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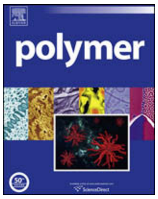

Synthesis and the third-order nonlinear optical properties of soluble polymers with different substituted azobenzene side chains

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ABSTRACT

A series of soluble polyacrylates containing different azobenzene side chains have been synthesized via atom transfer radical polymerization (ATRP) technique, from which the side-chain nonlinear optical (NLO) polymers with controllable molecular weight and low polydispersity (1.1–1.4) have been obtained. The third-order NLO absorption and refraction coefficients were simultaneously determined by Z-scan technique. The polymerization activity of the azobenzene-containing acrylate monomers and the third-order NLO properties of the obtained polyacrylates were both dominated by the electronic effect of the different substituents in the azobenzene side chain. The results of Z-scan with and without an aperture showed that all the azobenzene-containing monomers and polymers have both nonlinear absorption and nonlinear refraction. The third-order NLO susceptibility ($\chi^{(3)}$) of all the azobenzene-containing samples under the laser irradiation is 1.0–5.0 × 10^{-11} esu.

1. Introduction

In recent years, the third-order nonlinear optical (NLO) materials have been applied widely in many important technologies including optical recording, optical limiting for sensor protection, photonic switching, optical signal processing and optical computing [1–4]. During the last two decades, azobenzene-containing polymers based on (methyl) methacrylate, styrene, polyamide and polyester have been investigated on their potential applications in nonlinear optical (NLO) materials [5–9] because the soft main chain endues the azo polymers good solubility and film-forming ability, which are beneficial to form optical devices. The azo polymers with electron withdrawing group are well known to exhibit excellent third-order NLO susceptibilities and fast response capability for containing highly π-conjugated system and good fluidity of π electrons in their molecules [10–13]. Among the reported researches, one kind of polymers based on [4′-[(2-methacryloyloxy)ethyl]ethylamino]-4-nitroazobenzene DR1M are the most representative. The polymers containing nitro-substituted azobenzene group are widely synthesized and studied for various photonic applications [14–18]. But most researchers have introduced azobenzene group into the polymer side chain by post-coupling reaction, which is difficult to control the distribution and amount of the chromophores in the polymer [19–21]. In this paper, azobenzene-containing polymers were prepared via direct polymerization from a series of azobenzene monomers with similar structure to DRIM (Scheme 1). And here, one of the most attractive polymerization methods for preparing polymers with novel and controlled architectures in rather straightforward operating conditions, atom transfer radical polymerization (ATRP) technique [22–24], was employed to obtain azobenzene-containing side-chain polymers with controllable molecular weight and narrow polydispersity. The third-order nonlinear absorptive and refractive effect of the polymers containing different substituted azobenzene chromophores were investigated by using the Z-scan technique [25], which is a well-known technique that allows the simultaneous measurement of both nonlinear absorption coefficient (β) and the nonlinear refractive coefficient (n_2). All the samples displayed large third-order susceptibility ($\chi^{(3)}$). The influence of the push–pull electronic effect on the third-order NLO properties by changing the substituent which has different electronic effects on the azobenzene group was investigated.

2. Experimental section

2.1. Materials

N-ethyl-N-(2-hydroxyethyl) aniline (98%) was purchased from Tokyo Kasei Kogyo Co., Ltd. in Japan and used as-received. 4-Nitroaniline, 4-bromoaniline, 4-methoxyaniline and

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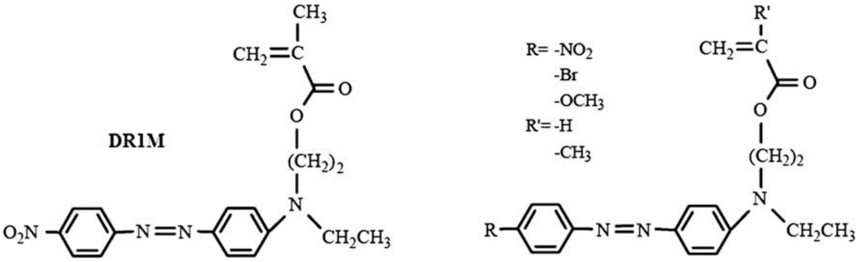


Scheme 1. Structure of DRIM and its similar azobenzene derivatives with different substituents.

triethylamine were all purchased from Shanghai chemical reagent Co., Ltd. as analytical regents and used without further purification (declared purity grade, ≥99%). Acryloyl chloride and methacryloyl chloride are produced by Haimen Best Fine Chemical Industry Co., Ltd. and used after redistillation. N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory) was dried with molecular sieve and distillated. Copper(I) bromide (CuBr) (A.R., Shanghai Zhenxin Chemical Reagent Factory) was purified with sodium sulfite and glacial acetic acid and stored under argon atmosphere at room temperature. Ethyl 2-bromoisobutyrate (EBiB) (Acros, 99%) was used without further purification. Tetrahydrofuran (THF), cyclohexanone and N,N-dimethyl formamide (DMF) were purified by reduced pressure distillation. Other reagents such as methanol were commercially available and used as-received.

2.2. *Instruments for characterization*

The FTIR spectra were recorded on a Perkin–Elmer 577 FTIR spectrophotometer in KBr disks. ^{1}H NMR spectra of monomers and polymers in CDCl$_3$ were obtained on an Inova 400 MHz FT-NMR spectrometer at ambient temperature. The UV–vis absorption spectra were carried out at room temperature in the 190–700 nm spectral region with a Perkin–Elmer Lambda spectrophotometer using cell path lengths of 0.5 cm. Molecular weights (M_n) and polydispersity (M_w/M_n) were measured on a gel permeation chromatography (GPC) utilizing Waters 515 pump and differential refractometer. THF was used as a mobile phase at a flow rate of 1.0 mL/min.

2.3. *Synthesis of monomer*

A series of azobenzene-containing monomers with different substituents were synthesized as a procedure modified from that described in the literature [26,27], as shown in Scheme 2.

2.3.1. *ANAzo*

^{1}H NMR (CDCl$_3$): δ (ppm) = 8.34 (d, 2H, benzene ring protons adjacent to –NO$_2$), 7.94–7.90 (d, 4H, benzene ring protons adjacent to –N=N–), 6.83 (d, 2H, benzene ring protons), 6.45 (d, 1H, vinyl proton), 6.14 (d, 1H, –CH=), 5.89 (t, 1H, vinyl proton), 4.39 (t, 2H, –OCH$_2$), 3.89 (t, 2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.58 (m, 2H, –CH$_2$ in ethyl), 1.27 (t, 2H, –CH$_3$ in ethyl). Anal. Calcd. for $C_{19}H_{20}N_4O_4$: C 61.948, H 5.4719, N 15.209; Found: C 62.165, H 5.6073, N 14.993.

2.3.2. *ABAzo*

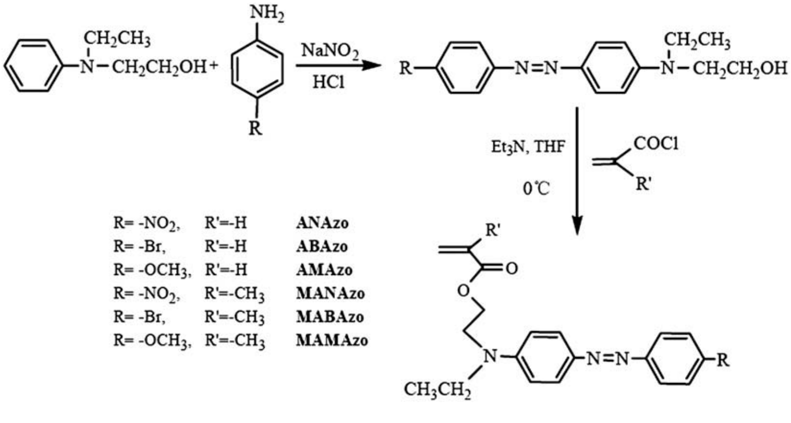
^{1}H NMR (CDCl$_3$): δ (ppm) = 7.90–7.75 (d, 4H, benzene ring protons adjacent to –N=N–), 7.65 (d, 2H, benzene ring protons adjacent to –Br), 6.80 (d, 2H, benzene ring protons), 6.44 (d, 1H, vinyl proton), 6.13 (t, 1H, –CH=), 5.88 (d, 1H, vinyl proton), 4.38 (t, 2H, –OCH$_2$), 3.71 (t, 2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.54 (m, 2H, –CH$_2$ in ethyl), 1.25 (t, 3H, –CH$_3$ in ethyl). Anal. Calcd. for $C_{19}H_{20}N_3BrO_2$: C 56.727, H 5.0108, N 10.445; Found: C 56.218, H 4.8964, N 10.112.

2.3.3. *AMAzo*

^{1}H NMR (CDCl$_3$): δ (ppm) = 7.85–7.26 (d, 4H, benzene ring protons adjacent to –N=N–), 6.97 (d, 2H, benzene ring protons adjacent to –OCH$_3$), 6.81 (d, 2H, benzene ring protons), 6.44 (d, 1H, vinyl proton), 6.11 (t, 1H, –CH=), 5.84 (d, 1H, vinyl proton), 4.37 (t, 2H, –OCH$_2$), 3.87 (s, 3H, methoxyl protons), 3.68 (t, 2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.48 (m, 2H, –CH$_2$ in ethyl), 1.23 (t, 3H, –CH$_3$ in ethyl). Anal. Calcd. for $C_{20}H_{23}N_3O_3$: C 67.797, H 6.5592, N 11.889, Found: C 68.021, H 6.6294, N 11.835.

2.3.4. *MANAzo*

^{1}H NMR (CDCl$_3$): δ (ppm) = 8.31 (d, 2H, benzene ring protons adjacent to –NO$_2$), 7.94–7.90 (d, 4H, benzene ring protons adjacent to –N=N–), 6.81 (d, 2H, benzene ring protons), 6.11 (s, 1H, vinyl proton), 5.59 (s, 1H, vinyl proton), 4.39 (t, 2H, –OCH$_2$), 3.72 (t, 2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.53 (m, 2H, –CH$_2$ in ethyl), 1.94 (s, 3H, methyl adjacent to vinyl), 1.27 (t, 3H, –CH$_3$ in ethyl). Anal. Calcd. for



Scheme 2. The synthetic route of the azobenzene monomers with different substituents.

$C_{20}H_{22}N_4O_4$: C 62.816, H 5.7983, N 14.651; Found: C 62.636, H 5.9426, N 14.516.

2.3.5. MABAzo

^{1}H NMR ($CDCl_3$): δ (ppm) = 7.88–7.73 (d, 4H, benzene ring protons adjacent to –N=N–), 7.60 (d, 2H, benzene ring protons adjacent to –Br), 6.82 (d, 2H, benzene ring protons), 6.11 (s, 1H, vinyl proton), 5.58 (s, 1H, vinyl proton), 4.38 (t, 2H, $–OCH_2$), 3.71 (t, 2H, $H_2C–N$ in $N–CH_2CH_2O$), 3.50 (m, 2H, $–CH_2$ in ethyl), 1.94 (s, 3H, methyl adjacent to vinyl), 1.25 (t, 3H, $–CH_3$ in ethyl). Anal. Calcd. for $C_{20}H_{22}N_3BrO_2$: C 57.701, H 5.3261, N 10.093; Found: C 57.588, H 5.4812, N 9.8862.

2.3.6. MAMAzo

^{1}H NMR ($CDCl_3$): δ (ppm) = 7.83–7.81 (d, 4H, benzene ring protons adjacent to –N=N–), 6.98 (d, 2H, benzene ring protons adjacent to $–OCH_3$), 6.80 (d, 2H, benzene ring protons), 6.09 (s, 1H, vinyl proton), 5.57 (s, 1H, vinyl proton), 4.34 (t, 2H, $–OCH_2$), 3.70 (s, 3H, methoxyl protons), 3.66 (t, 2H, $H_2C–N$ in $N–CH_2CH_2O$), 3.48 (m, 2H, $–CH_2$ in ethyl), 1.93 (s, 3H, methyl adjacent to vinyl), 1.23 (t, 3H, $–CH_3$ in ethyl); Anal. Calcd. for $C_{21}H_{25}N_3O_3$: C 68.644, H 6.857, N 11.436; Found: C 68.987, H 6.8526, N 11.524.

2.4. Preparation of azobenzene-containing side-chain polymers

An atom transfer radical polymerization (ATRP) technique was employed to prepare the azo polymers. A typical ATRP procedure of azobenzene monomer was carried out as follows. A round-bottom flask was equipped with a rubber septum, a magnetic stirrer and a gas inlet/outlet. 17 μL (0.1 mmol) of ethyl 2-bromoisobutyrate (EBiB), 15 mg (0.1 mmol) of CuBr and 20 μL (0.1 mmol) of PMDETA were added with 5.0 mmol of azobenzene monomer and 20 mL of cyclohexanone to the flask and the mixture was immediately degassed three times and flushed with nitrogen in an ice bath. The reaction mixture was then immersed in an oil bath connected with a thermal control meter with sufficient stirring. At different time intervals, a 1.5–2.0 mL solution mixture was withdrawn from the flask with a nitrogen-purged syringe. The mixture was poured into a large excess of methanol where 1:1 chlorhydric acid was added (100:1 v/v) to eluted the copper in the mixture. The suspension was filtered for the removal of residual monomer and most of the catalyst. The obtained polymers were purified by reprecipitation from THF into methanol and dried under vacuum for 24 h at room temperature. The ATRP kinetics of all the azo monomers was investigated under the same condition.

2.5. Measurement of the third-order optical nonlinearities

The Z-scan technique is a single-beam method for measuring the third-order optical nonlinearities through detecting the far-field sample transmittance of a focused Gaussian beam as a function of sample position (z), as depicted in Fig. 1. Superior to the other common techniques such as degenerate four-wave mixing (DFWM) and third harmonic generation (THG), the nonlinear absorption and refraction can be simultaneously determined by Z-scan technique. In Z-scan measurement, the intensity-dependent transmission of the sample measured without an aperture (open-aperture scan) gives information on purely absorptive nonlinearity whereas the apertured scan (closed-aperture scan) contains the information of both the absorptive and refractive nonlinearities. The nonlinear refractive component is obtained by dividing the normalized Z-scan data obtained under a closed-aperture configuration by the normalized Z-scan data obtained under the open-aperture configuration.

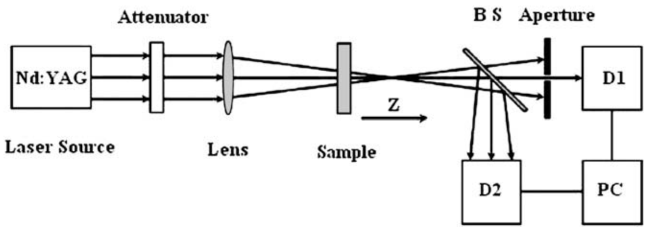


Fig. 1. Schematic illustration of the experimental set-up for the Z-scan measurements.

In this work, the third-order NLO coefficients were measured by the Z-scan technique using a Q-switching Nd:YAG laser which produces 4 ns (Full width at half-maximum) laser pulses at 532 nm with a repetition rate of 2 Hz. The single pulse incident energy is about 40 μJ. The input and output energies of the pulses were measured simultaneously with two energy detectors (laser Precision Rjp-735) controlled by computer.

3. Results and discussion

3.1. Preparation of azobenzene-containing side-chain polymers

ATRP was successfully used to prepare the homopolymers from the azo monomers. The polymer was prepared by using EBiB, CuBr, and PMDETA as initiator, catalyst and ligand, respectively. Each of the obtained polymers has a controlled number-average molecular weight and a low polydispersity confirmed by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC).

The kinetics of all the azo monomers was investigated under the same polymerization condition, as shown in Figs. 2 and 3. The results showed that the ln([M]$_0$/[M]) of each monomers and the conversion of polymers were enhanced with the increase of reaction time. And the polydispersity (M_w/M_n) of obtained polymers varied with reaction time a bit and remained all along relatively low values (1.15–1.4). In addition, the methyl-substituted vinyl monomers (azobenzene-containing methacrylates, **MANAzo**, **MABAzo**, **MAMAzo**) have higher activity than those without methyl group (azobenzene-containing acrylates, **ANAzo**, **ABAzo**, **AMAzo**) in this ATRP system for the electronic effect of the methyl group on the C adjacent to vinyl. By comparison, the nitro-substituted azobenzene monomers (**ANAzo** and **MANAzo**) had lower polymerization activity than the other azobenzene monomers substituted by bromo- and methoxy-group, which maybe caused by the inhibition

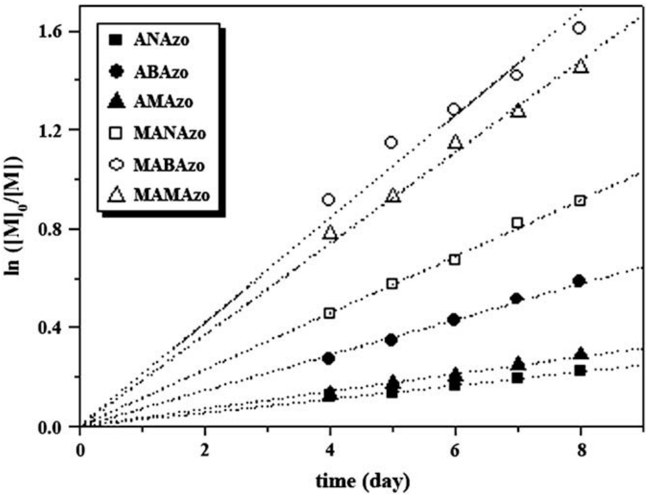


Fig. 2. First-order kinetic plots for ATRP of azo-containing acrylates and methacrylates (reaction conditions: [monomer]/[EBiB]/[CuBr]/[PMDETA] = 50:1:1:1, temperature = 80 °C).

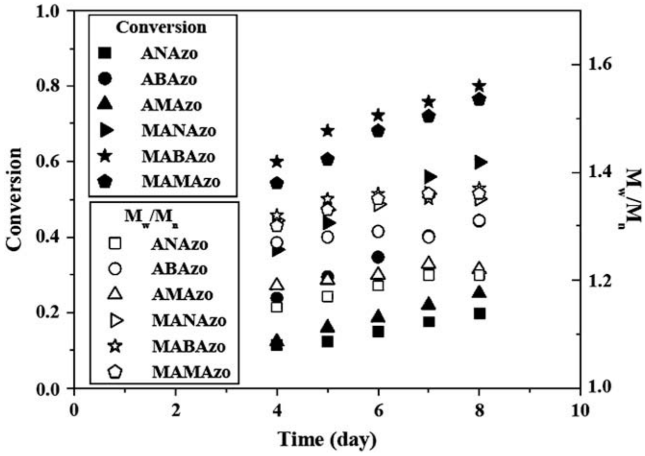


Fig. 3. Dependence of conversion and M_w/M_n on reaction time for ATRP of azobenzene-containing acrylates and methacrylates (reaction conditions: [monomer]/[EBiB]/[CuBr]/[PMDETA] = 50:1:1:1, temperature = 80 °C).

of the nitro-group [28] on the monomer in this polymerization system.

3.2. *Solubility of the azobenzene-containing side-chain polymers*

The azo intermediate products have poor solubility due to the high dipole moment introduced by its substituents on azobenzene group. But the azo-containing monomers and polymers show much better solubility after introducing apolar acryloyl groups. All of the azobenzene-containing side-chain polymers exhibit good solubility in a wide range of organic solvents, including $CHCl_3$, THF and DMF, and the solubility of polymers is improved than the corresponding monomers. It shows the potential on film-forming and further application in device.

3.3. *UV–vis spectra*

The UV–vis spectra of the azobenzene monomers in the $CHCl_3$ solutions are displayed in Figs. 4 and 5. Each of the azobenzene monomer shows the typical absorption peak at 400–500 nm which is associated to π–π^* electronic transitions of the azobenzene chromophores from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In comparison with their corresponding monomer, the typical absorption peaks of the azobenzene-containing homopolymers are red-shifted a bit, which maybe caused by the higher order of the macromolecules and the stronger conjugation in the polymer chain. The absorption peaks of bromo-substituted (**ABAzo** and **MABAzo**) and methoxy-substituted azobenzene monomers (**AMAzo** and **MAMAzo**) at around 418 and 408 nm, respectively only display weak ground state electron absorption at 532 nm for the laser output wavelength in Z-scan measurements. But the λ_{max} value of the nitro-substituted monomer (**ANAzo** and **MANAzo**) is located around 465 nm. The nitro-substituted monomers and polymers show certain ground state absorption and they display relatively low linear transmission at 532 nm. After the irradiation under the laser with 532 nm wavelength, resonant absorptions are exhibited to cause the concomitant heating effects those are contributive to the third-order nonlinearity. In our experiment, the solutions of the nitro-substituted monomers and polymers are prepared at lower concentration in order to avoid the heating effects.

3.4. *The third-order nonlinear optical (NLO) measurement*

The nonlinear coefficients of the azobenzene monomers and polymers were measured by using Z-scan technique, which is a well-known technique that allows the simultaneous measurement of both nonlinear absorption coefficient (β) and the nonlinear refractive coefficient (n_2).

In theory, the nonlinear absorption coefficient β value could be obtained by fitting the open-aperture normalized transmittance data to the following Eqs. (1)–(3) [25], which describe the third-order NLO absorption process of the sample.

$$T(z) = \frac{1}{\sqrt{\pi q(z)}}\int_{-\infty}^{\infty} \ln[1+q(z)]e^{-\tau^2}d\tau \tag{1}$$

$$q(z) = \alpha_2^{\mathrm{eff}} I(z)\frac{1-e^{-\alpha_0 L}}{\alpha_0} \tag{2}$$

$$\alpha(I) = \alpha + \beta I \tag{3}$$

where T is the normalized energy transmittance, z is the distance of the sample from the focus, α_0 and α_2^{eff} are the linear and effective

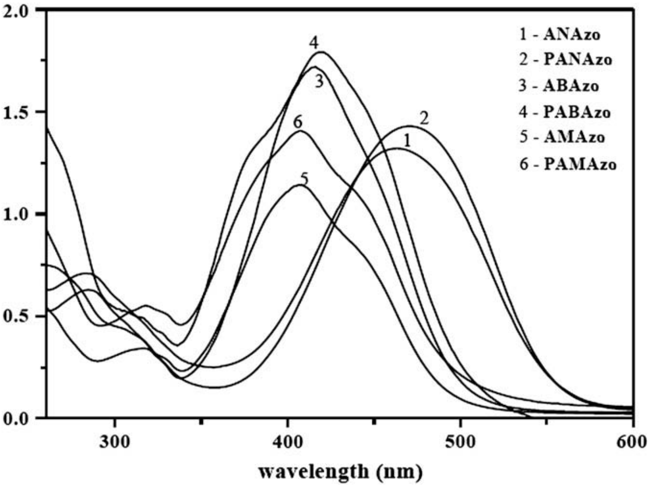


Fig. 4. UV–vis spectra of azobenzene-containing acrylates and their homopolymers (condition: 1×10^{-5} mol/L, $CHCl_3$ as solvent).

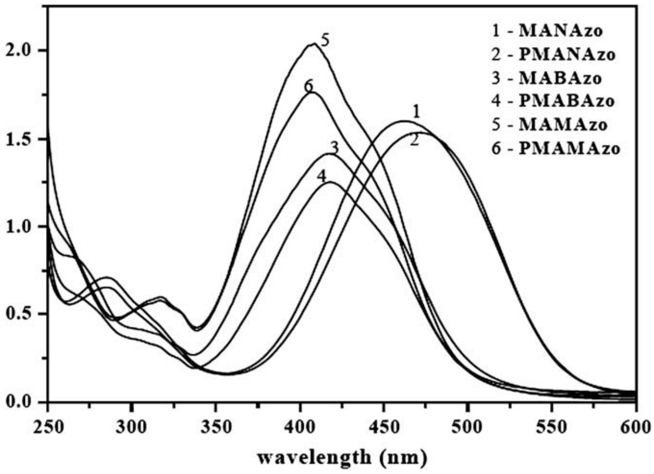


Fig. 5. UV–vis spectra of azobenzene-containing methacrylates and their homopolymers (condition: 1×10^{-5} mol/L, $CHCl_3$ as solvent).

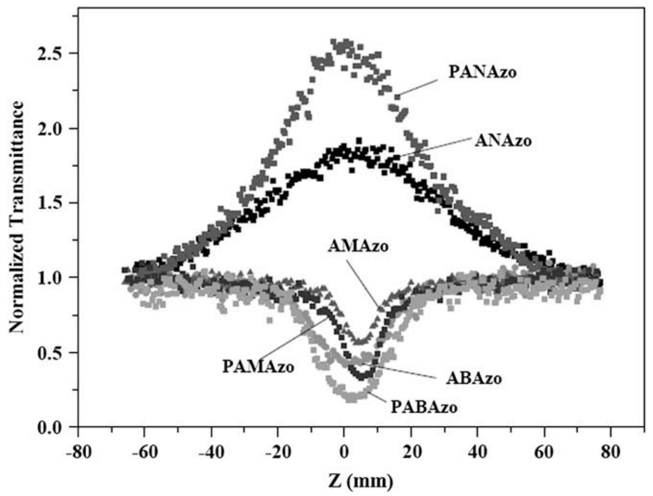


Fig. 6. Normalized open-aperture Z-scan curves of the azobenzene-containing acrylates and their polymers.

absorption indices, L is the thickness of the sample, τ is the time, and I is the radiation intensity.

The nonlinear refractive component of the sample was obtained by dividing the normalized Z-scan measured under a closed-aperture configuration by the normalized Z-scan data obtained under the open-aperture configuration. Thus, the refractive curves were obtained. The third-order nonlinear refractive index, n_2, could be got by fitting the refractive curves using Eq. (4):

$$n_2 = \frac{\alpha_0 \lambda \Delta T_{\mathrm{p-v}}}{0.812\pi I_0 (1-s)^{0.25}\left[1-\mathrm{e}^{-\alpha_0 L}\right]} \tag{4}$$

where $\Delta T_{\mathrm{p-v}}$ is the measured peak–valley transmittance difference from a normalized Z-scan curve, I_0 is the on-axis peak intensity at the focus ($z = 0$), s is the transmittance of the aperture ahead the detector in absence of a sample. Here, s is 0.13.

The real and imaginary parts of the third-order nonlinear susceptibility $\chi^{(3)}$ are related to the nonlinear refraction and absorption coefficients as shown in Eqs. (5) and (6).

$$\mathrm{Re}\chi^{(3)} = 2n_0^2\varepsilon_0 c n_2 \tag{5}$$

$$\mathrm{Im}\chi^{(3)} = n_0^2\varepsilon_0 c\beta/k \tag{6}$$

where k is the wave number, ε_0 and c are the permittivity and speed of the light in the vacuum, n_0 is the linear refraction index. The third-order nonlinear susceptibility $\chi^{(3)}$ could be calculated through Eq. (7).

$$\chi^{(3)} = \sqrt{\left(\mathrm{Re}\chi^{(3)}\right)^2+\left(\mathrm{Im}\chi^{(3)}\right)^2} \tag{7}$$

Thus, the larger the β and n_2 values of a sample, the larger $\chi^{(3)}$ is.

In our Z-scan experiment, the NLO properties of the samples were manifested by moving the samples along the axis of the incident laser irradiance beam (Z direction) with respect to the focal point and incident laser irradiance was kept constant. In order to avoid the resonant absorption from the laser irradiation, the concentration of the nitro-substituted samples in DMF is lower than the others. However, they possess much lower linear transmission than bromo- and methoxy-substituted samples.

The results of Z-scan with and without an aperture showed that all the azobenzene monomers and polymers have both nonlinear absorption and nonlinear refraction. Thus, the third-order susceptibility ($\chi^{(3)}$) of each sample result from dual is attributed to nonlinear absorption (β) and nonlinear refraction (n_2).

The nonlinear absorption component of the azobenzene monomers and polymers is evaluated under an open-aperture configuration. The open-aperture experimental Z-scan curves of azobenzene-containing acrylates and their polymers with different substituents are shown in Fig. 6. The normalized energy transmittance of **ANAzo** and **PANAzo** displays an increase at the focus indicating saturated absorption (SA) ($\beta < 0$), while other monomers and polymers display reverse saturated absorption (RSA) ($\beta > 0$). It is caused by the different electronic effects of the substituent on the azobenzene chromophore. As electron withdrawing nitro-group substituted in the azobenzene system, the π-electron conjugation is enhanced obviously and the absorption cross-section of its excited state is smaller than that of ground state under the irradiation of 532 nm laser, which caused saturated absorption (SA).

The pure NLO refractive effects were assessed by dividing the normalized Z-scan data obtained under the closed-aperture configuration by those under the open-aperture configuration. The peak–valley pattern of the normalized transmittance curves indicated that each of the azobenzene-containing monomers and polymers had a negative sign for the nonlinear refraction and exhibited a strong self-defocusing behavior. The peak–valley position of the normalized transmittance curves was not symmetrical with respect to the focus ($Z = 0$).

The third-order NLO coefficients values (β, n_2 and $\chi^{(3)}$) of all the samples were calculated by above equations and listed in Table 1. The nitro-substituted monomers and polymers have larger absorption for the contribution from heating effect caused by the resonant absorption at 532 nm and their β values are negative. In addition, the electron withdrawing nitro-substituent which forms

Table 1
Third-order NLO coefficients of azobenzene monomers and their homopolymers.

Sample	T_0	β (MKS) 10^{-11}	n_2 (esu) 10^{-11}	$\chi^{(3)}{}_{\mathrm{R}}$ (esu) 10^{-12}	$\chi^{(3)}{}_{\mathrm{I}}$ (esu) 10^{-12}	$\chi^{(3)}$ (esu) 10^{-12}
ANAzo	0.275	−41.7	−9.48	−21.6	−13.7	25.6
ABAzo	0.36	15.4	−4.76	−10.8	5.08	12.0
AMAzo	0.53	12.7	−2.87	−6.53	4.17	7.74
MANAzo	0.265	−21.8	−10.5	−23.9	−7.19	24.9
MABAzo	0.423	14.1	−4.96	−11.3	4.65	12.2
MAMAzo	0.625	12.6	−2.79	−6.35	4.14	7.58
PANAzo	0.435	−91	−20.4	−46.3	−30	55.2
PABAzo	0.455	33.3	−8.1	−18.4	11	21.5
PAMAzo	0.615	13	−3.26	−7.42	4.26	8.56
PMANAzo	0.255	−99.6	−20	−45.6	−32.8	56.1
PMABAzo	0.445	22.2	−9.19	−20.9	7.29	22.2
PMAMAzo	0.668	13.1	−3.43	−7.8	4.3	8.91

Conditions: All nitro-substituted samples are dissolved in DMF at 1×10^{-4} mol/L and 16 μJ, 2 Hz, 4 ns laser are used, others are dissolved in DMF at 1×10^{-3} mol/L and 40 μJ, 2 Hz, 4 ns laser are used.

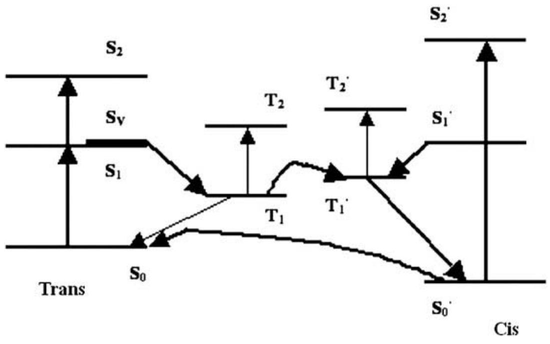


Fig. 7. Energy level scheme of azo molecule.

a push–pull (D–π–A) electron system with dimethylamino-group and enlarges π-conjugation system in the azobenzene molecule is favorable to increase the NLO susceptibility values. Thus, the nitro-substituted monomers and polymers have larger $\chi^{(3)}$ values than the others in spite of lower concentration. After polymerization, the azobenzene-containing polymers display higher NLO susceptibility values than their corresponding monomers. It maybe caused by the nonlinear superimposed NLO effect of the repeated azobenzene chromophores in the same molecular chain of polymer and the more ordered azobenzene chromophores enhance the delocalization effect of π-electron conjugation in the side chains of azobenzene-containing polymers.

It also can be verified by the one-dimensional molecule model founded by Sauteret et al. [29].

$$\chi^{(3)} = \frac{2^5}{45}\pi^2\frac{e^{10}}{\sigma}\left(\frac{\alpha_0}{d}\right)^3\left(\frac{1}{E_g^6}\right)$$

In which α_0 is Bohr radius and d is the average length of C–C bond, σ is the transversal surface area of the molecular chain and E_g is the energy gap of the polymer. The enhancement of π-electron conjugation can bring about a smaller energy gap and then exhibit a larger $\chi^{(3)}$ value.

The third-order NLO effect of all the azobenzene-containing samples is caused by the trans–cis isomerization [30–32] under the laser irradiation. The five-level model [32] of azobenzene molecule shown in Fig. 7 can accurately describe the photophysical dynamics of the azobenzene-containing samples we measured. In a general way, the azobenzene molecule exists as trans-configuration with lower energy. When the azobenzene molecule is excited by laser, the induced absorption and relaxation among the ground state (level S_0), the excited singlet state (level S_1) and the lowest triplet state (level T_1) can be occurred. The excited state S_1 or T_1 can be further excited to a high singlet state (level S_2) or a high triplet state (level T_2), respectively. Because the triplet states (T_1 and T_1') of trans-azobenzene and cis-azobenzene are approached and the relaxation of $T_1 \rightarrow S_0$ and $T_1 \rightarrow T_1' \rightarrow S_0$ can be achieved, the trans-azobenzene can be changed easily to the cis-azobenzene. When the irradiation of laser pulse is terminated, the cis-azobenzene comes back to trans-azobenzene by relaxing energy to the outside. During this process, we record the relationship between light intensity transmitted through the aperture and Z-position of sample by Z-scan measurement, so the nonlinear absorption and nonlinear refraction are observed. The electronic effect of the different substituents brings about different energy gaps among the energy levels in cis- and trans-azobenzene molecule, so different NLO coefficients of the azobenzene-containing monomers and polymers are displayed.

4. Conclusion

A new series of acrylates and methacrylates containing azobenzene chromophore have been synthesized and polymerized into side-chain NLO polymers by ATRP technique. The kinetics of the monomers is investigated and found that the activity of azobenzene-containing methacrylates is much higher than the azobenzene-containing acrylates. The well-controlled polymers with narrow polydispersities were obtained from the monomers with different substituents on the azobenzene side chain. All of the azo monomers and their polymers have both nonlinear absorption and nonlinear refraction. The third-order susceptibility ($\chi^{(3)}$) is influenced by the electronic effect of the different substituents on the azobenzene group. The electron withdrawing nitro-substituent which forms a push–pull (D–π–A) electron system with dimethylamino-group and enlarges π-conjugation system in the azobenzene molecule is favorable to increase the NLO susceptibility values. The results also can be verified by the one-dimensional molecule model and five-level model of azobenzene molecule.

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