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ScienceDirect
Dyes and Pigments 77 (2008) 223–228
DYES and PIGMENTS
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Preparation and nonlinear optical studies of a novel thermal stable polymer containing azo chromophores in the side chain

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Received 29 March 2007; received in revised form 15 May 2007; accepted 15 May 2007
Available online 26 May 2007

Abstract

A novel bisfluoro NLO chromophore monomer, 4-[(4-cyanophenyl)diazenyl]phenyl-2,6-difluorobenzoate was synthesized via a two-step synthetic procedure. Azobenzene-functionalized poly(aryl ether) (azo-PAE) was prepared via a nucleophilic aromatic substitution polycondensation based on this monomer. The obtained polymer was characterized and evaluated by FT-IR, UV–vis, ^{1}H NMR, DSC and TGA. The third-order NLO coefficient was measured by Z-scan technique. The results showed the azo-PAE has high glass transition temperature, good thermal stability and large third-order nonlinear susceptibility.

Keywords: Azo polymer; Chromophore; Poly(aryl ether); Third-order nonlinear optics; Z-scan

1. Introduction

In recent years, much attention has been devoted to materials with nonlinear opical (NLO) properties for their potential applications in optoelectronics, optical storage and photorefractive area [1–4]. The aromatic azobenzol compounds with electron withdrawing groups (such as cyano) are well known to exhibit excellent NLO properties for containing conjugate π-electron systems and good fluidity of π electrons in their molecules. Polymers bearing azobenzene moieties in their side chains have been considered as promising materials because of their potentially large third-order susceptibilities associated with fast response time [5–8]. Unless these, as polymeric NLO materials, they also need to have good solubility, high thermal/chemical stability and excellent processability [9]. Poly(aryl ether)s (PAEs) are a family of high-performance engineering thermoplastics with excellent thermal, mechanical and electrical properties [10–13]. Some researchers had tried to introduce azobenzene group into the side chain of the PAE by post-functional reaction [6–8]. The as-prepared polymers showed large nonresonant NLO coefficient, high thermal stability and good sizability. However, it is difficult to control the distribution and amount of the chromophores in the polymer by the post-functionalization. In this paper, we prepared a novel PAE containing azobenzene groups in side chains via direct polymerization from a new bisfluoro azobenzene monomer and 4,4′-isopropylidenediphenol. The thermal property and third-order NLO effect of the polymer are also investigated.

2. Experimental

2.1. Materials

2,6-Difluorobenzoyl chloride was purchased from Aldrich. Phenol (99.5%) was purchased from Beijing Chemical

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doi:10.1016/j.dyepig.2007.05.006

Factory. 4-Aminobenzonitrile (99.5%) and 4,4′-isopropylidenediphenol (BPA, 99.5%) were purchased from Shanghai Chemical Factory. All organic solvents were obtained from commercial sources and used as received. K_2CO_3 was dried at 120 °C for 24 h before used for polymerization.

2.2. Measurements

Mass spectra (MS) were performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). IR spectra (KBr pellet) were recorded on a Nicolet Impact 410FTIR spectrophotometer. ^{1}H NMR spectra were taken on a Bruker 510 instrument using dimethysulfoxide-d_6 (DMSO-d_6) or $CDCl_3$ as solvent. Elemental analysis results were obtained on a Flash Ea 1112 elemental analysis instrument. Gel permeation chromatograph (GPC) analyses were carried out using a Waters 410 instrument with tetrahydrofuran (THF) as an eluent and polystyrene as calibration standard. Inherent viscosity was determined on an Ubbelohde viscometer in thermostatic container with the polymer concentration of 0.5 g/dL in DMF at 25 °C. Glass transition temperatures (T_g) were determined using DSC (Mettler DSC821^e) instrument at a heating rate of 20 °C/min under a nitrogen flow of 100 mL/min. Thermo gravimetric analyses were performed on a PerkinElmer Pyris 1 TGA in nitrogen atmosphere (100 mL/min) at a heating rate of 10 °C/min. UV–vis absorption spectra were recorded on a UV2501-PC spectrophotometer in DMF solution at room temperature.

The nonlinear optical property of the sample was measured by Z-scan technique performed with a Q-switched ns Nd:YAG laser system (Surelite II-10) continuum with pulse width of 4.5 ns at 1 Hz repetition rate and 532 nm wavelength. The experiment was set-up as in Ref. [14]. The solution of the sample was contained in a 2-mm quartz cell. The relation between the normalized transmittance $T(z)$ and z position was obtained by moving the samples along the axis of the incident beam (z-direction) with respect to the focal point. The incident and transmitted energies were detected simultaneously by an energy meter (Laser Probe Corporation, Rj-7620 ENERGY RATIOMETER, RjP-735). The input energy was 43.7 μJ.

2.3. Synthesis

2.3.1. Synthesis of 4-(4-hydroxy-phenylazo)-benzonitrile (monomer *1*)

Monomer **1** was synthesized by diazotization reaction and followed by coupling with phenol. Hydrochloric acid (0.8 M, 67.2 mL) was added into the mixture of 4-aminobenzonitril (23.6 g, 0.2 mol) in 50 mL water, maintained at 0–5 °C. Then a concentrated aqueous solution of sodium nitrite (13.8 g, 0.2 mol) was added dropwise and stirred for 30 min at 0–5 °C. The resulting solution was filtered and added dropwise into a mixture of NaOH (8.0 g, 0.2 mol), phenol (18.8 g, 0.2 mol), and sodium bicarbonate (25.2 g, 0.3 mol) in 200 mL water. The reaction mixture was stirred at 0–5 °C for about 2 h and then for another 4 h at room temperature. Then the final solution was added slowly into 700 mL acid water (HCl) and orange-red precipitates of the azo compound were formed. The precipitates were washed with water containing a little amount of sodium hydrogen carbonate (pH = 8) and recrystallized in a mixture of ethanol/water ($V_1/V_2 = 3:2$). Finally, monomer **1** was obtained as orange-yellow crystal. Yield: 80%, mp: 207 °C (DSC); MALDI-TOF-MS: $C_{13}H_9N_3O$ $m/z = 224$ ($M^+ + H$); IR (KBr, cm^{-1}): 3311 (–OH), 3030 (Ar–H), 2234 (–CN); ^{1}H NMR (DMSO, δ, ppm): 10.56 (s, 1H, –OH), 8.02 (d, 2H), 7.93 (d, 2H), 7.86 (d, 2H), 6.98 (d, 2H). A typical elemental analysis for $C_{13}H_9N_3O$: calcd. C 69.95, H 4.04, N 18.82, O 7.17; found C 69.68, H 4.31, N 18.72, O 7.29.

2.3.2. Synthesis of 4-((4-cyanophenyl)diazenyl)phenyl-2,6-difluorobenzoate (monomer *2*)

Under N_2 atmosphere, a solution of 2,6-difluorobenzoyl chloride (8.875 g, 0.5 mol) in 20 mL benzene was added dropwise into a mixture of monomer **1** (11.15 g, 0.5 mol) and potassium carbonate (K_2CO_3, 10.35 g, 0.075 mol) in 80 mL benzene. Then the mixture was refluxed for 20 h. The resulting insoluble inorganic salt was removed by filtering and washed with hot benzene solution. After evaporating the filtrate and purifying the crude product by column chromatography (silica gel, dichloromethane as eluent), monomer **2** was obtained as orange crystal. Yield: 85%, mp: 194 °C (DSC); MALDI-TOF-MS: $C_{20}H_{11}F_2N_3O_2$ $m/z = 364.5$ ($M^+ + H$); IR (KBr, cm^{-1}): 3030 (Ar–H), 2234 (–CN), 1754 (–CO–), 1012 (–C–F); ^{1}H NMR ($CDCl_3$, δ, ppm): 8.05 (d, 2H), 8.00 (d, 2H), 7.83 (d, 2H), 7.54 (s, 1H), 7.46 (d, 2H), 7.06 (d, 2H). A typical elemental analysis for $C_{20}H_{11}F_2N_3O_2$: calcd. C 66.12, H 3.05, N 11.57, O 8.81; found C 66.41, H 3.25, N 11.39, O 8.51.

2.3.3. Synthesis of azobenzene-functionalized poly(aryl ether) (azo-PAE)

A 75-mL three necked flask equipped with a mechanical stirrer, a Dean–Stark trap, a cold water condenser, an N_2 inlet/outlet and a thermometer was charged with monomer **2** (3.6332 g, 0.01 mol), BPA (2.2829 g, 0.01 mol), anhydrous potassium carbonate (1.4504 g, 0.013 mol), 15 mL DMSO and 15 mL toluene. The reaction mixture was refluxed at 120 °C for 2 h under N_2 atmosphere to dehydrate the system. After dehydration and removal of toluene, the reaction temperature was then increased to 140 °C and maintained at this temperature for 8 h until a viscous solution was obtained. Then the viscous solution was slowly poured into water and the thread-like polymer was obtained. After pulverized into powders, the polymer was washed with hot deionized water and extracted in a Soxhlet extractor with alcohol. The resulting product was dried at 100 °C under vacuum for 24 h, the polymer (azo-PAE) was obtained as orange-yellow solid (yield: 87%). IR (KBr, cm^{-1}): 3030 (Ar–H), 2969 (–CH_3), 2223 (–CN), 1750 (–CO–), 1234 (–Ar–O–Ar–); ^{1}H NMR ($CDCl_3$, δ, ppm): 7.93 (m, 4H), 7.77 (m, 2H), 7.33 (m, 1H), 7.18 (m, 4H), 6.98 (m, 2H), 6.86 (m, 4H), 6.64 (m, 2H), 1.62 (s, 6H, –CH_3).

3. Results and discussion

3.1. Synthesis and characterization

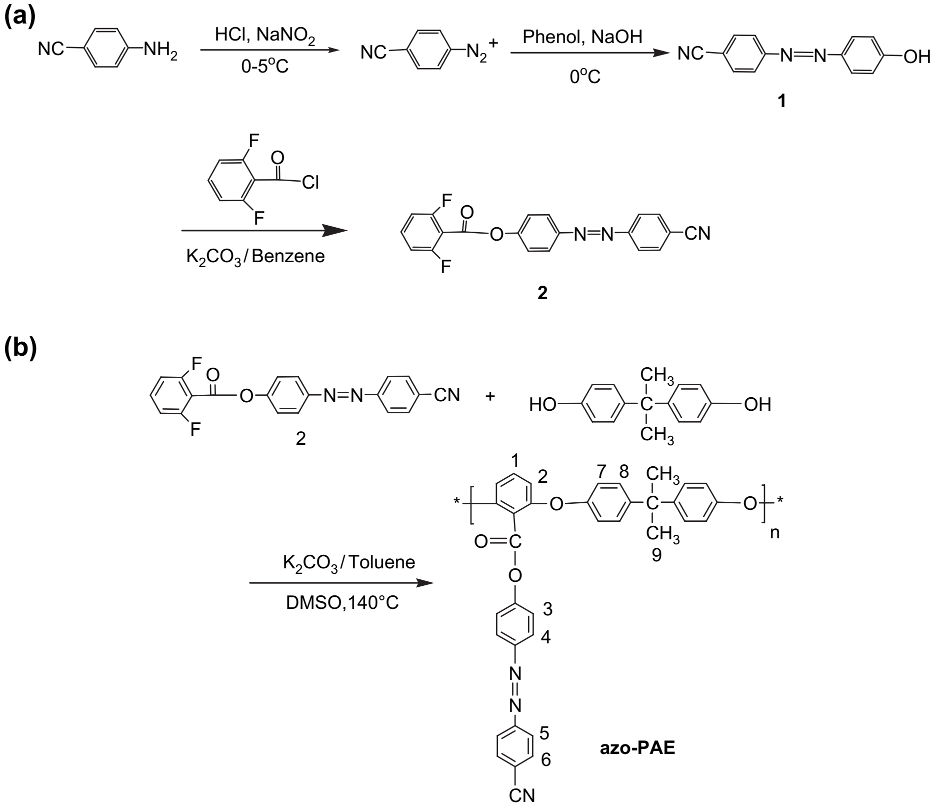
We designed a new bisfluoro monomer **2** containing azo group and the reaction mechanism for the preparation of the monomer is illustrated in Scheme 1a. The structure of monomer **2** was confirmed by MS, IR, and ^{1}H NMR. FT-IR spectrum exhibited characteristic bands of −CN at 2233 cm^{-1}, −CO− and C−F stretching vibrations at 1754 cm^{-1} and 1012 cm^{-1}, respectively. The azobenzene-functionalized poly(aryl ether) (azo-PAE) was synthesized by the typical nucleophilic substitution polycondensation reaction from 4-[(4-cyanophenyl) diazenyl]phenyl-2,6-difluorobenzoate (monomer **2**) and 4,4′-isopropylidenediphenol (BPA), as shown in Scheme 1b. The polymerization was carried out in DMSO with potassium carbonate as a base catalyzer and by using toluene for dehydration. The inherent viscosity of the resulting polymer azo-PAE was 0.32 dL/g in DMF at 25 °C and the number-average molecular weight (M_n) was 1.2×10^4 ($M_w/M_n = 6.1$, GPC measurement), which indicated successful polymerization. The polymer was well soluble in solvents such as chloroform, THF, DMF, DMAC, NMP and cyclohexanone, but insoluble in acetone and ethanol.

The chemical structure of azo-PAE was confirmed by FT-IR, UV−vis and ^{1}H NMR spectra. The FT-IR spectrum showed characterized absorption band of Ar−O−Ar at 1234 cm^{-1} and −CO− at 1758 cm^{-1}, indicating successful introduction of azo segments into the polymer chains. UV−vis absorption measurement of the azo-PAE was recorded at 25 °C in DMF solution (Fig. 1). In the spectrum, the absorptions at around 354 nm and 450 nm were corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of azo-aromatic chromophores, respectively. The high energy band was mainly attributed to the *trans*-isomer, whereas the low energy one was mainly derived from the metastable *cis*-isomer.

Fig. 2 showed the signal assignments in the aromatic region of the ^{1}H NMR spectrum of the polymer (azo-PAE) in $CDCl_3$. Although the signals in the ^{1}H NMR spectrum of the copolymer were greatly overlapped, the signals corresponding to the proton of $-CH_3$ (δ, 1.62) and the proton located at *ortho*-position of azo group (δ, 7.93) and −CN group (δ, 7.68) departed obviously from other protons and could be easily distinguished, which further confirmed the structure of the polymer.

3.2. Thermal property of azo-PAE

Thermal stability of azo-PAE was investigated by TGA analysis at a heating rate of 10 °C/min under a nitrogen atmosphere. From the TGA curve of azo-PAE (Fig. 3), it can be seen that 5% weight loss temperature and 10% weight loss temperature of azo-PAE were 403 °C and 417 °C, respectively, indicated that azo-PAE had good thermal stability. The T_g of azo-PAE was determined by differential scanning calorimetry (DSC) and is shown in Fig. 4. In DSC curve, no other



Scheme 1. (a) Synthetic route of monomer **2** and (b) synthetic route of the azo-PAE.

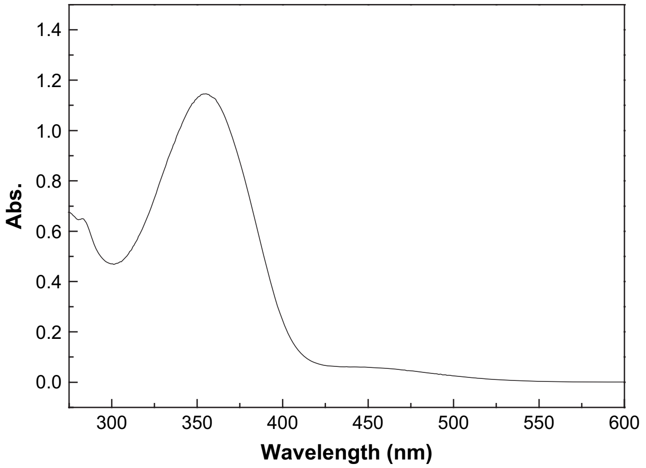


Fig. 1. UV–vis absorption spectrum of the azo-PAE in DMF solution at 25 °C.

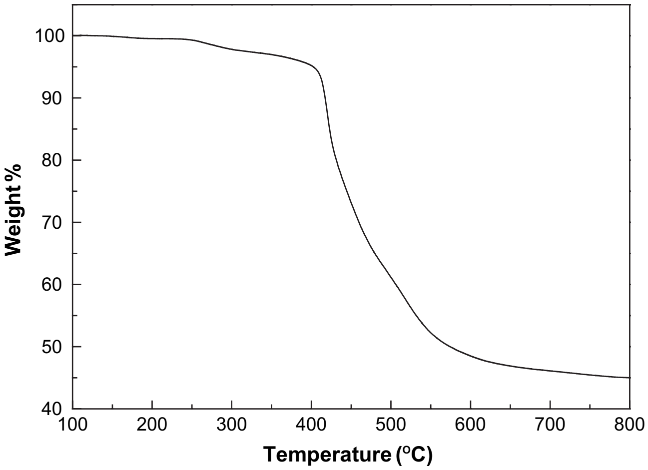


Fig. 3. TGA curve of azo-PAE in nitrogen.

thermo change except glass transition was observed below decomposition temperature, indicating that azo-PAE is amorphous. Due to the aromatic structure and the large dipole moment of the side groups, azo-PAE showed high glass transition temperature ($T_g = 163$ °C), which ensured it with good thermal property.

3.3. Nonlinear optical property of azo-PAE

The nonlinear coefficients of the polymers were measured by the Z-scan technique. Z-scan is a well-known technique that allows the simultaneous measurement of both nonlinear absorption coefficient (α_2) and the nonlinear refractive coefficient (n_2). The basic idea behind Z-scan technique is self-focusing or self-defocusing. A Gaussian beam is focused by a lens onto the sample and the variation in the beam profile is observed at the far field as the sample is taken through the focus of the lens. The beam propagation direction is taken as z-direction and hence this technique is known as Z-scan technique. By properly monitoring the transmittance change through a small aperture placed at the far-field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus and without placing an aperture at the detector (open aperture), one can measure the intensity dependent absorption as a change of transmittance through the sample.

In our experiment, the sample was moved forward or backward along the direction of the laser beam around the focus ($z = 0$). The transmittance was simultaneously recorded by an energy meter with and without an aperture in the far field of lens as the function of sample position. Fig. 5a shows the normalized transmittance plotted as a function of the sample position (z) measured with an open aperture, thus an intensity dependent absorption effect is observed. The open-aperture transmittance, which is symmetric with respect to the focus ($z = 0$), where it has a minimum transmittance, indicates that the nonlinear absorption in azo-PAE is unambiguous. From the linear absorption spectrum of azo-PAE (Fig. 1), the absorption maximum locates at 354 nm, but at 532 nm there is no single-photon absorption.

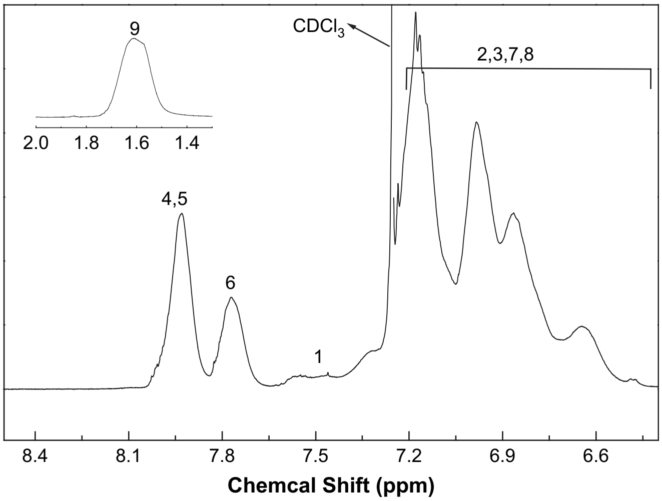


Fig. 2. ^{1}H NMR spectrum of azo-PAE in CDCl$_3$.

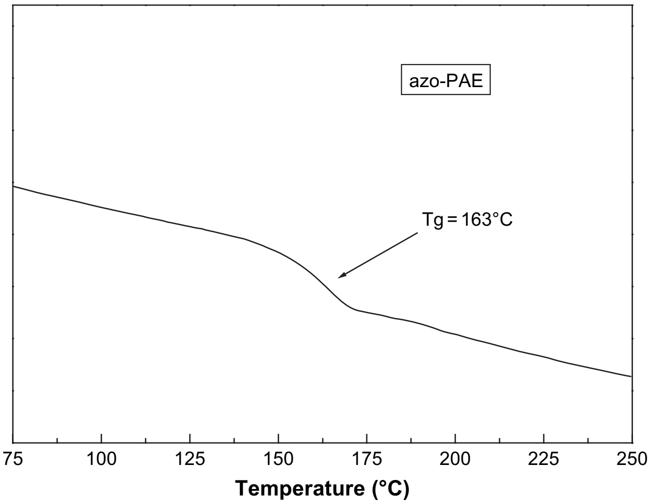


Fig. 4. DSC curve of azo-PAE.

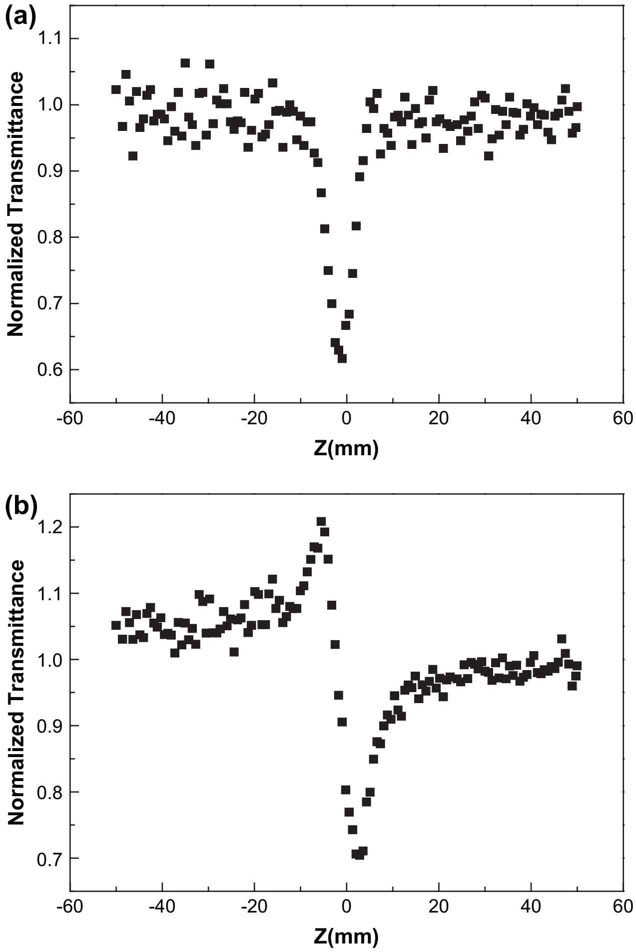


Fig. 5. (a) Z-scan data of opened aperture and (b) Z-scan data of closed aperture.

The pure nonlinear refraction curve of azo-PAE, shown in Fig. 5b, was obtained by the division of the closed aperture data by the corresponding open-aperture data. The Z-scan signature shows a large negative nonlinearity (self-defocusing) for azo-PAE.

Thus, the third-order nonlinear coefficient ($\chi^{(3)}$) of the polymer measured in this experiment was attributed to dual contributions of nonlinear absorption and refraction of the molecules. In theory, the normalized transmittance for the open aperture can be written as [14,15];

$$T(z,s=1)=\sum_{m=0}^{\infty}\frac{[-q_0(z)]^m}{(m+1)^{3/2}},\quad \text{for}|q_0|<1 \tag{1}$$

where $q_0(z)=\alpha_2 I_0(\mathrm{t})L_{\mathrm{eff}}/(1+z^2/z_0^2)$, with α_2 as the nonlinear absorption coefficient, $I_{0(\mathrm{t})}$ as the intensity of laser beam at focus ($z=0$), $L_{\mathrm{eff}}=[1-\exp(-\alpha_0 L)]/\alpha_0$ is the effective thickness with α_0 as the linear absorption coefficient and L as the sample thickness, z_0 as the diffraction length of the beam, and z as the sample position. Thus, the nonlinear absorption coefficient α_2 of azo-PAE is determined to be 1.33×10^{-10} MKS by fitting the experiment data using Eq. (1).

The normalized transmission for the closed aperture Z-scan is given by [14,15];

$$T(z,\Delta\Phi)=1+\frac{4\Delta\Phi\chi}{(\chi^2+9)(\chi^2+1)} \tag{2}$$

where $x=z/z_0$ and $\Delta\Phi$ is on-axis phase change caused by the nonlinear refractive index of the sample and $\Delta\Phi=\Delta\Phi=[2\pi I_0(1-\mathrm{e}^{-\alpha_0 L})n_2]/(\lambda\alpha_0)$. Thus, the nonlinear refractive coefficient n_2 of azo-PAE is determined to be -4.68×10^{-11} esu by fitting the experimental data using Eq. (2).

The $\chi^{(3)}$ can be calculated by the following equation [14,15];

$$\left|\chi^{(3)}\right|=\sqrt{\left|\frac{cn_0^2}{80\pi}n_2\right|^2+\left|\frac{9\times10^8\varepsilon_0 n_0^2c^2}{4\pi\omega}\alpha_2\right|^2} \tag{3}$$

where ε_0 is the permittivity of vacuum, c is the speed of light, n_0 is the refractive index of the medium and $\omega=2\pi c/\lambda$. Thus, the nonlinear susceptibility $\chi^{(3)}$ of azo-PAE is determined to be 1.15×10^{-11} esu, which is almost two orders of magnitude larger than those of poly(phenylacetylene) [16,17] and azobenzene polymers, such as poly(2-(4-(4-cyanopheny)diazenyl phenyloxy)ethoxyl methacrylate) [3,15] and poly(2-butoxy-5-(2′-(ethyl-(4′-(4′-nitrophenylazo)-phenyl)-amino)-ethoxy)1,4-phenylenevinylene) [18], a copolymer of maleic anhydride and octadecene containing disperse red or disperse orange type chromophores [19] and poly(cinylamine) containing sunset yellow [20].

4. Conclusions

A novel azobenzene-functionalized poly(aryl ether) (azo-PAE) had been synthesized via a nucleophilic aromatic substitution polycondensation. Large amount of chromophores can be introduced into the side chain of the polymer readily during the polycondensation step. The polymer was amorphous and has good solubility in organic solvents. This polymer possessed high glass transition temperature and high decomposition temperature. Z-scan measurements indicated that azo-PAE possessed large third-order NLO coefficient. Such a novel azo-functionized PAE is expected to be a potential candidate for optical limiting, optical switching and other fast photonic applications.

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