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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