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ФУНКЦИОНАЛЬНЫЕ ПОЛИМЕРЫ

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PREPARATION AND NONLINEAR OPTICAL PROPERTIES OF TWO ACRYLATE POLYMERS BEARING DIFFERENT LONG CONJUGATED PENDANTS[1]

© 2011 г. Weiju Zhu[a], Hongyao Xu[a, b], Zhenyu Wu[a], Cun Li[a], Min Fang[a]

[a] School of Chemistry and Chemical Engineering and the Key Laboratory of Environment-Friendly Polymer Materials of Anhui Province, Anhui University, Hefei 230039, China

[b] College of Material Science and Engineering and State Key Laboratory for Modification of Chemical Fibers and Polymeric Materials, Donghua University, Shanghai 201620, China

e-mail: hongyaoxu@163.com

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Abstract—Two new acrylate monomers containing different long π-election conjugation bridge structure, 4'-[(N, N-diethylacrylate) amino], 4-(pyridine-4-vinyl) stilbene (DAS) and 4'-[(N, N-diethylacrylate) amino], 4-(pyridine-4-vinyl) azobenzene (DAA), were synthesized and their copolymers with methyl methacrylate (MMA) were prepared by free radical polymerization method. Their structures and properties of these copolymers were characterized and evaluated by FTIR, ^{1}H-NMR, UV spectra, GPC and *Z*-scan technique with 8 ns pulses at 532 nm wavelength. The relationship between their structures and properties was investigated. The results show that the structure of these resultant copolymers can be effectively tuned by simply varying the feed ratio and these copolymers exhibit good solubility and large third-order nonlinear optical properties. The large third-order nonlinear optical properties are mainly attributed to the substituted NLO-chromophore with long D-π-A conjugated structure. Simultaneously, it is found that poly (DAA-*co*-MMA) with N=N double bond as conjugation bridge has larger third-order nonlinear optical susceptibility than poly (DAS-*co*-MMA) with C=C double bond as conjugation bridge owing to more effective π electron conjugation effect.

INTRODUCTION

With the fast development of modern laser technology, organic conjugated polymer materials have been intensively studied and applied in the field of nonlinear optics (NLO) in recent years because of their prominent performance such as large nonlinear optical properties, high damage threshold, easy of processing and structural modification, their applicability over a wide wavelength range and fast response time, etc. [1–6]. However, the relationship between molecular structure and nonlinear optical properties, so far, has not completely understood. Therefore, it is very important to design and synthesize new functional polymers for further exploring the relationship between molecular structure and nonlinear optical properties. The polymers bearing long conjugated chromophoric pendant often show good nonlinear optical properties, but exhibit poor solubility and film forming ability. Poly (methyl methacrylate) (PMMA), a commercially available polymer, has high light transmittance, good film forming properties and easy processing, make PMMA a valuable substitute for glass in optical device applications [7–9]. In this paper, we incorporated two NLO chromophore molecules (namely DAA and DAS) into the chain of macromolecule by copolymerization method to prepare two series new poly (DAA-*co*-MMA) and poly (DAS-*co*-MMA) (Scheme 1) with nonlinear optical properties. The relationship between their molecular structures and their poperties was investigated.

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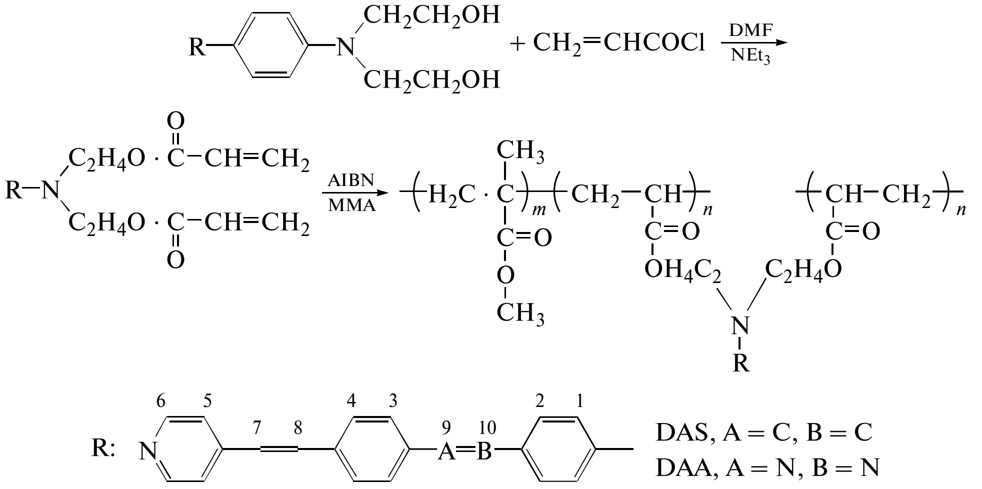

Scheme 1. Synthetic scheme of the functional copolymers

EXPERIMENTAL

FTIR spectra were recorded as KBr pellets on a Nicolet 170SX spectrometer. ^{1}H NMR spectra were obtained on an AVANCE/DMX-300 MHz Bruker NMR spectrometer. UV-vis spectra were recorded on a Shimadzu UV-265 spectrometer using a 1-cm square quartz cell. Molecular weights of the polymers were estimated on KNAVER Vapour Pressure Osmometer. The nonlinear optical properties of the polymers were measured in DMF solutions. Testing was performed using a frequency-doubled, Q-switched, mode-locked continuum ns/ps Nd: YAG laser, which provides linearly polarized 8 ns optical pulses at 532 nm wavelength with a repetition of 1 Hz. The experimental arrangement is similar to that in the literature [12, 13]. The input energy was 100 μJ. The sample solution was placed in a 2 mm quartz cell and moved along the axis of the incident beam (z direction).

4'-(N,N-dihydroxyethylamino), 4-(pyridine-4-vinyl) stilbene and 4'-(N,N-dihydroxyethylamino), 4-(pyridine-4-vinyl) azobenzene were synthesized according to the method reported [10]. Methylmethacrylate (MMA) was purchased from Fluka and distilled from calcium hydride under reduced pressure before use. N,N-dimethylformamide (DMF) was purified by distillation over CaH_2 prior to utilization. AIBN was purchased from Shanghai Chemical Reagent Company and purified before use. Technical-grade methanol was used to precipitate the polymer products.

Synthesis of Acrylic Ester (DAS)

A mixture of 4'-(N,N-dihydroxyethylamino)-4-(pyridine-4-vinyl) stilbene (0.38 g, 1 mmol), triethylamine (2 ml) and anhydrous DMF (50 ml) was placed in a flask and cooled in ice bath for 30 minutes. Then, the acryloyl chloride (0.16 ml, 2 mmol) in 10 ml DMF was added dropwise into above reaction mixture and stirred for 4 h at 0–10°C. After reaction for 24 h at room temperature, the solution was filtered and added dropwise into water to precipitate the product. The crude product was purified by column chromatography (Al_2O_3, ethyl acetate : petroleum ether = 1 : 1 as eluent) to give yellow-green powder in 35% yield. IR: ν 2928 (CH_2), 1722 (C=O), 1596, 1512(C=C phenyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ_H 3.72 (t, 4H, J = 6.4 Hz , $C\underline{H}_2CH_2$), 4.36 (t, 4H, J = 6.2 Hz, $CH_2C\underline{H}_2$), 5.85 (t, 2H, J = 9.2 Hz, H^a), 6.15 (m, 2H, H^c), 6.44 (d, 2H, J = 16.8 Hz, H^b), 6.76 (d, 2H, J = 8.8, H^1), 7.0 (d, 1H, J = 16.3 Hz, H^7), 7.12 (s, 1H, H^9), 7.34 (s, 1H, H^{10}), 7.40 (d, 2H, J = 8.5 Hz, H^2), 7.44 (s, 1H, H^8), 7.49 (d, 4H, J = 7.3 Hz, $H^{3,4}$), 7.52 (d, 2H, J = 6.1 Hz, H^5), 8.56 (d, 2H, J = 6.1 Hz, H^6) ppm.

For DAS($C_{31}H_{30}N_2O_4$) anal. Calcd. (%): C, 75.30; H, 6.07; N, 4.86.

Found (%): C, 75.25; H, 4.90; N, 6.11.

Synthesis of Acrylic Ester (DAA)

The synthesis process of DAA is similar to that of compound DAS. The crude product was purified by column chromatography (Al_2O_3, ethyl acetate : petroleum ether = 1 : 1 as eluent) to give deep-red powder in 40% yield. IR: ν 2926 (CH_2), 1721 (C=O), 1600, 1513(C=C phenyl) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ_H 3.80

Table 1. Copolymerization of DAS with MMA

Sample	Feed ratio		Measured ratio	Yield	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
	m(DAS) : m(MMA)	n(DAS) : n(MMA)					
P1	20 : 100	4.04 : 100	3.8 : 100	72.2	12.3	30.7	2.5
P2	50 : 100	10.1 : 100	9.1 : 100	71.0	9.32	21.2	2.27
P3	100 : 100	20.2 : 100	16.2 : 100	68.8	7.51	12.3	1.64
P4	200 : 100	40.4 : 100	28.2 : 100	67.8	7.15	13.5	1.89
P5	100 : 0	100 : 0	100 : 0	33.0	2.74	3.38	1.23

(t, 4H, J = 6.1 Hz, $N(C\underline{H}_2CH_2-)$), 4.40 (t, 4H, $N(CH_2C\underline{H}_2)$)), 5.86 (t, 2H, J = 10.5 Hz, H^a), 6.15 (m, 2H, H^c), 6.41 (d, 2H, J = 17.45 Hz, H^b), 6.87 (d, 2H, J = 9.05, H^1), 7.11 (d, 1H, J = 16.2 Hz, H^7), 7.25 (d, 2H, J = 7.8 Hz, H^4), 7.43 (d, 1H, H^8), 7.65 (d, 2H, H^3), 7.84 (d, 2H, H^2), 7.88 (d, 2H, J = 8.2 Hz, H^5), 8.59 (d, 2H, H^6) ppm.

For DAA($C_{29}H_{28}N_4O_4$) anal. Calcd. (%): C, 70.16; H, 5.65; N, 11.29.

Found (%): C, 70.25; H, 5.56; N, 11.11.

Synthesis of Copolymers

A typical procedure for the polymerization reaction was given below: monomer DAA (2.0 g, 5.3 mmol) and AIBN (5.5 mg) were added into a baked 20-ml Schlenk tube equipped with a side arm under N_2. Then, MMA (1.0 g, 10.0 mmol) solution in DMF (10 ml) was injected into the tube. After stirring at 70°C under nitrogen for 48 h, the reaction mixture was filtered. The filtrate was added dropwise into 100 ml of methanol under stirring to precipitate the polymer product. Then the product was redissolved in THF, and added dropwise through a cotton filter into methanol (300 ml). The dissolution-precipitation process was repeated three times, and the finally isolated precipitant was dried under vacuum to a constant weight.

Poly ($DAS_{16.2}$-*co*-MMA_{100}): yellow-green solid. Yield: 68.8%. GPC: M_w 7.51 × 10^3, M_w/M_n: 1.64 (polystyrene calibration). IR: ν 2948, 2840 (CH_3, CH_2), 1724 (C=O), 1600, 1450(C=C phenyl) cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.84–1.82 (br., $-COOCH_3$, $-CH_3$), 3.27~3.89 ($N(CH_2CH_2O)_2$, 6.41~8.75 (Ar–H and –CH=CH–), 8.56 (Py–H) ppm.

Poly ($DAA_{16.4}$-*co*-MMA_{100}): orange-red solid. Yield: 68.2%. GPC: M_w 8.69 × 10^3, M_w/M_n: 2.98 (polystyrene calibration). IR: ν 2975, 2845(CH_3, CH_2), 1731 (C=O), 1600, 1451(C=C phenyl) cm^{-1}. ^1H NMR ($CDCl_3$): δ_H 0.85~1.83 (br., $-C-CH_2-$, $-CH_3$), 2.79~3.01 (br., $-N(CH_2CH_2O)_2$), 3.27~3.84 (br., $-COOCH_3$), 6.68~8.03 (br., Ar–H and –CH=CH–), 8.56 (br., Py-H) ppm.

RESULTS AND DISCUSSION

Table 1 shows the results of the polymerization. The homopolymerization of monomers was first attempted in DMF using AIBN as initiator at 70°C. However, only low molecular weight products were obtained and showed poor solubility. To improve the solubility of resultant polymer and obtain polymer with high molecular weight, the MMA is selected to copolymerize with DAS due to the good solubility and film-forming ability of PMMA. There are a small amount of insoluble materials in the reaction products which may be produced by the formation of cross-link during copolymerization of these monomers with methylmethacrylate. The cross-linked copolymer was removed by repeating the dissolution–deposition process. Therefore we think that the product obtained is a linear or branched copolymer in the text. From Table 1, it can be seen that the copolymers with high molecular weight were obtained and the average molecular weight and yeild of resulting copolymers increase with increasing MMA monomer content. Simultanously, it is found that the chromophoric content in resultant polymers (poly(DAS-*co*-MMA)) increases with increase of DAS monomer feed ratio, which make the contallable preparation of copolymers with different chromophore content can be accomplied by varying the monomer feed ratio. The similar results were observed in polymerization of poly (DAA-*co*-MMA).

All the purified polymerization products gave satisfactory spectroscopic data corresponding to their expected molecular structures. Figure 1 displays the FTIR spectra of DAS, PMMA and poly (DAS-*co*-MMA). As can be seen from Fig. 1, the spectra of copolymers are different from that of monomers and PMMA. The intensity of the absorption band at 2948 and 2990 cm^{-1} assigning to $-CH_3$ and $-CH_2-$ streching vibration became stronger in copolymers, which proves that olefinic bond has transferred into

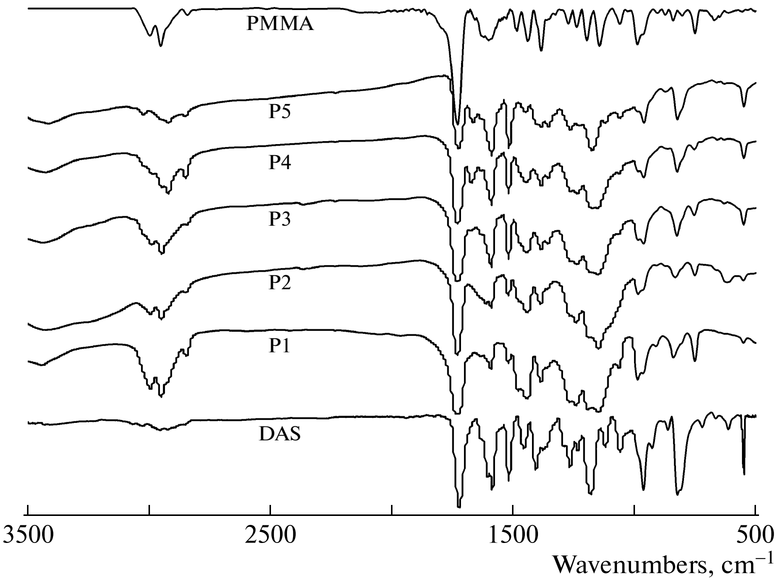

Fig. 1. IR spectra of DAS and copolymer and PMMA.

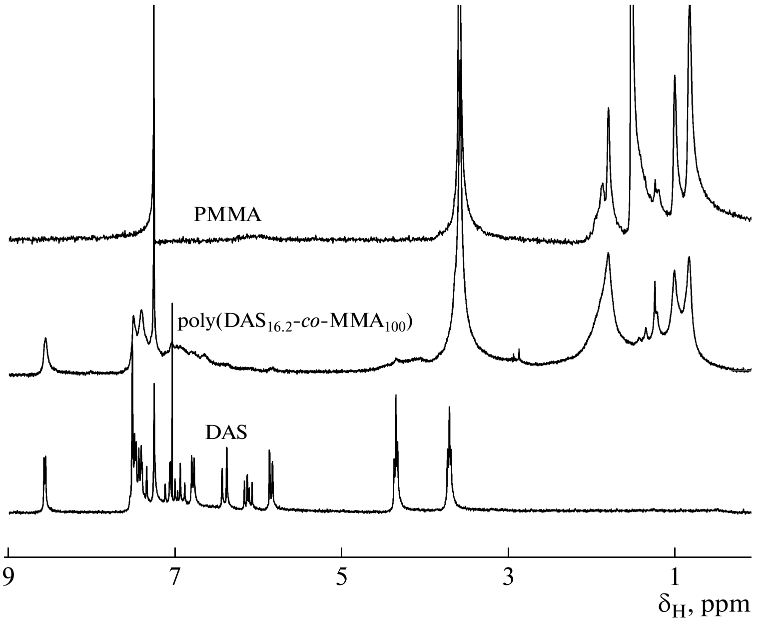

Fig. 2. ^{1}H NMR spectra of DAS and copolymer and PMMA.

carbon-carbon single bond after copolymerization of DAS and MMA. Similarly, the phenyl vibration band at 1590 and 1520 cm^{-1} from the DAS segment clearly appears in the poly (DAS-*co*-MMA) copolymer, and the intensity of the absorption band becomes stronger in copolymers with the DAS content increases. The appearance of the absorption band at 1590 and 1520 cm^{-1} assigning to phenyl streching vibration in the copolymers proves that the monomer DAS has copolymered with MMA, further supporting that copolymerization of DAS and MMA.

Figure 2 displays the ^{1}H NMR spectra of DAS, PMMA and poly (DAS$_{16.2}$-*co*-MMA$_{100}$). From Fig. 2 it can be seen that the characteristic proton absorbance band at δ 5.86, 6.12 and 6.41 ppm assigning to proton absorption of CH_2=CH– group of monomer DAS completely disappears, and a few new broad peaks appear at δ 0.84~1.82 which assigning to proton absorption of –CH_3 and –CH_2– group of MMA in the

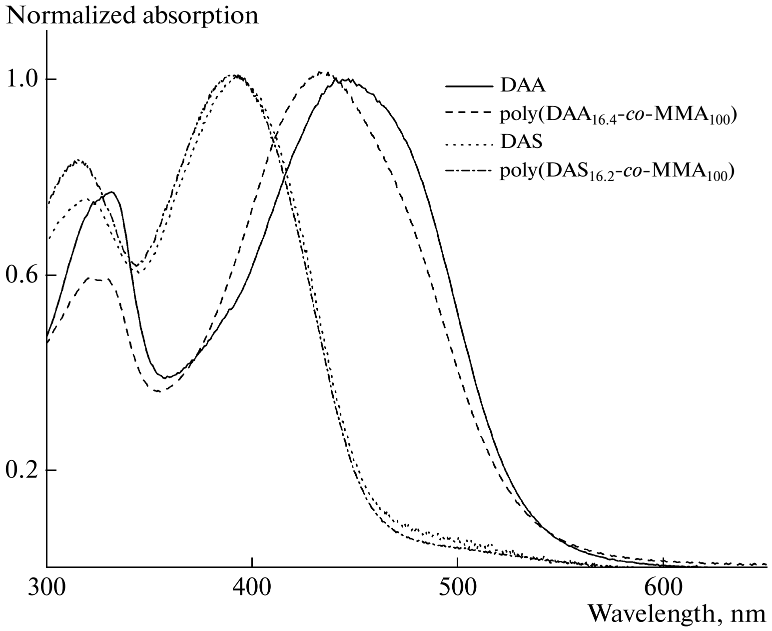

Fig. 3. UV-vis spectra of DMF solution of monomers and polymers (concentration: 0.01 mg/ml in DMF).

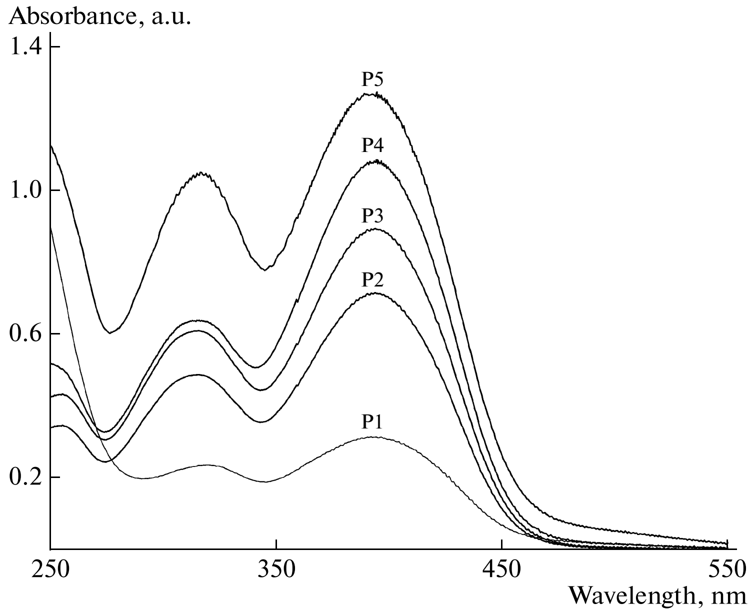

Fig. 4. UV-vis spectra of DMF solution of polymer (DAS-*co*-MMA) (concentration: 0.01 mg/ml in DMF).

^{1}H NMR spectra of the poly (DAS$_{16.2}$-*co*-MMA$_{100}$), which proves that the copolymerization has occurred. The aromatic proton peaks of DAS are obviously widened and shifted to upfield after the copolymerization with MMA, further supporting the conclusion that MMA is indeed copolymerized with DAS. The ^{1}H NMR spectrum was also used to determine the chromophoric content in the copolymer [10]. From Table 1 we observe that the DAS component contents in the copolymer increase with the increase of DAS feed ratio during the copolymerization, indicating that the nonlinear chromophoric pendants content can be effectively controled by changing the feed ratio. Similar results are found in poly (DAA-*co*-MMA).

Figure 3 shows the UV spectra of monomers and their copolymers in DMF. DAS has two absorption peaks at 318, 393 nm, which correspond to the absorption bands of the amino auxochromic group and the

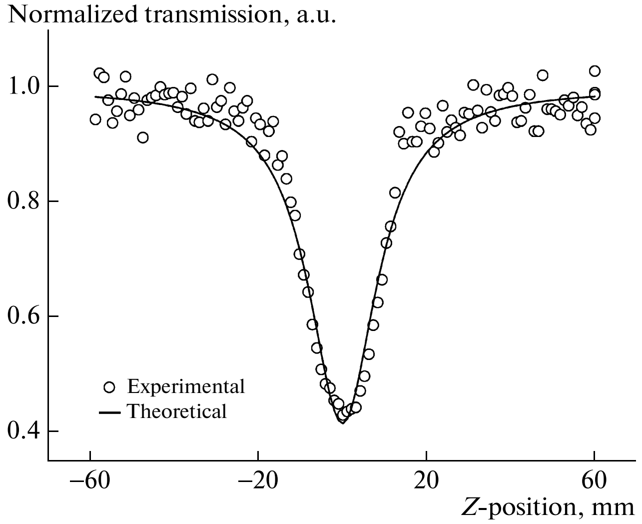

Fig. 5. Nonlinear absorption data of polymer ($\mathrm{(DAS_{16.2}\text{-}\mathit{co}\text{-}MMA_{100})}$).

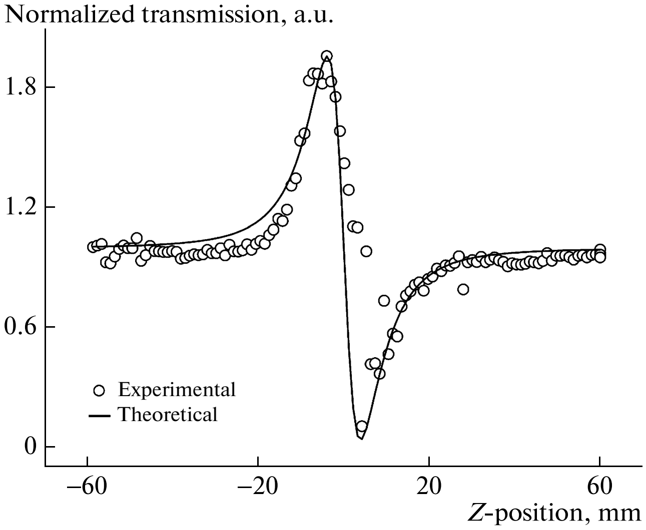

Fig. 6. Nonlinear refraction data of polymer ($\mathrm{(DAS_{16.2}\text{-}\mathit{co}\text{-}MMA_{100})}$).

π–π^* transition of the extended π electron conjugation structure of the NLO chromophore. Poly ($\mathrm{DAS_{16.2}}$-*co*-$\mathrm{MMA_{100}}$) exhibits two strong absorption peaks at 316, 391 nm, which is only slight blue-shifts from 393 nm of DAS to 391 nm, which is due to forming a long molecular chain. Compared with poly ($\mathrm{DAS_{16.2}}$-*co*-$\mathrm{MMA_{100}}$), poly ($\mathrm{DAA_{16.4}}$-*co*-$\mathrm{MMA_{100}}$) exhibits the absorption peak at 435 nm, which significantly red-shifts when the conjugation bridge of the NLO-chromophoric segment varies from C=C to N=N double bond, hinting that poly ($\mathrm{DAA_{16.4}}$-*co*-$\mathrm{MMA_{100}}$) with N=N double bond as conjugation bridge has larger π electron delocalization effect than poly ($\mathrm{DAS_{16.2}}$-*co*-$\mathrm{MMA_{100}}$) with C=C double bond conjugation bridge. In addition, with the increase of DAS component, UV absorption of copolymer peak intensity increased (Fig. 4), further confirming that the DAS has been incorporated into resulting copolymers owing to almost no absorption of PMMA in region of visible optical wavelength.

The nonlinear optical properties of copolymer, poly ($\mathrm{DAS_{16.2}}$-*co*-$\mathrm{MMA_{100}}$) and poly ($\mathrm{DAA_{16.4}}$-*co*-$\mathrm{MMA_{100}}$), were evaluated by *Z*-scan measurement technique [11–15]. The nonlinear absorption performance was evaluated under an open aperture configuration. The effective third-order nonlinear absorption coefficient β value can be obtained based on equation (1) and (2) by fitting theoretical curves of transmittance against the *z*-position of observed *z*-scan data.

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

$$q_0(z) = \beta I_0(t) L_{eff}/(1 + z^2/z_0^2), \tag{2}$$

where β is the nonlinear absorption coefficient, $I_0(t)$ is the intensity of laser beam at focus ($z = 0$), $L_{eff} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ is the effective thickness with α_0 the linear absorption coefficient and L is the sample thickness, z_0 is the diffraction length of the beam, and z is the sample position. Thus, the nonlinear absorption coefficients of the polymers can be determined by fitting the experimental data using Eq. (1).

The nonlinear refractive property of copolymers were assessed by dividing the normalized *Z*-scan data obtained in the close aperture configuration with those obtained in the open aperture configuration (Figs. 5–8). The effective third-order nonlinear refractive index n_2 can be derived from the difference between normalized transmittance values at valley and peak positions (ΔT_{v-p}) by using Eq. (3).

$$n_2 = \frac{\lambda \alpha_0}{0.812\pi I_0(1 - e^{-\alpha_0 L})(1 - S)^{0.25}} \Delta T_{v-p}, \tag{3}$$

Table 2. The nonlinear optical properties of poly ($\mathrm{DAS_{16.2}}$-*co*-$\mathrm{MMA_{100}}$) (a) and poly ($\mathrm{DAA_{16.4}}$-*co*-$\mathrm{MMA_{100}}$) (b)

Polymer	Sol. Conc. (mg/ml)	α_2 (m/W)	n_2 ($\mathrm{m^2/W}$)	$\mathrm{Im}\chi^{(3)}$ (esu)	$\mathrm{Re}\chi^{(3)}$ (esu)	$\chi^{(3)}$ (esu)
(a)	1.4	0.86×10^{-10}	18.53×10^{-18}	2.84×10^{-12}	45.5×10^{-12}	4.56×10^{-11}
(b)	1.4	0.54×10^{-10}	20.30×10^{-18}	1.76×10^{-12}	49.8×10^{-12}	4.97×10^{-11}

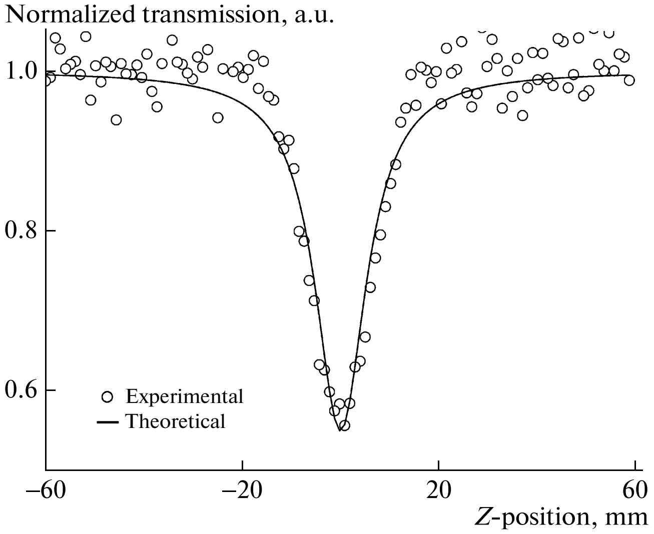

Fig. 7. Nonlinear absorption data of polymer ($DAA_{16.4}$-*co*-MMA_{100}).

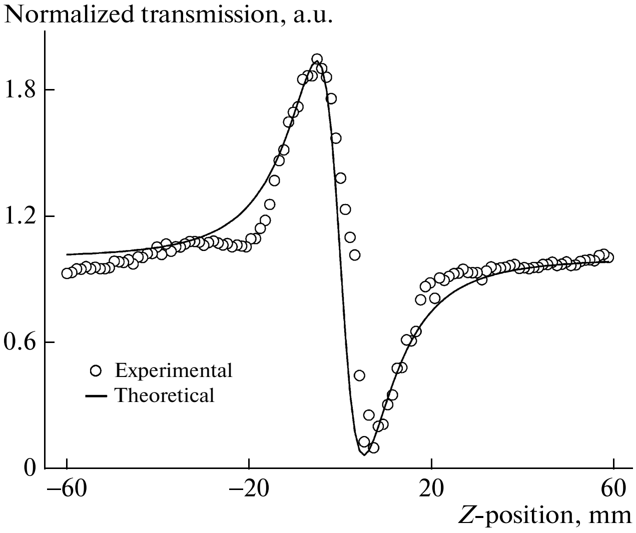

Fig. 8. Nonlinear refraction data of polymer ($DAA_{16.4}$-*co*-MMA_{100}).

where S is the aperture size ($S = 0.18$). Thus, the nonlinear refractive coefficients of the copolymers can be determined with Eq. (3).

In accordance with the observed β and n_2 values, the third-order susceptibility $\chi^{(3)}$ value can be calculated with the following equation:

$$\left|\chi^{(3)}\right| = \sqrt{\left|\frac{cn_0^2}{80\pi}n_2\right|^2 + \left|\frac{9\times 10^8\varepsilon_0 n_0^2 c^2}{4\pi\omega}\beta\right|^2}, \qquad (4)$$

where ε_0 is the permittivity of vacuum, c the speed of light, n_0 the refractive index of the medium and $\omega = 2\pi c/\lambda$. The results of Z-scan with and without an aperture show that copolymers had not only nonlinear refraction but also nonlinear absorption. The Z scan results of poly ($DAS_{16.2}$-*co*-MMA_{100}) and poly ($DAA_{16.4}$-*co*-MMA_{100}) are shown exemplarily in Figs. 5, 6 and Figs. 7, 8. The calculated nonlinear optical coefficients of the copolymers are 4.56×10^{-11} esu (C = 1.4 mg/ml) and 4.97×10^{-11} esu (C = 1.4 mg/ml) for poly ($DAS_{16.2}$-*co*-MMA_{100}) and poly ($DAA_{16.4}$-*co*-MMA_{100}) (Table 2) base on the experimental data, respectively. Their third-order susceptibility is larger than those of polyurethanes poly[4'-(N,N-dihydroxyethylamino),4-(pyridine-4-vinyl)stilbene] (5.7×10^{-12} esu, C = 0.117 mg/ml) and poly[4'-(N,N-dihydroxyethylamino),4-(pyridine-4-vinyl)azobenzene] (6.7×10^{-12} esu, C = 0.083 mg/ml) [10]. Thus, the introduction of the NLO-chromophoric segment into PMMA has endowed the resultant copolymers with large third-order nonlinear optical properties, good solubility and film forming ability. Simultaneously, it is found that poly ($DAA_{16.4}$-*co*-MMA_{100}) has larger nonlinear optical suscetibility than poly($DAS_{16.2}$-*co*-MMA_{100}), which is attributed with the more effective π electron conjugation when copolymer with N=N double bond as conjugation bridge than that with C=C double bond as conjugation bridge. It is consistent with that of UV spectra.

CONCLUSION

Two series novel functional copolymers bearing different long conjugation bridge structural nonlinear optical chromophores were successfully prepared. The incorporation of NLO chromophore into PMMA endowed copolymers large nonlinear optical properties, good solubility and film forming properties. Simultaneously, it is found that the nonlinear optical performances are strongly affected by π electron conjugation bridge structure of the NLO chromophores. Poly (DAA-*co*-MMA) with conjugation bridge structure has larger third-order nonlinear optical susceptibility than poly (DAS-*co*-MMA) with C=C double bond conjugation bridge structure owing to larger π electron delocalization effect. This work provides the way for designing new soluble functional polymers with large nonlinear optical property and well film forming ability.

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REFERENCES

1. L. W. Tutt and A. J. Kost, Nature **356**, 225 (1992).
2. P. Miles, J. Appl. Opt. **38**, 566 (1999).
3. Q. Zheng, G. S. He, A. Baev, and P. N. Prasad, J. Phys. Chem. B **110**, 14604 (2006).
4. X.-Y. Su, H.-Y. Xu, and Q.-Z. Guo, J. Polym. Sci. Part A: Polym. Chem. **46**, 4529 (2008).
5. S.-C. Yin, H.-Y. Xu, and. X.-Y. Su, J. Polym. Sci. Part A: Polym. Chem. **44**, 2346 (2006).
6. Q. Zheng, G.-S. He, and P. N. Prasad, J. Chem. Mater. **17**, 6004 (2005).
7. C.-Y. Chiu, Y.-J. Yen, and S. W. Kuo, Polymer **48**, 1329 (2007).
8. O. A. Lam, Y. Hervaud, and B. Boutevin, J. Polym. Sci, Part A: Polym. Chem. **44**, 4762 (2006).
9. M. M. Rao, J. S. Liu, W. S. Li, and Y. Liang, J. Memb. Sci. **322**, 314 (2008).
10. H.-Y. Xu, S.-C. Yin, and W.-J. Zhu, Polymer **47**, 6986 (2006).
11. J. E. Geusic, S. Singh, D. W. Tipping, and T. C. Rich, J. Phys. Rev. Lett. **19**, 1126 (1967).
12. M. Sheik-Bahae, A. A. Said, T.-H. Wei, et al., J. IEEE J. Quantum Electron **26**, 760 (1990).
13. X.-Y. Su, H.-Y. Xu, J.-Y. Yang, et al., Polymer **49**, 3722 (2008).
14. X. Wang, S.-Y. Guang, H.-Y. Xu, et al., J. Mater. Chem. **18**, 4204 (2008).
15. X Wang, J.-C. Wu, H.-Y. Xu, et al., J. Polym. Sci. Part A: Polym. Chem. **46**, 2072 (2008).