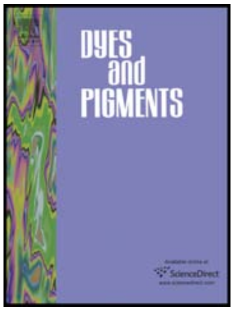

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Synthesis, characterization, and photoresponsive behaviour of a series of azobenzene-containing side-chain poly(ether sulfone)s with various lengths of flexible spacers

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Abstract:

A series of azobenzene-containing side-chain poly(ether sulfone)s (azo-PES) with various spacer lengths (2, 6 or 12 methylene units) were successfully synthesized via a nucleophilic substitution grafting reaction between poly(ether sulfone)s with hydroxylphenyl side groups and azobenzene monomers. Their chemical structures and properties were characterized by means of IR, UV-vis and ^{1}H NMR. These azo-polymers show good thermal stability with glass transition temperatures and 5% weight-loss temperatures above 119 ^{o}C and 347 ^{o}C, respectively. The results of photoisomerization experiments indicated that azo-PES polymer with longer spacers correspond to higher photoisomerization rates. Upon irradiation with a 532 nm neodymium doped yttrium aluminum garnet (Nd:YAG) laser beam, they presented remnant values of birefringence larger than 82% of the saturation value of birefringence, indicating the good stability of the photoinduced orientation. No fatigue phenomena have been observed after several cycles of inscription–erasure–inscription sequences.

Keywords: Poly(ether sulfone)s; Azobenzene; Photoinduced birefringence; Photoisomerization; Different length spacers; Grafting reaction

1. Introduction

In recent years, polymers containing azobenzene units (azo-polymers) have attracted considerable attention owing to their potential application in optical data storage, optical switching and nonlinear optical materials [1-6]. Because of the unique reversible photoisomerization and photoinduced anisotropy of the azobenzene chromophores, azo-polymers can show a variety of photoresponsive variations, such as photoinduced phase transition, photoinduced surface-relief-gratings (SRGs), and photoinduced birefringence [7-9]. Photoinduced birefringence is an important feature of azo-polymers that makes them suitable for optical storage applications. When azo-polymer films are illuminated by linearly polarized laser light, azobenzene chromophores undergo *trans-cis* isomerization accompanied by molecular reorientation. Through the hole-burning mechanism, an excess of chromophores occurs in the direction perpendicular to the laser polarization. This molecular reorientation induces birefringence property changing in the materials, which could be removed by irradiation with circularly polarized light or depolarized light [10].

Poly(arylene ether)s (PAEs) are a family of high-performance engineering thermoplastics known for their excellent thermal, mechanical, and environmental stabilities. Functionalized poly(arylene ether)s have received much attention due to their potential applications in proton-exchange membranes, light-emitting materials and optical materials [11-14]. In our previous work, we have reported some photoresponsive azo-poly(arylene ether)s synthesized by direct copolymerization, and investigated their corresponding optical properties [15-18]. These azo-PAEs present photoinduced birefringence behaviour with good stability of the photoinduced orientation and stable SRGs can be formed on them. However, most azo-PAEs show low photoisomerization rates because of their rigid structures. It was reported that azo-polymers with longer spacers could facilitate the alignment of azobenzene chromophores, which was a viable method to increase their photoisomeriztion rates [19, 20]. Herein, flexible alkyl units with different length were introduced between the main chain of poly(ether sulfone)s and azo chromophores via a grafting reaction in this work. The influence of spacer length on their thermal and photoresponsive properties were also investigated.

2. Experimental

2.1. Materials

Bis(4-fluorophenyl)sulfone was purchased from Acros Organics. 1,2-Dibromoethane and 1,6-dibromohexane were purchased from Aladdin Chemistry Co. Ltd. 1,12-Dibromododecane was purchased from TCI. 4-(4-Hydroxyphenylazo)benzonitrile and 2-(3-methoxyphenyl)hydroquinone was synthesized according to the literatures, respectively[14, 21]. All the solvents were purchased from commercial sources. Tetramethylene sulfone and *N*,*N*-dimethylformamide were dehydrated and distilled under reduced pressure for purification. K_2CO_3 was dried at 120 ^oC for 24 h before being used for polymerization.

2.2. Measurements

Gel permeation chromatography (GPC) was carried out using a Waters 410 instrument with *N*,*N*-dimethylformamide (DMF) as the eluent and polystyrene as the calibration standard. ^1H NMR spectra were recorded on a Bruker 510 (^1H, 500 MHz) instrument using dimethysulfoxide-d_6 (DMSO-d_6) and $CDCl_3$ as solvent. FI-IR spectra (KBr pellet) were recorded on a Nicolet Impact 410 FT-IR spectrophotometer. Elemental analyses of C, H and N were performed on an Elementar Vario Micro Cube elemental analyzer. Glass transition temperatures (T_gs) were determined by DSC (Model Mettler DSC821^e) instrument at a heating rate of 20 ^oC/min and under a nitrogen flow of 200 mL/min. The reported Tg value was recorded from the second scan after the sample was first heated and then quenched. Thermo-gravimetric analysis was performed on a Perkin Elmer Pyris 1 TGA analyzer under a nitrogen atmosphere (100 mL/min) at a heating rate of 10 ^oC/min. UV-visible absorption spectra were recorded on a UV2501-PC spectrophotometer at room temperature.

2.3. Synthesis

2.3.1. Synthesis of 1-Bromo-2-(4-((4-cyanophenyl)diazenyl)phenoxy)ethane(AZO_2, scheme 1)

A mixture of 4-(4-hydroxyphenylazo)benzonitrile (4.46 g, 0.02 mol), 1,2-dibromoethane (7.51 g, 0.04 mol), potassium carbonate (2.07 g, 0.015 mol) and acetone was heated under reflux with stirring for 24 h. The reaction mixture was filtered hot, and the residue was washed with acetone. The acetone was evaporated and petroleum ether (30-60 °C) was added to the concentrated organic extracts. The resulting precipitate was collected and dried. The crude product was recrystallized from ethanol twice. Yield: 56%; m.p. 165 °C; MALDI-TOF-MS: $C_{15}H_{12}BrN_3O$ m/z=335(M^+ + H); IR (KBr, cm^{-1}): 2929 2855 ($-CH_2-$), 2231 (-CN); ^1H NMR (DMSO-d_6, δ, ppm): 8.05(d, J=8.7 Hz, 2H), 7.98-7.95(m, 4H), 7.20(d, J= 9 Hz, 2H), 4.48(t, J=5.1 Hz, 2H), 3.87(t, J=5.4 Hz, 2H). A typical element alanalysis for $C_{15}H_{12}BrN_3O$: calcd. C 54.56, H 3.66, N 12.73; found C 54.22, H 3.83, N 12.89

2.3.2. Synthesis of 1-Bromo-6-(4-((4-cyanophenyl)diazenyl)phenoxy)hexane (AZO_6, scheme1)

This monomer was synthesized by a procedure similar to that used for synthesis of AZO_2.Yield:53%; m.p. 93 °C; MALDI-TOF-MS: $C_{19}H_{20}BrN_3O$ m/z=386 (M^+ + H); IR (KBr, cm^{-1}): 2929 2855 ($-CH_2-$), 2231 (-CN); ^1H NMR (DMSO-d_6, δ, ppm): 8.04(d, J=8.7 Hz, 2H), 7.97-7.93(m, 4H), 7.15(d, J=9 Hz, 2H), 4.11(t, J=6.6 Hz, 2H), 3.55(t, J=6.6 Hz, 2H), 1.75~1.85(m, 4H), 1.40~1.48(m.4H). A typical element alanalysis for $C_{19}H_{20}BrN_3O$: calcd. C 59.08, H 5.22, N 10.88,; found C 58.87, H 5.36, N 10.54.

2.3.3. Synthesis of 1-Bromo-12-(4-((4-cyanophenyl)diazenyl)phenoxy)dodecane (AZO_{12}, scheme 1)

This monomer was synthesized by a procedure similar to that used for synthesis of AZO_2.Yield:50%; m.p. 110 °C; MALDI-TOF-MS: $C_{25}H_{32}BrN_3O$ m/z=469 (M^+ + H); IR (KBr, cm^{-1}): 2929 2854 ($-CH_2-$), 2230 (-CN); ^1H NMR (DMSO-d_6, δ, ppm): 8.04(d, J=8.7 Hz, 2H), 7.97-7.93(m, 4H), 7.14(d, J=9 Hz, 2H), 4.11(t, J=6.6 Hz, 2H), 3.52(t, J=6.6 Hz, 2H), 1.72~1.81(m, 4H), 1.34~1.44(m.16H). A typical element alanalysis for $C_{25}H_{32}BrN_3O$: calcd. C 63.83, H 6.86, N 8.93; found C 63.52, H 7.17, N 8.71.

2.3.4. Synthesis of poly(ether sulfone)s with methoxy side groups (MPES, scheme 2)

2-(3-Methoxyphenyl)hydroquinone (4.3246 g, 0.02 mol), bis(4-fluorophenyl)-sulfone (5.085 g, 0.02 mol), K_2CO_3 (2.902 g, 0.021 mol), tetramethylene sulfone (TMS, 24 mL) and toluene (8 mL) were put into a three-necked flask fitted with a nitrogen inlet, a thermometer, a Dean–Stark trap, a condenser and a mechanical stirrer, and the apparatus was purged with nitrogen. The reaction mixture was heated under reflux at 130°C for 3 h to ensure complete dehydration. After dehydration and removal of toluene, the reaction mixture was heated at 170 °C for 6 h under a nitrogen atmosphere. After being poured into deionized water (500 mL), the precipitate was collected by filtration. The crude product was washed with hot deionized water and ethanol several times in sequence. The resulting product was dried at 100 °C under vacuum for 24 h and poly(ether sulfone)s with methoxy side groups (MPES) was obtained as a white powder. Yield: 93%; IR (KBr, cm^{-1}): 2932 , 2849 ($-OCH_3$), 1150 ($-SO_2-$), 1231 (-Ar-O-Ar-); ^1H NMR (DMSO-d_6, δ, ppm): 7.93-7.76 (m, 4H), 7.30 (s, H), 7.24-7.18 (m, 5H), 7.01 (t, 2H), 6.96(d, H), 6.92(s, H), 6.77(d, H), 3.55 (d, 3H)

2.3.5. Synthesis of poly(ether sulfone)s with hydroxyl side groups (HPES, scheme 2)

MPES (6.5 g) and freshly prepared pyridine hydrochloride (250 g) were put into a three-necked flask equipped with a nitrogen inlet, a thermometer, a condenser and a mechanical stirrer. The mixture was heated at 175 °C until the solution became homogeneous. After being cooled to 150 °C, the mixture was poured into water. The deposition was filtered and washed three times with water and dried under vacuum to give HPES as a grey powder. Yield: 90%; IR (KBr, cm^{-1}): 3423(-OH), 1150 ($-SO_2-$), 1231 (-Ar-O-Ar-); ^1H NMR (DMSO-d_6, δ, ppm): 9.44 (s, 1H), 7.95-7.78 (m, 4H), 7.24 (s, 1H), 7.21-7.17 (m, 4H), 7.08 (m, H), 7.03-7.00 (m, 2H), 7.00 (d, H), 6.81 (d, 2H), 6.64 (d, 1H).

2.3.6. Synthesis of azo-PES polymers (scheme 2)

AZO_i (6.0 mmol), HPES (6.0 mmol of repeating unit), K_2CO_3 (3.6 mmol) and DMF (50 mL) were added into a 100mL three-necked flask equipped with a nitrogen inlet, a thermometer, a condenser and a mechanical stirrer. The reaction mixture was heated under reflux at 120 °C for 12 h under a nitrogen atmosphere. Then the mixture was slowly poured into aqueous HCl (500 mL, 1 mol) and azo-polymer was obtained as a powder after washing with deionized water and ethanol several times, the orange polymers were dried under vacuum for 24h.

azo-PES2 Yield: 84%; IR (KBr, cm^{-1}): 2927 2855 ($-CH_2-$), 2230 (-CN), -1150 ($-SO_2-$), 1231 (-Ar-O-Ar-); ^1H NMR (DMSO-d_6, δ, ppm): 9.44 (s, -OH), 7.99-7.78 (m, ArH), 7.23-7.01 (m, ArH), 6.87-6.81(m, ArH), 6.65-6.64 (m, ArH), 4.26 (t,-OCH_2-)

azo-PES6 Yield: 82%; IR (KBr, cm^{-1}): 2927 2855 (-CH_2-), 2230 (-CN), -1150 (-SO_2-), 1231 (-Ar-O-Ar-); ^1H NMR ($CDCl_3$, δ, ppm): 7.90-7.76 (m, ArH), 7.16-6.88(m, ArH), 6.77 (t, ArH), 4.03 (s,-OCH_2-), 3.83 (s,-OCH_2-), 1.28-1.80 (m, -CH_2-)

azo-PES12 Yield: 79%; IR (KBr, cm^{-1}): 2927 2855 (-CH_2-), 2230 (-CN), 1150 (-SO_2-), 1231 (-Ar-O-Ar-); ^1H NMR ($CDCl_3$, δ, ppm): 7.89-7.73 (m, ArH), 7.15-6.87(m, ArH), 6.77 (t, ArH), 4.04 (s,-OCH_2-), 3.85 (s,-OCH_2-), 1.28-1.81 (m, -CH_2) (The azo-PES6 and azo-PES12 were soluble in $CDCl_3$ much better than in DMSO-d_6)

2.4. Preparation of polymer films

Polymer films were prepared by the following procedure. Polymers were dissolved in cyclohexanone (10 wt%) and then filtered through 0.8 μm syringe filters membranes. Polymer films were obtained by casting the polymer solution onto glass substrates, which were cleaned in an ultrasonic bath with DMF, THF, ethanol and then distilled water. The thickness of the casting films were about 8 μm for the photoinduced birefringence experiment. The films were dried under vacuum for 48 h to drive off the residual solvent and were then restored in a desiccator for further studies.

3. Results and discussion

3.1. Monomer synthesis

A series of azobenzene monomers (AZO_i) were designed and synthesized, as shown in Scheme 1. For example, AZO_2 was prepared from 4-(4-hydroxyphenylazo) benzonitrile and 1,2-dibromoethane via a nucleophilic substitution reaction. After recrystallized from ethanol twice, orange-red crystals of AZO_2 were obtained. AZO_6 and AZO_{12} were synthesized by a procedure similar to that used for synthesis of AZO_2. The structures of AZO_i were confirmed by MS, ^1H NMR and Elemental analyzer. The yields of AZO_2, AZO_6 and AZO_{12} were 56%, 53% and 54%, respectively.

Scheme 1

3.2. Polymer synthesis and structure characterization

Azo-PES polymers were synthesized via a nucleophilic substitution grafting reaction from AZO_i and poly(ether sulfone)s with hydroxyl side groups (HPES), as shown in Scheme 2. First of all, the precursor of HPES, poly(ether sulfone)s with methoxy side groups (MPES) was obtained by a typical nucleophilic substitution polycondensation reaction from 2-(3-methoxyphenyl)hydroquinone and bis(4-fluorophenyl)sulfone. Then, HPES was successfully obtained via hydrolysis of the methoxy groups on the MPES. At last, HPES was transformed into respective azobenzene-functionalized poly(ether sulfone)s via a nucleophilic substitution reaction between the -CH_2Br groups of the AZO_i and the hydroxyl groups on the HPES. From Table 1, it could be seen that all of azo-PES polymers had number average molecular weights above 8.5×10^4 g/mol. Compared to most of the reported azobenzene- containing poly(arylene ether)s, azo-PES polymers show higher molecular weights, indicating that using the grafting method is viable to synthesize azobenzene-containing poly(arylene ether)s with high molecular weight. All of azo-PES polymers showed good solubility in common organic solvents such as tetrahydrofuran, dimethylacetamide, *N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidone and cyclohexanone, but insoluble in ethanol.

Scheme 2

The chemical structures of azo-PES polymers were confirmed by IR, ^{1}H NMR and UV-vis spectra. The IR spectra of HPES and azo-PES polymers were shown in Fig. 1. Compared to the IR spectrum of HPES, the IR spectrum of azo-PES polymers showed characteristic absorption bands of -CN groups at 2230cm^{-1}, and -CH_2- groups at 2927 cm^{-1} and 2855 cm^{-1}, indicating that the azobenzene chromophores were successfully introduced into the polymer chains. Fig. 2 showed typical ^{1}H NMR spectra of MPES, HPES and azo-PES2 in DMSO-d_6 with signal assignment. Comparing the ^{1}H NMR spectra of MPES and HPES , it was observed that the signal corresponding to the proton of the methoxy group (δ, 3.55) disappeared with the signal of hydroxyl proton presented at 9.44 ppm which was absent in the spectrum of MPES. Compared to the ^{1}H NMR spectra of HPES, the ^{1}H NMR spectra of the azo-PES2 showed new peaks at around 4.26 ppm corresponding to the chemical shift of hydrogen in –OCH_2- group. The signal corresponding to the proton of –CH_2Br group (δ, 3.87) has not been observed, indicating that there is no monomer AZO_2 left in the azo-PES2. The ^1H NMR spectra of azo-PES6 and azo-PES12 could be characterized by a procedure similar to that used for characterizing the ^1H NMR spectra of azo-PES2. On the basis of ^1H NMR spectra, the molar percentage of the chromophore in azo-PES could be calculated from the integral ratio of the proton of the $–OCH_2$- group and the proton of the Ar-H group. The grafting ratio of azo-PES2, azo-PES6 and azo-PES12 were 67%, 65% and 59%, respectively. The UV–vis spectra of HPES and azo-PES polymers in DMF solution were shown in Fig. 3. The characteristic absorption bands at around 365 nm and 450 nm could be observed in the spectra of azo-PES polymers, corresponding to π-π*and n–π* transitions resulted from the intramolecular charge transfer of the azobenzene chromophores, respectively [22].

Fig. 1

Fig. 2

Fig.3

Table 1

Elemental analyzer of the polymers were performed on an Elementar Vario Micro Cube elemental analyzer and the detailed experimental were illustrated in Table 2. The measured values of C, H and N matched the calculated values well, and the slight departure may come from the instrument measuring error and minor water.

Table 2

3.3. Thermal properties of azo-PES polymers

Fig. 7 showed the DSC curves of polymers, and the experimental data were listed in Table 1. No thermal changes except for the glass transition was observed below decomposition temperature, indicating that the polymers are amorphous. Tg values of azo-PES polymers were much lower than that of HPES, because the introduction of azobenzene chromophores decreased the number of hydroxyl groups and weakened the hydrogen bonding interaction of polymer side chains. In addition the flexible alkyls units could further decrease the rigidity of polymer chains. As the methylene spacer length increased, Tg values of azo-PES polymers decreased from 171 °C of azo-PES2 to 119 °C of azo-PES12.

The detailed experimental data from the TGA analysis were illustrated in Table 1. From Table 1, it could be observed that the thermal stability decreased with spacer length from 358 ^{o}C to 347 ^{o}C. However, the temperatures at 5% weight loss (TGA-5%) of azo-PES polymers and HPES were all above 300 ^{o}C, indicating their good thermal stability.

Fig. 4

3.4. Photoisomerization behaviour of azo-PES polymers

The photoisomerization behaviour of the azo-PES polymers in DMF solutions were investigated by UV–vis spectroscopy after irradiated with 360 nm UV light. As shown in Fig. 5A , UV–vis spectra of azo-PES2 were recorded over different time intervals until the photostationary state was reached (irradiated for 70 s). When the solution was irradiated by 360 nm light, azobenzene chromophores underwent a *trans*-to-*ci*s photoisomerization process (Fig. 5A). The intensity of the π-π* transition band at 365 nm decreased gradually and the intensity of the n-π* transition band at 450 nm increased gradually with continued irradiation. The photostationary state of the photoisomerization was reached after irradiation for 70 s. As shown in Fig. 5B and Fig. 5C respectively, azo-PES6 and azo-PES12 displayed similar photoisomerization behaviour.

Fig. 5

The *trans*-to-*cis* photoisomerization rates of azo-PES polymers in DMF solution were analyzed using the UV absorption at 360 nm. The photoisomerization kinetic of azo-PES polymers were further studied and are presented in Fig. 6. It could be observed that $\ln((A_\infty-A_t)/(A_\infty-A_0))$ was linearly dependent on time (where A_0, A_t and A_∞ are the absorbances at time 0, time t and the photostationary state, respectively), confirming that the *trans*-to-*cis* photoisomerization of azo-PES polymers obey first-order kinetics, as reported previously. [23] The slope of the plots of $\ln((A_\infty-A_t)/(A_\infty-A_0))$ against time gave the first-order rate constants (k_P) for the *trans*-to-*cis* photoisomerization of azo-PES polymers. The rate constants of the photoisomerization of azo-PES2, azo-PES6 and azo-PES12 were 0.0541, 0.0821 and

1.4814 s^{-1}, respectively. As the spacer length decreased, it could be observed that the motion of the azobenzene chromophores became more difficult, which further restricted the photoisomerization process.

Fig. 6

3.5. Photoinduced birefringence of photochromic film samples

Birefringence measurements were produced by a pump beam (532 nm of Nd:YAG laser) polarized at 45^o with respect to the polarization of the probe beam (632.8 nm He:Ne laser). The samples were placed between two crossed polarizers (P and A) in the path of the probe laser beam. The transmitted probe beam was detected by a photodetector and connected through a lock-in amplifier to a computer. The probe light was modulated at 980 Hz by a mechanical chopper. The birefringence, Δn induced by 532 nm pump laser, resulted in transmission of the 632.8 nm probe beam through polarizer A. The intensity of this transmitted beam could be described by the well-known Eq. (1) [24]:

$$I_t=I_o\sin^2(\pi\Delta nd/\lambda) \tag{1}$$

where d is the sample's thickness, λ is the probe laser wavelength and I_o is the transmitted probe light intensity when the polarizer and analyzer are parallel to each other and the sample is not exposed to the polarized 532 nm laser light.

Fig. 7A showed the measured photoinduced birefringence of azo-PES polymers as a function of time. The moment at which the pump laser was switched on or off was marked with a letter. For azo-PES2, at the beginning of the experiments, it could be seen that no light is transmitted through the analyzer (0–10 s) due to the random orientation of the azobenzene chromophores. Under irradiation with a linearly polarized 532 nm laser beam (approximately 60 mW/cm^2, at point A), birefringence signals were induced immediately and reached approximately 0.1139 due to the alignment of azobenzene chromophores perpendicular to the pump laser polarization direction through multiple *trans-cis* isomerization cycles of the azobenzene moieties. The birefringence exhibited a decay after the pump laser was switched off (at point B) because of the thermal isomerization from *cis*-form to *trans*-form and dipole redistribution, which increase the entropy. The remaining photoinduced anisotropy could be erased with a circularly polarized beam (‘erasing’ beam) (at point C). Azo-PES6 and azo-PES12 exhibited photoinduced anisotropy behaviour similar to those described above, and the relative data are shown in Fig. 7A and Table 3. The order of the saturation values of birefringence which depended on the azobenzene chromophores contents was azo-PES2>azo-PES6>azo-PES12. The azobenzene chromophores contents of azo-PES polymers corresponded to the grafting ratios of azo-PES polymers. (The grafting ratios of azo-PES2, azo-PES6 and azo-PES12 were 67%, 65% and 59%, respectively.) With the length of flexible spacers increased, the decay of value of birefringence became larger. For azo-PES12, it decreased to 82% of the saturation value of birefringence. Compared to other azo-polymers [25-27], azo-PES polymers showed much smaller birefringence decay and possess remnant values of birefringence larger than 82% of the saturation values of birefringence, indicating the good stability of the photoinduced orientation. This stability is mainly attributed to the rigidity of the aromatic main chain structures of azo-PES polymers, which suppress the relaxation process of the photoalignment.

To allow qualitative comparison of the birefringence evolution with irradiation time for azo-PES polymers with different length spacers, the same evolution with the value of birefringence normalized to the saturation value of birefringence was shown in Fig. 7B.[28]. From the growth curves of the three polymers, it could be seen that the birefringence growth rate increased with increasing the methylene spacer length. Generally, the growth process of photoinduced birefringence is attributable to the multiple *trans–cis* isomerizations of the azobenzene moieties and the reorientation of azobenzene chromophores through these isomerization cycles. Therefore, their birefringence growth rates depended on their photoisomerization rates. As a result, polymer azo-PES12 which had the fastest photoisomerization rate as discussed in Section 3.4, showed the highest birefringence growth rate among these polymers.

Fig. 7

Table 2

The complete reversibility of the photoinduced birefringence of azo-PES polymers is related to fatigue resistance properties. As shown in Fig. 8, after several irradiation steps with linearly polarized and circularly polarized laser beams alternatively acting on the azo-PES12 film, the saturation values and remnant values of birefringence were similar. This result indicated that azo-PES polymers were promising for use in reversible optical storage applications and had excellent reproducibility, without any degradation of the signal or material fatigue.

Fig. 8

4. Conclusions

A series of novel azobenzene-functionalized poly(ether sulfone)s with different lengths of flexible spacers have been synthesized via a nucleophilic substitution grafting reaction. The azo-PES polymers exhibit high molecular weights, high Tg, good thermal stability and sensitive photoresponsive behaviour. The results of photoisomerization experiments show that azo-PES with longer spacers correspond to higher photoisomerization rates. Based on the results of photoinduced birefringence experiment, all polymers possess remnant values of birefringence larger than 82% of the saturation values of birefringence, indicating that introducing flexible spacers between azobenzene chromophores and rigid backbone of azo-PAEs could balance the conflict between photoisomerization rate and optic stability.

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References

[1] Natansohn A, Rochon P. Photoinduced motions in azo-containing polymers. Chem Rev 2002;102:4139–4175.

[2] Hvilsted S, Sanchez C, Alcala R. The volume holographic optical storage potential in azobenzene containing polymers. J Mater Chem 2009;19:6641–6648.

[3] Matharu AS, Jeeva S, Huddleston PR, Ramanujam PS. Synthesis and optical storage properties of a thiophene-based holographic recording medium. J Mater Chem 2007;17:4477-4482.

[4] Iftime G, Labarthet FL, Natansohn A, Rochon P. Control of chirality of an azobenzene liquid crystalline polymer with circularly polarized light. J Am Chem Soc 2000;122:12646–12650.

[5] Li NJ, Lu JM, Li H, Kang ET. Nonlinear optical properties and memory effects of the azo polymers carrying different substituents. Dyes and Pigments 2011;80: 18-24.

[6] Yu YL, Nakano M, IkedaT. Directed bending of a polymer film by light-Miniaturzing a simple photomechanical system could expand its range of applications. Nature 2003;425:145.

[7] Todorov T, Markovski P, Tomova N, Dragostinova V, Stoyanova K. Photopolymers-holographic investigations, mechanism of recording and applications. Optical Quantum Electronics 1986;16: 471-476.

[8] Ikeda T, Tsutsumi O. Optical switching and image storage by means of azobenzene liquid-crystal films. Science 1995;268:1873.

[9] Rochon P, Batalla E, Natansohn A. Optically induced surface gratings on azoaromatic polymer films. Appl Phys Lett 1995;66:136-138.

[10] Han DH, Tong X, Zhao Y, Galstian T, Zhao Y. Cyclic azobenzene-containing side-chain liquid crystalline polymers: synthesis and topological effect on mesophase transition, order, and photoinduced birefringence. Macromolecules 2010;43:3664–3671.

[11] Zhang HB, Pang JH, Wang D, Li XF, Jiang ZH. Sulfonated poly(arylene ether nitrile ketone)and its composite with phosphotungstic acid as materials for

proton exchange membranes. J. Membr Sci 2006;264:56–64.

[12] Liu D, Wang ZG, Yu H, You J. Fluorescence properties of novel rare earth complexes using carboxyl-containing polyaryletherketones as macromolecular ligands. European Polymer Journal 2009;45:2260-2268.

[13] Chen XB, Liu BJ, Zhang HB, Guan SW, Zhang JJ, Jiang ZH, Guiver MD. Fabrication of fluorescent holographic micropatterns based on azobenzene-containing host-guest complexes. Langmuir 2009;25:10444–10446.

[14] Chen XB, Zhang JJ, Zhang HB, Jiang ZH, Shi G, Song YL.Preparation and nonlinear optical studies of a novel thermal stable polymer containing azo chromophores in the side chain. Dyes and Pigments 2008;77:223–228.

[15] Chen XB, Zhang YH, Liu BJ, Zhang JJ, Wang H, Jiang ZH,.Novel photoactive hyperbranched poly(aryl ether)s containing azobenzene chromophores for optical storage. J Mater Chem 2008;18:5019–5026.

[16] Jiang XY, Chen XB, Yue XG, Zhang JJ, Guan SW, Zhang HB, Zhang WY, Chen D. Synthesis and characterization of photoactive poly(arylene ether sulfone)s containing azobenzene moieties in their main chains. React Funct Polym 2010;70:616–621.

[17] Jiang XY, Wang H, Chen XB, Li XJ, Mu JX, Zhang SL. A novel photoactive hyperbranched poly(aryl ether ketone)with azobenzene end groups for optical storage applications. React Funct Polym 2010;70:699–705.

[18] Zhang JJ, Zhang HB, Chen XB, Pang JH, Zhang YX, WangYP, Chen QD, Pei SH, Peng WX, Jiang ZH. Synthesis and photoresponsive behaviors of novel poly(arylene ether)s with di-azobenzene pendants. React Funct Polym 2011;71:553–560.

[19] Wu YL, Demachi Y, Tsutsumi O, Kanazawa A, Shiono T, Ikeda T. Photoinduced alignment of polymer liquid crystals containing azobenzene moieties in the side chain.1.effect of light intensity on alignment behavior. Macromolecules 1998;31:349-354.

[20] Cha SW, Choi DH, Oh DK, Han DY, Lee CE, Jin JI. Reversible polarization gratings on thin films of polyoxetanes bearing 4-(N,N-Diphenyl)amino-4’-

nitroazobenzene chromophores Adv Funct Mater 2002;12:670–678.

[21] Yue XG, Zhang HB, Chen WH, Wang YS, Zhang SL, Wang GB, Jiang ZH. Crosslinkable fully aromatic poly(aryl ether ketone)s bearing macrocycle of aryl ether ketone. Polymer 2007;48:4715-4722.

[22] Bandara HMD, Burdette SC. Photoisomerization in different classes of azobenzene. Chem Soc Rev 2012;41:1809-1825

[23] Kumar GS, Neckers DC. Photochemistry of azobenzene-containing polymers. Chem Rev 1989;89:1915–1925.

[24] Bian SP, He JA, Li L, Kumar J, Tripathy SK. Large photoinduced birefringence in azo dye/polyion films assembled by electrostatic sequential adsorption. Adv Mater 2000;12:1202–1205.

[25] Cha SW, Choi DH, Jin JI. Unusually fast optically induced birefringence in polyoxetanes bearing 4-(N,N-Diphenyl)amino-4’-nitroazobenzene chromophores. Adv Funct Mater 2001;11:355-360.

[26] Fernandez R, Mondragon I, Oyanguren PA, Galante MJ. Synthesis and characterization of epoxy polymers containing azobenzene groups that exhibit optical birefringence. React Funct Polym 2008;68:70–76.

[27] Wu YL, Natansohn A, Rochon P, Photoinduced birefringence and surface relief gratings in novel polyurethanes with azobenzene groups in the main chain. Macromolecules 2001;34:7822–7828.

[28] Forcén P, Oriol L, Sánchez C, Alcalá R, Hvilsted S, Jankova K, Loos J. Synthesis,characterization and photoinduction of optical anisotropy in liquid crystalline diblock azo-copolymers. J Polym Sci Pol Chem 2007;45:1899–1910.

Table 1 Properties of HPES and azo-PES polymers

Polymer	M_n	M_w/M_n	T_g (^oC) [a]	T_{d5} (^oC) [b]	T_{d10} (^oC) [c]
HPES	6.3×10^4	1.7	210	473	489
Azo-PES2	8.5×10^4	2.1	171	358	394
Azo-PES6	8.9×10^4	1.6	151	354	382
Azo-PES12	9.3×10^4	1.9	119	347	366

[a] Glass transition temperature by DSC.

[b] 5% weight-loss temperatures were detected at a heating rate of 10 ^oC/min in nitrogen with a gas flow of 100 mL/min.

[c] 10% weight-loss temperatures were detected at a heating rate of 10 ^oC /min in nitrogen with a gas flow of 100 mL/min.

Table 2 Elemental data of MPES, HPES and azo-PES polymers.

	Calculated			Found		
	C	H	N	C	H	N
MPES	69.75	4.21		69.53	4.42	
HPES	69.22	3.87		68.78	3.51	
Azo-PES2	69.98	4.02	4.23	70.53	3.69	3.91
Azo-PES6	70.73	4.53	3.78	70.32	4.67	3.43
Azo-PES12	71.46	5.06	3.07	71.96	4.73	2.86

All the values given are in percentages.

Table 3 Photoinduced birefringence characteristics of azo-PES polymers

Polymer	Saturation value of birefringence	Remnant value of birefringence	Remnant value of birefringence (%) [a]
Azo-PES2	0.1139	0.0988	87%
Azo-PES6	0.1129	0.095	84%
Azo-PES12	0.1106	0.0904	82%

[a] Remnant value of birefringence (%) = (remnant value of birefringence)/(saturation value of birefringence)×100

Figure Captions:

Table 1 Properties of HPES and azo-PES polymers.

Table 2 Elemental data of MPES, HPES and azo-PES polymers.

Table 3 Photoinduced birefringence characteristics of azo-PES polymers.

Fig. 1 IR (KBr) spectra of HPES and azo-PES polymers.

Fig. 2 ^{1}H NMR spectra of MPES, HPES and azo-PES2 in DMSO-d$_6$.

Fig. 3 UV-vis absorption spectra of HPES and azo-PES polymers in DMF solutions.

Fig. 4 DSC curves of HPES and azo-PES polymers in nitrogen.

Fig. 5 Changes in UV-visible absorption spectra of azo-PES in DMF solution at 25 ^{o}C with different irraiaton times under 360 nm irradiation. (A) azo-PES2 (B) azo-PES6 (C) azo-PES12.

Fig. 6 First-order *trans*-to-*cis* isomerization kinetics of azo-PES polymers.

Fig. 7 (A) Typical behaviour of the photoinduced birefringence of azo-PES polymers at room temperature: at point A, the writing laser was turned on; at point B, the writing laser was turned off; and at point C, the circularly polarized light was turned on. (B) Normalized photoinduced birefringence of the 10–50 s regions.

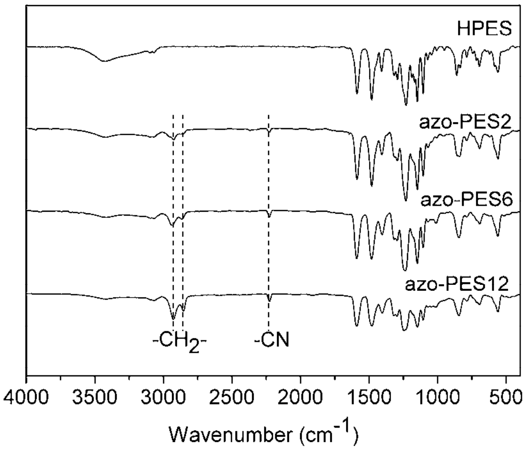
Fig. 8 Multiple writing-erasing cycles of azo-PES12 at room temperature: at point A, the writing laser was turned on; at point B, the writing laser was turned off; and at point C, the circularly polarized light was turned on.

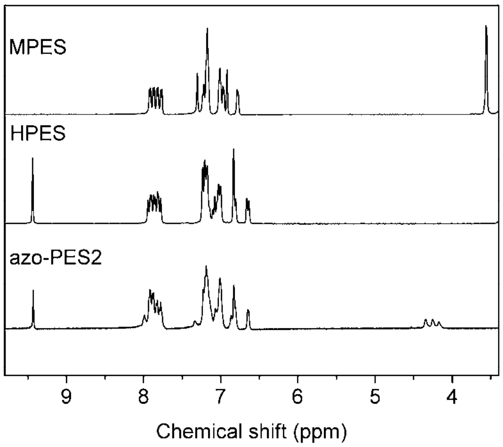
Scheme 1 Synthesis of monomers.

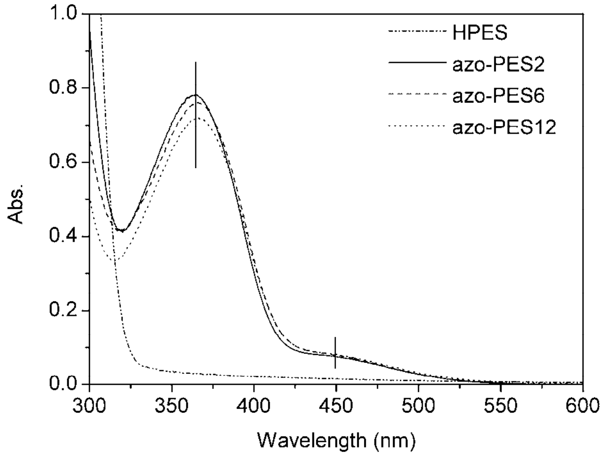
Scheme 2 Synthesis route of azo-PES polymers.

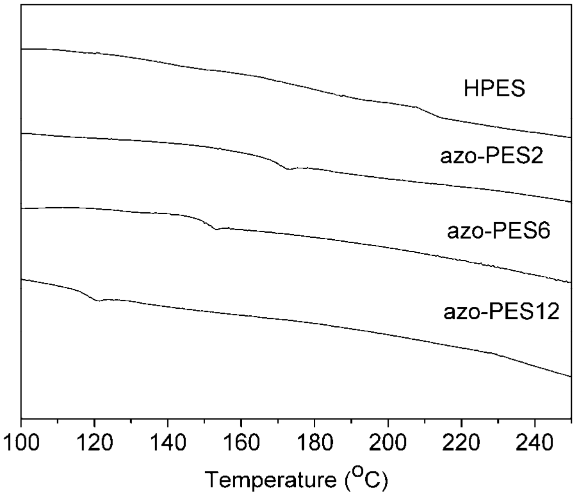
Highlights

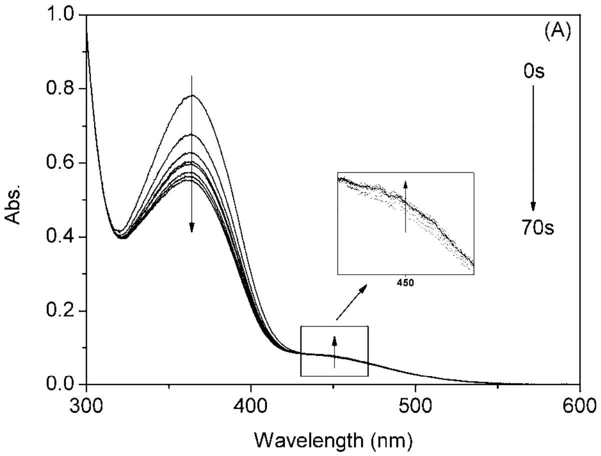
- Azobenzene-containing polyethersulfone with various spacer lengths were synthesized.
- All polymers show good thermal stability.
- The influence of spacer length on photoresponsive behaviour was investigated.
- The photoisomerization was more difficult to be induced for azobenzene-containing poly (ether sulfone)s with shorter spacers.
- All polymers possessed remnant values of birefringence larger than 84% of the saturation values of birefringence.

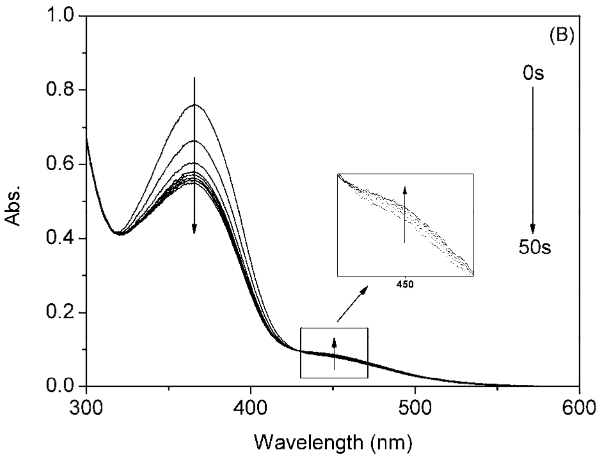

HPES
azo-PES2
azo-PES6
azo-PES12
-CH$_2$-
-CN
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

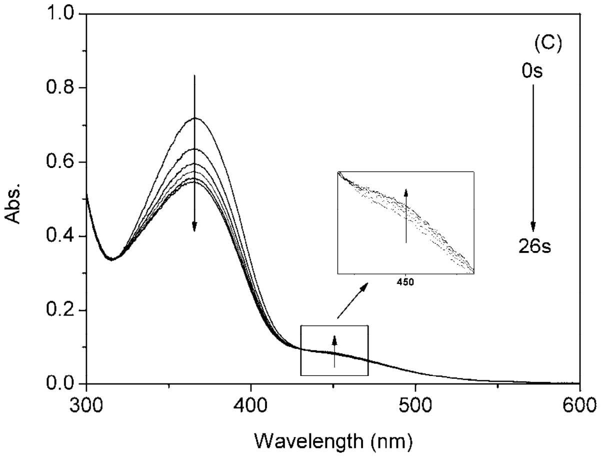

MPES
HPES
azo-PES2
9
8
7
6
5
4
Chemical shift (ppm)

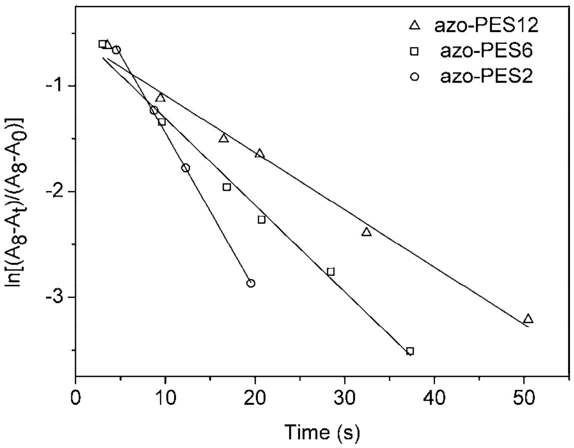

1.0
0.8
0.6
0.4
0.2
0.0
Abs.
300
350
400
450
500
550
600
Wavelength (nm)
HPES
azo-PES2
azo-PES6
azo-PES12

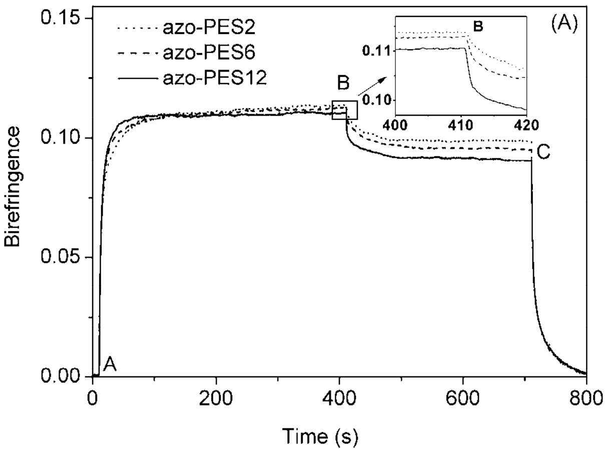

HPES
azo-PES2
azo-PES6
azo-PES12
100
120
140
160
180
200
220
240
Temperature (^{O}C)

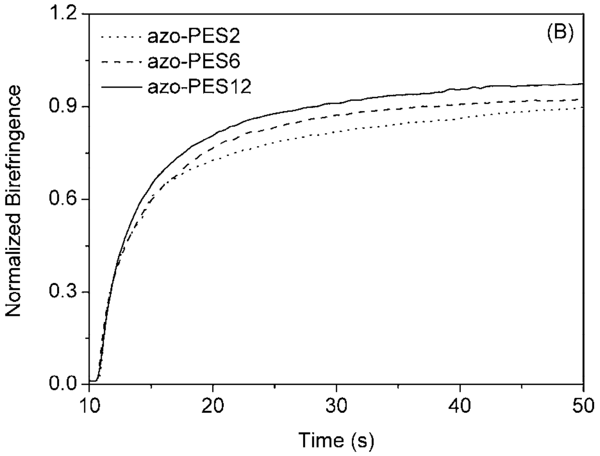

1.0
0.8
0.6
0.4
0.2
0.0
Abs.
300
400
500
600
Wavelength (nm)
(A)
0s
70s
450

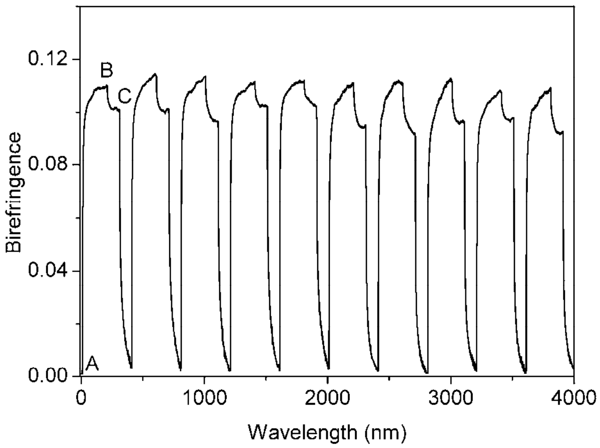

(B)
0s
50s
450
1.0
0.8
0.6
0.4
0.2
0.0
Abs.
300
400
500
600
Wavelength (nm)

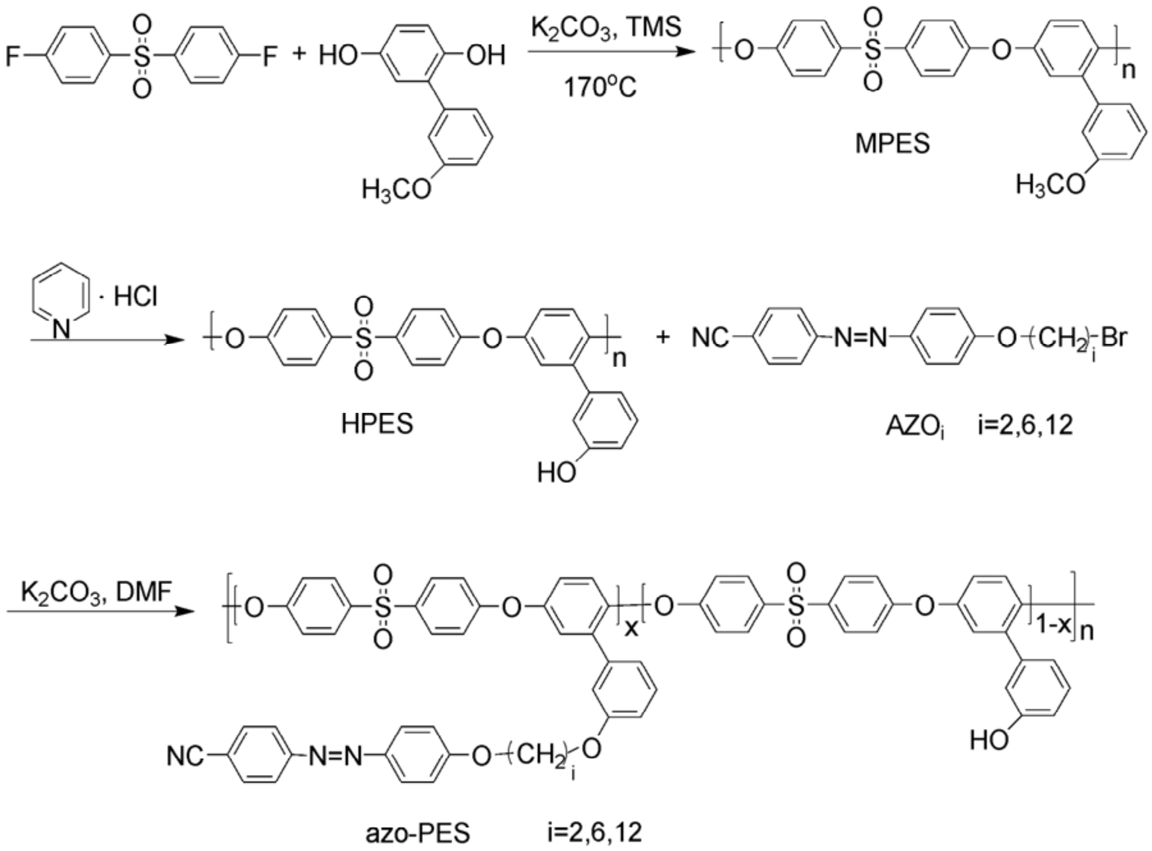

(C)
0s
26s
Abs.
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
450

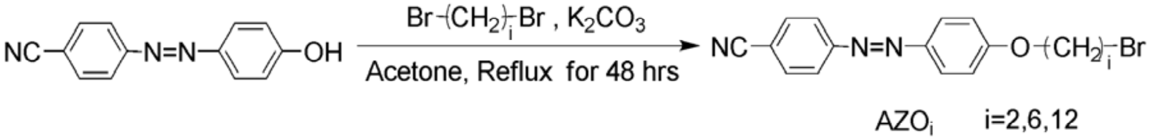

△ azo-PES12
□ azo-PES6
○ azo-PES2
ln[(A8-At)/(A8-A0)]
-1
-2
-3
0
10
20
30
40
50
Time (s)


(A)
azo-PES2
azo-PES6
azo-PES12
B
0.11
0.10
400
410
420
B
C
A
0.15
0.10
0.05
0.00
Birefringence
0
200
400
600
800
Time (s)


1.2
0.9
0.6
0.3
0.0
10
20
30
40
50
Normalized Birefringence
Time (s)
(B)
azo-PES2
azo-PES6
azo-PES12


0.12
0.08
0.04
0.00
Birefringence
0
1000
2000
3000
4000
Wavelength (nm)
A
B
C


K$_2$CO$_3$, TMS
170°C
MPES
HPES
AZO$_i$ i=2,6,12
K$_2$CO$_3$, DMF
azo-PES i=2,6,12


NC
N=N
OH
Br-(CH2)i-Br , K2CO3
Acetone, Reflux for 48 hrs
NC
N=N
O-(CH2)i-Br
AZOi
i=2,6,12