

EPOXY-BASED AZO POLYMERS WITH HIGH CHROMOPHORE DENSITY: SYNTHESIS, CHARACTERIZATION AND PHOTOINDUCED BIREFRINGENCE

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Abstract Three epoxy-based azo polymers (PEP-AZ-Cl, PEP-AZ-CN and PEP-AZ-NT) with high chromophore density were synthesized by using post-polymerization azo-coupling reactions between epoxy-based precursor polymer (PEP-AN) and diazonium salts of 4-chloroaniline, 4-aminobenzonitrile and 4-nitroaniline, respectively. The structures and properties of the azo polymers were characterized by using $^1\text{H-NMR}$, FT-IR, UV-Vis and thermal analyses. The photoinduced birefringence of the azo polymers was studied by irradiating spin-coated films of the polymers with laser beam at three different wavelengths (488, 532, and 589 nm). The results indicate that the photoinduced birefringence of the azo polymers is related with the electron-withdrawing group on azo chromophores and the excitation wavelength. The excitation wavelength that can cause the efficient responses is determined by the absorption band positions of the azo chromophores, which are mainly affected by the electron-withdrawing group on the chromophores. Therefore, the azo polymers containing chromophores with different electron-withdrawing groups show different responsive behavior to the irradiation light at different wavelengths. When irradiated with 488 nm light, PEP-AZ-Cl shows the shortest time to reach the saturated birefringence but with the lowest saturation birefringence level compared with the other two azo polymers. When irradiated with 532 nm light, PEP-AZ-CN shows the shortest time to reach the saturated birefringence. When irradiated with 532 and 589 nm light, PEP-AZ-NT shows the highest saturation birefringence level.

Keywords: Epoxy-based; Azo polymers; High chromophore density; Photoinduced birefringence.

INTRODUCTION

Due to the reversible photoinduced *trans-cis-trans* isomerization of the azo chromophore, polymers containing azo chromophores (azo polymers for short) have demonstrated distinctive photoinduced variations, such as photoinduced phase transition, photoinduced birefringence and dichroism, and surface-relief-grating (SRG) formation^[1–4]. Photoinduced birefringence has attracted considerable attention and has been intensively investigated as one of the most interesting properties of azo polymers^[5–7]. Birefringence induced by polarized light irradiation is a result of 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. Photoinduced birefringence for different kinds of azo polymers, such as side-chain azo polymers, main-chain azo polymers and liquid crystalline azo polymers has been widely investigated^[8–18]. In the fields of data-storage, optical sensors and optical switches, azo polymers with the property of photoinduced birefringence have extensive potential applications.

With good solubility, thermal stability and processibility, epoxy-based azo polymers have been synthesized by post-polymerization azo-coupling reactions and studied for the nonlinear optical properties and SRG formation^[19–21]. Epoxy-based azo polymers with high chromophore density are believed to have better photoinduced behaviors. The absorption band positions of azo polymers are significantly affected as the

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polymers bear different electron-withdrawing groups on azo chromophores. Consequently, the photoinduced birefringence of the azo polymers due to different excitation wavelengths will also depend on the electron-withdrawing groups on the chromophores.

In this study, three epoxy-based azo polymers (PEP-AZ-Cl, PEP-AZ-CN and PEP-AZ-NT) with high chromophore density were synthesized by using post-polymerization azo-coupling reactions. The different electron-withdrawing groups on azo chromophores of the polymers lead to the different absorption band positions and photoinduced birefringence behavior. Three lasers with different wavelengths (488, 532, and 589 nm) were used as excitation light source to study the photoinduced birefringence of the azo polymers. The influences of polymer structures and excitation wavelength on the photoinduced birefringence were investigated.

EXPERIMENTAL

Materials

Aniline (99%), 4-chloroaniline (98%), 4-aminobenzonitrile (98%) and 4-nitroaniline (98%) were purchased from Alfa Aesar. 2-(Chloromethyl)oxirane (AR) was purchased from Tianjin Kermel Chemical Reagent Co. Ltd. The other materials, reagents and solvents were commercial products and used as received without further purification.

Characterization

^1H -NMR spectra were recorded using a JEOL JNM-ECA600 NMR spectrometer. Infrared spectra were determined using a Nicolet 560-IR FT-IR spectrophotometer by incorporating samples in KBr disks. UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda Bio-40 spectrophotometer. Mass spectra were determined by Agilent 6300 Ion Trap LC/MS Systems. Molecular weights and molecular weight distributions were determined by using a gel permeation chromatography (GPC) apparatus at room temperature with THF as the eluent (1 mL min^{-1}). The instrument was equipped with a refractive index (RI) detector (Wyatt Optilab rEX) and fitted with a PLgel 5 μm mixed-D column. The molecular weights and distributions were obtained by calibration with linear polystyrene standards. Thermal phase transitions of the polymers were determined using a TA Instruments DSC 2920 with a heating rate of 10 K/min in nitrogen atmosphere. Thermal gravimetric analyses of the polymers were determined using a TGA Q5000 with a heating rate of 10 K/min in air.

Synthesis of Monomer

The monomer *N,N*-di(epoxypropyl)aniline was synthesized as follows: Silica gel (0.93 g, 100–200 mesh) as catalyst^[22] was added into a homogeneous mixture of aniline (9.3 g, 0.1 mol) and 2-(chloromethyl)oxirane (37 g, 0.4 mol). The reaction was carried out at 40°C for 5 h. After the reaction, the mixture was filtrated and added dropwise into petroleum ether to precipitate the white powder. The dried powder without purification was dissolved in a solution of THF (100 mL), and KOH (15 g) was added in. The solution was stirred at room temperature for 3 h and filtrated. The THF was removed by rotary evaporation and the residue was purified by column chromatography using a mixture of ethyl acetate and petroleum ether (1:10, *V/V*) as eluent. The final product was obtained as a yellow liquid. Yield: 54%. MS: m/z $[\text{M}]^+$: 204.97; calcd.: 205.11. ^1H -NMR (DMSO- d_6 , δ): 2.57 (m, 2H), 2.73 (m, 2H), 3.11 (m, 2H), 3.38 (m, 2H), 3.66 (m, 2H), 6.65 (m, 1H), 6.83 (m, 2H), 7.17 (m, 2H).

Synthesis of Precursor Polymer PEP-AN

Aniline (1.86 g, 20 mmol) and *N,N*-di(epoxypropyl)aniline (4.1 g, 20 mmol) were homogeneously mixed and stirred at 110°C for 10 h under the nitrogen protection. The crude product as a slightly yellow solid was dissolved in THF and added dropwise into a mixture of ethanol and petroleum ether (1:3, *V/V*) to obtain a sticky precipitate. The precipitate was collected by removing the liquid and was dried in a vacuum oven at 60°C for 48 h to get product. Yield: 31%. DSC: T_g 87°C . GPC: $M_n = 5000$, MWD = 1.56. ^1H -NMR (DMSO- d_6 , δ): 3.25 (1H), 3.40 (1H), 3.45 (1H), 3.60 (1H), 4.03 (1H), 5.28 (1H), 6.49 (1H), 6.60 (2H), 6.99 (2H).

Synthesis of Azo Polymer PEP-AZ-Cl

4-Chloroaniline (0.64 g, 5 mmol) was dissolved in a homogeneous mixture of glacial acetic acid (6 mL), propionic acid (3 mL) and sulfuric acid (98%, 0.7 mL). Diazonium salt was prepared by adding an aqueous solution of sodium nitrite (0.38 g, 5.5 mmol in 1 mL of water) dropwise into the 4-chloroaniline solution. The mixture was stirred at 5°C for 5 min and then added dropwise into a solution of PEP-AN (0.6 g, 4 mmol) in DMF (100 mL) at 0°C. The solution was stirred at 0°C for 12 h and then added dropwise into plenty of water. The precipitate collected by filtration was dried and then dissolved in THF, filtrated and precipitated with abundant petroleum ether. The product was collected by filtration and dried in a vacuum oven at 60°C for 48 h. Yield: 85%. DSC: T_g 160°C. $^1\text{H-NMR}$ (DMSO- d_6 , δ): 3.56 (2H), 3.78 (2H), 4.21 (1H), 5.46 (1H), 6.91 (2H), 7.47 (2H), 7.67 (4H). IR (KBr, cm^{-1}): 3313, 2902, 1599, 1510, 1477, 1390, 1360, 1313, 1232, 1155, 1142, 1086, 1009, 835, 542.

Synthesis of Azo Polymer PEP-AZ-CN

PEP-AZ-CN was synthesized *via* a similar procedure as the synthesis of PEP-AZ-Cl by an azo-coupling reaction between PEP-AN and the diazonium salt of 4-aminobenzonitrile. Yield: 84%. DSC: no obvious glass transition. $^1\text{H-NMR}$ (DMSO- d_6 , δ): 3.60 (2H), 3.81 (2H), 4.22 (1H), 5.49 (1H), 6.96 (2H), 7.74 (4H), 7.86 (2H). IR (KBr, cm^{-1}): 3363, 2904, 2225, 1597, 1510, 1443, 1419, 1387, 1313, 1243, 1159, 1138, 845, 823, 559.

Synthesis of Azo Polymer PEP-AZ-NT

PEP-AZ-NT was synthesized *via* a similar procedure as the synthesis of PEP-AZ-Cl by an azo-coupling reaction between PEP-AN and the diazonium salt of 4-nitroaniline. Yield: 81%. DSC: no obvious glass transition. $^1\text{H-NMR}$ (DMSO- d_6 , δ): 3.60 (2H), 3.82 (2H), 4.24 (1H), 5.51 (1H), 6.96 (2H), 7.78 (4H), 8.20 (2H). IR (KBr, cm^{-1}): 3342, 2914, 1601, 1514, 1443, 1421, 1389, 1336, 1234, 1140, 1103, 858, 823, 754, 688, 538.

RESULTS AND DISCUSSION**Polymer Synthesis and Characterization**

Figure 1 shows the synthetic route of the azo polymers with high chromophore density. The monomer containing epoxy groups was synthesized through the reaction between aniline and 2-(chloromethyl)oxirane. *Via* a step

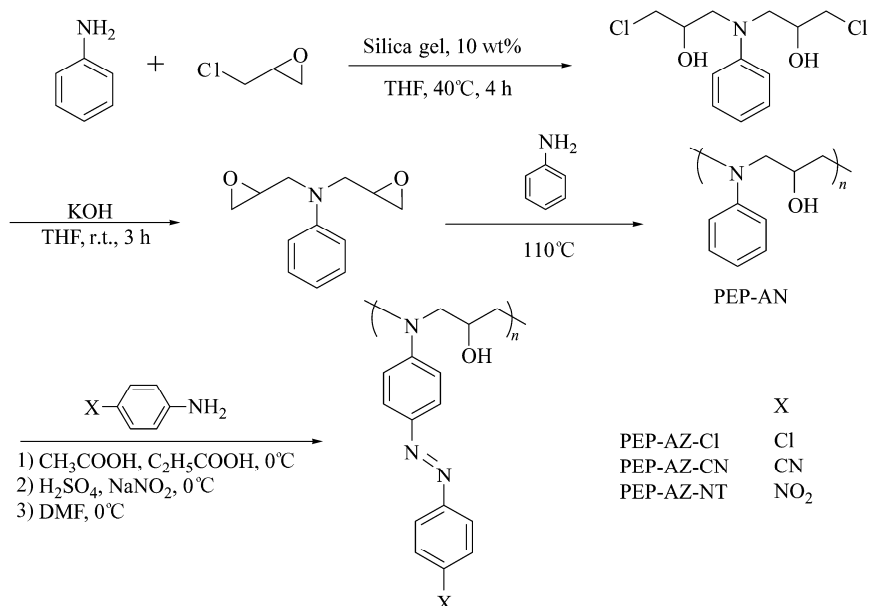


Fig. 1 Synthetic route of the azo polymers

polymerization between the monomer and aniline, the precursor polymer possessing a high density of aniline residues was subsequently synthesized. The density of aniline residues of this precursor polymer is extremely high and shows distinction from the epoxy-based precursor polymers used in previous study^[19, 21]. The polymerization temperature was controlled to be 110°C to avoid the possible side reaction between the hydroxy groups generated by ring-opening reaction and the unreacted epoxide rings. Low molecular weight oligomers, which were mainly cyclic oligomers, were removed by dissolving and precipitation. The number-average molecular weights (M_n) of PEP-AN is 5000 with the polydispersity indexes of 1.56, which were determined by GPC. Figure 2 shows the ^1H -NMR spectrum of precursor polymer PEP-AN. The ^1H -NMR spectrum of precursor polymer PEP-AN shows the resonance signals of the aniline moieties at $\delta = 6.49$, 6.99 and 6.60, which are attributed to the protons at *para*, *meta* and *ortho* positions of the amino group.

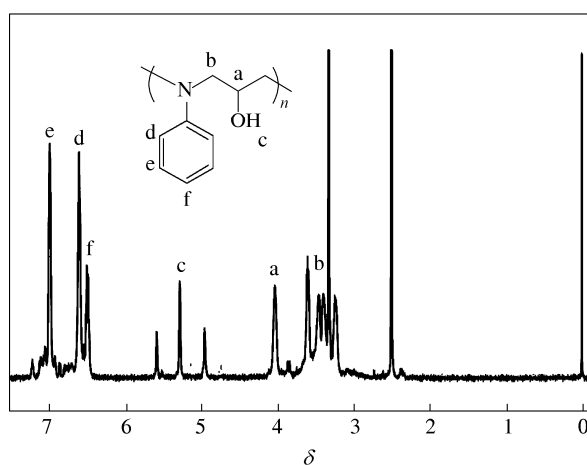


Fig. 2 ^1H -NMR spectrum of precursor polymer PEP-AN

As shown in Fig. 1, three kinds of azo polymers with high chromophore density, PEP-AZ-Cl, PEP-AZ-CN, and PEP-AZ-NT, were synthesized through the post-polymerization azo-coupling reactions between the precursor polymer PEP-AN and the diazonium salts of 4-chloroaniline, 4-aminobenzonitrile and 4-nitroaniline, respectively. The azo-coupling reactions were carried out in DMF. The molar ratios of diazonium salts to aniline moieties of the precursor polymer was 1.25:1, which ensured that almost every aniline residue in precursor polymer PEP-AN was functionalized with azo chromophore. After the azo-coupling reactions, the excess amount of diazonium salts and other solvents were removed through a precipitation/filtration processing. The abbreviated names of the azo polymers are consisted of three parts. The first two parts of the names specify the azo polymers obtained from the precursor polymer PEP-AN and the last part makes the distinctions of the substituents on the azo chromophores.

Figure 3 shows the ^1H -NMR spectra of the azo polymers. The resonance signal ($\delta = 6.49$) corresponding to the protons at *para* position of the amino group of precursor polymer completely disappears, which indicates that the aniline residues in precursor polymer were almost completely functionalized with azo chromophores. The signals of other protons in aniline residues (*ortho* and *meta* to the amino group in PEP-AN) shift to relative lower magnetic field. Meanwhile, additional resonance signals corresponding to the newly introduced benzenoid protons appear at the even lower magnetic field. These spectral changes are attributed to the introduction of the electron-withdrawing groups and the increase of the conjugation length after forming the azo bonds.

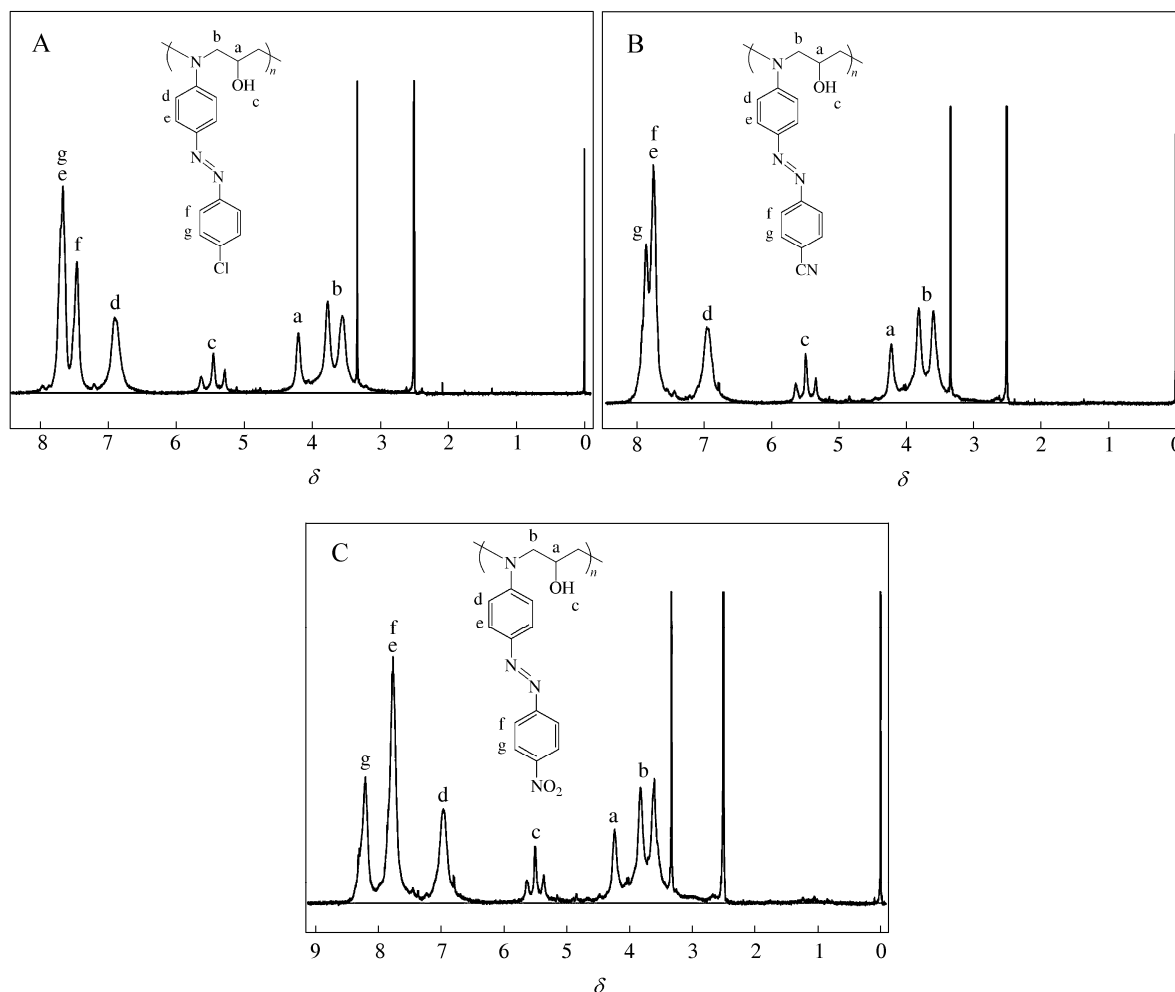


Fig. 3 ^1H -NMR spectra of azo polymers (A) PEP-AZ-Cl, (B) PEP-AZ-CN and (C) PEP-AZ-NT

Spectral and Thermal Properties

Figure 4 gives the UV-Vis absorption spectra of the azo polymers in DMF solution. The spectra show typical characteristics of the pseudo-stilbene type azo chromophores, of which the absorption bands corresponding to the $\pi\text{-}\pi^*$ transition appear in visible spectrum region. The λ_{max} s of the azo polymers PEP-AZ-Cl, PEP-AZ-CN, and PEP-AZ-NT are 427, 454 and 488 nm, respectively. The λ_{max} s of the azo polymers are strongly affected by the electron-withdrawing groups on the azo chromophores. As the ability of the electron-withdrawing groups increases from chloro to nitro group, the λ_{max} s show significant red-shift. The λ_{max} s of spin-coated films of the azo polymers PEP-AZ-Cl, PEP-AZ-CN and PEP-AZ-NT are 401, 440, and 459 nm, respectively. The λ_{max} s of the azo polymers as spin-coated films show blue-shifts compared with those in DMF solutions, which can be attributed to the aggregation of the azo chromophore as in spin-coated films and the strong solvatochromic effect of DMF.

Figure 5 gives the DSC curves of the precursor polymer PEP-AN and three azo polymers PEP-AZ-Cl, PEP-AZ-CN and PEP-AZ-NT. The glass transition temperature (T_g) of PEP-AN is 87°C determined by DSC. PEP-AZ-Cl shows a significantly higher T_g than that of the precursor polymer because of the existence of the azo chromophore. However, PEP-AZ-CN and PEP-AZ-NT do not show obvious glass transition. This observation can be rationalized by considering the high chromophore density in the side-chains and strong interaction among the azo chromophores. The strong interaction between the side-chains can inhibit the thermal-induced movement

of the segments. The thermal decomposition temperatures (T_d s) of the polymers are determined by TGA. After introducing the azo chromophore, the T_d s of the azo polymers are comparatively lower than the T_d of the precursor polymer PEP-AN due to the lower thermostability of the azo groups. The T_g s and T_d s of the polymers are listed in Table 1.

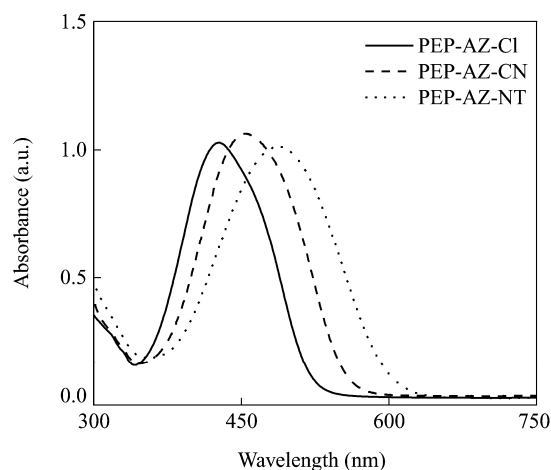


Fig. 4 The UV-Vis spectra of the azo polymers in DMF solution

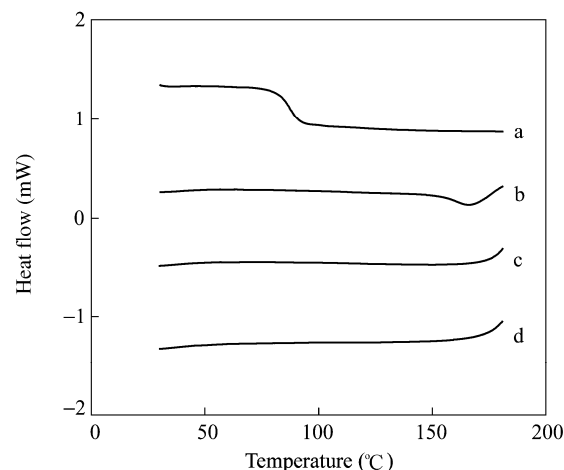


Fig. 5 The DSC curves of the azo polymers (a) PEP-AN, (b) PEP-AZ-Cl, (c) PEP-AZ-CN and (d) PEP-AZ-NT

Table 1. T_g s and T_d s of the prepared polymers

Polymers	T_g (°C)	T_d (°C)
PEP-AN	87	288
PEP-AZ-Cl	160	250
PEP-AZ-CN	—	275
PEP-AZ-NT	—	266

Photoinduced Birefringence

Solid films of the azo polymers with smooth surfaces were prepared by spin-coating. The homogeneous solutions of the azo polymers were obtained by dissolving a suitable amount of the materials in DMF with a typical concentration of 10 wt%. The solutions were filtered through 0.45 μ m membranes and spin-coated onto glass slides. The films were dried at 60°C under vacuum for 48 h before use with a thickness in a range from 400 nm to 600 nm. A linearly polarized laser beam with the wavelength of 488 nm (Ar^+ laser), 532 or 589 nm (diode-pumped frequency doubled solid state lasers) was used as the light source. A piece of the azo polymer films was placed between two crossed linear polarizers. A low power He-Ne laser beam at 632.8 nm was used to measure the transmitted power through this optical setup. The writing laser beam with intensity of 100 mW/cm² was incident perpendicular to the sample and the polarization angle of the incident laser beam was set to be 45° with respect to the optical axes of both polarizers. The angle between incident laser beam and probing laser beam was fixed to be 8°. The photoinduced birefringence was estimated from the change in transmittance of the probe beam^[23].

Figure 6 shows the birefringence growth curves as a function of time of the three azo polymers upon the laser irradiation with different wavelengths. Upon the irradiation with 488 nm laser beam (Fig. 6a), the saturation birefringence levels of three azo polymers PEP-AZ-Cl, PEP-AZ-CN and PEP-AZ-NT are 0.093, 0.161 and 0.147, respectively. The saturated times are 350 s, 1500 s and 3000 s, respectively. Azo polymer PEP-AZ-Cl, which contains chloro as the electron-withdrawing group, shows the fastest birefringence growth rate with a saturated time of 350 s. However, the saturation birefringence level of PEP-AZ-Cl is the lowest with a value of 0.093. PEP-AZ-CN shows a highest saturation birefringence level with a value of 0.161 and PEP-AZ-NT shows

the slowest birefringence growth rate with a saturated time of 3000 s. Upon the irradiation with 532 nm laser beam (Fig. 6b), the saturation birefringence levels and the saturated times of three azo polymers PEP-AZ-Cl, PEP-AZ-CN and PEP-AZ-NT are 0.098, 0.147, 0.200 and 1000 s, 500 s, 2000 s, respectively. The saturated time of PEP-AZ-Cl is obviously longer than that upon the irradiation with 488 nm laser beam. PEP-AZ-CN shows the fastest birefringence growth rate with a saturated time of 500 s. PEP-AZ-NT shows the highest saturation birefringence level and slowest birefringence growth rate. Upon the irradiation with 589 nm laser beam (Fig. 6c), PEP-AZ-Cl does not show birefringence signal due to its very weak absorption at 589 nm. The saturation birefringence levels and the saturated times of two azo polymers PEP-AZ-CN and PEP-AZ-NT are 0.156, 0.231 and 1200 s, 3600 s, respectively. PEP-AZ-NT shows higher saturation birefringence level and slower birefringence growth rate.

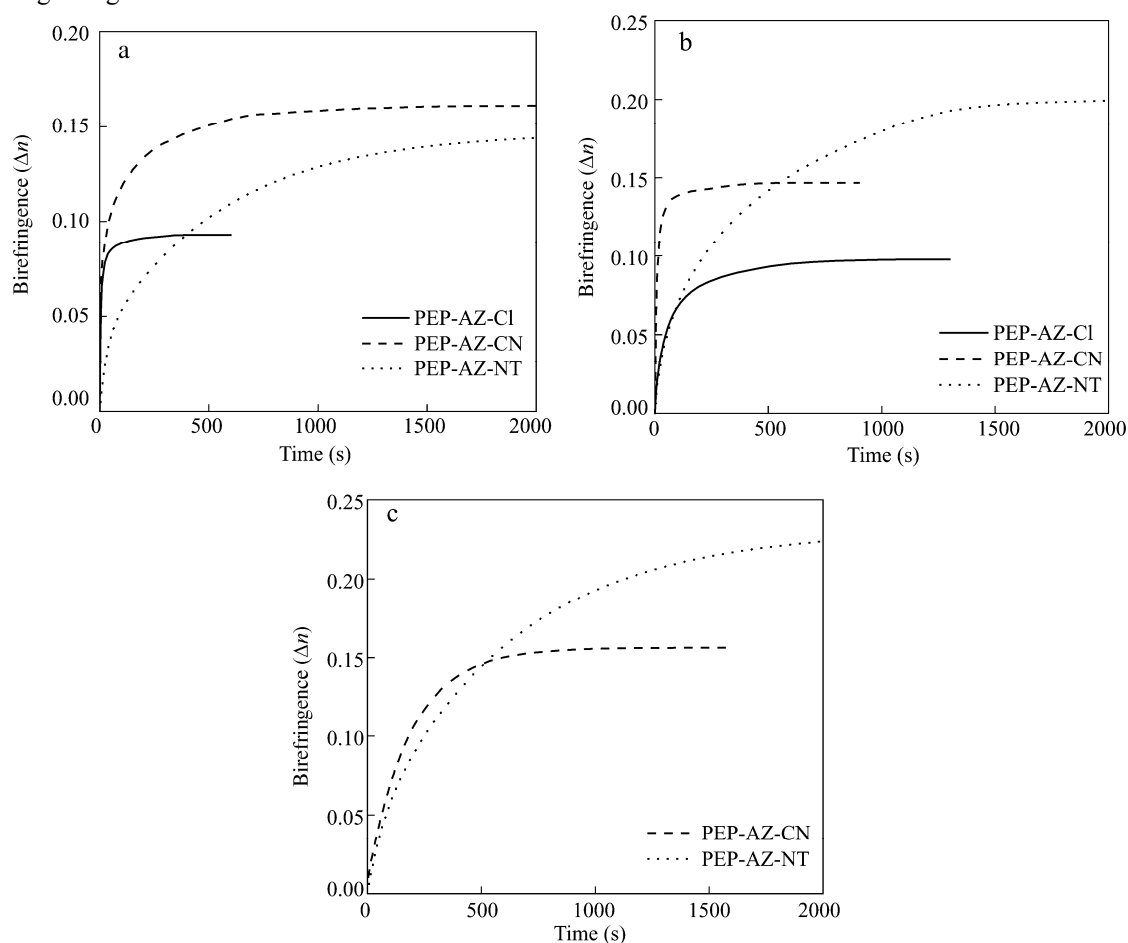


Fig. 6 The birefringence as a function of time of the azo polymers with the incident laser beam at different wavelengths: (a) 488 nm, (b) 532 nm and (c) 589 nm

The above results indicate that the photoinduced birefringence behavior is closely related with the excitation wavelength and the electron-withdrawing groups on azo chromophores. When the excitation wavelengths are between the $\lambda_{\max}$ s of the azo polymers and absorption band tails at the longer wavelength side, the azo polymers show a relatively fast birefringence growth rate (such as PEP-AZ-Cl at 488 nm and PEP-AZ-CN at 532 nm). On the other hand, when the excitation wavelength is too close to the absorption band tails, the birefringence growth rate decreases (such as PEP-AZ-Cl at 532 and 589 nm). These results are consistent with those reported before^[24]. For the three excitation wavelengths, the azo polymer containing chloro as the electron-withdrawing group (PEP-AZ-Cl) always shows the lowest saturation birefringence level, and the azo polymer

containing nitro as the electron-withdrawing group (PEP-AZ-NT) shows the highest saturation birefringence level upon the irradiation at 532 and 589 nm. This observation indicates that as the ability of the electron-withdrawing groups on azo chromophore increases, the saturation birefringence level also increases when irradiated with the proper irradiation wavelength. It indicates that the type of the electron-withdrawing groups on the azo chromophore shows close correlation with the photoinduced birefringence behavior of the azo polymers. The correlation between the absorption band position and excitation wavelength plays an important role in the process.

CONCLUSIONS

Three epoxy-based azo polymers with high chromophore density bearing different electron-withdrawing groups on azo chromophores were synthesized. The structures and properties of the azo polymers were characterized by spectroscopic methods and thermal analysis. The photoinduced birefringence behavior of the azo polymers was studied by irradiation of the laser beam at three different wavelengths of 488, 532, and 589 nm. The results indicate that the photoinduced birefringence behavior is closely related with the excitation wavelength and the electron-withdrawing groups on azo chromophore. PEP-AZ-Cl at 488 nm and PEP-AZ-CN at 532 nm show the fastest birefringence growth rate, respectively. PEP-AZ-Cl does not show birefringence upon the irradiation at 589 nm. When irradiated at 488 and 532 nm, PEP-AZ-Cl shows the lowest saturation birefringence level. Upon the irradiation at 532 and 589 nm, PEP-AZ-NT shows the highest saturation birefringence level.

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