Dyes and Pigments 80 (2009) 73–79

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis of third-order nonlinear optical polyacrylates containing an azobenzene side chain via atom transfer radical polymerization

Najun Li, Jianmei Lu*, Xuewei Xia, Qingfeng Xu, Lihua Wang

Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, Su Zhou 215123, Jiangsu, PR China

ARTICLE INFO

Article history:
Received 11 April 2008
Received in revised form 23 May 2008
Accepted 23 May 2008
Available online 3 June 2008

Keywords:
Azobenzene
ATRP
Side chain
Homopolymer
Copolymer
NLO

ABSTRACT

A series of polyacrylates containing different substituted-azobenzene chromophores were synthesized and polymerized via atom transfer radical polymerization. Nonlinear optical homopolymers containing an azobenzene side chain, of controllable molecular mass and low polydispersity (1.1–1.4) were obtained. In addition, side-chain copolymers were prepared in which the composition of the copolymers was controlled by using different feed ratios of the azobenzene monomer and methyl methacrylate. The third-order nonlinear optical properties of azobenzene monomers and their polymers were measured using the degenerated four-wave mixing technique. Each of the polymers displayed a high $\chi^{(3)}$ of about 10^{-11} esu and rapid response time in femto-second magnitude. The effect of substituents on the azobenzene group and the composition of the polymer chain on the third-order nonlinear optical properties of the polymers were investigated.

1. Introduction

In recent years, azobenzene-containing polymers have been widely studied for their potential applications in many fields including optical data storage [1,2], liquid crystal displays [3–5], holographic surface relief gratings (SRG) [6–8], nonlinear optical (NLO) materials [9,10], and so forth. Various azobenzene bound within the host–guest doping mixtures and on the side or main chain of the homopolymers or copolymers of (methyl) methacrylate, styrene, polyamide and polyester have been investigated. Among the azo-containing polymers reported in the literature, polymers based on [4′-[(2-methacryloyloxy) ethyl] ethylamino]-4-nitroazobenzene (DR1M) are the most representative. Whilst many homopolymers [11–15] and copolymers [16–25] obtained by free radical polymerization of DR1M have been studied for various photonic applications, there have been only a few reports of azobenzene-containing polymers synthesized by atom transfer radical polymerization (ATRP) [26–28].

ATRP is one of the most attractive methods for the synthesis of novel and controlled architectures under straightforward operating conditions, and furnishes polymers with well-defined molecular mass and narrow polydispersity [29–32]. In our previous work, we have synthesized NLO polymers containing an azobenzene side chain using ATRP [33] which had well-defined molecular mass and narrow polydispersity, but the activity of ATRP for these azo monomers was not high enough because of the steric effect of the azo side chain in the acrylate backbone.

This paper concerns the synthesis of a series of azobenzene-containing acrylates and methacrylates with relatively high activity, including DR1M (named as **MANAzo** in this paper) whose structures are shown in Scheme 1. The ATRP technique has been employed to synthesize the azobenzene-containing side-chain homopolymers with controllable molecular weight. We further attempted to carry out the copolymerization of the azo monomers with methyl methacrylate (MMA) to improve the activity of ATRP. The composition of the copolymers was controlled using different feed ratios of the azobenzene monomer and MMA. The influence of the push–pull electronic effect and the azobenzene content in copolymer chain to the macroscopical NLO properties of homopolymers and copolymers were investigated.

2. Experiment

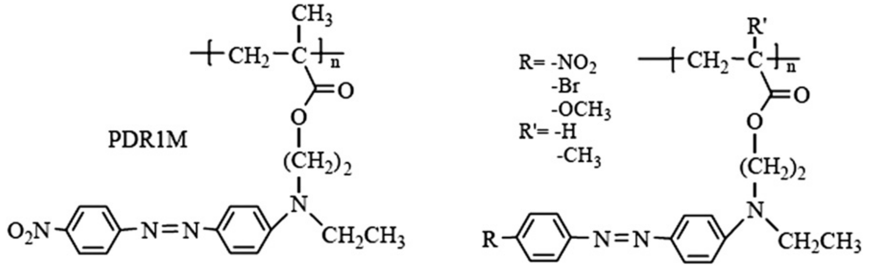
2.1. Materials

4-Nitroaniline, 4-bromoaniline, 4-methoxyaniline and triethylamine were purchased from Shanghai chemical reagent Co. Ltd. as analytical reagents and used without further purification (declared purity grade, ≥99%). Acryloyl chloride and methacryloyl chloride

---

* Corresponding author. Tel./fax: +86 512 65882875.
E-mail address: lujm@suda.edu.cn (J. Lu).

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.05.004



Scheme 1. The structure of PDRIM and azobenzene side-chain homopolymers.

were 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 a 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%) and *N*-ethyl-*N*-(2-hydroxyethyl) aniline (Tokyo Kasei Kogyo Co. Ltd.) were used without further purification. MMA (A.R., Shanghai Chemical Reagent Co. Ltd.) was vacuum-distilled after being dried by anhydrous magnesium sulfate. Tetrahydrofuran (THF), cyclohexanone and *N*,*N*-dimethyl formamide (DMF) were purified by reduced pressure distillation. Other reagents were used as received.

2.2. Synthesis of monomer

Six monomers with side-chain azobenzene groups, 4′-[*N*-(2-(meth)acryloyloxy ethyl)-*N*-ethyl] amino-4-nitro azobenzene (**ANAzo** and **MANAzo**), 4′-[*N*-(2-(meth)acryloyloxy ethyl)-*N*-ethyl] amino-4-bromo azobenzene (**ABAzo** and **MABAzo**) and 4′-[*N*-(2-(meth)acryloyloxy ethyl)-*N*-ethyl] amino-4-methoxy azobenzene (**AMAzo** and **MAMAzo**) were synthesized following a procedure modified from that described in the literature [34,35], as shown in Scheme 2.

ANAzo: ^{1}H NMR (CDCl$_3$): δ (ppm) = 8.34 (2H, benzene ring protons adjacent to –NO$_2$), 7.94–7.90 (4H, benzene ring protons adjacent to –N═N–), 6.83 (2H, benzene ring protons), 6.45 (1H, vinyl proton), 6.14 (1H, –CH═), 5.89 (1H, vinyl proton), 4.39 (2H, –OCH$_2$), 3.89 (2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.58 (2H, –CH$_2$ in ethyl), 1.27 (2H, –CH$_3$ in ethyl); Elem. 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.

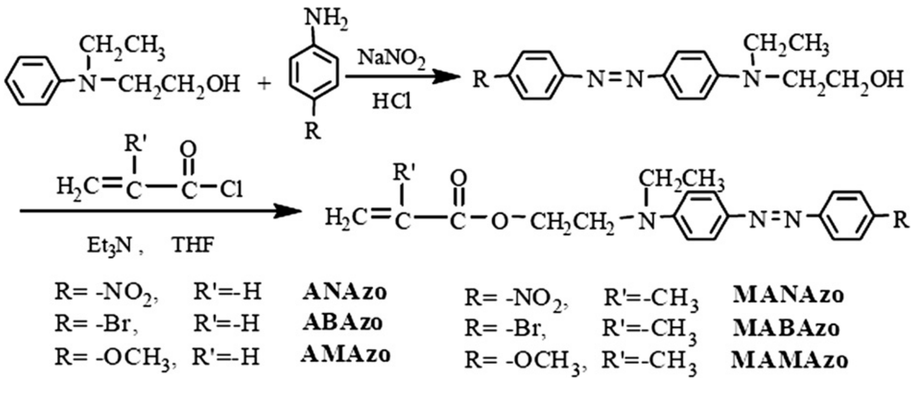
ABAzo: ^{1}H NMR (CDCl$_3$): δ (ppm) = 7.90–7.75 (4H, benzene ring protons adjacent to –N═N–), 7.65 (2H, benzene ring protons adjacent to –Br), 6.80 (2H, benzene ring protons), 6.44 (1H, vinyl proton), 6.13 (1H, –CH═), 5.88 (1H, vinyl proton), 4.38 (2H, –OCH$_2$), 3.71 (2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.54 (2H, –CH$_2$ in ethyl), 1.25 (3H, –CH$_3$ in ethyl); Elem. 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.

AMAzo: ^{1}H NMR (CDCl$_3$): δ (ppm) = 7.85–7.26 (4H, benzene ring protons adjacent to –N═N–), 6.97 (2H, benzene ring protons adjacent to –OCH$_3$), 6.81 (2H, benzene ring protons), 6.44 (1H, vinyl proton), 6.11 (1H, –CH═), 5.84 (1H, vinyl proton), 4.37 (2H, –OCH$_2$), 3.87 (3H, methoxyl protons), 3.68 (2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.48 (2H, –CH$_2$ in ethyl), 1.23 (3H, –CH$_3$ in ethyl); Elem. 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.

MANAzo: ^{1}H NMR (CDCl$_3$): δ (ppm) = 8.31 (2H, benzene ring protons adjacent to –NO$_2$), 7.94–7.90 (4H, benzene ring protons adjacent to –N═N–), 6.81 (2H, benzene ring protons), 6.11 (1H, vinyl proton), 5.59 (1H, vinyl proton), 4.39 (2H, –OCH$_2$), 3.72 (2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.53 (2H, –CH$_2$ in ethyl), 1.94 (3H, methyl adjacent to vinyl), 1.27 (3H, –CH$_3$ in ethyl); Elem. Anal. Calcd. for $C_{20}H_{22}N_4O_4$: C, 62.816; H, 5.7983; N, 14.651; Found: C, 62.636; H, 5.9426; N, 14.516.

MABAzo: ^{1}H NMR (CDCl$_3$): δ (ppm) = 7.88–7.73 (4H, benzene ring protons adjacent to –N═N–), 7.60 (2H, benzene ring protons adjacent to –Br), 6.82 (2H, benzene ring protons), 6.11 (1H, vinyl proton), 5.58 (1H, vinyl proton), 4.38 (2H, –OCH$_2$), 3.71 (2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.50 (2H, –CH$_2$ in ethyl), 1.94 (3H, methyl adjacent to vinyl), 1.25 (3H, –CH$_3$ in ethyl); Elem. Anal. Calcd. for $C_{10}H_{22}N_3BrO_2$: C, 57.701; H, 5.3261; N, 10.093; Found: C, 57.588; H, 5.4812; N, 9.8862.

MAMAzo: ^{1}H NMR (CDCl$_3$): δ (ppm) = 7.83–7.81 (4H, benzene ring protons adjacent to –N═N–), 6.98 (2H, benzene ring protons adjacent to –OCH$_3$), 6.80 (2H, benzene ring protons), 6.09 (1H, vinyl proton), 5.57 (1H, vinyl proton), 4.34 (2H, –OCH$_2$), 3.66 (2H, H$_2$C–N in N–CH$_2$CH$_2$O), 3.70 (3H, methoxyl protons), 3.48 (2H, –CH$_2$ in ethyl), 1.93 (3H, methyl adjacent to vinyl), 1.23 (3H, –CH$_3$ in ethyl); Elem. 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.



Scheme 2. The synthetic route of azobenzene monomers.

2.3. Homopolymerization via ATRP

A typical ATRP procedure was carried out as follows. A polymerization pipe was equipped with a magnetic stirrer and a gas inlet/outlet. Ethyl 2-bromoisobutyrate (EBiB, 1.7 μL, 0.01 mmol), 1.5 mg (0.01 mmol) of CuBr and 2.0 μL (0.01 mmol) of PMDETA were added with 184 mg (0.5 mmol) of **ANAzo** and 2.0 mL of cyclohexanone to the pipe 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 for a certain reaction time. Then the mixture was poured into about 200 mL of methanol where 1:1 chlorhydric acid was added (100:1 v/v) to elute the copper in the mixture. The suspension was filtered for removal of residual monomer and most of the catalyst. The obtained polymers were purified by reprecipitation from THF into methanol twice and dried under vacuum for 24 h at room temperature.

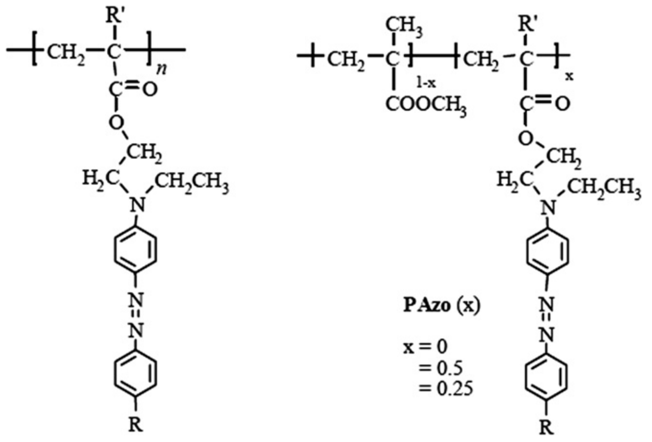
A similar procedure was followed when other conditions were applied in the homopolymerization. The ATRP of all the azo monomers was investigated under the same condition.

2.4. Copolymerization with MMA via ATRP

The procedure of copolymerization was similar to the synthesis of homopolymers, but the sole azo monomer was changed into azo monomer and MMA together in different feed ratios. The ratio of 0.25 mmol azo monomer/0.25 mmol MMA ($x = 0.5$) and 0.25 mmol azo monomer/0.75 mmol MMA ($x = 0.25$) was used in this ATRP system. The composition of the copolymer was well controlled by feed ratio of azo monomer and MMA, which is confirmed by elemental analysis of N concentration in copolymers and the ^{1}H NMR spectra of the obtained copolymers. The structure of the obtained homopolymers and copolymers containing azobenzene chromophores is shown in Scheme 3.

2.5. Instruments for characterization

^{1}H NMR spectra of monomers and polymers in $CDCl_3$ were obtained on an Inova 400 MHz FT-NMR spectrometer at ambient temperature. UV–vis absorption spectra were carried out at 25 °C in the 700–190 nm spectral region with a Perkin–Elmer Lambda spectrophotometer using cell path lengths of 0.5 cm. The elemental analysis was performed by Italian 1106FT analyzer. Monomer conversion was determined by gravimetry. 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. The glass transition temperature values were determined by differential scanning calorimetry (DSC) on a 2010 DSC TA Instrument at a heating rate of 10 K/min under nitrogen atmosphere.



Scheme 3. The structure of azobenzene-containing homopolymers and copolymers.

2.6. Measurements of the third-order optical nonlinearities

The phase conjugated forward three-dimensional degenerate four-wave mixing (3D DFWM) technique was used with the femtosecond pulse Solid-state Laser (wavelength is 800 nm, pulse-width is 45.7 fs, repetition rate is 10 Hz and pulse power is about 720 mW) to measure the third-order nonlinear optical (NLO) susceptibility. Solutions of 0.1 mM azo polymers in DMF were used in NLO measurements. The third-order NLO coefficients $\chi^{(3)}$ and the response time $Y_{1/2}$ can be obtained by comparing the measured signals of the samples with that of carbon disulfide (CS_2) as reference by the procedure presented in our previous work [36].

3. Results and discussion

3.1. Preparation of azobenzene-containing homopolymers by ATRP

ATRP was successfully used to prepare the homopolymers from the azo monomers with controlled number-average molecular weight and a low polydispersity. The polymer was prepared by using EBiB, CuBr, and PMDETA as initiator, catalyst and ligand, respectively. Kinetics of all the azo monomers was investigated under the same polymerization condition, as shown in Figs. 1 and 2. The results showed that the molecular weights and the conversion of polymers increased with the increase of reaction time and PDI (M_w/M_n) of obtained polymers remained at relatively low values (1.15–1.4). The $\ln([M]_0/[M])$ of each monomer increased with reaction time linearly, although the activity of each azobenzene-containing acrylate is much lower than the corresponding methacrylate. The azo monomers synthesized with methacryloyl chloride have higher activity in this ATRP system for the electronic effect of the methyl group on the C adjacent to vinyl. So the azobenzne-containing side-chain polymers with higher molecular weight can be obtained by ATRP of azobenzene-containing methacrylates.

The structure of each obtained polymer was confirmed by ^{1}H NMR spectra. As shown in Fig. 3, the chemical shifts at $\delta = 5.6$ ppm and 6.10 ppm assigned to the vinyl protons of monomer

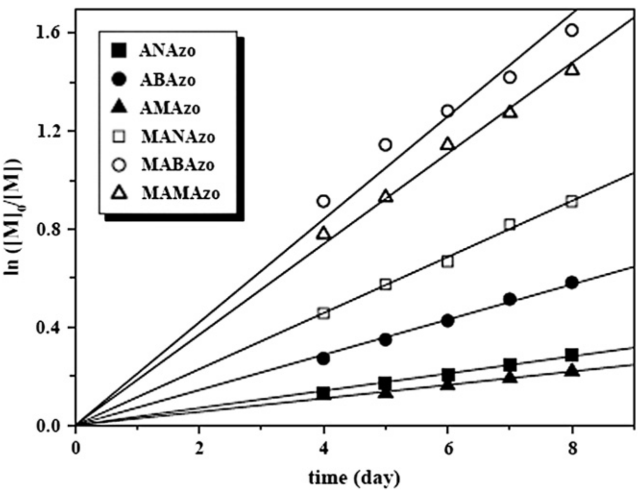


Fig. 1. First-order kinetic plots for ATRP of azo-containing methacrylates and methyl methacrylates (reaction conditions: [monomer]/[EBiB]/[CuBr]/[PMDETA] = 50:1:1:1, temperature = 80 °C).

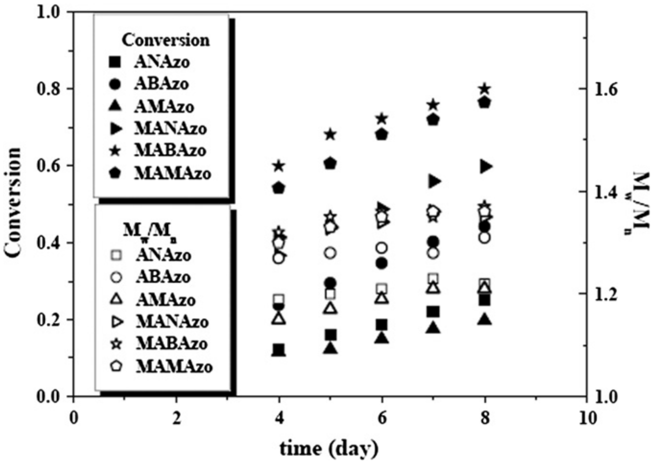


Fig. 2. Dependence of conversion and M_w/M_n on reaction time for ATRP of azo-containing methacrylates and methyl methacrylates (reaction conditions: [monomer]/[EBiB]/[CuBr]/[PMDETA] = 50:1:1:1, temperature = 80 °C).

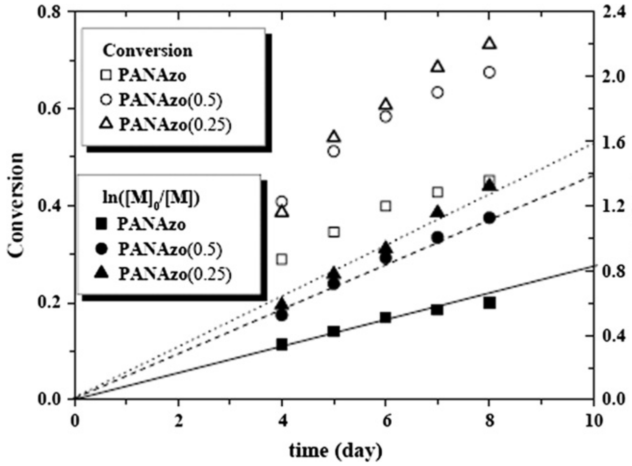


Fig. 4. Dependence of conversion and $\ln([M]_0/[M])$ for ATRP of azo monomer and MMA (reaction conditions: **PANAzo**: [**ANAzo**]/[EBiB]/[CuBr]/[PMDETA] = 50:1:1:1, **PANAzo**(0.5): [MMA]/[**ANAzo**]/[EBiB]/[CuBr]/[PMDETA] = 25:25:1:1:1, **PANAzo**(0.25): [MMA]/[**ANAzo**]/[EBiB]/[CuBr]/[PMDETA] = 75:25:1:1:1, temperature = 80 °C).

disappeared after the polymerization. At the same time, an additional chemical shift of $–CH_2–$ was observed at $\delta = 1.0$ ppm in the spectra of the homopolymer. In addition, other chemical shifts corresponding to those caused by its monomer were much wider, which also certified the successful polymerization.

3.2. Preparation of azobenzene-containing copolymers by ATRP

Considering the low activity of the acrylates containing azobenzene side chain, MMA was employed as the second high-active monomer to copolymerize with each azo monomer, respectively. The copolymerization was carried out at 80 °C with the feed molar ratio of azo monomer: MMA = 1:1 and 1:3 under the same reaction condition of the homopolymerization. As shown in Fig. 4, the "living"/controlled characteristics of ATRP like the result of homopolymerization were observed in the copolymerization system while it was much faster than that of the homopolymerization of each azo monomer.

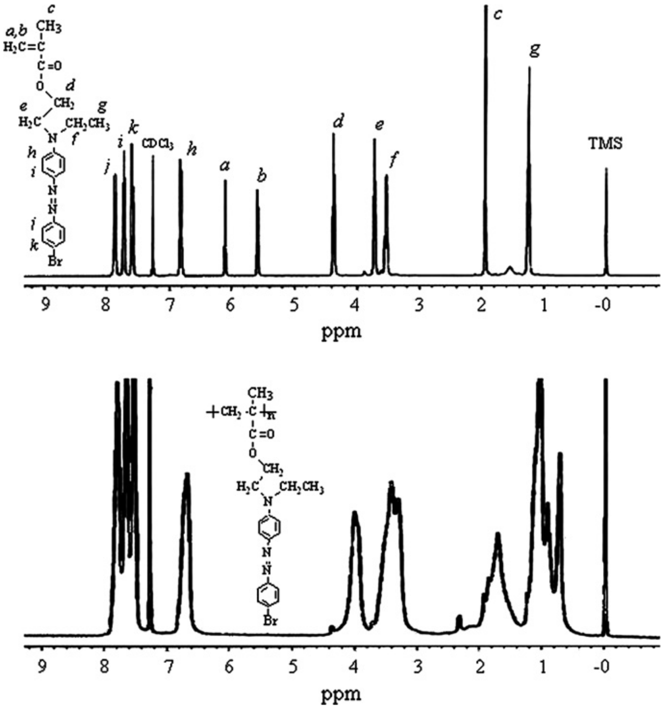


Fig. 3. ^{1}H NMR spectra in $CDCl_3$ of **MABAzo** and its homopolymer by ATRP.

The copolymerization of the azobenzene-containing methacrylates with MMA was much faster than that of acrylates containing azobenzene group, which is similar to the behavior of their homopolymerization. From the results listed in Table 1 we can see that the obtained copolymers have higher molecular weight than that of homopolymers under the same condition of ATRP. The higher the molar feed ratio of MMA is, the bigger the molecular weight of the copolymer is.

The structure of the polymers was also confirmed by ^{1}H NMR spectra and elemental analysis of N concentration in copolymers. As the ^{1}H NMR spectra of **PABAzo**(0.5) and **PABAzo**(0.25) shown as example in Fig. 5, the composition of the copolymers was confirmed by the integral area ratio of the H proton from azo monomer and MMA in the ^{1}H NMR spectra of copolymer. The composition of the copolymer was well controlled as the feed ratio of the azo monomer and MMA. When the feed ratio of **ABAzo**/MMA is 0.5/0.5, the composition ratio of azobenzene units to methyl methacrylate units in the copolymer is 0.5/0.5 approximately. When the feed ratio of **ABAzo**/MMA is changed into 0.25/0.75, the composition ratio of azobenzene units to methyl methacrylate units in the copolymer is also turned to 0.25/0.75 accordingly. It is also confirmed by the elemental analysis for N concentration of copolymer. Since there is no N element in methyl methacrylate unit, we can calculate the concentration of azobenzene unit in the copolymer in terms of N concentration of copolymer. The results showed that the composition of copolymer is corresponded with the feed ratio of azobenzene monomer and MMA.

Table 1
The copolymerization results of MMA and the azobenzene-containing methyl acrylates

Monomer	[Monomer]:[MMA] feed molar ratio[a]	[Monomer]:[MMA] measured molar ratio	Conversion (%)	M_n	M_w/M_n
MANAzo	25:25	20:30	41.7	3800	1.24
MABAzo	25:25	19: 31	81.8	5800	1.27
MAMAzo	25:25	23:27	58.7	7250	1.35
MANAzo	25:75	21:79	43.2	5900	1.47
MABAzo	25:75	20:80	76.2	7700	1.45
MAMAzo	25:75	29:71	65.9	11000	1.46

[a] ATRP condition: [monomer]/[MMA]/[EBiB]/[CuBr]/[PMDETA] = 25:25:1:1:1 or [monomer]/[MMA]/[EBiB]/[CuBr]/[PMDETA] = 25:75:1:1:1 by mol., 80 °C, 4 days.

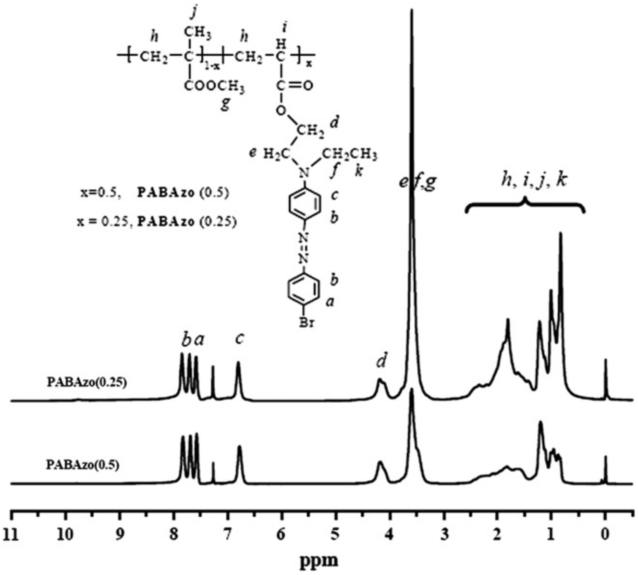


Fig. 5. ^{1}H NMR spectra in CDCl$_3$ of the copolymers of **ABAzo** and MMA by ATRP.

3.3. UV–vis spectra of azo side-chain polymers

Figs. 6 and 7 show the UV–vis spectra of the homopolymers and copolymers polymerized by azobenzene-containing acrylates, respectively. Each homopolymer of the azobenzene-containing acrylates showed the maximum absorption with a little red shift (Fig. 6). It may be caused by ordered and localized arrangement of the azo side chain on the polymer chain, which reduced the sterically hindered effect among the azobenzene chromophores and enhanced the conjugation of the polymer chain.

Fig. 7 shows the UV–vis spectra of the azo copolymers with different molar feed ratio of azo monomer/MMA. As the copolymers with the same substituent prepared by different feed ratio, their maximum absorption is red-shifted a little and the absorption intensity is reduced corresponding to the decrease of the azo concentration that is coincident with the feed ratio. As the monomer **ANAzo** for example, **PANAzo** > **PANAzo**(0.5) > **PANAzo**(0.25). After the copolymerization of methyl methacrylate with azo monomer, the sterically hindered effect in the chain of resulted copolymer is cut down in comparison with its homopolymer, which results in a red shift in the maximum absorption of the UV–vis spectra. The results of each azo homopolymer and copolymer are listed in Table 2.

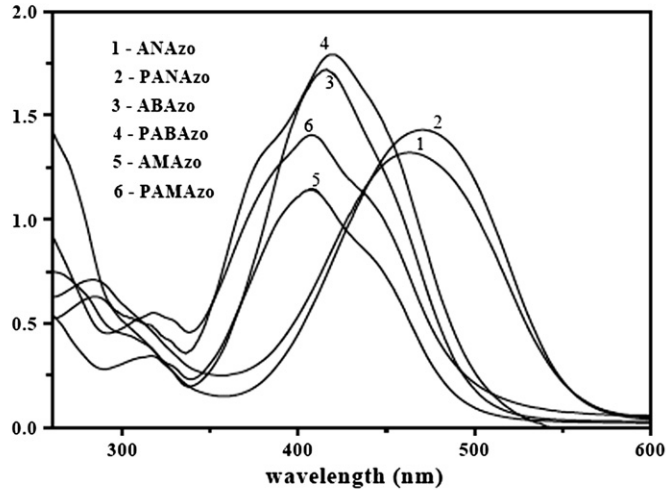


Fig. 6. UV–vis spectra of azobenzene-containing acrylates and their homopolymers (condition: 1×10^{-5} mol/L, CHCl$_3$ as solvent).

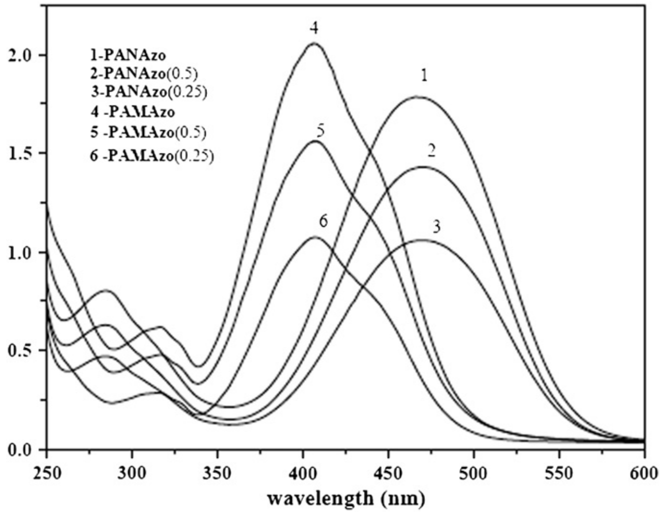


Fig. 7. UV–vis spectra of azobenzene-containing acrylates and their copolymers (condition: 1×10^{-5} mol/L, CHCl$_3$ as solvent).

3.4. Solubility of azo side-chain polymers

The solubility of the azo intermediate products is not good due to the azobenzene group. But the azo-containing acrylates and methacrylates show much better solubility after the introduction of acryloyl group. Homopolymers with azo side chain exhibit good solubility and the higher the molecular weight, the better the solubility. In addition, the solubility of the azo-containing copolymers is further improved after the introduction of methyl methacrylate unit in the polymer chain. All of the azobenzene-containing side-chain polymers exhibit good solubility in a wide range of organic solvents, including CHCl$_3$, THF and DMF, which shows the potential to film-forming and further application in optical devices.

3.5. The third-order nonlinear optical (NLO) properties

All the samples have no linear absorption under the irradiation of the laser with 800 nm wavelength and no heating effect existed during the measurements for NLO properties. Firstly, the DFWM measurements performed on DMF solutions of six azo monomers and their side-chain homopolymers with different number-average molecular weight are reported and the DFWM response curves are displayed in Gaussian distribution, as the examples shown in Fig. 8.

Table 2
UV–vis absorption data of azo monomers and their polymers

(Poly)acrylate	λ_{max}[a]	(Poly)methacrylate	λ_{max}[a]
ANAzo	462	**MANAzo**	460
ABAzo	415	**MABAzo**	417
AMAzo	403	**MAMAzo**	405
PANAzo	465	**PMANAzo**	462
PABAzo	418	**PMABAzo**	420
PAMAzo	405	**PMAMAzo**	407
PANAzo(0.5)	470	**PMANAzo**(0.5)	472
PABAzo(0.5)	418	**PMABAzo**(0.5)	422
PAMAzo(0.5)	408	**PMAMAzo**(0.5)	409
PANAzo(0.25)	472	**PMANAzo**(0.25)	475
PABAzo(0.25)	420	**PMABAzo**(0.25)	425
PAMAzo(0.25)	409	**PMAMAzo**(0.25)	411

[a] UV–vis spectra were measured under this condition: 1×10^{-5} mol/L, CHCl$_3$ as solvent.

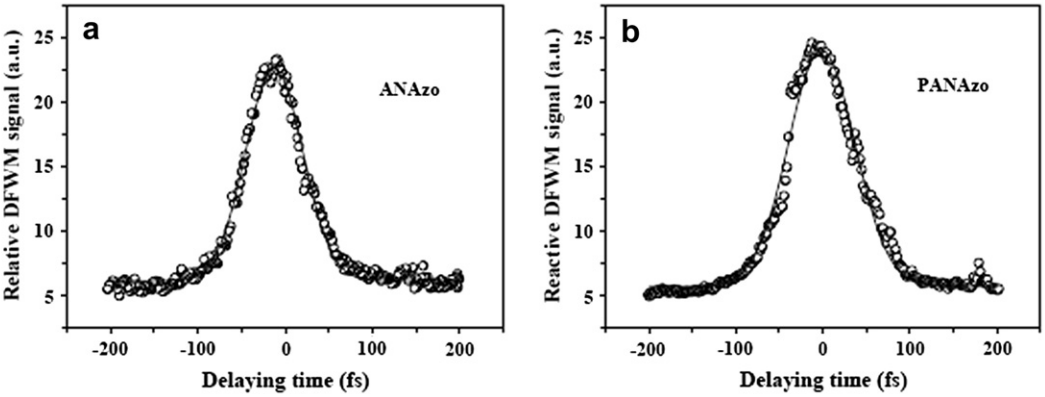


Fig. 8. The third-order NLO response curves of **ANAzo** and **PANAzo** in DMF solution by DFWM.

The calculated values of their third-order nonlinear coefficient $\chi^{(3)}$ and response time $Y_{1/2}$ are listed in Table 3.

As the monomers with different substituent, the electron-withdrawing nitro group on the end of azobenzene can form a push–pull electronic structure with the dibasic amine group on the other end of azobenzene in the molecules of monomers **ANAzo** and **MANAzo**. So the fluidity of the delocalized π electrons within the conjugated azobenzene system is enhanced and the induced polarization of the electric moment in the azo molecules is accelerated, which intensify the macroscopical third-order NLO effect obviously. Thus, the $\chi^{(3)}$ value of the monomers and their homopolymers containing nitro group on the end is much higher than methoxyl- and bromo-substituted monomers and polymers, which is in the 10^{-11} order of magnitude [37–39]. It also can be verified by the one-dimensional molecule model founded by Sauteret et al. [40]:

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

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 significant improvement of the polarization in the azobenzene-containing side chain is caused by the formation of D–π–A structure, which brings about a smaller energy gap and then an excellent NLO property with higher $\chi^{(3)}$ value is exhibited in the azo polymers with strong electron-withdrawing nitro group.

After polymerization, the macroscopical third-order NLO coefficient $\chi^{(3)}$ value of azo polymer is enhanced by the nonlinear superimposed NLO effect of the repeated azobenzene chromophores in the same molecular chain of polymer and some other effect such as photoelectric conjugation and orientation selectivity in polymer chain. Although the polymerization reactivity of azo monomers is not very high, which is influenced by the steric effect of azobenzene chromophore in the side chain, the increase of the number-average molecular weight of the side-chain polymers influenced their third-order NLO properties a little. The polymer with higher molecular weight has higher third-order NLO coefficient $\chi^{(3)}$ value. It implicates us to synthesize azo polymers with high molecular weight and defined molecular structure via other effective techniques.

The copolymers of MMA and azo monomer were also investigated by DFWM technique. Fig. 9 shows the NLO response curves of **PANAzo**(0.5) and **PANAzo**(0.25). It can be clearly seen that the third-order NLO effect of **PANAzo**(0.5) is stronger than the latter because of a higher concentration of the azo NLO chromophores in the copolymer chain. From the data listed in Table 4 we can see that the $\chi^{(3)}$ value of azo side-chain copolymers decreased with increasing the molar feed ratio of MMA/azo monomer. Since the concentration of azo NLO chromophore in the obtained copolymers decreased with increasing the feed ratio of MMA/azo monomer, the copolymer containing higher ratio of methyl methacrylate unit exhibits lower macroscopical third-order NLO coefficient $\chi^{(3)}$ values. But the copolymers containing higher MMA unit ratio have better solubility and film-forming ability, which is

Table 3
The third-order NLO coefficient and response time of azo monomers and their homopolymers

Sample	M_n	$\chi^{(3)}$ (10^{-12} esu)	$Y_{1/2}$ (10^{-15} s)
ANAzo	–	13.0	86
ABAzo	–	7.48	85
AMAzo	–	7.30	81
MANAzo	–	13.8	99
MABAzo	–	7.82	89
MAMAzo	–	7.58	90
PANAzo	3000	14.9	99
PABAzo	3450	8.23	95
PAMAzo	3650	8.14	93
PMANAzo	4500	15.1	101
PMANAzo	5650	15.7	104
PMABAzo	5850	8.90	92
PMABAzo	7000	9.11	97
PMAMAzo	5000	8.46	90
PMAMAzo	6500	8.55	93

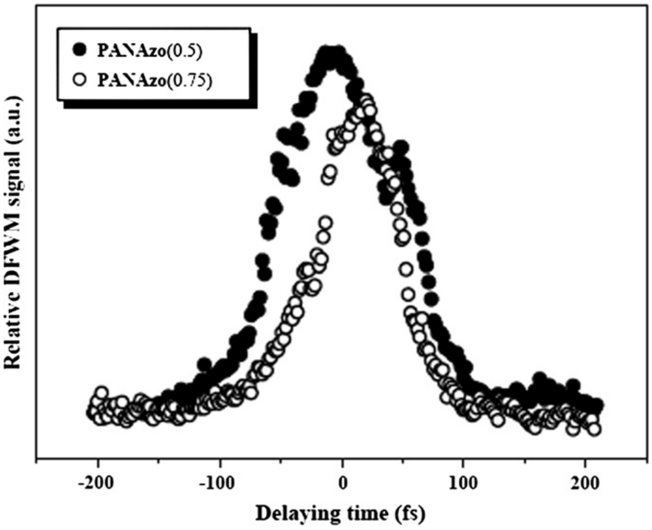


Fig. 9. The third-order NLO response curves of **PANAzo**(x) in DMF solution by DFWM.

Table 4
Characterization data and the third-order NLO coefficient $\chi^{(3)}$ of the copolymers of MMA and the azobenzene-containing (methyl) acrylates

Copolymer (x)	GPC result		$\chi^{(3)}$ (10^{-12} esu)
	M_n	M_w/M_n	
PANAzo(0.5)	4550	1.23	14.1
PANAzo(0.25)	6500	1.32	12.9
PABAzo(0.5)	4750	1.23	8.09
PABAzo(0.25)	5900	1.35	7.88
PAMAzo(0.5)	4350	1.28	8.10
PAMAzo(0.25)	8450	1.39	7.96
PMANAzo(0.5)	4050	1.25	14.3
PMANAzo(0.25)	5900	1.47	12.6
PMABAzo(0.5)	5800	1.27	8.69
PMABAzo(0.25)	7700	1.45	7.88
PMAMAzo(0.5)	7250	1.35	8.30
PMAMAzo(0.25)	11000	1.46	7.96

also important for the application of the azo-containing polymers as polymeric NLO materials. In our experiment, the third-order NLO coefficient of the copolymers **PAzo**(0.5) (MMA/azo monomer = 1:1 by mole) is close to that of the homopolymers with the same substituent. Although the concentration of the azo chromophores in the copolymer chain is reduced, the flexible methyl methacrylate unit introduced in copolymer main chain can weaken the sterically hindered effect and the azobenzene-containing side chain can be a better ordered arrangement in the same polymer chain, which is contributed to the NLO effect. However, when the feed ratio is up to [MMA]/[azo monomer] = 3:1, the concentration of the azo chromophores in the copolymer chain is too low to bring about a high NLO response. So it is important for us to adjust an optimized concentration of the azo chromophores to obtain the good NLO material of azo copolymers. Here **PAzo**(0.5) has both high NLO effect and good processability for device application.

4. Conclusion

A new series of acrylates and methacrylates containing azo NLO chromophore have been synthesized and polymerized into side-chain NLO polymers by ATRP technique. The kinetics of the monomers are investigated and found that the activity of azo-containing methacrylates is much higher than that of azo-containing acrylates. The well-controlled homopolymers and copolymers with narrow polydispersity and well-defined molecular weights were obtained from the monomers with different substituents on the azo side chain and MMA. All the azo monomers and their polymers have high third-order NLO properties. The electronic effect of the substituent on the azobenzene group impacts the third-order NLO property in evidence. When the push–pull electronic structure is formed, the electron in the molecular chain flow well and the energy gap of the conjugate system decreases, which contributes much to enhancing the NLO coefficient. After polymerization, the $\chi^{(3)}$ value of the polymers is higher than their monomers and it is increased a little with the increase of molecular weight. With increasing feed ratio of MMA, the obtained copolymers have much better solubility for introduction of methyl methacrylate unit, but the content of azobenzene chromophore in the copolymer chain is decreased and the macroscopical third-order NLO coefficient $\chi^{(3)}$ of polymers is weakened. There is further work for us to optimize the reaction condition of polymerization and the composition of copolymers containing azo NLO chromophore for application of polymeric NLO materials.

Acknowledgement

This work is financially supported by Chinese Natural Science Foundation No. 20476066, the Natural Science Foundation of China No. 20571054 and the “Project of High-Level Elitist in Suzhou” for financial supports.

References

[1] Rainer H, Thomas B. Adv Mater 2001;13(23):1805.
[2] Darracq B, Canva M. Appl Phys Lett 1997;70(3):292.
[3] Thieghi LT, Bonvent JJ, Oliveira EA, Giacometti JA, Balogh DT. Appl Phys A 2003;77:911.
[4] He X, Yan D, Mai Y. Eur Polym J 2004;40:1759.
[5] Silong S, Lutfor MR, Ab Rahman MZ, Wan Yunus WMZ, Haron MJ, Ahmad MB, et al. J Appl Polym Sci 2002;86:2653.
[6] Carlos JLC, Ricardo FA, Cleber RM, Sarita VM, Debora TB, Sergio CZ, et al. Adv Funct Mater 2001;11(1):65.
[7] Kim MJ, Chun C, Nakayama T, Kim DY. Jpn J Appl Phys 2006;45(6):L169.
[8] Ozaki M, Nagata T, Matsui T, Yoshino K, Kajzar F. Jpn J Appl Phys 2000;39:L614.
[9] Liang Z, Ming H, Wang P, Zhang J, Xie J. J Appl Physiol 2001;90(12):5866.
[10] Jia Y, Wang G, Guo B, Su W, Zhang Q. J Opt A Pure Appl Opt 2004;6:833.
[11] Luigi A, Renato B, Loris G, Danilo P, Giovanni T, Alessandro D. Chem Eur J 2002; 8(18):4241.
[12] Lagugne-Labarthet F, Bruneel JL, Buffeteau T, Sourisseau C. J Phys Chem B 2004;108:6949.
[13] Rodriguez V, Adamietz F, Sanguinet L, Buffeteau T, Sourisseau C. J Phys Chem B 2003;107:9736.
[14] Shen Y, Xia Y, Gu F, Zhang J. Mater Chem Phys 2005;91:468.
[15] Lagugne-Labarthet F, Buffeteau T, Sourisseau C. Phys Chem Chem Phys 2005; 91:468.
[16] Hubert C, Malcor E, Maurin I, Nunzi JM, Raimond P, Fiorini C. Appl Surf Sci 2002;186:29.
[17] Takeshi M, Keijiro Y, Kanae N, Keiji M, Masanobu H, Masami T. J Appl Polym Sci 2006;100:3913.
[18] Takashi F, Hiro M, Takao S, Tatsumi K, Masao K, Nirmal KV, et al. Macromolecules 2000;33:4220.
[19] Brown D, Natansohn A, Rochon P. Macromolecules 1995;28:6116.
[20] Takami U, Etsuya O, Toshikuni K. Mol Cryst Liq Cryst 2002;374:303.
[21] Hideaki T, Almeria N, Paul R. Polymer 2003;44:7345.
[22] Meng X, Natansohn A, Barrett C, Rochon P. Macromolecules 1996;29:946.
[23] Mamiko N, Fumihiko H, Makoto M, Masaaki T, Osamu W. Macromolecules 2007;40:623.
[24] Nahata A, Shan J, Yardley JT, Wu C. J Opt Soc Am B 1993;10(9):1553.
[25] Nagata T, Matsui T, Ozaki M, Yoshino K, Kajzar F. Synth Met 2001;119:607.
[26] Cui L, Tong X, Yan XH, Liu GJ, Zhao Y. Macromolecules 2004;37:7097.
[27] He XH, Yan DY. Macromol Rapid Commun 2004;25:949.
[28] Jin M, Lu R, Bao CY, Xu TH, Zhao YY. Polymer 2004;45:1125.
[29] Matyjaszewski K, Xia JH. Chem Rev 2001;101:2921.
[30] Kamigaito M, Ando T, Sawamoto M. Chem Rev 2001;101:3689.
[31] Matyjaszewski K. Polym Int 2003;52:1559.
[32] Pyun J, Kowalewski T, Matyjaszewski K. Macromol Rapid Commun 2003;24: 1043.
[33] Li NJ, Xu QF, Lu JM, Xia XW, Wang LH. Macromol Chem Phys 2007;208:399.
[34] Natansohn A, Rochon P, Gosselin J, Xie S. Macromolecules 1992;25:2268.
[35] Cristina C, Paul R. J Mater Chem 2004;14:2909.
[36] Li NJ, Lu JM, Xu QF, Wang LH. Opt Mater 2006;28:1412.
[37] Tirelli N, Suter UW, Altomare A, Solaro R, Ciardelli F, Follonier S, et al. Macromolecules 1998;31(7):2152.
[38] Facchetti A, Abbotto A, Beverina L, van der Boom ME, Dutta P, Evmenenko G, et al. Chem Mater 2002;14(12):4996.
[39] Gopalan P, Katz HE, McGee DJ, Erben C, Zielinski T, Bousquet D, et al. J Am Chem Soc 2004;126(6):1741.
[40] Sauteret C, Hemann JP, Frey R. Phys Rev Lett 1976;36(16):956.