

# Synthesis and characterization of polysiloxanes containing carbazolyl and sulfonyl-indole based chromophore as side chains

Zhen Li<sup>a</sup>, Jun Li<sup>a</sup>, Jingui Qin<sup>a,\*</sup>, Anjun Qin<sup>b</sup>, Cheng Ye<sup>b</sup>

<sup>a</sup>Department of Chemistry, Wuhan University, Wuhan 430072, China

<sup>b</sup>Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

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## Abstract

A new post-functional strategy was developed to prepare polysiloxanes with the sulfonyl-indole based chromophore and carbazolyl side groups. Thus a polysiloxane (**P1**) with indole and carbazolyl groups as side chains was first synthesized through hydrosilylation reaction, and then the post-azo coupling of *p*-ethylsulfonylbenzenediazonium fluoroborate toward the indole rings afforded the multifunctional sulfonyl-indole based chromophore-functionalized polysiloxane (**P2** and **P3**). The polymers were easily soluble in common organic solvents, and their maximum absorption appeared at 394 nm, which is about 30 nm blue-shifted compared to the corresponding chromophore with nitro acceptors, and could result in a wider transparency window. The poled films of **P2** and **P3** reveals a resonant  $d_{33}$  value of 12 and 18 pm/V, respectively, by second harmonic generation (SHG) measurements.

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**Keywords:** Polysiloxane; Synthesis; Sulfonyl

## 1. Introduction

While the traditional carbon-chain polymers have been studied more thoroughly and encountered some problems, polymers with inorganic backbones have attracted more and more interest recently due to their special properties and some advantages over the former ones [1]. Among them, polysiloxanes are one of the largest kinds of inorganic polymers. There are many types of commercial products of polysiloxanes for the applications in industry and daily life due to their excellent properties, such as temperature resistance, resistance to weather and good electrical properties [2]. Furthermore, polysiloxanes generally possess low glass transition temperature due to its flexible backbone, and can be easily prepared by various methods including hydrosilylation. On the other hand, organic nonlinear optical (NLO) chromophore-containing polymeric materials are considered as the most promising NLO materials for their huge potential photonics

applications and many advantages over single crystals such as the superior chemical flexibility, processability, and low cost [3,4]. By utilizing their advantages mentioned above, some polysiloxanes containing NLO chromophore as side chains have been prepared by us [5–7] and other scientists [8,9], and showed good properties for the potential practical NLO applications. Especially, the low glass transition temperature of polysiloxanes is possibly suitable for NLO switching at room temperature. However, the syntheses of them were relatively complex [8,9], or there were still some unreacted SiH groups remained which resulted in the cross-linking of the polysiloxanes and led to the sharply decrease of their solubility in the storage [7]. Therefore, some new synthetic strategies are needed to develop the NLO polysiloxanes.

The sulfonyl moieties are good acceptor groups, similar to the nitro groups, but not been widely studied like the latter in NLO field. According to literatures [10–13] and our previous work [14], the chromophores exhibit similar molecular hyperpolarizabilities when the nitro groups were replaced by the sulfonyl groups, but the sulfonyl compounds showed much increased visible spectrum

\* Corresponding author. Tel.: +86 27 67864117; fax: +86 27 67856757.  
E-mail address: [jgqin@whu.edu.cn](mailto:jgqin@whu.edu.cn) (J. Qin).

transparency (hypsochromic shift 20–40 nm) which is also an important parameter of NLO polymers besides the high stability and the large macroscopic optical nonlinearity [15–17]. In addition, the sulfonyl ones are bifunctional groups, which permit greater freedom in the design of compounds for specific applications and allows more flexibility for synthetically tailoring the physical properties. However, studies on sulfonyl groups for NLO applications are still not enough.

In this paper, a novel synthetic strategy was developed to prepare polysiloxanes with sulfonyl-indole based chromophore side chains, and the synthetic route was shown in Scheme 1. The polysiloxanes (**P1–P3**) were easily soluble in common solvents, and very stable during the storage. And the poled films of **P2** and **P3** reveals a resonant  $d_{33}$  value of 12 and 18 pm/V, respectively, by second harmonic generation (SHG) measurements. This synthetic route is very simple, and the purification of the products was very easy. Therefore, it can be applied to prepare many other NLO polymers with sulfonyl-indole based side groups.

## 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. Dicyclopentadienedichloroplatinum is synthesized according to the method of Doule [18]. *N*-allylcarbazole was prepared as reported previously [5]. *N*-allylindole was prepared by the reaction between indole and allyl chloride in DMF at the presence of excess of potassium hydroxide. *N*-methylpyrrolidone (NMP) was dried over and distilled from  $\text{CaH}_2$  under an atmosphere of dry

nitrogen. All other reagents were used as received. The hydrosilylation reaction of poly(hydrogenmethylsiloxane) was carried out in a dry nitrogen atmosphere using Schlenk technique.

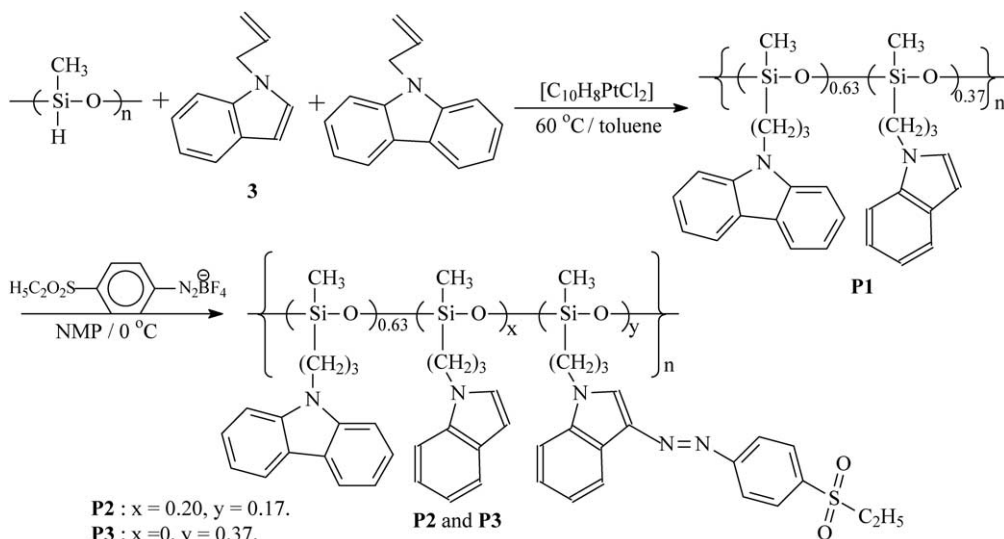
$^1\text{H}$  NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer. FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 series in the region of  $3000\text{--}400\text{ cm}^{-1}$  on KBr pellets. UV–vis spectra were obtained using a Shimadzu 160A spectrometer in the polymer DMF solution. Molecular weights were determined by gel permeation chromatography (GPC) combined with light scattering (LS) in THF solution. Differential scanning calorimetry (DSC) analyses were performed in a Rigaku Themoflex DSC8131 at a scan rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Thermal analysis was performed on SHIMADZU DT-40 thermal analyzer at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  in nitrogen at a flow rate of  $50\text{ cm}^3/\text{min}$  for thermogravimetric analysis (TGA).

### 2.2. Synthesis of *p*-ethylsulfonylbenzenediazonium fluoroborate

*p*-Ethylsulfonylaniline (0.56 g, 3 mmol) was dissolved in fluoroboric acid (40%), and then the solution was cooled to  $0\text{ }^\circ\text{C}$ . A solution of sodium nitrite (0.21 g, 3 mmol) in water (1.5 ml) was added dropwise. The resultant mixture was stirred at  $0\text{ }^\circ\text{C}$  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 (0.7 g).

### 2.3. Synthesis of polysiloxane **P1**

Poly(hydrogenmethylsiloxane) (0.384 g, 6.4 mmol), *N*-allylindole (**3**) (0.30 g, 2.0 mmol) and toluene (12 ml) were placed in a Schlenk tube with a nitrogen inlet. After the



Scheme 1.

addition of a small amount of dichlorodicyclopentadiene platinum ( $10^{-4}$  mol/mol SiH), the mixture was agitated at 60 °C for 48 h. Then *N*-allylcarbazole (2.0 g, 9.7 mmol) was added, and the resultant mixture was reacted at 60 °C for three days. After the reaction, the main parts of the solvent were distilled under vacuum. Some methanol was added to precipitate the white solid. The resultant product was purified by several precipitations from chloroform into methanol. (1.1 g).

#### 2.4. Preparation of polysiloxane **P2** and **P3**

Polysiloxane **P1** (0.25 g) was dissolved in 1.8 ml of *N*-methylpyrrolidone (NMP), and then *p*-ethylsulfonylbenzenediazonium fluoroborate (51 mg) was added under cooling with an ice bath. The color of the solution changed to red immediately. After stirring for 8 h at 0 °C, excessive anhydrous potassium carbonate was added and the mixture was stirred for additional 1 h, and then filtered. The residue was washed with THF, and the filtrates were collected and THF was removed under reduced pressure. Then some methanol was added dropwise to precipitate the polymer. Reprecipitation from chloroform into methanol gave 0.17 g orange product **P2**.

**P3** was prepared similar as that of **P2**, but the weight of *p*-ethylsulfonylbenzenediazonium fluoroborate was 120 mg. At last, 0.19 g orange product of **P3** was obtained.

#### 2.5. Polymer film preparation

**P2** and **P3** was dissolved in THF, and the solution (4 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*-dimethylformide, 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 0.42 μm for **P2** and 0.61 μm for **P3** measured by TENCOR 500 Surface Profiler.

#### 2.6. Characterization of poled films

The second-order optical nonlinearity of **P2** and **P3** 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: 41 °C for **P2** and 48 °C for **P3**, voltage: 8.5 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

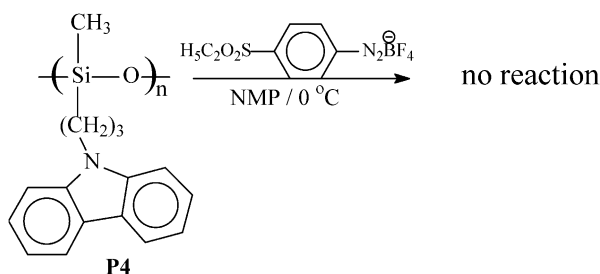
#### 3.1. Polymer synthesis

The synthetic strategy to **P2** and **P3** is a post-functional method. It includes two steps. First, a hydrosilylation reaction of poly(hydrogen-methylsiloxane) with the terminal double bonds of the allyl chains of *N*-allylindole and *N*-allylcarbazole occurred to produce **P1**, which is the precursor polymer for the next reaction. Then in the following step, *p*-ethylsulfonylbenzenediazonium fluoroborate attacked the indole rings of **P1** in the solvent of NMP to yield **P2** and **P3** by the post-azo coupling reaction. As the NLO chromophores was not linked to the polysiloxane backbone directly from the hydrosilylation reaction but post-coupling reaction, it avoids the possibility of some unreacted SiH bonds remaining due to the steric hinder of bulky azo chromophores [7]. That is to say, in the first step, by adding excess *N*-allylcarbazole to the reacting mixture, the Si–H bonds could be reacted completely. This was supported by the following structural characterization.

The post-coupling reaction is a convenient method to introduce azo chromophores into the side chains of NLO polymers, which was first used by Katz et al. [19] and developed by Tripathy et al. [20]. Recently, we successfully extended the post-azo coupling reaction to prepare polymers with the indole azo chromophore side chains at the first time [21]. However, in all the above cases, the acceptors of the NLO chromophores are nitro groups, and there are no reports about other acceptors. But we still expect that **P2** and **P3** could be synthesized as both sulfonyl and nitro groups are strong acceptors, and both of *p*-alkylsulfonylaniline and *p*-nitroaniline could form diazonium salts in hydrochloric acid. So, by the method similar to that for *p*-nitrobenzenediazonium fluoroborate [22], *p*-ethylsulfonylbenzenediazonium fluoroborate was prepared, though there was no report about the preparation.

This overall route is very simple, and the reaction conditions are mild. Especially, it provides a novel method to prepare NLO polymers with sulfonyl-based chromophores, and it is believed that many other NLO polymers could be synthesized by this novel strategy.

At the very beginning of this research, we worried if the *p*-ethylsulfonylbenzenediazonium fluoroborate might attack the carbazolyl ring to form azo carbazolyl moieties. If it is the case, then the structure of the resultant product would be very complicated. So another polysiloxane (**P4**) instead of **P1** was stirred with *p*-ethylsulfonylbenzenediazonium fluoroborate at the same conditions as the preparation of **P2** and **P3** (Scheme 2). However, there was no absorption assigned to the azo carbazolyl chromophore in the UV–vis spectroscopy of the resultant solid, and no absorption of the sulfonyl groups appeared in the IR spectroscopy. On the contrary, the UV–vis, IR and NMR spectra of the resultant product were essentially the same as those of **P4**. These results demonstrated that the azo salts did not attack the



Scheme 2.

carbazoyl ring in the side chain of **P4** at these reacting conditions. Therefore in the preparation procedure of **P2** and **P3**, the *p*-ethylsulfonylbenzenediazonium fluoroborate would only attack the indole groups, and the structure of them was just as shown in Scheme 1.

### 3.2. Structural characterization

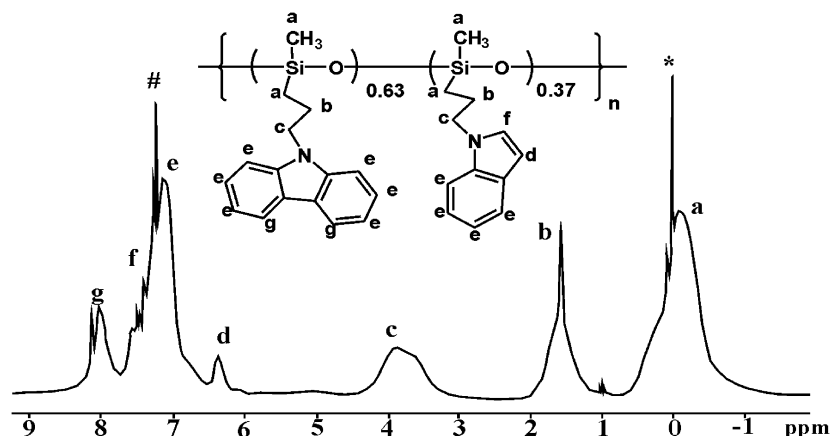
In the IR spectra of **P1–P3**, there is no absorption at  $2155\text{ cm}^{-1}$  assignable to the Si–H stretching, indicating that the Si–H has been completely reacted. The absorption in the range of  $1100\text{--}1000\text{ cm}^{-1}$  was assignable to the intense stretching vibration of Si–O–Si bonds, and the absorptions for the Si–CH<sub>3</sub> bonds were at  $1265$  and  $843\text{ cm}^{-1}$ . In **P2** and **P3**, an apparently strong absorption band appeared at  $1129\text{ cm}^{-1}$  is assignable to the absorption of the sulfonyl unit. This confirmed that the *p*-ethylsulfonylbenzenediazonium fluoroborate had reacted with the indole ring and the sulfonyl units were introduced into the polymer side chains.

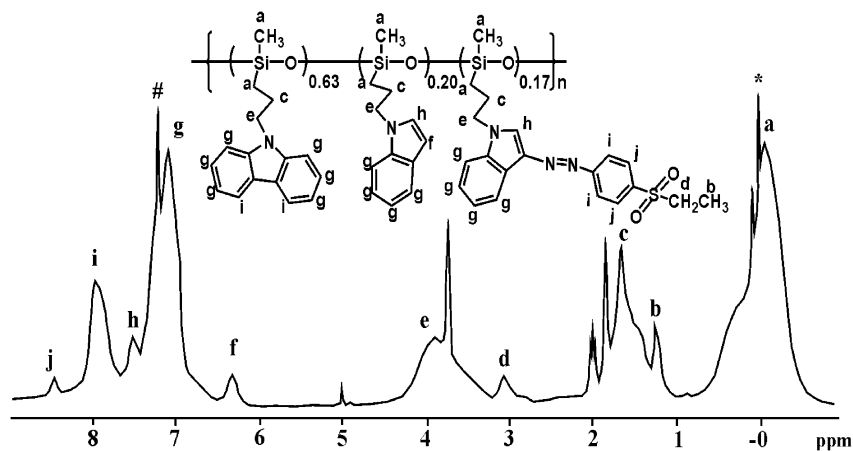
The <sup>1</sup>H NMR spectra of **P1** and **P2** were shown in Figs. 1 and 2, and the assignment of peaks was also demonstrated. The component concentrations of **P1** could be calculated from the <sup>1</sup>H NMR peak integration of one proton resonance of the indole group at 6.22 ppm and the total integration of two proton resonances of the carbazoyl moieties in the range of 7.80–8.20 ppm. After the azo coupling reaction, some resonance peaks appeared in the downfield, which were due to the *p*-sulfonyl phenyl moieties, and two new

peaks assigned to the ethyl groups linked to the sulfonyl moieties were also present. These new appeared peaks also confirmed that the azo coupling reaction was successful and the azo chromophore really formed. And the component concentrations of **P2** could be calculated from the integration of one proton resonances of the unreacted indole groups at 6.25 ppm and the integration of two proton resonances of the phenyl moieties near the sulfonyl groups at 8.43 ppm, combining the total concentration of the indole moieties in the polymer including the unreacted indole groups and the indole azo groups. The <sup>1</sup>H NMR spectrum of **P3** is similar to that of **P2** except that the peak at 6.25 ppm assigned to the three positions of the indole group has disappeared completely. This indicated that all of the indole groups in **P1** have reacted with *p*-ethylsulfonylbenzenediazonium fluoroborate to yield the corresponding azo chromophores. Therefore, **P3** should take the structure as shown in Scheme 1. In all the three <sup>1</sup>H NMR spectra of **P1–3**, the SiH peak (at about  $\delta$  4.6 ppm) was absent to prove the successful completed reaction of SiH bonds in the procedure of the hydrosilylation reaction once more.

**P1–3** were easily soluble in common organic solvents, such as toluene, CHCl<sub>3</sub>, THF, DMSO and DMF, etc. Fig. 3 showed the UV–vis spectra of **P1–3**. After the post-azo coupling reaction, a new strong absorption maximum of the  $\pi$ – $\pi^*$  transition of sulfonyl-indole based chromophore appeared at about 394 nm, with a cutoff at ca 500 nm in both of **P2** and **P3**. And the absorption peak of **P3** at 394 nm is relatively higher than that of **P2**, which coincides well with the higher chromophore concentration in **P3**. This maximum absorption is about 30 nm blue-shifted compared to the corresponding chromophore with nitro acceptor, and could result in better transparency of polysiloxanes, which is an important parameter of NLO materials. The molecular weights of the polymers were determined by GPC experiments with the use of THF solvent. The  $M_n$  and  $M_w$  of **P2** were  $4.9 \times 10^3$  and  $2.3 \times 10^4$ , respectively, while that of **P3** were  $5.1 \times 10^3$  and  $2.6 \times 10^4$ .

The polysiloxanes did not show any significant low-

Fig. 1. <sup>1</sup>H NMR spectra of polysiloxanes **P1**.

Fig. 2.  $^1\text{H}$  NMR spectra of polysiloxanes **P2**.

temperature weight loss. The high-temperature weight loss for **P2** commenced at about 350 °C, while **P3** at about 330 °C, and increased gradually at high temperature. The DSC thermograms of polymers exhibited a glass transition ( $T_g$ ) at about 46 °C of **P2** and 52 °C of **P3**. The  $T_g$ 's are relatively low, indicating that the backbone has good flexibility.

### 3.3. Nonlinear optical property

The thin films of **P2** and **P3** were prepared for SHG measurement to evaluate the NLO activity. Calculation of the  $d_{33}$  value for the poled **P2** is based upon the equation as shown below [23],

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{\frac{I_s l_{c,q}}{I_q l_s}} F$$

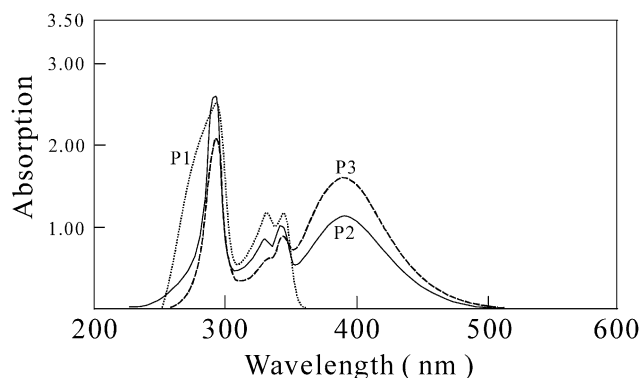
where the  $d_{11,q}$  is  $d_{11}$  of the quartz crystals, which is 0.45 pm/V,  $I_s$  and  $I_q$  are the SHG intensities of the sample and the quartz, respectively,  $l_{c,q}$  is the coherent length of the quartz,  $l_s$  is the thickness of the polymeric film, and  $F$  is the correction factors of the apparatus and equals 1.2 when  $l_{c,q} \gg l_s$ . The  $d_{33}$  values of **P2** and **P3** were calculated to be 12 and 18 pm/V, respectively, at 1064-nm fundamental

wavelength. The higher value of **P3** may be due to the higher chromophore concentration in **P3**. The values were relatively high, similar to those of polysiloxanes containing Dispersed Red-1 (DR-1) or similar chromophores reported in the literature [24] but lower than the cases reported by Park et al. in 2000 [25]. However, the  $d_{33}$  value of the same NLO polymer could be different when tested by different method or different testing system. Compared with the values of our other polymers containing Dispersed Red-1 (DR-1) or nitro-based indole azo groups as NLO chromophores tested at the same testing equipment [21,26–28], the  $d_{33}$  values were only a little lower though the sulfonyl groups were in place of the nitro groups as the acceptor groups.

Generally the photorefractive (PR) effect can occur in materials that simultaneously possess electro-optical activity and photoconductivity [1,2]. Here in **P2** and **P3**, every unit contains one carbazolyl or indolyl group (including indole and indole azo groups), therefore the carbazolyl and 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 these two moieties as they are good charge-transporting agents [1,25] to ensure the photoconductivity. As **P2** and **P3** has demonstrated the second order nonlinear optical property, therefore, it is expected that **P2** and **P3** could show PR effect, and the low  $T_g$ 's of the polymers would enhance the PR properties due to an orientational enhancement effect. The PR researches are currently in progress.

## 4. Conclusion

A new synthetic strategy is presented to prepare polysiloxanes **P2** and **P3** with a high density of the sulfonyl-indole based chromophore and carbazole groups. The polymers exhibit excellent solubility in common organic, such as toluene,  $\text{CHCl}_3$ , THF, DMSO and DMF, etc. and are very stable during storage. The poled films of **P2**

Fig. 3. UV-vis spectra of polysiloxanes **P1-3**.

and **P3** reveals a resonant  $d_{33}$  value of 12 and 18 pm/V by second harmonic generation (SHG) measurements. This synthetic route is very simple, and the purification of the products is very easy. Also the reaction conditions are mild. Therefore, we hope that this novel strategy will promote the preparation of more other polymers containing sulfonyl-based chromophore for NLO applications.

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