

# Thermooxidative Degradation Behavior of Poly(silphenylene-siloxane)s

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**ABSTRACT:** Copolymers of poly(silphenylene-siloxane) with dimethylsiloxane and diphenylsiloxane with various end groups were synthesized through an Si-H/Si-OR polycondensation process. The thermooxidative degradation behaviors of the copolymers were investigated by thermogravimetric analysis and IR spectrometry techniques. All of the polymers were characterized by a two-step mass loss. The first one, which peaked at 510–545°C in differential thermogravimetric curves, was mostly caused by the main-chain depolymerization, whereas the second one, which reached its maximum around 650°C, was caused by side-group oxidation and

Si-C bond scission. The main-chain depolymerization occurred over a temperature range of some 470–580°C, whereas Si-C bond scission and side-group oxidation occurred over a temperature range of about 585°C to above 720°C. The incorporation of phenyl groups in the end groups greatly retarded the temperature for the degradation onset of the main chain to 120°C higher. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 926–933, 2010

**Key words:** degradation; elastomers; high performance polymers; high temperature materials; polysiloxanes

## INTRODUCTION

Polymers containing halogens, nitrogen, or phosphorous, such as fluorocarbon polymers, polyimide, and polyphosphazenes<sup>1</sup> are widely used as heat-resistant or fire-retardant polymers. However, the drawback of these materials is the emission of toxic and corrosive gasses upon combustion. Poly(silarylene-siloxane)s are known as one class of harmless high-temperature elastomers. The incorporation of silarylene units in the polysiloxane backbone significantly enhances its thermal stability under oxidative and inert atmospheres.<sup>2</sup> Poly(silarylene-siloxane) is generally prepared by the polycondensation of difunctional organosilanes or oligosiloxanes, such as the dehydration of 1,4-bis(hydroxydimethylsilyl)benzene and 1,3-bis(hydroxydimethylsilyl)benzene<sup>3</sup> or the polycondensation of 1,4-bis(hydroxydimethylsilyl)benzene and bis(dimethylamino)-,<sup>4–7</sup> bisureido-,<sup>8</sup> or dichlorodialkylsilanes.<sup>6,9</sup> The dehydrogenative coupling of organohydrosilanes with organosilanols or other compounds containing active hydrogens, such as water, is particularly convenient because of its high selectivity and easy removal of the byproduct,

hydrogen.<sup>10–16</sup> Silyl hydride/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, generally Ph<sub>3</sub>HSi/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or Et<sub>3</sub>SiH/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, is a useful system in organic chemistry.<sup>17–24</sup> The coupling reaction of silyl hydrides with alkoxysilanes catalyzed by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is a new and efficient method for the preparation of linear polysiloxanes with merits of high selectivity, low level of catalyst, and easy removal of the byproduct alkane.<sup>25,26</sup> Crosslinkable vinyl-substituted poly(silphenylene-siloxane) (PTMS) can also be synthesized through this process.<sup>27</sup>

Three different mechanisms have been proposed for the thermal degradation of polydimethylsiloxanes: (1) the unzipping mechanism for Si-OH terminated polymers, (2) the random main-chain-scission mechanism for trimethylsilyl (TMS)-terminated polymers, and (3) the externally catalyzed mechanism for polymers containing impurities.<sup>2</sup> Both organic substituents and end groups have effects on the thermal stability of polysiloxanes. The introduction of methylhydridosiloxy units in the polysiloxane backbone decreases their thermal stability in nitrogen and thermooxidative stability in air,<sup>28</sup> whereas phenyl substituents on silicon increase the thermal stability of polysiloxanes.<sup>2,29</sup> Vinyl end groups decrease the thermal stability and the amount of degradation residue of both polydimethylsiloxanes and polymethylhydridosiloxanes in an inert atmosphere.<sup>28</sup>

Dvornic et al.<sup>30</sup> investigated the thermal stability and degradation behavior of a series of exactly

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alternating silphenylene-siloxane polymers that contained methyl, vinyl, hydrido, 3,3,3-trifluoropropyl, and tridecafluoro-1,1,2,2-tetrahydrooctyl side groups or their combinations by dynamic and isothermogravimetric analyses in air and in nitrogen. A strong thermostabilizing effect by the vinyl side groups on the degradation behavior of these polymers was observed, which was also established by many other studies.<sup>31-33</sup> The hydrido and fluoroalkyl side groups reduced the overall polymer thermal stability in terms of the degradation onset temperature.

Grassie and Beatty<sup>34,35</sup> studied the thermal degradation behavior of poly(tetramethyl-*p*-silphenylene-siloxane) and a series of copolymers of varied compositions. Thermal volatilization analysis revealed that the predominantly linear products gave way to cyclics as the proportion of dimethylsiloxane (DMS) structures in the copolymers increased. At a lower degradation temperature, the formation of cyclic oligomers was ascribed to the intramolecular exchange reaction of Si-O bonds; at higher temperatures, linear oligomers with Si-H or Si-Ph end groups were detected, which indicated Si-C bond scission. Below the apparent degradation temperature, an alternating TMPS/DMS copolymer thermally arranged to a random copolymer by the intermolecular exchange of Si-O bonds; this took place at a lower temperature than the intramolecular exchanges.<sup>36</sup>

Although the effects of organic side groups on the thermal stability of the TMPS/DMS copolymers and the formation and structure of the volatile degradation products have been well studied, the effects of the end groups on the degradation behavior have not yet been investigated. We believe that the end groups of PTMS and its copolymers will affect their thermal degradation behavior. The aim of this study was to investigate the thermooxidative degradation behavior of PTMS copolymers and the effect of end groups on them.

## EXPERIMENTAL

### Materials

Toluene was refluxed upon sodium sand to blue with benzophenone as an indicator and then distilled; 1,4-bis(dimethylsilyl)benzene (BDSB) and dimethylphenylsilane (DMPS) were prepared under ultrasonic radiation according to a process described in our previous work.<sup>27</sup> B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (95%), trimethylmethoxysilane (TMMS; 97%), and diphenyldimethoxysilane (97%) were purchased from Aldrich (St. Louis, MO).

### Thermogravimetric (TG)/IR measurement

A TG/IR system, which combined a Netzsch TG 209 thermoanalyzer (Germany) and a Bruker Vector-22

Fourier transform infrared (FTIR) spectrometer (Germany), was used to perform the TG/IR analysis. Samples of 8.0–8.9 mg were heated from room temperature to 720°C at a heating rate of 10°C/min in air, and the air flow rate was 20 mL/min. The evolved gases were led to the Vector-22 FTIR spectrometer directly through a heated gas line to obtain three-dimensional FTIR spectra. The IR frequency range was 600–4500 cm<sup>-1</sup>. The IR scan rate was 12 scans/s, and the resolution was 4 cm<sup>-1</sup>.

### Preparation and nomenclature of the polymer

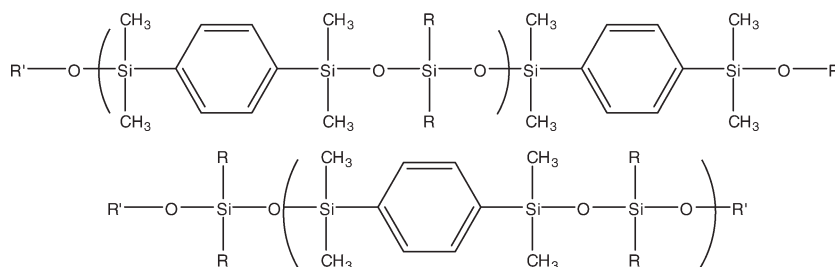
A dry, 50-mL, three-necked flask equipped with a magnetic stirrer, condenser (the outlet was connected to a dry tube filled with calcium chloride), thermometer, and rubber septum seal was evacuated and then filled back with nitrogen. The flask was charged with 10 mL of toluene, 1.40 g (7 mmol) of BDSB, and 4.0 mg (7.4 × 10<sup>-3</sup> mmol) of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. The flask was heated to 45°C, and 1.30 g of a mixture of diphenyldimethoxysilane and DMDMS (molar ratio = 1 : 1, total = 7 mmol) was added dropwise via a glass syringe over a period of 2 h. When the addition of the alkoxy silane was complete, the reaction mixture was stirred for an additional 2 h at 45°C to complete the polymerization, and the excess alkoxy silane was added to the reaction mixture until no bubbles were observed. An excess of BDSB or DMPS was added to the reaction mixture, and the mixture was stirred for another 1 h to end-cap the polymer to form TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-BDSB or TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMPS. The reaction mixture was poured into 100 mL of methanol. The solvent was decanted from the precipitated polymer, and the residue was dissolved in methylene chloride. The polymer solution was filtered through anhydrous CaSO<sub>4</sub>, the solvent was removed *in vacuo*, and the polymer was dried on the vacuum line to yield a colorless gumlike polymer. Gel permeation chromatography analysis indicated that the weight-average molecular weight was 12,088 g/mol and the weight-average molecular weight/number-average molecular weight was 1.91.

The synthesis procedures of TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-TMS and TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMMS were similar to that of TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-BDSB and TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMPS. The nomenclature and structure of the prepared polymers are listed in Table I.

## RESULTS AND DISCUSSION

Polysiloxanes show relatively complex mass loss processes in air compared to those in nitrogen; these correspond to three thermal degradation mechanisms: main-chain decomposition, Si-C scission, and side-chain oxidation. Main-chain decomposition

**TABLE I**  
Nomenclature and Structure of the Polymers



R=50% Me + 50% Ph

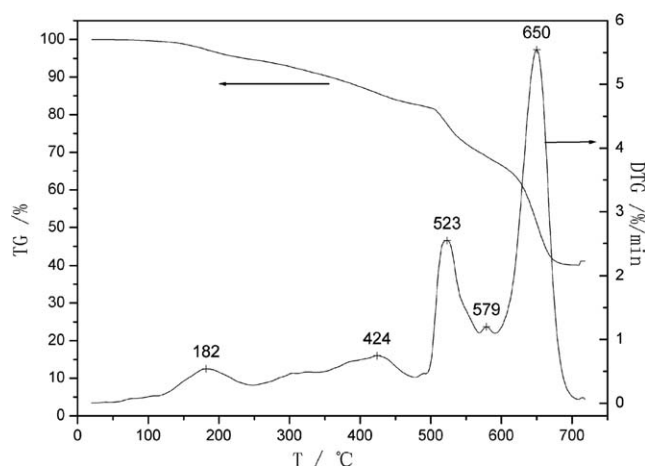
Nomenclature	End-capped reagent	End group (R')
TMPS(DM <sub>50</sub> DP <sub>50</sub> )S-DMMS	DMDMS	
TMPS(DM <sub>50</sub> DP <sub>50</sub> )S-TMS	TMMS	
TMPS(DM <sub>50</sub> DP <sub>50</sub> )S-BDSB	BDSB	
TMPS(DM <sub>50</sub> DP <sub>50</sub> )S-DMPS	DMPS	

yields volatile siloxane oligomers via intramolecular Si—O bond exchange, Si—C scission produces oligomers with Si—H end groups, and side-chain oxidation produces CO<sub>2</sub>, CO, H<sub>2</sub>O, and H<sub>2</sub>CO<sub>3</sub>, accompanied by a crosslink process initiated by free radicals.

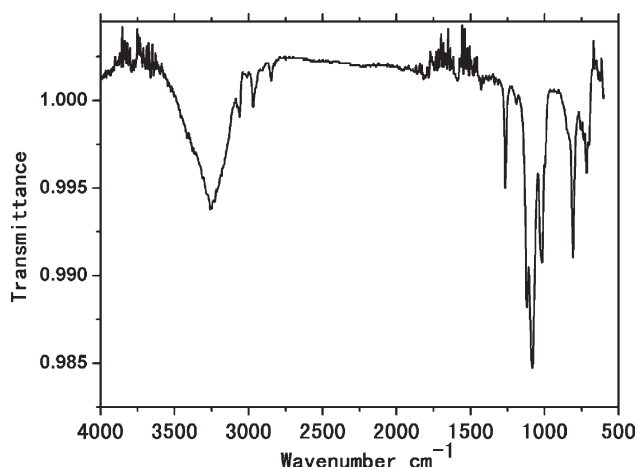
### Thermooxidative degradation behavior of TMPS(DM<sub>50</sub>DP<sub>50</sub>)S

TG/IR analysis of TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMMS

The TG and differential thermogravimetry (DTG) curves obtained for TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMMS are shown in Figure 1. The DTG curve was characterized by four maximums: two remarkable weight loss peaks at 523 and 650°C and two inconspicuous weight loss peaks at 182 and 424°C (Fig. 1). The IR



**Figure 1** TG and DTG curves obtained in air for TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMMS.



**Figure 2** Representative IR spectra of the thermooxidative degradation products obtained for TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMMS at 194°C.

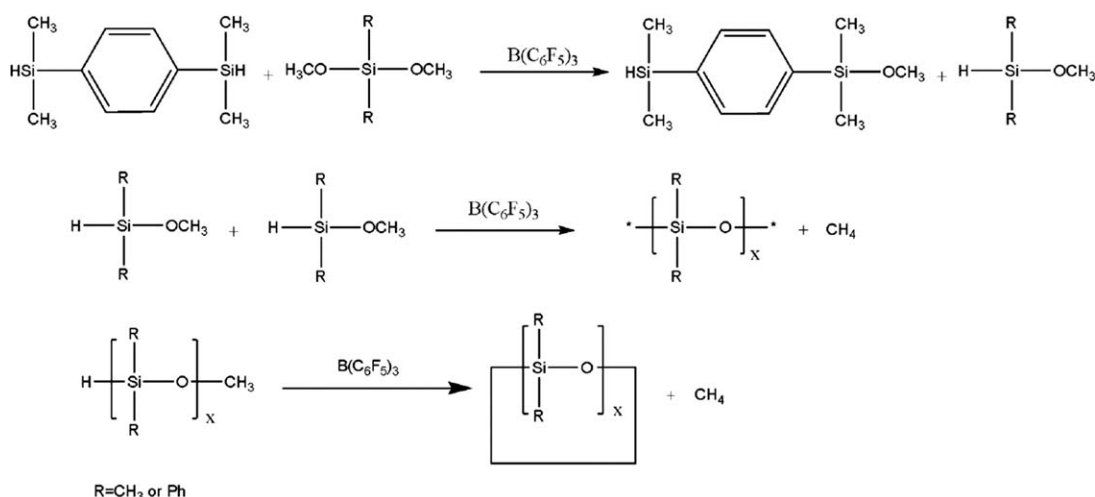
spectrum collected at 194°C showed absorptions at 1084 and 1018 cm<sup>-1</sup> (Fig. 2), which were the characteristic absorptions of Si—O—Si bonds of linear or cyclic DMS oligomers; this indicated that the weight loss peak centered at 182°C was caused by the volatilization of the impurities of low-molecular-weight polydimethylsiloxanes. These polydimethylsiloxanes oligomers were probably the products of the reaction of Si—H/Si—OCH<sub>3</sub> exchange (Scheme 1). The broad IR peaks centered at 3259 cm<sup>-1</sup> were the background absorption and were irrelevant to the degradation products. The products of weight loss peak centered at 424°C showed IR absorption at 1024 cm<sup>-1</sup>, which was also the absorption of Si—O—Si bonds; this indicated the onset of thermal depolymerization of the main chain via the formation of volatile linear or cyclic siloxane oligomers.

The IR spectrum collected at 523°C showed intensive IR absorptions at 1028 (ν<sub>Si—O—Si</sub>) and 1065 cm<sup>-1</sup>

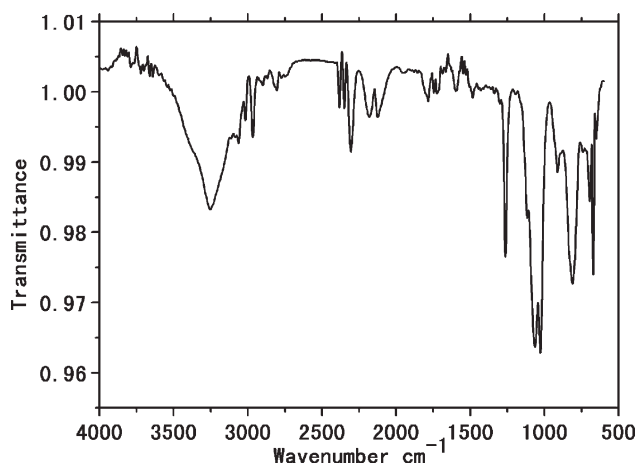
(ν<sub>Si—O—Si</sub>) (Fig. 3); this indicated that this stage of weight loss was mainly caused by the main-chain degradation. The degradation products at 650°C showed IR absorptions at 669 (δ<sub>C—O</sub> of CO<sub>2</sub>), 2110 (ν<sub>Si—H</sub>), 2183 (ν<sub>Si—H</sub>) and 2359 cm<sup>-1</sup> (ν<sub>C—O</sub> of CO<sub>2</sub>), and no absorptions over 1000–1100 cm<sup>-1</sup> were observed (Fig. 4); this indicated that only side-group oxidation and Si—C bond scission occurred during this stage. The weak but complex IR absorptions over 1350–1850 and 3500–3900 cm<sup>-1</sup> were ascribed to the absorptions of the product of H<sub>2</sub>O. From 496 to 567°C (the first-stage degradation, with the DTG peak centered at 523°C, Fig. 1), a 12% weight loss was observed, whereas a 27% weight loss was observed from 592 to 700°C (the second-stage degradation, with the DTG peak centered at 650°C, Fig. 1). This result showed that the weight loss of TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMMS was mostly caused by side-group oxidation, which was distinctly unlike the thermal degradation behavior of silanol-terminated dimethylsiloxanes (PDMS-OHs). TG/IR analysis showed that PDMS-OH underwent main-chain depolymerization over a broad temperature range over 100°C to above 720°C with relatively slight side organogroup oxidation (Fig. 5). The three-dimensional FTIR spectra acquired for these two polymers were much more illustrative (Figs. 5 and 6).

#### TG/IR analysis of TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-TMS

The TG and DTG curves obtained for TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-TMS are shown in Figure 7. TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-TMS had similar thermooxidative degradation behavior as TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMMS. However, two tiny differences were found after careful examination of the IR spectra and DTG curves. First, although there was no significant difference in the second-stage degradation temperature,



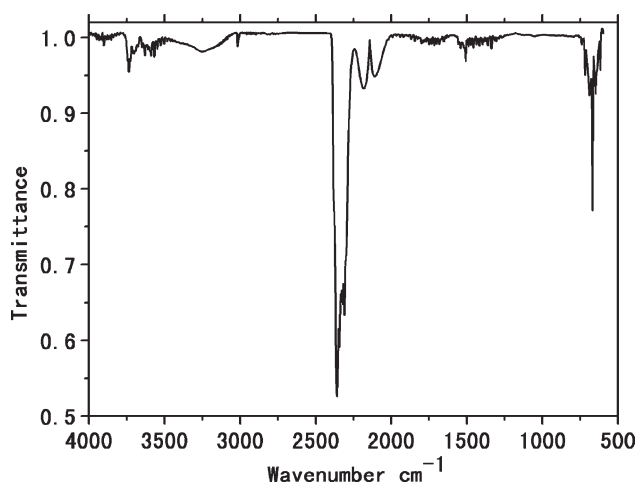
**Scheme 1** Side reactions for the formation of linear or cyclic polysiloxane oligomers.



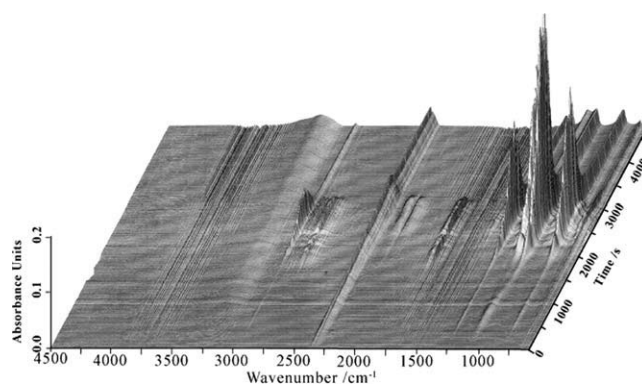
**Figure 3** Representative IR spectra of the thermooxidative degradation products obtained for TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMMS at 523°C.

the first-stage degradation temperature for TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-TMS shifted to a relatively lower temperature, 510°C, which was lower by 13°C. Second, the IR absorption of CO<sub>2</sub> at 2360 cm<sup>-1</sup> in the first stage for TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-TMS (Fig. 8) was more intensive than that of TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMMS (Fig. 3), which indicated earlier side-chain oxidation occurrence.

From the TG/IR analyses of the polymers terminated by TMS and dimethyldimethoxysilyl (DMMS), we observed that, unlike Si-OH, the end-group Si-OCH<sub>3</sub> did not cause an unzipping degradation reaction. Generally, the unzipping degradation mechanism caused by terminal silanol decreases the thermal stability of polydimethylsiloxanes by 50°C. Actually, in our investigation, the Si-OCH<sub>3</sub> terminated polymer, that is, TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMMS, exhibited a higher temperature for main-



**Figure 4** Representative IR spectra of the thermooxidative degradation products obtained for TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMMS at 650°C.

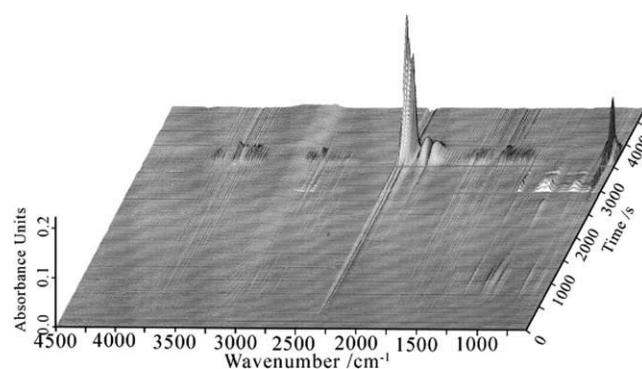


**Figure 5** Three-dimensional FTIR spectra of PDMS-OH in air.

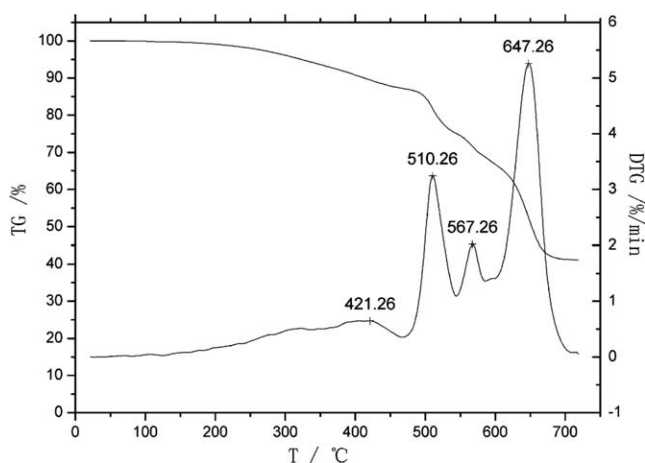
chain depolymerization than the TMS-terminated polymer, that is, TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-TMS, the first maxima in the DTG curves, which were ascribed to main-chain decomposition for these two kinds of samples, were 523 and 510°C, respectively. Moreover, the amounts of the first-stage mass loss observed for these polymers were almost the same, 12%.

#### TG/IR analysis of TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMPS

The TG and DTG curves of TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMPS are presented in Figure 9. TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMPS showed a two-step weight loss in air, which was similar to the polymers terminated by DMMS or TMS. The temperature for the second-step weight loss was 650°C, which was almost the same as that of TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMMS and TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-TMS, but the first weight loss peak shifted to a higher temperature, 545°C. TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMPS also showed a small mass loss peak around 421°C, but the IR absorptions of the volatile products of this stage were quite different. The IR spectrum collected at 418°C exhibited absorptions at 669 and 2360 cm<sup>-1</sup>, and almost no

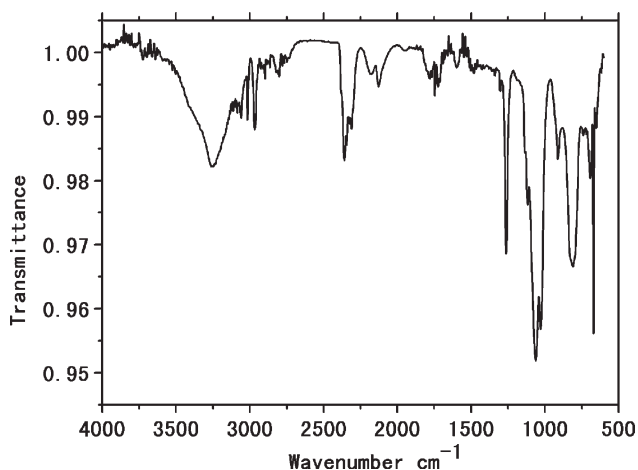


**Figure 6** Three-dimensional FTIR spectra of TMPS(DM<sub>50</sub>DP<sub>50</sub>)-S-DMMS in air.

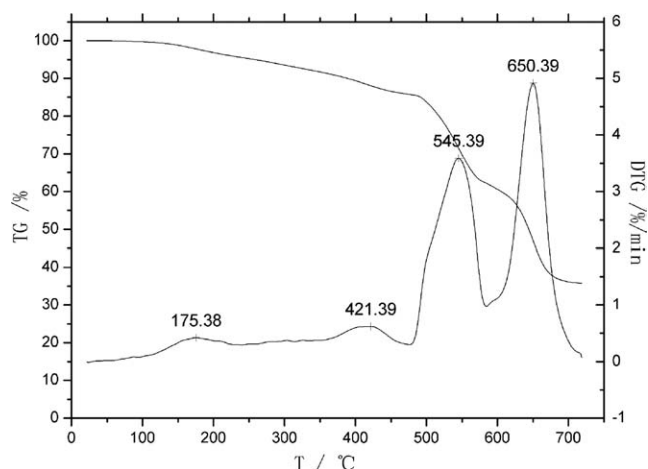


**Figure 7** TG and DTG curves obtained in air for TMPS-(DM<sub>50</sub>DP<sub>50</sub>)S-TMS.

absorptions were observed over 1000–1100  $\text{cm}^{-1}$  (Fig. 10); this indicated that the weight loss of the peak centered at 421°C of TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-TMPS was mostly caused by side organogroup oxidation instead of main-chain decomposition. The IR spectrum collected at 545°C exhibited absorptions at 671, 1063, and 2361  $\text{cm}^{-1}$  (Fig. 11); this indicated that this step of the weight loss was mostly caused by the depolymerization of the main chain and the oxidation of side groups. The absorption at 2361  $\text{cm}^{-1}$  was more intensive than that of the polymer terminated by DMMS (Fig. 3) or TMS (Fig. 8) during this mass loss stage; this indicated that the ratio of the products of side-group oxidation increased. The volatile products of the peak centered at 650°C showed IR absorptions at 669, 2110, and 2359  $\text{cm}^{-1}$ , the same as those of TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMMS (Fig. 4); this indicated that only side-group oxidation and Si–C bond scission occurred during this stage. From



**Figure 8** Representative IR spectra of the thermooxidative degradation products obtained for TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-TMS at 510°C.

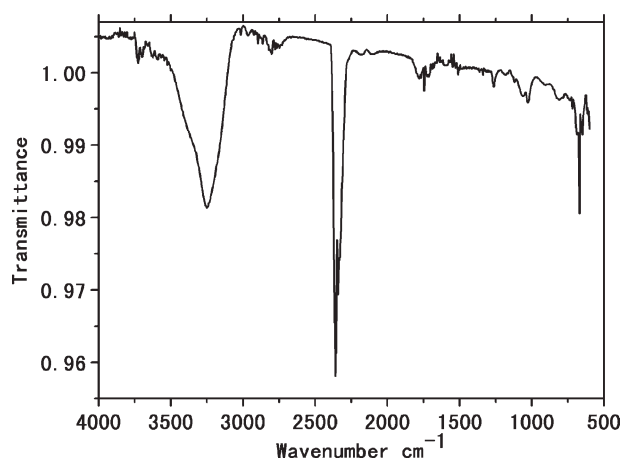


**Figure 9** TG and DTG curves obtained in air for TMPS-(DM<sub>50</sub>DP<sub>50</sub>)S-DMPS. T, temperature.

477 to 584°C (the first-stage degradation, with the peak centered at 545°C, Fig. 9), 14% weight loss was observed, whereas 26% weight loss was observed from 592 to 700°C (the second-stage degradation, with the peak centered at 650°C, Fig. 9).

#### TG/IR analysis of TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-BDSB

TG analysis indicated that TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-BDSB showed two steps of weight loss, which peaked at 540 and 647°C, respectively, in the DTG curves. The weight loss peak centered at 540°C was caused by the side-group oxidation and main-chain depolymerization, whereas the peak centered at 647°C was caused by side-chain oxidation and Si–C bond scission. The temperature range for the main-chain depolymerization evidenced by IR absorptions over 1000–1100  $\text{cm}^{-1}$  was 470–565°C, whereas the temperature range for side-group oxidation evidenced by



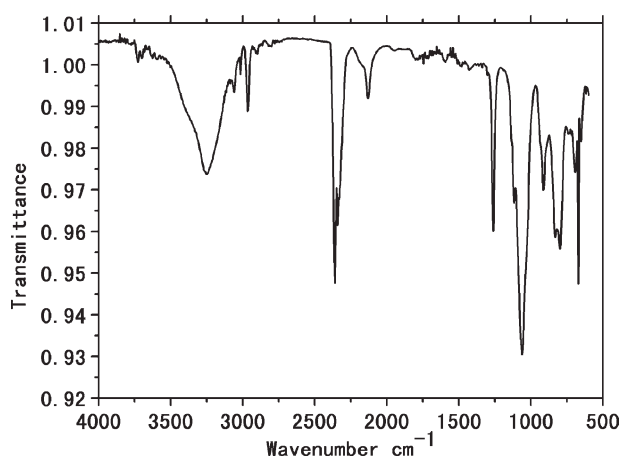
**Figure 10** Representative IR spectra of the thermooxidative degradation products obtained for TMPS(DM<sub>50</sub>DP<sub>50</sub>)S-DMPS at 418°C.

the IR absorptions of  $\text{CO}_2$  around  $2360\text{ cm}^{-1}$  was some  $360^\circ\text{C}$  to above  $720^\circ\text{C}$ . The three-dimensional FTIR spectra showed that the thermooxidative degradation behavior of  $\text{TMPS}(\text{DM}_{50}\text{DP}_{50})\text{S}-\text{BDSB}$  was similar to that of  $\text{TMPS}(\text{DM}_{50}\text{DP}_{50})\text{S}-\text{TMPS}$ , but the IR absorptions of  $\text{CO}_2$  were much more intensive over the whole thermal degradation period.

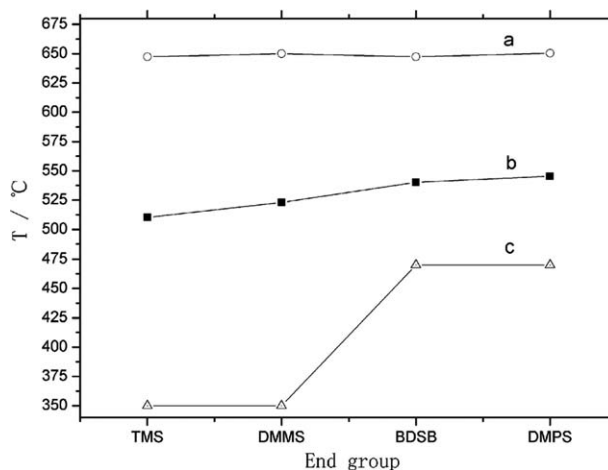
On the basis of the previous discussion, the thermooxidative degradation behavior of  $\text{TMPS}(\text{DM}_{50}\text{DP}_{50})\text{S}$  can be summarized as follows: (1) main-chain depolymerization through intramolecular Si—O exchange mainly occurred over a temperature range of some  $470\text{--}580^\circ\text{C}$ , and the products were mostly PTMS oligomers; (2) Si—C bond scission and side-group oxidation mainly occurred over a temperature range of about  $585$  to over  $720^\circ\text{C}$ , and the degradation products were mostly  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and oligomers with Si—H end groups; and (3) unlike Si—OH, the end-group Si— $\text{OCH}_3$  did not cause an unzipping degradation reaction and thus did not decrease the thermal stability of the main chain.

### Effects of the end groups on the thermooxidative degradation behavior

The relationships between the end groups and the characteristic temperatures of TG/IR analysis are shown in Figure 12. The temperatures for the second-step weight loss were not affected by the end groups, but the temperatures for the first-step weight loss, which were  $510$ ,  $523$ ,  $540$ , and  $545^\circ\text{C}$  for the polymers terminated by TMS, DMMS, BDSB, and DMPS, respectively, were notably different. The temperatures for the degradation onset of the main chain evidenced by IR absorptions of the Si—O—Si bond over  $1000\text{--}1100\text{ cm}^{-1}$  were affected much more prominently by the end groups; this was about  $350^\circ\text{C}$  for the polymers terminated by TMS and



**Figure 11** Representative IR spectra of the thermooxidative degradation products obtained for  $\text{TMPS}(\text{DM}_{50}\text{DP}_{50})\text{S}-\text{DMPS}$  at  $545^\circ\text{C}$ .



**Figure 12** Relationships between the characteristic temperatures and end groups: ( $\Delta$ ) temperatures for the second-stage degradation, ( $\blacksquare$ ) temperatures for the first-stage degradation, and ( $\circ$ ) temperatures for the degradation onset of the main chain evidenced by the IR absorptions of Si—O—Si bond over  $1000\text{--}1100\text{ cm}^{-1}$ .

DMMS but  $120^\circ\text{C}$  higher, that is, some  $470^\circ\text{C}$ , for the polymers terminated by BDSB and DMPS. This thermostabilizing effect of the BDSB and DMPS end groups was readily ascribed to the bulk and rigid phenyl group, which hindered the main-chain depolymerization via the formation of volatile cyclic oligomers by intramolecular Si—O exchange.

### CONCLUSIONS

All of the PTMS/DMS/diphenylsiloxane polymers with various end groups exhibited a two-steps weight loss in air. The first-step weight loss peaked at  $510\text{--}545^\circ\text{C}$  in the DTG curves and shifted to higher temperature with the augmentation of the bulk and rigidity of the end groups, whereas the second step centered around  $650^\circ\text{C}$  and was approximately the same for all of polymers with various end groups. The main-chain depolymerization via intramolecular Si—O bond exchange and side-group oxidation accounted for the first-step weight loss; however, as the bulk and rigidity of the end groups increased, the predominantly main-chain depolymerization products gave way to the side-group oxidation products. In the second-stage mass loss, only the products of side-group oxidation and Si—C bond scission were observed. The temperature for degradation onset of the main chain was greatly retarded to  $120^\circ\text{C}$  higher by termination of the polymer with DMPS or BDSB. Unlike Si—OH, the end-group Si— $\text{OCH}_3$  did not cause unzipping depolymerization and thus did not decrease the thermal stability of the PTMSs.

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