

# Synthesis and Characterization of a Series of New Functional Poly(ferrocenylenesilanes) for Nonlinear Optics<sup>†</sup>

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A series of new poly(ferrocenylenesilanes) containing carbazole as charge transporting agent and Dispersed Red 1 (DR-1) as second-order nonlinear optical (NLO) chromophore was synthesized. The resulting polymers represent the first example of NLO polymer with ferrocenyl groups in the backbone. This series of polymers was characterized with <sup>1</sup>H NMR, UV-vis, IR spectroscopies, differential scanning calorimeter (DSC) and gel permeation chromatography (GPC). A preliminary measurement on NLO property of the polymers was carried out with *in-situ* second-harmonic generation (SHG) measurement.

**Keywords** poly(ferrocenylenesilane), nonlinear optical (NLO), photorefractive, multifunctional, synthesis, chromophore, SHG

## Introduction

Poly(ferrocenylenesilanes) are a novel class of transition metal organometallic polymers with a backbone consisting of alternating ferrocene and organosilane units. High molecular weight poly(ferrocenylenesilanes) was first synthesized via thermal ring-opening polymerization (ROP) by Manners and co-worker in 1992.<sup>1</sup> Since then the polymers have received considerable attention<sup>2-7</sup> with respect to their interesting physical and chemical properties and

potential application in such fields as liquid crystal,<sup>8</sup> electronic materials<sup>9</sup> and magnet<sup>10-15</sup> materials.

We are interested in exploring the nonlinear optical (NLO) properties, including electro-optical and photorefractive (PR) properties, of poly(ferrocenylenesilanes) due to several considerations. The transition metal organometallic polymeric NLO materials, though have received little attention thus far, may show some different behavior from organic polymers. The high molecular weight poly(ferrocenylenesilanes) are highly processible polymers with relative ease to introduce a variety of functional groups to the backbone. For a polymer to show photorefractive effect, they must simultaneously exhibit photoconductive and electro-optical properties.<sup>16</sup> It was expected that poly(ferrocenylenesilanes) may exhibit weak photoconductive behavior due to a weak electron conjugation in the backbone. On the other hand, carbazole unit is an effective charge transporting agent for increasing the photoconductivity and has been utilized in many applications,<sup>17</sup> and Disperse Red-1 (DR-1) is an effective NLO chromophore for electro-optical effect. Thus, we recently have synthesized a series of new multifunctional poly(ferrocenylenesilanes) containing different ratios of charge trans-

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Received May 20, 2002; revised and accepted September 26, 2002.

Project supported by the Education Ministry of China and by a grant (No. 99078) from the National Key Fundamental Research Program of China.

<sup>†</sup>Dedicated to Professor HUANG Yao-Zeng on the occasion of his 90th birthday.

porting agents and NLO chromophores as pendant groups for nonlinear optical application. The synthetic reaction sequence is shown in Scheme 1. Poly(ferrocenylmethylchlorosilane) (**3**) matrix was synthesized firstly via transition-metal catalyzed ROP of 1,1'-ferrocenediylmethylchlorosilane (**2**), and then DR-1 (**4**) (as second-order nonlinear optical chromophore) and *N*-(6-hydroxyhexyl)carbazole (**5**) (as charge-transporting agents) were introduced onto the backbone of **3** through post-functionalization. To the best of our knowledge, these polymers represent the first examples of poly(ferrocenylenesilanes) for NLO purpose. In this paper, we report the synthesis and structural characterization of multifunctional poly(ferrocenylenesilanes) as well as the preliminary results of the second-order NLO property measurement.

## Experimental

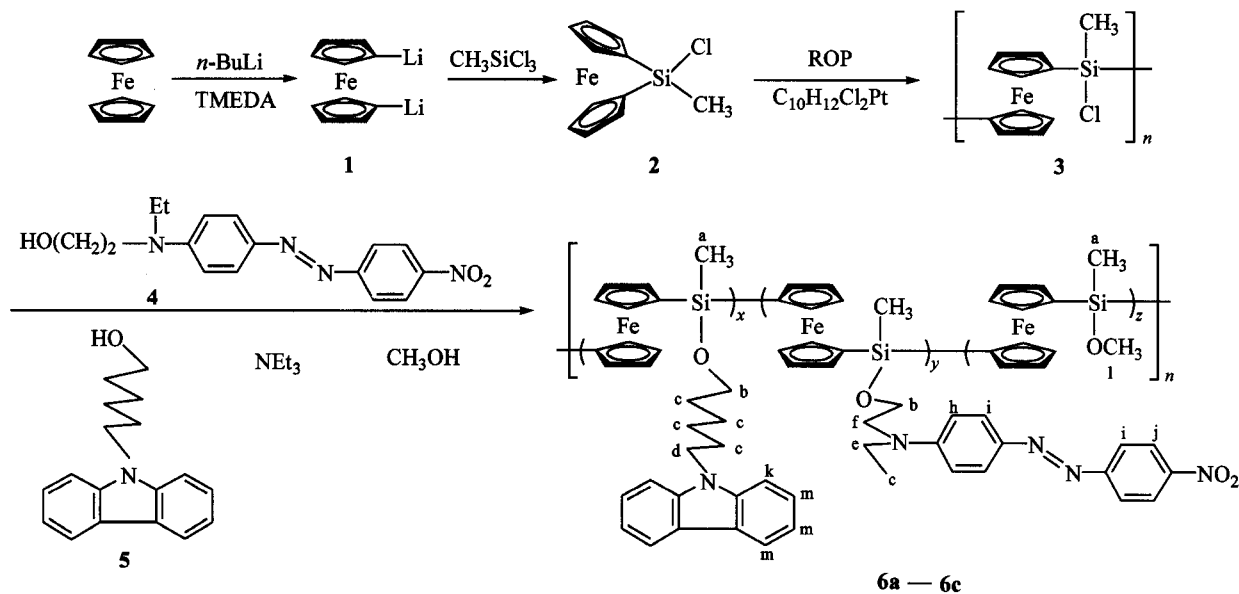
### General procedures

All of reactions with air- or moisture-sensitive materials were carried out under an atmosphere of argon using either standard Schlenk techniques or in an inert-atmosphere glove box.

### Materials and equipment

Ferrocene and trichloromethylsilane were purified by sublimation or distillation respectively before use. Tetramethylethylenediamine (TMEDA) was distilled from calcium hydride. *n*-Butyllithium (2.5 mol/L hexane solution) was purchased from Acros Organic Co. Tetrahydrofuran (THF) and petroleum ether were dried and distilled from Na-K alloy under an atmosphere of dry argon. 1,1'-Dilithioferrocene (**1**),<sup>18</sup> **2**,<sup>19</sup> **3**,<sup>19</sup> **5**,<sup>20</sup> and the catalyst dichloro(dicyclopentadiene)platinum<sup>21</sup> were prepared according to the respective literature procedure. Freshly distilled, dry and oxygen-free solvents were used throughout. <sup>1</sup>H NMR spectra were recorded on a Varian Mercury 300 spectrometer. Molecular weight ( $M_w$  and  $M_n$ ) and polydispersity indexes were estimated by gel permeation chromatography (GPC) using Waters 2960D separation Moduel containing Styragel HR1 THF column and Waters 2410 Refractive Index Detector with a calibration curve for polystyrene standards. THF was used as an eluent at a flow rate of 1.0 mL/min. Infrared spectra were recorded on a Testscan Shimadzu FT-IR 3000 series in the region of 4000–400  $\text{cm}^{-1}$ . UV-visible spectra were recorded

**Scheme 1** Synthetic route of polymers **6a**, **6b** and **6c**



$$\mathbf{6a} \quad x = 0.50 \quad y = 0.10 \quad z = 0.40$$

$$\mathbf{6b} \quad x = 0.54 \quad y = 0.12 \quad z = 0.34$$

$$\mathbf{6c} \quad x = 0.29 \quad y = 0.27 \quad z = 0.44$$

on a Shimadzu 160A spectrometer in dichloromethane solution. A Rigaku Thermoflex DSC 8131 was used to study the thermal behavior at a scan rate of 10 °C/min. The thickness of the thin film was monitored with Tencor 500 surface profiler.

#### Preparation of **6a**

To a solution of **2** (1 g, 3.8 mmol) in 15 mL of THF under argon was added several milligrams of dichloro(dicyclopentadiene)platinum(II) as a catalyst. The polymerization was left stirring at 60 °C over 24 h, then DR-1 (0.19 g, 0.6 mmol), *N*-(6-hydroxyhexyl)carbazole (0.9 g, 3.4 mmol) and Et<sub>3</sub>N (2 mL, 14 mmol) were added and stirred for another 24 h at room temperature. NH<sub>4</sub>Cl was removed by filtration. The red filtrate was concentrated under vacuum and then the red fibrous powder polymer **6a** (1.05 g) was collected after precipitation with methanol three times. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.29 (br, 2H, aromatic protons), 8.11 (2H, aromatic protons), 7.81–7.89 (m, 4H, aromatic protons), 7.20–7.40 (m, br, 6H, aromatic protons), 6.55 (br, 2H, aromatic protons), 4.30 (br, 8H, H-Cp), 3.58 (br, 2H, –SiOCH<sub>2</sub>–), 3.39 (br, 4H, –NCH<sub>2</sub>–), 1.12–1.81 (m, 8H, –(CH<sub>2</sub>)<sub>4</sub>–), 0.51 (br, 3H, –SiCH<sub>3</sub>); IR (KBr) ν: 3442, 3080, 2929, 2859, 1708, 1632, 1594, 1515, 1456, 1418, 1332, 1248, 1163, 1130, 1094, 1030, 821, 775, 749, 720, 625, 465 cm<sup>-1</sup>; UV-vis λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>): 493, 346, 332, 297 nm.

Polymers **6b** and **6c** were prepared in the same procedure, except the quantities of DR-1 and *N*-(6-hydroxyhexyl)carbazole are 1 mmol and 3 mmol for **6b**, and 2 mmol and 2 mmol for **6c**, respectively.

#### Film fabrication

For the second-harmonic generation measurement, thin films of **6a**, **6b** and **6c** were prepared. Polymers (**6a–6c**) were dissolved in 1,2-dichloroethane with a concentration of about 8% (*w/w*) and then filtered through syringe filter. The resulting solution was spin-coated onto indium-tin-oxide (ITO) covered glass. After being dried under vacuum at 40 °C for 36 h, the thin polymer film was obtained. The film thickness was estimated to be 0.77 μm for **6a**, 0.97 μm for **6b** and 0.5 μm for **6c**, respectively, by measurement with Tencor

500 surface profiler.

#### NLO characterization of the poled films

The second-order optical nonlinearity of polymers (**6a–6c**) was determined by *in-situ* second harmonic generation (SHG) experiments using a closed temperature-controlled oven with optical windows and three needle electrodes.<sup>22,23</sup> The film, which was kept at 45° angle to the incident beam, was poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature: 45 °C for polymer **6a**, 47 °C for polymer **6b**, and 80 °C for **6c**. Voltage: 7 kV at the needle point, gap distance between the needle and the film: 0.8 cm. SHG measurements were carried out with a Nd: YAG laser operating with a 10 Hz repetition rate and a 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

#### Results and discussion

Dichloro(dicyclopentadiene)platinum(II) was chosen as the catalyst due to its good solubility in THF and high catalytic activity for this ring opening polymerization. Polymer **3** was not separated from the reaction mixture since it is moisture-sensitive due to Si–Cl, and used directly for the further reaction with *N*-(6-hydroxyhexyl)carbazole (**4**) and DR-1 (**5**). <sup>1</sup>H NMR spectrum indicated that **4** and **5** can not react with all chlorine atoms because of the steric hindrance effect, though an excessive amount of **4** and **5** was used in this reaction. In order to avoid the possible cross-linking due to the existence of remaining Si–Cl, the resulting polymer was treated with methanol three times to ensure that the chlorine atoms can be substituted completely.<sup>24</sup> The resulting polymers **6a–6c** can be dissolved by ordinary organic solvents such as THF, chloroform, and toluene and are easy to form film. Gel permeation chromatography (GPC) measurements in THF indicate the number average molecular weights (*M<sub>n</sub>*) were 3.4 × 10<sup>4</sup>, 3.8 × 10<sup>4</sup> and 4.6 × 10<sup>4</sup>, and the weight molecular weights (*M<sub>w</sub>*) were 6.2 × 10<sup>4</sup>, 5.8 × 10<sup>4</sup> and 6.9 × 10<sup>4</sup>, respectively, for **6a**, **6b** and **6c**. The polydispersity index (PDI) was 1.82 for **6a**, 1.52 for Polymer **6b**, and 1.50 for **6c**. The glass transition temperatures (*T<sub>g</sub>*) of polymers **6a**, **6b** and **6c** were determined to be 48 °C, 52 °C and 96 °C, respec-

tively, by means of DSC. The concentration of the components and some characterization data of **6a**–**6c** are listed in Table 1.

Poly(ferrocenylenesilanes) **6a**–**6c** have been structurally characterized by  $^1\text{H}$  NMR, IR, and UV-visible spectroscopies. Infrared spectra (Fig. 1) are compatible with the structure of polymers **6a**, **6b** and **6c**. The IR spectra showed the characteristic vibrational band of ferrocenyl groups at  $821\text{ cm}^{-1}$ , associated with asymmetric C—C stretching and the out of plane C—H vibration, respectively, together with the cyclopentadienyl-Fe-cyclopentadienyl located at  $462\text{ cm}^{-1}$ . The absorptions at  $1594$ ,  $1456$ ,  $749$  and  $720\text{ cm}^{-1}$  were attributed to carbazolyl groups, and those at  $1515$  and  $1332\text{ cm}^{-1}$  to nitro groups, which indicated that the functional groups **4** and **5** have been successfully introduced into the polymer backbone.

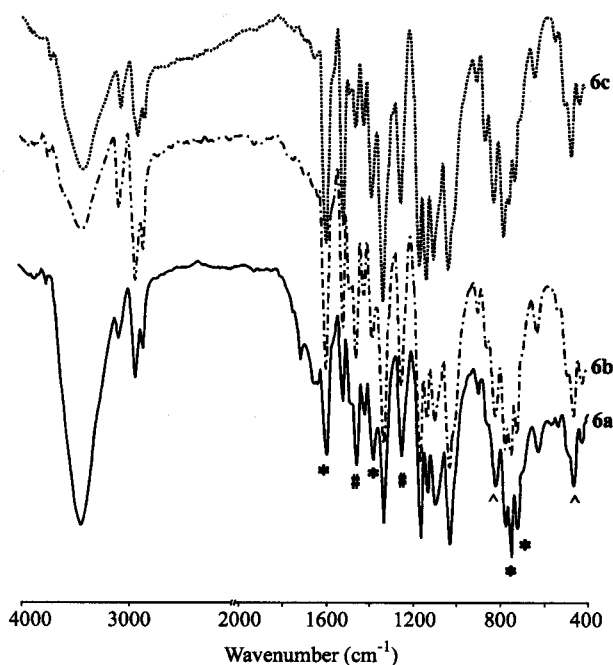


Fig. 1 IR spectra of polymers **6a**, **6b** and **6c**. \*, Carbazole absorption peaks; #, nitro absorption peaks; ^, ferrocene absorption peaks.

The  $^1\text{H}$  NMR spectra of polymers **6a**–**6c** and the assignment of the resonance signals are shown in Fig. 2. The wide peak at  $\delta$  4.25 was attributed to H-Cp. The peak of  $-\text{CH}_2\text{N}$  at  $\delta$  4.15 and the peak of  $-\text{OCH}_3$  at  $\delta$  4.05 were hidden by that of H-Cp. The ratio of carbazolyl group ( $x$ ), azo chromophore ( $y$ ) and methoxyl ( $z$ ) was estimated to be 0.50:0.10:0.40, 0.54:0.12:0.34 and 0.29:0.27:0.44, respectively for polymers **6a**, **6b** and **6c**, by the calculation of their corresponding signal integration in  $^1\text{H}$  NMR spectra. The UV-visible absorption spectra of polymers **6a**–**6c** in  $\text{CH}_2\text{Cl}_2$  showed clearly the absorption peak of the azo chromophore at 493 nm and that of the carbazolyl group at 346, 332 and 297 nm (Fig. 3).

The second-order NLO property can be shown only in a noncentrosymmetric system. The noncentrosymmetric alignment of the chromophores can be achieved by corona-poling. The second-order optical nonlinearity of the poled films of polymers **6a**–**6c** was determined by *in-situ* second-harmonic generation (SHG) experiments. The poling temperature for the polymers is slightly lower than the glass transition temperature. The detailed description of the poling conditions and process has been published elsewhere<sup>22,23</sup>. The  $d_{33}$  value of **6a**–**6c** films was found to be 7.0, 7.7 and 18.4 pm/V, respectively. The reason for **6c** to show an obviously higher  $d_{33}$  value is believed to be that **6c** contains a higher density of the chromophore (27%) than **6a** (10%) and **6b** (12%). The study on their photorefractive effect of the poly(ferrocenylenesilanes) is in progress.

## Conclusion

The first series of multifunctional poly(ferrocenylenesilanes) with carbazolyl group as charge transporting agent and DR-1 as NLO chromophore have been successfully synthesized and characterized. The resulting polymers **6a**, **6b** and **6c** showed good solubility in

Table 1 The components and structural characterization of **6a**–**6c**

Polymer	Composition			$M_w (\times 10^4)$	$M_n (\times 10^4)$	PDI	$T_g (\text{ }^\circ\text{C})$	$d_{33} (\text{pm/V})$
	$x$	$y$	$z$					
<b>6a</b>	0.50	0.10	0.40	6.2	3.4	1.82	48	7.0
<b>6b</b>	0.54	0.12	0.34	5.8	3.8	1.52	52	7.7
<b>6c</b>	0.29	0.27	0.44	6.9	4.6	1.50	94	18.4

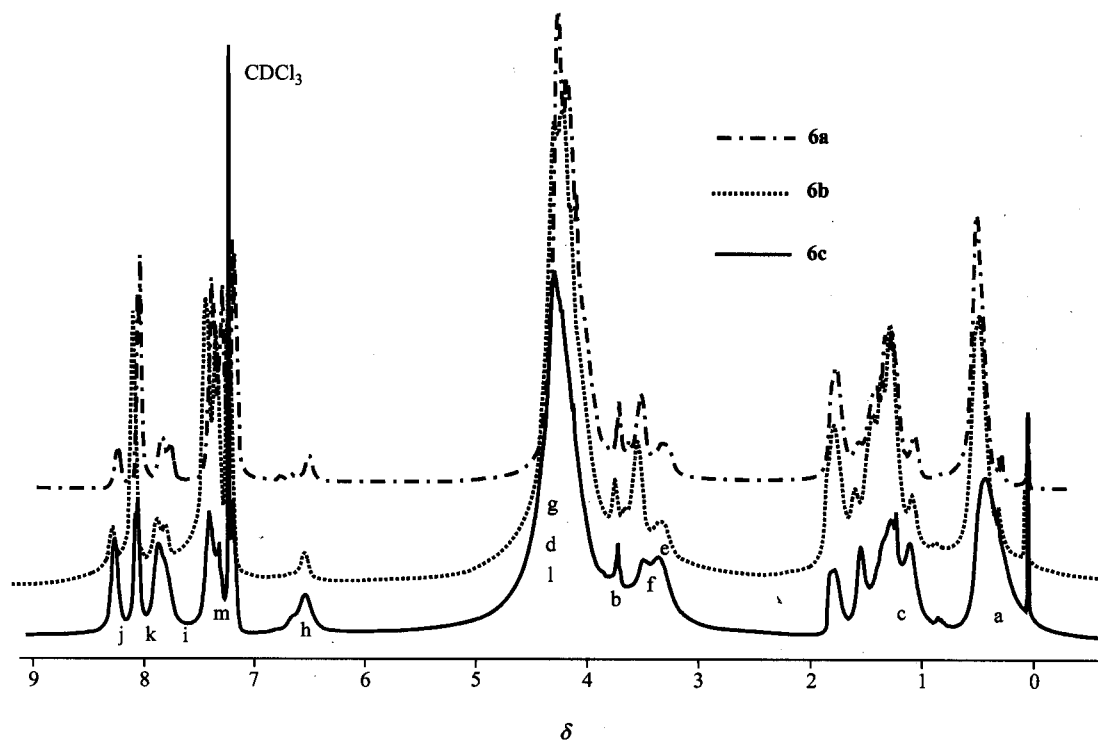


Fig. 2  $^1\text{H}$  NMR spectra of **6a**, **6b** and **6c**.

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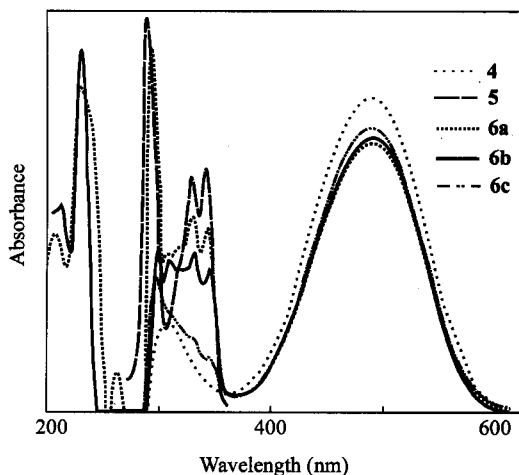


Fig. 3 UV/vis spectra of **4**, **5**, **6a**, **6b** and **6c** (in  $\text{CH}_2\text{Cl}_2$ ).

common organic solvents and good processibility. The  $d_{33}$  value of **6a**, **6b** and **6c** was found to be 7.0, 7.7 and 18.4 pm/V, respectively, by SHG measurement. This work may open a new door for the research on transition metal organometallic NLO polymers.

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(E0205201 ZHAO, X. J.; DONG, H. Z.)