

Synthesis and Characterization of α,ω -Bis(3-hydroxypropyl)-Functionalized Poly{dimethylsiloxane-co-methyl[3-(2-acetyl-acetoxy)]propylsiloxane}

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ABSTRACT: With the purpose to develop polysiloxane-modified waterborne polyurethane (WPU) which was expected to have better water resistance than WPU and better mechanical strength and abrasion characteristics than polysiloxane, a novel reactive polysiloxane bearing hydroxypropyl group at both chain ends and carbonyl groups at the side chain was synthesized by five-step reactions. The prepared compounds in each step were characterized; the results showed that each step synthesis was successfully carried out and objective products were achieved. This novel reactive polysiloxane combines the properties of difunctional hydroxyalkyl terminated polysiloxane and crosslinking agent. When it was incorporated

with WPU, the latex film properties of reactive polysiloxane-modified WPU were investigated compared with that of pure WPU. The results indicated that siloxane segments could lower the water absorption of WPU, and that the crosslinking reaction between the dihydrazide and carbonyl group could improve the physical-mechanical characteristics of polysiloxane-modified WPU after post-added dihydrazide. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 595–607, 2012

Key words: hydrosilylation; equilibrium reaction; polysiloxane; ketone-hydrazine reaction; waterborne polyurethane

INTRODUCTION

Waterborne polyurethane has been found a variety of applications in recent years because of its excellent mechanical properties and its environmental friendliness.^{1–3} Typical applications of these materials include textile coatings, leather finishing, adhesives, sealants, plastic coatings, wood finishes, and glass fiber sizing.⁴ However, some properties of waterborne polyurethane when used as coating, such as water resistance and weather resistance, need to be improved to be competitive with solvent-based polyurethane.⁵ To improve the water resistance and surface hydrophobicity of the films for waterborne polyurethane, the polyurethane was often modified by the difunctional hydroxyalkyl terminated polysiloxane.⁶ But the incorporation of polysiloxane often had a negative effect on the physical-mechanical properties of the polyurethane. It is well known that polysiloxanes demonstrate superior

flexibility, resistance to humidity but poor physical-mechanical properties, and on the other hand, the waterborne polyurethanes are more hydrophilic, but have excellent physical-mechanical characteristics. With the purpose of combining the valuable properties of the two types of polymers, the polysiloxane-polyurethane systems were often designed to form the crosslinking structure.

In the early stage of polyurethane development, the crosslinked polysiloxane-polyurethane systems has been prepared by inner crosslinking, such as either by the crosslinking of Si—O—Si bond through the hydrolysis condensation process,^{7,8} or by incorporation of multifunctional oligosiloxane polyols to crosslink the prepolymer,⁹ or by addition of chain extenders with functionalities greater than two in the dispersion stage.¹⁰ The aforementioned systems formed the crosslinking structure in the process of synthesizing, but they could not design a high crosslinking structure, because inner crosslinking through these methods often result in highly viscous prepolymers, which are hard to be dispersed and lead to gel formation in certain cases.¹¹ To avoid the disadvantage of inner crosslinking, much attention has been attracted on an alternative which is so-called post-crosslinking. The post-crosslinking refers to a chemical reaction designed to occur during or shortly after film formation by adding a second

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component as a crosslinking agent.¹² As we know, ketone–hydrazine crosslink reaction is one of the common practices used to prepare self-crosslinking waterborne polyurethane,¹³ because ketone or hydrazine are groups stable in aqueous phase and can react at ambient temperature.

In this article, to improve the disadvantages of the polysiloxane–polyurethane crosslinking as mentioned above, a novel reactive polysiloxane bearing hydroxypropyl group at both chain ends and carbonyl groups at the side chain was synthesized by five-step reactions which included transesterification, hydroxyl protection, hydrosilylation, equilibrium reaction, and deprotection. The prepared compounds in each step were characterized by FTIR and NMR. Based on this novel reactive polysiloxane, reactive polysiloxane-modified waterborne polyurethane was prepared, the latex film properties of reactive polysiloxane-modified WPU were studied by a variety of techniques.

EXPERIMENTAL

Materials

Tetramethyldisiloxane (TMDS, Institute of Chemical Engineering of Wuhan), hexamethyldisilylamine (HMDSA, Shanghai Huitian New Chemical Material), and octamethyltetracyclosiloxane (D₄, Dow Chemical Company), dimethylol propionic acid (DMPA, Dow Chemical Company), adipic dihydrazide (ADH, Japan Kyowa Hakko Chemical), all industrial grade, were used as received without further treatment. Toluene 2,4-diisocyanate (TDI-100, Tianjin Fuchen Chemicals) was stored in the dark at 10°C and was melted at 30°C before using. Ethyl acetoacetate, triphenylphosphine (TPP), diethylene-triamine (DEA), toluene, methanol, hydrochloric acid, potassium hydroxide, and acetic acid were all A.R. and were received from Sinopharm Chemical Reagent. Allyl alcohol was product of Shanghai General Factory of Chemicals. The 2,4,6,8-tetramethylcyclotetrasiloxane (D₄^H) and trifluoromethanesulfonic acid (TFMSA) were purchased from ABCR (Karlsruhe, FRG). Polypropylene glycol with molecular weight 1000 (PPG210) and 2000 (PPG220), all industrial grade, were vacuum-distilled before use. *N,N*-dimethylformamide (DMF), triethylamine (TEA), and acetone were immersed in 4 Å molecular sieves for more than 1 week before use.

Measurements

Fourier transformed infrared spectra (FT-IR) were obtained on a Nicolet 470 FT-IR spectrometer in dry air, at room temperature, on KBr or thallium bromide-iodide pellets, in the range of 4000–400 cm⁻¹.

¹H NMR, ¹³C NMR, and ²⁹Si NMR spectra were recorded at 27°C on Bruker AVANCE 400 with CDCl₃ as solvent and tetramethylsilane (TMS, δ = 0 ppm) as internal standard. GC analysis was carried out on GC-2010 instrument (Shimadzu, Japan). A DB-5 capillary column (30.0 m × 0.25 mm × 0.75 μm) was used with helium as the carrier. The column temperature profile was programmed with initial temperature at 100°C maintained for 2 min, followed by a constant increase to 250°C at 10°C min⁻¹ and maintained at 250°C for 3 min. Both injection port and FID detector temperature were set at 280°C. The flow rate was adjusted at 1.0 mL min⁻¹ and split ratio at 100 : 1. Toluene was used as solvent in all sample tests. Gel permeation chromatography (GPC) was performed with Waters 1525 Binary HPLC Pump using Waters 2414 refractive index detector, Styragel HT 2, 3, 4 as columns, THF as eluant, and polystyrene as the polymer standard. Differential scanning calorimetry measurements were carried out using a Perkin–Elmer PYRIS Diamond DSC instrument. The samples (2.3 mg), sealed under aluminum pans are scanned in the temperature range of 0–100°C. The heating rate is 10°C min⁻¹ under the nitrogen atmosphere with a flow rate of 40 mL min⁻¹.

The tensile strength and elongation of the films were determined by Instron testing machine (Instron Model 5569, USA). The films were stamped using a standard die, and tested at room temperature using a crosshead speed of 10 cm min⁻¹. The Shore hardness of the films was measured at room temperature by LX-A rubber durometer (Jiangdu, China). For water and toluene absorption, a piece of the latex film with known weight (*m*₁) was immersed in water or toluene, the sample was taken out of the test liquid after 24 h of equilibration. Excess liquid on film surface was wiped up using a Kleenex and the film weighed again (*m*₂). The water and toluene absorptions were expressed as the weight percentage of water or toluene in the swollen sample:

$$\text{water or toluene absorption (\%)} = \frac{m_2 - m_1}{m_1} \times 100\%$$

Latex crosslinking was tested by Soxhlet extractor using toluene as extraction solvent. An accurately known amount of dried polymer (*G*₁) was put in a preconditioned and weighed cellulose thimble (weight of thimble denoted as *G*), and extracted with toluene for 48 h. Crosslinked polymer was assumed to remain in the thimble while linear polymer went down to the toluene balloon by toluene circulation. The polymer containing thimble was weighed again afterward (*G*₂). Crosslink extent of the polymer was obtained through following equation:

$$\text{polymer crosslinking (\%)} = \frac{G_2 - G}{G_1} \times 100\%$$

Synthesis of allyl acetoacetate (I)

According to published procedures,¹⁴ 13.03 g ethyl acetoacetate, 7.54 g allyl alcohol, 2.62 g TPP and 20 mL toluene were added sequentially into the flask. The solution was heated to 110°C and kept at this temperature for 8 h. The resulting crude material was concentrated *in vacuo* and distilled at 77°C (1.13 KPa) to give 10.82 g allyl acetoacetate with a yield of 76%. FT-IR (KBr, ν , cm^{-1}): 3434 (C—OH), 2947 (C—H), 1745 (O=C—O), 1718 (CH_3 —C=O), 1648 (C=C), 1031 (C—O—C). ¹H NMR (CDCl_3 , 400 MHz, δ ppm): 5.16, 5.19, 5.24, and 5.28 (2H, q, CH_2 =CH), 5.78–5.88 (1H, m, $\text{CH}=\text{CH}_2$), 4.55 (2H, d, CH_2 —O), 3.40 (2H, s, O=C— CH_2), 2.19 (3H, s, CH_3 —C=O).

Synthesis of 2,4,6,8-tetramethyl-2,4,6,8-tetra[3-(2-acetyl-acetoxy)]propylcyclotetrasiloxane (II)

A round-bottomed flask equipped with a thermometer, a stirrer, a nitrogen purge, and a reflux condenser (the later equipped with a tubular dryer filled with anhydrous calcium chloride), was charged consecutively with 2.86 g I, 15 mL toluene, and 0.10 g chloroplatinic acid solution (2% in isopropanol). The flask was heated to 90°C, followed by dropwise addition of 1.20 g D_4^{H} . The reaction mixture was then slowly heated to 110°C and kept at this temperature for 6 h. Toluene and excessive I were removed under vacuum (5.32 KPa). About 3.49 g of brown yellow transparent liquid was obtained with a yield of 86%. FT-IR (KBr, ν , cm^{-1}): 1742 (O=C—O), 1719 (CH_3 —C=O), 1269 (Si— CH_3), 1081 (Si—O—Si). ¹H NMR (CDCl_3 , 400 MHz, δ ppm): 0.03 (12H, s, Si— CH_3), 0.49 (8H, t, Si— CH_2), 1.62 (8H, m, Si— CH_2 — CH_2), 2.20 (12H, s, CH_3 —C=O), 3.39 (8H, s, O=C— CH_2), 4.02 (12H, t, CH_2 —O). ¹³C NMR (CDCl_3 , 150 MHz, δ ppm): -1.822 (Si— CH_3), 11.738 (Si— CH_2), 21.083 (Si— CH_2 — CH_2), 29.013 (CH_3 —C=O), 48.996 (CH_2 —C=O), 66.384 (CH_2 —O), 166.072 (O=C=O), 199.393 (CH_3 —C=O).

Synthesis of allyloxytrimethylsilane (III)

Nearly 23.23 g of allyl alcohol was located into a 100 mL round-bottomed flask, and then 35.52 g HMDSA was dropwise added into the flask under agitation at room temperature. This mixture solution was heated to 98°C and kept at this temperature for 6 h. The product, allyloxytrimethylsilane (ATMS), was separated through fractionation from the crude products, the distillate between 98 and 100°C was collected and 44.75 g colorless liquid was obtained with a yield of 86%. Refractive index of the collected distillate was measured as $n_{\text{D}}^{20} = 1.3940$, which

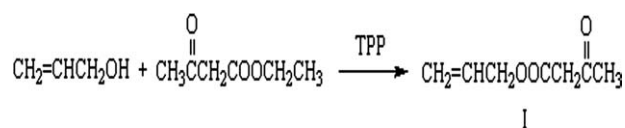
agreed well with reported value of $n_{\text{D}}^{20} = 1.3940$.¹⁵ FT-IR (KBr, ν , cm^{-1}): 1646 (C=C), 1252 (Si— CH_3), 1087 (Si—O—C). ¹H NMR (CDCl_3 , 400 MHz, δ ppm): 5.01, 5.03, 5.15, and 5.20 (2H, q, CH_2 =CH), 5.81–5.90 (1H, m, $\text{CH}=\text{CH}_2$), 4.06 (2H, d, CH_2 —O), 0.06 (9H, s, Si— CH_3).

Synthesis of 1,3-bis(3-trimethylsiloxypropyl)tetramethyldisiloxane (IV)

A round-bottomed flask equipped with a thermometer, a stirrer, a nitrogen purge, and a reflux condenser (the later equipped with a tubular dryer filled with anhydrous calcium chloride), was charged consecutively with 31.25 g III, 15 mL toluene, and 0.10 g chloroplatinic acid solution (2% in isopropanol). The flask was heated to 90°C, followed by dropwise addition of 13.41 g TMDS. The reaction mixture was then slowly heated to 110°C and kept at this temperature for 6 h. IV was separated through distillation under reduced pressure (0.27 KPa) from the crude products. The distillate between 122 and 124°C was collected and 35.36 g colorless liquid was obtained with a yield of 90%. Refractive index of the collected distillate was measured as $n_{\text{D}}^{20} = 1.4220$, which agreed well with reported value of $n_{\text{D}}^{20} = 1.4240$.¹⁵ FT-IR (KBr, ν , cm^{-1}): 1252 (Si— CH_3), 1097 (Si—O—Si), 1062 (Si—O—C). ¹H NMR (CDCl_3 , 400 MHz, δ ppm): -0.03 (18H, s, Si—(CH_3)₃), 0.04 (12H, s, Si—(CH_3)₂), 0.39 (4H, t, Si— CH_2), 1.46 (4H, m, Si— CH_2 — CH_2), 3.45 (4H, t, CH_2 —O). ¹³C NMR (CDCl_3 , 150 MHz, δ ppm): -0.969 (Si—(CH_3)₃), -0.273 (Si—(CH_3)₂), 13.552 (Si— CH_2), 26.070 (Si— CH_2 — CH_2), 64.952 (CH_2 —O). ²⁹Si NMR (CDCl_3 , 79 MHz, δ ppm): 7.727 (Si—(CH_3)₃), 16.778 (Si—(CH_3)₂).

Synthesis of α,ω -bis(3-hydroxypropyl)-functionalized poly{dimethylsiloxane-co-methyl-3-(2-acetyl-acetoxy)propylsiloxane} (V)

To produce the final product, a nitrogen purged reaction vessel with agitation was charged with II, IV and D_4 , the ratio of II/IV/ D_4 was varied in different equilibrium polymerization. Stirring was provided by a magnetic bar. The mixture was heated to 65°C followed by injection of 30 μL TFMSA as catalyst. The equilibrium polymerization was kept going on for 20 h. After the mixture cooled down to room temperature, TFMSA was then neutralized by adding 0.50 mL of potassium hydroxide methanol solution (1 mol L^{-1}). KOH in excess was neutralized by subsequent addition of 0.20 mL of hydrochloric acid (1 mol L^{-1} in methanol). Methanol and the cyclic side products were removed by vacuum stripping under 8.5 KPa until cessation of distillate condensation.



Scheme 1 Synthesis of compound I.

After removing KCl precipitate, the product of equilibrium polymerization and 100 mL methanol were charged into 250 mL three-necked round bottom flask. Acetic acid (0.1 mL) was added as catalyst. The reaction mixture was refluxed at 65°C for 6 h. Acetic acid, $\text{CH}_3\text{OSi}(\text{CH}_3)_3$ and excessive methanol were removed under vacuum. FT-IR (KBr, ν , cm^{-1}): 3405 (OH), 1742 (C=O), 1261 (Si-CH₃), 1094 (Si-O-Si). ¹H NMR (CDCl₃, 400 MHz, δ ppm): 0.00 (s, Si-CH₃), 0.46 (m, Si-CH₂), 1.55 (m, Si-CH₂-CH₂), 2.11 (s, CH₂-OH), 2.19 (s, CH₃-C=O), 3.36 (s, O=C-CH₂), 3.52 (t, CH₂-OH), 4.02 (m, CH₂-O-C=O).

Synthesis of waterborne polyurethane modified with compound V

About 2.84 g V and 17.42 g TDI were charged into the flask and heated to 70°C for 30 min. While stirring, 7.64 g PPG 210 and 20.02 g PPG 220 were then added to the mixture for an additional 30 min at 70°C. Nearly 3.18 g DMPA and 2.10 g EG were added to the flask at the same temperature and the mixture was continuously being stirred. Two hours later, the NCO content of the prepolymer was determined by the standard dibutylamine back-titration method. The reaction was allowed to proceed until the content of NCO reached the theoretical value (theoretical value: 3.4%, measured value: 3.0%). And then, 30 g acetone was added to reduce the viscosity of the prepolymer and stirring continued until a homogeneous mixture was obtained at ambient temperature. About 2.40 g TEA was added to neutralize the carboxylic group in the side chain of prepolymer. Aqueous dispersions were obtained by adding

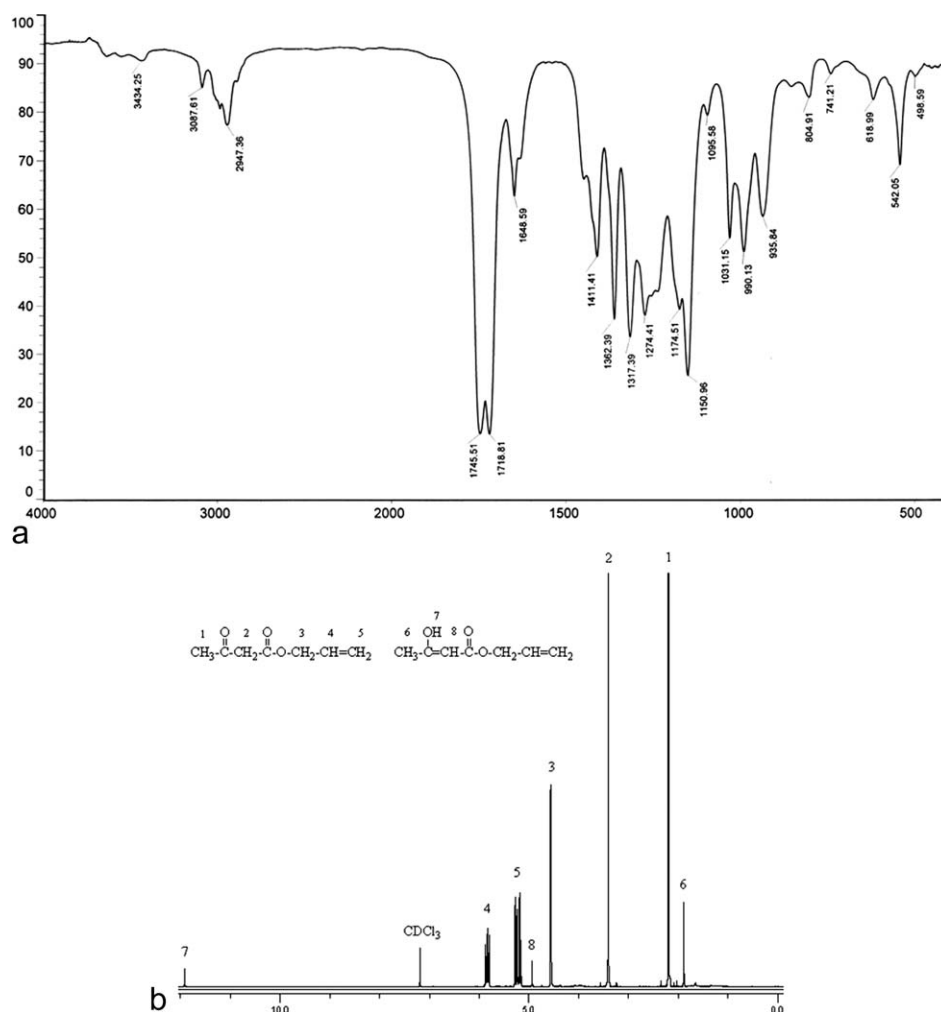
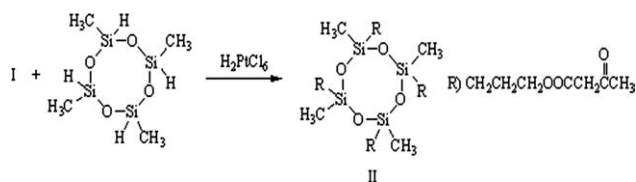


Figure 1 (a) FT-IR spectra of compound I. (b) ¹H NMR spectra of compound I.



Scheme 2 Synthesis of compound II.

the prepolymer while high speed stirred to the water containing DEA, which mass was determined by the NCO value. The chain-extension reaction was allowed to proceed at ambient temperature for 40 min. After removal of acetone, the resulting product was waterborne polyurethane dispersion with solids content of 25%. For the waterborne polyurethane latexes with the designed crosslinking, ADH was post-added with its amount controlled to be half of the carbonyl group in mol. Latex films was cast from a Teflon plate at room temperature.

RESULTS AND DISCUSSION

Synthesis and characterization of compound I

Allyl acetoacetate, compound I, was prepared via transesterification reaction between ethyl acetoacetate and allyl alcohol as depicted by Scheme 1.

The structure of compound I was first studied by FT-IR analysis [Fig. 1(a)]. The FT-IR spectrum of compound I present the characteristic absorption of both precursors. The very low intensity of the C—OH band in the region $3500\text{--}3400\text{ cm}^{-1}$ shows that the proportion of the enol form is small. The peaks in the region $3000\text{--}2800\text{ cm}^{-1}$ are mainly caused by the CH₃ asymmetric stretching vibration, the CH₂ asymmetric stretching vibration, and the CH₃ symmetric stretching vibration, respectively. The peak at 1031 cm^{-1} is the characteristic absorption peak of C—O—C group. Two strongly absorption bands associated to C=O bond were evidently observed at 1745 and 1718 cm^{-1} . The former belongs to ester group and the latter belongs to carbonyl

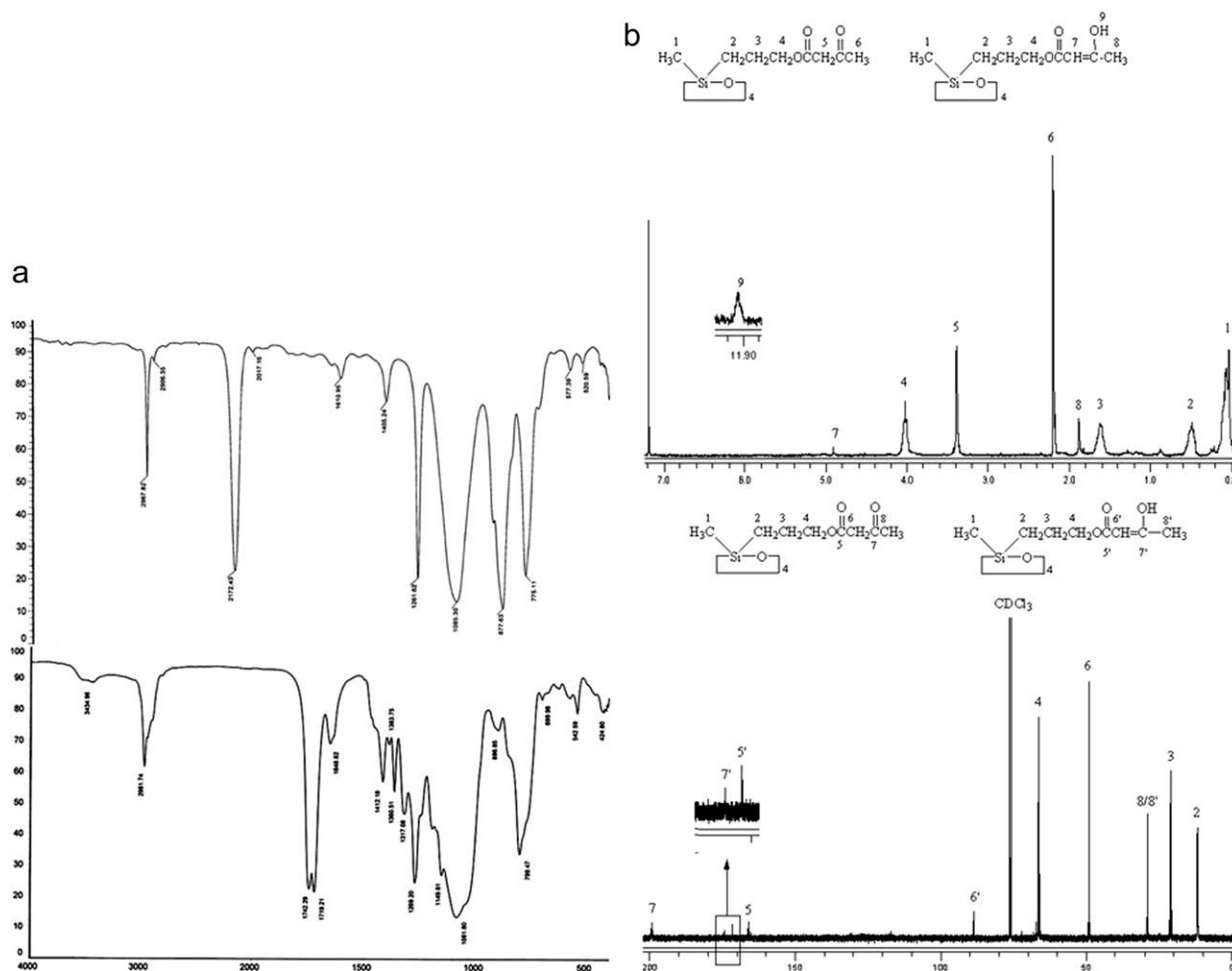
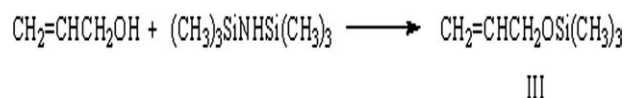


Figure 2 (a) FT-IR spectra of D₄H (upper) and compound II (bottom). (b) ¹H (upper), ¹³C (bottom) NMR spectra of compound II.



Scheme 3 Synthesis of compound III.

group. In addition, the band assigned to allylic double bond and that assigned to C—H from double bond allylic group were also observed at 1648 and 3087 cm^{-1} .

To confirm the formation of compound I better, I was then subjected to ^1H NMR analysis [Fig. 1(b)]. One point should be noted. Because allyl acetoacetate is one of special β -dicarbonyl compounds, there exists a tautomeric system which is the equilibrium between a ketone and its enol form. The interconversion of the two forms involves the migration of a proton and the shifting of bonding electrons. Because of the existence of tautomeric system, eight different peaks were found. From the chemical shifts and the peak area integrations, the peaks representing protons labeled from 1 to 8 are easily assigned. Based on this information, it becomes possible to estimate amounts of ketone form and enol form. There are several ways to make this estimation. Knowing the total number of all protons in the

molecules or the number of protons in each assigned group, one can easily calculate the responsive unit area value for an individual proton. By comparing either the area of the peak at $\delta = 2.19$ ppm (protons on methyl in ketone form) to that at $\delta = 1.88$ ppm (protons on methyl in enol form), or one of the peak areas to the total integration, the amount of enol form was estimated to be 9.7%. This value can be equally estimated from the peak at $\delta = 11.92$ ppm (proton on hydroxyl in enol form), which gave 9.1% as the amount of enol form.

Synthesis and characterization of compound II

The compound II was prepared via hydrosilylation reaction between compound I and D_4^{H} as depicted by Scheme 2.

As for compound I, compound II was first subjected to FT-IR analysis, the spectrum is presented in Figure 2(a). In comparison with the spectra of the reacting materials, the spectrum of II exhibits the following characteristics: (1) Complete disappearance of Si—H vibration, which was observed as the third largest peak at 2172 cm^{-1} amongst all peaks on D_4^{H} spectrum; (2) Complete disappearance of C—H

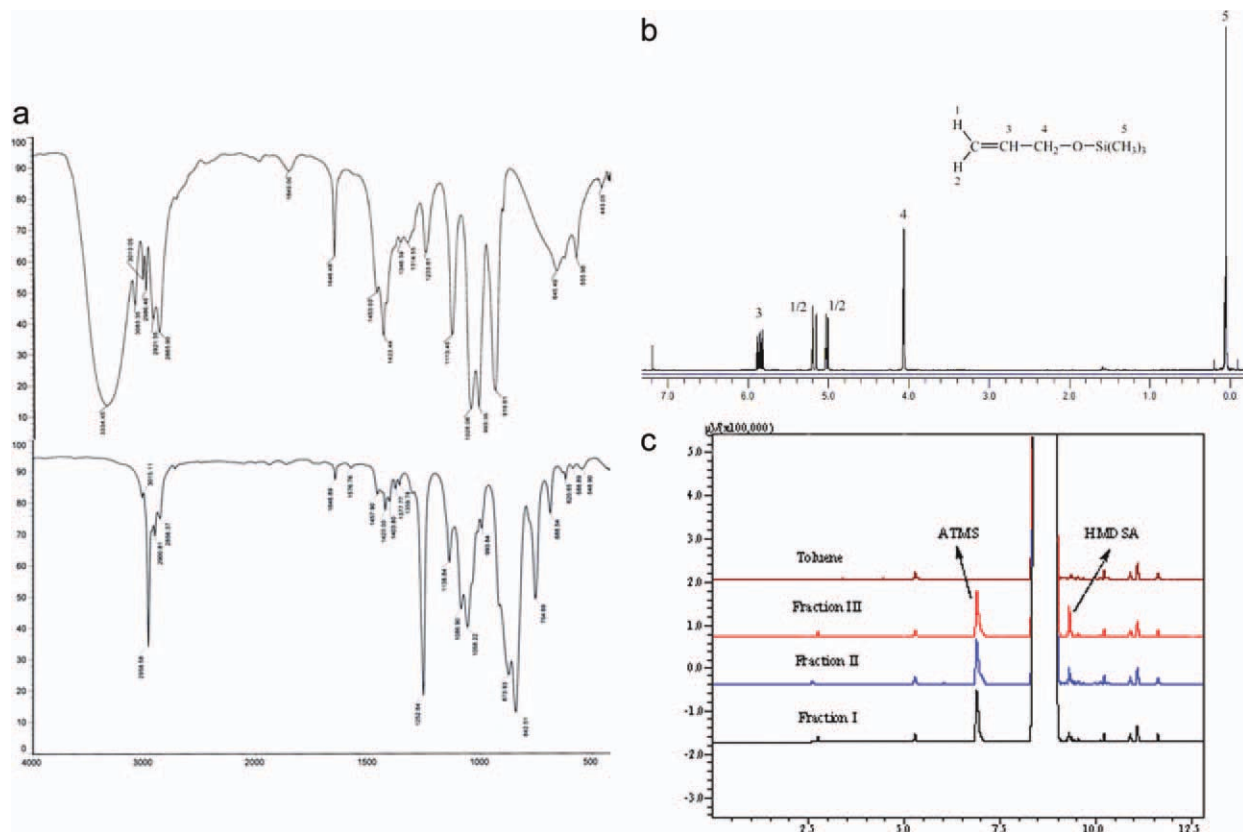


Figure 3 (a) FT-IR spectra of allyl alcohol (upper) and compound III (bottom). (b) ^1H NMR spectra of compound III. (c) Gas chromatograms of toluene, fraction I, II, and III. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
The GC Analysis Data of Fractions Collected in Different Boiling Range

Fraction	Boiling range (°C)	Retention time (min)		Peak area ratio, ATMS/HMDSA
		ATMS	HMDSA	
I	91–92	6.882	9.306	12.98
II	92–96	6.880	9.310	7.95
III	96–98	6.887	9.315	3.38

vibration, which was observed at 3087 cm^{-1} assigned to C—H from double bond allylic group on I spectrum; (3) Appearance of C=O ester bond and C=O carbonyl bond at 1742 and 1719 cm^{-1} , these peaks were absent on D_4^{H} spectrum; (4) Vibration peaks due to stretching of methylene and methyl, situated in between 2800 and 3000 cm^{-1} , as well as those around 1300 – 1480 cm^{-1} due to bending vibration of the adjacent methenyl and methylene are all present; (5) Other peaks, i.e., Si—O—Si stretching vibration at 1081 cm^{-1} , Si—CH₃ stretching vibration at 1269 cm^{-1} and its swing vibration at 799 cm^{-1} , are also observed.

In the presence of Speier catalyst, hydrosilylation of allyl acetoacetate was considered to be unfavorable because the reaction of Si—H group with the C=O group was doubtful.^{16,17} However, a few references reported that 3-allylpentane-2,4-dione was hydrosilylated by this method successfully.^{18,19} Note that the replacement of a hydrogen atom in Si—H group by a hydroxyl group of the ketone in the enol form is possible in principle. Yao et al.²⁰ investigated the hydrosilylation of 3-allylpentane-2,4-dione by NMR method. According to the result of NMR analysis, they reached to the conclusion that the addition of Si—H to C=O was negligible. In the present work, we have investigated the hydrosilylation reaction between allyl acetoacetate and D_4^{H} by the similar method.

The ^1H NMR spectrum of compound II [Fig. 2(b) upper] shows one intense multiplet (0.03 ppm) for the Si—CH₃ groups. Resonances for the methyl protons in the CH₃C(=O)CH₂— (2.20 ppm) and CH₃C(=C)O— (1.88 ppm) fragments, the methylene protons in the C(=O)CH₂— (3.39 ppm) and three multiplets (0.49, 1.62, and 4.02 ppm) corresponding to methylene substituents in the 3-(2-acetyl-acetoxy)-propyl group are also observed. Two signals of

much lower intensity at 4.91 and 11.91 ppm are assigned to the hydrogen atom of CH(=C)O— and to the hydrogen atom of the hydroxy group in the enol form. The position and integration of signals in the spectrum fit the formula of compound II very well with consideration of the tautomerism. From the ^{13}C NMR spectrum of compound II [Fig. 2(b) bottom], the chemical shifts for carbon atom labeled on the molecular formula agree with the chemical structure of compound II as well as with that of its tautomerism.

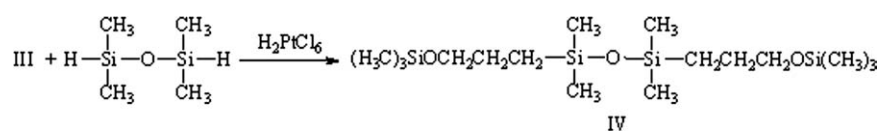
Based on the result of ^1H NMR and ^{13}C NMR analysis, it is confirmed that the hydrosilylation between allyl acetoacetate and Si—H group could proceed in the normal way without interference by the C=O group.

Synthesis and characterization of compound III (ATMS)

Hydroxyl group protection is important in the synthesis of organic molecules, particularly the hydrosilylation of alkenols with Si—H group.^{21–23} Because Si—H group can react with hydroxyl group to release hydrogen gas which reduces the yield of final compound. One way to protect hydroxyl groups is to transform the molecules to their corresponding silyl ethers.^{24–27} The trimethylsilyl group has been used for hydroxyl protection, partly because of its specific and mild removal by methanol.²⁸ This protection is normally accomplished by using HMDSA as depicted by Scheme 3.

An interesting phenomenon was observed during the distillation of ATMS. ATMS and HMDSA can form a double binary azeotrope. The azeotrope system was confirmed by GC analysis [see Fig. 3(c)]. Three kinds of fractions were collected in different boiling range, and the GC analysis data of them are listed in Table I. Based on the GC analysis, ATMS can not be separated completely by traditional distillation. A Vigreux fractionating column was used for ATMS separation, the distillate between 98 and 100°C was collected. The purity of ATMS thus obtained exceeded 98%, examined by GC analysis.

The chemical structure of compound III was confirmed by FT-IR and ^1H NMR analysis. Figure 3(a) shows the FT-IR spectra of compound III, in which the absorptions of stretch vibrations of double bond and that of C—H on CH=CH₂ were observed at 1646 cm^{-1} and 3015 cm^{-1} , respectively. Peak of



Scheme 4 Synthesis of compound IV.

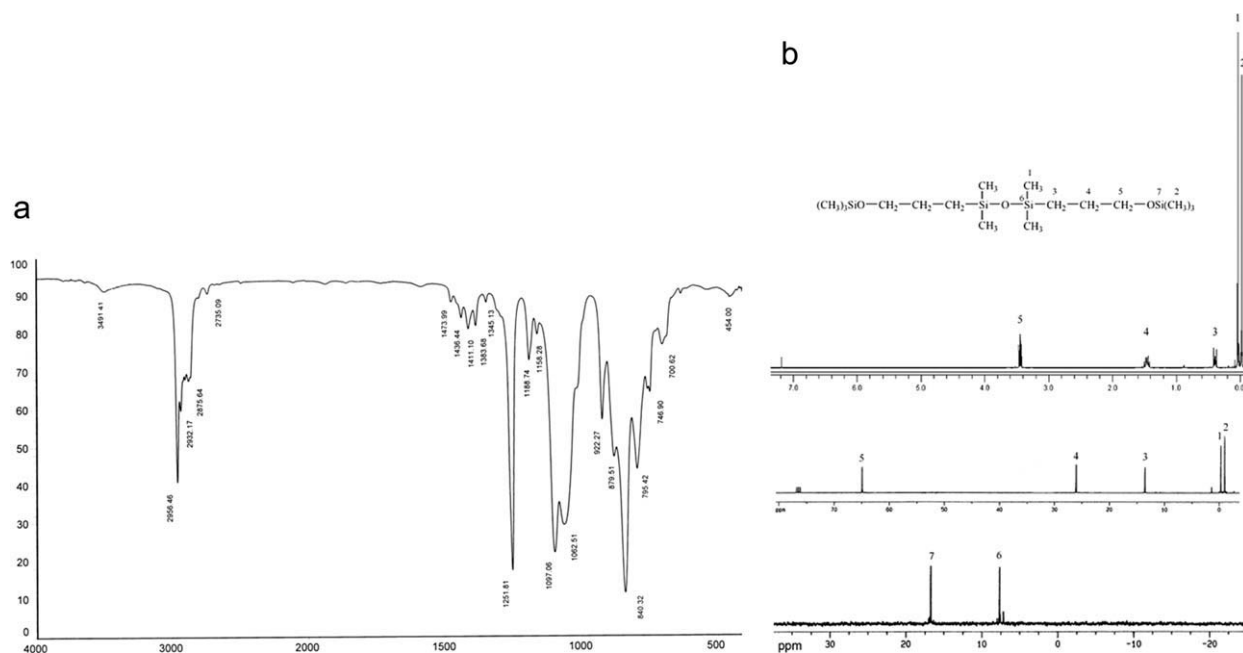


Figure 4 (a) FT-IR spectra of compound IV. (b) ^1H (upper), ^{13}C (middle), and ^{29}Si (bottom) NMR spectra of compound IV.

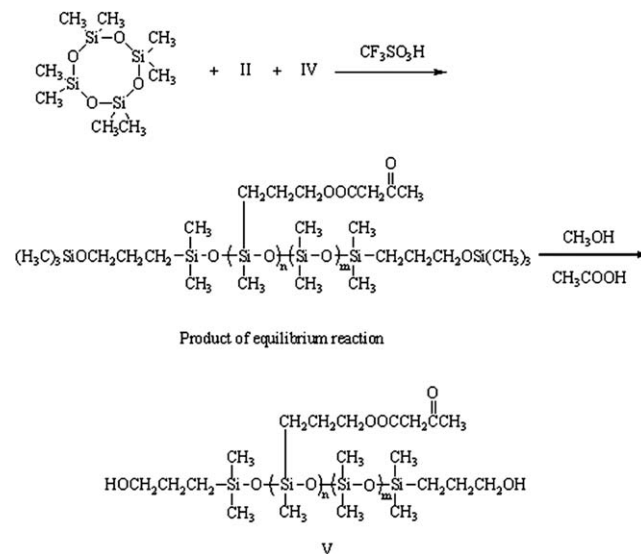
stretch vibration of hydroxyl group at 3331 cm^{-1} in allyl alcohol disappeared in ATMS spectrum. The characteristic absorption of $\text{Si}-\text{CH}_3$ and $\text{Si}-\text{O}-\text{C}$ also appeared at 1252 and 1087 cm^{-1} . Figure 3(b) shows the ^1H NMR spectra of compound III in CDCl_3 . All the signals corresponding to the proposed structures were observed.

Synthesis and characterization of compound IV

The compound IV was synthesized by hydrosilylation reaction as shown in Scheme 4. From the aforementioned refractive index of the objective product IV given in experimental section, it was seen that the experimental value, $n_D^{20} = 1.4220$, agreed well with reported value of $n_D^{20} = 1.4240$. Figure 4(a) presents the FT-IR spectrum of compound IV. In comparison with the spectra of ATMS and TDMS, the spectrum of IV exhibits the following characteristics: (1) Complete disappearance of $\text{C}=\text{C}$ double bond vibration, which was observed in ATMS spectrum at 1646 cm^{-1} ; (2) Complete disappearance of $\text{Si}-\text{H}$ vibration, which was observed as the third largest peak at 2127 cm^{-1} amongst all peaks on TMDs spectrum; (3) Appearance of $\text{Si}-\text{O}-\text{C}$ bond at 1097 cm^{-1} due to its stretch vibration, this peak was absent on TMDs spectrum; (4) Vibration peaks due to stretching of methylene and methyl, situated in between 2800 and 3000 cm^{-1} , as well as those around $1300\text{--}1480\text{ cm}^{-1}$ due to bending vibration of the adjacent methenyl and methylene are all present; (5) Other peaks, i.e. $\text{Si}-\text{O}-\text{Si}$ stretching vibration at 1062 cm^{-1} , $\text{Si}-\text{CH}_3$ bending vibration at 840 cm^{-1}

and its swing vibration at 795 cm^{-1} , are also observed. All these observations indicated that the $\text{C}=\text{C}$ double bond and $\text{Si}-\text{H}$ bond disappeared after hydrosilylation, while $\text{Si}-\text{O}-\text{C}$ bond remained, and new chemical groups such as methenyl, methene have been formed by hydrosilylation as expected. This confirms the formation of compound IV through the hydrosilylation reaction.

The compound IV was then subjected to ^1H NMR [Fig. 4(b) upper], ^{13}C NMR [Fig. 4(b) middle], and ^{29}Si NMR [Fig. 4(b) bottom] analysis. In the ^1H NMR spectrum of compound IV, the methyl protons of $\text{Si}-\text{CH}_3$ (H_1 and H_2) were observed at 0.04 and



Scheme 5 Synthesis of compound V.

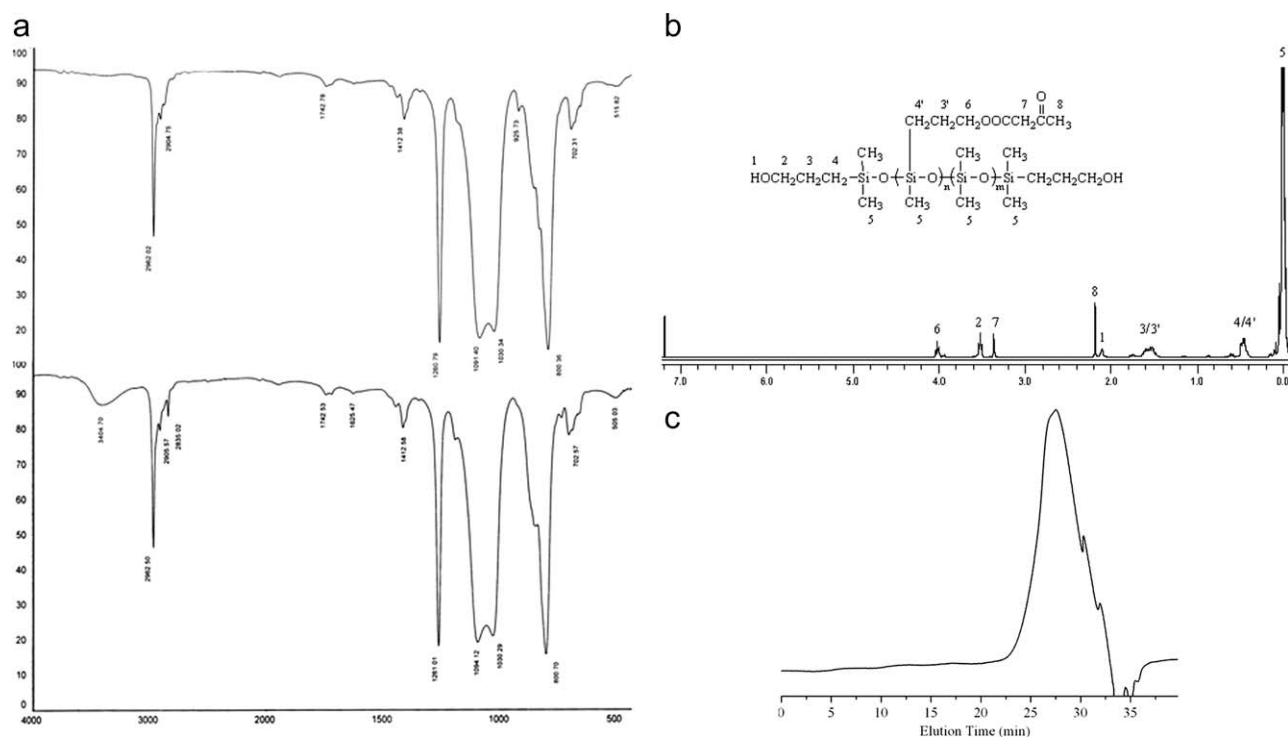


Figure 5 (a) FT-IR spectra of equilibrium product (upper) and compound V (bottom). (b) ¹H NMR spectra of compound V. (c) GPC curve of compound V.

−0.03 ppm. The propyl protons H₃, H₄, and H₅ showed in the region of 0.36–0.43, 1.41–1.50, and 3.40–3.48 ppm, respectively. To further provide a supplementary confirmation for the accuracy of these identifications, a ¹³C NMR was then conducted. From the chemical shifts, the peaks representing carbon atoms labeled 1, 2, 3, 4, and 5 on the molecular formula were easily assigned. Based on the analysis of ¹H NMR and ¹³C NMR, compound **IV** was synthesized as successfully as expected. To consolidate the conclusion that compound **IV** was indeed the designed product, a ²⁹Si NMR was then followed, which showed two neat resonance peaks at $\delta = 7.727$ and 16.778 ppm, this agrees with the chemical structure depicted in Scheme 4.

Synthesis and characterization of compound V

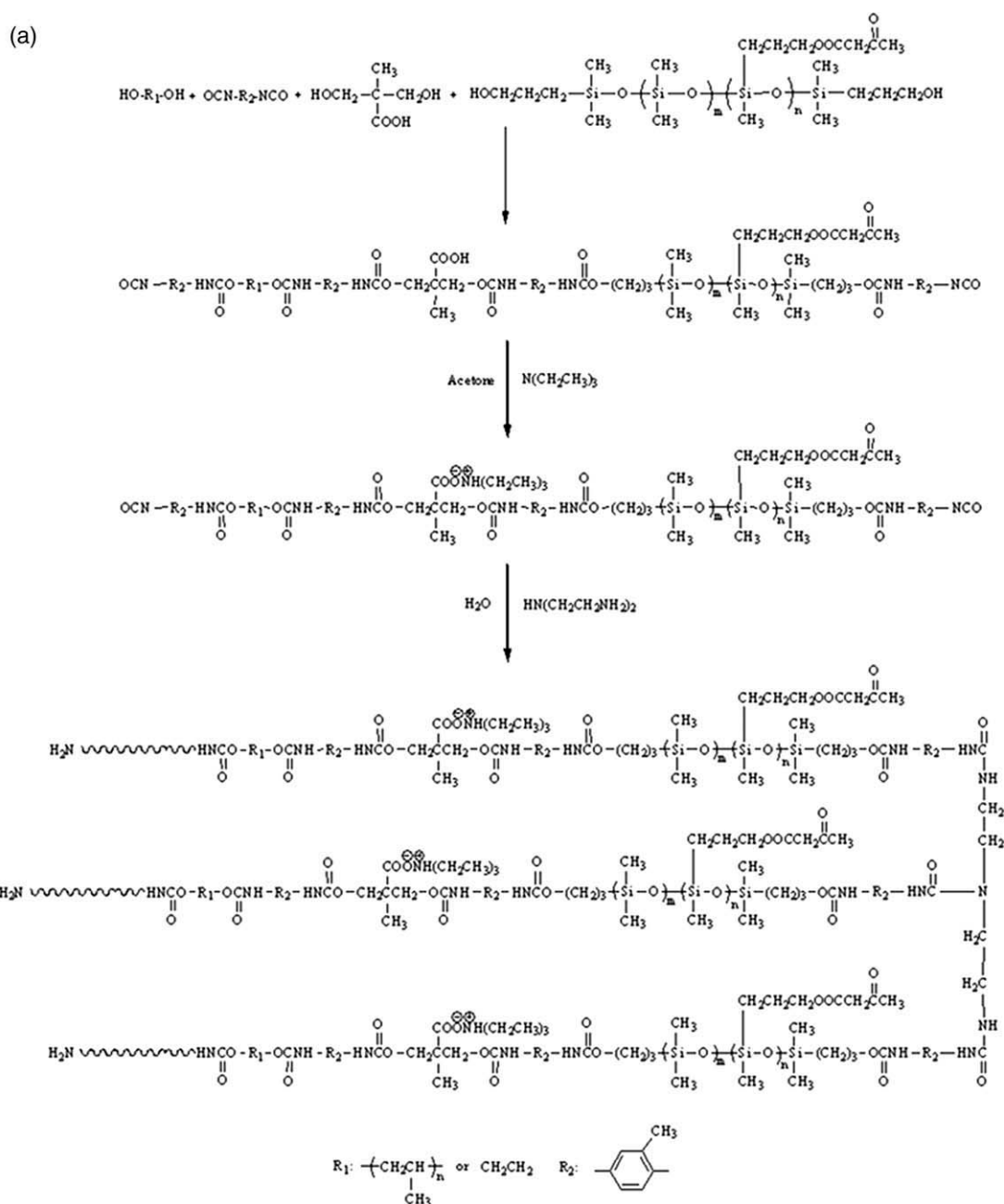
The final product was obtained through a two-step procedure including equilibrium reaction and deprotection (Scheme 5). First, the objective of the equilibrium or redistribution reaction was to extend the siloxanes segment length through insertion of the

siloxane oligomer originated from ring-opened **D**₄ and **II** condensation. This equilibrium reaction has been used in the literature and proved to be effective, chain expansion was successfully achieved.²⁹ Second, the protective groups in the equilibrium product should be removed to create two hydroxyl groups in the molecule, so that it became reactive towards isocyanate group in a subsequent step to prepare polyurethane modified by polysiloxane. It is assumed that the ester and carbonyl groups are not affected by this process; the resultant product will possess the main chemical structure as both **II** and **IV**. The FT-IR spectrum of equilibrium product and compound **V** are given in Figure 5(a). A strong hydroxyl vibration peak appeared at 3405 cm^{-1} , a sign of hydroxyl formation following the breakage of trimethylsilyl group. The absorption band associated to C=O bond was also observed at 1742 cm^{-1} . For the ¹H NMR spectrum of compound **V** given in Figure 5(b), it displays the same characteristic as those of **II** and **IV**. The GPC curve of the compound **V** was shown in Figure 5(c). Based on the proton

TABLE II
Molecular Weight of V

Samples	M_n by theory	M_n by ¹ H NMR	m/m'^a	n/n'^a	M_n by GPC	PDI
V ₁	996	990	6.8/7.0	1.2/1.1	2396	1.39
V ₂	1499	1536	13.6/14.1	1.2/1.2	2657	1.28

^a $m(n)$: theory value, $m'(n')$: determined value by NMR spectroscopy.

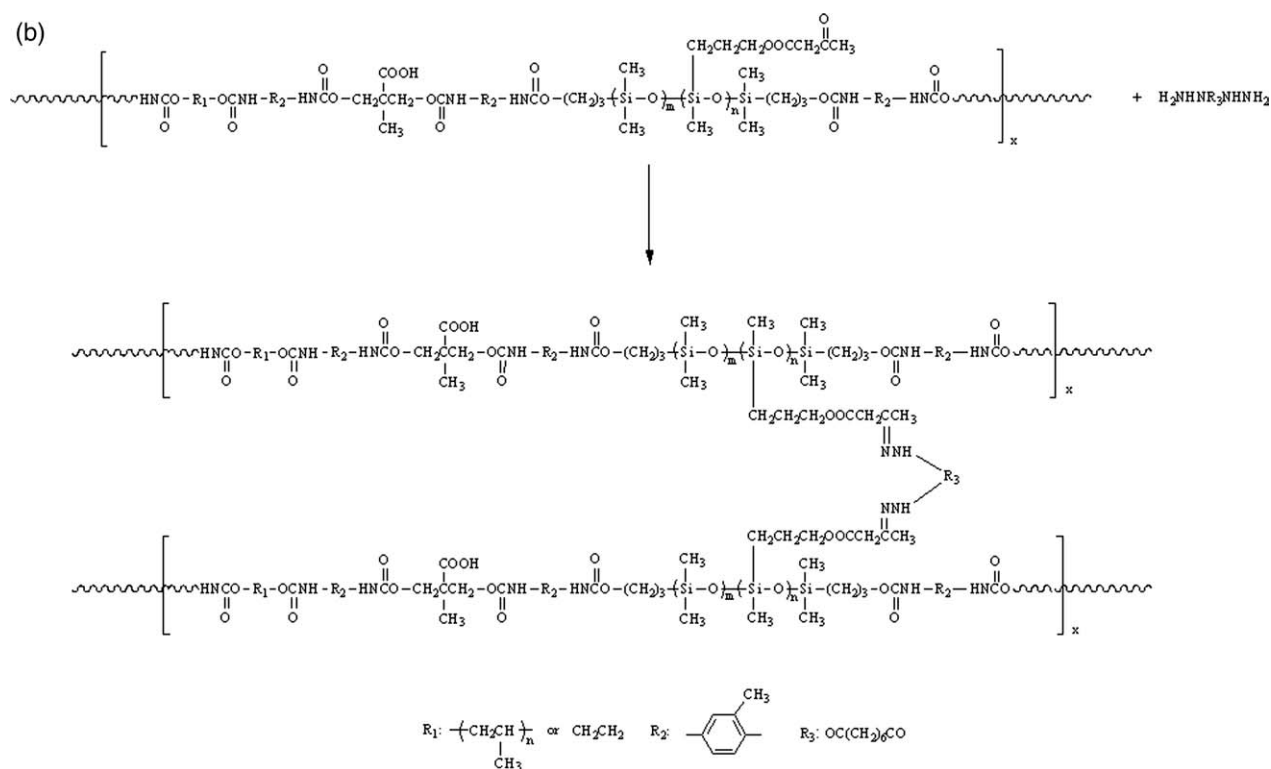


Scheme 6 (a) Synthesis of polyurethane modified with V. (b) Crosslinking of WPU-V bearing aceto acetylated groups with a dihydrazide.

peak integration, the molecular weight of the compound V (Table II) was estimated along with that obtained via GPC as well as the theoretical value. It is noteworthy that the theoretical molecular weight of the compound V is in good agreement with the value measured from ^1H NMR. However, the value from GPC is slightly larger than the theoretical value. This might be because of the fact that the polystyrene was used as the polymer standard in these test, which may lead to inaccurate result knowing that these two polymers were of very different natures.

Synthesis and characterization of waterborne polyurethane modified with V (WPU-V)

The compound V combines the properties of difunctional hydroxyalkyl terminated polysiloxane and crosslinking agent. On the one hand, polysiloxane segments could be inserted into polyurethane chains to form block copolymers by the reaction between isocyanate groups and hydroxypropyl groups, and on the other hand, when a dihydrazide was post-added upon polyurethane preparation and crosslinking was thus achieved by the reaction between the dihydrazide and carbonyl group during film



Scheme 6 (Continued).

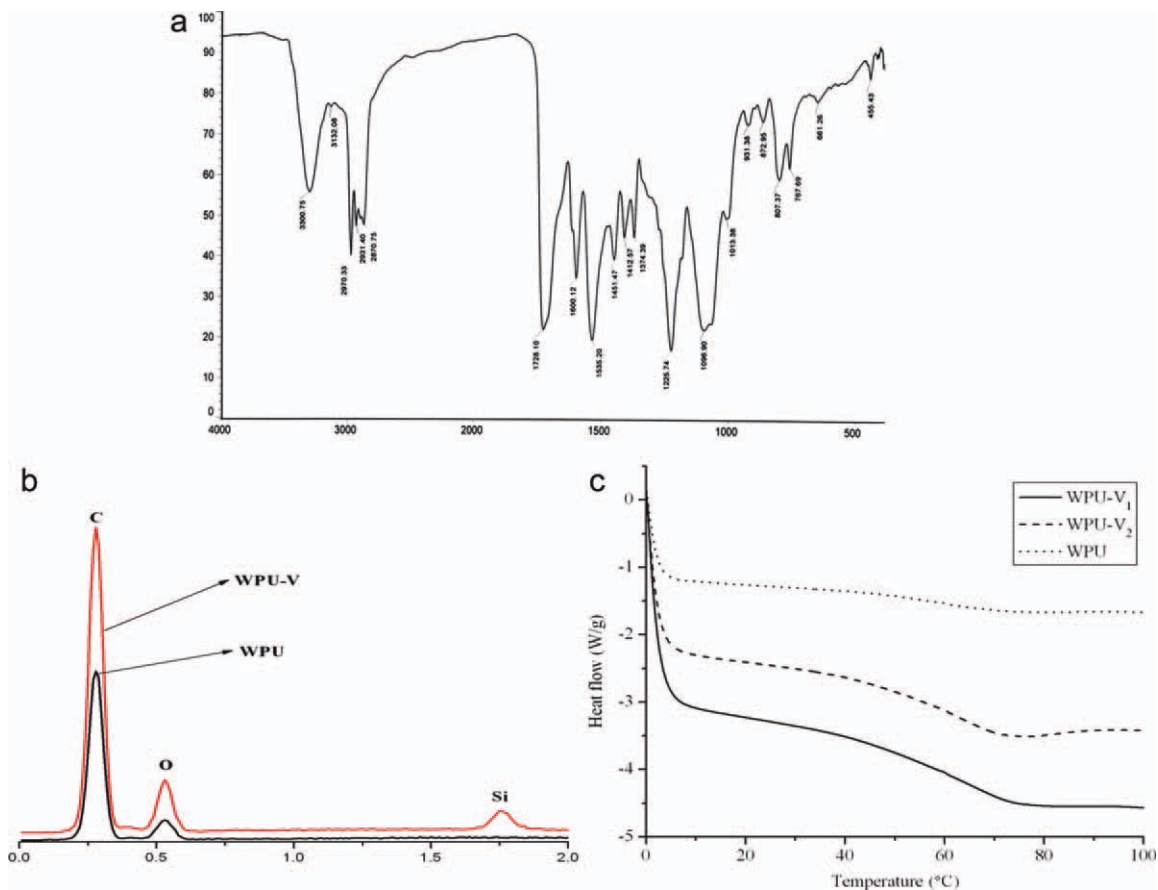


Figure 6 (a) FT-IR spectrum of WPU-V. (b) EDS spectra of WPU and WPU-V. (c) DSC curves of WPU, WPU-V₁, and WPU-V₂. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE III
Properties of Latex Films of WPU and WPU-V

	Sample		
	WPU	WPU-V ₁	WPU-V ₂
Crosslinking (%)	85.54	90.03	91.75
Hardness (shore A)	82.1	77.2	82.5
Tensile strength (MPa)	16.6	20.6 ^a (16.5) ^b	22.7 (19.5)
Elongation at break (%)	266	207 ^a (246) ^b	189 (227)
Water absorption (%)	75.23	61.28	56.86
Toluene absorption (%)	84.75	76.57	76.82
T _g (°C)	52.86	59.28	55.03

^a Tensile strength (or elongation at break) of latex films of WPU-V with ADH.

^b Tensile strength (or elongation at break) of latex films of WPU-V without ADH.

formation. The compound **V** with different chemical structures and molecular weights reacted with TDI, PPG, DMPA, and EG by the prepolymer process to synthesize WPU-V. For the polyurethane latexes with the designed crosslinking, ADH was post-added with its amount controlled to be half of the carbonyl group in mol. The synthesis route of WPU-V and crosslinking of WPU-V bearing aceto acetylated groups with a dihydrazide were shown in Scheme 6(a,b), respectively.

Figure 6(a) shows the FT-IR spectrum of WPU-V. The absorption peaks of typical polyurethane at 3300 cm⁻¹ [ν (NH)], 2870–2970 cm⁻¹ [ν (CH₂) and ν (CH₃)], 1728 cm⁻¹ [ν (C=O)] and 1535 cm⁻¹ [δ (NH)] can be seen clearly in the spectra. Furthermore, the peaks at 1225 cm⁻¹ [ν (Si–CH₃)], 1096 cm⁻¹ [ν (Si–O)] and 807 cm⁻¹ [(Si–CH₃ rocking)] indicates that siloxane segments have been successfully introduced into the polyurethane chain. The elemental identification of latex films were measured by energy-dispersive X-ray spectroscopy (EDS). The EDS spectra [Fig. 6(b)] indicates the presence of C, O, and Si atoms after the compound **V** linking to WPU, and this result is in agreement with that obtained by FT-IR analysis.

Properties study of WPU-V

Table III presents properties of latex films of WPU and WPU-V. Comparing WPU with those cross-linked with **V** and post-added ADH, it is clearly seen that crosslinking was indeed enhanced in the films prepared with the compound **V**. The crosslinking was 85% in WPU due to DEA, and it increased with presence of the compound **V**. Film hardness was no obvious changed with crosslinking. Tensile strength of WPU-V increased after post-added ADH, combined with a decrease in film elongation at break. It indicates that the post-crosslinking reaction can improve the physical–mechanical characteristics

of films prepared by the compound **V**. The most remarkable improvements were water and toluene adsorptions of the latex films, which were significantly reduced by this designed crosslinking. Water adsorption was reduced from 75 to 56%. Similar effects were observed for toluene adsorption but at a lessened significance. This indicates that the compound **V** was indeed a very effective ambient temperature self-crosslinking agent for WPU.

The glass transition temperature values (T_g) were also listed in Table III and the differential scanning calorimeter (DSC) curves of WPU, WPU-V₁, and WPU-V₂ were illustrated in Figure 6(c). As shown in Table III, WPU exhibited a T_g of 52.86°C. Comparing WPU with WPU-V, the T_g of WPU-V increased, but the T_g change among them was not evident. This might be because of the fact that the T_g of polysiloxane was around –120°C, when WPU was bonded with polysiloxane, the T_g of WPU-V would be decreased. On the other hand, crosslinking could increase the T_g of WPU-V.

CONCLUSIONS

A novel reactive polysiloxane bearing hydroxypropyl group at both chain ends and carbonyl groups at the side chain was synthesized by five-step reactions. The prepared compounds in each step were characterized by FTIR and NMR. The results indicated that each step synthesis was successfully carried out and objective products were achieved. This novel reactive polysiloxane combines the properties of difunctional hydroxyalkyl terminated polysiloxane and crosslinking agent, which can be utilized for double modification of waterborne polyurethane and is indeed a very effective ambient temperature self-crosslinking agent for waterborne polyurethane.

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