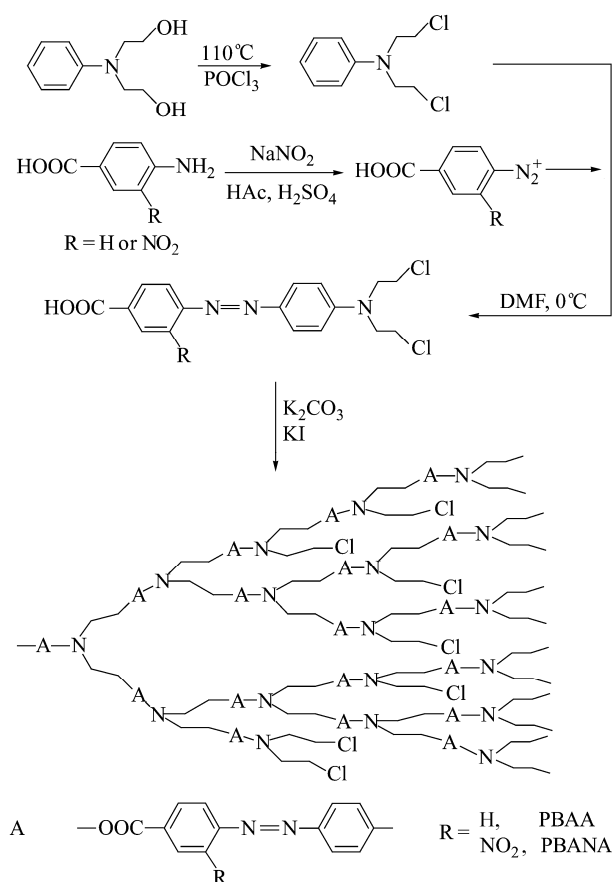
Photoinduced dichroism study of the hyperbranched polymer films was performed by using a polarized Ar⁺ laser beam with a wavelength of 488 nm as the writing beam. The polymer films were irradiated long enough to guarantee that the molecular reorientation caused by the writing beam had reached saturation. The optically induced dichroism was detected by using polarized UV-Vis spectroscopy.

The experimental setup for SRG fabrication was similar to that reported before^[30]. A *p*-polarized Ar⁺ laser beam (488 nm, 150 mW/cm²) was used as the light source. SRGs were optically inscribed on the polymer films with the interfering laser beams, where the Ar⁺ laser beam was split by a mirror and the reflecting half beam coincided with the other half on the film surfaces. The surface profiles of the resulting gratings were recorded by using a nanoscope atomic force microscope (AFM) in the tapping mode. The diffraction efficiency of the gratings was probed for the first-order diffracted beam of an unpolarized low power He-Ne laser beam (633 nm) in transmission mode. Even only weak absorption at the probed wavelength, the absorption effect of the polymer films was corrected in the calculation of the diffraction efficiency.

RESULTS AND DISCUSSION

Synthesis and Characterization of Azo Hyperbranched Polymers

The synthetic route of the two hyperbranched polymers is shown in Scheme 1. Monomer BAA was synthesized by the azo-coupling reaction between BCA and 4-aminobenzenic acid. Monomer BANA was synthesized by the azo-coupling reaction between BCA and 3-nitro-4-aminobenzenic acid. The hyperbranched azo polymers PBAA and PBANA were prepared through the nucleophilic substitution reaction of BAA and BANA in DMSO using K₂CO₃ and KI as HCl absorbent and catalyst, respectively.



Scheme 1 Synthetic route of the azo hyperbranched polymers

The resonances of protons that are ortho to the carboxyl group, azo group and amino group of PBAA appear at $\delta = 7.90\text{--}8.15$, $7.60\text{--}7.90$ and $6.60\text{--}7.15$, respectively. The resonances of protons that are ortho to the carboxyl group, azo group and amino group of PBANA appear at $\delta = 7.90\text{--}8.25$, $7.40\text{--}7.90$ and $6.60\text{--}7.40$, respectively. Compared to the monomers BAA and BANA, two new resonances corresponding to the protons of $-\text{COOCH}_2\text{CH}_2\text{N}-$ and $-\text{COOCH}_2\text{CH}_2\text{N}-$ appear at $\delta = 4.40\text{--}4.70$ and $3.80\text{--}4.20$ in the ^1H spectra of PBAA and PBANA respectively due to the polymerization. The resonances corresponding to the protons of unreacted $\text{ClCH}_2\text{CH}_2\text{N}-$ ($\delta = 3.6\text{--}3.8$) of the hyperbranched polymers appear at the same range as the monomer. The number average molecular weight (M_n) and polydispersity index of PBAA are 6500 and 1.8, respectively. The number average molecular weight (M_n) and polydispersity index of PBANA are 6700 and 2.0, respectively. Both ^1H -NMR and GPC results suggest that the designed hyperbranched azo polymers with a reasonably high molecular weight have been successfully synthesized.

The phase transition behavior of the series of HBPs was studied by using differential scanning calorimetry (DSC). From the DSC curves given in Fig. 1, the T_g s of PBAA and PBANA are determined to be 161°C and 163°C , respectively. Thermal stability of the polymers was characterized by thermogravimetric analysis (TGA). From the TGA curves given in Fig. 2, the T_d s of PBAA and PBANA are determined to be 287°C and 244°C , respectively.

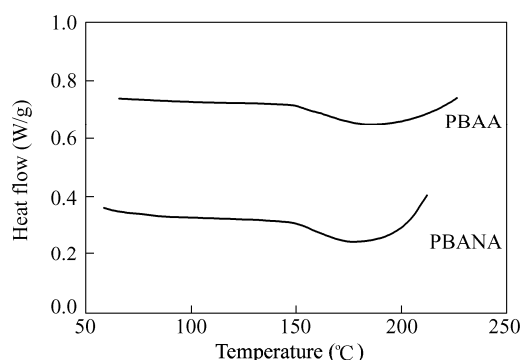


Fig. 1 DSC curves of PBAA and PBANA

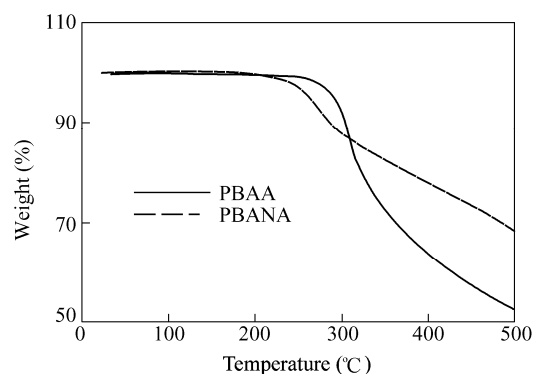


Fig. 2 TGA curves of PBAA and PBANA

UV-Vis spectra of the azo monomers and polymers in DMF solutions and polymers as spin-coated thin films are shown in Fig. 3. The wavelength at the absorption maximum (λ_{max}) is listed in Table 1. The spectra show typical absorption behaviors of the pseudo-stilbene type azo chromophores. The chromophores exhibit strong absorption in the visible light region. The spectra of the HBPs, PBAA and PBANA, in DMF solutions show the maximum absorption at 438 and 476 nm, respectively. The spectra of the HBPs, PBAA and PBANA, as spin-coated films show the maximum absorption at 427 and 462 nm, respectively. The λ_{max} of PBANA exhibited a red-shift compared with that of PBAA. That is because of the existence of the nitro groups. The λ_{max} was strongly affected by the electron-withdrawing groups due to their inductive and conjugative effect on both the ground and excited states. Spectra of PBAA and PBANA solutions show a red-shift compared with the corresponding spectra of the solid films because of the solvatochromic effect of DMF. Owing to the stronger intermolecular interaction of the hyperbranched polymers in the solid state, the absorption bands are broader compared to those of the solutions.

Table 1. λ_{max} of the monomers in DMF solutions and HBPs in DMF solutions and as spin-coated films

Samples	BAA ^a	BANA ^a	PBAA ^a	PBANA ^a	PBAA ^b	PBANA ^b
λ_{max} (nm)	422	452	438	476	427	462

^a in DMF solution; ^b as spin-coated film

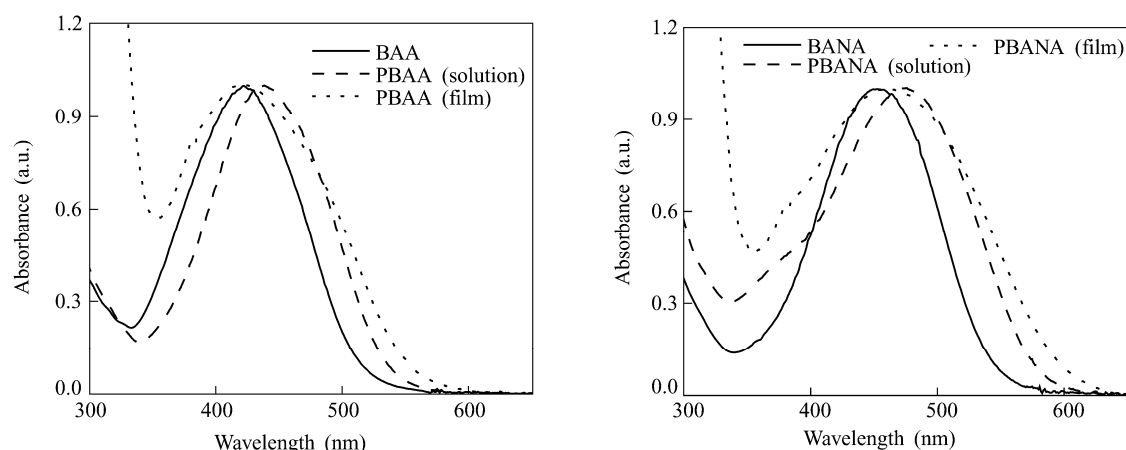


Fig. 3 UV-Vis spectra of monomers in DMF solutions and HBPs in DMF solutions and as spin-coated films

Photoinduced Dichroism and SRGs

To study the photoinduced dichroism, the spin-coated thin films were irradiated with linearly polarized Ar^+ laser beam. The films were exposed to the laser beam for 20 min to guarantee that the photo-induced chromophore orientation had reached the saturated states. In-plane dichroism was induced in PBAA films and indicated by the polarized UV-Vis spectroscopy (Fig. 4). It can be seen that the absorbance in the direction perpendicular to the polarization of the laser beam is larger than that in the direction of the polarization of the laser beam. From the UV-Vis spectroscopy, the orientation order parameter of PBAA is estimated to be 0.073. With the same experimental setup and conditions, PBANA film cannot show photoinduced dichroism and the orientation order parameter of PBANA is about 0.

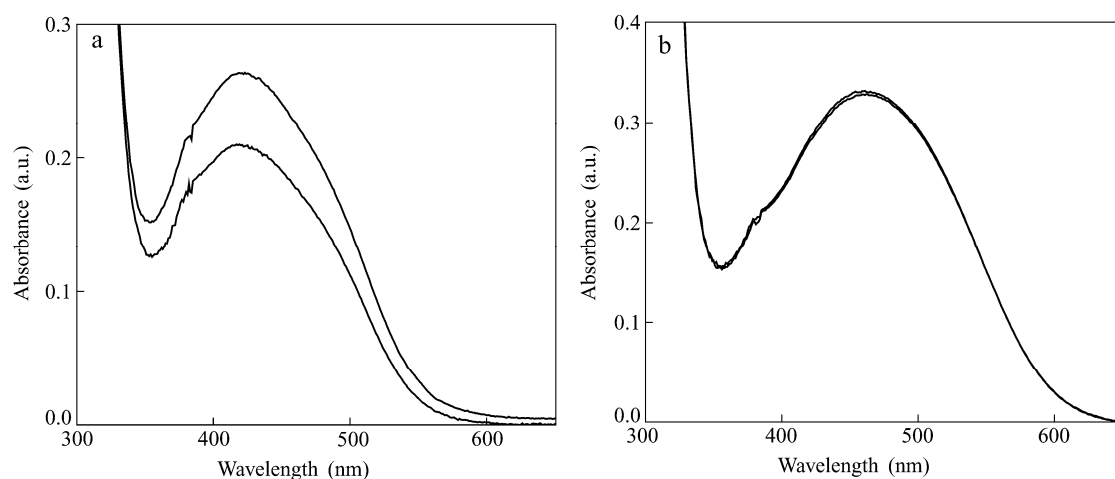


Fig. 4 UV-Vis spectra of PBAA (a) and PBANA (b) films: the upper curve, perpendicular to the polarization direction of laser beam; the lower curve, parallel to the polarization direction of laser beam. The films were irradiated with a linearly polarized Ar^+ laser beam for 20 min.

Spin-coated films of newly synthesized HBPs with a thickness of about 1 μm were used to carry out photoprocessing experiments. The experimental setup and conditions were similar to that reported before^[30]. The interference pattern of Ar^+ laser beams was produced by two *p*-polarized beams. After irradiation for 2000 s at room temperature, SRGs with large surface modulation were formed on the surface of PBAA film. Figure 5 shows the atomic force microscopic (AFM) image of the sinusoidal surface relief structures with regular spaces formed on the polymer film. The surface modulation depth is about 83 nm, and the grating spacing is about

770 nm. The modulation depth depends on the irradiation energy and the spatial period depends on both the angle θ between the two interfering beams and the wavelength λ of the writing beam. The first order diffraction efficiency of the SRGs recorded *in situ* was used to characterize the surface modulation. Diffraction efficiency from the surface-relief-gratings was monitored during the grating formation. A plot of the diffraction efficiency as a function of irradiation time for PBAA is given in Fig. 6. On the contrary, PBANA could hardly form SRGs after the irradiation even with longer time by using the same experimental setup and conditions. The relief depths of PBAA and PBANA films, after the irradiation under the same condition, were measured with atomic force microscopy (AFM), and the results are shown in Fig. 7 for comparison.

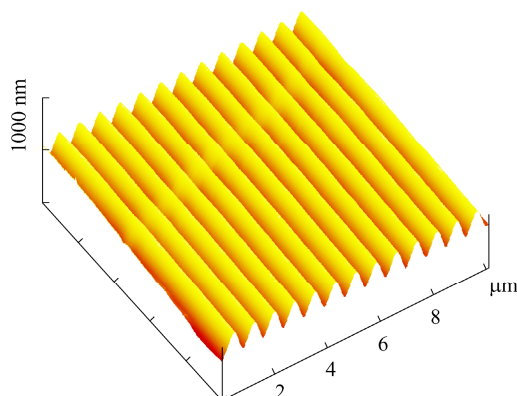


Fig. 5 AFM image of the SRGs formed on the PBAA film ($10.0\ \mu\text{m} \times 10.0\ \mu\text{m}$)

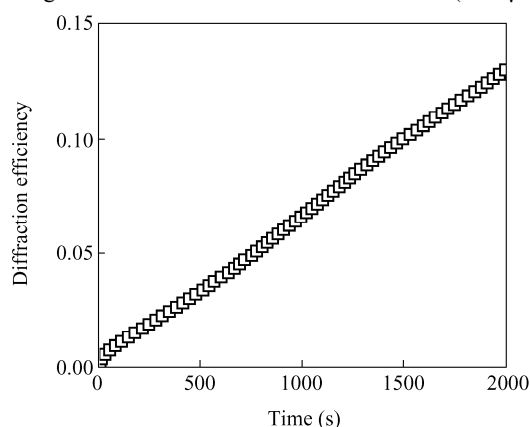


Fig. 6 Diffraction efficiency of the surface gratings inscribed on the films of PBAA as a function of irradiation time

The intensity of irradiation beam is about $150\ \text{mW}/\text{cm}^2$.

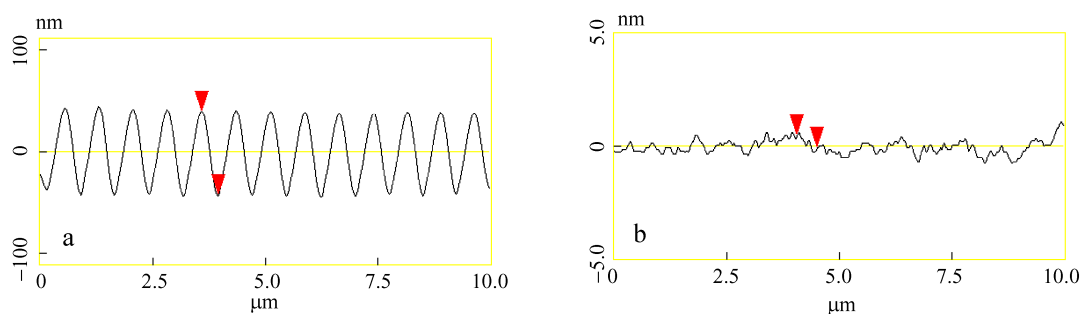


Fig. 7 Relief depth of SRGs formed on the (a) PBAA film and (b) PBANA film

In order to correlate the photoinduced dichroism and the SRG-forming behavior with the chromophore structure, the other factors that could influence the photoinduced dichroism and the SRG formation were carefully controlled in the experiments. In the photoinduced dichroism study, the light intensity was controlled to be the same. In the photoinduced SRG study, the light intensity and the angle between the two interfering beams were strictly controlled to be the same. The films used for carrying out SRGs had the approximately same thickness (of or over 1 μm). According to the report^[31], the dependence of inscription rates on the film thickness can be ignored when the films are relatively thick ($> 0.5 \mu\text{m}$). Therefore, the influences of the above factors are trivial in the above study. The structures of the two kinds of HBPs are almost the same. The only difference between PBAA and PBANA is the nitro groups at the ortho position of the azo groups. Therefore, it is believed that the substitution is the major factor to influence the photoinduced dichroism and the SRG formation. The steric hindrance caused by the nitro groups at the ortho position of the azo groups of PBANA can inhibit or retard the isomerization of the azobenzene groups. The mechanism of photoinduced dichroism and SRGs are still not fully understood. This study suggests that the dichroism and SRG formation are closely related to the photoinduced *trans-cis* isomerization of the azobenzene groups. The effect is related to the details about how the molecule evolves on the potential energy surfaces of the excited states and how it interconverts to the ground states. Our study suggests the close correlation between the isomerization and the photoinduced variations, which is a factor that needs further investigation.

CONCLUSIONS

We have successfully synthesized two kinds of hyperbranched polymers (PBAA and PBANA) through nucleophilic substitution reactions. The obtained hyperbranched polymers were characterized by $^1\text{H-NMR}$, DSC and GPC measurements. The UV-Vis spectra of the HBPs both in DMF solutions and as spin-coated films show the typical behavior of the azobenzene chromophores. After the irradiation of a polarized Ar^+ laser beam at 488 nm, the dichroism was only observed in the PBAA spin-coated film. After exposed to interfering illumination of Ar^+ laser beams (488 nm) at modest intensities (150 mW/cm^2), surface-relief-gratings were only observed on the surface of the PBAA film. Failing the photoresponses for PBANA can be attributed to the steric hindrance of the nitro group at the ortho position of the azo group, where the photoinduced *trans-cis* isomerization is inhibited or retarded.

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