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Polysilanes with NLO chromophores as pendant groups by utilizing different synthetic strategies

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Abstract

This paper summarizes our research on the synthesis and properties of several kinds of functionalized polysilanes (FPSs) containing nonlinear optic (NLO) chromophores in the side chain. They have been synthesized successfully through utilizing different synthetic strategies: chloromethylation of poly(methylphenylsilanes) and the following etherification with the hydroxy-containing NLO chromophore in water–chloroform two-phase system with Brij35 as a phase-transfer catalyst; hydrosilylation of polyhydrosilanes with the NLO chromophore containing the terminal double bond; etherification of chlorine-containing polysilanes with the hydroxy-containing NLO chromophore; and post-functionalization of phenyl group-containing polysilanes through azo coupling with *p*-nitrobenzenediazonium fluoroborate or tricyanovinylolation with the oxidant tetracyanoethylene. FPSs were characterized with FT-IR, UV–vis spectra, differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and elemental analysis. The second-order optical nonlinear properties of the polysilanes were determined by in situ second harmonic generation (SHG) experiments.

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1. Introduction

Extensive researches in optoelectronics and photonics of polymers have led to the development of many novel organic materials for optoelectronic application. Recently, there has been increasing interest in the chemical synthesis and optoelectronic application potentials of polysilanes, which possess an interesting σ – σ conjugated system [1–4]. However, the functionalization of polysilanes is still a challenge for the synthetic chemists, although there have been 20 more years since the first soluble high-molecular weight polysilane was synthesized successfully [5]. The direct synthesis of functionalized polysilanes (FPSs) have been restricted to few dichlorosilane monomers with functional groups such as aryloxy, dimethylamino, and trimethylsilyl groups due to the drastic conditions of the Wurtz coupling reaction [6–8]. Post-functionalization or chemical modification

of the polymer affords alternative way to introduce a reactive functional group into parent polysilanes. Ban et al. [9] reported the Friedel-Crafts chloromethylation of aryl-containing polysilanes by using chloromethyl methyl ether with stannic chloride as a catalyst; Kminek et al. [10] transformed chloromethyl into aldehyde group and successfully prepared the polysilanes bearing directly attached nonlinear optic (NLO) chromophores.

It is well known that polysilanes are semiconducting polymers that show σ -conjugation along the Si–Si main chain [11]. A high photoconductivity has been reported for linear polysilanes and a mobility of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, approximately 4 orders of magnitude higher than that of poly(vinylcarbazole), was measured [1]. As we know, the research of polysilanes attached with NLO chromophores as pendant groups would be of interest, especially in the research of the photorefractive effect and its corresponding application in optical storage, exchange, and manipulation of information [12]. The photorefractive effect is described as a multi-step process, involving the production of mobile charges, followed by charge transport through diffusion and

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drift. The free charges subsequently generate a space-charge field that modulates the refractive index. To manifest photorefractive effect, the polymers must possess both photoconductive and electro-optical properties. Polysilanes functionalized with NLO chromophores as side groups is just the good candidate for photorefractive effect, where the backbone of polysilanes offers photoconductivity and the NLO chromophores activate electro-optical effect.

Our groups started focusing to design and synthesize of FPS in 1995 [13,14]. Because the polymerization conditions of the Wurtz reductive coupling are quite demanding for most of NLO chromophores with push-pull structures, the post-functionalization strategies have to be adopted to prepare FPSs with NLO chromophores as the pendant groups. We have synthesized successfully several kinds of FPSs containing NLO chromophore in side chain by utilizing different synthetic strategies.

1.1. Route 1

The poly(methylphenylsilane) was first chloromethylated using chloromethyl methyl ether [15] and then etherified with *N*-hydroxyethyl-*N*-methyl-4-(4'-nitrophenyl)azobenzeneamine in water–chloroform two-phase system with Brij35 as a phase-transfer catalyst.

1.2. Route 2

The polyhydrosilane was prepared by standard Wurtz reductive coupling and subsequently hydrosilylated with *N*-allyl-*N*-ethyl-4-(4'-nitrophenyl)azobenzeneamine to afford chromophore-functionalized polysilane under the catalysis of dicyclopentadienedichloroplatinum.

1.3. Route 3

The parent poly(dimethyl-co-methylphenyl)silane was treated with acetyl chloride and aluminum chloride to give a polysilane with chlorine substitution; replacement of the chlorine with a hydroxy-containing chromophore was achieved by etherification in the presence of triethylamine to afford the chromophore-functionalized polysilanes.

1.4. Route 4

The polysilane containing 3-(*N*-ethyl, *N*-phenyl)aminopropyl group was conveniently prepared by means of Wurtz coupling technique and then further functionalized by azo-coupling reaction with *p*-nitrobenzenediazonium fluoroborate as azo coupling agent; the polysilane containing 3-(*N*-ethyl, *N*-phenyl)aminopropyl group was also post-functionalized by tricyanovinylolation with the oxidant tetracyanoethylene (TCNE).

In this paper, we report mainly on the synthesis and characterization of polysilanes functionalized by NLO chromophores in the side chain through the above-mentioned synthetic routes. The preparation of the film samples and characterization of photorefractive effect are in progress.

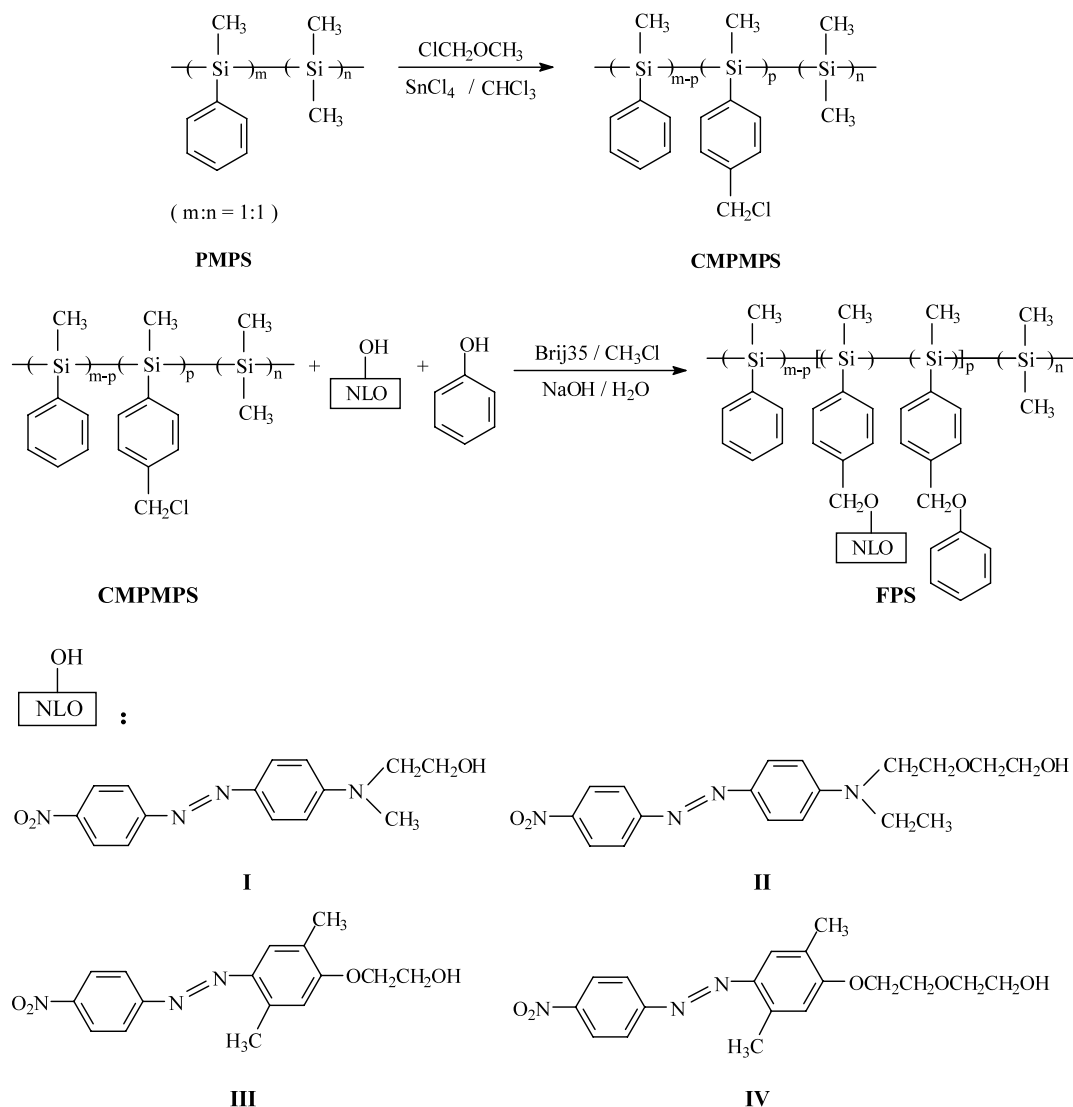
2. Results and discussion

2.1. Synthesis and characterization of NLO polysilanes through the route 1

A very useful chemical modification of aryl-containing polysilanes is the Friedel-Crafts chloromethylation using chloromethyl methyl ether with stannic chloride as a catalyst [9]. The chloromethylated polysilane is a good intermediate for further derivatization since chloromethyl groups are quite reactive toward nucleophilic displacement under mild conditions.

Four FPSs have been synthesized through the route 1 shown in Scheme 1. Here the percentage chloromethylation of the phenyl groups was calculated to reach 90% by integration of ¹H-NMR signals for the different groups. NLO chromophores were linked to the chloromethylated polysilane CMPMPS through a phase-transfer catalysis reaction with Brij35 as catalyst. During the reaction, an excess of phenol was added in order to make chloromethyl groups to be exhausted as completely as possible. The obtained polymers, FPSs, were soluble in ordinary organic solvents such as toluene, chloroform, etc. The appearance of the nitro group absorption at 1521 and 1341 cm⁻¹ and absorption band at 1020–1120 cm⁻¹ assignable to ether bonds vibration in IR spectrum of FPSs indicates that the NLO chromophore groups have been successfully introduced into the chloromethylated polysilane, and the absorption peak assigned to chloromethyl group at 1260 cm⁻¹ in the IR spectrum of CMPMPS was concealed by the new absorption peak at 1245 cm⁻¹ in the IR spectrum of FPSs.

The UV–vis absorption spectra of the polymers in CHCl₃ also show clearly the absorption peak of the chromophore group at visible spectral region and that of the catenated silica chain at 313 nm (Fig. 1). The relative low absorption peak of the chromophore group compared to that of the catenated silicon chain manifests the low concentration of the chromophore in the polysilane. Elemental analysis finds it only about 10 wt.% (Table 1). The gel permeation chromatography (GPC) measurements in THF using polystyrene as the standard indicated that the number-average molecular weights (*M_n*) were among from 2500 to 3500 and the weight-average molecular weights (*M_w*) were among from 8900 to 12 000 for the resulting polysilane FPS in contrast to 9356 of *M_n* and 39 340 of *M_w* for the starting polysilane



Scheme 1.

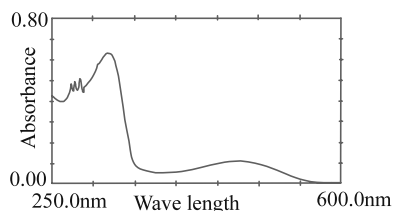


Fig. 1. UV-vis spectrum of the polysilane FPS-I in chloroform.

PMPS. A distinct reduction in molecular weight probably results from the aggressive reaction conditions of the chloromethylation and phase-transfer catalytic etherification reaction. The glass transition temperatures (T_g s) of the polysilanes FPS are around room temperature or below (heating rate $10\text{ }^\circ\text{C min}^{-1}$) and they are thermally stable up to $320\text{ }^\circ\text{C}$. Due to the low T_g , an orientational enhancement effect that has been

Table 1
The characterization data of four FPSs synthesized through route 1

Polysilanes	Concentration of the NLO group (wt.%)	DSC-TGA		Molecular weight (Da)	
		T_g ($^\circ\text{C}$)	T_d ($^\circ\text{C}$)	M_n	M_w
FPS-I	6.2	~ 20	~ 320	3580	11964
FPS-II	12.1	–	~ 330	3765	14538
FPS-III	12.3	–	~ 280	3279	10763
FPS-IV	10.8	–	~ 300	2586	8978

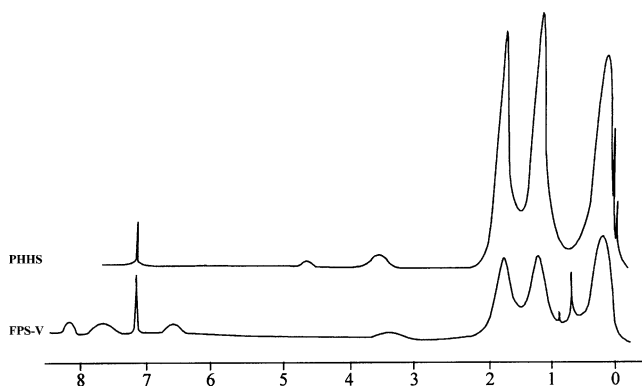


Fig. 2. The $^1\text{H-NMR}$ spectra of the hydrogen-containing polysilane (PHHS) and the FPS (FPS-V).

recently revealed is expected to improve the photorefractive efficiency [16].

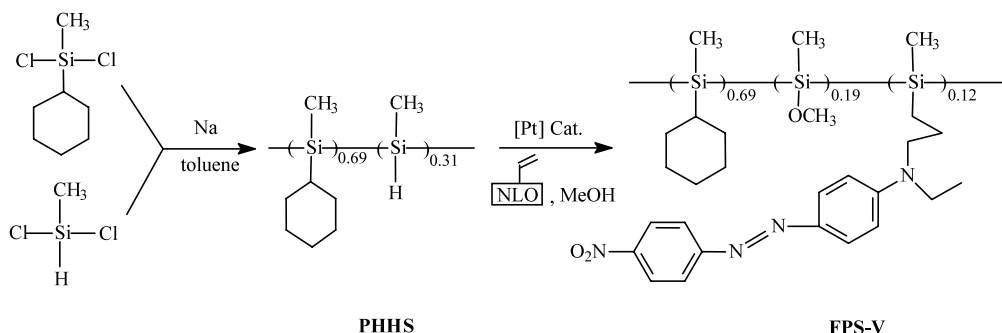
2.2. Synthesis and characterization of NLO polysilanes through the route 2

Hydrosilylation reaction has been verified to be an important approach for the preparation of functionalized polysiloxanes. However, there were few reports where hydrosilylation reaction was utilized to prepare FPSs [1,17] since it has been well known for many years that hydro-polysilanes underwent readily the platinum-catalyzed degradation [18]. We have ever used dicyclopentadienedichloroplatinum to catalyze the hydrosilylation reaction of hydro-containing polysiloxane with NLO group and found that it was a very efficient catalyst compared to H_2PtCl_6 [19]. So we wanted to attempt to catalyze the hydrosilylation reaction of hydro-polysilane with NLO group by using the same catalyst. According to Scheme 2, a new FPS with the NLO chromophore as the pendant group has been synthesized through the hydrosilylation reaction. Thus, a polyhydrosilane PHHS was first prepared in 16% yield

by standard Wurtz reductive coupling and subsequently hydrosilylated with *N*-allyl-*N*-ethyl-4-(4'-nitrophenyl)azobenzeneamine to afford the resulting polysilane FPS-V under the catalysis of dicyclopentadienedichloroplatinum. FPS-V was purified by reprecipitation of its THF solution in methanol, and at this stage the remaining Si-H reacted with methanol because of the trace of platinum catalyst. The $^1\text{H-NMR}$ and IR spectral data of PHHS and FPS-V are in good agreement with the expected structures. The peak at $\delta = 3.57$ ppm is assigned to Si-H proton. The mole ratio of methylcyclohexylsilylene unit and methylhydrosilylene unit in PHHS is about 0.69:0.31 by calculation from $^1\text{H-NMR}$ data, which is similar to the feeding ratio (2:1) of the monomers. On the other hand, after hydrosilylation the Si-H proton resonance disappeared and two new broad peaks appeared at $\delta = 4.0$ and 3.3 ppm assigned to the N-CH₂ proton resonance and Si-O-CH₃ proton resonance, respectively. From the signals for the different groups in $^1\text{H-NMR}$, the content of the chromophore (mole ratio) is calculated to be about 12%. At the same time, in the IR spectra it also can be found that the Si-H absorption maximum of PHHS presents at 2083 cm^{-1} ; the peaks at 540, 510, and 420 cm^{-1} are related to Si-Si stretching vibration. After hydrosilylation of PHHS, the Si-Si stretching absorption is still present, the Si-H absorption disappeared, while phenyl skeletal breathing appeared (Fig. 2).

PHHS shows UV absorption maxima at 265 and 293 nm. FPS-V shows strong λ_{max} at 456.5 nm assigned to the absorption of the NLO chromophore besides the absorption at 265 nm. The weight-averaged molecular weight of PHHS and FPS-V, determined by GPC based on polystyrene standard, are 2400 and 3460, respectively. Based on the molecular weight measurement data, it seems to us that hydrosilylation under the catalysis of dicyclopentadienedichloroplatinum may still be a choice for functionalization of polysilanes.

The thermal transition behavior of polysilanes PHHS and FPS-V is investigated by differential scanning calorimetry (DSC). No apparent glass transition is observed from 25 to $300\text{ }^\circ\text{C}$.



Scheme 2.

2.3. Synthesis and characterization of NLO polysilanes through the route 3

The reaction of the poly(dimethyl-co-methylphenyl)silanes PMPS with acetyl chloride/aluminum chloride yielded the chlorine-substituted polysilane PI. Because the Si–Ph bonds were much more reactive toward acetyl chloride than Si–Me bonds, Si–Ph bonds were transformed to Si–Cl firstly [20]. The chlorine-substituted polysilanes were air-sensitive and they were directly used in the next reaction without further purification and characterization. The reaction of chlorine-substituted polysilane PI with hydroxy-containing NLO chromophores was performed in the presence of triethylamine as acid acceptors in THF. THF was selected as solvent due to the higher reactivity of nucleophilic-substituted reaction in it. Because of the bulkiness of the chromophores, the reaction mixture was refluxed in order to assist chlorine substitution. In order to minimize the residue Si–Cl bonds, which may cause the polymer cross-linking in the storage, excess *n*-BuOH was added and butoxy-substituted compound was formed. The polysilanes PII-1 and PII-2 were precipitated twice from THF solution into methanol. Polysilanes PIIs showed good solubility in common organic solvents such as THF and CHCl₃ (Scheme 3).

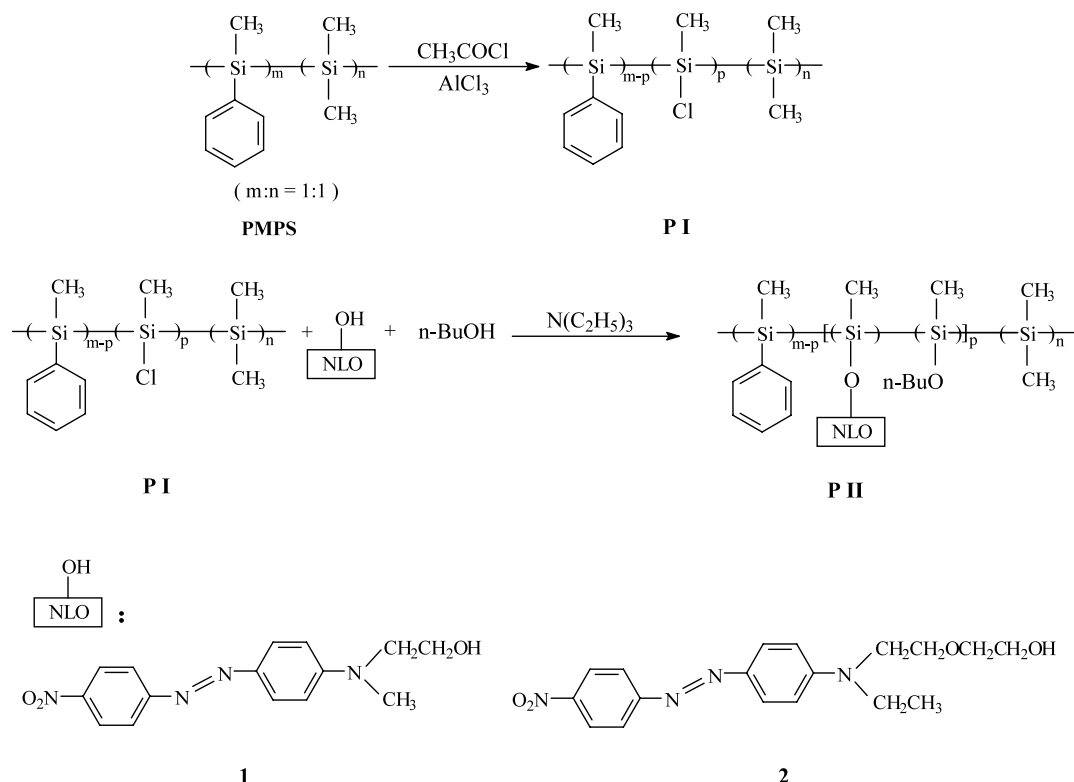
The presence of expected organic groups in the polysilanes was confirmed by ¹H-NMR and FT-IR spectra. The copolymer composition (listed in Table 2)

was calculated from the ¹H-NMR peak integration. The composition was further examined by the results of elemental analysis. The molar contents of NLO group in PII-1 and PII-2 were 6 and 7%, respectively.

In Fig. 3, FT-IR spectra of poly(dimethyl-co-methylphenyl)silanes (PMPS) and chromophore-substituted polysilanes PIIs were compared. The appearance of the phenyl absorption at 1595, 1455, 748, and 720 cm⁻¹ and nitro group absorption at 1521 and 1341 cm⁻¹, and stronger absorption band at 1020–1120 cm⁻¹ assignable to ether bonds vibration in the IR spectra of polysilanes PIIs indicated that the chromophores were successfully introduced into the polysilanes backbone. Moreover, no change had happened to the adsorption at 461 cm⁻¹ assigned to Si–Si vibration.

Due to the delocalization of σ -electrons in backbones, polysilane precursor showed strong UV maximum absorption at 331 nm. After substitution of the NLO chromophore, the adsorption band at 331 nm had made no significant changes, while the new strong adsorption band that appeared around 498 nm corresponded to the intra-molecular charge transfer of the NLO chromophore.

The average molecular weights (M_n) of PMPS, PII-1 and PII-2, determined by GPC were 1.28×10^4 , 7.7×10^3 , and 7.9×10^3 , and the polydispersity M_w/M_n was 5.03, 1.92, and 1.84, respectively. After post-functionalization the polydispersity had changed to a remarkably lower value than that of the parent polysilane. These



Scheme 3.

Table 2

The composition and physical properties of the FPSs PII-1 and PII-2 synthesized through route 3

	x	y	Elemental analysis (Found/Calc.)			T_g (°C)	M_w ($\times 10^4$)	d (M_w/M_n)	λ_{max} (nm)
			C	H	N				
PII-1	0.13	0.06	56.30/57.92	7.59/7.67	3.16/3.27	143	1.5	1.92	498
PII-2	0.19	0.07	56.33/57.24	7.81/7.93	2.78/2.83	132	1.5	1.84	498

results were explained as all-anti regions of similar length being broken by sharp gauche turns in the treatment of PMPS with acetyl chloride and aluminum chloride [21,22].

DSC and thermogravimetric analysis (TGA) studied the thermal behaviors of PII-1 and PII-2 in the air. The results were presented in Figs. 4 and 5.

From the DSC curves of PII-1 and PII-2, the glass transition temperatures of them could be determined as 143 and 132 °C, respectively. PII-2 had higher T_g than PII-1 resulting from the longer spacer providing more free volume, which made chromophore molecule move flexible. In the DSC curves, PII-1 and PII-2 both showed an exothermal peak at about 240–260 °C, which probably resulted from the oxidization by oxygen in the air. A slight weight increase at 240–260 °C in TGA curves could further confirm this. Estimated by TGA curves, PII-1 started to decompose at 285 °C and the

PII-2 at 287 °C, both of them showing good thermal stability.

2.4. Synthesis and characterization of NLO polysilanes through the route 4

Poly{methylphenyl-co-methyl[3-(*N*-ethyl, *N*-phenyl)aminopropyl]}silanes CPS-a and CPS-b were conveniently prepared by means of Wurtz coupling technique. In order to lower the glass transition temperatures and provide more room to increase the contents of chromophore, much more 3-(*N*-ethyl, *N*-phenyl)aminopropyl group unit were introduced in CPS-b. The ratio of two kinds of units in CPS, respectively bearing phenyl and *N,N*-dialkyl-substituted aniline as the pendant groups, is estimated by carefully analyzing the spectra (Table 3). The polymers CPS-a and CPS-b are easily soluble in common organic solvents such as chloroform and THF.

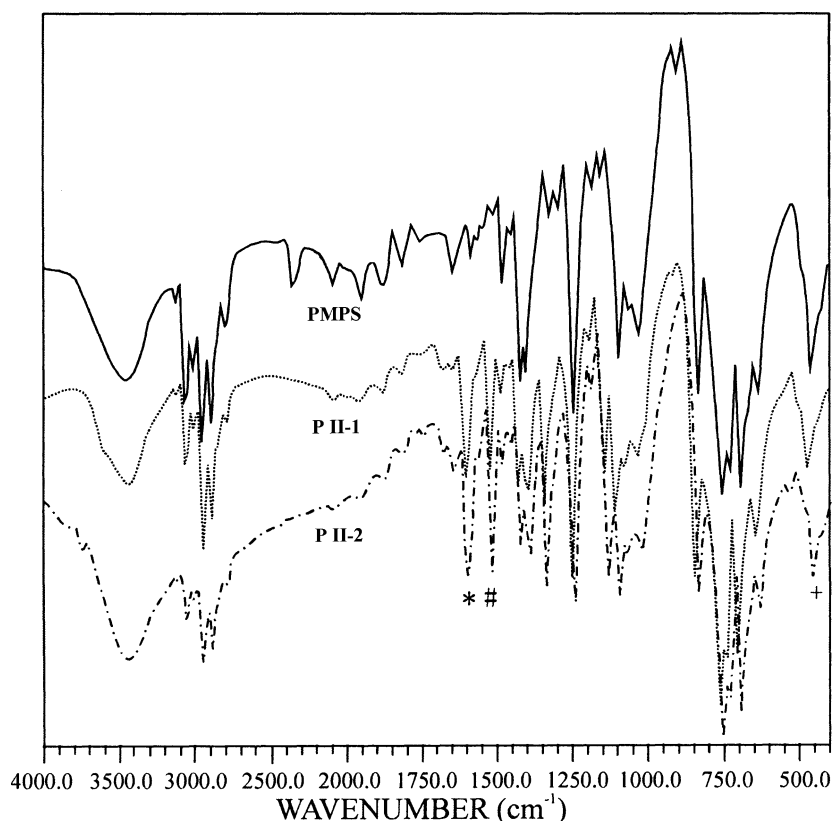


Fig. 3. The FT-IR spectra of PMPS, PII-1, and PII-2. (#, nitro absorption peaks; *, phenyl absorption peaks; +, Si-Si resonances absorption peak.)

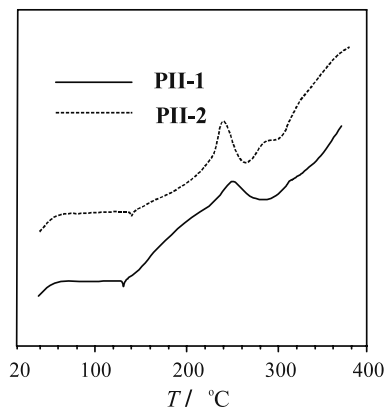


Fig. 4. The DSC curves of PII-1 and PII-2.

The polymers AZOFPS were synthesized through post-azo coupling reaction. The *p*-nitrobenzenediazonium fluoroborate as azo coupling agent and NMP as solvent were chosen due to a homogeneous phase reaction condition. Diazonium salt readily attacks the *para* position with rich electron in the benzeneamine ring. Compared to the $^1\text{H-NMR}$ spectrum of CPS-a, in that of AZOFPS-a additional two new peaks around the range 7.6–8.4 ppm emerge distinctively assignable to the aromatic protons in the attached NLO chromophore. The density (molar ratio) of NLO chromophore is calculated to be about 16% for AZOFPS-a and 42% for AZOFPS-b based on $^1\text{H-NMR}$. Thus, a conversion ratio up to about 80% in this step has been achieved. Moreover, IR spectra of CPS and AZOFPS show basically the same strong adsorption at 462 cm^{-1} as respective to the stretch vibration of Si–Si catenation. Therefore, the condition of azo coupling reaction is so mild that the degradation of the backbone of polysilane is believed to be minimized.

The $^1\text{H-NMR}$ spectra (Fig. 6) confirmed that the tricyanovinyl group was introduced at the *para* position of the aniline groups. After tricyanovinylization, the new peak at $\delta = 7.99\text{ ppm}$ could be attributed to the *ortho*-protons of the tricyanovinyl group, for which the strong electron-withdrawing ability made the *ortho*-protons resonance to down field. The content of *p*-tricyanovinylaniline chromophore was calculated from

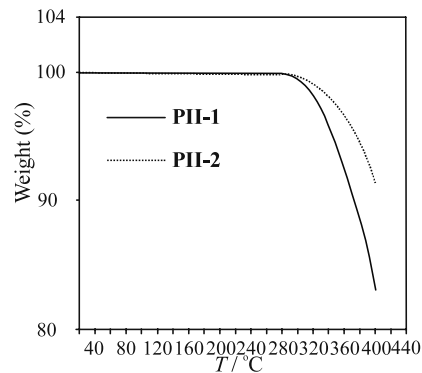


Fig. 5. The TGA curves of PII-1 and PII-2.

the integration of $^1\text{H-NMR}$ at $\delta = 7.99\text{ ppm}$ and from $\delta = 6.8$ to 7.2 ppm to be 18% for TCYFPS-a and 34% for TCYFPS-b. In FT-IR spectra of TCYFPS-a and TCYFPS-b, a new strong absorption at 2212 cm^{-1} assignable to the nitrile stretching vibration and a weak absorption at 1620 cm^{-1} contributed to the C=C stretching vibration of conjugated double bonds also demonstrated that the tricyanovinylaniline chromophore had been successfully introduced in the polysilane side chain. Comparing the absorption strength at 462

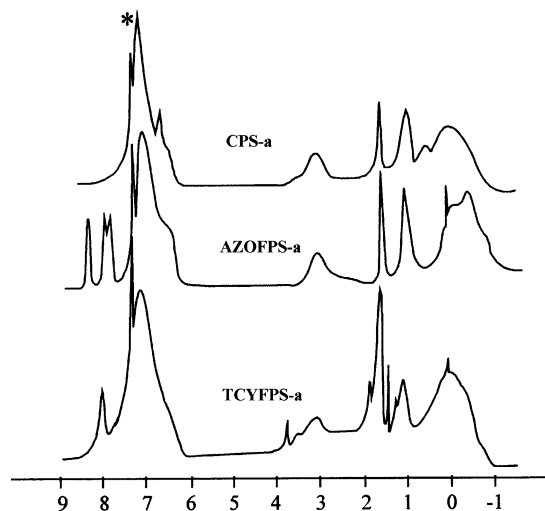
Fig. 6. $^1\text{H-NMR}$ spectra of CPS-a, AZOFPS-a, and TCYFPS-a.

Table 3

The compositions and physical properties of the polysilanes synthesized through route 4

	Composition			Elemental analysis (Found/Calc.)			Molecular weight		λ_{max} (nm)	T_g ($^{\circ}\text{C}$)	T_d ($^{\circ}\text{C}$)
	<i>x</i>	<i>y</i>	<i>z</i>	C	H	N	M_{ww}	<i>d</i>			
CPS-a	0.80	0.20	0	70.21/70.07	7.29/7.44	2.12/2.04	18500	1.22	330	96	334
AZOFPS-a	0.80	0.16	0.04	66.32/66.45	6.35/6.46	5.76/5.99	18400	1.19	494	104	260
TCYFPS-a	0.80	0.18	0.02	69.03/68.82	6.39/6.46	6.53/6.68	10300	3.77	525	47	267
CPS-b	0.46	0.54	0	70.15/70.06	8.51/8.40	4.62/4.56	19000, 4500	2.90, 2.31	310	10.7	306
AZOFPS-b	0.46	0.42	0.12	63.42/63.65	6.92/6.86	11.42/11.23	21000	4.81	496	42	165
TCYFPS-b	0.44	0.34	0.22	68.45/68.34	6.97/6.84	10.79/10.95	5400	4.07	525	–4	230

cm^{-1} of TCYFPS-a and TCYFPS-b with that of CPS-a and CPS-b, no obvious change had happened in TCYFPS-a, but a significant degradation observed in TCYFPS-b. The average molecular weight (M_w) estimated to be 10300 with $d=3.77$ for TCYFPS-a and 5400 with $d=4.07$ for TCYFPS-b indicated that the degradation of polysilane main chain was influenced by the level of tricyanovinylolation, which also preliminarily was confirmed from the UV–vis spectra.

The UV–vis spectra of CPS-b, AZOFPS-b, and TCYFPS-b are shown in Fig. 7. Strong absorption bands with the absorption maximum (λ_{max}) at about 330 nm for CPS-a and CPS-b are observed due to the delocalization of σ -electron of polysilanes backbone. After post-azo coupling and post-tricyanovinylolation reactions, these absorption bands have no significant change, while a new strong absorption band with the λ_{max} around 494 nm appears in AZOFPS-a and AZOFPS-b corresponded to the intra-molecular charge transfer of NLO chromophore, and a new strong absorption at λ_{max} around 525 nm owing to the intra-molecular charge transfer of the tricyanovinylated chromophore was also observed in TCYFPS-a and TCYFPS-b. The new absorption band at 380 nm appeared in TCYFPS-b, which could be attributed to the formation of complex between dialkylbenzeneamine and tricyanovinylated chromophore (Scheme 4).

2.5. NLO properties measurement

Several FPSs (FPS-I, FPS-V, PII-1, AZOFPS-a, AZOFPS-b) were chosen for the measurement of NLO properties. The samples were dissolved in THF and the solution (3 wt.%) was filtered through syringe filters. Polymer films were spin-coated onto indium-tin-oxide (ITO)-coated glass substrates (which were cleaned in the ultrasonic bath with *N,N*-dimethylformide, acetone, distilled water, and THF subsequently). Residual solvent was removed by heating the films in a vacuum oven, at 45 °C, for 2 days. The film thickness was 0.47 μm

measured by TENCOR 500 Surface Profiler. The second-order optical nonlinearity of the film sample 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 °C to the incident beam, was poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows—temperature: around T_g , voltage: 7.5 kV at the needle point, and gap distance: 0.8 cm. SHG measurements were carried out with an Nd:YAG laser operating with a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal was used as the reference. Calculation of the d_{33} value for the poled film 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 $d_{11,q}$ is d_{11} of the quartz crystals, which is 0.45 pm V^{-1} , I_s and I_q the SHG intensities of the sample and the quartz, respectively, $l_{c,q}$ the coherent length of the quartz, l_s the thickness of the polymeric films, and F the correction factors of the apparatus and equals 1.2 when $l_c \gg l_s$. The d_{33} values were calculated to be 13, 19, and 28 pm V^{-1} at 1064 nm fundamental wavelength for PII-I, AZOFPS-a, and AZOFPS-b, respectively. Any SHG signals were not observed for the samples (FPS-I and FPS-V) because T_g of them was too low and the NLO chromophore groups could not be effectively electro-poled at room temperature. The d_{33} value of AZOFPS-b was much higher than that of AZOFPS-a, which indicates that the concentration of NLO chromophores plays an important role in the second NLO response.

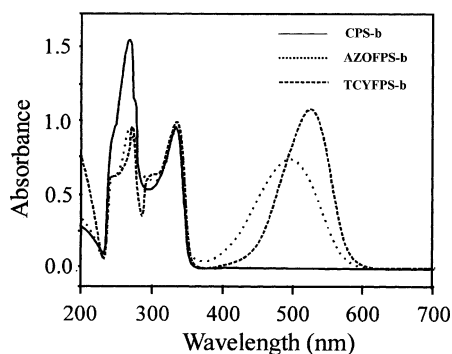


Fig. 7. UV–vis spectra of CPS-b, AZOFPS-b, and TCYFPS-b.

3. Concluding remarks

In summary, we have synthesized successfully several kinds of functionalized polysilanes containing NLO chromophore in the side chain by utilizing different synthetic strategies. Post-functionalization or chemical modification of the parent polysilanes has been proved to be an effective route for introducing NLO chromophores as the side groups into the Si–Si main chain. The second-order optical nonlinear property of the resulting polysilanes, combined with the inherent photoconductivity of the Si–Si backbone, makes themselves become the potential photorefractive polymeric materials.

methanol, filtered, vacuum-dried, and weighted (2.4 g, 80% yield).

Under avoiding light chloromethylated polysilane (CMPMPS) (2.4 g, 0.01 mol), NLO chromophore (0.0017 mol) and a little Brij35 were dissolved in 10 ml of chloroform solution. After the addition of 2 ml of 50% sodium hydroxide aqueous solution, the reaction mixture was stirred for 24 h at 50 °C. Then, an excess of phenol was added and kept stirred for another 24 h. Subsequently, the mixture was washed with water till pH 7, then poured into excessive petroleum ether. The precipitated polymer was filtered off, washed thoroughly with methanol, and dried (1.0 g, 30% yield).

4.3. Procedure of route 2

A 100 ml, three-necked, round-bottomed flask is fitted with a reflux condenser, a pressure-equalizing addition funnel, magnetism stirrer, and argon inlet. The sodium dispersion (2.45 g) is made by high-speed stirring of Na particles in 60 ml refluxed toluene under the protection of dry argon atmosphere. The mixture of dichloromethylsilane (2.7 ml, 25.4 mmol) and dichloromethylcyclohexylsilane (5 g, 25.4 mmol) in 5 ml toluene was slowly added dropwise at a rate so as to maintain vigorous reflux. The mixture is refluxed for additional 3 h, cooled down to room temperature (r.t.), and filtered. The filtrate was concentrated and precipitated in the mixture solvent of 75 ml methanol and 25 ml isopropanol. The white precipitate (PHHS) was collected and dried in vacuum at 45 °C (0.71 g, 16.4% yield).

PHHS (0.25 g), *N*-allyl-*N*-ethyl-4-(4'-nitrophenyl)azobenzeneamine (0.25 g, 0.81 mmol), and a little dicyclopentadienedichloroplatinum were added into 15 ml toluene and the mixture was warmed up to 100 °C. After stirring for 24 h, the reaction was cooled down to r.t., and toluene was evaporated off under reduce pressure. The residue was dissolved in appropriate THF and filtered. The filtrate was precipitated by adding excess methanol. The solid was collected and precipitated from THF and methanol twice. The red powder was obtained after drying in vacuum at 40 °C (0.21 g, 42% yield).

4.4. Procedure of route 3

In a typical experiment, 0.5 g of [(Me₂Si)_{0.5}(Ph-SiMe)_{0.5}] was dissolved in 10 ml of dry petroleum ether and then 0.19 g (1.42 mmol) of anhydrous AlCl₃ was added and stirred at 0–5 °C for 5 min. Subsequently, 0.12 ml of freshly distilled acetyl chloride was added through a syringe. The solution was turned to dark brown gradually. After stirring at 0–5 °C for 18 h and then at r.t. for 24 h, 0.2 ml of dry acetone was added and stirred for 2 h, and then the colorless upper layer was separated and the yellowish residue washed twice with

dry petroleum ether (10 ml × 2). The combined petroleum ether solution was concentrated in a vacuum to give a white semisolid PI. Without further purification and measurement, PI was used directly for the next step.

To a THF solution (5 ml) of PI prepared as above was added the THF solution of 1.4 mmol of NLO chromophore and 0.4 ml of NEt₃ (2.8 mmol) dropwise at r.t. Stirring for another 2 h at r.t. and 4 h at 60 °C, the excess 1-butanol was added to react with residue Si–Cl bond. After removing NEt₃·HCl, THF and excess 1-butanol and triethylamine were tripped off at vacuum to give a solid. Precipitation from THF into methanol twice gave a red solid.

4.5. Procedure of route 4

A 100 ml, three-necked, round-bottomed flask is fitted with a reflux condenser, a pressure-equalizing addition funnel, magnetism stirrer, and argon inlet. The sodium dispersion is made by high-speed stirring of Na particles (excess of 10% relative to Si–Cl) in dry argon atmosphere. A mixture of the monomers with different feed ratios in dry toluene is added dropwise at a rate so as to maintain vigorous reflux. The mixture is refluxed for additional 5 h and cooled down to r.t. under argon atmosphere and then excessive ethanol is added until no gas produces. Then, the mixture is filtered and the residue is washed with dry toluene and ethyl ether. The filtrates are collected and the solvent is removed under reduced pressure, the colorless oily residue is redissolved in 5 ml of THF and then 20 ml of methanol is added. Reprecipitating in THF/methanol twice and drying under vacuum at 45 °C gave white crystalline solid polysilanes CPS.

Polysilane CPS is dissolved in *N*-methylpyrrolidone (NMP), and *p*-nitrobenzenediazonium fluoroborate (excess 10% relative to aniline units) is added in an ice bath. The color of the solution changes to red immediately. After stirring for additional 12 h under argon atmosphere, excessive anhydrite potassium carbonate is added and the mixture is stirred for half an hour, then filtered. The residue is washed with THF, the filtrates are collected, and THF is tripped off under reduced pressure. Then, largely excess methanol is added dropwise to precipitate the polymer. Reprecipitating in THF/methanol twice gave red polysilane AZOFPS.

Polysilane CPS is dissolved in NMP, and TCNE (excess 10% relative to aniline units) is added and heated to 100 °C. The color of the solution changes to violet red immediately. After stirring for additional 5 h under argon atmosphere, excessive anhydrite potassium carbonate is added and the mixture is stirred for 5 min, then filtered. The residue is washed with THF, the filtrates are collected, and THF is tripped off under reduced pressure. Then, largely excess methanol is added drop-

wise to precipitate the polymer. Reprecipitating in THF/methanol twice gave red-violet polysilane TCYFPS.

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