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Synthesis of novel poly{methyl-[3-(9-indolyl)propyl]siloxane}-based nonlinear optical polymers via postfunctionalization

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Abstract

A novel series of nonlinear optical (NLO) polysiloxanes with a high density of chromophore moieties based on poly{methyl-[3-(9-indolyl) propyl]siloxane} (PMIPS) were synthesized by a post functional strategy. First, PMIPS (**P1**) was prepared through hydrosilylation reaction, then **P1** is partially formylated by the reaction between **P1** and the reagents of dimethylformamide (DMF) and phosphorus oxychloride under the standard Vilsmeier reaction conditions, and these formyl groups with high reactivity are condensed with four predesigned cyanoacetylated chromophores to afford the series of chromophore functionalized polysiloxanes (**P3–6**). The most special point is the molar concentrations of chromophore moieties are the same in polymers **P3–6**, which makes it convenient to study the behavior of different chromophores in the polymeric system. The poled films of **P3–6** reveal the resonant d_{33} values in the range of 7.9–55.2 pm/V by second harmonic generation (SHG) measurements.

Keywords: Polysiloxane; Synthesis; Indole

1. Introduction

In the past decade, organic nonlinear optical (NLO) chromophore-containing polymers have attracted considerable interest, and are considered as the most promising NLO material due to their potential photonics applications and many advantages over single crystals [1]. Thanks to the enthusiastic synthetic efforts of polymer chemists, a rich variety of NLO polymers has been designed and synthesized to improve their comprehensive properties for the practical applications [2]. Among them, some polysiloxanes containing NLO chromophore as side chains were obtained by various methods and showed good properties [3], in which perhaps the most important point is their low glass transition temperature derived from the flexible inorganic backbone [4], offering the possibility of NLO switching at room temperature and the appearance of the orientational enhancement effect [1].

We are interested in the designing and preparing of NLO polymers during the past several years, and developed some new synthetic strategies in which the post functional method [5], especially the post azo coupling reaction, is our favorite. By using the post azo coupling reaction, we have not only successfully simplified the preparation procedure for the NLO polysiloxanes [6], but also avoided the presence of unreacted SiH groups in our previous case [3g], which resulted in the cross-linking of the obtained polysiloxanes and led to the sharply decrease of their solubility in the storage. However, there are still some defects present in the post azo coupling method, and the most obvious one should be the limitation of the donor groups in the formed push–pull structure of the chromophore moieties. To further develop NLO polysiloxanes, focusing on the introduction of different types of chromophore groups with different donor moieties to this special inorganic backbone, new synthetic strategies are still needed.

On the other hand, polymers with indole side chains for the NLO applications appeared recently. The initially work of Park et al. revealed that polymers with indole-based chromophores demonstrate large nonlinear optical coefficients and photoconductive sensitivity, since the structure of indole is similar to carbazole except its smaller bulk, which improves the poling behavior and the consequent NLO performance [7]. In 2001,

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Brustolin et al. reported the syntheses and charge-transfer properties of a series of poly(1-vinylindole)s, and considered them valid substitutes for poly(*N*-vinylcarbazole) (PVK) as host matrix in NLO composite materials [8]. Also, we reported the syntheses of polymers with indole-based chromophore as side chains recently [5a,b]. However, the study on the indole-containing polymers is still very scarce.

In this paper, a novel post functional strategy was developed to prepare a series of nonlinear optical (NLO) polysiloxanes with a high density of chromophore moieties based on poly{methyl-[3-(9-indolyl)propyl]siloxane} (PMIPS). First, PMIPS (**P1**) was prepared through hydrosilylation reaction, then **P1** is partially formylated by the reaction between **P1** and the reagents of DMF and phosphorus oxychloride under the standard Vilsmeier reaction conditions, and these formyl groups with high reactivity are condensed with four predesigned cyanoacetylated chromophores to afford the series of chromophore functionalized polysiloxanes (**P3–6**) in complete conversion. This synthetic method is very simple, and the purification procedure is very easy. The polymers were easily soluble in common organic solvents, and showed good comprehensive properties.

2. Experimental

2.1. Materials and measurements

Toluene was dried over and distilled from sodium under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Phosphorus oxychloride was distilled twice before use. Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Dicyclopentadienedichloroplatinum is synthesized according to the method of Doule [9]. *N*-allylindole was prepared by the reaction between indole and allyl chloride in DMF in the presence of excess of potassium hydroxide. *p*-Ethylsulfonylaniline was synthesized according to the literature [10]. *N*-ethyl-*N*-(6-hydroxyhexyl)aniline (**1**) was synthesized according to the literature method [11]. *N*-(6-hydroxyhexyl)carbazole (**2**) was prepared as reported previously [12]. The *p*-nitrobenzenediazonium fluoroborate was synthesized following a procedure described in the literature [13]. Poly(hydrogenomethylsiloxane) was obtained from Xinhuo Campany, Jiangxi Province, China ($M_n = 500$). All other reagents were used as received. The hydrosilylation reaction of poly(hydrogenmethylsiloxane) was carried out in a dry nitrogen atmosphere using Schlenk technique.

^1H NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer. FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 series in the region of 3000–400 cm^{-1} on KBr pellets. UV–visible spectra were obtained using a Schimadzu 160A spectrometer in the chloroform solutions of polymers. FAB-MS spectra were used with VJ-ZAB-3F-Mass spectrometer. Elemental analysis was tested by a CARLOERBA-1106 micro-elemental analyzer. Melting points were measured on a SGW X-4 apparatus and the thermometer is not corrected. Differential scanning calorimetry (DSC) analyses were performed in a Rigaku Themoflex DSC8131 at a scan rate of 10 °C/min. Molecular weights were determined in THF solution by Waters 2960D separation Module containing Styragel HR1 THF column and Waters 2410 Refractive Index Detector with a calibration curve for polystyrene standards. Thermal analysis was performed on SHIMADZU DT-40 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).

2.2. Synthesis of *p*-ethylsulfonylbenzenediazonium fluoroborate

p-Ethylsulfonylaniline (2.79 g, 0.015 mol) was dissolved in fluoroboric acid (40%), and then the solution was cooled to 0 °C. A solution of sodium nitrite (1.04 g, 0.015 mol) in water (4 ml) was added dropwise. The resultant mixture was stirred at 0 °C for half an hour. The yellow solid was filtered quickly and washed with cold ethanol and ether for several times. After this, the product was stored in the refrigerator (4.05 g, 95%).

2.3. Synthesis of **3–4**

4-Nitroaniline (0.69 g, 5 mmol) was dissolved in a solution of concentrated hydrochloric acid (1.3 ml) in 7 ml of water. The mixture was cooled to 0 °C in an ice bath, and then a solution of sodium nitrite (0.35 g, 5 mmol) in 2 ml of water was added slowly to the 4-nitroaniline solution. After stirred below 2 °C for 20 min, some sodium acetate was added to the above mixture to adjust pH about 7.0. Then a solution of **1** (1.1 g, 5 mmol) in 2 ml of ethanol was added. The mixture was agitated below 2 °C for 3 h. The red precipitate was filtered, washed with water, and air-dried. Mp: 116–117 °C. IR: 1604 cm^{-1} (C=C), 1514, 1339 cm^{-1} ($-NO_2$), 1258 cm^{-1} (C–N). ^1H NMR ($CDCl_3$) δ (ppm): 1.32 (t, $J = 7.5$ Hz, 3H, $-CH_3$), 1.2–1.7 (m, 8H, $-(CH_2)_4-$), 3.38 (t, $J = 7.2$ Hz, 2H, $-N-CH_2CH_2$), 3.48 (q, 2H, $-N-CH_2CH_3$), 3.67 (t, $J = 7.2$ Hz, 2H, $-O-CH_2-$), 6.71 (m, 2H, ArH), 7.90 (m, 4H, ArH), 8.30 (m, 2H, Ar*H*).

By the similar procedure, **4** was prepared. The solid was recrystallized from ethanol/water to give red powder product (60%). Mp: 64–66 °C. IR: 1600, 1515 cm^{-1} (–C=C–), 1377 cm^{-1} (C–N), 1271, 1129 cm^{-1} ($-SO_2-$). ^1H NMR ($CDCl_3$) δ (ppm): 1.23 (t, $J = 7.0$ Hz, 3H, $-CH_3$), 1.29 (t, $J = 7.5$ Hz, 3H, $-CH_3$), 1.41–1.68 (m, 8H, $-(CH_2)_4-$), 3.14 (q, $J = 7.5$ Hz, 2H, $-SO_2CH_2-$), 3.38 (t, $J = 7.0$ Hz, 2H, $-NCH_2CH_2$), 3.48 (q, 2H, NCH_2CH_3), 3.66 (t, $J = 7.2$ Hz, 2H, $-O-CH_2-$), 6.74 (d, $J = 7.0$ Hz, 2H, ArH), 7.90 (d, $J = 7.0$ Hz, 2H, ArH), 7.97 (m, 4H, ArH).

2.4. Synthesis of **5–6**

The compound **5** was prepared by a modified method developed by Tagaki [14]. To a solution of **2** (3.81 g, 0.014 mol) in CH_2Cl_2 (200 ml) were added solid *p*-nitrobenzene diazonium tetrafluoroborate (3.35 g, 0.014 mol) and silica gel (20 g). The reaction mixture was agitated at 0–5 °C in an ice bath for 30 h and then filtered to remove the silica gel. After the silica gel was washed several times by CH_2Cl_2, the filtrate was evaporated to remove the bulk of CH_2Cl_2 and the residue recrystallized twice from CH_2Cl_2/CH_3OH to give red crystal (4.7 g, 82%). Mp: 130–132 °C. IR: 1625, 1587 cm^{-1} (C=C), 1516, 1339 cm^{-1} ($-NO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 1.42–2.05 (m, 8H, $-(CH_2)_4-$), 3.38 (t, $J=7.2$ Hz, 2H, $-N-CH_2CH_2$), 4.35 (t, $J=7.0$ Hz, 2H, $-CH_2-O-$), 7.26 (m, H, ArH), 8.04–8.37 (m, 5H, ArH), 8.67 (s, H, ArH).

By the similar procedure presented above, **6** was synthesized. The solid was recrystallized from CH_2Cl_2/CH_3OH to give red powder product (40%). Mp: 100–102 °C. IR: 1626, 1591, 752 cm^{-1} (carbazole), 1305, 1126 cm^{-1}($-SO_2-$), 1233 cm^{-1} (C–N). ^1H NMR ($CDCl_3$) δ (ppm): 1.33 (t, $J=7.5$ Hz, 3H, $-CH_3$), 1.43–1.94 (m, 8H, $-(CH_2)_4-$), 3.18 (q, $J=7.5$ Hz, 2H, $-SO_2CH_2-$), 3.61 (t, $J=7.2$ Hz, 2H, $-OCH_2-$), 4.36 (t, $J=7.0$ Hz, 2H, $-NCH_2-$), 7.32 (s, 1H, ArH), 7.44–7.56 (m, 3H, ArH), 8.07 (m, 4H, ArH), 8.18 (t, 2H, ArH), 8.75 (s, 1H, ArH).

2.5. Synthesis of **7–10**

The general synthetic procedure was similar, and that of **8** was described in detail for an example. **4** (1.25 g, 3 mmol), cyanoacetic acid (0.27 g, 3.15 mmol), 4-(*N*,*N*-dimethyl)aminopyridin (0.03 g, 0.3 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) (0.63 g, 3 mmol) was dissolved in dry THF (20 ml), and the resultant mixture stirred at room temperature for 24 h. The precipitate was filtered out and washed with THF for several times. The solvent of the solution was evaporated under reduced pressure, and then the obtained red solid was washed with hydrochloric acid (0.5 N), diluted aqueous solution of sodium bicarbonate, and water subsequently. The crude product was purified on a silica gel column using petroleum/ethyl acetate (1:1, v/v) to afford compound **8** as a red powder (1.05 g, 68%). Mp: 90–91 °C. IR: 2260 cm^{-1} (CN), 1747 cm^{-1} (C=O), 1598, 1516 cm^{-1} (–C=C–), 1360 cm^{-1} (C–N), 1267, 1128 cm^{-1} ($-SO_2-$). ^1H NMR ($CDCl_3$) δ (ppm): 1.22 (t, 3H, $-CH_3$), 1.28 (t, 3H, $-CH_3$), 1.41–1.72 (m, 8H, $-(CH_2)_4-$), 3.13 (q, $J=7.5$ Hz, 2H, $-SO_2CH_2-$), 3.37 (t, $J=7.2$ Hz, 2H, $-NCH_2CH_2-$), 3.46 (s, 2H, $CNCH_2COO-$), 3.47 (q, 2H, $-NCH_2CH_3$), 4.25 (t, $J=7.2$ Hz, 2H, $-COOCH_2-$), 6.70 (d, $J=9.0$ Hz, 2H, ArH), 7.87 (d, $J=9.0$ Hz, 2H, ArH), 7.95–7.98 (q, 4H, ArH).MS (FAB), *m/z* [M^+]: 484, 100%. $C_{23}H_{32}N_4O_4S$ (EA) (%, Calcd/found): C, 61.98/62.03; H, 6.61/6.64; N, 11.57/11.52.

7: Yield: 72%, Mp: 122–123 °C. IR: 2263 cm^{-1} (CN), 1745 cm^{-1} (C=O), 1602, 1587 cm^{-1} (C=C), 1513, 1337 cm^{-1} ($-NO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 1.27 (t, $J=7.5$ Hz, 3H, $-CH_3$), 1.36–1.74 (m, 8H, $-(CH_2)_4-$), 3.39 (t, $J=7.2$ Hz, 2H, $-NCH_2CH_2-$), 3.46 (s, 2H, $CNCH_2COO-$), 3.52 (q, 2H, $-NCH_2CH_3$), 4.22 (t, $J=7.0$ Hz, 2H, $-COOCH_2-$), 6.75 (d, $J=9.0$ Hz, 2H, ArH), 7.87 (d, $J=9.0$ Hz, 2H, ArH), 8.30–8.34 (q, 4H, ArH). MS (FAB), *m/z* [M^+], 437, 100%. $C_{25}H_{27}N_5O_4$ (EA) (%, Calcd/found): C, 63.15/63.09; H, 6.18/6.15; N, 16.02/16.04.

9: Yield: 74%, Mp: 148–149 °C. IR: 2216 cm^{-1} (CN), 1745 cm^{-1} (C=O), 1624, 1590, 754 cm^{-1} (carbazole), 1514, 1338 cm^{-1} (NO_2-). ^1H NMR ($CDCl_3$) δ (ppm): 1.43–2.05 (m, 8H, $-(CH_2)_4-$), 3.40 (s, 2H, $CNCH_2COO-$), 4.16 (t, $J=7.2$ Hz, 2H, $-NCH_2-$), 4.40 (t, $J=7.0$ Hz, 2H, $-OCH_2-$), 7.37 (t, 1H, ArH), 7.45–7.57 (m, 4H, ArH), 8.04 (d, 1H, ArH), 8.31 (t, 2H, ArH), 8.40 (d, 2H, ArH), 8.77 (s, 1H, ArH).MS (FAB), *m/z* [M]: 469, 100%. $C_{27}H_{25}N_4O_4$ (EA) (%, Calcd/found): C, 69.08/69.04; H, 5.33/5.29; N, 11.94/11.89.

10: Yield: 64%, Mp: 99–100 °C. IR: 2262 cm^{-1} (CN), 1746 cm^{-1} (C=O), 1626, 1587, 744 cm^{-1}(carbazole), 1123 cm^{-1}($-SO_2-$), 1235 cm^{-1} (C–N). ^1H NMR ($CDCl_3$) δ (ppm), 1.27 (t, $J=7.2$ Hz, 3H, $-CH_3$), 1.35–1.87 (m, 8H, $-(CH_2)_4-$), 3.15 (q, $J=7.5$ Hz, 2H, $-SO_2CH_2-$), 3.34 (s, 2H, $CNCH_2COO-$), 4.09 (t, $J=7.2$ Hz, 2H, $-NCH_2-$), 4.31 (t, $J=7.0$ Hz, 2H, $-OCH_2-$), 7.27 (t, 1H, ArH), 7.41–7.51 (m, 3H, ArH), 8.01 (t, 4H, ArH), 8.11 (t, 2H, ArH), 8.75 (s, 1H, ArH). MS (FAB), *m/z* [M^+]: 516, 100%. $C_{29}H_{30}N_3O_4S$ (EA) (%, Calcd/found): C, 67.44/68.01; H, 5.18/5.79; N, 8.14/8.09.

2.6. Synthesis of **P1**

Poly(hydrogenmethylsiloxane) (0.39 g, 6.4 mmol), *N*-allylindole (1.60 g, 10.0 mmol) and toluene (12 ml) were placed in a Schlenk tube with a nitrogen inlet. After the addition of a small amount of dichlorodicyclopentadiene platinum (10^{-4} mol/mol SiH), the mixture was agitated at 60 °C for 48 h. After the reaction, the main parts of the solvent were distilled under vacuum. Some methanol was added to precipitate the light green solid. The resultant product was purified by several precipilations from chloroform into methanol. (1.20 g, 88%) FT-IR (cm^{-1}, neat): 2931, 2865 (indole), 1262, 843 (CH_3Si-O-), 1241 (C–N), 1040 (Si–O–Si). ^1H NMR ($CDCl_3$)δ(ppm): −0.4–0.6 ($-CH_3Si$ and $-CH_2Si$), 1.4–1.8 ($-CH_2-$), 3.4–4.1 ($N-CH_2-$), 6.2–6.5 (ArH), 6.6–7.0 (ArH), 7.0–7.2 (ArH), 7.3–7.5 (ArH).

2.7. Synthesis of **P2**

To a solution of **P1** (0.9 g) in DMF (10 ml) at 0 °C, phosphorus oxychloride (1.2 ml) was added dropwise. The resultant solution stirred at 0 °C for 1 h, then heated to 50 °C, and left at this temperature for another 1 h. The solution was filtered and poured into ice water (100 ml). The resultant mixture was neutralized to pH 7 with the solution of sodium hydroxide (2 N). The precipitate was collected, washed with water and methanol, and further purified by several reprecipitations from its clear chloroform solution to methanol. After dried in vacuum at 50 °C, the product was weighted to be 0.76 g (about 74%). FT-IR (cm^{-1}, neat), 2930, 2880 (indole), 1658 (CHO), 1263, 785 (CH_3Si-O-), 1241 (C–N), 1031 (Si–O–Si). ^1H NMR ($CDCl_3$)δ(ppm): −0.5–0.6 ($-CH_3Si$ and $-CH_2Si$), 1.4–2.0 ($-CH_2-$), 3.4–4.2 ($N-CH_2-$), 5.9–6.1 (ArH), 6.6–7.0 (ArH), 7.0–7.4 (ArH), 7.4–7.7 (ArH), 7.8–8.4 (ArH), 9.4–10.0 (ArCHO).

2.8. Synthesis of **P3–6**

The general procedure was alike to prepare **P3–6**, and the synthesis of **P3** was given as an example.

P2 (120 mg, 0.49 mmol), **7** (240 mg, 0.55 mmol) and some piperidine (three drops) were dissolved in DMF (2.5 ml) under an argon atmosphere. The reaction mixture stirred at 50 °C for 48 h, and then poured into methanol. The precipitant was collected and further purified by several reprecipitations from its clear chloroform solution to methanol. After dried in vacuum at 50 °C, the product was weighted to be 0.17 g (about 55%) of dark red powder (**P3**). FT-IR (cm^{-1}, neat), 2931, 2859 (indole), 2207 (CN), 1712 (C=O), 1516, 1336 ($–NO_2$), 1102 (Si–O–Si). ^1H NMR ($CDCl_3$) δ(ppm): -0.2–0.2 ($–CH_3Si$), 0.3–0.6 ($–CH_2Si$), 1.22 ($–CH_3$), 1.3–2.0 ($–CH_2–$), 3.2–3.6 ($N–CH_2–$), 3.8–4.4 ($COOCH_2–$), 6.0–6.2 (ArH), 6.6–6.8 (ArH), 7.0–7.4 (ArH), 7.7–8.0 (CN–CH=CH– and ArH), 8.2–8.3 (ArH), 8.3–8.6 (ArH).

P4: Red powder, 57%. FT-IR (cm^{-1}, neat), 2932, 2852 (indole), 2213 (CN), 1713 (C=O), 1129 ($–SO_2$), 1084 (Si–O–Si). ^1H NMR ($CDCl_3$)δ(ppm): -0.2–0.2 ($–CH_3Si$), 0.3–0.6 ($–CH_2Si$), 1.1–1.3 ($–CH_3$), 1.3–2.0 ($–CH_2–$), 3.02–3.17 ($SO_2CH_2–$), 3.3–3.5 ($N–CH_2–$), 3.8–4.3 ($COOCH_2–$), 6.0–6.2 (ArH), 6.6–6.8 (ArH), 7.0–7.4 (ArH), 7.6–8.0 (CN–CH=CH– and ArH), 8.2–8.6 (ArH).

P5: Orange red powder, 53%. FT-IR (cm^{-1}, neat): 2932, 2859 (indole), 2213 (CN), 1712 (C=O), 1518, 1339 ($–NO_2$), 1104 (Si–O–Si). ^1H NMR ($CDCl_3$)δ(ppm): -0.2–0.2 ($–CH_3Si$), 0.3–0.6 ($–CH_2Si$), 1.43 ($–CH_3$), 1.5–2.0 ($–CH_2–$), 3.8–4.4 ($NCH_2–$ and $COOCH_2–$), 6.0–6.1 (ArH), 7.0–7.3 (ArH), 7.4–7.5 (CN–C=CH–), 7.6–7.8 (ArH), 7.8–8.2 (ArH), 8.3–8.5 (ArH), 8.6–8.8 (ArH).

P6: Orange powder, 58%. FT-IR (cm^{-1}, neat): 2934, 2859 (indole), 2213 (CN), 1712 (C=O), 1119 ($–SO_2$), 1086 (Si–O–Si). ^1H NMR ($CDCl_3$)δ(ppm): -0.2–0.2 ($–CH_3Si$), 0.3–0.6 ($–CH_2Si$), 1.1–1.3 ($–CH_3$), 1.3–2.0 ($–CH_2–$), 3.1–3.2 ($SO_2CH_2–$), 3.8–4.1 ($NCH_2–$), 4.2–4.4 ($COOCH_2–$), 6.0–6.1 (ArH), 7.1–7.3 (ArH), 7.4–7.5 (CN–C=CH–), 7.6–7.8 (ArH), 7.9–8.2 (ArH), 8.3–8.5 (ArH), 8.6–8.7 (ArH).

2.9. Polymer film preparation

P3–6 was dissolved in THF, and the solution (3 wt%) was filtered through syringe filters respectively. Polymer films were spin coated onto indium–tin-oxide- (ITO-) coated glass substrates (which were cleaned by *N*,*N*-dimethyformide, acetone, distilled water and THF subsequently in ultrasonic bath). Residual solvent was removed by heating the films in a vacuum oven at 40 °C for 2 days. The film thickness of the active layer was measured by TENCOR 500 Surface Profiler and was shown in Table 1.

2.10. Characterization of poled films

The second-order optical nonlinearity of **P3–6** was determined by in situ second harmonic generation (SHG) experiments using a closed temperature-controlled oven with optical windows and three needle electrodes. The film, which was kept at 45° to the incident beam, was poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows; temperature: the best poling temperature was different for **P3–6** and was shown in Table 1; voltage: 7.7 kV at the needle point, gap distance: 0.8 cm. SHG measurements were carried out with a Nd:YAG laser operating with 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

Compounds **3–4** were prepared by the normal azo coupling reaction. Compounds **5–6** were synthesized by a modified method reported previously [14], and in the experiment, the silica gel should be washed several times till the filtrate became colorless to improve the product yields, because the silica gel can absorb the product in the synthetic process (Scheme 1). Compounds **7–10** were prepared by the reaction between the cyanoacetic acid and the corresponding alcohol, and all the

Table 1
The physical data of **P1–6**

No.	T_g (°C)[a]	λ_{max} (nm)[b]	T_d (°C)[c]	M_n ($\times 10^3$)[d]	M_w ($\times 10^4$)[d]	d_{33} (pm/V)[e]	d_{33} (∞) (pm/V)[f]	l_s (μm)[g]
P1		289		3.9	1.7			
P3	77	492	297	5.3	2.3	55.2	6.28	0.41
P4	86	460	296	5.2	2.4	7.9	1.62	1.36
P5	97	403 (460)	330	5.6	2.6	14.0	2.87	1.28
P6	99	402	325	5.8	2.9	32.9	12.1	0.53

[a] Glass transition temperature (T_g) of polymers detected by the DSC analyses under nitrogen at a heating rate of 10 °C/min.

[b] Absorption maximum wavelength measured in the chloroform solutions of the polymers.

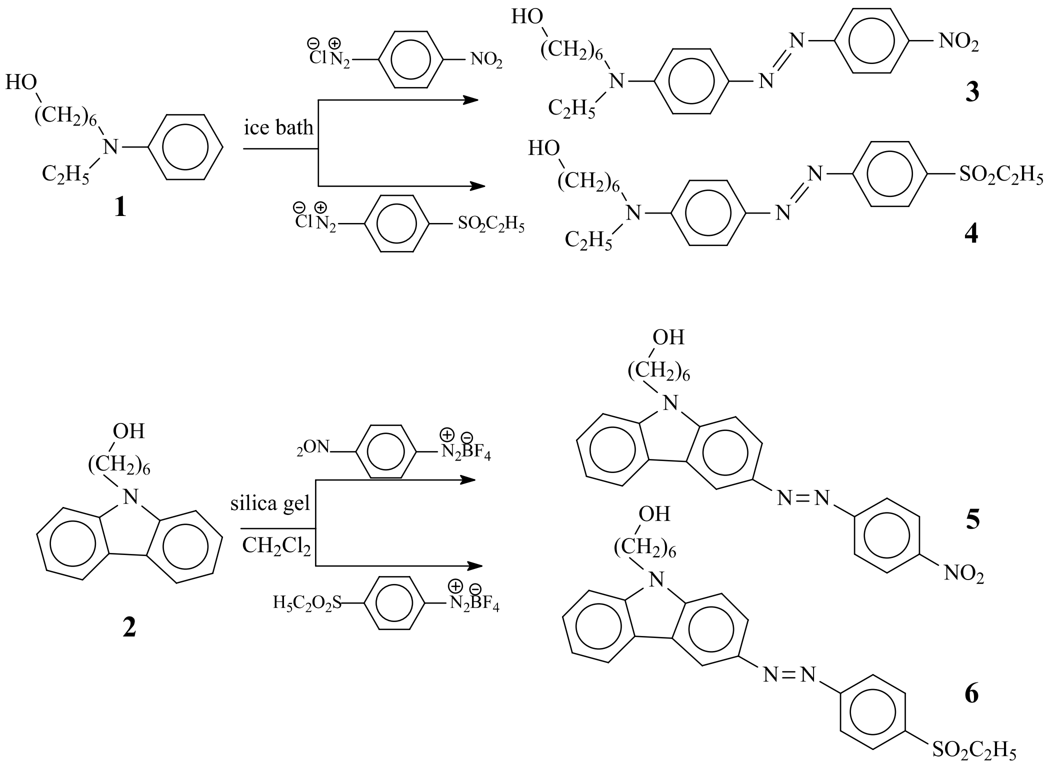
[c] The 10% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 20 °C/min.

[d] Determined by GPC in THF on the basis of a polystyrene calibration.

[e] Second harmonic generation (SHG) coefficient.

[f] The nonresonant d_{33} values calculated by using the approximate two-level model.

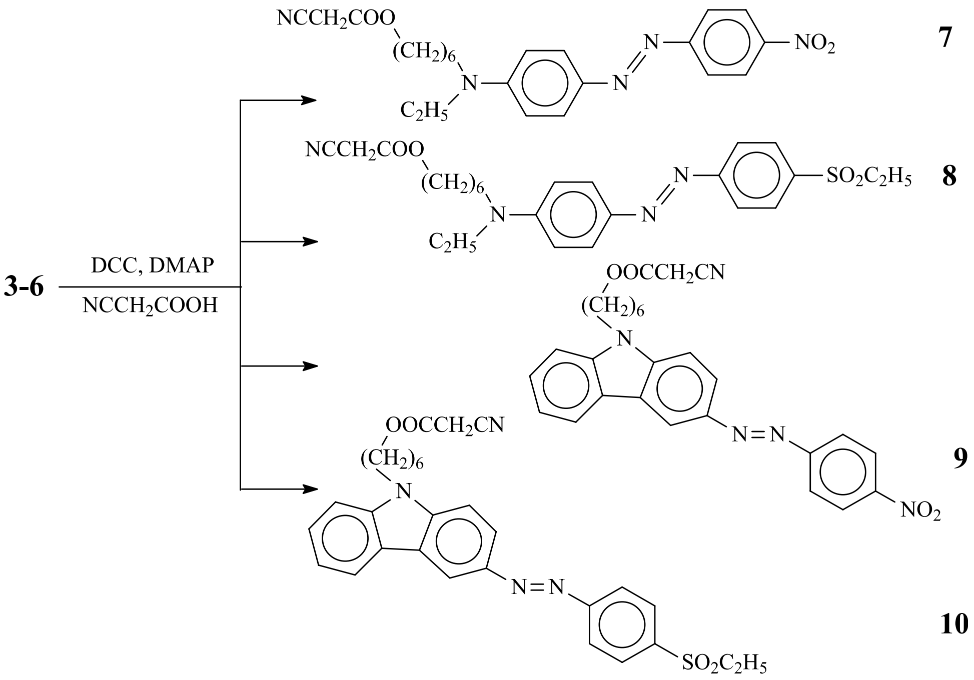
[g] Film thickness.



Scheme 1.

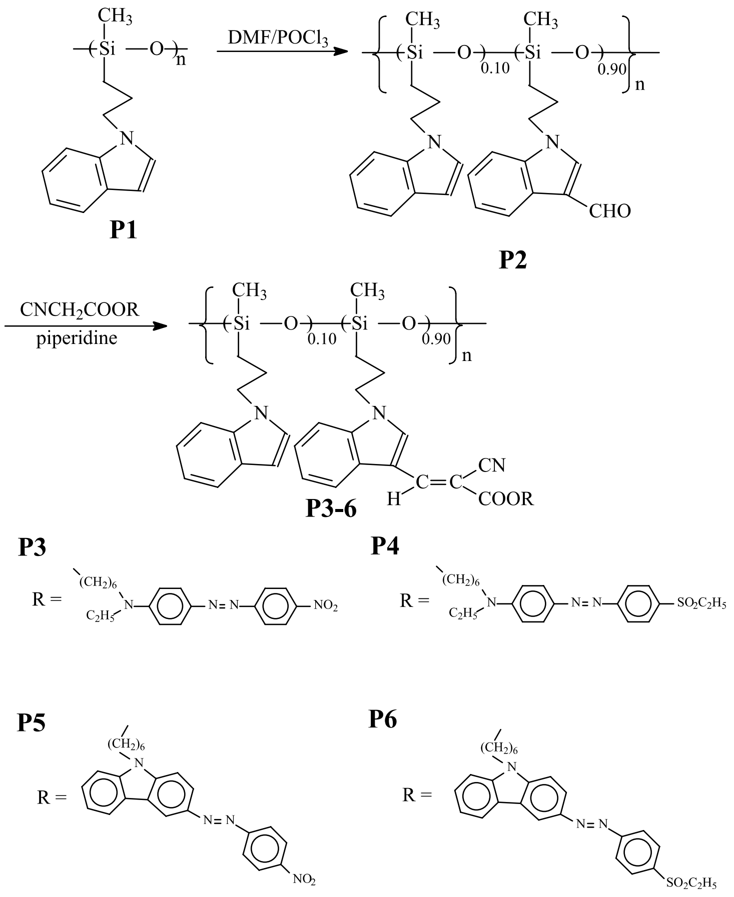
reacting compounds and the solvent should be well dried (Scheme 2).

As shown in Scheme 3, **P3–6** was prepared by the post functional method. First, a hydrosilylation reaction between poly(hydrogen-methylsiloxane) and *N*-allylindole occurred to yield **P1**; secondly **P1** was partially formylated by the standard Vilsmeier reaction to give **P2**; and then **P3–6** were prepared by the knoevenagel condensation between **P2** and the corresponding cyanoacetylated chromophore. In the hydrosilylation reaction, excess of *N*-allyindole was added to react with the SiH bonds completely in enough reaction time, since the polysiloxane would crosslink if there were some unreacted SiH bonds remained in the product. By the normal Vilsmeier reaction, most of the indole groups in **P1** were formylated



Scheme 2.

Scheme 3



Scheme 3.

successfully, and this is the first example concerned the Vilsmeier reaction of indole moieties bonded on polymers, though small indolecarbaldehyde molecules were reported to be synthesized [7]. The formylation degree of **P1** could be adjusted by controlling the molar ratio of the reagents and the reaction time. The formyl groups have high reactivity toward Knoevenagel condensation, and the cyanoacetate is selected as the active hydrogen species for its high reactivity and minimized byproduct in this reaction [15]. The whole approach to **P3–6** comprised only two steps. The special feature of this method was that different chromophores with hydroxyl groups could be easily converted to the cyanoacetylated chromophores, which were then linked to **P2** by Knoevenagel condensation. The reaction conditions are mild, and the purification is easy. It is believed that other polymers with indole side groups could be the precursor for the preparation of many NLO polymers. This method avoided the limitation of the reported methods to the indole-based NLO polymers in some degree, and made the synthesis of indole-based NLO polymers more flexibility.

Here, four different chromophores were linked to polysiloxanes, the donor groups are aniline or carbazole groups, and the acceptor groups are nitro or sulfonyl groups. Normally, the aniline groups are better donor than carbazole groups, and can offer high d_{33} values, while the latter possess better thermal stability and good photoconductivity. The sulfonyl groups possess strong acceptor properties, though a little weaker than that of nitro groups, but the sulfonyl compounds showed much wider transparency in visible region (with hypsochromic shift of 20–40 nm) and the synthetic flexibility, and the chromophores exhibited similar first molecular hyperpolarizability (β) when the nitro groups were replaced by the sulfonyl groups [16]. Therefore, we would like to compare the comprehensive properties of **P3–6** by using these four chromophores at the same molar concentration in the polymers.

3.2. Structural characterization

Compounds **3–10** were well characterized, and the analytical data were shown in the experimental part. Since **7–10** were new compounds, the elemental and the mass spectral analysis were also conducted. **P1–6** were confirmed by ^{1}H NMR, IR and UV–vis spectra, gel permeation chromatograply (GPC) and differential scanning calorimetry (DSC). The ^{1}H NMR and IR data were shown in the experimental part, and the others were listed in Table 1. Also their spectra were demonstrated in this paper, and those of **P4** were selected from **P3–6** for example.

Fig. 1 showed the IR spectra of **P1**, **P2** and **P4**. The absorption in the range of 1100–1000 cm^{-1} was assignable to the intense stretching vibration of Si–O–Si bonds, the absorptions around 2932 and 2851 cm^{-1} were assigned to the indole groups, and the absorption of the $Si–CH_3$ bonds was at about 1265 and 843 cm^{-1}. An apparently strong absorption band appeared at 1658 cm^{-1} in **P2** confirmed that the high concentration of formyl groups were introduced to the indole side chains in polysiloxane by the Vilsmeier reaction. And this strong absorption disappeared completely in **P4**, while new absorption bands at 1712 and 2213 cm^{-1} emerged, respectively contributed by the carbonyl stretching vibration of a conjugated carboxylic ester and the nitrile stretching vibration. Moreover, new absorption band at 1129 cm^{-1} can be attributed to the characteristic peak of sulfonyl groups. This indicated that all the formyl groups in **P2** reacted with the cyanoacetylated chromophore **8**, and the latter was linked to the polymer successfully. Similar changes could also be easily found in the spectra of **P3**, **P5** and **P6**. In all the spectra of **P1**–**6**, there is no absorption at 2155 cm^{-1}, the typical absorption band of the Si–H stretching, indicating that all the Si–H bonds have underwent the hydrosilylation reaction in the preparation procedure of **P1**. The same situation happens in the ^{1}H NMR spectra, where the SiH peak (at about δ 4.6 ppm) was absent in **P1**–**6**.

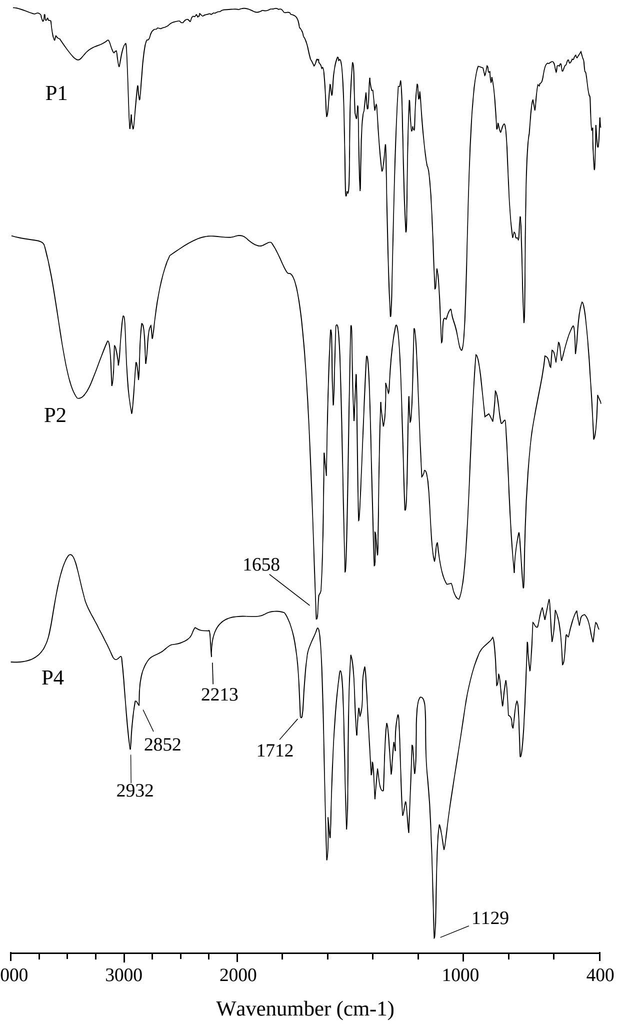


Fig. 1. IR spectra of **P1**, **P2** and **P4**.

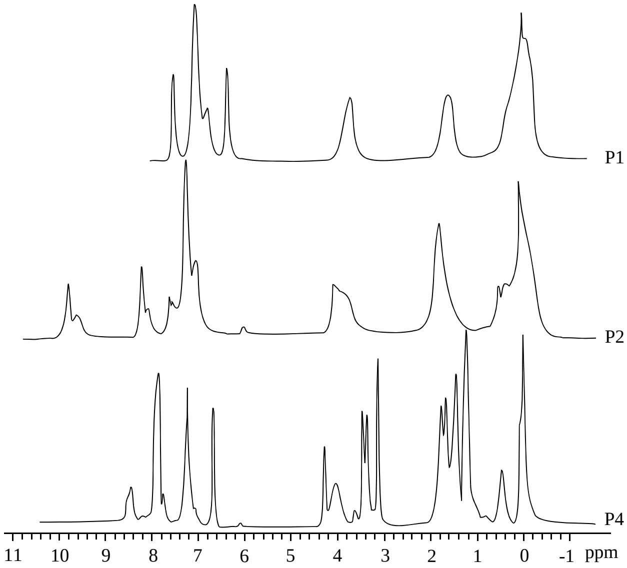


Fig. 2. ^{1}H NMR spectra of **P1**, **P2** and **P4**.

The ^{1}H NMR spectra of **P1**, **P2** and **P4** were shown in Fig. 2. For **P1**, the side chain was only the indole group, and the ^{1}H NMR peak integrations coincide with the structure shown in Scheme 3. In **P2**, the component concentrations of two indole moieties could be calculated to be 1:9 from the ^{1}H NMR peak integration of one proton resonance of the indole group at 6.22 ppm and the integration of the aldehyde proton. After the Knoevenagel condensation, some resonance peaks appeared in the downfield, which were due to the *p*-ethylsulfonyl phenyl moieties, and new peak assigned to the $–SO_2CH_2–$ groups appeared around 3.1 ppm, confirming that the condensation reaction was successful and the azo chromophore was really linked to the polymer. As the peak around 9.9 ppm assigned to the aldehyde proton has disappeared completely, it was considered that all of the aldehyde groups in **P2** have reacted with cyanoacetylated chromophore **8** as they possess high reactivity toward Knoevenagel condensation. Therefore, **P4** should take the structure as shown in Scheme 3, and the ^{1}H NMR peak integration coincides with the structure. The structure of **P3**, **P5** and **P6** could also be determined as shown in Scheme 3 by calculating the ^{1}H NMR peak integration carefully, combining the fact that there were no peaks around 9.9 ppm of aldehyde proton in the ^{1}H NMR spectra of them.

P1–**6** were easily soluble in common organic solvents, such as toluene, $CHCl_3$, THF, DMSO and DMF, etc. Fig. 3 showed the UV–Vis spectra of them in chloroform. After the linkage of the corresponding cyanoacetylated chromophores, new strong absorption maximum of the π–π* transition of chromophores appeared in **P3**–**6**, which were similar to those of their corresponding free small chromophores and all the data were shown in Table 1. As mentioned above, the sulfonyl-based chromophore moieties in **P4** and **P6** really showed blue-shifted

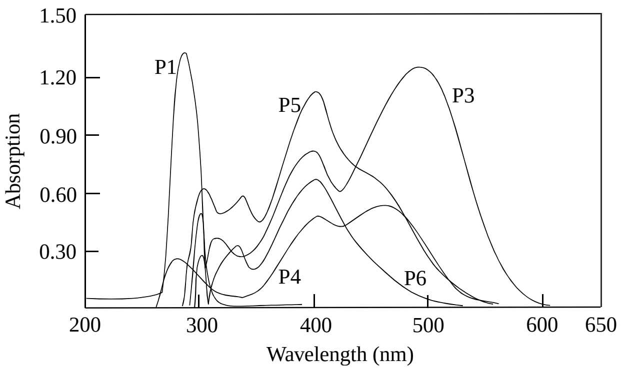


Fig. 3. UV–Vis spectra of **P1–6**.

maximum absorption. It is about 32 nm for **P4** compared to that in **P3**, while not obvious in **P6**, but the shoulder peak at 460 nm disappeared, showing wider transparency than **P5**.

The polysiloxanes did not show any significant low-temperature weight loss. The 10% weight loss temperature of polymers was detected to be nearly 300 °C for **P3–4**, while those of **P5–6** even up to 330 °C. The molecular weights of the polymers were determined by GPC experiments with the use of THF as solvent. The DSC thermograms of polymers exhibited that the glass transition temperature are relatively low, indicating that the backbone possesses good flexibility. All the results were demonstrated in Table 1.

3.3. Nonlinear optical property

To evaluate the NLO activity of the poled polymer films, thin films of **P3–6** were prepared for SHG measurement. Calculation of the d_{33} values for the poled films is based upon the equation as shown below [17],

$$\frac{d_{33,\mathrm{s}}}{d_{11,\mathrm{q}}} = \sqrt{\frac{I_\mathrm{s}}{I_\mathrm{q}}}\frac{l_{\mathrm{c,q}}}{l_\mathrm{s}}F$$

where the $d_{11,\mathrm{q}}$ is d_{11} of the quartz crystals, which is 0.45 pm/V, I_s and I_q are the SHG intensities of the sample and the quartz, respectively, $l_{\mathrm{c,q}}$ is the coherent length of the quartz, l_s is the thickness of the polymeric film, and F is the correction factors of the apparatus and equals 1.2 when $l_{\mathrm{c,q}} \gg l_\mathrm{s}$. The d_{33} values of **P3–6** were calculated at 1064-nm fundamental wavelength, and the results were shown in Table 1.

Although the d_{33} value of the same NLO polymer could be different when tested by different method or in different testing system. We can still compare the obtained results of these four polymers with each other and other polymers tested at the same testing equipment before. **P3** showed the highest d_{33} value, coinciding with the highest β value of chromophore **7** [16f], measured by HRS technique in chloroform using the fundamental excitation wavelength of 1064 nm, among the four chromophores [18]. And also, this value is similar to that we tested before in the polyphosphazene system with almost the same chromophore structure despite the different molar concentration of chromophore [5h]. The second higher d_{33} value was found in **P6**, which is much lower than that of **P3**. It is reasonable since the carbazolyl group is not a good donor moiety as aniline groups, while sulfonyl moieties are not so strong acceptors as nitro groups. It seems very strange when we saw the results of **P4** and **P5**. Both of them are much lower than those of **P3** and **P6**. As we knew, the β values of chromophores are in the order of **7**>**8**>**9**>**10** [16f], then the d_{33} values should be as **P3**>**P4**>**P5**>**P6** provided other conditions are the same, especially the molar concentrations of these chromophores are the same in the polymer system, which is another advantage of this new synthetic method presented here. However, the actual results are in the order of **P3**>**P6**>**P5**>**P4**. We have tried to prepare films again, but obtained the similar results. Although we could explain that the much thicker film thickness of **P4** and **P5** may result in the low poling efficiency and led to the low tested d_{33} values directly. But we can not attribute the lower value of **P4**, compared with that of **P5**, to the same reason as the thickness of their films is similar. Also by using the approximation two-level model, the nonresonant d_{33} value of polymers are estimated (Table 1), but the results still not coincide with the tested β values of chromophores polymers contain. Then, perhaps, we could raise another question as other scientists mentioned: the behavior of chromophore moieties in the polymeric system is complicated, and many factors could affect the poling behavior of chromophors [19]. Therefore, how to transform the high β values of the chromophores to the high macroscopic d_{33} values of polymeric materials is still a big challenge ahead of us. This problem should be solved to further push the development of NLO polymeric materials, and bring this kind of promising material into practical applications.

Generally the photorefractive (PR) effect can occur in materials that simultaneously possess electro-optical activity and photoconductivity [1]. Here in **P3–6**, every unit contains one indole group, therefore the indole groups are close enough in space due to its high density and the good flexibility of polysiloxane backbone. And the charge carrier can transport between them, as it is charge-transporting agent and the photocunductivity has been proved [7,8], to ensure the photoconductivity. As **P3–6** have demonstrated the second order nonlinear optical property, therefore, it is expected that **P3–6** could show PR effect.

4. Conclusion

A novel post functional strategy was presented, and it was successfully applied to prepare a series of NLO polysiloxanes with high density of chromophore. The whole synthetic route comprised hydrosilylation reaction, Vilsmeier reaction and Knoevenagel condensation. All the reaction conditions are mild and with high product yields. This synthetic method is very simple, and the purification procedure is very easy. The polymers were easily soluble in common organic solvents, and showed good properties. We hope that this method will promote the preparation of more other polymers containing indole-based chromophore for NLO applications.

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