

SYNTHESIS AND CHARACTERIZATION OF POLYMERS BEARING AZOBENZENE AND CARBAZOLE GROUPS VIA POST-AZO-COUPLING REACTION*

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Abstract A series of polymers bearing azobenzene and carbazole groups for photorefractive purpose were prepared via post-azo-coupling reaction. The successful reaction was identified by spectroscopic analysis and gel permeation chromatography. This approach is more facile compared with the direct polymerization of corresponding functional monomer. The polymers prepared have weight average molecular weight of higher than 1.5×10^4 and are easily soluble in common organic solvents like chloroform and tetrahydrofuran, polymer films with high optical quality could be easily fabricated through solution casting. Glass transition temperature (T_g) of the polymers ranges from 60°C to 182°C, depending on the alkylene spacer length between the functional side group and the polymer backbone, and the polymers are relatively stable under 300°C.

Keywords: Post-azo-coupling; Carbazole; Azobenzene; Photorefractive.

INTRODUCTION

Polymers with both photoconductive and electrooptic functionalities can be regarded as suitable materials for a wide range of optical and electrooptic applications. There has been much interest in these multifunctional materials that combine the photoconductive and electrooptic components into polymer backbone^[1, 2]. One of the present challenges is to fully exploit the tailorability of polymers so as to design novel electrooptic materials with optimized properties, and to find facile preparation method.

Carbazole-based azo-containing polymers are especially attractive because of their unique electrooptic properties^[3–5]. Conventional synthesis of these polymers, the polymerization of the intrinsic monomers containing both azo and carbazole groups^[2, 6], makes it difficult to obtain a polymer with high molecular weight owing to the bulky volume of the monomers^[6]. In addition, the synthesis of monomer itself is basically complicated and the yield is very low. A noticeable trend for the preparation of electrooptic polymers in the past few years is the post-functionalization approach^[7–10]. The azo coupling reaction was first used to functionalize a copolymer of methyl methacrylate and methacrylate ester of *N*-ethyl-*N*-(hydroxyethyl)aniline in acetic acid medium by Katz *et al.*^[11] Wang and coworkers found that the azo coupling reaction between a polymer and the diazonium salt could be carried out in a polar organic solvent with high product yield^[12], while most post-azo-coupling reaction reported was used in the functionalization on benzene rings.

The present paper presents our recent results using the azo coupling reaction to prepare a series of potential photorefractive polymers. Such an azo coupling reaction enabled us to introduce an nonlinear optical (NLO) chromophore to the polymer bearing carbazole group, and at the same time, the conjugation length of the chromophore was extended as a result. Compared with the conventional direct polymerization, the post-azo-

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coupling reaction gave polymers with much higher molecular weight, and the chromophore content could be easily adjusted. In addition, the result is more facile for the polymeric product purification. Based on this two-step approach, a series of polymers bearing azobenzene and carbazole groups for photorefractive purpose were prepared. The characterization and the thermal properties of these polymers are also discussed.

EXPERIMENTAL

Material

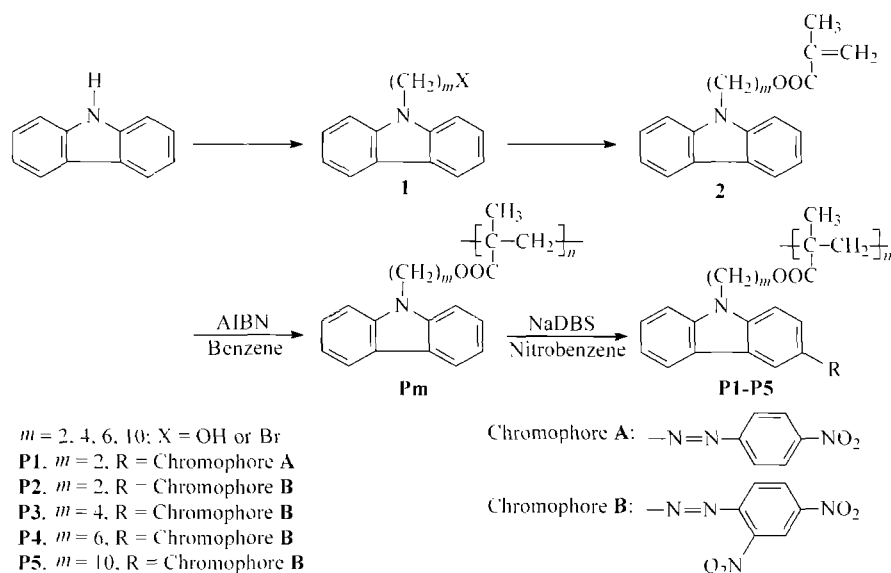
Methacryloyl chloride was prepared from methacrylic acid. Chemicals like carbazole, 4-nitroaniline, 2-chloroethanol and 2,4-dinitroaniline were commercially supplied and used as received. Tetrahydrofuran (THF) and *N,N*-dimethyl formamide (DMF) were dehydrated over calcium hydride and molecular sieves, respectively. Dry pyridine was obtained by refluxing commercial pyridine over potassium hydroxide pellets for 3 h under nitrogen and subsequent distillation.

Measurements

FTIR spectra were recorded on a Nicolet-460 FTIR spectrometer. ^1H -NMR spectra were obtained by a Bruker DRX-400 NMR spectrometer using CDCl_3 as solvent. UV/vis spectra were recorded with a Shimadzu 3010 UV/vis spectrometer using DMF as solvent. Gel permeation chromatography (GPC) analysis was carried out on Waters 515 chromatograph equipped with a refractive index detector; THF was used as the eluent and the calibration was performed with polystyrene standards. Elemental analysis was measured with an MOD-1106 elemental analysis system. Differential scanning calorimetry (DSC) analysis were performed on TA DSC-2920 differential scanning calorimeter at a heating rate of 10 K/min. Thermogravimetric analysis (TGA) was carried out on a Netzsch TGA systems at a heating rate of 10 K/min.

Synthesis

The synthetic procedures for all the polymers are summarized in Scheme 1. Compounds **1** and **2** and polymers Pm were synthesized following literature procedures^{12, 13}. Polymers **P1-P5** were prepared as follows.



Scheme 1 Synthesis route of polymers

Preparation of polymer P1

4-Nitroaniline (5 mmol) was dissolved in a solution of concentrated HCl (2.5 mL) in water (75 mL). The mixture was cooled with an ice bath to lower than 4°C , then an aqueous solution containing sodium nitrite (0.06 g) was slowly added, the mixture was kept stirring for further 30 min. Sodium dodecyl benzenesulfonate

(NaDBS) (1 g) and a solution of polymer Pm (1.4 g) in nitrobenzene (50 mL) were successively added. The resultant mixture was vigorously stirred at room temperature for 30 h, another part of diazonium salt, which was prepared from 5 mmol of 4-nitroaniline and 0.06 g of sodium nitrite, was added. After being vigorously stirred at room temperature for another 30 h, polymer **P1** was isolated by precipitation from methanol as an orange precipitate. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 0.2–1.8 (α -methyl and CH_2 in main chain), 3.7–4.9 ($\text{NCH}_2\text{CH}_2\text{O}$), 6.8–9.0 (aromatic protons).

Preparation of polymers **P2**, **P3**, **P4**, **P5**

Sulphuric acid (10.5 mL) was cooled with an ice bath to below 4°C , sodium nitrite (0.3 g) was added. The mixture was stirred under cooling with an ice bath cooling for a while, then warmed up to 70°C and kept for 3 min. Upon being cooled down again to room temperature, 2,4-dinitroaniline (0.69 g) was added. When a bright yellow clear diazonium salt solution was observed, ice (22.5 g), NaDBS (0.6 g) and a solution of polymer Pm (1.05 g) in nitrobenzene (50 mL) were successively added. The resultant mixture was vigorously stirred at room temperature for 24 h, and the polymer was isolated by precipitation from methanol as a dark red precipitate. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 0.6–2.1 (α -methyl, CH_2 in main chain and $(\text{CH}_2)_n$ in side chain), 3.7–4.8 (NCH_2 and CH_2O), 6.9–8.9 (aromatic protons).

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

The precursor polymers Pm were obtained by radical polymerization of carbazole group bearing methacrylate monomer with different alkylene chain length. The precursor polymers were then functionalized to introduce the chromophore in the second stage of the reaction. The bulkiness of the introduced functional group and steric hindrance of the resulting product would control the electrophilic substitution to take place exclusively at the third position of carbazole. After several experiments, nitrobenzene was selected as the reaction medium in the preparation of the five polymers because of its excellent solubilizability to the precursor polymers. An interesting phenomenon was found: another part of diazonium salt could be added to the system when the diazonium salt in the system was exhausted. A series of polymers P1 with different chromophore contents were prepared using such a method.

The post-azo-coupling reaction was monitored through FTIR measurement. The representative FTIR spectra of polymer **P1** and its precursor are showed in Fig. 1. Polymer **P1** shows the absorption of $\text{N}=\text{N}$ band a 1596 cm^{-1} , and the absorptions of nitro group ($-\text{NO}_2$) appeared around 1522 and 1341 cm^{-1} . Special absorptions for phenyl ring appeared at 820 and 860 cm^{-1} . These evidences indicated the successful introduction of chromophores onto the backbone of the precursor polymer. Similar IR spectral change can also be found for the rest polymers and their precursors.

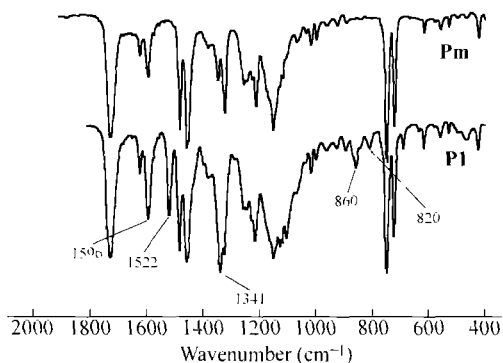


Fig. 1 IR spectra of Pm and polymer 1

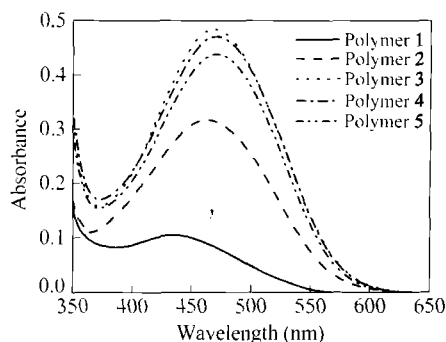


Fig. 2 UV-Vis spectra of polymers
In DMF solution with the concentration of $0.1\text{ }\mu\text{mol/L}$

After the post-azo-coupling reaction, a new broad absorbance in the range of 430–470 nm (in DMF solution with the concentration of 0.1 $\mu\text{mol/L}$) can be observed in the UV-vis spectra of polymers showed in Fig. 2, which could not be observed in the corresponding precursor polymer. The absorbance extension to longer wavelength indicated the enlargement of conjugated structure in the resultant polymers. The data listed in Table 1 also indicated that the λ_{max} of polymers **P2** to **P5** have little difference, which suggests that there is no appreciable variation in the electronic environment of the chromophores in this series of polymers. While the λ_{max} of polymer **P1** has been obviously blue-shifted compared to other polymers owing to the less content in the nitro group.

Table 1. Properties of the resultant polymers

Polymer	M_n^a	M_w^a	M_w/M_n^a	NLO (mol% $\pm 10\%$) ^b	λ_{max} (nm) ^c
P1	13000	25000	2.10	80	434
P1 [*]	3300	4700	1.42	100	434
P2	13000	27000	2.10	77	468
P2 [*]	3300	4800	1.43	100	468
P3	9900	15569	1.57	70	469
P4	23700	37700	1.59	30	471
P5	12500	21000	1.68	103	470

^a Measured by GPC; ^b Calculated from elemental analysis; ^c Measured by UV/vis spectroscopy in DMF solution with the concentration of 0.1 $\mu\text{mol/L}$. ^{*} Direct polymerization related to Ref. [6].

The content of NLO chromophore in polymers was calculated based on elemental analysis measurements, and the results are also listed in Table 1. Polymer **P5** has relatively higher chromophore contents. A possible reason for the high content is comparatively far distance between the polymer backbone and the attaching functional group ($m = 10$). The less steric hindrance resulted in the easier attack for the azo group to the carbazole group. All the polymers with different alkylene spacers ($m = 2$ –10) between the polymer backbone and the functional attacking group exhibits good solubility in common organic solvents, such as chloroform, THF and DMF as illustrated in Table 2. Polymer films with high optical quality could be easily fabricated through solution casting.

Table 2. Solubility of the polymers

Polymer	m	Solubility ^a		
		CHCl_3	THF	DMF
P1	2	+	++	++
P2	2	+	+	++
P3	4	+	+	++
P4	6	+	+	++
P5	10	+	++	++

^a ++ Soluble at room temperature; + Soluble on warming

From the molecular weight comparison of the polymers shown in Table 1, it can be realized that the polymers obtained by post-azo-coupling reaction have obviously higher molecular weight than that of the polymers obtained by conventional direct polymerization. The carbazole monomer bearing the chromophore contains azobenzene and nitro- group that may act as an inhibitor for the free radical polymerization.

Thermal Properties

The DSC curves of polymers **P1**–**P5** are shown in Fig. 3, the T_g of the polymers was depressed with the increase in the alkylene chain length. This suggests that there is a substantial increase in the segmental mobility from shorter to longer spacer length. The tendency in T_g changes is in agreement with the characterization results of a similar series of poly(*n*-methylenecarbazole) photorefractive polymers^[6]. It can also be observed that the T_g of the

polymer containing one nitro group in the chromophore (**P1**) is lower than that of the corresponding polymer containing two nitro groups in the chromophore (**P2**). The thermal stability of the polymers was characterized by thermogravimetric analysis (TGA) as showed in Fig. 4. It can be observed that all the polymers started to lose weight in the temperature range of 285–300°C. Different shapes of the TGA curves exhibited the difference in the mechanism of decomposition process according to different chromophore and spacer length.

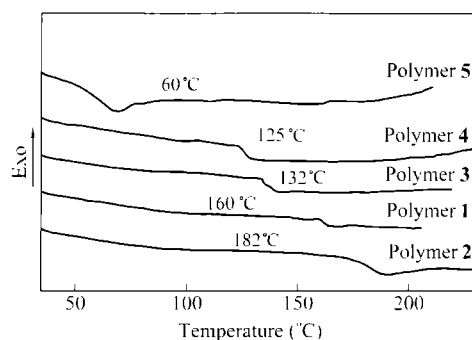


Fig. 3 DSC curves of polymers heating rate 10 K/min

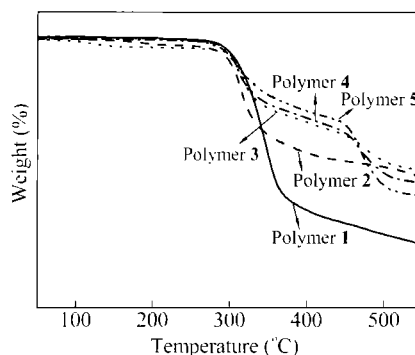


Fig. 4 TGA curves of polymers heating rate 10 K/min

Detailed examination on NLO and photorefractive properties of these carbazole-based polymers will be carried out in future work.

CONCLUSION

A series of new carbazole-based azo group containing polymers with high molecular weight have been prepared by post-azo-coupling reaction. The preparation of these polymers via post-azo-coupling reaction is more facile and gave higher molecular weight than conventional direct polymerization. Chromophore content in these polymers changes from 30 mol% to 103 mol% ($\pm 10\%$). All these polymers are soluble in common organic solvents and relatively stable under 300°C.

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