

# Polysilaethers bearing Si–H and its functionalization via hydrosilylation with acrylic acid

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## Abstract

The polysilaether polymers bearing Si–H bonds (PSEHs) were synthesized using Wurtz coupling reaction of dichlorosilanes, mediated by alkali metals, after alcoholysis, the reactant was further hydrolyzed and polycondensation. The Si–H bonds in the macromolecular side chains provide tremendous potentials to prepare a variety of functionalized polysilaethers via hydrosilylation. In this work, the functionalization of PSEHs was carried out via hydrosilylation with acrylic acid and the functionalized derivative was characterized by means of nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, gel permeation chromatography and thermal analysis. It is noted that both PSEHs and the functionalized derivative polymer displayed the characteristics of ultraviolet (UV) absorption and photoluminescence. The functionalized polymers show a considerable blue shift ( $\sim 325$  nm) and red shift ( $\sim 390$  nm) in comparison with the starting polymer, which provides the potential to obtain some tunable optoelectronic properties via the structural modifications of PSEHs.

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**Keywords:** Polysilaether; Si–H bonds; Hydrosilylation reaction

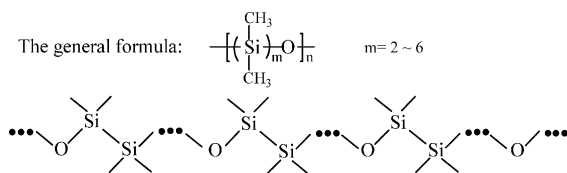
## 1. Introduction

Recently, the photo-luminescent and electroluminescent polymers [1–3] have received an unabated attention in the design and synthesis of functional polymers. Polysilane containing silicon–silicon bonds have attracted considerable interest during the past years since this class of polymers possesses important optoelectronic properties [4–6]. However, the low processing properties greatly limited their application. In addition, the fully saturated structures of the substituted groups make them intractable in further functionalization. In fact, some new polymers containing silicon in the backbone [7–9] has been prepared via

hydrosilylation between Si–H bonds and unsaturated monomers recently. It is expected that the introduction of Si–O–Si and Si–H into the macromolecular backbones of polysilanes could significantly improve the processability and functionalizability of the polymers while their optoelectronic properties will be basically reserved. Kumada et al. [10] first reported the synthesis of the simplest silicon analogues of polyethers, fully substituted with hydrogen in 1968. Unfortunately, the polymers were very unstable because each Si atom connected with two reactive Si–H bonds in the backbone. More recently, Chojnowski and co-workers [11,12] reported that the polysilaethers with permethyl-substituted groups (e.g. poly[oxy(multidimethylsilylene)s]). In the macromolecular backbones of permethyl polysilaethers, Si–Si bonds are regularly intercalated by oxygen atoms (Scheme 1) and the polymers are highly crystalline [13]. It was reported that permethyl-substituted polysilaethers can be synthesized via polycondensation of  $\alpha$ ,  $\omega$ -functionalized linear oligosilanes or oligosiloxanes [14–18] and the ring-opening polymerization (ROP) of cyclic silaethers [19–21], respectively.

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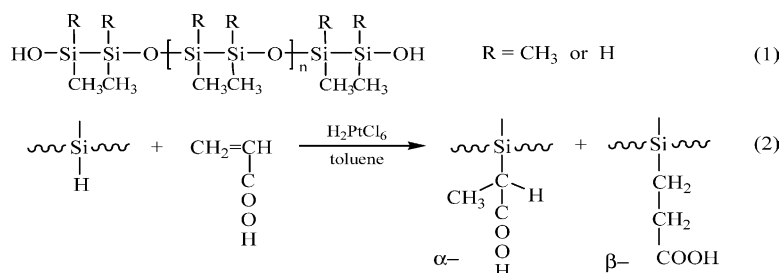
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Scheme 1. The general formula of polysilaethers.

Although the solubility of these polymers is good enough, their processibility is not satisfied; more importantly, it is hard to be further modified (or functionalized) via chemical reactions due to their fully saturated structures.

Some investigators [11–14] have studied the properties of pemethylpolysilaethers, which displayed some properties different from those of polysilanes [22] due to the introduction of oxygen atoms. Poly-O(SiMe<sub>2</sub>)<sub>m</sub> ( $m=2\text{--}6$ ) shows the crystallinity with various melting points [15,23], radiation sensitivity [24], UV absorption [18,23,25] and other related properties [26]. It is expected that when the Si–H bonds are introduced into the macromolecular backbones, the polysilaethers will exhibit some novel features owing to the electronic effect of hydrogen. In addition, the presence of Si–H bonds will provide tremendous potentials to prepare a variety of functionalized derivatives through hydrosilylation. Recently, we have reported the synthesis of a novel polysilaether bearing moiety Si–H bonds in the side chain (PSEMH) [27] and the styrene-graft-polysilaether copolymer prepared by hydrosilylation reaction [28]. We found that styrene-graft-polysilaether does inherit the UV absorption and the fluorescence of the parent polymer. But we wondered why the fluorescence of the polysilaether bearing partly Si–H bonds is very sensitive to the grafted styryls. In the present work, we report on the controllable synthesis of the polysilaethers bearing partly Si–H bonds in the side chain (PSEH) and its functionalization of PSEH via hydrosilylation with the monomer of acrylic acid (Scheme 2). The purpose of this work is to prepare a PSEH derivative with good hydrophilicity and its optoelectronic properties are reserved. The hydrosilylation is carried out with a water-soluble polymer monomer, acrylic acid and the optoelectronic behavior of both apparent and derivative polymers will be addressed based on the results of UV–vis and photoluminescence spectroscopy.



Scheme 2. The structure of target polymers and the synthetic strategy of functionalized polymers.

## 2. Experimental

### 2.1. Materials

Dichloromethylsilane (MeHSiCl<sub>2</sub>, 99%) was kindly provided by Xinghuo Chemical Plant, Jiangxi province, People's Republic of China. Dichlorodimethylsilane (Me<sub>2</sub>SiCl<sub>2</sub>, 99%) was obtained from Xin'an Chemical Industrial Co. Ltd, Zhejiang province, People's Republic of China. The dichorosilane monomers were further purified by distillation before use. *N,N*-Dimethylamino pyridine (DMAP) was purchased from Acros Chemical Co. (USA) and was used as received. Na, K, Br<sub>2</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and acrylate acid (AA) were of analytically pure grade, purchased from Shanghai Chemical Reagents Co. (People's Republic of China). Highly pure nitrogen was used as the protecting gas. The organic solvents such as methanol, ethanol and toluene were obtained from chemical commercial sources and were further purified in generally ways. Before using, toluene was refluxed with Na over 24 h, and then distilled and sealed in the presence of 4 Å molecular sieve to eliminate any traces of water.

### 2.2. Measurements and techniques

#### 2.2.1. Gel permeation chromatography (GPC)

The molecular weight was measured on a Perkin–Elmer series 200 gel permeation chromatography (GPC) with PL mixed-B10μ column at 30 °C. Toluene was used as eluent at a flow rate of 1 mL/min. The retention time were calibrated against polystyrene as standards: 156,000, 156,000, 18,500, 2950 and 680 g/mol.

#### 2.2.2. Fourier-transform infrared spectroscopy (FT-IR)

The FTIR measurements were conducted on a Perkin–Elmer Paragon 1000 Fourier transform spectrometer at room temperature (25 °C). The samples were prepared via casting the liquid polymers onto KBr windows. The specimens were sufficiently thin to be within a range where the Beer–Lambert law is obeyed. In all cases 16 scans at a resolution of 0.1 cm<sup>−1</sup> were used to record the spectra.

#### 2.2.3. Nuclear magnetic resonance spectroscopy (NMR)

The <sup>1</sup>H and <sup>29</sup>Si NMR measurements were carried out on

a Varian Mercury Plus 400 MHz NMR spectrometer at 25 °C. The samples were dissolved with deuterated chloroform and the solutions were measured with TMS as the internal reference.

#### 2.2.4. Ultraviolet–visible spectroscopy (UV–vis)

The UV–vis measurements were carried out on Perkin–Elmer Lambda 20/2.0 spectrometer in the range of 200–800 nm. The polymers were determined in toluene solution ( $\sim 10^{-5}$  mol/L) at room temperature (22 °C). The neat toluene was used as the reference solution.

#### 2.2.5. Photoluminescence spectroscopy (PL)

The luminescence spectra were obtained on a Perkin–Elmer Luminescence spectrometer LS-50B in the range of 200–800 nm at room temperature (22 °C). The liquid polymers were determined by coating them on the KBr wafer.

#### 2.2.6. Thermogravimetric analysis (TGA)

The TGA experiments were performed on a Perkin–Elmer Pyris-7 instrument at a flow rate of 20 ml of nitrogen. The temperature was increased 20 °C/min from 18 to 900 °C.

#### 2.2.7. Determination of Si–H bond contents

The Si–H bonds content of the synthetic PSEHs was determined by  $\text{Na}_2\text{S}_2\text{O}_3$  oxidation–reduction titration [29].

### 2.3. Preparation of samples

#### 2.3.1. Synthesis of PSEH

Approximately 6 g ( $\sim 0.15$  mol) potassium and 150 ml toluene were charged to a 250 ml four-necked round bottom flask, equipped with a stirrer, a condenser with a drying tube, a thermometer and a constant pressure dropping funnel under the nitrogen atmosphere. The flask was immersed into an oil bath at 75 °C in which the ultrasonic irradiation can be generated. In this system, the ultra-fine potassium dispersed in toluene was formed by ultrasonic technique [30] with vigorously stirring. Wurtz coupling reaction between an equimolar of potassium and dichlorosilanes (the different mole ratio of  $\text{Me}_2\text{SiCl}_2$  and  $\text{MeHSiCl}_2$  used in here were given in Table 1) was carried out under the present condition. The alcoholysis of Wurtz coupling resultants was in situ performed at the temperature lower than 5 °C with ethyl alcohol and the polycondensation of hydrolysis occurred simultaneously at 0–5 °C with de-ionized water in the presence of a small amount of DMAP [31]. After the salt was separated out, the products were washed with de-ionized water to pH=7.0. The organic phase (toluene solution) was dried with anhydrous  $\text{MgSO}_4$  overnight. Toluene was removed under vacuum at 100 °C. To separate the low-molecular weight side products, the residue was dissolved in methylene chloride, and the polymer was precipitated with methanol. The precipitate was heated up to

120 °C on a vacuum oven at  $10^{-4}$  mmHg for 4 h. The slight yellow, transparent and viscous liquid polymers were obtained (Table 1).

#### 2.3.2. Hydrosilylation of PSEH with acrylic acid

Acrylic acid (AA) of 3.57 g (49.5 mmol) was added to a solution of PSEH B (5.11 g, 0.181 mmol, 10% solution in toluene) with 0.2 g chloroplatinic acid isopropanol solution (1% in weight) as catalyst at room temperature. A small amount of hydroquinone (0.001 g) was added to the mixture. The mixture was heated at 70 °C for 18 h, and then the reactant was washed with de-ionized water. After separated the water phase, the solvents were removed by heating to 110 °C under reduced pressure to yield a slight yellow transparent viscous liquid, 6.62 g (96.0%).

## 3. Results and discussion

### 3.1. Characterization of PSEHs and PSEH-AA

The Wurtz coupling reaction can be performed between dichlorosilane [ $\text{CH}_3\text{SiHCl}_2$  and  $(\text{CH}_3)_2\text{SiCl}_2$ ] and metal potassium (K). In order to facilitate the reaction, the metal potassium was dispersed by ultrasonic irradiation in this work. By controlling the molar ratio of dichlorosilanes to metal potassium to be 1:1, the Wurtz reductive coupling reaction mainly affords the dichlorodisilane (theoretical intermediates:  $\text{ClSiR}_2\text{SiR}_2\text{Cl}$ , R =  $\text{CH}_3$  or H). In the reactive system, the byproduct HCl was exterminated from system due to its insolubility with the solvent of toluene. The toluene solution of dichlorodisilane in situ formed was employed to prepare the polysilaether bearing Si–H bonds via hydrolytic polycondensation. In this work, the alcoholysis of dichlorodisilane was employed to ensure that the hydrolytic polycondensation is carried out under a mild condition to avoid the cleavage of Si–H bonds due to direct hydrolysis due to the vigorous exothermal effect of direct hydrolysis reaction. Only in the last stage of reactions was the hydrolysis performed at 0–5 °C. The hydrolytic polycondensation of the alcoholysis resultants in toluene was readily carried out in the presence of a small amount of catalyst (i.e. DMAP). The polymers were obtained by precipitation from methylene chloride solution with methanol. The Si–H bonds contents of the synthetic polymers determination by  $\text{Na}_2\text{S}_2\text{O}_3$  oxidation–reduction titration are coincidence with theoretical value (Table 1). The fact that the measured contents of Si–H bonds in accordance with the predicted values suggests that the Si–H bonds were survived in the synthetic procedures.

$^1\text{H}$  and  $^{29}\text{Si}$  NMR, FT-IR and GPC were used to characterize the polymers. The ratio of monomers used in synthesis of PSEHs and the results of characterization data were summarized Table 1. All the GPC results showed that the PSEHs displayed the mono-modal molecular weight distributions. Shown in Fig. 1 are the FT-IR spectra of

Table 1  
The determination results of PSEHs and PSEH-AA

Polymers	Monomers mole ratio <sup>a</sup>	$\bar{M}_n \times 10^4$	PDI	Yield (%)	Si–H (H%)		IR (cm <sup>-1</sup> ) <sup>b</sup>	<sup>29</sup> Si NMR (ppm) <sup>c</sup>	<sup>1</sup> H NMR (ppm) <sup>d</sup>
					Cal.	Found			
PSEH A	1:1	2.26	1.34	74	0.85	0.83	2160, 2078; 377	–17.18; –35.31, –37.42	5.0–5.05 (w, Si–H), 0.1–0.16 (Si–CH <sub>3</sub> )
PSEH B	3:7	2.82	1.36	74.2	0.485	0.47	2160, 2071; 368	–17.09; –35.15, –37.33	4.81–4.92 (w, Si–H), 0.2 (Si–CH <sub>3</sub> )
PSEH-AA	–	–	–	96	–	–	Si–H disappeared	–	2.32–2.42 (m, β-, –CH <sub>3</sub> ), 1.25 (m, α-, –CH <sub>2</sub> -), 1.18 (w, α-, –SiCH <sub>3</sub> ), 0.87 (w, β-, –SiCH <sub>2</sub> -), 0.01–0.30 (s, CH <sub>3</sub> –Si) <sup>e</sup>

<sup>a</sup> The mole ratio of monomers used in Wurtz reductive coupling reaction is MeSiHCl<sub>2</sub> to Me<sub>2</sub>SiCl<sub>2</sub>.

<sup>b</sup> The split of  $\nu_{\text{Si-H}}$  and  $\nu_{\text{Si-Si}}$ .

<sup>c</sup> End groups were not detected perhaps due to the high molecular weight.

<sup>d</sup> The chemical shift of <sup>1</sup>H NMR vs CDCl<sub>3</sub>.

<sup>e</sup> α-Type metamerism of addition, β-type metamerism of addition.

PSEHs and PSEH-AA. The stretching vibration bands of Si–H bonds ( $\nu_{\text{Si-H}}$ ) in PSEHs appeared in the range of 2200–2045 cm<sup>-1</sup> and split into two peaks at 2160 and 2078 cm<sup>-1</sup>, respectively. This phenomenon of the stretching vibration split of Si–H bonds is observed in FT-IR spectra of PSEHs just as in PSEMH [27]. It is possible that the two peaks at 2160 and 2078 cm<sup>-1</sup> are from the different sequence distribution of the chain structure, for example, –SiMeHSiMeH– and –SiMe<sub>2</sub>SiMeH–. The double bands also could be related to the difference in conformation of the chiral Si atoms. But with the contents of Si–H bonds in the polysilaethers changed, the intensities of two split peaks show a great difference. From the FT-IR spectra of PSEH A, it can be found that the intensities of two split peaks are almost equally. However, the intensity of the lower wavenumber split peak is higher than that of the higher wavenumber in PSEH B. It is noted that the relative intensity of the splitting bands are quite related to the contents of Si–H units in the macromolecular skeletons of PSEHs. With increasing the content of Si–H bonds in the polymers (from PSEH A to PSEH B), the intensity of the

split peak at 2160 cm<sup>-1</sup> increased while that at 2078 cm<sup>-1</sup> decreased. All the PSEHs show single moderately strong absorption bands in the range of 370–400 cm<sup>-1</sup>, indicative of the presence of Si–Si bonds in the polymers. With increasing the percentage of –SiMe<sub>2</sub>– units in the macromolecules, the Si–Si stretching vibration bands were observed to shift to the lower frequencies. This observation could be responsible for the methyl groups, which act as electron donating group and reduce the conjugate of  $\sigma_{\text{Si-Si}}$  in the macromolecular skeleton. From the spectra of PSEHs, it can be found that the stretching vibration bands of Si–O–Si ( $\nu_{\text{Si-O-Si}}$ ) appeared in the range of 1080–1050 cm<sup>-1</sup>, and the widths of bands are quite narrower than those of Si–O–Si in typical polysiloxanes (viz. 1130–1000 cm<sup>-1</sup>). This is due to the percentage of Si–O–Si units is equal to that of Si–Si units.

The <sup>29</sup>Si NMR spectra of PSEHs are shown in Fig. 2. The <sup>29</sup>Si NMR signals of PSEHs appear at ca. –17.10, –35.30 and –37.40 ppm, suggesting that PSEHs could contain –((SiMe<sub>2</sub>)<sub>2</sub>O)–, –(SiMeHSiMe<sub>2</sub>O)– and –((SiMeH)<sub>2</sub>O)– units, respectively. This result was in marked contrast to

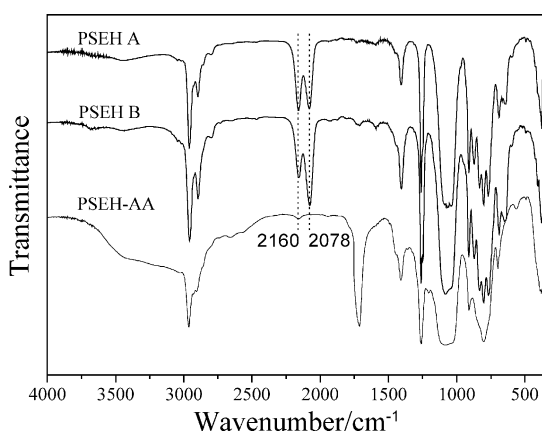


Fig. 1. FT-IR spectra of PSEHs and PSEH-AA.

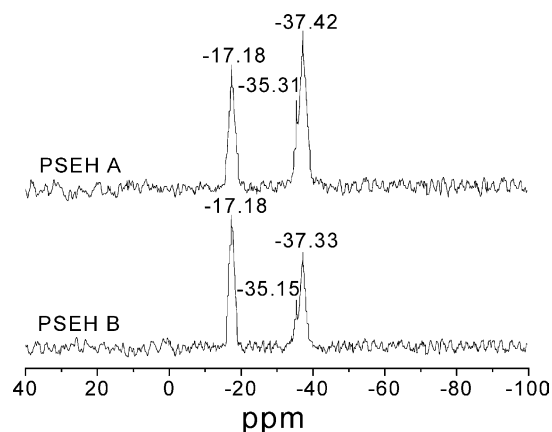


Fig. 2. <sup>29</sup>Si NMR spectra of PSEH A and PSEH B.

the chemical shift of  $^{29}\text{Si}$  nucleus in  $-(\text{SiMe}_2)-$  and  $-(\text{SiMe}_2\text{O})-$  units, the chemical shift values of which were reported to be  $-34$  ppm [32] and  $-20$  ppm [33,34], respectively. The  $^1\text{H}$  NMR spectra of PSEHs are exhibited in Fig. 3. The signals present at 7.25–6.95 and 2.36 ppm are the residue of the solvent toluene. From the  $^1\text{H}$  NMR spectrum of PSEHs, it was found that the integral ratios of  $\text{CH}_3$  and  $\text{Si-H}$  are 9:1 and 17:1 for PSEH A and PSEH B, respectively, which coincide with the theoretical values and implied that  $\text{Si-H}$  bonds were protected in the course of synthesis successfully.

The results of  $^1\text{H}$ ,  $^{29}\text{Si}$  NMR and FTIR spectroscopy indicate that the polymers with intended structures were successfully obtained. The GPC experiment shows that under the present condition the PSEHs possess the high molecular weight (viz.  $M_n = 2.26\text{--}2.82 \times 10^4$ ,  $M_w = 3.02\text{--}3.84 \times 10^4$ ) [27].

The functionalization of PSEH B (PSEH-AA) was carried out by means of its hydrosilylation reaction with acrylic acid (AA). It should be pointed out that two types of addition products (i.e.  $\alpha$ - and  $\beta$ -additions) could exist in the system of hydrosilylation (Scheme 2). After 18 h, the integration area ratio of the  $\text{Si-H}$  band (residue  $\text{Si-H}$  bonds) is about 7%. The completion of hydrosilylation was evidenced by the nearly disappearance of the stretching vibration bands of  $\text{Si-H}$  bonds ( $\nu_{\text{Si-H}}$ ) in FT-IR. To avoid the self-polymerization of allyl monomer, a small amount of hydroquinone was used as the polymerization inhibitor and the temperature of hydrosilylation reaction was as low as possible. To separate hydroquinone the reactive system was washed with de-ionized water. The FT-IR spectrum of functionalized PSEH (PSEH-AA) was shown in Fig. 1 in the ranges of  $4000\text{--}350$   $\text{cm}^{-1}$ . The appearance of the band at  $1710$   $\text{cm}^{-1}$  indicates the carbonyl of grafted acrylic groups. The stretching vibration band at  $3550\text{--}3300$   $\text{cm}^{-1}$  could be ascribed to the hydroxyl groups of acrylic acid grafted in PSEH B and the simple frequency multiplication of  $\nu_{\text{C=O}}$ . The stretching vibration band at  $3300\text{--}2500$   $\text{cm}^{-1}$  is ascribed to the effect of hydrogen-bonded between the macromolecules of PSEH-AA. The  $^1\text{H}$  NMR spectrum of

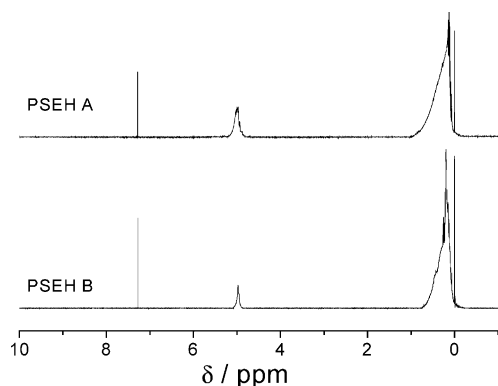


Fig. 3.  $^1\text{H}$  NMR spectra of PSEHs.

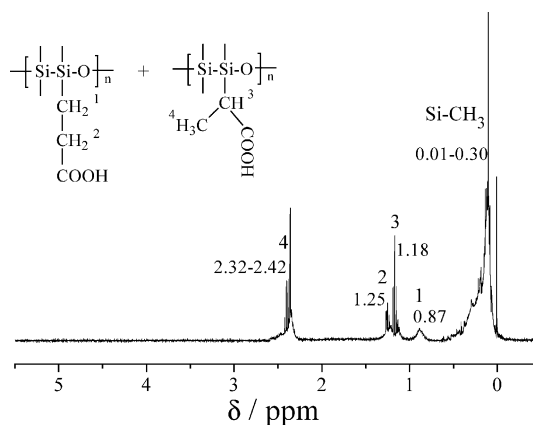


Fig. 4.  $^1\text{H}$  NMR spectra of PSEH-AA.

PSEH-AA shown in Fig. 4 and the results were summarized in Table 1. The integration ratio of  $\text{Si-CH}_3$ : $\text{=CH}_2(\alpha)$ : $\text{=CH}_2(\alpha)$ : $\text{=CH}(\beta)$ : $\text{=CH}_3(\beta)$  is about 34:1:1:2:6. Based on the intensity of integration, the ratio of  $\alpha$ - to  $\beta$ -addition type is calculated to be 2:3. The results of  $^1\text{H}$  NMR and FT-IR spectroscopy indicate that the functionalized PSEH with intended structures were successfully obtained.

The FT-IR spectra of the functionalization PSEH during the hydrosilylation reaction were determined at different time by taking a small liquid sample coating on KBr wafers (solvent and unreacted monomer are easy to be volatilized under the radiation of infrared lamp). The FT-IR spectra of PSEH B, PSEH-AA (18 h) and the products in reaction process are shown in Fig. 5. It is interesting to note that the disappearance manner of the splitting  $\nu_{\text{Si-H}}$ . With development of hydrosilylation reaction, the intensity of the lower wavenumber split peak at  $2078$   $\text{cm}^{-1}$  disappeared gradually at first. At the same time, the intensity of the higher wavenumber split peak is higher than that of the lower wavenumber in product of the hydrosilylation reaction. Afterward, the higher wavenumber split peak at  $2160$   $\text{cm}^{-1}$  almost disappeared gradually in the end (about 18 h). To the best of our knowledge, it is plausible to propose that the chiral center Si atoms are associated with some spatial configuration of these macromolecules of polymers. We think that the two  $\text{Si-H}$  bond split peaks are in correspondence with two different space conformations and different energies. The chemical activity of  $\text{Si-H}$  bonds corresponding to the lower wavenumber split peak at  $2078$   $\text{cm}^{-1}$  could be higher than that of the higher wavenumber split peak at  $2160$   $\text{cm}^{-1}$ . There would be two competitive reactions between acrylic acid and two types of  $\text{Si-H}$  bonds. So the  $\text{Si-H}$  bonds of the lower wavenumber split peak at  $2078$   $\text{cm}^{-1}$  could firstly react with acrylic acid in the competitive reaction. Our recent quantum chemistry calculation suggests that this phenomenon could be germane to the different of the space conformations the exchange of  $\text{Si-O-Si}$  and  $\text{Si-Si}$  segments and along with the polymers backbone [35].



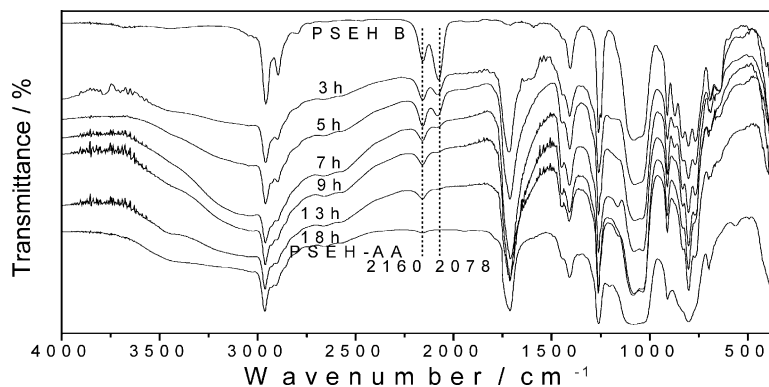


Fig. 5. FT-IR spectra of PSEH B, PSEH-AA (18 h) and the products in reaction process.

### 3.2. Properties of functionalized polymers

#### 3.2.1. UV-vis spectroscopy

The ultraviolet absorption spectra of synthetic PSEHs and PSEH-AA measured in toluene about  $10^{-5}$  mol/L shown in Fig. 6. The UV-vis absorption maxima of the synthetic PSEHs and PSEH-AA are summarized in Table 2. It is found PSEHs have absorption bands in the near-UV region and the PSEH-AA show the shoulder peak feature in Fig. 6. The UV absorptions of the polymers are due to the synergism of the  $\sigma_{\text{Si-Si}}$  delocalization and the  $p_{\pi(\text{O})} - \sigma_{\pi^*(\text{Si-O})}^*$  delocalization in the polymer backbone. The ultraviolet absorption property of the PSEMH has been reported [27]. With the increasing of  $-\text{SiMe}_2-$  segments in the polymer skeleton (from PSEH A to PSEH B), the UV absorption of PSEHs shift towards the shorter wavelength (blue shift). This observation could be responsible for the methyl groups, which act as the electron donating groups and boost up the conjugate interaction of  $\sigma_{\text{Si-Si}}$  in the skeleton of PSEHs. The maximum absorption wavelength of PSEHs are higher than that of poly[( $\text{Me}_2\text{Si}$ ) $_m\text{O}]_n$ ,  $m=2-6$ , which are reported by Chojnowski et al. [11,18,25]. These phenomena maybe indicate that the more the methyl groups, the lower the electrons of d-p orbital conjugated interactions ( $\pi_{\text{d-p}}$ ) between oxygen lone pairs in 2p and the 3d

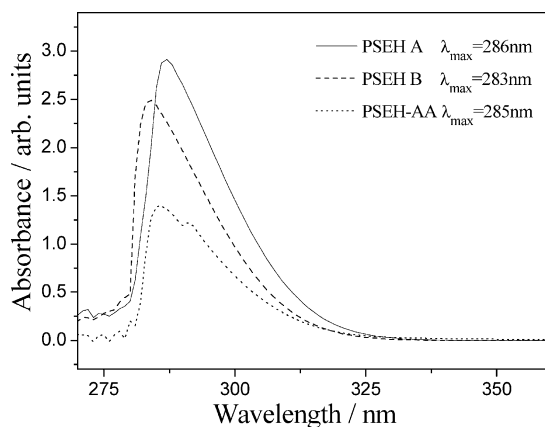


Fig. 6. Ultraviolet absorption spectra of synthetic PSEHs and PSEH-AA in toluene about  $10^{-5}$  mol/L.

empty orbital of Si atom in the polymer backbone. As a result, the interaction lead to the increase of difference energy level of  $\sigma \rightarrow \sigma^*$  ( $\Delta E_{\sigma \rightarrow \sigma^*}$ ). However, the absorption peaks of these polymers show a considerable blue shift in comparison with that of dialkyl-substituted polysilanes (300–350 nm) [36,37] and a considerable red shift in comparison with that of dimethylsilane oligomers [ $\text{Me}(\text{SiMe}_2)_m\text{Me}$ ,  $m=2-6$ , 197–260 nm] [38]. The absorption spectra of PSEH-AA show two peaks at 285 and 291 nm in the near-UV region, which are due to the different addition types of acroleic acid, for example,  $\alpha$ -type addition and  $\beta$ -type addition. PSEH-AA presents the low absorption intensity, which indicates that the grafted groups induced the hypochromic effect.

#### 3.2.2. Photoluminescence properties

The photoluminescence spectra of PSEH B are present in Fig. 7. In the near-UV regions, there are two fluorescence bands were identified at  $\sim 335$  and  $\sim 350$  nm, respectively. Generally, the S band emission was observed typically in alkyl- and aryl-substituted polysilanes [39], which was ascribed to the emission from the 1-D exaction state on the Si conjugated skeletons. There are the two types of conjugations in PSEH B skeletons, which are d-p orbital conjugation ( $\pi_{\text{d-p}}$ ) (between oxygen lone pairs in 2p orbital and the 3d empty orbital of Si atom in the polymer backbone) and  $\sigma_{\text{Si-Si}}$  conjugation (between Si atoms in polymer skeleton), respectively. In the present case, the two fluorescence bands maybe result from the vibronic structures or the interaction of these two conjugations of the polymer chain. With increasing of  $-\text{SiMe}_2-$  segments in the polymer skeleton (from PSEMH [27] to PSEH B), the photoluminescence bands were observed to shift towards higher wavelength (red shift, from 345 nm shift to 355 nm)

Table 2  
UV and PL data for the polymers

Polymers	UV $\lambda_{\text{max}}$ (nm)	PL $\lambda_{\text{max}}$ (nm)
PSEH A	286	–
PSEH B	283	336, 355
PSEH-AA	285, 291 (shoulder)	322, 392

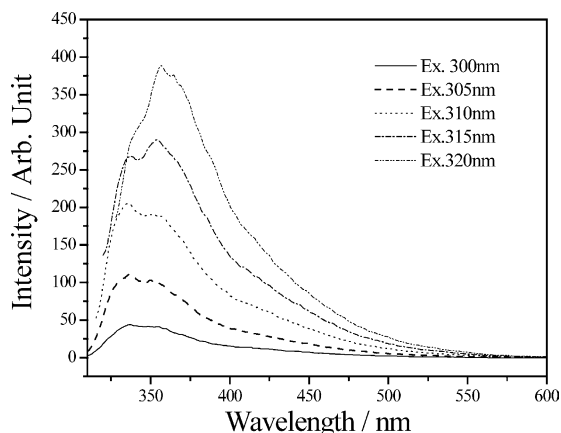


Fig. 7. The photoluminescence spectra of PSEH B.

and the intensity increasing in the meantime. Perhaps they are ascribed to the introduction of the electron-donating group (i.e. methyl group), which leads to a hyperconjugation between Si and methyl containing in the polymer side chain. It is seen that with increasing the content of methyl groups, the extent of the hyperconjugation along the polymer skeleton was strengthened.

The photoluminescence spectra of PSEH-AA show in Fig. 8. It is interesting to note that there are significant differences between PSEH B and PSEH-AA in photoluminescence properties. From the photoluminescence spectra of PSEH-AA, it is found that the fluorescence of this functionalized polymer is very sensitive to the grafted groups although they are not typical conjugated groups just as styrene-*graft*-polysilaether [28]. This phenomenon could be ascribed to the specific structure and the conformation of the parent polymer. The photoluminescence spectra of PSEH-AA displayed two fluorescence bands in the near-UV regions. However, the fluorescence bands show the considerable tendencies of blue shift (from 336 to  $\sim$ 320 nm) and red shift (from 355 to  $\sim$ 390 nm), respectively, in comparison with PSEH B. The different shifts of fluorescence bands could be ascribed to the structures resulting from  $\alpha$ - and  $\beta$ -addition products. It is proposed that the blue shift is the result of  $\alpha$ -type addition, since in the case; the electron density of Si in polymer skeleton is reduced whereas the red shift is attributed to  $\beta$ -type addition due to the increase of electron density of Si in polymer skeleton. The S band emission of PSEH-AA at  $\sim$ 320 nm is weaker than that of PSEH B, implying that the grafted acrylic groups restrain the stimulated emission of the PSEH-AA. However, the photoluminescence spectra of PSEH-AA show the emission intensity of the S band at  $\sim$ 325 nm decreasing with the increase of the energy of excitation light; by contraries, the emission intensity of the S band at  $\sim$ 390 nm increasing with the increase of the energy of excitation light.

### 3.2.3. Thermal stability (TGA)

The TGA experiments were performed in the atmosphere

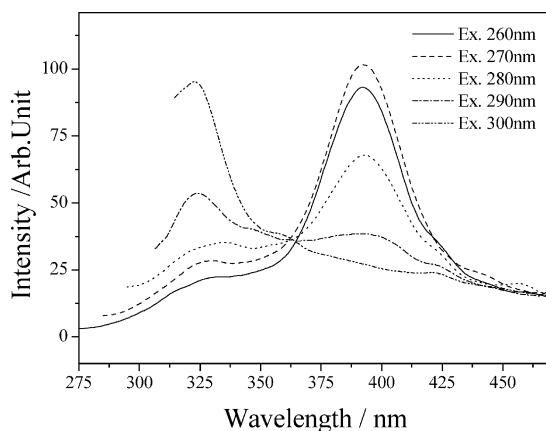


Fig. 8. The photoluminescence spectra of PSEH-AA.

of nitrogen and TGA curves were shown in Fig. 9. PSEH A displayed three decomposition stages and the third thermal degradation occurred at about 700 °C. PSEH A exhibited thermal decomposition behavior and the residue yield is some different from that of permethyl polysilaethers [18]. The TGA curve of PSEH B indicated that the pyrolytic process occurs in two main stages, the first one between 220 and 470 °C, and the second between 470 and 710 °C. With the decreasing of the Si–H bonds content, the stability of PSEH increases below 250 °C. After functionalized PSEH B was observed that there are two obviously decomposition stages in PSEH-AA. The first degradation steps which occurred in the range of  $\sim$ 180–300 °C are attributable to the decomposition of the grafted groups. The second maximal loss of weight took place at  $\sim$ 360 °C, which could be ascribed to the cracking of Si–CH<sub>3</sub>. The residues of PSEH A, PSEH B and PSEH-AA are 35.9, 22.4 and 20.3%, respectively.

## 4. Conclusions

PSEHs with different contents of Si–H bonds were synthesized through Wurtz reductive coupling reaction by

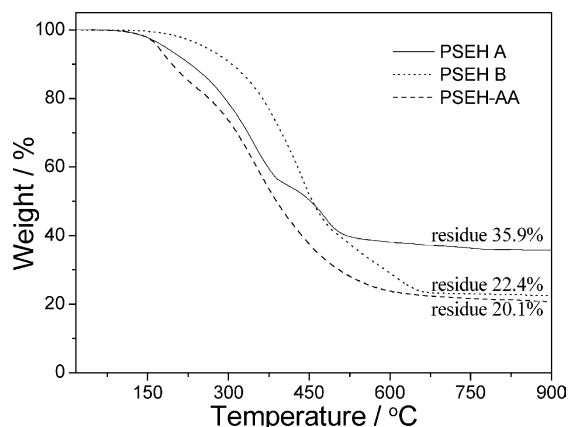


Fig. 9. The TGA curves of PSEH A,B and PSEH-AA.

equimolar of dichlorosilanes and alkali metal, followed by alcoholysis and hydrolyzation. The two percentage contents of Si–H bonds in the polymer side chain could be synthesized by controlling the ratios of dichlorosilanes. Polysilaethers bearing partly Si–H bonds in the side chain could be taken a class of modified polysilanes, which contains both Si–Si and Si–O–Si in macromolecular backbone, and used as the starting point for further functionalization via hydrosilylation. Through hydrosilylation reaction, we successfully synthesized a grafted polymer by using acrylic acid as the unsaturated monomer. The grafted polymer reserved the UV absorption and photoluminescence properties of polysilanes. More importantly, the photoluminescence properties of PSEH-AA are very sensitive to the grafted groups; although, the grafted groups are neither strong electron donating groups, nor intense electron withdraw groups. These results included the properties of styrene-grafted-polysilaether [28] could be ascribed to the special structure of alternate between Si–Si and Si–O–Si in macromolecular backbone.

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