

# Synthesis and Characterization of 3-(2,3-Dihydroxypropoxy)propyl-Terminated Polydimethylsiloxanes

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**ABSTRACT:** 3-(2,3-Dihydroxypropoxy)propyl-terminated polydimethylsiloxanes (DHT-PDMS) samples were prepared through the copolymerization of 1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane ( $D_4$ ) and 1,3-bis[3-(2,3-dihydroxypropoxy)propyl]-1,1,3,3-tetramethyldisiloxane by acid-catalyzed equilibration. Their structures were characterized with IR and  $^1\text{H-NMR}$  spectra. The molecular weights were determined with gel permeation chromatography and  $^1\text{H-NMR}$  spectra, respectively. Differential scanning calorimetry and thermogravimetric analysis were used to investigate the thermodynamic properties and thermal degrada-

tion of DHT-PDMS. The effects of various factors on the synthesis of DHT-PDMS were also examined. However, the preparation of DHT-PDMS through the base-catalyzed equilibrium copolymerization of  $D_4$  and 1,3-bis[3-(2,3-epoxypropoxy)propyl]-1,1,3,3-tetramethyldisiloxane, followed by the hydrolysis of the epoxy groups, was unsuccessful. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 110–115, 2004

**Key words:** cationic polymerization; differential scanning calorimetry (DSC); polysiloxanes; thermogravimetric analysis (TGA)

## INTRODUCTION

Polysiloxanes possess a variety of unique and superior properties, such as high- and low-temperature resistance, aging resistance, corrosion resistance, climate resistance, electric characteristics, good UV stability, physiological inertness, biocompatibility, and flexibility. The copolymerization of polysiloxanes and organic polymers (e.g., graft or block) can endow the organic polymers with the excellent properties of the polysiloxanes so that new polymer materials with special properties can be obtained. Of course, the copolymerization of polysiloxanes and organic polymers can also endow the polysiloxanes with the good properties of the organic polymers; in other words, the organic polymers and polysiloxanes can modify each other through their copolymerization. Akiyama et al.<sup>1</sup> found that polysiloxane–polyimide copolymers were good, oxygen-rich membrane materials with heat resistance and gas permeability. Polysiloxanes/polyethers exhibit good antistatic ability, antifoaming ability, releasing properties from adhesive surfaces and/or mold surfaces, wettability, and lubricity and have been widely used as surfactants.<sup>2–4</sup> The mechanical

strength and solvent (oil) resistance of polysiloxanes can be improved by their copolymerization with methyl methacrylate.<sup>5</sup> Polysiloxanes/polyurethanes can be used as selective gas permeation membranes,<sup>6</sup> soil stabilizers,<sup>7</sup> copolymerization activating agents,<sup>8</sup> sealing materials,<sup>9</sup> non-water-solvent dispersing agents,<sup>10</sup> paper finishing agents,<sup>11</sup> optical materials,<sup>12</sup> and so forth and show great potential in many fields. In the copolymerization of organic polymers and polysiloxanes, carbofunctionalized polysiloxanes (also called modified silicone oils) play an important role.

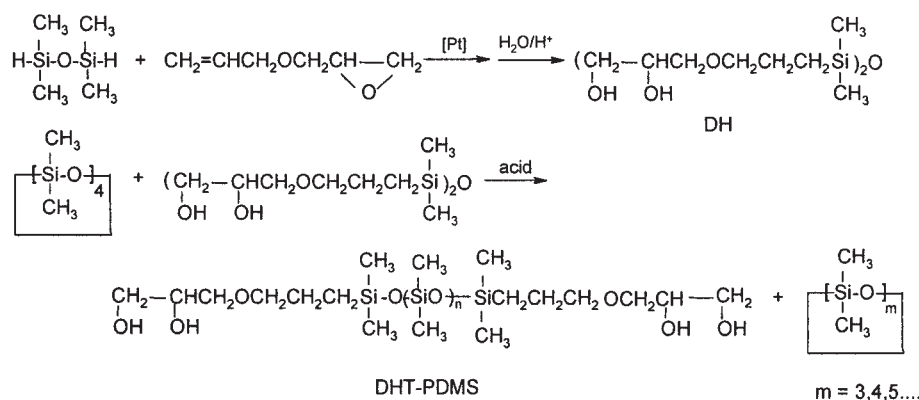
Modified silicone oils are polysiloxanes formed by the substitution of carbofunctional groups for partial methyl groups of polydimethylsiloxanes.<sup>13(a)</sup> The carbofunctional groups may be hydroxyalkyl, aminoalkyl, carboxylalkyl, epoxy, or mercaptoalkyl groups. They may be in the ends or on the chains pendant to the sides of the polysiloxane molecular chains. The intermodification of polysiloxanes and organic polymers can be performed with the aid of the reaction activity of the carbofunctional groups.

Hydroxyalkylated polysiloxanes are important modified silicone oils. There have been many research reports on their use in the improvement of organic polymers.<sup>13(b)</sup> However, studies on dihydroxy-terminated polysiloxanes (tetrahydroxyl-functional polysiloxane oligomers), particularly with respect to their synthesis and characterization, have been rare. Riffle and Yilgor<sup>14</sup> prepared the tetrahydroxyl-functional polysiloxane oligomers which were crosslinked with isocyanates to form polysiloxane networks having im-

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Scheme 1 Synthetic route of DHT-PDMS.

proved mechanical strength. Buchholz and Mülhaupt<sup>15</sup> synthesized low-molecular-weight tetrahydroxyl-functional polysiloxanes through the addition of bis(hydridosilane)-terminated polysiloxanes to glyceryl-1-*O*-allylether in the presence of a platinum catalyst and obtained polysiloxane-polycaprolactone block copolymers. Yilgor and Yilgor<sup>16</sup> investigated the thermal stabilities of  $\alpha,\omega$ -hydroxypropyl-,  $\alpha,\omega$ -hydroxybutyl-,  $\alpha,\omega$ -hydroxypentyl-, and  $\alpha,\omega$ -hydroxyhexyl-terminated polydimethylsiloxane oligomers and found that the thermal stabilities of the end groups were directly related to the structures of the hydrocarbon bridges between the functional groups and silicon atom. For modification, the dihydroxy-terminated polysiloxanes are perhaps preferable to hydroxyalkyl-terminated polysiloxanes for providing polysiloxane copolymers retaining the desirable properties of crosslinked polysiloxane elastomers with improved mechanical properties. Understanding the synthesis and characterization of dihydroxy-terminated polysiloxanes as well as their properties is a matter of primary importance for studying and using them in the modification of organic polymers. In this work, high-molecular-weight 3-(2,3-dihydroxypropoxy)propyl-terminated polydimethylsiloxane (DHT-PDMS) samples were prepared through the copolymerization of 1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane ( $D_4$ ) and 1,3-bis[3-(2,3-dihydroxypropoxy)propyl]-1,1,3,3-tetramethyldisiloxane (DH) by acid-catalyzed equilibration (Scheme 1). Their structures were characterized, and their properties were investigated. It was expected to promote the synthesis and application of dihydroxy-terminated polysiloxanes.

## EXPERIMENTAL

### Materials

$D_4$  and allyl glycidyl ether (AEP) were industrial chemicals and were distilled before use. 1,1,3,3-Tetramethyldisiloxane ( $M^H M^H$ ; 97%) and trifluoromethane sulfonic acid (TFMSA; 98%) were from Acros Organics

(Fairlawn, New Jersey). Acetone, sodium hydroxide, concentrated hydrochloric acid, anhydrous magnesium sulfate, dichloromethane, and toluene were chemical reagents and were used without further purification. A 1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum catalyst (Pt-cat) and tetramethylammonium silanolate (TMAS) were prepared according to refs. 17(a) and 17(b), respectively. Activated clay (0.1N NaOH) was acquired from Zhoucun Activated Clay Plant (Zhoucun, China).

### General data

The  $^1\text{H-NMR}$  spectra were recorded on a JEOL FX-300Q instrument (Tokyo, Japan) in  $\text{CDCl}_3$ . IR spectra were obtained on a Nicolet FI/IR 20SX spectrometer (Tokyo, Japan). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out on DSC-SP and TGA-2 thermogravimetric instruments, respectively, manufactured by Perkin-Elmer Corp. (Piscataway, New Jersey) under an atmosphere of  $\text{N}_2$ . The epoxy values of the siloxanes or polysiloxanes containing epoxy groups were determined with a method described in the literature.<sup>18</sup> Gel permeation chromatography (GPC) analyses were performed on a Waters 515 instrument (Milford, Massachusetts) with polystyrene as a standard and toluene for elution at 25°C. The number-average molecular weights ( $M_n$ 's) were determined from the GPC analyses and  $^1\text{H-NMR}$  spectra.

### Preparation of 1,3-bis[3-(2,3-epoxypropoxy)propyl]-1,1,3,3-tetramethyldisiloxane (DOTMDS)

As previously reported in the literature,<sup>19</sup> with AEP (40.5 g, 0.355 mol),  $M^H M^H$  (20.3 g, 0.151 mol), Pt-cat (0.1 g), and toluene (20 mL), DOTMDS was obtained as a colorless liquid.

Yield: 42.6 g (78.0%). bp: 190–193°C at 1 mmHg.  $n_D^{25}$ : 1.4508. Epoxy value: 0.5478 mol/100 g (calcd.: 0.5518 mol/100 g).

TABLE I  
Experimental Results for the Preparation and  $M_n$  and  $d$  Values of DHT-PDMS

Sample	D <sub>4</sub> (g)	DH (g)	A-clay (g) <sup>a</sup>	TFMSA (μL)	Yield (%)	M <sub>n</sub> , NMR (g/mol)	M <sub>n</sub> , GPC (g/mol)	$d$
1	20.00	0.50		6.0	70.0	8,200		
2	22.50	0.60		6.0	77.6	9,600		
3	28.65	1.57	1.50		82.8	15,000	17,540	1.58
4	24.60	0.92	1.50		85.6	20,800	24,960	1.45
5	25.50	0.70	1.50		90.5	23,500	27,830	1.51
6	25.00	0.35		4.0	80.0	26,200		
7	26.55	0.49	1.50		90.2	27,900	31,200	1.47
8	25.25	0.39	1.50		90.3	31,900	34,650	1.48
9	25.00	0.30		4.0	75.2	39,500		

<sup>a</sup> Activated clay.

### Preparation of DH

A 500-mL, round-bottom flask equipped with an N<sub>2</sub> purge, a reflux condenser, a thermometer, and an agitator was charged with 27.5 g (0.076 mol) of DOTMDS, 55.0 g (3.056 mol) of water, and 150 mL of acetone. After 1.0 g of a 10% aqueous sodium hydroxide solution was added, the reaction mixture was heated to reflux under N<sub>2</sub>, and the temperature was maintained for 10 h. Concentrated hydrochloric acid (0.3 mL) was then added, and the resulting mixture was refluxed for 0.5 h more. Acetone and water were vacuum-removed, and the product was extracted with 200 mL of dichloromethane. The extract was washed with water, dried over anhydrous magnesium sulfate overnight, and then filtered. The removal of dichloromethane afforded 28.2 g (93.2% yield) of DH as a light yellow liquid.

<sup>1</sup>H-NMR (δ, ppm): 0.01 (s, 12H), 0.43–0.63 (t, 4H), 1.45–1.75 (m, 4H), 3.46–3.70 (m, 14H), 3.80–4.05 (m, 4H). IR (cm<sup>-1</sup>): 790, 1260, 1409, 2963 (Si—CH<sub>3</sub>), 1024–1092 (Si—O—Si), 2905 (CH<sub>2</sub>), 3400 (OH).

### Preparation of DHT-PDMS by acid-catalyzed equilibration

Activated clay as a catalyst

A 100-mL, four-necked, round-bottom flask equipped with an N<sub>2</sub> purge, a reflux condenser, a thermometer, and an agitator was charged with 24.4 g (0.082 mol) of D<sub>4</sub> and 1.2 g of activated clay. The reaction mixture was heated to 90°C under N<sub>2</sub>, and the temperature was maintained for 0.5 h. Then, 0.6 g (1.51 mmol) of DH was added slowly dropwise. The equilibration reaction was kept at 90°C for 6 h. The resulting mixture was dissolved in 200 mL of toluene and then was filtered to remove the catalyst. The filtrate was washed with water to neutrality and then dried over anhydrous magnesium sulfate. After the removal of toluene and low-boiling-point compounds at 145°C and 10 mmHg, 20.5 g of DHT-PDMS was obtained as a colorless, transparent, and viscous liquid.

Yield: 82.0%.  $M_n$ : 15,000. <sup>1</sup>H-NMR (δ, ppm): 0.01 (s, Si—CH<sub>3</sub>), 0.43–0.63 (m, Si—CH<sub>2</sub>), 1.45–1.75 (m, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.37–3.70 (m, CH—OH, CH<sub>2</sub>—OH, CH<sub>2</sub>OCH<sub>2</sub>), 3.80–4.05 (m, OH). IR (cm<sup>-1</sup>): 790, 1260, 1409, 2963 (Si—CH<sub>3</sub>), 1024–1092 (Si—O—Si), 2905 (CH<sub>2</sub>), 3400 (OH).

A series of DHT-PDMS samples with various molecular weights were obtained through changes in the ratios of the reactants (see Table I).

TFMSA as a catalyst

A 100-mL, four-necked, round-bottom flask equipped with an N<sub>2</sub> purge, a reflux condenser, a thermometer, and an agitator was charged with 20.0 g (59.2 mmol) of D<sub>4</sub> and 0.5 g (1.26 mmol) of DH and was heated to 80–90°C. Then, 6.0 μL of TFMSA was added. The mixture was heated for 24 h at 80–90°C. The resulting mixture was neutralized with 1N potassium hydroxide in methanol under stirring at 70 ± 5°C for 10 min. The unreacted and low-boiling-point compounds were removed from the reaction mixture at 1 mmHg and up to 150°C, and 14.4 g of DHT-PDMS was obtained as a colorless, viscous liquid. The yield was 70.0%, and  $M_n$  from NMR was 8200. The spectra were similar to those taken when activated clay was used as a catalyst.

### Preparation of DHT-PDMS by base-catalyzed equilibration

As previously reported in the literature,<sup>18</sup> 29.6 g (0.1 mol) of D<sub>4</sub> and 0.5 g of TMAS were placed in a 100-mL, four-necked, round-bottom flask equipped with an N<sub>2</sub> purge, a reflux condenser, a thermometer, and an agitator. The mixture was dewatered at 40°C and 50 mmHg for 0.5 h and then heated to 80–85°C to react for 0.5 h. To the mixture was added dropwise 0.47 g (1.3 mmol) of DOTMDS. The resulting mixture was stirred under N<sub>2</sub> at 82 ± 2°C for 8 h and then heated to 140°C for 0.5 h to decompose the catalyst. After the final mixture was vacuum-distilled at 140°C



Scheme 2 Synthetic route of polysiloxane oligomers.

to remove low-boilingpoint compounds, 25.9 g of epoxy-terminated polydimethylsiloxane (EP-PDMS) was obtained as a colorless, viscous liquid.

EP-PDMS was placed in a 100-mL, four-necked, round-bottom flask, and 1.5 mL of 0.5% dilute  $\text{H}_2\text{SO}_4$  and 25 mL of toluene or acetone were added. The reaction mixture was heated to reflux for 20 h. After cooling to room temperature, the resulting mixture was washed with water to neutrality and then dried over anhydrous magnesium sulfate. After low-boiling-point compounds were vacuum-stripped, 24.8 g of the product was obtained. The  $^1\text{H-NMR}$  and IR data showed that the product was EP-PDMS. Therefore, the epoxy groups of EP-PDMS were not hydrolyzed under the conditions used.

## RESULTS AND DISCUSSION

### Preparation of DHT-PDMS

Generally, polysiloxane oligomers can be prepared by acid- or base-catalyzed equilibration reactions of cyclic polysiloxanes and disiloxanes as chain-terminating agents, as shown in Scheme 2. *R* represents the same or different organic groups; *n* is 3 or 4; and *p* is 3, 4, 5, and so forth. *X* represents hydrogen, alkyl, or carbofunctional groups. When we prepared DHT-PDMS, we investigated two different methods.

### Preparation of DHT-PDMS by base-catalyzed equilibration

Because the hydroxyl groups of DH react with basic catalysts,<sup>20</sup> we tried to prepare DHT-PDMS by base-catalyzed equilibration reactions of  $\text{D}_4$  and DOTMDS as a chain-terminating agent with TMAS as a catalyst,<sup>21</sup> followed by hydrolysis ring opening of the epoxy groups of the resulting polysiloxanes (EP-PDMS).

The base-catalyzed equilibration of cyclosiloxane monomers is one of the most convenient and common methods for preparing polysiloxanes, especially polysiloxanes with high molecular weights. However, in the preparation of polysiloxanes containing epoxy groups, the reactivity of the epoxy groups must be considered because the epoxy rings are easily opened under strongly acidic or basic conditions. Although the amount of TMAS used was not so large that the epoxy rings would be destroyed,  $\text{D}_4$  would not ring-open to polymerize when DOTMDS was added in the beginning of the reaction. So  $\text{D}_4$  was first prepolymerized, DOTMDS was added dropwise to equilibrate,

and EP-PDMS was obtained successfully in good yields. It was demonstrated by analysis that the experiments agreed well with the expected results.

Si—O bonds of polysiloxanes are stable under weakly acidic conditions, and the epoxy groups are ring-opened more easily under acidic conditions than basic ones. Therefore, we chose the acidic hydrolysis of EP-PDMS in toluene–water or acetone–water solutions to prepare DHT-PDMS. Unfortunately, EP-PDMS was intact after the reaction, and the expected product, DHT-PDMS, was not obtained. This may have happened because the epoxy groups of EP-PDMS are enveloped in the polysiloxane chains and water molecules consequently have difficulty reaching them. This suggests that an attempt to prepare DHT-PDMS by a base-catalyzed equilibrium copolymerization of  $\text{D}_4$  and DOTMDS, followed by the hydrolysis of epoxy groups (i.e., via EP-PDMS intermediates), would be unsuccessful.

### Preparation of DHT-PDMS by acid-catalyzed equilibration

The acid-catalyzed equilibration of cyclosiloxanes can be carried out in concentrated sulfuric acid, alkyl or arylsulfonic acid, chlorosulfonic acid, aluminum sulfate, inorganic acids, organic acids, Lewis acids, or activated clay as a catalyst. For the convenience of the workup, activated clay and TFMSA were used in these experiments.

For the preparation of methylsilicone oils,  $\text{D}_4$  and 1,1,1,3,3,3-hexamethyldisiloxane as a chain-terminating agent are often equilibrated together. However, if  $\text{D}_4$  and DH were added together for the preparation of DHT-PDMS with activated clay as a catalyst, the equilibration reaction would not occur, perhaps because DH would react with the catalyst more easily than  $\text{D}_4$  and the activity of the activated centers formed by the reaction of DH with the catalyst would be low so that the ring opening of  $\text{D}_4$  would be difficult. Therefore,  $\text{D}_4$  was first prepolymerized by the catalysis of activated clay for a period of time, and then DH was dropwise added slowly to the reaction mixture to equilibrate. Thus, the expected products could be obtained. The experiments showed that after equilibration for 6 h, the reaction yield reached a maximum of about 90%. When the reaction time was further extended, the yield no longer increased. Because the resulting mixture was viscous, it had to be dissolved in toluene for the removal of the activated clay. In addition, no back-biting reactions causing cyclization of the polysiloxane backbones by the terminated hydroxyl groups were found in equilibration. Compared with the base-catalyzed equilibration reactions, this method is a good one for preparing DH-terminated polysiloxane oligomers with low molecular weights. However, using TFMSA as a catalyst would be better because of the small amount used and

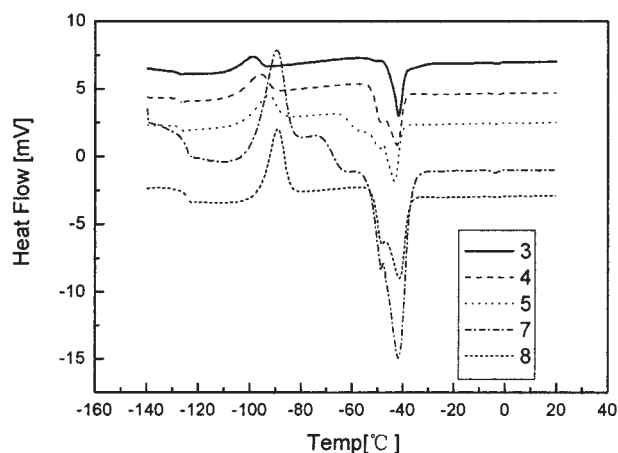


Figure 1 DSC curves of samples 3, 4, 5, 7, and 8.

the easy workup. At the same time, TFMSA is more suitable for preparing high-molecular-weight DHT-PDMS.

#### Determination of $M_n$ of DHT-PDMS

Each DHT-PDMS molecule has two hydroxyl groups on each terminal group, that is, four hydroxyl groups. Theoretically, the  $M_n$  value of DHT-PDMS can be obtained by the determination of its hydroxyl group content. The periodate oxygenation method is a common one for determining adjacent dihydroxyl groups.<sup>22</sup> However, because this method uses water as a solvent in which DHT-PDMS does not dissolve, there exists a large measurement error in its use for determining the hydroxyl group content of DHT-PDMS. Using an esterification method with phthalic anhydride and pyridine as a solvent can successfully determine the hydroxyl values of samples with single or intervallic hydroxyl groups in each molecule. However, because of the large steric hindrance and low activity of adjacent dihydroxyl groups, the determination of the hydroxyl groups of DHT-PDMS with this method did not succeed, although the esterification of the adjacent dihydroxyl groups could be completed in a long time according to the literature.<sup>23</sup> The absolute errors caused in this way were all greater than 10%. Therefore, we chose GPC and proton ratios from  $^1\text{H-NMR}$  spectra to determine the  $M_n$  values of DHT-PDMS and the corresponding polydispersity index ( $d$ ). The results are collected in Table I. The  $d$  values of DHT-PDMS were between 1.45 and 1.59; therefore, DHT-PDMS with a narrow dispersion of molecular weights could be obtained by the acid-catalyzed equilibration of cyclosiloxanes and DH.

#### DSC analysis of DHT-PDMS

DSC analysis is a good means of studying chain and aggregated state structures of polymers and an impor-

tant method of investigating the relationship between the structures and properties of polymers by molecular motion.

Studies on the molecular motion of methyl-, hydroxy-, and hydroxypropyl-terminated polydimethylsiloxanes can be found in many articles.<sup>24–27</sup> However, to our knowledge, no reports on the thermodynamic properties of DHT-PDMS have been made. Therefore, we carried out DSC analyses of several DHT-PDMS samples in this work. The results are shown in Figure 1 and Table II. For comparison, the DSC analyses of methyl-terminated polydimethylsiloxane (PDMS),  $\alpha,\omega$ -dihydroxypolydimethylsiloxane (107 gum), and  $\alpha,\omega$ -dihydroxypropyl polydimethylsiloxane (HPPS) are also given in Table II.

The analytical results in Table II show that the glass-transition temperature ( $T_g$ ) of DHT-PDMS gradually rises with increasing  $M_n$  and this agrees with general laws, although the change is small. The hydrogen bonds from the two hydroxy groups on each terminal group reduce the flexibility of the molecular chains of DHT-PDMS; meanwhile, the large steric hindrance of the two hydroxy groups hinders intrarotation of single bonds in the polymer chains, thus reducing the segment motion of the polysiloxane main chains. When  $M_n$  of DHT-PDMS is large enough, its  $T_g$  will be the same as that of high-molecular-weight PDMS because of the small proportion of the hydroxyl groups in the whole molecule. Table II also shows that  $T_g$  of DHT-PDMS is slightly lower than that of HPPS or 107 gum with a close molecular weight.

For the same kinds of polymers,  $M_n$  has an obvious effect on the crystallization rates. To reach the same crystallinity, high-molecular-weight polymers will require a longer heat-treatment time than those with low molecular weights. This is because the flexibility of high-molecular-weight polymers is poorer than that of low-molecular-weight polymers and because barriers of the former, preventing molecular chains from diffusing into crystallization phases, are higher than those of the latter. The crystallization temperature ( $T_c$ ) of DHT-PDMS rises with increasing  $M_n$  (see Table II).

The melting temperature ( $T_m$ ) of polymers is related to their  $T_c$ . The lower  $T_c$  is, the lower  $T_m$  is and the

TABLE II  
DSC Analyses of DHT-PDMS, PDMS,  
HPPS, and 107 Gum

Sample	$M_n$	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)
3	15,000	-128.1	-98.8	-41.6
4	20,800	-128.1	-97.5	-41.9
5	23,500	-127.8	-97.9	-42.6
7	27,900	-127.6	-96.5	-40.6
8	31,900	-127.4	-93.3	-40.0
PDMS	$1.2 \times 10^5$	-126.1		
HPPS	28,800	-126.4	-89.4	-43.2
107 gum	25,000	-127.3	-93.1	-39.9

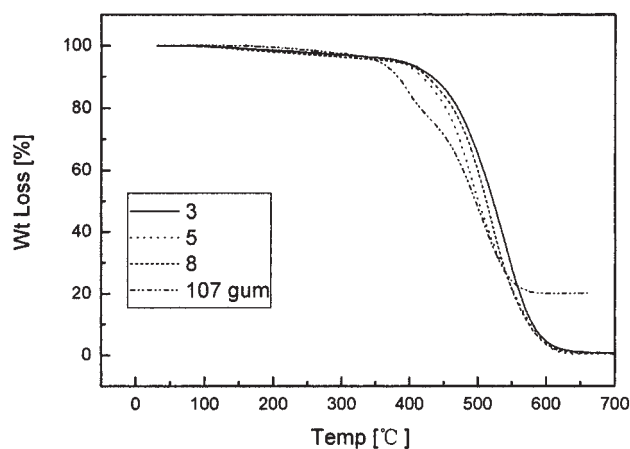


Figure 2 TGA curves of samples 3, 5, and 8 and 107 gum.

wider the  $T_m$  range is because crystals formed at low temperatures are imperfect and inhomogeneous on account of the poor activity of the molecular chains. Naturally, these crystals will melt at low temperatures and over a wide range. Conversely, crystals formed at high temperatures will have high  $T_m$ 's and narrow melting ranges. That is the case for DHT-PDMS. As  $M_n$  of DHT-PDMS increases,  $T_m$  rises. When  $M_n$  of DHT-PDMS is greater than 20,000, two melting peaks occur on DSC curves (see Fig. 1). This is because with increasing  $M_n$ , the molecular chains will twine, and this leads to the formation of microcrystals under supercooling. These microcrystals are still existent above  $T_c$ , but they melt early at  $T_m$  to cause a small melting peak.

### TGA of DHT-PDMS

TGA curves of some DHT-PDMS samples are shown in Figure 2. For comparison, a TGA curve of 107 gum is also presented. In comparison with 107 gum, DHT-PDMS has higher thermal stability. The weight loss of DHT-PDMS at 400°C is less than 7%, whereas that of 107 gum is almost 7% at 360°C and more than 15% at 400°C. As the weight loss here is caused by the degradation of polysiloxane chains, it suggests that end Si—OH groups of polysiloxane cause the degradation of the polysiloxane chains more easily than end Si—C<sub>n</sub>—OH groups [Si—CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—O—CH<sub>2</sub>CH(OH)—CH<sub>2</sub>OH]. The degradation of DHT-PDMS of various molecular weights begins around 380°C, and this indicates that the degradation of DHT-PDMS occurs first at the ends of molecular chains and is unrelated to its  $M_n$ . However,  $M_n$  of DHT-PDMS influences the maximum degradation rate. The higher  $M_n$  of DHT-PDMS is the higher the temperature is corresponding to the maximum degradation rate. This is because when  $M_n$  of DHT-PDMS is low, the proportion of end hydroxy groups is large. Therefore, the

degradation accelerates, and the temperature corresponding to the maximum degradation rate is low.

### CONCLUSIONS

DHT-PDMS can be prepared through the copolymerization of D<sub>4</sub> and DH by acid-catalyzed equilibration with activated clay or TFMSA as a catalyst. The molecular weight can be determined by GPC or <sup>1</sup>H-NMR spectroscopy. DSC results show that  $T_g$ ,  $T_c$ , and  $T_m$  of DHT-PDMS rise with increasing  $M_n$ . TGA shows that the weight loss of DHT-PDMS at 400°C is less than 7%. DHT-PDMS has high thermal stability. The preparation of DHT-PDMS by the base-catalyzed equilibrium copolymerization of D<sub>4</sub> and DOTMDS, followed by the hydrolysis of epoxy groups, was unsuccessful.

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