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Polymer 48 (2007) 3650–3657

polymer

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Controlling nonlinear optical effects of polyurethanes by adjusting isolation spacers through facile postfunctional polymer reactions

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Received 11 February 2007; received in revised form 21 April 2007; accepted 26 April 2007
Available online 3 May 2007

Abstract

With the aim to control nonlinear optical (NLO) effects of polyurethanes, especially to efficiently translate the fixed $\mu\beta$ values of the organic chromophore to possibly higher macroscopic NLO activities of polymers, a facile synthetic strategy, consisting of the postazo coupling and esterification reactions, was developed to prepare a series of second-order nonlinear optical polyurethanes (**P2**–**P5**). And in the polymers, different isolation groups were introduced to the sulfonyl-based chromophore moieties at the acceptor side. Thus, polyurethane **P1** containing aniline groups was obtained from the copolymerization of 2,4-toluenediisocyanate (TDI) and *N*,*N*-2-(2-hydroxyethyl)aniline directly; then a post-azo coupling reaction of *p*-(2-hydroxyethyl)sulfonylbenzenediazonium fluoroborate toward the aniline ring afforded the sulfonyl-based chromphore-functionalized polyurethane **P2**, which underwent the subsequent esterification reactions between the hydroxyl groups in **P2** and different organic acids to link different isolation spacers (changing from small groups to much larger ones such as carbazolyl groups), to the chromophore moieties at the acceptor side, to yield polyurethanes **P3**, **P4** and **P5**. The polymers exhibit good solubility in common organic solvents and are thermally stable. The maximum absorption appeared at about 436 nm with a cutoff at ca. 570 nm, resulting in a wider transparency window. The tested NLO properties demonstrate that the resonant d_{33} values of polymers could be improved about 1.5 times by attaching isolation spacers with suitable bulkiness.

Keywords: Polyurethanes; Nonlinear optical effect; Postfunctional synthetic method

1. Introduction

Organic and polymeric second-order nonlinear optical (NLO) materials have extensive potential for use in integrated optical devices, and thus attracted considerable attentions over the past two decades [1,2]. One of the major problems still encountered in optimizing organic NLO materials is to efficiently translate the large $\mu\beta$ values of the organic chromophores, where μ and β are the dipole moment and the first hyperpolarizability, into high macroscopic NLO activities of polymers [3]. By the attachment of some isolation spacers, or through the introduction of the NLO chromophore moieties to dendrimers, this problem could be alleviated in some degree, according to the site isolation principle [4–6]. And recent researches demonstrate that the macroscale NLO properties of NLO dendrimers and polymers containing dendronized NLO chromophores as side groups are heavily related to the subtle difference in architectural design [7]. However, there are still scarce information concerning the relationship between the structure of isolation spacers and the resultant macroscopic NLO effects of the polymers. Or, in other words, we do not know which size, including length, flexibility and polarity of isolation spacer should be adapted for a certain chromophore to boost its microscopic $\mu\beta$ value to possibly higher macroscopic NLO property efficiently. Thus, it is needed to study the structure–property relationship in detail.

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0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.04.062

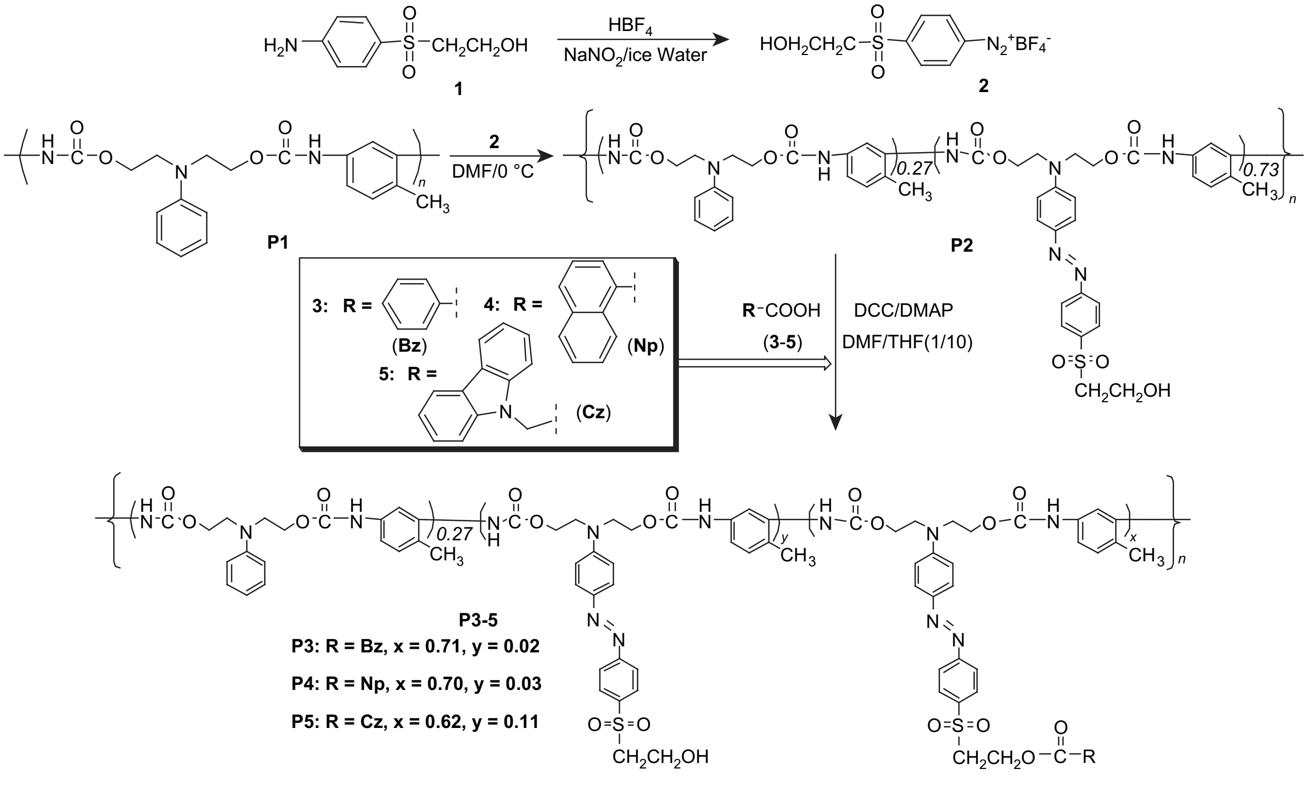
In the past several years, we are interested in the design and preparation of functional polymers (most of them are NLO polymers), and developed some new synthetic strategies with the aim to obtain polymers with good properties easily and conveniently, in which the postfunctional methods through the polymer reactions are our favorite [8,9]. Using the postfunctional polymer reactions, we have not only successfully simplified the preparation and purification procedures of functional polymers, but also solved some synthetic difficulties, for example, avoiding the unreacted SiH groups in the polysiloxane system encountered in the straightforward preparation method [9e,g,10], increasing the linked concentrations of NLO chromophores in the polyphosphazene system [8a,b,9d], obtaining some functional disubstituted polyacetylenes which perhaps could not be prepared from the direct polymerization of their corresponding monomers [9a,b], and introducing C_{60} and carbon nanotubes to different polymeric systems [8g,9b,c].

In this work, we tried to study the effect of the different size of isolation spacer on the resultant NLO properties, and based partly on our previous work [8,9], we would like to prepare the target polymers through postfunctional strategy. The common azo chromophores with sulfonyl groups as the acceptor were used as the NLO active units, since they are easily obtained, widely studied, combined with some advantages such as much wider transparency in visible region (with hypsochromic shift of 20–40 nm compared to their analogues with nitro groups as the acceptor) and synthetic flexibility [11]. The designed polymers (Scheme 1), in which the size of isolation spacer changed from small atoms such as hydrogen to much larger groups (carbazolyl groups), were synthesized by the postazo coupling and esterification reactions, which were frequently used in our previous work [8,9] and reported in the literatures [2g,6c,7b]. The synthetic procedure is very simple, and the polymers could be purified easily by several precipitations from their THF solutions into methanol. The tested NLO properties demonstrate that the NLO values of the polymers are not always increased with increasing size of the isolation spacer. Herein, we would like to report the syntheses, characterization, and NLO properties of these polymers.

2. Experimental section

2.1. Materials

Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. *N*,*N*-Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. 2,4-Toluenediisocyanate (TDI) was purified by distillation under reduced pressure before use. All other reagents were used as received. *p*-(2-Hydroxyethyl)sulfonylaniline (**1**) and *N*-carbazolylacetic acid (**5**) were synthesized according to the methods reported in the literatures [12]. Polyurethane **P1** was obtained from the copolymerization of 2,4-toluenediisocyanate (TDI) and *N*,*N*-2-(2-hydroxyethyl)aniline under similar polymerization conditions as reported previously [13]. Chromophore **6** was



Scheme 1.

synthesized from *N*,*N*-2-(2-hydroxyethyl)aniline and *p*-(2-hydroxyethyl)sulfonylaniline (**1**) through the normal azo coupling reaction for comparison [14].

2.2. Instrumentation

^{1}H NMR spectroscopy study was conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 4000–400 cm^{-1}. UV–vis spectra were obtained using a Shimadzu UV-2550 spectrometer. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent and the flow rate was 1.0 mL/min. Thermal analysis was performed on Netzsch STA449C thermal analyzer at a heating rate of 20 °C/min in nitrogen at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a Mettler differential scanning calorimeter DSC822e under nitrogen at a scanning rate of 10 °C/min. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

2.3. Synthesis of p-(2-hydroxyethyl)sulfonylbenzenediazonium fluoroborate (**2**)

p-(2-Hydroxyethyl)sulfonylaniline (**1**) (1.01 g, 5.00 mmol) was dissolved in fluoroboric acid (40%), and then the solution was cooled to 0 °C. A solution of sodium nitrite (0.45 g, 6.52 mmol) in ice water (1 mL) was added dropwise. The resultant mixture was stirred at 0 °C for half an hour and then was put into a refrigerator overnight. The yellow solid was filtered quickly and washed with cool ethanol and ether for several times. After this, the product **2** was stored in the refrigerator (1.53 g, 96.8%).

2.4. Synthesis of **P2**

Polyurethane **P1** (1.44 g) was dissolved in DMF (14.5 mL), and then compound **2** (1.42 g) was added under cooling with an ice bath. The color of the solution changed to red immediately. After stirring for 10 h at 0 °C, excessive anhydrous potassium carbonate was added, and the mixture was stirred for an additional 0.5 h, and then filtered. The residue was washed with THF, the filtrates were collected, and THF was removed under reduced pressure. Then the solution was added dropwise to the stirring methanol to precipitate the polymer. The solid was further purified by several precipitations from THF into methanol. The solid obtained was dried in a vacuum at 40 °C to yield an orange-red product **P2** (1.73 g, 73.3%). $M_w = 7100$, $M_w/M_n = 1.33$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1722 (C=O), 1599 (–C=C–), 1128 (–SO$_2$). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.1 (–CH$_3$), 3.4–3.5 (–CH$_2$SO$_2$–), 3.6–3.9 (–N–CH$_2$– and –CH$_2$OH), 4.1–4.4 (–CH$_2$OCO–), 6.6 (ArH), 6.8 (ArH), 6.9–7.2 (ArH), 7.5 (ArH), 7.8–8.0 (ArH), 8.8–9.0 (–NH–), 9.5–9.7 (–NH–). UV–vis (THF, 0.02 mg/mL): λ_{max} (nm): 437.

2.5. General procedure for the synthesis of **P3–P5**

P2 (1.00 equiv), compound **3** or **4** or **5** (5.00 equiv), and 4-(*N*,*N*-dimethyl)aminopyridine (DMAP) (0.4 equiv) were dissolved in THF/DMF (10:1 in volume), then dicyclohexylcarbodiimine (DCC) (5.00 equiv) was added. The resultant mixture was allowed to stir at room temperature for 72 h under nitrogen, then filtered to remove the insoluble solid. The filtrate was added to the stirring methanol to precipitate the polymer. The resultant precipitate was collected, and washed with large amount of methanol and diethyl ether to afford polymer **P3–P5**.

P3. Orange-red powder with the yield of 90.3%. $M_w = 9500$, $M_w/M_n = 1.33$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1727 (C=O), 1603 (–C=C–), 1132 (–SO$_2$). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.1 (–CH$_3$), 3.5–3.7 (–N–CH$_2$–), 3.7–4.0 (–N–CH$_2$– and –CH$_2$SO$_2$– and –CH$_2$OH), 4.1–4.4 (–CH$_2$OCO–), 4.5–4.7(–CH$_2$OCO–), 6.6 (ArH), 6.8 (ArH), 6.9–7.3 (ArH), 7.4–7.6 (ArH), 7.7–7.9 (ArH), 7.9 (ArH), 8.0–8.1 (ArH), 8.8–9.0 (–NH–), 9.5–9.7 (–NH–). UV–vis (THF, 0.02 mg/mL): λ_{max} (nm): 436.

P4. Orange-red powder with the yield of 90.6%. $M_w = 10\,200$, $M_w/M_n = 1.60$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1722 (C=O), 1599 (–C=C–), 1128 (–SO$_2$). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.1 (–CH$_3$), 3.5–3.7 (–N–CH$_2$–), 3.7–4.0 (–N–CH$_2$– and –CH$_2$SO$_2$– and –CH$_2$OH), 4.1–4.4 (–CH$_2$OCO–), 4.5–4.7 (–CH$_2$OCO–), 6.6 (ArH), 6.8 (ArH), 6.9–7.2 (ArH), 7.2–7.3 (ArH), 7.4–7.6 (ArH), 7.7–7.9 (ArH), 7.9–8.1 (ArH), 8.1 (ArH), 8.7 (ArH), 8.8–9.0 (–NH–), 9.5–9.7 (–NH–). UV–vis (THF, 0.02 mg/mL): λ_{max} (nm): 436.

P5. Orange-red powder with the yield of 97.2%. $M_w = 10\,600$, $M_w/M_n = 1.33$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1731 (C=O), 1603 (–C=C–), 1128 (–SO$_2$). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.1 (–CH$_3$), 3.5–3.6 (–N–CH$_2$–), 3.7–4.0 (–N–CH$_2$– and –CH$_2$SO$_2$– and –CH$_2$OH), 4.1–4.5 (–CH$_2$OCO–), 5.0 (–N–CH$_2$CO–), 6.8 (ArH), 6.9–7.2 (ArH), 7.3–7.6 (ArH), 7.7–7.9 (ArH), 7.9–8.2 (ArH), 8.8–9.0 (–NH–), 9.5–9.7 (–NH–). UV–vis (THF, 0.02 mg/mL): λ_{max} (nm): 437.

2.6. Preparation of polymer thin films

The polymers were dissolved in THF (concentration ~3 wt%) and the solutions were filtered through syringe filters. Polymer films were spin-coated onto indium-tin-oxide (ITO)-coated glass substrates, which were cleaned by DMF, acetone, distilled water and THF sequentially in ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

Table 1
Polymerization results and characterization data

No.	Yield (%)	M_w[a]	M_w/M_n[a]	λ_{max}[b] (nm)	T_g[c] (°C)	T_d[d] (°C)	T[e] (°C)	l_s[f] (μm)	d_{33}[g] (pm/V)
P1	90.8	6800	1.64						
P2	73.3	7100	1.33	437	131	223	135	0.31	31.6
P3	90.3	9500	1.33	436	111	213	128	0.35	39.3
P4	90.6	10 200	1.60	436	114	223	124	0.24	45.6
P5	97.3	10 600	1.33	437	126	213	128	0.29	41.8

[a] Determined by GPC in THF on the basis of a polystyrene calibration.
[b] The maximum absorption wavelength of polymer solutions in THF.
[c] Glass transition temperature (T_g) of polymers detected by the DSC analyses under nitrogen at a heating rate of 10 °C/min.
[d] The 5% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 20 C/min.
[e] The best poling temperature.
[f] Film thickness.
[g] Second harmonic generation (SHG) coefficient.

2.7. NLO measurement of poled films

The second-order optical nonlinearity of the polymers was determined by in-situ second harmonic generation (SHG) experiment using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously while the poling temperature was increased from room temperature to the best poling temperature. That is to say, the SHG signals were collected when the films were poled and the temperature was increased. Poling conditions were as follows: temperature: different for each polymer (Table 1); voltage: 7.5 kV at the needle point; gap distance: 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating at a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

3. Results and discussion

3.1. Synthesis

As shown in Scheme 1, **P2**–**P5** were easily yielded through the simple postfunctional methods. First, polyurethane **P1** was obtained from two cheap commercial products, TDI and *N*,*N*-2-(2-hydroxyethyl)aniline; secondly, **P2** with terminal hydroxyl groups in the side chains was synthesized *via* a postazo coupling reaction between **P1** and *p*-(2-hydroxyethyl)sulfonylbenzenediazonium fluoroborate, similar as we have reported previously in other cases [8a,b,d]; and then different isolation spacers were bonded to the chromophore moieties through the normal esterification reaction to give **P3**, **P4** and **P5** with high yields conveniently. Therefore, the structures of **P3**, **P4** and **P5** are similar, except the different isolation group at the terminal side. And the linkage of the isolation groups would not affect the electronic properties of the sulfonyl-based chromophore moieties, since there are no conjugation bridges between the chromophore moieties and the isolation spacers. Thus, it is convenient to compare the NLO properties of the resultant polymers, in which the size of the isolation spacers changed from small groups, such as hydrogen atoms in **P2**, to much larger ones such as carbazolyl groups in **P5**.

The reaction conditions are mild, and the purification is simple. The most special point is that different isolation groups with different size, could be easily linked to the chromophore moieties on the acceptor side, to control the subtle architecture of the resultant polymers, leading to the possible adjustment of the macroscopic NLO effects of the resultant polymers. Thus, from the postesterification reaction, more NLO polymers with different isolation spacers could be prepared conveniently to boost the high microscopic β values of the chromophores to possibly larger macroscopic NLO property of the corresponding polymers efficiently. Actually, so far, there are few examples reported in the literatures, in which a hydroxyl group could be easily handled on the chromophore moieties for further functionalization.

Also, it should be pointed out that **P2** could not be prepared from the direct polymerization procedure, but only be obtained from the postfunctional method, indicating the synthetic flexibility of the postfunctional strategy. And in this work, the different reactive property of the amino and hydroxyl groups was rationally utilized to fulfill the whole synthetic process, with the combination of the postazo and esterification reactions. Thus, our preliminary results partially demonstrate the power of the cooperating usage of different kinds of reactions in the postfunctional strategy, and might attract increasing interests of other scientists to contribute in this area for the further development of the polymer chemistry, in addition to the traditional straightforward synthetic methods of polymers.

3.2. Structure characterization

The polymers were characterized by spectroscopic methods, and all give satisfactory data (see Section 2 and Table 1 for detailed analysis data). In all the IR spectra of **P1**–**P5** (Fig. 1), a strong absorption peak appeared at 1720 cm^{-1}, which was attributed to the vibration of the carbonyl groups. After the postazo coupling reaction, the absorption band peaked at 1128 cm^{-1} became much stronger in **P2**, which was ascribed to the absorption of the sulfonyl groups. This confirmed that the sulfonyl groups were introduced to the polymer side chains successfully. The curves of **P3**–**P5** were similar to that of **P2**, the absorption of the new bonded carbonyl groups in the process of the postesterification

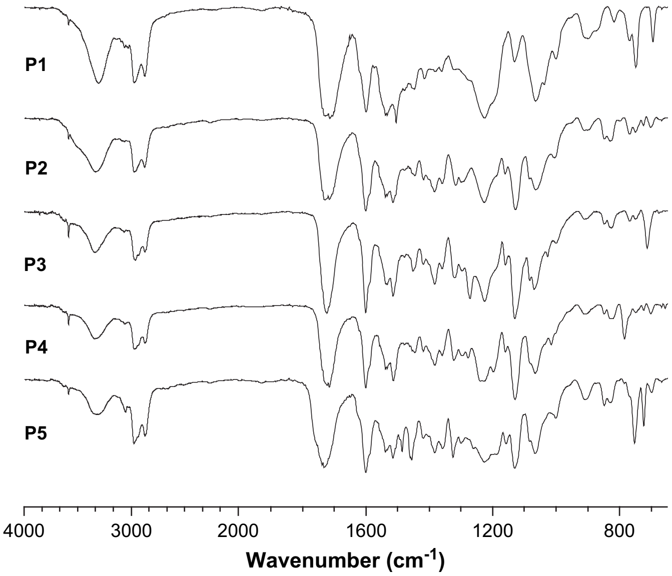


Fig. 1. IR spectra of polymers **P1**–**P5**.

reaction was masked by those of many carbonyl ones present in the main chains of the polymers.

In all the ^{1}H NMR spectra of the polymers **P1**–**P5**, the chemical shifts are consistent with the proposed polymer structures demonstrated in Scheme 1. Fig. 2 shows the ^{1}H NMR spectra of **P1**, **P2** and **P4** as examples. Some resonance peaks appearing at about 7.9 ppm in **P2**, which were due to the *p*-(2-hydroxyethyl)sulfonylphenyl moieties, also confirmed that the azo coupling reaction was successful and the azo chromophore really formed. The ratio of the two kinds of aniline groups in **P2**, aniline and sulfonylazoaniline moieties, could be determined accurately as 0.27:0.73, by UV–vis absorption spectra as discussed below. After the esterification reaction, the concentrations of the aniline moieties in **P3**–**P5** are the same as that in **P2**, the signal of the methylene groups linked to the hydroxyl groups previously, would appeared at about 4.6 ppm rather than 3.9 ppm in **P2**, so the ratio of two kinds of azo chromophores in **P3**, without isolation groups and with isolation groups, was estimated to be 0.02:0.71 by analyzing the peaks of two protons in the range of 4.5–4.7 ppm and four protons in the range of 4.1–4.4 ppm carefully. By the same method, for **P4**, the ratio was estimated to be 0.03:0.70, and for **P5**, the ratio was 0.11:0.62. Also, the ratio could be calculated by analyzing the integration area of the new signals appearing in the down field derived from the proton in the organic acid with those of other methylene groups; for example, as shown in Fig. 2, in **P4**, there is a typical signal at 8.7 ppm ascribed to one proton in naphthyl moieties, and the peak of the methylene groups linked with nitrogen atoms was at about 4.2 ppm, thus it was easy to calculate the molar ratio of the two different azo chromophore moieties by comparing their integration carefully. In **P5**, there is also a typical signal at 5.0 ppm, ascribed to two protons in methylene of carbazolyl acid moieties, thus we could calculate the molar ratio of the two different azo chromophore moieties by comparing their integration carefully.

P1–**P5** are soluble in common organic solvents, such as THF, DMF and DMSO. Their solutions could be easily spin-coated into thin solid films, and therefore, it is convenient to test their NLO properties based on the thin films. The UV–vis absorption spectra of polymers in THF solution are shown in Fig. 3. After the azo coupling reaction, **P2** exhibits a new strong absorption peak at ~437 nm due to the π–π^* transition of the sulfonyl azo chromophore, with a band edge of ~570 nm. The polymer thus has a wide transparency window, which should contribute to low optical loss, and confirmed the advantages of sulfonyl-based chromophore again. It is noticed that **P2**–**P5** have about the same λ_{max} (437 nm), further indicating that the attachment of the isolation spacers did not

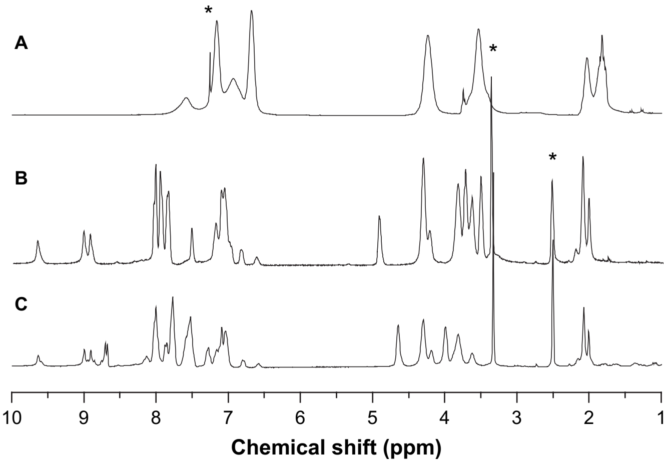


Fig. 2. ^{1}H NMR spectra of (A) **P1** in $CDCl_3$, (B) **P2**, and (C) **P4** in DMSO-d_6. The solvent and water peaks are marked with asterisks (*).

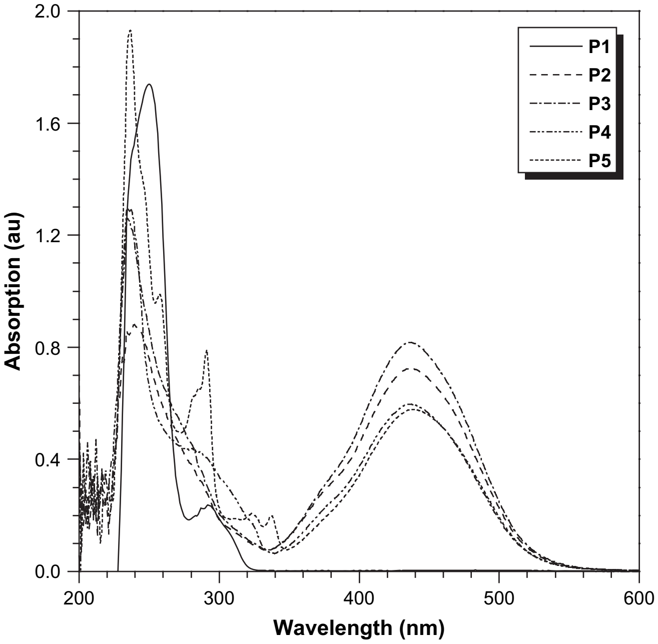
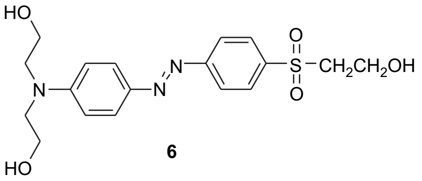


Fig. 3. UV–vis absorption spectra of THF solutions of polymers **P1**–**P5** (concentration: 0.02 mg/mL).



6

Fig. 4. The structure of chromophore **6**.

influence the electronic properties of the chromophore moieties in the polymers, thus it is feasible to compare their NLO properties and study the structure–property relationship at nearly the same level.

To determine the concentration of the azo moieties in **P2**, a model compound (**6**, Fig. 4) was prepared. A series of THF solutions of **6** with concentration in the range of 1×10^{-5}–5×10^{-5} mol/L were prepared and a calibration curve was drawn from their absorption data in UV–vis spectra at 437 nm. The spectrum of a THF solution of **P2** (0.02 mg/mL) was then measured. Using the calibration curve, the molar ratio of the sulfonylazoaniline moieties in **P2** was calculated to be 0.73.

The molecular weights of polymers were determined by gel permeation chromatography (GPC), with THF as an eluent and polystyrene standards as calibration standards. All the results are summarized in Table 1, and most of polymers possess similar molecular weights, which would facilitate the comparison of their properties on the same level. The polymers are thermolytically resistant. Their TGA thermograms are shown in Fig. 5, and the 5% weight loss temperature of polymers are listed in Table 1. All of the polymers exhibited nearly the same thermal stability. The glass transition temperature (T_g) of the polymers was investigated using a Setaram differential scanning calorimeter (Table 1). **P3** and **P4** have a moderate T_g (~110 °C), and **P5** has a higher T_g of 126 °C, partially due to the strong secondary forces between polymer chains. And the introduced bulky isolation groups might also contribute to the higher T_g of **P5**.

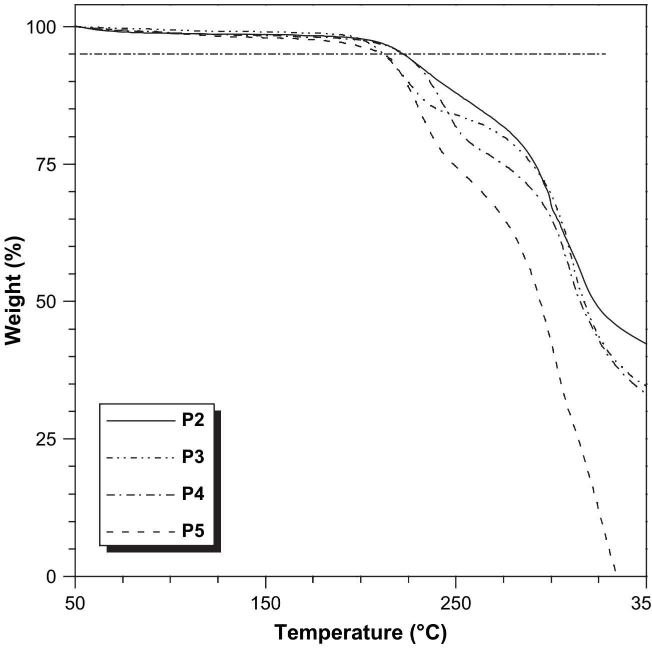


Fig. 5. TGA thermograms of **P2**–**P5** measured in air at a heating rate of 20 °C/min.

3.3. NLO properties

To evaluate the NLO activity of the polymers, their poled thin films are prepared. The most convenient technique to study the second-order NLO activity is to investigate the second harmonic generation (SHG) processes characterized by d_{33}, an SHG coefficient. To check the reproducibility, we repeated the measurements several times for each sample. The method for the calculation of the SHG coefficients (d_{33}) for the poled films has been reported in our previous papers [8]. From the experimental data, the d_{33} values of **P2**–**P5** are calculated at 1064 nm fundamental wavelength (Table 1).

It is not strange that the four polymers exhibit different d_{33} values for their different structures. However, it seems that there are no rules present in the tested results at the first glance. Fig. 6(A) shows the comparison of the d_{33} values of the polymers, using **P2** as the reference. It is seen that the d_{33} values are not always increasing as the isolation groups enlarged, and the naphthalene group (Np) is the best isolation moieties in this system.

As discussed above, the four polymers contain the same active NLO chromophore moieties, and the linkage of the isolation spacers did not affect the electronic properties of the chromophore moieties, thus the different NLO properties of the polymers should be caused by the difference in the isolation groups, and especially related to their size. However, on

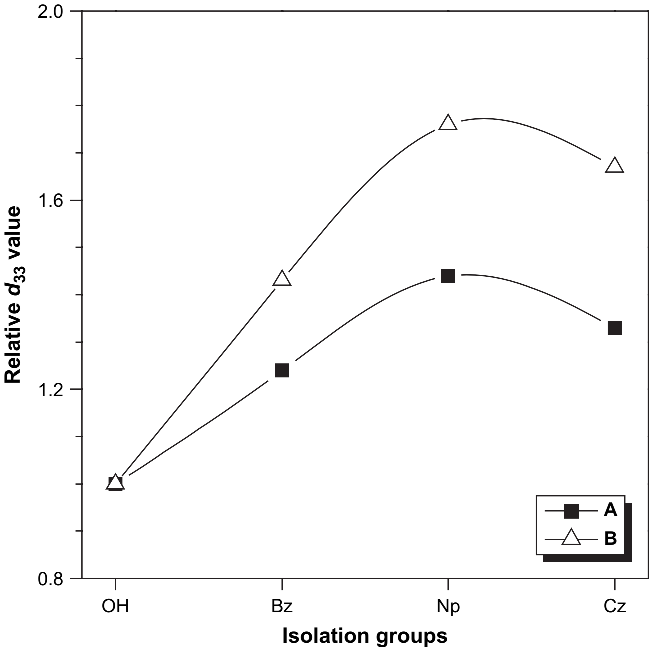


Fig. 6. (A) The comparison of the d_{33} values of the polymers using **P2** as the reference. (B) The comparison of the calculated d_{33} values, which were obtained using the tested d_{33} values dividing the concentration of the active chromophore moieties of the polymers using **P2** as the reference.

the other hand, the introduction of different isolation groups would surely lead to the different molar weights of the obtained chromophores. According to the one-dimensional rigid orientation gas model [15]:

$$d_{33} = \frac{1}{2} N\beta f^{2\omega}(f^{\omega})^2 \langle \cos^3 \theta \rangle \qquad (1)$$

where N is the number density of the chromophore, β is its first hyperpolarizability, f is the local field factor, 2ω is the double frequency of the laser, ω is its fundamental frequency, and $\langle \cos^3\theta \rangle$ is the average orientation factor of the poled film. Here, the active NLO chromophore moieties are the same, which exhibit the same first hyperpolarizability (β), thus under identical experimental conditions, d_{33} should be proportional to the number density of the chromophore moieties in the polymers. Therefore, we considered the different molar concentrations of the active chromophore moieties in the polymers, used the tested d_{33} values dividing the molar concentrations of the active chromophore moieties in the polymers, and compared the results again with that of **P2** as the reference.

Fig. 6(B) demonstrates the comparison of the calculated d_{33} values of the polymers. Similar to the results shown in Fig. 6, the d_{33} value reaches the peak value while the isolation group is naphthalene group (Np). Then it is obvious that for a special NLO chromophore, the d_{33} values of the resultant polymers are not always increasing as the isolation groups enlarged, even only when the concentration of the active chromophore moieties in the system is considered.

As we know, the push–pull NLO chromophores with large dipole moments tend to compactly pack in a centrosymmetric manner due to the strong intermolecular dipole–dipole interactions, making poling-induced noncentrosymmetric alignment of chromophores a daunting task. And the purpose of controlling the shape of the chromophores or introducing isolation groups is to minimize the strong intermolecular dipole–dipole interactions and reduce chromophore aggregation at high loading density (positive effect), in order to improve the d_{33} values of the materials. And in our case, we also would like to minimize the interactions using different isolation groups on the acceptor side. However, the addition of the isolation groups would increase the bulky of the resultant chromophore moieties, which makes the noncentrosymmetric alignment of the chromophores under the electronic field more difficult (negative effect). So, while the bulky of isolation groups introduced were increased gradually, the NLO properties, however, do not always increase at the same time. When the isolation groups are moderate, such as the benzene (Bz) and naphthalene (Np) groups, the positive effect is obvious while the negative effect, perhaps, is negligible, so the NLO properties becomes better; but when the isolation group is even larger, such as carbazolyl (Cz) group, the positive effect is still okay or even better, however, the negative effect does work now, cancels the positive effect partly, so the NLO properties begin to decrease.

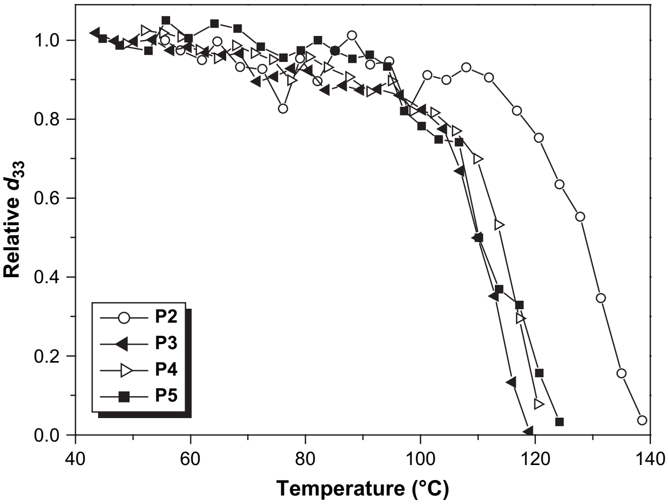


Fig. 7. Decays of SHG coefficient of **P2**–**P5** as a function of temperature.

The dynamic thermal stabilities of the NLO activities of the polymers are investigated by the depoling experiment, in which the real time decays of their SHG signals are monitored as the poled films are heated from 45 to 150 °C in air at the rate of 4 °C/min (Fig. 7). The results indicated that the long-term temporal stability of the polymers are relatively good with the onset temperatures for decays in the d_{33} values around 100 °C, and the better stability of **P2** should be due to the presence of the hydroxyl groups, which might undergo thermal crosslinking process between the hydroxyl groups and the isocyanate moieties during the experiment. Indeed, **P2** demonstrates a large exothermic peak starting from 79 to 113 °C in its DSC thermograms, indicating the crosslinking reactions upon heating.

4. Conclusions

A series of polyurethanes containing sulfonyl-based NLO chromophores, which could not easily be obtained from the direct synthetic route, were prepared through a two-step polymer reaction conveniently with high yields. The obtained polymers were soluble in common polar solvents and well characterized. Our preliminary study demonstrates the following.

1. A postfunctional approach was successfully developed with the combination of the postazo and esterification reactions, confirming the synthetic flexibility of the postfunctionalization method again, and demonstrating the power of the cooperating usage of different kinds of reactions in the postfunctional strategy. The total synthesis is very simple, and the purification of the polymers is very easy.
2. The NLO properties of the polymers do not always increase accompanying with the enlargement of the isolation groups linked to the chromophore moieties. However, for a given chromophore moiety and given linked position, there should be a suitable isolation group present to boost its microscopic $\mu\beta$ value to possibly higher macroscopic NLO property efficiently.

Thus, our synthetic strategy to the polymers offers a new synthetic route to functional polymers that cannot be obtained directly from the traditional polymerization of their corresponding monomers.

Acknowledgements

We are grateful to the National Science Foundation of China (nos. 20402011 and 20674059), the National Fundamental Key Research Program and Hubei Province for financial support.

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