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 $^1$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
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
$^1$H-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 $\text{N},\text{N}$-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 [M]$^+$: 204.97; calcd.: 205.11. $^1$H-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 $\text{N},\text{N}$-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. $^1$H-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).