

# Thermal Properties of Polyurethane Binder with 2-(Ferrocenylpropyl)dimethylsilane-grafted Hydroxyl-Terminated Polybutadiene

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**ABSTRACT:** We synthesized a ferrocene-based burning rate catalyst, 2-(ferrocenylpropyl) dimethylsilane (FPDS). FPDS-grafted hydroxyl-terminated polybutadiene (FPDS-g-HTPB) was synthesized using hydrosilylation with a Pt catalyst. The structures of FPDS and FPDS-g-HTPB were investigated by Fourier transform infrared spectroscopy and nuclear magnetic resonance. HTPB-based polyurethanes were prepared from HTPB,  $\epsilon$ -hexamethylenediisocyanate (HDI), and HDI-trimer. Polyurethane network was prepared with an (NCO)/(OH) ratio of 1.05 and an [isocyanate trimer]/[total NCO] ratio of 0.3 then subjected to accelerated aging at 80°C. The thermal behaviors of the polyurethane

network were compared using differential scanning calorimetry and thermal gravity analysis. The glass transition temperatures ( $T_g$ ) of HTPB and FPDS-g-HTPB were  $-76^\circ\text{C}$  and  $-47^\circ\text{C}$ , respectively. The value of  $T_g$  for the networked polyurethane was not influenced by HDI-trimer content but by FPDS content. The decomposition temperature of the neat HTPB-based polyurethane network was lower than that of the FPDS-g-HTPB-based polyurethane networks. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3560–3568, 2011

**Key words:** HTPB; ferrocenyl silane; hydrosilylation; DSC; TGA

## INTRODUCTION

Propellants are used in a wide range of applications such as the military, aerospace, and automobile.<sup>1</sup> Composite propellants with reduced smoke and high burning rates are composed of about 85% oxidizers and 15% metallic fuels and polymeric materials and other materials.

Inorganic oxidizers are oxygen-rich crystalline inorganic perchlorate such as ammonium perchlorate. Oxidizers should have high density, low heat of formation, high oxygen content, high thermal stability, low hygroscopicity, compatibility with other ingredients, and a high energy release during combustion to form large volumes of gas. Metallic fuels, such as lithium, aluminum, and magnesium, are incorporated into the propellant to achieve high volumetric energy due to their high heat of combustion, high propellant density, and high combustion temperature.<sup>2,3</sup> Polymeric materials are used as binders for solid particles (oxidizers, metallic fuels, etc.) to formulate composite propellants. The polymeric materials impart dimensional stability, structural integrity to the propellant grain, compatibility with

other propellant ingredients, good mechanical properties, and act as fuel during combustion.

Recent research focuses on polyurethane binder. Polyurethane binders synthesize with polyol and diisocyanate. HTPB prepolymers, because of their high specific impulse, impart a low-glass transition temperature, good mechanical properties at low temperature, and good ballistic resistance, are used as binder in rocket or missile solid propellant.<sup>4–10</sup>

Besides an oxidizer, metallic fuel, and binder, a composite propellant needs a metal catalyst control the burning rate. Ferric oxide is used as a burning rate catalyst for composite solid propellants. Inorganic ferric oxide particles have several drawbacks: (1) they have poor compatibility with organic binders, (2) they induce heterogeneous combustibility due to their low dispersity and homogeneity, and (3) they are characterized by poor storage stability. To mitigate the weaknesses of ferric oxides, ferrocene derivatives, having property of good stability and compatibility, are often used. Ferrocene derivatives have some drawbacks, such as their migration to insulation composition during storage, evaporation, or sublimation loss during processing, and phase separation by crystallization. To solve these problems and to improve the efficiency of the ferrocene catalyst, attempts have been made to use the appropriate ferrocene derivative to covalently link the ferrocene moiety to the propellant binder via grafting to the binder backbone during its synthesis.<sup>11–13</sup>

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In this study, to overcome these disadvantage, we synthesized a ferrocene-based burning rate catalyst, 2-(ferrocenylpropyl)dimethylsilane. 2-(Ferrocenylpropyl)dimethylsilane-grafted hydroxyl-terminated polybutadiene (HTPB) was synthesized using hydrosilylation with a Pt catalyst. The structures of 2-(ferrocenylpropyl)dimethylsilane and 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB were investigated by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR). 2-(Ferrocenylpropyl)dimethylsilane-grafted HTPB-based polyurethanes were prepared from HTPB prepolymer, 1,6-hexamethylenediisocyanate (HDI), and HDI-trimer. Polyurethane network was prepared with an (NCO)/(OH) ratio of 1.05, and an (isocyanate trimer)/(total NCO) ratio of 0.3 then was subjected to accelerated aging at 80°C. The thermal behaviors of HTPB, 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB, and polyurethane networks were compared using differential scanning calorimetry (DSC) and thermal gravity analysis (TGA).

## EXPERIMENTAL

### Materials

Ferrocene (Aldrich Co; 98%), aluminum chloride (Aldrich Co; 99.99%), toluene (Aldrich Co; 99%), hexachloroplatinic acid (Aldrich Co; 99.9%), and magnesium sulfate (samchun Co; 99.5%) were used without further purification. Allyl dimethyl chlorosilane (ADCS; Gelest) was distilled before use. HDI and hexamethyleneisocyanurate (TLA-100; Asahikasei Chemical Co.) were used as purchased. Dibutyltindilaurate (DBTDL; Aldrich Co.) was used as received. HTPB (Satomer; 1,2-addition content 20%) was dried under reduced pressure at 85°C for 24 h. Materials for protecting and deprotecting, aluminum chloride hexahydrate, 3,4-dihydro-2H-pyran, and methanol, were used as received. Tetrahydrofuran (THF) was kept under refluxed over a mixture of sodium metal and benzophenone for 48 h, then distilled.

### Synthesis

#### Synthesis of 2-(ferrocenylpropyl)dimethylsilane<sup>14</sup>

The compound was prepared first by the alkylation of ferrocene, allyl dimethyl chlorosilane, and aluminum chloride in methylene chloride under argon atmosphere and then stirred for 1.5 h at 0°C to create 2-(ferrocenylpropyl)chloro dimethylsilane. The solvent was removed by vacuum evaporation. The remaining mixture was dissolved in dried THF and added dropwise to a suspension of lithium aluminum hydride in dried THF, then heated for 1 h and hydrolyzed with water. The organic layer was

extracted with diethyl ether, and the extracts were washed with aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate, and then filtered. The solvent was distilled off.

<sup>1</sup>H-NMR(300MHz) δ0.15 (6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.9(1H, SiCH<sub>a</sub>H<sub>b</sub>), 1.1(1H, SiCH<sub>a</sub>H<sub>b</sub>), 1.4(3H CHCH<sub>3</sub>), 2.8 (1H, CHCH<sub>3</sub>), 3.6 (1H, SiH)4.11–4.25 (9H, Cp)

### Protecting of HTPB

A mixture of hydroxyl-terminated polybutadiene (HTPB) and aluminum chloride hexahydrate in tetrahydrofuran (THF) was stirred at room temperature. After 3,4-dihydro-2H-pyran was dropped, the reaction mixture was refluxed at 60°C and the progress of the reaction was monitored by FTIR. The product was purified by filtering, extraction using toluene, and then evaporation under reduced pressure. The reaction scheme of the hydrosilylation of 2-(ferrocenylpropyl)dimethylsilane with hydroxy-terminated polybutadiene is shown in Scheme 1.

### Synthesis of 2-(ferrocenylpropyl)dimethylsilane with protected HTPB

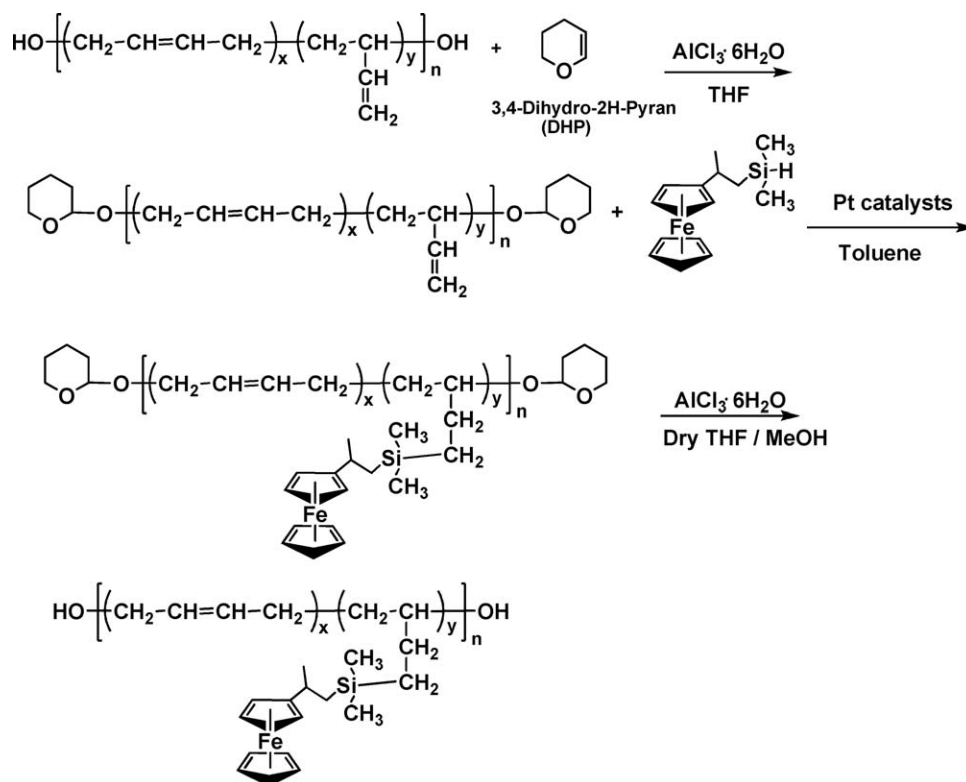
A mixture of hydroxyl-terminated polybutadiene (HTPB; 18 g) and hexachloroplatinic acid (0.1 g) in dried toluene (100 mL) under argon atmosphere was stirred for 1 h at 60°C. Then, 2-(ferrocenylpropyl)dimethylsilane was dropped. The reaction mixture was refluxed for another 16 h at 80°C. The end point of the reaction was determined by FTIR monitoring. When the absorption band at 910 cm<sup>-1</sup>, 1,2-addition in HTPB, disappeared, the reaction was ended. The product was purified by filtering, extraction using toluene, and then evaporation under reduced pressure.

### Deprotecting of 2-(ferrocenylpropyl)dimethylsilane grafted protected HTPB

2-(Ferrocenylpropyl)dimethylsilane-grafted protected hydroxyl-terminated polybutadiene (HTPB), aluminum chloride hexahydrate, and excess methanol were mixed at 60°C for 24 h, allowing affording regeneration of the 2-(ferrocenylpropyl)dimethylsilane grafted protected HTPB. 2-(Ferrocenylpropyl)dimethylsilane-grafted HTPB (FPDS-*g*-HTPB) was purified using the methanol precipitation process. FPDS-*g*-HTPB was determined in the presence of unreacted FPDS through thin-layer chromatography, using *n*-hexane-THF (2 : 1, v/v %) mixed solvent as the eluent.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ0.15 (SiCH<sub>3</sub>), 0.9, 0.7, 0.4 (CH<sub>2</sub>) 1.2 (CH<sub>2</sub> of HTPB and CH<sub>3</sub>) 2.05 (CH<sub>2</sub> of HTPB), 2.3 (CH<sub>2</sub>), 4.0 (C<sub>10</sub>H<sub>9</sub>), and 5.4 (C=C of HTPB);

Fe content: determination 10%, calculation 9.1%; M<sub>w</sub>: 10,000.

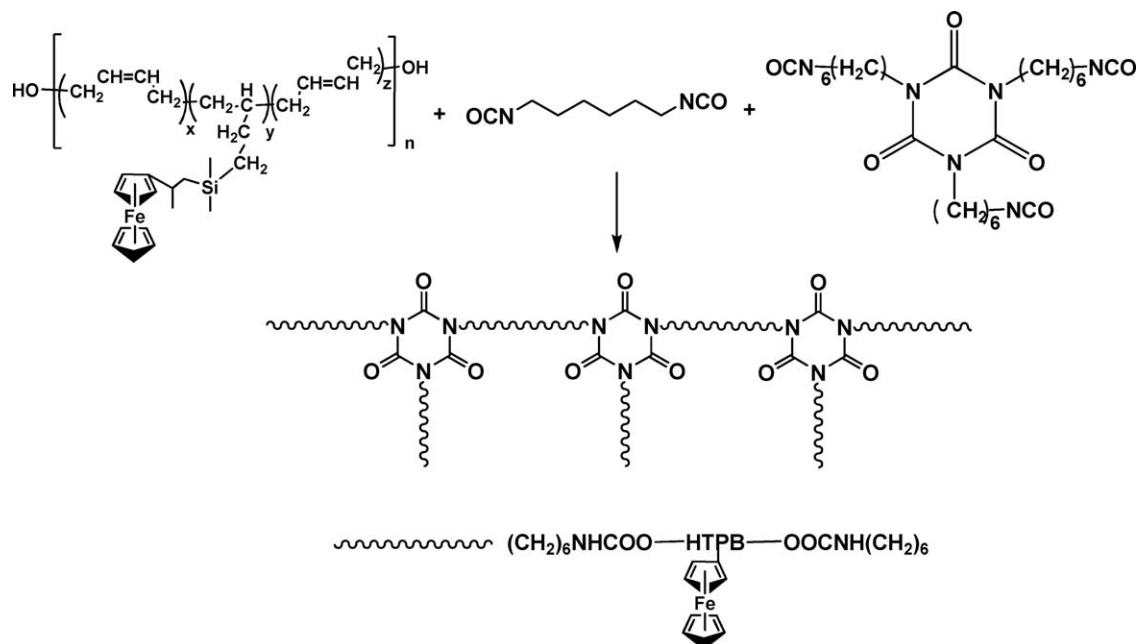


**Scheme 1** Synthesis of 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB.

#### Purification of FPDS-g-HTPB

After the reaction, purification process was conducted. FPDS-grafted hydroxyl-terminated polybutadiene (FPDS-g-HTPB), which was insoluble in methanol, was obtained by methanol-precipitation process. In the methanol-precipitation process, the

reaction mixture was poured into methanol for washing out the low-molecular weight material and precipitating the polymer. The precipitated polymer was dissolved in THF and precipitated again in methanol, and this process was repeated at least five times to remove FPDS in the product.



**Scheme 2** Preparation of networked polyurethane.

**TABLE I**  
Swelling Values of FPDS-*g*-HTPB-Based Polyurethane Networks for Several Solvents

Solvent name	Swelling value (w/w) after 12 h
Tetrahydrofuran	0.65
<i>N</i> -methyl-2-pyrrolidone	0.70
<i>N,N'</i> -Dimethylformamide	0.35

#### Preparation of polyurethane networks

HTPB prepolymer-based polyurethane networks were prepared by one-step and casting processes. The polyurethane networks were prepared from a dibutyltin dilaurate-catalyzed urethane reaction of polyol (HTPB or FPDS-*g*-HTPB), HDI, and HDI-trimer in THF, as shown in Scheme 2. Polyurethane networks were prepared with an (NCO)/(OH) ratio of 1.05 and an (isocyanate trimer)/(total NCO) ratio of 0.3. The concentration of reactants in the reaction mixture was 20%. The solution was mixed for 3 h at room temperature, poured onto a Teflon plate, and cured for 72 h at 80°C. The preparation conditions, such as the curing times and temperatures, for the neat HTPB-based polyurethane networks were fixed.

#### Measurement

##### Sol content

The sol content is very important, when studying thermal and mechanical properties. The sol content in a network should be below ~ 1% for an accurate analysis. The sol contents of the HTPB prepolymer-

based polyurethane networks were determined by extraction at room temperature in THF. After 24 h, the extracted polymer was dried, and its mass was determined. The sol fraction ( $W_s$ ) was calculated with the following relationship:

$$W_s = (1 - W_d/W_0) \times 100(\%)$$

where  $W_d$  is the mass of the dry residue, and  $W_0$  is the initial mass of the polymer.

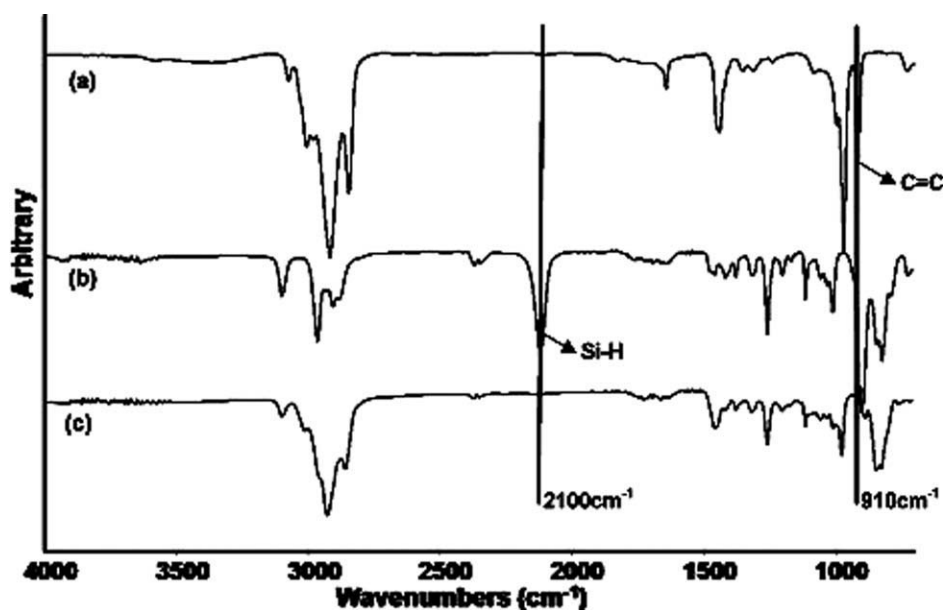
##### Structural analysis

ATR-FTIR spectra were collected using an AVATAR 360 E.S.P IR spectrometer equipped with a diamond ATR window (Nicolet Instrument Corp). All spectra were recorded in the spectral range of 4000–400  $\text{cm}^{-1}$  with 128 scans at a spectral resolution of 4  $\text{cm}^{-1}$  resolution.

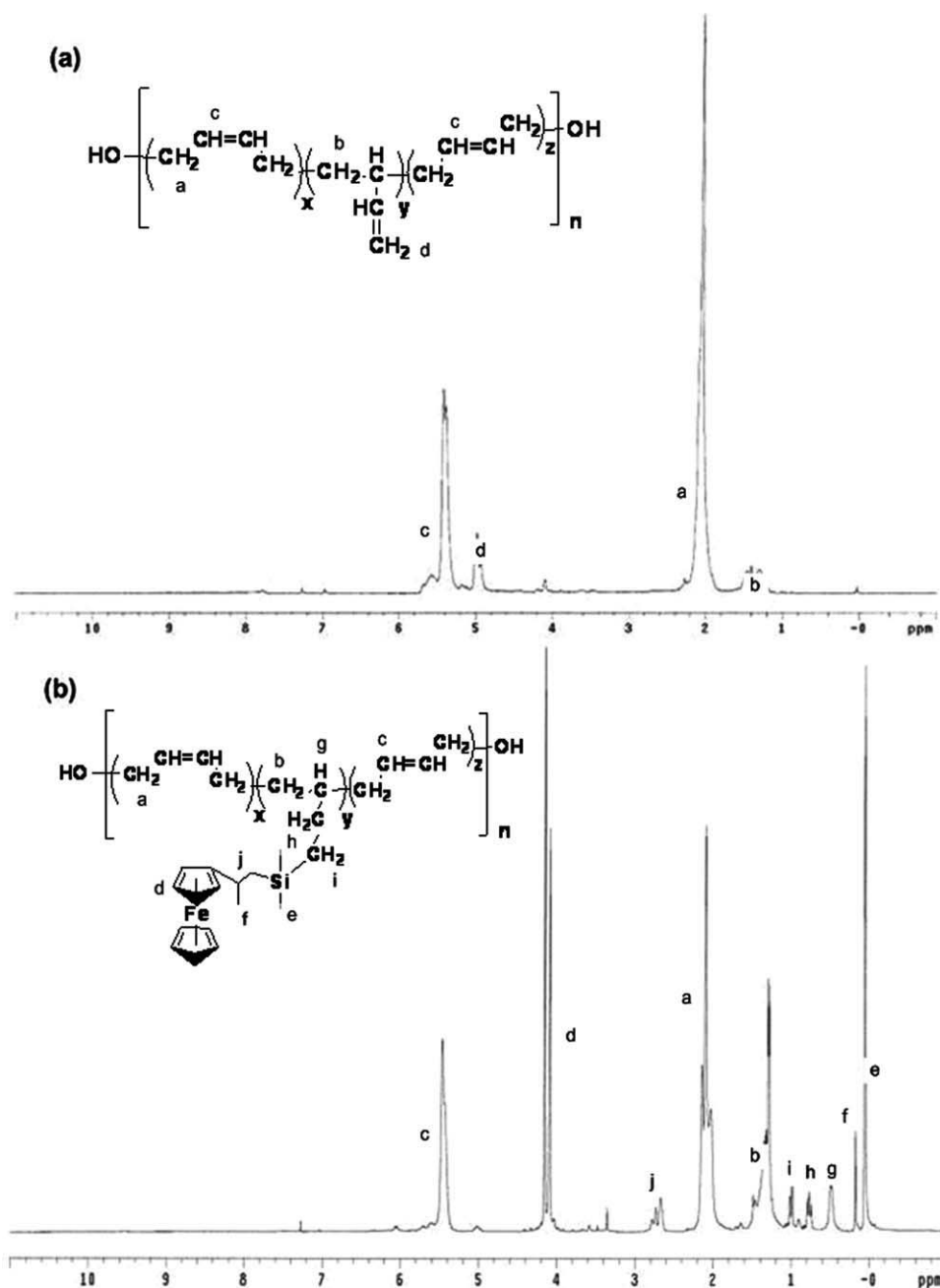
$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded on a Varian Mercury-500 NMR spectrometer at 500 MHz in deuterated chloroform.  $^1\text{H-NMR}$  spectra were referenced to the solvent signal ( $\text{CDCl}_3$ , 7.19 ppm), and  $^{13}\text{C-NMR}$  spectra to the solvent signal ( $\text{CDCl}_3$ , 77.0 ppm).

##### Thermal analysis

DSC experiments were performed with a TA Instrument 2010 DSC equipped with an aluminum pan under nitrogen purge. The DSC was calibrated using indium. Samples were scanned in two experiments: 25–100°C and –100–100°C at a heating rates of 10°C/min. Liquid nitrogen was used to cool the



**Figure 1** IR spectra of (a) HTPB, (b) 2-(ferrocenylpropyl)dimethylsilane, and (c) 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB.



**Figure 2**  $^1\text{H-NMR}$  spectra of (a) HTPB and (b) 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB.

sample during the low-temperature measurement from room temperature to  $-100^\circ\text{C}$ . Measurements were performed under nitrogen atmosphere at a rate of 60 mL/min. An empty pan was used as a reference. The glass transition temperature ( $T_g$ ) was reported as the midpoint temperature of the baseline shift measured during the transition. The sample weight was 8–10 mg.

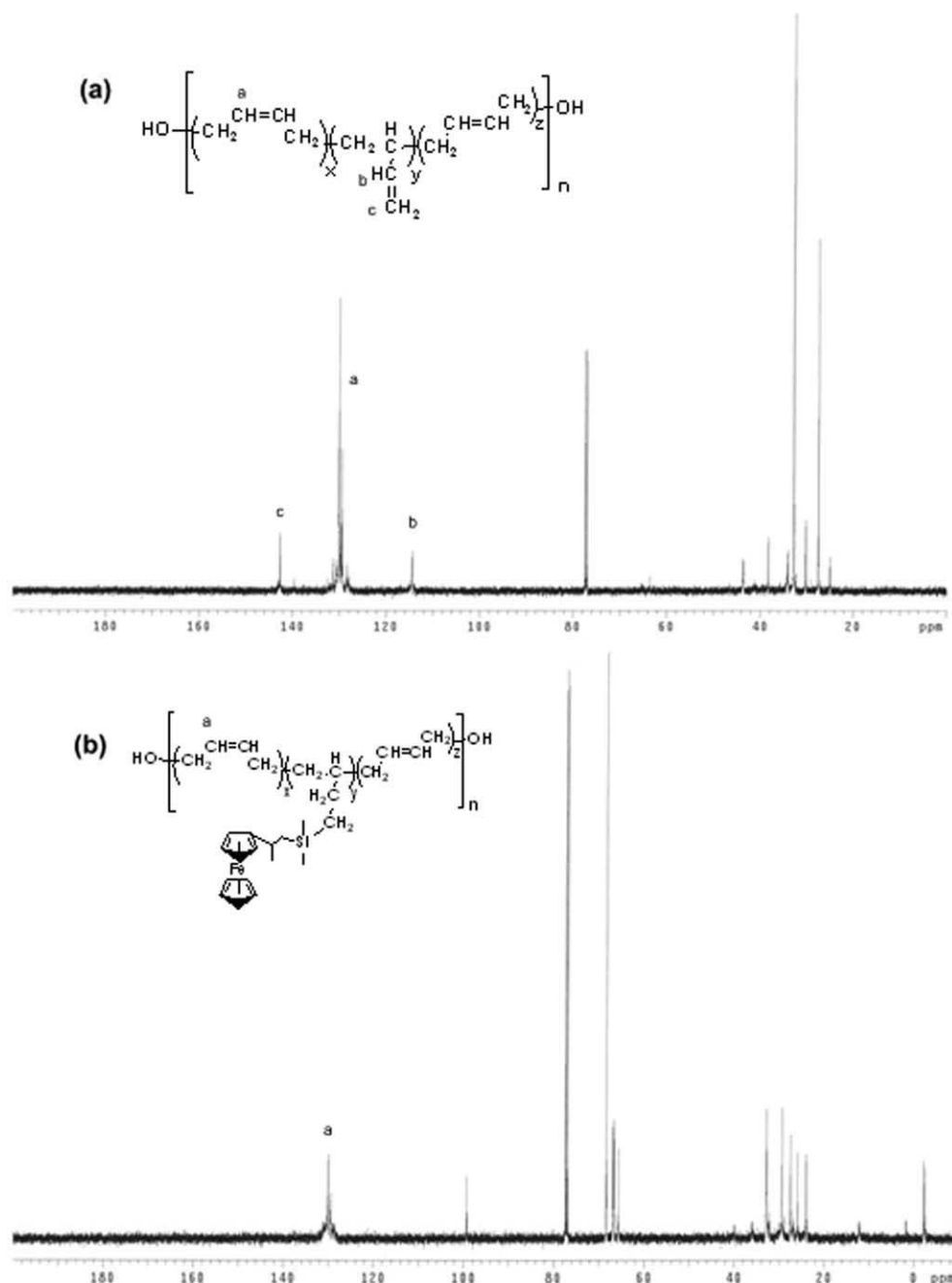
Thermo gravimetric analysis was recorded on a TA Instrument TGA-Q5000, and was carried out between room temperature and  $700^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere at 20 mL/min. The sample weight was 8–10 mg.

#### Fe content

The Fe content in the FPDS-grafted HTPB (FPDS-g-HTPB) was estimated by inductively coupled plasma-optical emission spectrometer on a Ultima 2 (Jobin-Yvon Co.). The solution was prepared by mixing 50 mg of the sample with nitric acid in a microwave oven.

#### Swelling studies

Swelling values were determined by sample in THF, *N*-methyl-2-pyrrolidone, and *N,N'*-dimethylformamide at room temperature for 12 h. Subsequently, the



**Figure 3**  $^{13}\text{C}$ -NMR spectra of (a) HTPB and (b) 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB.

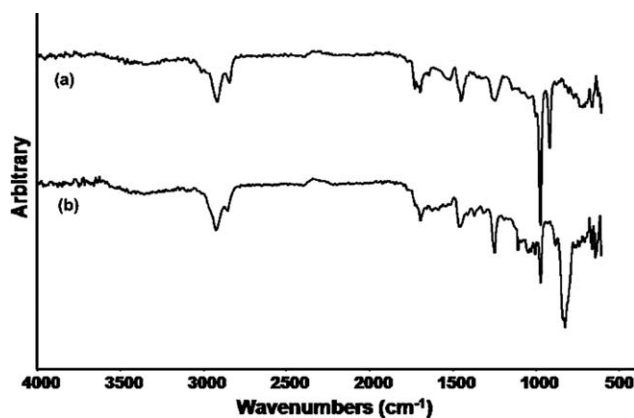
specimens were removed, and swollen weight ( $W_s$ ) was determined, after wiping off the liquid adhered to the surface.  $W_i$  is initial weight of sample. The swelling value ( $S_v$ ) is given by  $S_v = (W_s/W_i) - 1$ . The swelling values of FPDS-g-HTPB-based polyurethane networks in THF, *N*-methyl-2-pyrrolidone, and *N,N'*-dimethylformamide are given in Table I.

## RESULTS AND DISCUSSION

### Structural analysis

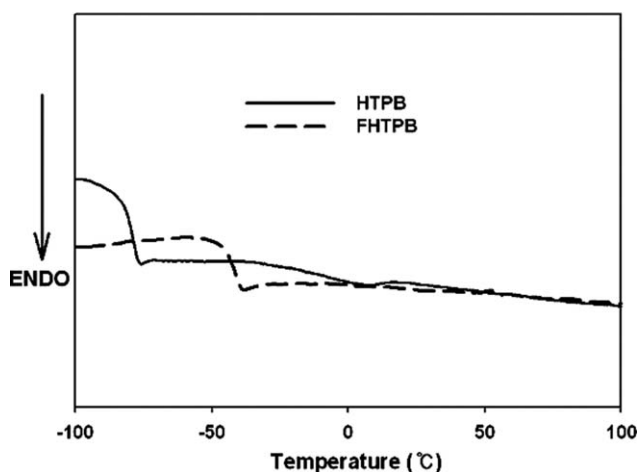
The reaction scheme for the hydrosilylation of 2-(ferrocenylpropyl)dimethylsilane with hydroxy-termi-

nated polybutadiene is shown in Scheme 1. The end point of the reaction was characterized by FTIR and was confirmed by the disappearance of the 1,2-addition ( $-\text{C}=\text{C}$ ) peak of HTPB and the silane group ( $\text{Si}-\text{H}$ ) peak of FPDS. The IR spectra of HTPB, FPDS, and FPDS-g-HTPB are shown in Figure 1(a-c). In Figure 1(a,b), the bending vibration for the 1,2-addition ( $-\text{C}=\text{C}$ ) of HTPB at around  $910\text{ cm}^{-1}$  and the stretching vibration for  $\text{Si}-\text{H}$  of FPDS at around  $2100\text{ cm}^{-1}$  appeared, but the peaks at  $910\text{ cm}^{-1}$  and  $2100\text{ cm}^{-1}$  disappeared in Figure 1(c). Stretching vibration for Cp ring ( $-\text{C}=\text{C}$ ) of FPDS at  $3090\text{ cm}^{-1}$  appeared, and stretching vibration for  $-\text{C}=\text{C}$  of HTPB at  $3070\text{ cm}^{-1}$

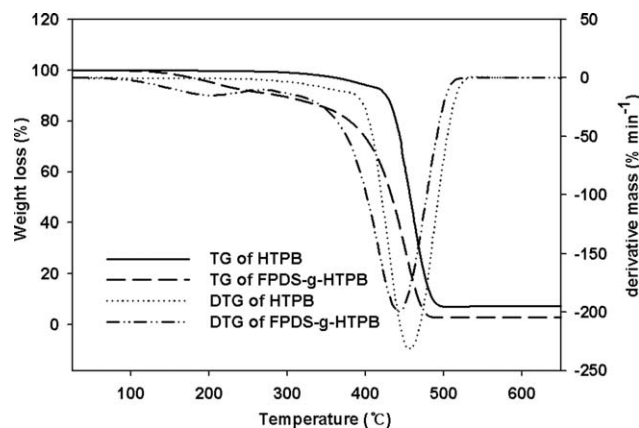


**Figure 4** IR spectra of (a) HTPB-based polyurethane networks and (b) 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB-based polyurethane networks.

disappeared in Figure 1(c). The  $^1\text{H-NMR}$  spectra of HTPB and FPDS-g-HTPB recorded at 500 MHz are shown in Figure 2. In the  $^1\text{H-NMR}$  spectrum of HTPB, the absorption peaks at 1.2–1.6 ppm and 2.0–2.4 ppm were assigned to the 1,2- $\text{CH}_2$  proton and 1,4- $\text{CH}_2$  proton, those at 3.4–4.1 ppm were assigned to the hydroxyl group (geraniol type, hexane-2-1 type, and vinyl type), and those at 4.8–5.2, 5.4, and 5.5–5.8 ppm were assigned to 1,4-(cis and trans) proton and 1,2-vinyl proton. In the  $^1\text{H-NMR}$  spectrum of 2-(ferrocenyl propyl) dimethylsilane, the absorption peak at 3.8 ppm was assigned to Si-H. In the  $^1\text{H-NMR}$  spectra of FPDS-g-HTPB, the absorption peak at 0.05, 0.4–0.9, 1.2, 2.0, 2.3, 4.0, and 5.4 ppm was assigned. The peaks at 3.8 and 4.8 ppm disappeared in FPDS-g-HTPB. The  $^{13}\text{C-NMR}$  spectra of HTPB and FPDS-g-HTPB recorded at 500 MHz are shown in Figure 3. In the  $^{13}\text{C-NMR}$  spectra of HTPB, the absorption peak at 25–28, 30–33, 35–39, and 44 ppm was assigned to the 1,2- $\text{CH}_2$  proton and the 1,4- $\text{CH}_2$  proton, and the peaks at 114, 127–132, 143 ppm were assigned to the



**Figure 5** DSC thermogram for (a) HTPB and (b) 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB.



**Figure 6** TG trace and DTA curve of 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB.

1,4-(cis and trans) proton and the 1,2-vinyl proton. In the  $^{13}\text{C-NMR}$  spectra of FPDS-g-HTPB, the absorption peaks were assigned. The peaks for 1,2-addition( $-\text{C}=\text{C}$ ) of HTPB at 114 and 143 ppm disappeared in FPDS-g-HTPB.<sup>15</sup>

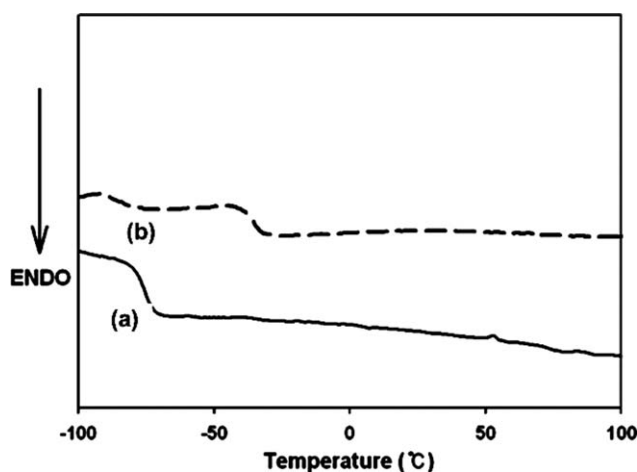
The reaction scheme for the polyurethane networks is shown in Scheme 2. The polyurethane networks were investigated using ATR-FTIR. The end point of the reaction was characterized by ATR-FTIR and confirmed by the disappearance of the isocyanate group ( $-\text{NCO}$ ) peak of HDI or the HDI trimer and hydroxyl group ( $-\text{OH}$ ) peak of HTPB prepolymer and the appearance of the amine group ( $-\text{NH}$ ) and carboxyl group ( $-\text{C}=\text{O}$ ) peaks of the polyurethane networks.

Figure 4(a,b) shows the ATR-FTIR result for the HTPB-prepolymer polyurethane networks. In the ATR-FTIR spectra of the HTPB prepolymer-based polyurethane networks, the stretching vibrations for the isocyanate group at  $2270\text{ cm}^{-1}$  and for the hydroxyl group at  $3400\text{ cm}^{-1}$  disappeared, while the stretching vibration for the amine group at  $3300\text{ cm}^{-1}$  and for the carboxyl group at  $1725\text{ cm}^{-1}$  appeared. The low sol fractions and the results of the ATR-FTIR analyses indicated that the amount of residue from the unreacted hydroxyl and isocyanate group was negligible.

**TABLE II**  
Thermal Property for HTPB and FPDS-g-HTPB

	$T_{1\%}$	$T_{10\%}$	$T_{50\%}$	$T_{90\%}$	$T_{\text{max}1}$	$T_{\text{max}2}$	$T_g$
HTPB	305°C	414°C	457°C	486°C	460°C	–	–76°C
FPDS-g-HTPB	140°C	248°C	433°C	467°C	195°C	440°C	–43°C

$T_{1\%}$  is the temperature at decomposition of 1% the sample;  $T_{10\%}$  is the temperature at decomposition of 10% the sample;  $T_{50\%}$  is the temperature at decomposition of 50% the sample;  $T_{90\%}$  is the temperature at decomposition of 90% the sample;  $T_{\text{max}1,2}$  is the D.T.G maximum peak temperature for the first, second decomposition stage.



**Figure 7** DSC thermogram for (a) HTPB-based polyurethane networks and (b) 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB-based polyurethane networks.

### Thermal properties

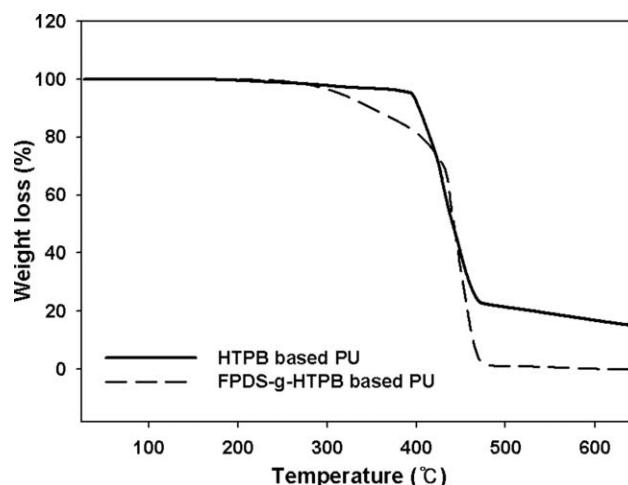
Figure 5 shows the DSC thermogram for HTPB and FPDS-*g*-HTPB. Thermal properties, including the glass transition temperature ( $T_g$ ), were determined from DSC. The value of  $T_g$  for FPDS-*g*-HTPB was  $-41^\circ\text{C}$ , which is about  $35^\circ\text{C}$  higher than that for HTPB. Gautier et al.<sup>16</sup> reported that  $T_g$  of HTPB shifts toward higher temperatures with the addition of (4-butylferrocenyl) dimethylsilane. Figure 6 shows the TG traces and DTA for HTPB and FPDS-*g*-HTPB. The decomposition temperature of HTPB was  $460^\circ\text{C}$ . The decomposition temperature of FPDS-*g*-HTPB was  $195^\circ\text{C}$  and  $440^\circ\text{C}$ . In FPDS-*g*-HTPB, the first-stage decomposition was due to the burning rate catalyst, and the second was attributed to the HTPB. The decomposition temperature of the HTPB was lower than that of the FPDS-*g*-HTPB due to ferrocene-based burning rate catalyst. Table II gives a summary of thermal properties for HTPB and FPDS-*g*-HTPB.

Figure 7 shows the DSC thermocurve of the HTPB prepolymer-based polyurethane networks at  $10^\circ\text{C}/\text{min}$ . The value of  $T_g$  for the soft segment of the HTPB-based polyurethane networks and the FPDS-*g*-HTPB-based polyurethane networks was  $-76^\circ\text{C}$  and  $-43^\circ\text{C}$ , respectively. The value of  $T_g$  for the polyurethane networks was not influenced by diisocyanate and isocyanate trimer, but was influenced by polyol (HTPB and FPDS-*g*-HTPB). It was observed that the FPDS-*g*-HTPB-based polyurethane networks showed higher  $T_g$  value than the HTPB-based polyurethane networks. This is because the linear structure of HTPB provides greater flexibility and mobility to the chain, resulting in a lowering of  $T_g$ , whereas the pendant ferrocenyl silane groups in FPDS-*g*-HTPB restrict the movement of the chain. TGA was carried out on the polyurethane networks

in air to investigate the thermal stability, decomposition temperature, and decomposition mechanism. The thermal analysis of the HTPB-based polyurethane networks is shown in Figure 8. The TGA thermogram of the HTPB-based polyurethane networks displays two distinct regions of weight loss. The first decomposition was complete at around  $340^\circ\text{C}$ , and the second decomposition was complete at around  $440^\circ\text{C}$ . The first-stage decomposition was due to the urethane linkage, and the second was attributed to the HTPB. The TGA thermogram of the FPDS-*g*-HTPB-based polyurethane networks displays three distinct regions of weight loss. The first decomposition was complete at around  $220^\circ\text{C}$ , the second was complete at around  $400^\circ\text{C}$ , and the third was complete at around  $440^\circ\text{C}$ .

### CONCLUSIONS

FPDS was grafted onto HTPB by hydrosilylation. Its thermal properties, including glass transition temperature ( $T_g$ ), were determined from DSC. The value of  $T_g$  for the FPDS-*g*-HTPB was  $-41^\circ\text{C}$ , which was about  $35^\circ\text{C}$  higher than that of HTPB. HTPB prepolymer-based polyurethane networks were prepared by one-step and casting processes. FPDS-*g*-HTPB-based polyurethane networks showed higher  $T_g$  value than the HTPB-based polyurethane networks, because the linear structure of HTPB provides greater flexibility and mobility to the chain, resulting in the lowering of  $T_g$ , whereas the pendant ferrocenyl silane groups in FPDS-*g*-HTPB restrict the movement of the chain. The FPDS-*g*-HTPB-based polyurethane networks were decomposed faster than the HTPB-based polyurethane networks, due to the use of ferrocene as a burning rate catalyst.



**Figure 8** TG trace of (a) HTPB-based polyurethane networks and (b) 2-(ferrocenylpropyl)dimethylsilane-grafted HTPB-based polyurethane networks.



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