Nunchaku-like molecules containing both an azo chromophore and a biphenylene unit as a new type of high-sensitivity photo-storage material

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A series of nunchaku-like molecules containing both an azo chromophore and a rigid biphenylene unit (AZBP-X, X = CA, CN, and NT) was designed and synthesized in this study. The azo compounds were amorphous solids at room temperature with glass transition temperature (T_g) values of 98, 87, and 79 °C for AZBP-CA, AZBP-CN, and AZBP-NT, respectively. Thin solid films of the azo molecular glasses could be readily obtained by spin-coating. Photoinduced anisotropy (PIA) and surface-reliefgrating (SRG) formation were investigated by irradiating the films with a linearly polarized Ar⁺ laser (488 nm) beam or interfering Ar⁺ laser beams. Upon Ar⁺ laser irradiation, photoinduced orientation occurred rapidly and the films showed significant birefringence and dichroism. When the irradiating light was switched off, the orientation did not show relaxation, as is observed for most azo polymers, and the birefringence even increased slightly. When irradiated with p-polarized interfering Ar⁺ laser beams with modest intensity (80 mW cm⁻²), SRGs were observed to be formed on the films in a high inscription rate. The grating with trough depth of 380 nm could be inscribed in 1200 s, which showed the diffraction efficiency of 27% for a He-Ne probe beam. In the initial stage of the SRG formation, a viscous flow process was visualized for the AZBP-CA film, which underwent a transition from doublet fringes on the grating crests to the final sinusoidal profile. Both PIA and SRG behavior showed a close correlation with the electron-withdrawing groups of the azo chromophores. The nunchaku-like azo molecules could be a new promising type of photo-storage materials for future applications.

Introduction

Polymers containing azobenzene and its derivatives (azo polymer for short) have been intensively studied in recent years due to their interesting properties and potential applications in the areas such as diffractive optical elements, information storage, optical switching, nonlinear optics, sensor and actuators.¹⁻⁸ When irradiated with light at appropriate wavelengths, azo polymers can show a variety of photoresponsive properties related to the trans-cis isomerization of azo chromophores.^{1,2} The photoinduced anisotropy (PIA) and surface-relief-grating (SRG) formation are two important properties attracting much recent attention.5-7 Photoinduced birefringence and dichroism of azo polymer films as typical PIA processes have been investigated by many research groups for years.^{3-6,9,10} The processes are attributed to repeated trans-cis-trans photoisomerization of azo chromophores, which forces the chromophores and related groups to gradually line up in a direction perpendicular to the polarization direction of the excitation.⁶ SRG formation is generally referred to as the surface modulation induced by irradiation with interfering laser beams.^{5-7,11,12} SRGs on azo polymer films can be inscribed at a temperature well below the glass transition temperature (T_g) of the azo polymers.¹³ The surface structures are stable below the $T_{\rm g}$ of the polymers and can be erased by heating samples to a temperature above their $T_{\rm g}$ or by irradiation with a uniform laser beam. SRG formation is also

believed to be related to the photoinduced *trans-cis* isomerization of azo chromophores.^{6,7} Although it has been actively studied in recent years, the mechanism of SRG formation still remains a puzzling issue requiring further elucidation.¹⁴⁻²⁰

Amorphous molecular materials are organic compounds that can exist in a stable glass state below their T_g but whose molecular weights are much lower than those of polymers.^{21,22} Similar to amorphous polymers, thin solid films of amorphous molecular materials can be prepared by spin-coating. Owing to attractive features such as high chromophoric density and absence of chain entanglement, amorphous molecular materials containing azo chromophores (azo molecular glasses) are promising as a new type of photoresponsive materials.^{23–25} The well-defined structures of azo molecular glasses enable them to be an ideal candidate for mechanism study. Several types of azo molecular glasses have been developed through different molecular design motifs and synthetic methods.²¹⁻³⁰ SRGs can be inscribed on the films with a fast forming-rate and large surface modulation.²⁸⁻³⁰ Nevertheless, at the current stage, the types of azo molecular glasses are still quite limited. A rigid molecular backbone is usually required to maintain the amorphous state at room temperature. Biphenyl or biphenylene units have been widely used as building blocks to construct molecular glasses.²¹⁻²⁷ Because of the rigid rod-like structure, the units can potentially take preferential orientation induced by intermolecular interaction or an external field. However, for most reported azo molecular glasses, the biphenyl or biphenylene units and azobenzene are tightly anchored by rigid tris(phenyl) cores. The rigid structure is difficult to drive by light in the photoresponsive processes.

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In this study, a new molecular design was adopted to develop photoresponsive azo molecular glasses. The molecules were constructed by connecting an azo chromophore and a rigid biphenylene unit *via* a flexible spacer. Owing to the molecular shape, it is designated as nunchaku-like molecules in this article. This molecular architecture could be reminiscent of the liquid crystal (LC) dimers, where two identical or different mesogenic units are connected by a flexible spacer.^{31–33} In contrast with the LC dimers, the aminoazobenzene unit used in this study is not a mesogenic unit. Therefore, the nunchaku-like molecules show phase behavior of an amorphous material rather than LC. Transparent solid films could be obtained by spin-coating with the azo compound solutions. The structure and properties of the azo molecular glass materials, especially those related with their responses to light irradiation, were investigated in detail.

Experimental section

Materials synthesis

Biphenyl-4,4'-diol (99%) was purchased from Tokyo Chemical Industry Co., Ltd (TCI). *N*-Methylaniline, 6-chlorohexan-1-ol, and 4-aminobenzonitrile were purchased from ACROS and Aldrich. All other chemicals and solvents were commercially purchased and used as received without further purification.

6-(*N*-Methyl-*N*-phenylamino)hexan-1-ol (1). *N*-Methylaniline (10.752 g, 100 mmol) and 6-chlorohexan-1-ol (14.05 g, 100 mmol) were added dropwise into a mixture of K_2CO_3 (13.8 g, 100 mmol) and KI (18.26 g, 100 mmol) in *N*,*N*-dimethylformamide (DMF, 100 mL) with violent stirring. After reaction at 80 °C for 5 h, the mixture was poured into an excess of water. The product was extracted from water with ethyl acetate (100 mL). The extract was desiccated and concentrated by rotary evaporation. The final product was obtained by silica gel chromatography with a mixture of ethyl acetate and petroleum ether (v/v = 1/2) as the eluent. $R_f = 0.75$ (SiO₂, ethyl acetate : petroleum ether (1 : 2)). Yield: 77%. ¹H NMR (300 MHz, CDCl₃): δ 1.33 (m, 4H), 1.55 (m, 4H), 1.95 (br, 1H), 2.90 (s, 3H), 3.28 (t, 2H), 3.57 (t, 2H), 6.70 (m, 3H), 7.20 (t, 2H).

N-(6-Chlorohexyl)-*N*-methylaniline (2). 6-(*N*-Methyl-*N*-phenylamino)hexan-1-ol (1) (10.35 g, 50 mmol) was added dropwise into a flask containing phosphoryl trichloride (23.475 g, 150 mmol) with ice-bath cooling. Then, the mixture was slowly heated to 110 °C and the reaction was kept at that temperature for 2 h. After that, the mixture was poured into an excess of water. The product was extracted from the water using benzene (100 mL). After desiccating and concentrating the organic phase, the final product as yellowish liquid was obtained. Yield: 60%. ¹H NMR (300 MHz, CDCl₃): δ 1.33 (m, 2H), 1.45 (m, 2H), 1.55 (m, 2H), 1.75 (m, 2H), 2.90 (s, 3H), 3.28 (t, 2H), 3.50 (t, 2H), 6.70 (m, 3H), 7.20 (t, 2H).

4-(6-(N-Methyl(N-phenyl)amino)hexyloxy)biphenyl-4'-ol (3). Biphenyl-4,4'-diol (5.58 g, 30 mmol) and N-(6-chlorohexyl)-Nmethylaniline (**2**) (6.765 g, 30 mmol) were added into a mixture of K_2CO_3 (6.90 g, 50 mmol) and KI (0.913 g, 5 mmol) in anhydrous N,N-dimethylformamide (100 mL) with violent stirring. After reaction at 80 °C for 12 h, the mixture was poured into an excess of NaOH aqueous solution (0.1 mol L⁻¹). The precipitate was collected by filtration and washed adequately with deionized water. After drying in a vacuum oven at room temperature for 24 h, the final product was obtained. Yield: 86%. ¹H NMR (300 MHz, CDCl₃): δ 1.35 (m, 2H), 1.55 (m, 4H), 1.78 (m, 2H), 2.90 (s, 3H), 3.30 (t, 2H), 3.95 (t, 2H), 6.70 (m, 3H), 6.90 (m, 4H), 7.20 (t, 2H), 7.40 (t, 4H).

 α -(N-Methyl-N-(4-(4'-carboxyphenylazo)phenyl)amino)- ω -(4hydroxylbiphenylene)-hexane (AZBP-CA) (4). 4-Aminobenzoic acid (0.59 g, 5 mmol) was dissolved in a mixture of acetic acid (15 mL) and sulfuric acid (1 mL) at 0 °C. NaNO₂ (0.414 g, 6 mmol) dissolved in 2 mL water was slowly dripped into the acidified 4aminobenzoic acid solution. The mixture was stirred in an ice bath for 10 min to obtain a yellowish solution of the diazonium 4-(6-(N-methyl-N-phenylamino)hexyloxy)biphenyl-4'-ol salts. (3) (1.5 g, 4 mmol) was dissolved in 80 mL DMF and the solution was cooled down to 0 °C. The diazonium salt solution was added dropwise into the DMF solution and the temperature was controlled to be below 5 °C. After reaction for 5 h, the raw product was obtained by pouring the reaction solution into 500 mL deionized water. The precipitate was collected by filtration and washed with plenty of water until the neutral state was achieved. After drying, the raw product was dissolved in THF and precipitated into a suitable amount of petroleum ether. The final product was obtained by vacuum drying at 60 °C for 24 h. Yield: 81%. ¹H NMR (300 MHz, *d*-DMSO): δ 1.39 (m, 2H), 1.47 (m, 2H), 1.63 (m, 2H), 1.76 (m, 2H), 3.08 (s, 3H), 3.50 (t, 2H), 3.99 (t, 2H), 6.88 (m, 6H), 7.43 (m, 4H), 7.83 (m, 4H), 8.10 (t, 2H), 9.41 (s, 1H), 12.90 (s, 1H). ¹³C NMR (600 MHz, d-DMSO): § 25.9, 26.6, 27.0, 29.2, 38.9, 52.0, 67.9, 111.9, 115.3, 116.2, 122.2, 126.0, 127.5, 127.7, 131.0, 131.3, 132.7, 133.2, 143.0, 152.6, 155.7, 157.0, 158.0, 167.4. IR (KBr): 3200 (m; OH), 2972 (m; CH), 1725 (s; C=O), 1600, 1510 (s; benzene ring), and 1223 (C-O) cm⁻¹. *m*/*z* (MALDI-TOF): 523.4 (M⁺, calc. for C₃₂H₃₃N₃O₄, 523.25).

 α -(N-Methyl-N-(4-(4'-cyanophenylazo)phenyl)amino- ω -(4hydroxylbiphenylene)-hexane (AZBP-CN) (5). AZBP-CN was synthesized and purified via a procedure similar to that described above for the AZBP-CA preparation. In the reaction, the diazonium salt of 4-aminobenzonitrile was reacted with 3 to obtain AZBP-CN. Yield: 83%. ¹H NMR (300 MHz, d-DMSO): δ 1.38 (m, 2H), 1.47 (m, 2H), 1.61 (m, 2H), 1.73 (m, 2H), 3.05 (s, 3H), 3.49 (t, 2H), 3.97 (t, 2H), 6.90 (m, 6H), 7.47 (m, 4H), 7.85 (m, 4H), 7.95 (t, 2H), 9.42 (s, 1H). ¹³C NMR (600 MHz, *d*-DMSO): δ 25.9, 26.6, 27.0, 29.2, 38.9, 52.1, 67.9, 111.4, 112.0, 115.3, 116.1, 119.3, 122.9, 126.4, 127.5, 127.7, 131.1, 133.1, 134.1, 143.0, 153.0, 155.4, 157.0, 158.0. IR (KBr): 3300 (m; OH), 2970 (m; CH), 2220 (s; CN), 1728 (s; C=O), 1590, 1502 (s; benzene ring), and 1230 (C-O) cm^{-1} . m/z (MALDI-TOF): 504.4 (M⁺, calc. for C₃₂H₃₂N₄O₂, 504.25).

 α -(N-Methyl-N-(4-(4'-nitrophenylazo)phenyl)amino- ω -(4hydroxylbiphenylene)-hexane (AZBP-NT) (6). AZBP-NT was synthesized and purified *via* a procedure similar to that described above for the AZBP-CA preparation. In the reaction, the diazonium salt of 4-nitroaniline was reacted with **3** to obtain AZBP-NT. Yield: 89%. ¹H NMR (300 MHz, *d*-DMSO): δ 1.40 (m, 2H), 1.48 (m, 2H), 1.60 (m, 2H), 1.75 (m, 2H), 3.10 (s, 3H), 3.49 (t, 2H), 3.98 (t, 2H), 6.89 (m, 6H), 7.43 (m, 4H), 7.90 (m, 4H), 8.37 (t, 2H), 9.40 (s, 1H). ¹³C NMR (600 MHz, *d*-DMSO): δ 25.9, 26.6, 27.0, 29.2, 52.0, 67.9, 112.1, 115.3, 116.1, 123.0, 125.5, 126.6, 127.5, 127.7, 131.3, 133.2, 143.2, 147.3, 153.2, 156.8, 157.0, 158.0. IR (KBr): 3300 (m; OH), 2968 (m; CH), 1719 (s; C=O), 1605, 1518 (s; benzene ring), and 1235 (C–O) cm⁻¹. *m*/*z* (MALDI-TOF): 524.4 (M⁺, calc. for C₃₁H₃₂N₄O₄, 524.24).

Characterization

¹H NMR spectra were obtained on a JOEL JNM-ECA300 NMR spectrometer. ¹³C NMR spectra were obtained on a JOEL JNM-ECA600 NMR spectrometer. IR spectra were determined using a Nicolet 560-IR FT-IR spectrophotometer by incorporating the powder samples in KBr disks. Mass spectra were determined using MALDI-TOF mass spectroscopy (BIFLEX III, Bruker Daltonics, Inc.). The UV-vis spectra of the samples were recorded using a Perkin-Elmer Lambda Bio-40 spectrophotometer. The thermal properties of the azo molecular glasses were investigated with TA instrument (DSC 2910 and Hi-Res TGA 2950) at a heating rate of 10 °C min⁻¹ under N₂ protection. The surface profiles of the surface-relief-gratings were monitored using an atomic force microscope (AFM) (Nanoscope IIIa, tapping mode).

PIA and SRG study

The azo compounds were dissolved in DMF with a concentration of 0.1 g mL⁻¹. After being filtered through 0.45 µm membrane, the solutions were spin-coated onto clean glass slides. By adjusting the spinning rate, the thickness of the films was controlled to be about 0.75 µm for PIA investigation and about 1.0 µm for SRG inscription. After being dried at 70 °C under vacuum for 48 h, the transparent solid films with good optical quality were obtained, which were stored in a desiccator for further studies. The birefringence and dichroism of the films were induced by irradiation with a linearly polarized beam from an Ar⁺ laser (488 nm, 80 mW cm⁻²). The photoinduced birefringence was probed in a real-time manner by an unpolarized beam from a He-Ne laser (633 nm) with low intensity, which transmitted through a pair of crossed linear polarizers at $\pm 45^{\circ}$ with respect to the polarization direction of exciting light. The optical setups for the experiments were similar to those reported previously.^{3,25,34,35} When the variation reached the saturated state, the exciting beam was turned off to investigate the relaxation process. The dichroism was detected by polarized UV-vis spectroscopy immediately after the irradiation.⁵ For SGR inscription, a linearly polarized Ar⁺ laser beam (488 nm, 80 mW cm⁻²) was used as the light source. After the p-polarized laser beam was expanded and collimated, half of the collimated beam was incident on the films directly and the other half of the beam was reflected onto the films from a mirror. The diffraction efficiency of the first order diffracted beam from the gratings was probed with an unpolarized low power He-Ne laser beam at 633 nm in transmission mode.11,12

Results and discussion

Synthesis and characterization

The synthetic route towards the nunchaku-like molecules containing both an azo chromophore and a rigid biphenylene unit is depicted in Scheme 1. The molecules differ from each other only in the chromophoric electron-withdrawing groups, which are carboxyl, cyano, and nitro for AZBP-CA, AZBP-CN, and AZBP-NT, respectively. All of the target molecules were obtained from the same precursor (3) by an azo-coupling reaction using diazonium salts of the corresponding compounds. This reaction route could introduce azo chromophores with different electron-withdrawing groups at the final stage of the preparation under mild conditions. The diazonium salts readily attack the benzene rings of the anilino groups at positions with high electron densities. The bulkiness of the attacking groups and resulted steric hindrance allow the electrophilic substitution to take place exclusively at the para position. This synthetic route can be used to prepare a series of nunchaku-like molecules bearing different electron-withdrawing groups. The chemical structure of the nunchaku-like molecules was confirmed by spectroscopic analyses and MALDI-TOF measurements.

The thermal transition and phase behavior of AZBP-X (X =CA, CN or NT) were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The DSC curves of the azo compounds are given in Fig. 1. The glass transition temperature (T_g) values were obtained from DSC and are summarized in Table 1. The T_{g} values of the AZBP-CA, AZBP-CN and AZBP-NT are 98, 87 and 79 °C, respectively. AZBP-CA containing the 4-carboxylazobenzene moiety shows a higher T_g than those of the other two compounds. This can be attributed to the hydrogen bonding between the COOH groups. POM observations indicated that before and after the glass transition, the AZBP-X films were isotropic without preferential molecular orientation. Thermogravimetric analysis (TGA) was used to investigate the thermal stability of the azo compounds. TGA curves of the azo compounds are shown in Fig. 2 and the thermal decomposition temperature (T_d) values obtained from TGA are summarized in Table 1. The T_d values of the AZBP-CA, AZBP-CN and AZBP-NT are 198, 220, and 223 °C, respectively.

The UV-vis spectra of the azo compounds in DMF solutions are shown in Fig. 3. The spectral features are typical for pseudostilbene-type azo compounds.² The absorption bands corresponding to the π - π * transition appear at the longest wavelength and the azo compounds show strong absorption in the visible region. The positions of the absorption bands are strongly affected by the electron-withdrawing groups on the azobenzene moieties, which can be attributed to their inductive and conjugative effect on both the ground and excited states. The λ_{max} of AZBP-CA, AZBP-CN and AZBP-NT is 435, 469, and 493 nm (Table 1).

Photoinduced anisotropy

Photoinduced birefringence of the azo compounds films was investigated at 633 nm. The value of the birefringence (Δn) can be calculated from the equation:⁹



Scheme 1 Synthetic route of the nunchaku-like molecules containing both an azo chromophore and a biphenylene unit.



Fig. 1 DSC curves of the azo molecular glasses.

Table 1 T_g , T_d and λ_{max} values of AZBP-CA, AZBP-CN and AZBP-NT

Sample	$T_{\rm g}(^{\circ}{ m C})$	$T_{\rm d}$ (°C)	$\lambda_{\max} (nm)^{a}$
AZBP-CA	98	198	435
AZBP-CN	87	220	469
AZBP-NT	79	223	493
AZBP-NT ^a In DMF soluti	79 on.	223	493

 $I = I_0 \sin^2(\pi \Delta n d/\lambda)$

where I is the intensity of the light transmitted through the crossed polarizer, I_0 is the intensity of the incident laser beam, d is



Fig. 2 TGA curves of the azo molecular glasses.

the thickness of the film, and λ is the wavelength of the laser beam (633 nm). Fig. 4 shows variations of the photoinduced birefringences of the AZBP-X thin films with the irradiation time. The birefringences increase rapidly at the initial stage and then gradually saturate after the rapid increases. The time needed to reach the saturated values is different for the three samples. It is shortest for AZPB-CN, which can reach the saturated value in less than 100 s. In contrast, AZPB-NT does not reach the saturated level even in 600 s. The saturated birefringence of AZBP-CA is the highest in the series, which can reach 0.22. The value is much higher compared with most azo polymers and amorphous molecular materials.^{4-6,25,29,36} The saturated birefringence of



Fig. 3 UV-vis spectra of AZBP-CA, AZBP-CN, and AZBP-NT in DMF solutions.



Fig. 4 Photoinduced birefringence of AZBP-X (X = CA, CN and NT) films. Linearly polarized Ar⁺ laser beam at 488 nm with 80 mW cm⁻² of intensity was used as the pump light. After saturation, the birefringence was further monitored for several minutes. The time when the irradiating light is switched off is marked on the curves.

AZBP-NT is much smaller than those of its counterparts, which is only 0.03 after irradiation for 10 min. The above results indicates that the photoinduced birefringence of the molecular azo glasses is closely related with the electron-withdrawing groups on the azobenzene moieties. But the exact influence of the electronwithdrawing groups on the saturated birefringence and its developing rate could be complicated. AZBP-CA shows a much larger saturated birefringence than that of AZBP-CN, but the initial increase of the birefringence of the former is slower than that of the latter.

In contrast to azo polymers, no birefringence decay (relaxation) is observed for azo molecular glasses after switching off the irradiating light (Fig. 4). Such decay is typical for azo polymers and related materials.^{4–6,25,29,36} On the contrary, even a slight increase in the birefringence can be observed when switching-off the irradiating light. This unusual property can be attributed to the structure of the nunchaku-like molecules. For azo polymers, polymer backbones are usually not easy to drive by the orientational movement of azo chromophores. Therefore, after switching off the pumping light, the stress built-up in the system could force some of the azo chromophores to reorientate, which results in the birefringence decay. In contrast, for the nunchakulike molecules studied here, the alignment of azo chromophores is easier to drive the flexible aliphatic spacers and even biphenylene units to take the corresponding orientation. In this case, the correlation in the molecules will not show obvious restriction to cause the birefringence decay.

Dichroism associated with the photoinduced azo chromophore orientation was also investigated. Fig. 5 shows the UV-vis spectra of the AZBP-X films (750 nm thick) after irradiation with the polarized Ar^+ laser beam (80 mW cm⁻²) for 20 min. Consistent with the birefringence study, obvious dichroism is observed for the films after the irradiation. The films possess much stronger absorption in the direction perpendicular to the polarization of the pumped beam. It reveals that the predominant amounts of azo chromophores have taken the orientation perpendicular to the polarization direction of the excitation beam.

By comparing the spectra given in Fig. 5, it can be seen that the electron-withdrawing groups show a significant influence on the dichroic behavior of the materials. AZBP-CA and AZBP-NT, with a carboxyl and nitro substituents, show the largest and smallest dichroism. The orientation order parameter *S*, which is used to describe the degree of orientation, can be estimated from the dichroic ratio:

$$S = (A_{\perp} - A_{\parallel})/(A_{\perp} + 2A_{\parallel})$$

where A_{\perp} and A_{\parallel} are the maximum absorbance in the directions perpendicular and parallel to the polarization.^{5,37,38} The *S* values for the AZBP-CA, AZBP-CN and AZBP-NT are calculated to be about 0.43, 0.17 and 0.10, respectively. The order parameter of AZBP-CA is the largest in the series and also much larger than those of the polymeric counterparts. The observation is consistent with the photoinduced birefringence results mentioned above. Both the birefringence and dichroism are related to the molecular orientation, but the latter is almost exclusively related to the azo chromophore orientation. The large birefringence and dichroism induced by the light irradiation could be explored for optical data-storage and used to prepare optical devices such as polarizers.

Photoinduced surface-relief-gratings

Photoinduced SRG formation on AZBP-X films was investigated by using interfering p-polarized Ar⁺ laser beams (80 mW cm⁻²) as the inscribing light and a He-Ne laser beam at 633 nm as the probe beam. The SRG formation was monitored by measuring the diffraction efficiencies of the probe beam in a realtime manner. The profiles and trough depths of the gratings were detected by AFM. Upon exposure to the interference pattern of laser beams at the modest intensity, SRGs were observed to be formed on films of all three azo molecular glasses. Fig. 6(a) shows a typical AFM image of the sinusoidal surface relief structures with regular spaces formed on the AZBP-CA film. The spatial period depends on the wavelength and the incident angle of the writing beams. Fig. 6(b) shows the AFM image of the surface



Fig. 5 UV-vis spectra of 750 nm thick films of (a) AZBP-CA, (b) AZBP-CN, (c) AZBP-NT, after irradiation by the polarized Ar^* laser (80 mW cm⁻²) for 20 min. Curve 1: perpendicular to the polarization direction of the laser beam; curve 2: parallel to the polarization direction of the laser beam.

relief structures composed of two-set fringes orthogonal to each other at the same location. Like those reported for azo polymer films, the SRGs are stable below the T_g of the amorphous materials and can be removed by optical erasure or by heating samples to a temperature above their T_g .



Fig. 6 AFM images of the surface-relief-structures on AZBP-CA films, (a) typical SRG; (b) pattern composed of two-set fringes recorded orthogonally to each other at the same location.

For a comparative study, the films of three azo molecular glasses were exposed to the laser light when the experimental conditions, such as laser intensity, incident angle and film thickness were controlled to be identical. Fig. 7 shows the firstorder diffraction efficiency (DE) as a function of irradiation time for AZBP-X (X = CA, CN and NT). Result shows that the SRGforming rate and saturated level are closely related to the electron-withdrawing groups of the azo chromophores. AZBP-CA shows the fastest inscription rate during the SRG formation among the series. Its diffraction efficiency can reach 27% after irradiation for 1200 s. The saturated depths of AZBP-CA, AZBP-CN, AZBP-NT measured by AFM are 380, 353, and 315 nm after irradiation for 1200 s. A similar dependence of the SRG formation behavior on the electron-withdrawing groups has been observed for epoxy-based azo polymers, hyperbranched polymers, and dendritic azobenzene-containing azo compounds.^{30,34,39} The SRG-forming rate and modulated amplitude depend on the experimental parameters such as light polarization manner, film thickness and grating space period. Under the same conditions, the SRG formation rate of AZBP-CA is much faster than that of BP-AZ-CA, an epoxy-based polymer bearing the same type of azo chromophores.³⁴ In this study, the SRGs were inscribed with p-/p-polarized interfering beams. The saturated surface modulation and diffraction



Fig. 7 Diffraction efficiency as a function of the irradiation time for AZBP-X.

efficiency of AZBP-CA are obviously larger than those of typical azo polymers obtained under the same experimental conditions.^{11–14} It indicates that the response to the light irradiation is significantly influenced by the molecular architecture. The nunchaku-like molecular structure is more favorable for the light-driven movement.

An interesting feature of the diffraction efficiency (DE) variation can be observed for the AZBP-CA film (Fig. 7). When the writing beams are switched on, DE starts to increase rapidly at the first stage. After about 50 s, the increase slows down and a platform can be seen for the DE-time curve, which appears that the saturated level has been obtained. However, after irradiation for another 100 s, the diffraction efficiency starts to increase again with a relatively slower rate. It finally reaches a much higher and truly saturated DE after irradiation for 1200 s. The DE variation with irradiation time can be understood by considering the contribution from the polarization (birefringence) grating and SRG.40,41 When the diffraction efficiency from both gratings is comparable, the phase shift between the gratings has a considerable effect on the dynamics of diffraction efficiency.41 The rapid DE increase in the initial stage can be attributed to the formation of the polarization grating caused by the molecular orientation. In order to verify this point, the DE variation in the first 300 s is plotted in Fig. 8 and the AFM images corresponding to the marked time periods (10, 35, 45, 60, 80 s) are given in Fig. 9. In the stage of the DE rapid increase, the SRG formed is shallow as it is a relatively slow process. Comparing the results given in Fig. 4 and Fig. 9, it can be seen that both polarization grating and SRG will increase in the period from 50 to 150 s. The DE platform for this time period can only be attributed to the phase shift of polarization grating and SRG in the space. In this case, the diffraction efficiency can not reflect the real inscription depth. As AZBP-CA shows the most significant birefringence induced by the polarized light, the superimposed effect from both gratings can be clearly observed. When the surface modulation is large (such as 200 nm), the diffraction effect from the bulk refractive index grating can be ignored.⁴⁰ The viscous flow of the material involved in the surface structure formation could disrupt the birefringence grating. The



Fig. 8 Diffraction efficiency varying with time in the initial stage of the SRG formation for the AZBP-CA film. The points marked correspond to the time to obtain the AFM images given in Fig. 9.



Fig. 9 Development of the surface morphology of the AZBP-CA film at the initial stage.

DE increase with a relative slow rate after irradiation for 150 s can be mainly attributed to the diffraction contribution from SRG.

Fig. 9 reveals more details of the SRG formation process of AZBP-CA, which is the most efficient one in the series. After exposing the film to the interfering beams for 10 s, the grating starts to form on the surface. Because of the small modulation

amplitude, the profile is hardly perceivable by AFM (Fig. 9(a)). After irradiation for 35 s, the surface relief structure can be clearly seen (Fig. 9(b)). However, in contrast to the final SRG, there is a shallower trough on every relief crest. In order to identify the difference, it is named as shallow trough to distinguish it from the true trough. The separation between the true troughs corresponds to the grating period and is determined by the incident angle and the wavelength of the laser beam. It can be estimated from AFM that the depth of the shallow trough is about 5 nm and the depth of the true grating trough is about 12 nm. After irradiation for 45 s, the depth of the true trough obviously increases but the depth of the swallow trough is almost the same (Fig. 9(c)). When the irradiation time further increases, the modulation amplitude of the grating keeps increasing and the shallow trough on the relief crest gradually disappears (Fig. 9(d) and 9(e)). The result presents a visualized picture of the SRG formation on the film through viscous flow. During the process, the material in the bright areas of the interfering fringes becomes soft and starts to migrate to the dark area at the initial stage. As the irradiation time increases, the mass-migration process gradually develops and spreads to the dark regions of the fringes. This observation can be used to better understand the SRGs formation mechanisms.

Conclusions

A series of nunchaku-like azo compounds (AZBP-X, X = CA, CN, and NT) was synthesized in this work. The materials showed amorphous solid behavior at room temperature without special treatment such as quenching. The type of the electronwithdrawing groups of the azo chromophores played an important role to influence the photoresponsive abilities of the materials. Some of the materials (such as AZBP-CA) showed a very sensitive response to the light irradiation as exhibited by the photoinduced birefringence, dichroism, and SRG formation. In contrast to azo polymers, when the irradiating light was switched off, no orientation relaxation occurred and the birefringence even increased slightly. SRG on the AZBP-CA film showed a high diffraction efficiency of 27% for the probed beam. The nunchaku-like molecules as an amorphous material are promising for the high PIA efficiency, rapid SRG formation rate and large surface modulation. The molecular design using the flexible aliphatic spacer between the functional and rigid units can be further explored for materials development and better understanding of the structure-property relationship.

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