

Synthesis and Characterization of Bi-functional Photorefractive Polymers with High Molecular Weight and Low Glass Transition Temperature^{*}

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Abstract Carbazole-based bi-functional photorefractive polyacrylates were prepared *via* free radical polymerization and post-azo-coupling reaction. The structure of polymers was characterized by Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (¹H-NMR) spectroscopy. The differential scanning calorimetry (DSC) and the thermal gravimetric analysis (TGA) were used to characterize the thermal property of polymers. The results indicate that though the glass transition temperature (T_g) of polymers increases with increasing the ratio of NLO groups, the polymers with different ratios of NLO groups still all show low glass transition temperatures around 60 °C, and good thermal stability, which are favorable to the practical application of these polymers. The gel permeation chromatographic (GPC) result indicates that these polymers all have high-molecular-weight which is favorable to the long term stability of the material. Further, these polymers have good solubility in chloroform solvent, and the solutions can easily be fabricated into optically transparent films. Gain coefficients of 75 cm⁻¹, 185 cm⁻¹ and 66 cm⁻¹ can be observed at zero external electric field without any addition agent or pre-poling for polymers P-2, P-3 and P-4 respectively. The different contents of NLO groups result in the different properties of polymers P-2, P-3 and P-4.

Keywords: Photorefractive; Polyacrylate; Post-azo-coupling reaction; High molecular weight; Low T_g .

INTRODUCTION

Photorefractive (PR) materials are such multifunctional materials that may combine photoconductivity and nonlinear optical (NLO) response to modulate the refractive index of the medium^[1, 2], which have attracted considerable attention due to their potential applications in the fields of digital holographic data storage, image processing, optical pattern recognition, holographic interferometry, wavelength demultiplexing and medical imaging^[3, 4].

Organic photorefractive materials are emerging as key materials for advanced information and telecommunication technology^[5, 6]. Owing to their high performance, structural flexibility and light weight, these polymers are expected to play a major role in optical technology. Since then, numerous organic photorefractive materials have been developed, and the effect of different groups in various organic materials has been extensively investigated for many years^[7–11].

At present, the single-component polymers with low T_g which exhibited PR performance at room temperature and without an external electric field or pre-poling have attracted more and more concentration of

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researchers due to their large advantages in the application fields^[12–14]. Further, the steady-state PR performance of all these single-component polymers could be enhanced significantly by use of a charge-transporting plasticizer.

According to the structure of backbone, the low- T_g single-component polymers can be divided into three kinds; they are polyphosphazene backbone, siloxane backbone and polyacrylate backbone. The polymers with siloxane backbone are usually synthesized through a post-azo coupling technique^[15] and can get a high content of chromophore, but still presented a low gain coefficient^[16, 17]. The polymers of polyphosphazene backbone can get a gain coefficient of 91 cm^{-1} , but for the preparation of polyphosphazenes the usual methods, including the direct nucleophilic substitution reaction of the chlorine atoms in the highly reactive macromolecular intermediate poly(dichlorophosphazene) or the One-pot *in situ* synthesis of poly(dichlorophosphazene) from PCl_3 , are complicated and lack of the controllability of the molecular weight of polymers^[18, 19].

The polymers of polyacrylate backbone have shown a gain coefficient of 140 cm^{-1} and a diffraction efficiency of 8.3% at zero electric field^[20, 21]; these values are the highest reported among the three kinds of low T_g single-component organic PR materials at present.

In our work, we first prepared the monomers with the conjugated bond and the charge transport groups (carbazole), and then synthesized the PR polymers through the free-radical polymerization. Through this method, the molecular weight of polymers can be controlled easily and more exactly, further, other structure units can be easily introduced into the backbone through free-radical polymerization to improve the combination property of polymers. According to the reported work about the photorefractive polymers of polyacrylate backbone, the α -methyl groups connected to the backbone of polymers can improve the T_g of the polymers and decrease the flexibility of polymer chains, we proposed an idea for synthesis of the low T_g photorefractive polymers of polyacrylate backbone without the α -methyl groups in the structure. It was found that these single component polymers exhibited excellent PR performance at room temperature without an external electric field or pre-poling.

EXPERIMENTAL

Materials

Carbazole (AR, Shanghai Jiangchun Reagent Co. Ltd.); toluene (AR), sodium hydroxide (AR), triethyl benzyl ammonium chloride (AR), petroleum ether (AR), tetrahydrofuran (THF, AR), chloroform (AR), acrylic acid (AR), ethyl acetate (AR), sodium dodecyl benzenesulfonate (NaDBS, AR), hydrochloric acid (HCl, AR), 4-nitroaniline (AR), sodium nitrite (AR) and nitrobenzene (AR) all supplied by Kelong Chemical Reagents Factory (Chengdu, China); silica gel grit 300 (Sea Wave Company of Qingdao); 1'6-dibromohexane (97%, Aladdin Chemistry Co. Ltd.); tetrabutylammonium bromide (AR) purchased from Kemiou Chemical Reagents Factory (Tianjin, China). *N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. 2,2'-Azobisisobutyronitrile (AIBN) was supplied by Kelong Chemical Reagents Factory (Chengdu, China) and was recrystallized twice from methanol.

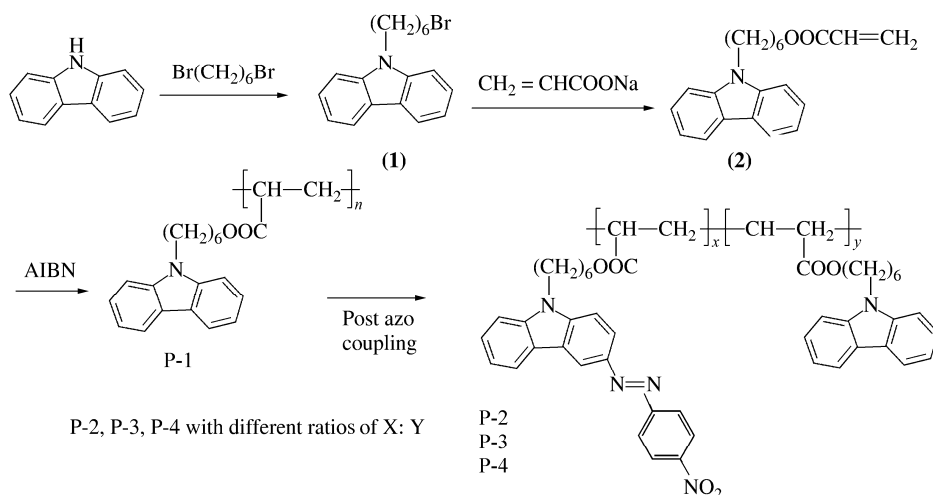
Synthesis of Photorefractive Polymers

The synthetic procedure for photorefractive polymers P-2~P-4 is shown in Scheme 1.

Synthesis of *N*-(6-Bromohexanyl) carbazole (**1**)

50 wt% sodium hydroxide aqueous solution and 0.60 g triethyl benzyl ammonium chloride were stirred in 60 mL toluene at room temperature for 15 min. The mixture was then stirred with 12.0 g carbazole for another 30 min. 90 mL 1'6-dibromohexane was added slowly under stirring at $50\text{ }^\circ\text{C}$ and the resultant mixture was allowed to react at $50\text{ }^\circ\text{C}$ for 12 h.

The mixture was first washed by deionized water and separated through separating funnel until the unreacted sodium hydroxide was totally removed and the pH of aqueous phase reached 7. After then, the organic phase was rotate evaporated to remove the residual solvent, and then the organic phase was subjected to column chromatography purification (300 mesh silica gel 500 g, 5% THF in petroleum ether). Yield: 93%.



Scheme 1 Synthetic route for bi-functional photorefractive polymers P-2, P-3 and P-4

Synthesis of *N*-(6-acrylatehexanyl) carbazole (2)

First, 37 mL acrylic acid was added slowly in 20 wt% sodium hydroxide aqueous solution under stirring at 0–3 °C for 2 h to prepare the sodium acrylate. In order to avoid the homopolymerization of sodium acrylate, the react temperature must be exactly controlled at 0–3 °C.

Tetrabutylammonium bromide 1.5 g, *N*-(6-Bromohexanyl) carbazole 8.3 g were stirred in 40 mL chloroform at 45 °C for 30 min, and then added the prepared sodium acrylate aqueous solution. The mixture solution was allowed to react for 60 h at 45 °C.

The mixture was first washed by deionized water and separated through separating funnel until the pH of the aqueous phase was lower than 7. And then the organic phase was subjected to column chromatography purification (300 mesh silica gel 500 g, 10% ethyl acetate in petroleum ether). Yield: 70%.

Synthesis of poly(*N*-(6-acrylatehexanyl) carbazole) (P-1)

The poly(*N*-(6-acrylatehexanyl) carbazole) can be synthesized through free radical polymerization. 5 g *N*-(6-acrylatehexanyl) carbazole was stirred in 20 mL DMF at 60 °C for 2 h, and then added 0.25 g AIBN to initiate the reaction. The reaction was allowed to proceed in stirring for 48 h with the protection of nitrogen. The mixture was poured into cold methanol and the precipitate was filtered out, dried and then dissolved in a minimum amount of DMF. The product was purified by reprecipitation from methanol for three times, then dried in vacuum at 60 °C for 24 h. Yield: 85%.

Post-azo-coupling reaction (P-2~P-4)

The formulation for post-azo-coupling reactions is shown in Table 1. In a typical synthetic process, *p*-nitroaniline (0.1424 g 1.03 mmol) was dissolved in a solution of 30 HCl (20 mL deionized water and 10 mL hydrochloric acid). The mixture was cooled with an ice bath to lower than 4 °C, and then 0.3 mL aqueous solution containing sodium nitrite (20.13 wt%) was slowly added. The mixture was stirred for 30 min. Sodium dodecyl benzenesulfonate (NaDBS) (0.4 g) and a solution of polymer P-1 (1 g, 3.12 mmol carbazole groups) in nitrobenzene (30 mL) were successively added.

The resultant mixture was vigorously stirred at room temperature for 48 h, and then washed with deionized water. The mixture was poured into cold methanol and the precipitate was filtered out, dried and then dissolved in a minimum amount of THF. The product was purified by reprecipitation from methanol for three times, then dried in vacuum at 40 °C. The productivity is about 90%.

Table 1. Formulation for post-azo-coupling reaction

Sample	<i>p</i> -Nitroaniline (g)	HCl aqueous solution	20.13 wt% NaNO ₂ aqueous solution (mL)	NaDBS (g)	P-1 (g)
P-2	0.1424 (1.03 mmol)	10 mL HCL + 20 mL deionized water	0.3	0.4	1
P-3	0.2374 (1.72 mmol)	10 mL HCL + 20 mL deionized water	0.5	0.4	1
P-4	0.3323 (2.41 mmol)	10 mL HCL + 20 mL deionized water	0.7	0.4	1

Polymer Characterization

All synthesized products were characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet NEXUS-670) in a KBr flake and the proton nuclear magnetic resonance (¹H-NMR) spectroscopy, the spectrum of each sample was obtained from a 400 MHz VARIAN spectrometer using CDCl₃ as solvent. The gel permeation chromatographic (GPC) analysis of the polymer samples were done on an Agilent 1100 Series high performance liquid chromatograph, equipped with an Agilent PLgel column using chloroform (Fisher, HPLC grade) as eluent at a flow rate of 1 mL/min. The number (*M_n*) and weight (*M_w*) average molecular weights of the polymers were determined with Polyethylene Glycol standards purchased from Agilent. The optical properties of polymers were characterized by UV-spectroscopy (UV-3010 spectrophotometer, Hitachi, Japan) and fluorescence (LS55, Perkin Elmer). The glass transition temperature (*T_g*) of purified polymers was characterized by differential scanning calorimetry (DSC-204, Netzsch). The temperature range was from 10 °C to 200 °C, the rate of temperature increasing was 10 K/min, the samples were in a nitrogen-cooling atmosphere (50 mL/min). The thermal gravimetric analysis (TGA-SDTA851, Mettler) was used to characterize the thermal stability of purified polymers.

Photorefractive Measurements

For the photorefractive measurement, polymers P-2~P-4 dissolved in chloroform (1 wt%) were filtered through a 0.22 μm pore Teflon membrane filter, and then dipped onto two indium tin oxide (ITO) glass plates at room temperature. Residual solvent was removed by heating the film at temperatures around *T_g* in vacuum for 12 h. The dried samples were warmed on a hot plate and then the melted samples were sandwiched between the two ITO glass plates by applying a gentle pressure. The sandwiches were cooled quickly to room temperature under pressure, and the thickness of the films was 15 μm. The photorefractive property of 15 μm thick films of P-2~P-4 were determined by two-beam-coupling (TBC) experiments as shown in Scheme 2^[8, 17, 18]. The normal of the samples surface was tilted 35° (in air) relative to the bisector of the incident beams, and the external interbeam angle was 40°. In the TBC experiment, two coherent *p*-polarized laser beams at a wavelength of 442 nm overlapped on the samples. The gain coefficient *Γ* could be calculated by the following approximate formula:

$$\Gamma = \frac{\cos \phi_{\text{in}}}{d} \ln \left(\frac{\beta \gamma_0}{\beta + \gamma_0 - 1} \right) \quad (1)$$

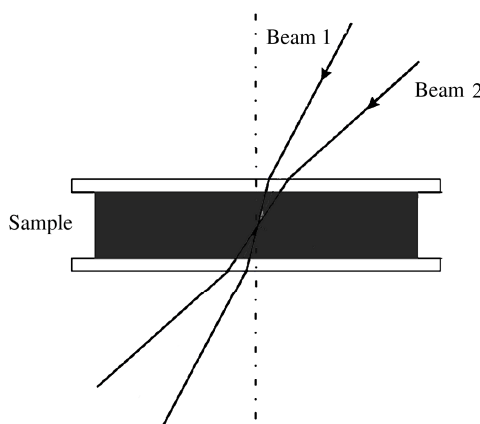
where, *d* is the thickness of the sample, ϕ_{in} is the incident angle of the beam 1 inside the sample, β is the initial intensity ratio of beams after the sample (in the absence of coupling), and $\gamma_0 = I/I_0$ is the beam coupling ratio where *I*₀ is the signal intensity without the pump beam, and *I* is the signal intensity with the pump intensity.

RESULTS AND DISCUSSION

Chemical Structure of Photorefractive Polymers

Polymers P-1~P-4 were characterized by FTIR, the results are shown in Fig. 1. It can be observed that there are some common absorbencies of P-1~P-4: 3050 cm⁻¹, 1596 cm⁻¹, 1484 cm⁻¹, 1452 cm⁻¹ (carbazole); 2933 cm⁻¹ (alkyl—H); 1720 cm⁻¹ (C=O stretching vibration); 1120 cm⁻¹ (C—O—C stretching vibration). Except that, the polymers P-2~P-4 show an intense N=N stretching vibration at 1596 cm⁻¹, and the absorbencies at 1520 cm⁻¹

and 1340 cm^{-1} are assignable to the —NO_2 group, the characteristic absorbance from the phenyl ring is found at 860 cm^{-1} . The results of FTIR proved the successful introduction of the nitrophenyl groups into polymer P-1 and the expected structure of the polymers P-2~P-4.



Scheme 2 The typical tilted geometry for the two-beam coupling experiment

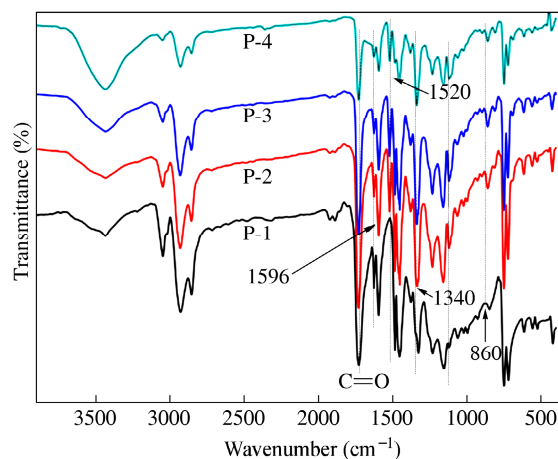


Fig. 1 Infrared spectra of P-1~P-4

The structure of polymers P-1~P-4 were further characterized by $^1\text{H-NMR}$ spectra, the results are shown in Fig. 2. In the $^1\text{H-NMR}$ spectra, there are some similar signals for P-1~P-4. Signals at $\delta = 1.0\text{--}2.2$ are derived from the alkyl groups; Signals at $\delta = 3.5\text{--}4.2$ can be attributed to —NCH_2 or —OCH_2 groups; $\delta = 7.95$ is the signal from the carbazole groups. Except that, there are several new signals appear in the $^1\text{H-NMR}$ spectra of P-2~P-4 at around $\delta = 8.2$ and 8.6 that are not found for P-1. These new signals are derived from the *p*-nitrophenyl moiety, which illustrate the successful formation of the azo-carbazole chromophore. Also, the mole concentration of azobenzene moieties could be calculated from the $^1\text{H-NMR}$ spectra of P-2~P-4. As shown in Fig. 2, after the post-azo coupling reaction, new signal peaks appear at $\delta = 8.2$ and 8.6 . The signal at $\delta = 8.2$ should be ascribed to the carbazole groups linked to the $\text{N}=\text{N}$ groups after the post-azo coupling reaction, because of the influence of the $\text{N}=\text{N}$ groups, the signal peak of the carbazole groups shifts from $\delta = 7.95$ to $\delta = 8.2$. The signal at around $\delta = 8.6$ should be ascribed to the nitrobenzene groups. The mole ratio of the azobenzene moieties in P-2~P-4 can be calculated by comparing the integrations of signal peaks at $\delta = 7.95$ (carbazole groups), 8.2 (carbazole groups) and 8.6 (nitrobenzene groups). The mole ratio of the azobenzene moieties in P-2~P-4 can be calculated by Eq. (2) and the results are shown in Table 2.

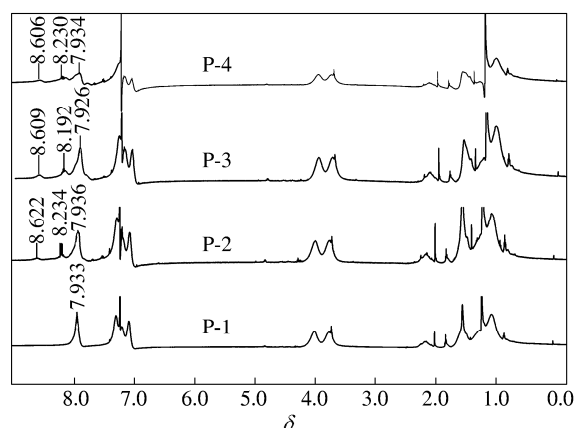


Fig. 2 ^1H -NMR spectra of P-1~P-4

Table 2. The mole ratio of the azobenzene moieties in polymers

Sample index	P-1	P-2	P-3	P-4
Signal area ($\delta 7.95$)	1	1	1	1
Signal area ($\delta 8.2$)	0	0.23	0.27	0.92
Signal area ($\delta 8.6$)	0	0.13	0.18	0.49
Mole percent of the azobenzene groups	0%	18.50%	24.80%	44.66%
X:Y (Scheme 1)	0	1:4.41	1:3.03	1:1.24

$$M = \frac{(S_{\delta 7.95} + S_{\delta 8.2}) / 7}{S_{\delta 8.6} / 4} \quad (2)$$

where, M is the mole ratio of azobenzene moieties; $S_{\delta 7.95}$ is the signal area at $\delta = 7.95$; $S_{\delta 8.2}$ is the signal area at $\delta = 8.2$; 7 means every carbazole group contains seven H atoms after the post-azo coupling reaction. $S_{\delta 8.6}$ is the signal area at $\delta = 8.6$; 4 means every nitrobenzene group contains four H atoms.

From above results and analysis, we can get the conclusion that with increasing of *p*-nitroaniline in feed (Table 1), the mole percent of the azobenzene groups in the structure of polymers P-1~P-4 increases also. In other words, polymers P-1~P-4 have different mole percent of the azobenzene groups in their structure, and the mole ratio of NLO groups in polymers P-1~P-4 is 0%, 18.50%, 24.80% and 44.66% respectively.

The Molecular Information of Polymers P-1~P-4

It can be observed from Table 3 that the number average molecular weight of all polymers P-1~P-4 reaches hundreds of thousands g/mol; the large molecular weight of polymers is favorable to improve the stability of the polymers. With increasing the content of NLO groups, the number average molecular weight and the polydispersity index M_w/M_n of polymers both increase. Because polymers P-2~P-4 have the same precursor P-1, so in theory they should have the same molecular weight and molecular weight distribution before post-azo-coupling reaction. Thus, the differences of their molecular weight and distribution are caused by the different contents of NLO groups which are introduced in their structure through post-azo-coupling reaction. The wide molecular weight distribution of polymers may be caused by the radical polymerization step (P-1) and the post-azo-coupling reaction (P-2~P-4).

Table 3. Molecular weight and molecular weight distribution of polymers P-1~P-4

Sample index	M_n (g/mol)	M_w (g/mol)	M_w/M_n
P-1	0.13×10^6	1.05×10^6	8.08
P-2	0.28×10^6	2.75×10^6	9.82
P-3	0.42×10^6	3.98×10^6	9.48
P-4	0.55×10^6	7.08×10^6	12.83

The Optical Properties of Polymers P-1~P-4

The UV-Vis absorption spectra of the polymers were measured in THF solutions, and the concentration was 0.5 mg/mL. It can be observed from Fig. 3 that after the azo-coupling reaction, a broad absorption ranging from 360 nm to 570 nm with a maximum at 439 nm is observed for polymers P-2~P-4, which is not found for polymer P-1. This broad absorption peak is derived from the increase in the conjugation length (due to the π - π^* transition of the nitro azo chromophore moieties), which further confirms the successful attachment of azobenzene groups to the polymer backbone. Further, it can be observed that with increasing of NLO groups, the absorption band of nitro azo chromophore moieties also increases.

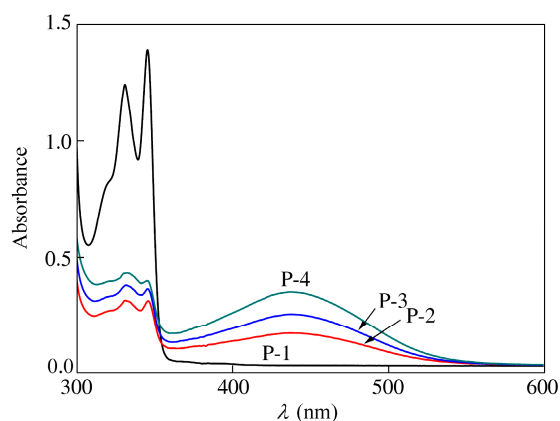


Fig. 3 The UV-Vis absorption spectra of the polymers P-1~P-4 in THF solutions (concentration:0.5 mg/L)

Figures 4 and 5 show the fluorescence excitation and emission spectra of polymers P-1~P-4 in THF solutions. Two fluorescence excitation peaks at around 258 nm and 290 nm for polymer P-1 and one fluorescence excitation peak at around 372 nm for polymers P-2~P-4 can be apparently observed in the Fig. 4. So we use the illuminant of 290 nm to excite the polymer P-1 and that of 372 nm to excite the polymers P-2~P-4, and the fluorescence emission spectra are shown in Fig. 5. It can be observed that polymer P-1 only has one emission peak at around 352 nm, which can be ascribed to fluorescence emission of carbazole moieties. After post-azo coupling reaction, because of the increase of conjugation length (due to the π - π^* transition of the nitro

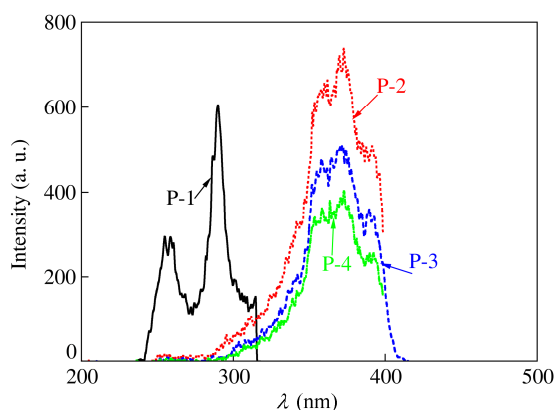


Fig. 4 Variation of fluorescence excitation spectra of polymers P-1~P-4 in THF solutions with the concentration of 0.025 mg/L (P-1: λ_{em} = 352 nm; P-2~P-4: λ_{em} = 405 nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C)

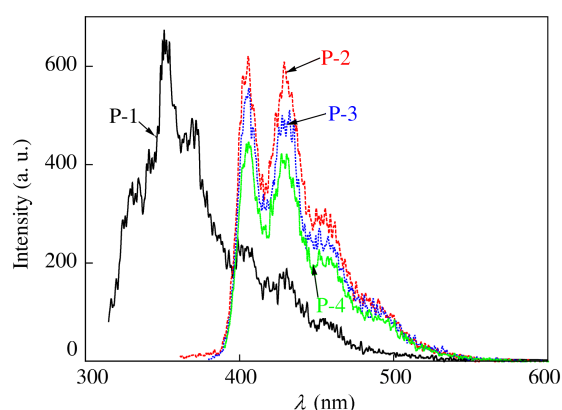


Fig. 5 Variation of fluorescence emission spectra of polymers P-1~P-4 in THF solutions with the concentration of 0.025 mg/L (P-1: λ_{ex} = 290 nm; P-2~P-4: λ_{ex} = 372 nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C)

azo chromophore moieties), the fluorescence emission peaks of P-2~P-4 exhibit red shift, and two fluorescence emission peaks at around 404 nm and 430 nm can be observed apparently. The two peaks are ascribed to the fluorescence emission of carbazole moieties and nitro azo chromophore moieties respectively. With the increasing content of NLO groups, the intensity of emission bands at 404 nm and 430 nm decreases obviously due to the increasing fluorescence quenching effect from $-\text{NO}_2$ groups.

The Thermal Properties of Polymers P-1~P-4

The thermal properties of P-1~P-4 were investigated by thermal gravimetric analysis (TGA) (Fig. 6) and differential scanning calorimetry (DSC) (Fig. 7). The TGA results indicate that polymer P-1 (without NLO groups in structure) has excellent thermal stability with 5% weight loss when the temperature reaches 354.1 °C. It can be observed from the TGA results that polymer P-1 starts to decompose at about 348 °C, and only 2% weight remains when the temperature reaches 400 °C. Its glass transition temperature is found to be about 50 °C. As measured by DSC, the low glass transition temperature of P-1 is due to the flexible backbone of polyacrylate. No melting transition is detected in the DSC curve, which implies polymer P-1 is amorphous. Comparing to P-1, P-2~P-4 (T_g : 59.1 °C, 63.2 °C and 66.4 °C; respectively) have higher glass transition temperature (T_g) due to the introducing of NLO chromophore groups, and the T_g of polymers P-2~P-4 increases with increasing the mole ratio of NLO groups in their structure. The reason is that the NLO group has a long conjugate structure, and is rather rigid, so with increasing the mole ratio of NLO groups, the flexibility of polymers decreases and the T_g increases. However, the T_g of P-2~P-4 is still significantly lower than that of the previously reported polymethacrylate containing the same NLO side groups^[20, 21], and can present the photorefractive effect at room temperature^[16, 17], which is primarily a consequence of the highly flexible character of the polyacrylate backbone. The TGA results indicate that P-2~P-4 have good thermal stability. The TGA curves of polymers P-2~P-4 can be divided into three parts; at the range of 0 °C to about 300 °C, the polymers are stable and just lose very little weight; all these polymers start to decompose quickly at about 320.1 °C until around 500 °C similar to polymer P-1; finally, the decomposition rate decreases with increasing temperature, and the final residual weight increases with increasing the content of NLO chromophore groups.

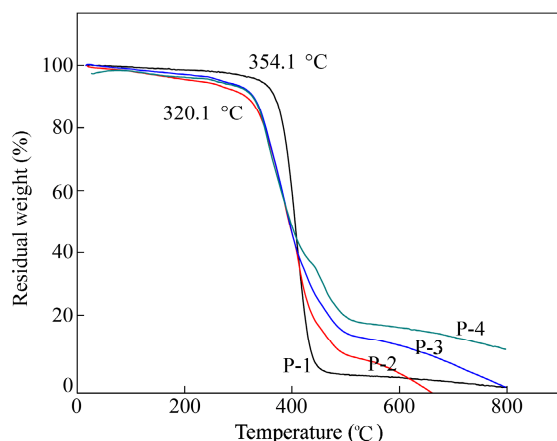


Fig. 6 The thermal gravimetric analysis (TGA) curves of polymers P-1~P-4

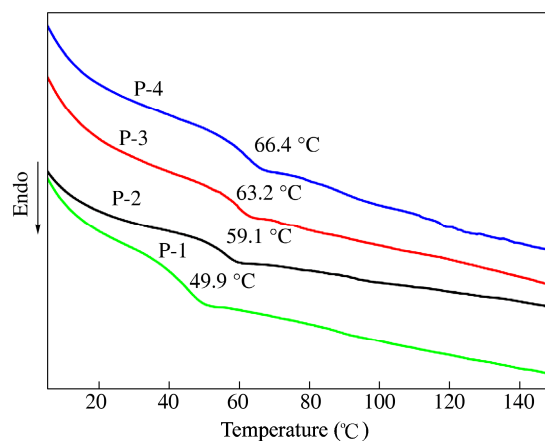


Fig. 7 The differential scanning calorimetry (DCS) curves of polymers P-1~P-4

Photorefractive Properties

The photorefractive performances of the polymers P-2~P-4 were characterized by the two-beam coupling (TBC) experiment. This technique provides a real proof of the photorefractive effect, because it may outrule other possible grafting forming mechanisms as photochromic or thermal gratings. The gain coefficients of 75 cm^{-1} , 185 cm^{-1} and 66 cm^{-1} can be observed at zero external electric field without any addition agent or pre-poling in polymers P-2, P-3 and P-4 respectively. Because polymer P-3 has the best photorefractive effect (185 cm^{-1}), so

the result of energy transfer in TBC experiment of polymer P-3 at zero electric field is shown in Fig. 8. Although there was a high gain coefficient of 214 cm^{-1} reported before for PR polymer composites^[8], our work is the first that reports a single component PR polymer with so excellent photorefractive property. Further, the results indicate that the content of NLO groups in polymers severely influences the photorefractive effect of polymers. When the content of NLO groups is too low, the PR polymer may lack the orientation strengthen and polarization effect, and its PR effect is weak (P-2 with a gain coefficient of 75 cm^{-1}). But when the content of NLO groups is too high, the NLO groups intend to aggregation, weaken the orientation strengthen and polarization effect, the PR effect is weak (P-4 with a gain coefficient of 66 cm^{-1}). Only when the content of NLO groups at a proper range, the PR polymers can present excellent photorefractive property (P-3 with a gain coefficient of 185 cm^{-1}).

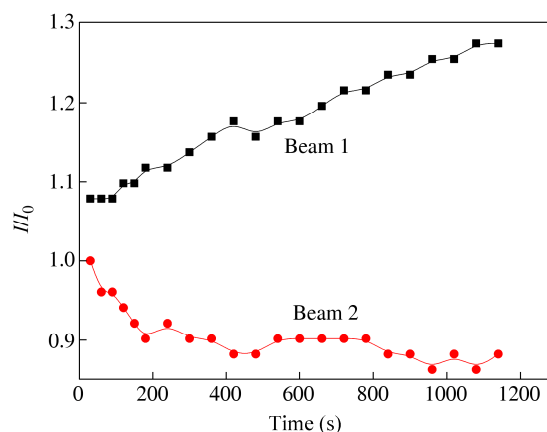


Fig. 8 Energy transfer in TBC experiments of polymer P-3 at zero electric field

CONCLUSIONS

By applying post-functional strategy, the bi-functional photorefractive polyacrylates with NLO chromophores were synthesized. The free radical polymerization was also used in the preparation process. As a result, the polymerization process has good controllability, and it is easy to introduce other copolymerization unites to the backbone to improve the combination property of polymers. These polymers with different mole ratios of NLO groups all show low glass transition temperature around $60\text{ }^{\circ}\text{C}$ and good thermal stability. They all have good solubility in chloroform and can easily be fabricated into optically transparent films with long-term stability. The GPC results show that the polymers prepared through free radical polymerization all have large molecular weight which is favorable to improve the stability of the polymers. The single polymer P-3 has excellent photorefractive property, under the conditions of zero electric field and without any addition agent or pre-poling, its gain coefficient can reach 185 cm^{-1} .

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