

Novel second-order nonlinear optical main-chain polyurethanes: Adjustable subtle structure, improved thermal stability and enhanced nonlinear optical property

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Abstract

A series of main-chain polyurethanes containing sulfonyl-based NLO chromophores in the polymer backbone were prepared, the subtle structure of the chromophore moieties could be easily modified to adjust the property of the resultant polymers. The polymers exhibit improved stability of their enhanced NLO effects, besides their good processability, thermal stability, and relatively good transparency. The tested NLO properties of the polymers demonstrate that there is a suitable isolation group present for the sulfonyl-based chromophore to boost its microscopic β value to possibly higher macroscopic NLO property efficiently, and BOP moieties are the best choice for this series of polymers to achieve optimized properties.

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1. Introduction

To realize their huge potential applications in photonic devices, organic second-order nonlinear optical (NLO) materials should simultaneously demonstrate large macroscopic optical nonlinearity, high physical and chemical stabilities, and good optical transparency. Also, it is very important for the device-quality NLO materials to maintain their NLO effects, derived from the poling-induced noncentrosymmetric alignment of chromophores under electric field, for a long term during the practical usage [1–3]. However, the relaxation of the noncentrosymmetric order occurs even at temperatures well below ($T_g - 50^\circ\text{C}$) the glass transition temperature (T_g) [4]. Thanks to the great efforts of scientists, many strategies and approaches have been reported for the development of polymeric NLO materials [1–3]. Among several types of polymeric

NLO materials, the main-chain NLO polymers have been of more interest since NLO chromophores with flexible arrangements, such as head-to-head, head-to-tail, tail-to-tail, accordion, and random, can be covalently attached to the polymeric main-chain backbone, resulting in large second-order optical nonlinearity and stabilized oriented dipoles at elevated temperatures [5,6]. Recently, Dalton et al. and Jen et al. reported that the macroscopic nonlinearity of the polymeric materials (including dendrimers) can be even enhanced by controlling the shape of the chromophore according to the site isolation principle [7–9]. The additional linked isolation moieties were really helpful to minimize the strong intermolecular dipole–dipole interactions between the chromophore groups, which account for the facts that the NLO properties of the polymers are only enhanced several times while the $\mu\beta$ values of chromophores have been improved by up to 250 folds [7–9]. However, so far, there are no reports concerning the main-chain polymers with chromophore moieties containing additional linked isolation groups, though many side-chain polymers containing dendronized chromophores

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in the side chains have already demonstrated good, even excellent NLO properties due to the reduction of intermolecular electrostatic interactions [9].

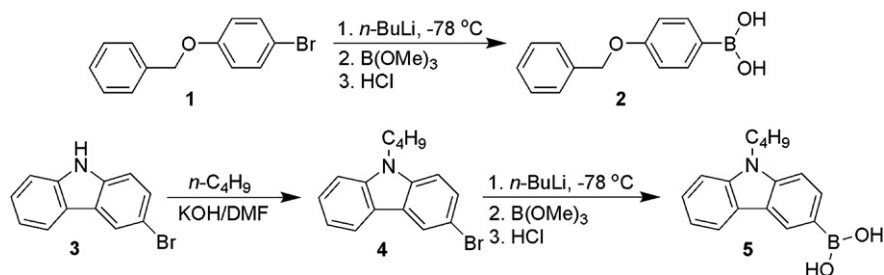
Therefore, to deepen the exploration of the fundamental architectural design parameters, based partly on our previous research [10], in this work, we prepared a series of main-chain polyurethanes containing sulfonyl-based chromophores, in which different isolation moieties, changed from small atoms such as hydrogen to much larger groups (Schemes 1–3), were introduced to the chromophore moieties on the donor side with the efforts to study the effect of the different size of isolation spacer on the resultant NLO properties. The common azo chromophores with sulfonyl groups as the acceptor were used as the NLO active units in this study 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 [5f,11]. Polyurethanes were chosen as the polymer backbone, for they can form extensive hydrogen bonding between urethane linkages and increase rigidity to prevent the

relaxation of the induced dipoles. Also, they could be conveniently synthesized [12]. The tested NLO properties demonstrate that the NLO values and the poling efficiency of the polymers are not always improved with increasing the size of the isolation spacer, and there is a suitable isolation group to boost the NLO properties of the polymers to possibly high level. Herein, we would like to report the syntheses, characterization and NLO properties of these main-chain NLO polymers.

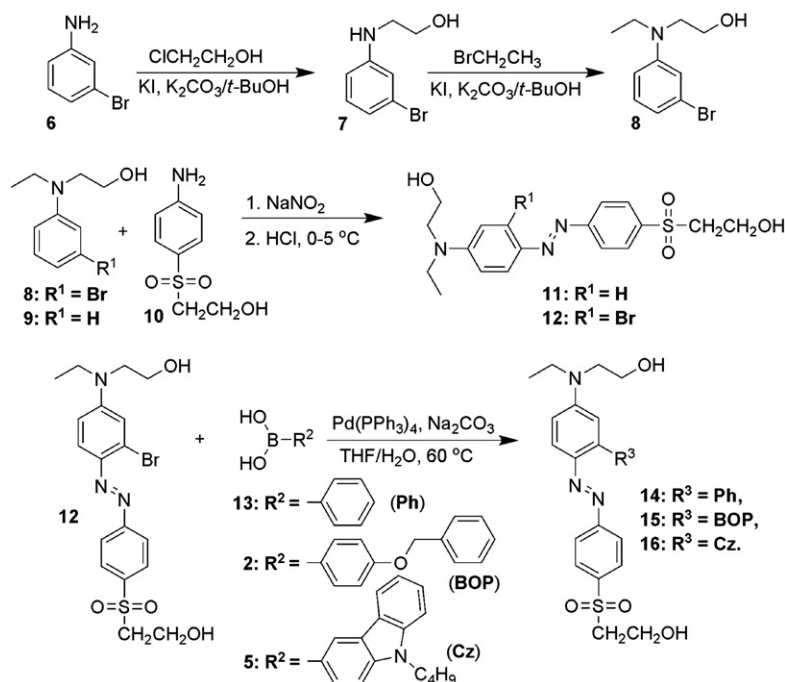
2. Experimental section

2.1. Materials

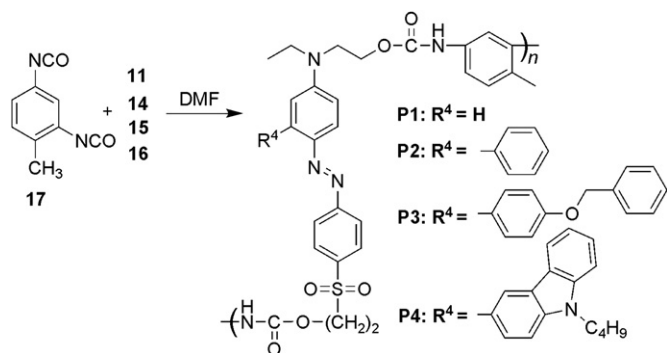
Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. *N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH₂ under an atmosphere of dry nitrogen. 2,4-Toluenediisocyanate (TDI) was purified by distillation under reduced pressure before use. All other reagents were used as received. 1-Benzyloxy-4-bromobenzene (**1**), 3-bromocarbazole (**3**), *N*-ethyl-*N*-(2-



Scheme 1.



Scheme 2.



Scheme 3.

hydroxyethyl)aniline (**9**) and *p*-(2-hydroxyethyl)sulfonylaniline (**10**) were synthesized according to the literature methods [13].

2.2. Instrumentation

¹H NMR spectroscopic study was conducted with a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer-2 spectrometer in the region of 3000–400 cm^{-1} on KBr pellets. UV–vis spectra were obtained using a Shimadzu UV-2550 spectrometer. FAB-MS spectra were recorded with a VJ-ZAB-3F-Mass spectrometer. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. Gel permeation chromatography (GPC) was used to determine the molecular weights of the polymers. GPC analysis was performed on a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC. DMF 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 $^{\circ}\text{C}/\text{min}$ in argon 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 $^{\circ}\text{C}/\text{min}$. The thermometer for measurement of the melting point was uncorrected. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

2.3. Synthesis of 4-(benzyloxy)phenylboronic acid (**2**)

A solution of compound **1** (3.68 g, 14.00 mmol) in THF (10 mL) was added dropwise to a solution of *n*-BuLi (7.7 mL, 15.40 mmol, 2.00 M in *n*-hexane, Aldrich) in THF (25 mL) at -78°C under nitrogen, the mixture was stirred for 1 h, then trimethyl borate (3.05 g, 29.40 mmol) was added dropwise, the reaction mixture was stirred for another 1 h at -78°C , and then stirred overnight at room temperature. After the addition of hydrochloric acid (2 M) (34 mL), the mixture was further stirred for 30 min. The resultant mixture was

extracted with ether and washed with distilled water for three times. The organic layer was dried over magnesium sulfate and evaporated to dryness. The crude product was purified with column chromatography on silica gel using ethyl acetate/hexane (2/1) as eluent to afford white solid **2** (2.06 g, 64.5%). ¹H NMR (CDCl_3) δ (ppm): 5.16 (s, 2H, $-\text{CH}_2\text{O}-$), 7.08 (d, $J = 8.7$ Hz, 2H, ArH), 7.3–7.5 (m, 5H, ArH), 8.16 (d, $J = 8.4$ Hz, 2H, ArH).

2.4. Synthesis of *N*-(*n*-butyl)-3-bromocarbazole (**4**)

3-Bromocarbazole (**3**) (2.46 g, 0.01 mol) was dissolved in DMF (30 mL) and then powdered potassium hydroxide (2.80 g, 0.05 mmol) was added. After the mixture was stirred for 1 h, the solution of 1-bromobutane (2.50 g, 0.02 mol) was added slowly. After stirred for 20 h at room temperature, the mixture was poured into ice water (200 mL), then extracted with chloroform, and washed with water. The organic layer was dried over magnesium sulfate. The crude product was purified with column chromatography on silica gel using chloroform/hexane (1/2) as eluent to afford the colorless oil **4** (2.30 g, 76.4%). ¹H NMR (CDCl_3) δ (ppm): 0.96 (t, $J = 6.6$ Hz, 3H, $-\text{CH}_3$), 1.40 (m, 2H, $-\text{CH}_2-$), 1.85 (m, 2H, $-\text{CH}_2-$), 4.30 (t, $J = 6.6$ Hz, 2H, $-\text{N}-\text{CH}_2-$), 7.25 (m, 2H, ArH), 7.40–7.55 (m, 3H, ArH), 8.08 (d, $J = 7.2$ Hz, 1H, ArH), 8.21 (s, 1H, ArH).

2.5. Synthesis of 3-*N*-(*n*-butyl) carbazole boronic acid (**5**)

The procedure was similar as that for compound **2**. Compound **4** (1.80 g, 6.00 mmol), *n*-BuLi (4.0 mL, 6.60 mmol, 1.65 M in *n*-hexane), $\text{B}(\text{OCH}_3)_3$ (1.31 g, 12.60 mmol). The crude product was dissolved in ether and dropped into 40 mL *n*-hexane, then filtered, and washed with *n*-hexane to afford white solid **5** (0.85 g, 53.1%). ¹H NMR (CDCl_3) δ (ppm): 1.01 (t, $J = 7.2$ Hz, 3H, $-\text{CH}_3$), 1.45 (m, 2H, $-\text{CH}_2-$), 1.93 (m, 2H, $-\text{CH}_2-$), 4.41 (t, $J = 7.5$ Hz, 2H, $-\text{N}-\text{CH}_2-$), 7.35 (m, 1H, ArH), 7.4–7.6 (m, 3H, ArH), 8.37 (d, $J = 7.8$ Hz, 1H, ArH), 8.50 (d, $J = 8.4$ Hz, 1H, ArH), 9.13 (s, 1H, ArH).

2.6. Synthesis of 3-bromo-*N*-(2-hydroxyethyl) aniline (**7**)

3-Bromoaniline (**6**) (8.60 g, 0.05 mol) and 2-chloroethanol (13.5 mL, 0.20 mol) were dissolved in *t*-BuOH (100 mL) in the presence of potassium carbonate (21.40 g, 0.16 mol) as an acid acceptor with potassium iodide (1.20 g, 6.8 mmol) as catalyst. The resultant mixture was stirred at 100 $^{\circ}\text{C}$ for 7 days. Then the residue was filtered, and most of the solvent in the filtrate was removed under reduced pressure. The crude product was purified with column chromatography on silica gel using ethyl acetate/hexane (4/1) as eluent to afford brown oil **7** (4.66 g, 42.3%). ¹H NMR (CDCl_3) δ (ppm): 3.25 (t, $J = 4.8$ Hz, 2H, $-\text{N}-\text{CH}_2-$), 3.88 (br s, 2H, $-\text{O}-\text{CH}_2-$), 6.58 (d, $J = 9.0$ Hz, 1H, ArH), 6.80 (m, 2H, ArH), 7.05 (t, $J = 8.4$ Hz, 1H, ArH).

2.7. Synthesis of 3-bromo-N-ethyl-N-(2-hydroxyethyl)aniline (**8**)

The procedure was similar as that of compound **7**. Compound **7** (2.43 g, 11.3 mmol), bromoethane (3.08 g, 28.3 mmol). Purified by column chromatography on silica gel using ethyl acetate/hexane (1/1) as eluent to afford yellow oil **8** (2.10 g, 76.5%). $^1\text{H NMR}$ (CDCl_3) δ (ppm): 1.18 (t, $J = 7.5$ Hz, 3H), 3.46 (m, 4H, $-\text{N}-\text{CH}_2-$), 3.80 (t, $J = 5.7$ Hz, 2H, $-\text{O}-\text{CH}_2-$), 6.67 (d, $J = 7.8$ Hz, 1H, ArH), 6.82 (m, 2H, ArH), 7.05 (t, $J = 8.1$ Hz, 1H, ArH).

2.8. General procedure for the synthesis of chromophores **11** and **12**

p-(2-Hydroxyethyl)sulfonylaniline (**10**) (1.05 equiv) was dissolved in a water solution of 35% hydrochloric acid. The mixture was cooled to 0–5 °C in an ice bath, and then a solution of sodium nitrite (1.05 equiv) in water was added dropwise to the above cooled solution with stirring. After stirred below 5 °C for 15 min, a solution of **8** or **9** (1.00 equiv) in ethanol was added slowly. The mixture was left in the ice bath for another 1 h, and then some sodium bicarbonate was added to adjust the pH to 7.0. The reaction mixture was further stirred for 0.5 h, the orange red precipitate was filtered, washed with water, and dried in a vacuum desiccator. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (5/1) as eluent.

2.8.1. Chromophore **11**

Compound **9** (0.17 g, 1.00 mmol), **10** (0.21 g, 1.05 mmol). Orange red powder (0.26 g, 68.9%). Mp = 130–131 °C. $^1\text{H NMR}$ (CDCl_3) δ (ppm): 1.26 (t, $J = 7.2$ Hz, 3H, $-\text{CH}_3$), 3.39 (t, $J = 5.1$ Hz, 2H, $-\text{SO}_2\text{CH}_2-$), 3.60 (m, 4H, $-\text{N}-\text{CH}_2-$), 3.90 (br s, 2H, $-\text{O}-\text{CH}_2-$), 4.04 (t, $J = 5.4$ Hz, 2H, $-\text{O}-\text{CH}_2-$), 6.82 (d, $J = 9.0$ Hz, 2H, ArH), 7.89 (d, $J = 9.3$ Hz, 2H, ArH), 8.00 (q, $J = 8.9$ Hz, 4H, ArH). MS (FAB), m/z [M^+]: 377.1; calcd: 377.1. UV–vis (THF, 2.5×10^{-5} mol/L): $\lambda_{\text{max}} = 449$ nm; $\epsilon_{\text{max}} = 3.52 \times 10^4$ mol $^{-1}$ L cm $^{-1}$.

2.8.2. Chromophore **12**

Compound **8** (1.00 g, 4.10 mmol), **10** (0.87 g, 4.32 mmol). Orange red powder (1.18 g, 63.3%). Mp = 143–145 °C. $^1\text{H NMR}$ (CDCl_3) δ (ppm): 1.26 (t, $J = 6.9$ Hz, 3H, $-\text{CH}_3$), 3.38 (t, $J = 4.8$ Hz, 2H, $-\text{SO}_2\text{CH}_2-$), 3.58 (m, 4H, $-\text{N}-\text{CH}_2-$), 3.90 (t, $J = 5.1$ Hz, 2H, $-\text{O}-\text{CH}_2-$), 4.04 (br s, 2H, $-\text{O}-\text{CH}_2-$), 6.72 (d, $J = 9.9$ Hz, 1H, ArH), 7.06 (s, 1H, ArH), 7.81 (d, $J = 9.6$ Hz, 1H, ArH), 8.00 (br s, 4H, ArH). MS (FAB), m/z [M^+]: 455.3; calcd: 455.1. UV–vis (THF, 2.5×10^{-5} mol/L): $\lambda_{\text{max}} = 448$ nm; $\epsilon_{\text{max}} = 3.42 \times 10^4$ mol $^{-1}$ L cm $^{-1}$.

2.9. General procedure for the synthesis of chromophores **14–16**

A mixture of chromophore **12** (1.00 equiv), the boronic acid **13**, **2** or **5** (1.10 equiv), sodium carbonate (10.0 equiv), THF (monomer concentration is about 0.05 M)/water (3:1 in

volume), and tetrakis(triphenylphosphine)palladium $\text{Pd}(\text{PPh}_3)_4$ (3–5 mol%) was carefully degassed and charged with nitrogen. The reaction mixture was stirred for 30 h at 80 °C. After cooled to room temperature, the organic layer was separated, dried over sodium sulfate, and evaporated to dryness. The crude product was purified by recrystallization or column chromatography.

2.9.1. Chromophore **14**

Compound **12** (0.30 g, 0.66 mmol), **13** (0.88 g, 0.72 mmol). Purified by recrystallization from ethanol to afford orange red powder (0.26 g, 85.8%). Mp = 147–148 °C. IR (thin film), ν (cm^{-1}): 1598 ($-\text{C}=\text{C}-$), 1299, 1117 ($-\text{SO}_2$), 849 ($-\text{C}-\text{N}$). $^1\text{H NMR}$ (CDCl_3) δ (ppm): 1.28 (t, $J = 6.9$ Hz, 3H, $-\text{CH}_3$), 3.34 (t, $J = 5.4$ Hz, 2H, $-\text{SO}_2\text{CH}_2-$), 3.60 (m, 4H, $-\text{N}-\text{CH}_2-$), 3.92 (t, $J = 3.9$ Hz, 2H, $-\text{O}-\text{CH}_2-$), 4.04 (t, $J = 5.1$ Hz, 2H, $-\text{O}-\text{CH}_2-$), 6.81 (m, 2H, ArH), 7.43 (m, 3H, ArH), 7.51 (d, $J = 6.6$ Hz, 2H, ArH), 7.80 (d, $J = 7.8$ Hz, 2H, ArH), 8.00 (m, 3H, ArH). MS (FAB), m/z [M^+]: 453.4; calcd: 453.2. $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_4\text{S}$ (EA) (%), found/calcd): C, 63.47/63.56; H, 6.07/6.00; N, 9.21/9.26. UV–vis (THF, 2.5×10^{-5} mol/L): $\lambda_{\text{max}} = 452$ nm; $\epsilon_{\text{max}} = 3.87 \times 10^4$ mol $^{-1}$ L cm $^{-1}$.

2.9.2. Chromophore **15**

Compound **12** (0.35 g, 0.76 mmol), **2** (0.19 g, 0.83 mmol). Purified by recrystallization from ethanol to afford orange red powder (0.36 g, 84.6%). Mp = 148–150 °C. IR (thin film), ν (cm^{-1}): 1594 ($-\text{C}=\text{C}-$), 1290, 1117 ($-\text{SO}_2$), 849 ($-\text{C}-\text{N}$). $^1\text{H NMR}$ (CDCl_3) δ (ppm): 1.28 (t, $J = 6.9$ Hz, 3H, $-\text{CH}_3$), 3.36 (t, $J = 4.5$ Hz, 2H, $-\text{SO}_2\text{CH}_2-$), 3.61 (m, 4H, $-\text{N}-\text{CH}_2-$), 3.91 (br s, 2H, $-\text{O}-\text{CH}_2-$), 4.00 (br s, 2H, $-\text{O}-\text{CH}_2-$), 5.16 (s, 2H, $-\text{O}-\text{CH}_2-$), 6.79 (m, 2H, ArH), 7.05 (d, $J = 8.4$ Hz, 2H, ArH), 7.3–7.5 (m, 7H, ArH), 7.82 (d, $J = 8.4$ Hz, 2H, ArH), 7.94 (m, 3H, ArH). MS (FAB), m/z [M^+]: 559.6; calcd: 559.2. $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_5\text{S}$ (EA) (%), found/calcd): C, 66.22/66.53; H, 6.06/5.94; N, 7.32/7.57. UV–vis (THF, 2.5×10^{-5} mol/L): $\lambda_{\text{max}} = 452$ nm; $\epsilon_{\text{max}} = 3.84 \times 10^4$ mol $^{-1}$ L cm $^{-1}$.

2.9.3. Chromophore **16**

Compound **12** (0.29 g, 0.65 mmol), **5** (0.19 g, 0.71 mmol). Purified by column chromatography on silica gel using ethyl acetate/hexane (4/1) as eluent to afford red powder (0.34 g, 87.4%). Mp = 104–105 °C. IR (thin film), ν (cm^{-1}): 1598 ($-\text{C}=\text{C}-$), 1290, 1117 ($-\text{SO}_2$), 849 ($-\text{C}-\text{N}$). $^1\text{H NMR}$ (CDCl_3) δ (ppm): 0.99 (t, $J = 7.2$ Hz, 3H, $-\text{CH}_3$), 1.31 (m, 3H, $-\text{N}-\text{CH}_2-\text{CH}_3-$), 1.45 (m, 2H, $-\text{CH}_2-$), 1.92 (m, 2H, $-\text{CH}_2-$), 3.30 (t, $J = 5.7$ Hz, 2H, $-\text{SO}_2\text{CH}_2-$), 3.67 (m, 4H, $-\text{N}-\text{CH}_2-$), 3.95 (br s, 4H, $-\text{O}-\text{CH}_2-$), 4.38 (t, $J = 7.2$ Hz, 2H, $-\text{N}-\text{CH}_2-$), 6.83 (d, $J = 7.5$ Hz, 1H, ArH), 6.92 (s, 1H, ArH), 7.20 (m, 1H, ArH), 7.46 (m, 3H, ArH), 7.58 (d, 1H, ArH), 7.8 (q, $J = 8.7$ Hz, 4H, ArH), 8.01 (m, 2H, ArH), 8.19 (s, 1H, ArH). MS (FAB), m/z [M^+]: 598.2; calcd: 598.3. $\text{C}_{34}\text{H}_{38}\text{N}_4\text{O}_4\text{S}$ (EA) (%), found/calcd): C, 67.83/68.20; H, 6.52/6.40; N, 9.36/9.36. UV–vis (THF, 2.5×10^{-5} mol/L): $\lambda_{\text{max}} = 455$ nm; $\epsilon_{\text{max}} = 3.97 \times 10^4$ mol $^{-1}$ L cm $^{-1}$.

2.10. General procedure for the synthesis of polyurethanes **P1–P4**

NLO chromophore and TDI with equivalent molar ratios were reacted in appropriate anhydrous DMF solution at 80 °C for 30 h under an atmosphere of dry nitrogen. After cooled to ambient temperature, the resultant mixture was dropped into methanol to remove monomers. The polymer was filtered and dried in a vacuum desiccator.

2.10.1. P1

Chromophore **11** (0.148 g, 0.39 mmol), TDI (0.071 g, 0.39 mmol). Red powder (0.10 g, 45.7%). $M_w = 22,000$, $M_w/M_n = 1.08$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1728 (C=O), 1598 (–C=C–), 1299, 1126 (–SO₂), 849 (–C–N). ¹H NMR (CDCl₃) δ (ppm): 1.2–1.3 (–CH₃), 2.3 (–CH₃), 3.4–3.6 (–SO₂CH₂–), 3.6–3.8 (–N–CH₂–), 4.3–4.5 (–O–CH₂–), 6.7–6.9 (ArH), 7.0 (ArH), 7.7–8.0 (ArH). UV–vis (THF, 0.02 mg/mL): $\lambda_{\text{max}} = 443$ nm.

2.10.2. P2

Chromophore **14** (0.199 g, 0.44 mmol), TDI (0.080 g, 0.44 mmol). Red powder (0.116 g, 41.6%). $M_w = 25,800$, $M_w/M_n = 1.15$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1707 (C=O), 1594 (–C=C–), 1303, 1122 (–SO₂), 844 (–C–N). ¹H NMR (CDCl₃) δ (ppm): 1.2–1.4 (–CH₃), 2.0–2.2 (–CH₃), 3.2–3.8 (–SO₂CH₂– and –N–CH₂–), 4.1–4.4 (–O–CH₂–), 6.4–6.9 (ArH), 7.3–7.5 (ArH), 7.6–8.0 (ArH). UV–vis (THF, 0.02 mg/mL): $\lambda_{\text{max}} = 447$ nm.

2.10.3. P3

Chromophore **15** (0.294 g, 0.52 mmol), TDI (0.095 g, 0.52 mmol). Red powder (0.314 g, 80.6%). $M_w = 30,900$, $M_w/M_n = 1.18$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1732 (C=O), 1594 (–C=C–), 1295, 1122 (–SO₂), 849 (–C–N). ¹H NMR (CDCl₃) δ (ppm): 1.1–1.3 (–CH₃), 2.2 (–CH₃), 3.3–3.8 (–SO₂CH₂– and –N–CH₂–), 4.2–4.5 (–O–CH₂–), 5.0–5.2 (–OCH₂–), 6.5–6.8 (ArH), 6.8–7.1

(ArH), 7.3–7.5 (ArH), 7.6–8.0 (ArH). UV–vis (THF, 0.02 mg/mL): $\lambda_{\text{max}} = 448$ nm.

2.10.4. P4

Chromophore **16** (0.239 g, 0.40 mmol), TDI (0.072 g, 0.40 mmol). Red powder (0.260 g, 83.4%). $M_w = 27,600$, $M_w/M_n = 1.16$ (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1732 (C=O), 1594 (–C=C–), 1295, 1117 (–SO₂), 844 (–C–N). ¹H NMR (CDCl₃) δ (ppm): 0.8–1.0 (–CH₃), 1.1–1.3 (–CH₃), 1.3–1.5 (–CH₂–), 1.8–2.0 (–CH₂–), 2.0–2.1 (–CH₃), 3.2–3.9 (–SO₂CH₂– and –N–CH₂–), 4.2–4.5 (–O–CH₂– and –N–CH₂–), 6.7–6.9 (ArH), 7.1–7.2 (ArH), 7.3–7.5 (ArH), 7.5–7.7 (ArH), 7.7–7.9 (ArH), 7.9–8.1 (ArH), 8.1–8.2 (ArH). UV–vis (THF, 0.02 mg/mL): $\lambda_{\text{max}} = 450$ nm.

2.11. 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 *N,N*-dimethylformamide, 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.

2.12. 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. 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 an Nd:YAG laser operating at a 10 Hz repetition rate and an

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)	ϕ^h
P1	45.7	22,000	1.08	443 (449)	115	209	119	0.31	39.5	0.07
P2	41.6	25,800	1.15	447 (452)	120	243	119	0.23	54.6	0.15
P3	80.6	30,900	1.18	448 (452)	117	225	121	0.24	55.9	0.19
P4	83.4	27,600	1.16	450 (455)	128	247	149	0.31	36.2	0.13

^a Determined by GPC in DMF on the basis of a polystyrene calibration.

^b The maximum absorption wavelength of polymer solutions in THF, while the maximum absorption wavelength of the corresponding small chromophore molecules in diluted THF solutions are given in the parentheses.

^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 argon at a heating rate of 20 °C/min.

^e The best poling temperature.

^f Film thickness.

^g Second harmonic generation (SHG) coefficient.

^h Order parameter $\Phi = 1 - A_1/A_0$, A_1 and A_0 are the absorbances of the polymer film after and before corona poling, respectively.

8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

3. Results and discussion

3.1. Synthesis

Compound **8** was synthesized through a two-step procedure, first, 3-bromoaniline reacted with 2-chloroethanol at the molar ratio of 1:4 to give the mono-substituted product, compound **7**, which underwent a further substitution reaction with bromoethane under the similar reaction conditions as those of compound **7**. These two compounds, **7** and **8**, could not be easily obtained, their preparation process took a relatively long time, while *t*-BuOH was chosen as the solvent similarly as we did previously [10h]. However, compound **9** could be easily prepared according to the literature method [13d]. Under the normal azo coupling reaction conditions, chromophores **11** and **12** were conveniently yielded. Unlike phenylboronic acid (**13**), which was directly purchased from Aldrich, 4-(benzyloxy)phenylboronic acid (**2**) and 3-*N*-(*n*-butane) carbazole boronic acid (**5**) were prepared from a series of reactions as shown in Scheme 1, the detailed synthetic procedure was presented clearly in Section 2. Following the general Suzuki approach [14], chromophores **14–16** were synthesized smoothly with high yields. Therefore, from chromophore **11** to **14**, then to **15** and **16**, the linked isolation moieties, which are labeled as R¹ or R³ in Scheme 2, were adjusted from the hydrogen atoms (or we could say there is no isolation group in this case), to very large and bulky groups such as carbazolyl groups, step by step. Thus, it is not difficult to study the size effect of the isolation moieties linked to the NLO chromophore groups on the macroscopic nonlinearity of the resultant main-chain polymeric materials.

The main-chain polyurethanes, **P1–P4**, were synthesized from the corresponding chromophores and TDI under similar conditions as reported in the literatures for the preparation of polyurethanes [12]. Also, as there are nearly no different reactivity between the two hydroxyl groups in the chromophores, it was expected that the chromophore dipoles should be randomly arranged in the polymer backbone (i.e., the dipoles can be head-to-tail, tail-to-tail, or head-to-head) as the cases reported in the literatures [5,6,11c]. This structure, perhaps, might benefit the alignment of chromophore moieties upon poling, we would discuss this point in the part of *NLO properties*.

3.2. Structural characterization

The chromophores and polymers were characterized by spectroscopic methods, and all give satisfactory spectral data (see Section 2 and Table 1 for detailed analysis data). The NLO chromophores are new compounds (except chromophore **11**), and further confirmed by elemental analysis. Polymers **P2–P4** were not reported yet, while polymer **P1** was prepared here for comparison. In the IR spectra of chromophores **11**, and **14–16**, the absorption bands associated with the sulfonyl groups are at about 1290 and 1120 cm⁻¹. After these

chromophores reacting with TDI, the absorption bands of the sulfonyl groups remained in the IR spectra of the resultant polymers **P1–P4**, while another strong absorption peak appears at about 1730 cm⁻¹, which is attributed to the vibration of the carbonyl group in a urethane group, indicating the formation of urethane linkages during the polymerization process as shown in Scheme 3 [12].

In all the ¹H NMR spectra of the polymers **P1–P4**, the chemical shifts are consistent with the proposed polymer structure as demonstrated in Scheme 3, however, showing an inclination of signal broadening due to polymerization. For example, Fig. 1 shows the spectra of chromophore **15** and its corresponding polymer **P3**, which were conducted in chloroform-*d*. As an example, it is easily seen that the signal of the methylene groups linked with the benzene ring in chromophore **15** is a sharp peak, however, becomes very broad in the spectrum of **P3** after the polymerization procedure.

All the polymers are soluble in common polar organic solvents such as chloroform, THF, DMF, and DMSO. Their solutions can be easily spin-coated onto thin solid films; therefore, it is convenient to test their NLO properties based on these thin films. The UV–vis absorption spectra of polymers are shown in Fig. 2, the maximum absorption wavelength for the π – π^* transition of the azo moieties in them are listed in Section 2 and Table 1. In the literatures and our previous cases, the maximum absorption wavelength of the chromophore moieties often blue-shifted (up to 15 nm) compared with those of the free chromophore molecules after they were introduced to the side-chain polyurethanes, due to the presence of the electronic interaction between the chromophore moieties and the polymer chain [9,12]. Here, the difference of the maximum absorption wavelength is minor (not more than 6 nm), indicating the similarity of the environments of the chromophore moieties either at free molecular state or in polymers. This, perhaps, demonstrates the difference between the side-chain and main-chain polyurethanes in some degree [15]. Also, it is noticed that the maximum absorption wavelength of the chromophore molecules is similar, the difference among them is less than 6 nm, indicating that the introduction of the different isolation

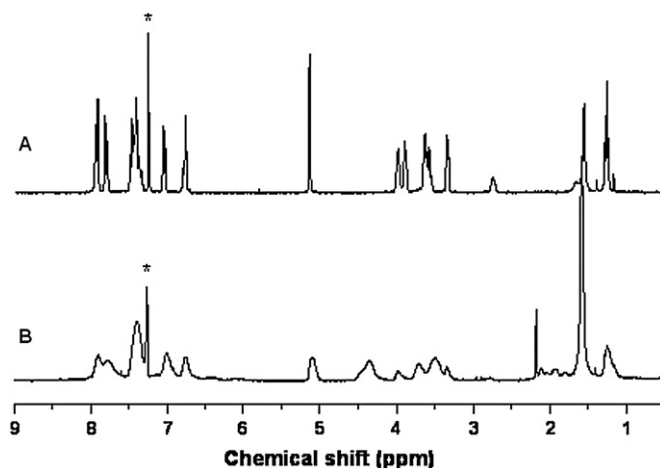


Fig. 1. ¹H NMR spectra of chromophore **15** (A) and **P3** (B) in chloroform-*d*.

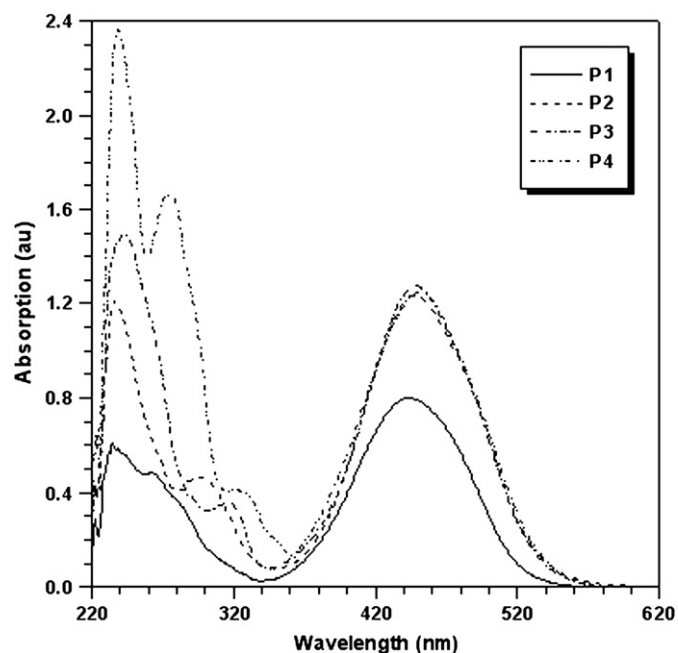


Fig. 2. UV-vis spectra of THF solutions of **P1–P4**.

groups to the donor side of the chromophore molecules did not affect their electronic structure properties at a large extent, or in other words, chromophores **11** and **14–16** would exhibit similar NLO properties, regardless of the different isolation moieties linked. Thus, it is reasonable for us to focus our eyes on the relationship between the size of the isolation groups and the resultant NLO properties of the main-chain polymers. Also, it should be pointed out that all the polymers have a wide transparency window with a band edge of the UV-vis curves shorter than 575 nm, which should contribute to their low optical loss, confirming the advantages of sulfonyl-based chromophore again [5f,11].

The molecular weights of polymers were determined by gel permeation chromatography (GPC) with DMF as an eluent, with polystyrene standards as calibration standards. All the results are summarized in Table 1. All the polymers possess relatively high molecular weight (M_w higher than 22,000), which would perhaps facilitate the comparison of their properties on the same level. The polymers are thermally stable, and the 5% weight loss temperature of polymers is listed in Table 1. After linked with the isolation groups, the polymers exhibited better thermal stability than **P1**, which is, perhaps, another advantage of the presence of the isolation moieties. **P3** is not so stable as **P2** and **P4**, possibly due to the unstable point of the benzyl groups. The glass transition temperature (T_g) of the polymers was investigated using a differential scanning calorimeter (Table 1); all the polymers generally have moderate T_g of about 120 °C due to the strong secondary forces between polymer chains.

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. The method for the calculation of the SHG coefficients (d_{33}) for the poled films has been reported in our previous papers [10]. From the experimental data, the d_{33} values of **P1–P4** are calculated at fundamental wavelength of 1064 nm (Table 1).

P1–P4 demonstrate different NLO properties as we found in the previous case [10], due to their different structures, especially the introduced different isolation groups linked to the chromophore moieties in the donor side. For a visual look at the results, we compared the d_{33} values of the polymers using **P1** as reference (Fig. 3A). As easily seen, the d_{33} value of **P2** is about 1.38 times that of **P1**, while that of **P3** being about 1.42, indicating that the introduction of the isolation groups to the chromophore moieties really benefits the improvement of the NLO properties of the resultant polymeric materials by minimizing the strong intermolecular dipole–dipole interactions between the chromophore groups as in the previously reported cases [7–9]. However, the d_{33} value of **P4** decreases, this seems strange. Also, there is another point to be considered: the introduced isolation groups would dilute the concentrations of the chromophore moieties in the polymers. Thus, according to the one-dimensional rigid orientation gas model [16]:

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

where N is the number density of the chromophore, β is its first hyperpolarizability, f is the local field factor, 2ω is the double

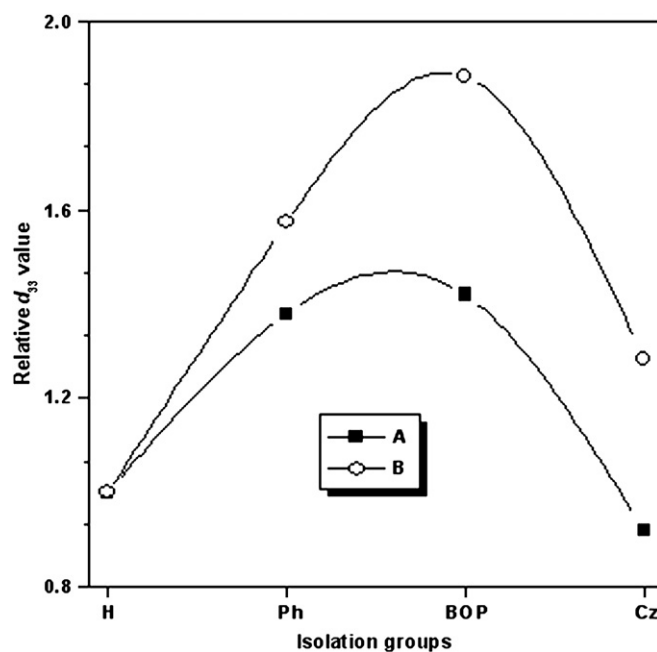


Fig. 3. (A) The comparison of the d_{33} values of the polymers and (B) the comparison of the calculated d_{33} values, which were obtained by using the tested d_{33} values dividing the concentration of the active chromophore moieties of the polymers, using **P1** as reference.

frequency of the laser, ω is its fundamental frequency, and $\langle \cos^3 \theta \rangle$ is the average orientation factor of the poled film; the d_{33} values of the polymers should be proportional to the number density of the chromophore moieties in the polymers. Therefore, we considered the different concentrations of the active chromophore moieties in the polymers, using the tested d_{33} values dividing the concentrations of the active chromophore moieties in the polymers, and comparing the results again with that of **P1** as reference. As shown in Fig. 3B, the difference of the relative d_{33} values becomes even larger. **P3** still exhibits the highest relative d_{33} value, which is about 1.88 times that of **P1**. Also, **P4** shows higher relative d_{33} value than **P1**. However, it is sure that the d_{33} values of the polymers are not always increasing as the isolation groups enlarged in both of the above cases, while further increasing the size of the isolation group without limitation, the tested d_{33} values will drop to even lower than that of the original polymer, in which there is no isolation moieties (or hydrogen atoms as the isolation part). Thus, there should be a suitable isolation group present for a special chromophore to boost its fixed $\mu\beta$ value to possibly higher macroscopic NLO activities of polymers. In our case, the part introduced to the chromophore moieties in **P3** is the best isolation moieties. In fact, these phenomena are reasonable, if we consider carefully and deeply. The linkage of the isolation group to the chromophore moieties in the polymers would mainly cause three impacts:

1. to minimize the strong intermolecular dipole–dipole interactions to some degree, leading to the improvement of the d_{33} values of the polymers as many scientists expected;
2. to dilute the active concentration of the chromophore moieties, generally reducing the d_{33} values;
3. to increase the bulky of the resultant chromophore moieties, making the noncentrosymmetric alignment of the chromophore upon poling in the electronic field more difficult, which would generate complicated effects on the resultant d_{33} values (at the beginning, the enlargement of the size would benefit the alignment due to the minimized electrostatic interaction, but would restrain the alignment when the size is too bulky).

Thus, the macroscale NLO properties of polymers containing chromophores with isolation groups are expected to be heavily related to the subtle difference in architectural design, and there is a balance present according to the above mentioned three impacts. Or we could say: there is a suitable isolation group to realize this balance, leading to the possibly highest macroscopic NLO activities of polymers containing the preferred NLO chromophores. Therefore, based on this point, it is promising that the reported NLO polymers with dendronized chromophore as side chains might achieve even better NLO properties if more suitable isolation groups were used. In addition, it should be pointed out that the suitable isolation group might be different for a same NLO chromophore if the linked position in the chromophore or the chemical environments of the chromophore were changed. Thus, to study the structure–property relationship of NLO polymers in detail,

to realize the wide practical application of NLO materials, more work is still needed.

To further explore the alignment of the chromophore moieties in the polymers, we measured their order parameter (Φ). After the corona poling, the dipole moments of the chromophore moieties in the polymers were aligned, and the absorption curves decrease due to birefringence. From the absorption change, the Φ value for the polymers can be calculated according to the following equation:

$$\Phi = 1 - A_1/A_0 \quad (2)$$

where A_1 and A_0 are the absorbances of the polymer film after and before corona poling, respectively. The calculated Φ values are summarized in Table 1. Fig. 4 also describes the results more visually. As we analyzed above, the Φ value increases till a peak point with the isolation groups enlarging, then decreases while the isolation groups become even bigger, coinciding well with the trends observed in the tested and relative d_{33} values of the polymers, further confirming the above discussion from another approach.

The dynamic thermal stability of the NLO activity of the polymers were investigated by depoling experiments, in which the real time decays of their SHG signals were monitored as the poled films were heated from 35 to 150 °C in air at a rate of 4 °C/min. The results indicated that the long-term temporal stability of the polymers is relatively good, and the introduction of the large size of the isolated groups to the sulfonyl-based chromophores benefits the thermal stability of the resultant polymers. Fig. 5 shows the decay of SHG coefficient of polymers as a function of temperature. The onset temperature for the decay of **P1** is found to be 100 °C, which is relatively higher, much better than those obtained in the side-chain polymers, even the side-chain polyurethanes, due to the main-chain

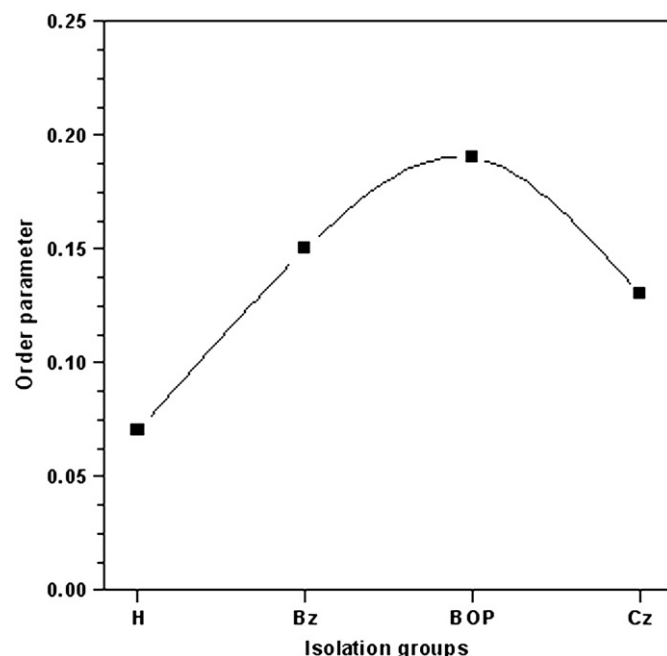


Fig. 4. Order parameter (Φ) of polymers (**P1**–**P4**).

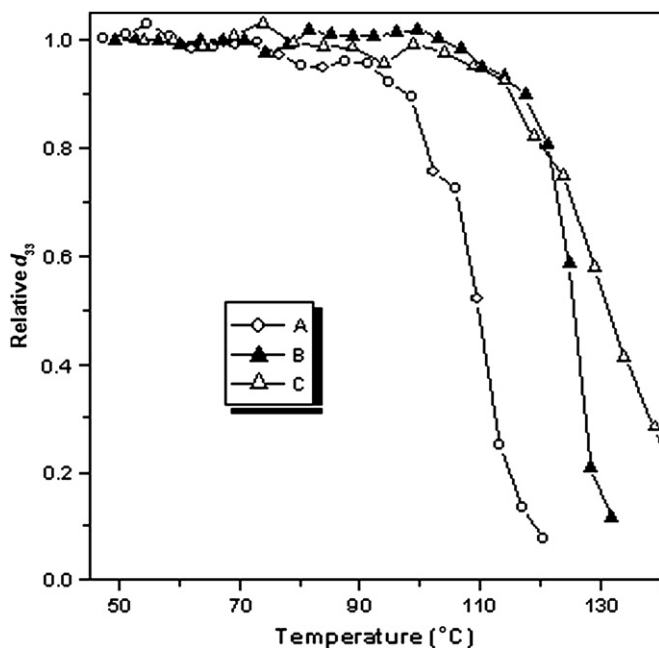


Fig. 5. Decay curves of SHG coefficient of **P1** (A), **P3** (B) and **P4** (C) as a function of temperature.

structure of the polymer. Actually, as mentioned in Section 1, the polymeric main-chain backbone results in large second-order optical nonlinearity and stabilized oriented dipoles at elevated temperatures. These advantages prove themselves in our case: **P1** exhibits a little higher d_{33} value in comparison with polyurethane containing the same chromophore in the side chain (**P5**, Fig. 6); as to the stability of the NLO effects, **P1** is much better than its side-chain analogue, **P5**, which nearly could not maintain its NLO coefficient as the temperature is higher than 60 °C [10h]. Similar phenomena were also observed in the literatures [11c], and this advantage should be due to the structure of the random arrangement of the chromophore moieties in the polymer backbone as discussed in the above synthetic part. After the introduction of the isolation groups, the thermal stability of the resultant polymers was even better, and the onset temperature for the decay of **P3** is as high as 119 °C (Fig. 6), while that of **P4** is 117 °C, indicating the much improved long-term temporal stability of its NLO effects, which would benefit their practical application.

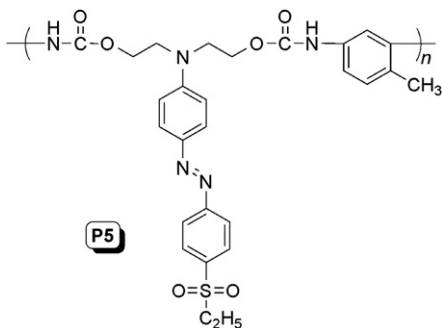


Fig. 6. The structure of **P5**.

4. Conclusions

A series of main-chain polyurethanes containing sulfonyl-based chromophores were prepared, in which different isolation groups were linked to the chromophore moieties at the donor side. The isolation groups were changed from small atoms to much larger groups. Our preliminary study demonstrates that:

1. all the polymers exhibit good stability of the NLO effects, in addition to their good processability, thermal stability, relatively good transparency and NLO effects. Thus, they could be good candidates for the practical application in the photonic fields.
2. The site isolation principle is applied to the main-chain polymers for the first time. The tested d_{33} value and the poling efficiency of the resultant polymers demonstrated that BOP is the best isolation group for this series of the main-chain polymers, due to the complicated impacts present after introducing the isolation groups to the chromophore moieties.

Thus, our study may provide some useful information for the design of new NLO polymers and be helpful to obtain even better NLO properties by using the present chromophores.

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