# New Method for Evaluation of Kinetic Parameters and Mechanism of Degradation from Pyrolysis–GC Studies: Thermal Degradation of Polydimethylsiloxanes

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ABSTRACT: Thermal degradation of polydimethylsiloxane (PDMS) polymers having hydroxyl (PS) and vinyl (PS-V) terminals was studied by pyrolysis-gas chromatography (PGC) in the temperature range from 550 to 950°C. The degradation products were primarily cyclic oligomers ranging from trimer (D<sub>3</sub>) to cyclomer D<sub>11</sub> and minor amounts of linear products and methane. The product composition varied significantly with pyrolysis temperature and extent of degradation. A new method was developed to derive a mass loss-temperature curve (pyrothermogram, PTG) and to determine the kinetic parameters of decomposition (k, n, and  $E_a$ ) from sequential pyrolysis studies. It was shown that isothermal rate constants can be derived from repeated pyrolysis data. Good agreement between the rate constants derived from the two methods validates the methodology adopted. This was further confirmed from thermogravimetric studies. The  $E_a$  values for the decomposition of PS and PS-V derived from sequential pyrolysis were  $40 \pm 2$  and  $46 \pm 2$  kcal mol<sup>-1</sup>, respectively. Various mechanisms for the degradation of PDMS were reviewed and discussed in relation to the PGC results. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 441–450, 1999

**Key words:** pyrolysis-GC; thermal degradation; kinetic parameters; polydimethylsiloxanes

## **INTRODUCTION**

Thermal degradation of diorganosiloxane polymers has received considerable attention as these polymers find various applications over a wide range of temperatures by virtue of their inherent thermal stability and unique thermal properties.<sup>1-4</sup> There have been many studies on the thermal degradation of polydimethylsiloxanes (PDMS). The volatile degradation products under vacuum or inert atmosphere are a mixture of cyclic dimethylsiloxane oligomers from trimer (D<sub>3</sub>) onward.<sup>5-16</sup> Trace or small amounts of linear products have also been reported.<sup>5,6,10,13-15</sup> How-

ever, there are significant differences in the reported product composition. Thus, the reported yield of  $D_3$  varied from a value as high as  $99\%^{17}$  to a much lower value of 44%.<sup>5,10</sup> Methane has also been found as a minor product of degradation of hydroxyl terminated PDMS in some of the studies<sup>18,19</sup> against the data of others.<sup>10,12,17,20</sup> There is disagreement about the mechanism of degradation among investigators.<sup>7,8,10,15,17–19</sup> Different mechanisms have been proposed for the depolymerization by siloxane rearrangement. Grassie and Macfarlan<sup>12</sup> have pointed out that much of the disagreement was because of variations in the method of polymerization, the level of impurities and catalyst residues, and the degradation conditions. Although thermal degradation of methyl end-blocked and hydroxyl terminated polydi-

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methylsiloxanes has been investigated by many people, the literature has no detailed studies on vinyl terminated PDMS.

Most of the studies above were carried out under relatively mild pyrolysis conditions of isothermal heating for prolonged periods in vacuum or sealed tubes or low heating rates (thermogravimetry). Random degradation is proposed for the depolymerization of methyl end-blocked PDMS<sup>10,12,15,17</sup>: whereas, depolymerization from the chain end is suggested for hydroxyl terminated PDMS.<sup>7,8,12,17,19</sup> However, the mechanism of degradation and product composition may greatly vary with the temperature and the extent of degradation. PGC is a very convenient and powerful technique for thermal degradation studies permitting flash pyrolysis at various temperatures. Data from TG can be coupled to provide a wealth of information for characterization of thermal degradation of polymers over a wide range of temperatures and conditions. We reported earlier on thermal degradation of polysulfides<sup>21,22</sup> and polybutadienes $^{23,24}$  and have shown the variation of product composition and mechanism of degradation with pyrolysis temperature and extent of degradation. In this article, these studies are further extended to the functionally terminated polydimethylsiloxanes (having hydroxyl and vinyl end groups) because of our interest in these polymers for high-temperature applications in our space programs. Kinetic parameters are evaluated, and the mechanism of degradation is discussed in light of earlier reports.

# **EXPERIMENTAL**

## **Materials**

The silanol terminated polydimethylsiloxane PS (viscosity, 6500 cst; mol. wt., 54,000) and vinyl terminated polydimethylsiloxane, PS-V (viscosity, 1000 cst; mol. wt. 28,000) samples used in this study were commercial samples obtained from Reliance Silicones Ltd., India and Gelest, Inc., USA, respectively.

# Pyrolysis–Gas Chromatography (PGC)

Pyrolysis experiments were carried out using a CDS 100 Pyroprobe interfaced with Fisons HRGC MEGA 2 gas chromatograph equipped with a digital temperature programmer and thermal conductivity detector (TCD). About 0.5–1 mg of sample was taken in a quartz sample boat and kept in

the coil probe of the pyrolyzer. The probe was placed in the heated interface, and the sample was pyrolyzed in helium (carrier gas) at the desired temperature for 10 or 20 s. The volatile degradation products were analyzed by the GC. The injector and detector were maintained at  $250^{\circ}$ C. The carrier gas (helium) flow was 40 mL min<sup>-1</sup>.

For identification of the products, analyses were carried out using two columns  $(2 \text{ m} \times \frac{1}{16} \text{ in. o.d.},$ stainless steel, 15% SP-2100 and 3% OV-101 columns). For all other studies, the latter column was used so that faster elution of the higher boiling products was achieved to aid better quantification. The column temperature was programmed from 100 to 200°C at 20°C min<sup>-1</sup>. The initial temperature was held for 2 min for adequate separation of initial peaks. The chromatogram was processed by a Shimadzu CR-1 data processor as well as Fisons Chromcard GC software using a PC, and quantitative data were obtained by the area summation method.

# Thermogravimetry (TG)

Dynamic thermogravimetric experiments (TG) were carried out in dry N2 (50 mL min<sup>-1</sup> flow) on a DuPont 951 Thermal Analyzer in combination with a DuPont Thermal Analyzer 2000. About 10 mg of sample was heated in a platinum crucible from ambient to 650°C at a heating rate of 10°C min<sup>-1</sup>.

# **RESULTS AND DISCUSSION**

# **Characterization of Pyrolysis Products**

About 0.5 mg of sample was taken in a quartz boat and pyrolyzed for 20 s using the CDS pyrolyzer. The decomposition products were separated using GC by temperature programming the column and detected by a TCD. The pyrogram was recorded and processed using a data processor, and the amounts of individual products were calculated by the area summation method.

The products were identified based on the knowledge of pyrolysis products of polydimethylsiloxane in vacuum or inert atmosphere reported earlier<sup>5,6,10,15</sup> and by comparing the GLC traces reported by Grassie and Macfarlan<sup>12</sup> and Nielsen.<sup>13</sup> Identification of lower cyclomers was confirmed by comparing the retention times of standard samples and higher members of the ho-



**Figure 1** Pyrogram of hydroxyl terminated polydimethylsiloxane (PS) at 750°C.

mologous series by using retention index. A typical pyrogram of hydroxyl terminated PDMS, obtained at a pyrolysis temperature of 750°C, is shown in Figure 1. The degradation products were primarily cyclic oligomers consisting largely of  $D_3$  (trimer,  $\sim$  46%) and  $D_4$  (tetramer,  $\sim$  20%) and lower amounts of  $D_5~(\sim~9\%),\,D_6~(\sim~11\%),\,D_7$ (~ 8%), and  $D_8$  (~ 3%), with smaller amounts of higher members up to  $D_{11}$  in decreasing proportions. The cyclic oligomers constitute nearly 99.5% of the total volatiles formed. Trace amounts of linear products formed are seen as small peaks in between the cyclomer peaks. Almost similar product distribution was obtained for vinyl terminated PDMS also at this temperature.

Methane also was found to be a minor product. The first peak in the pyrogram was identified as methane by separating it well away from other peaks using SP-2100 and OV-101 columns connected in series and maintaining the column temperature at 50°C and a low carrier gas flow. The retention time of the peak was close to that of air peak. The identity was further confirmed by comparing the retention times of  $C_1$  and  $C_2$  hydrocarbons in the pyrogram of polypropylene under the same GC conditions. The concentration of methane in the products was significantly more at elevated temperatures, especially in the case of PS-V, as indicated in the pyrograms at 950°C shown in Figure 2.

#### **Evaluation of Kinetic Parameters**

Kinetic parameters such as extent  $(\alpha)$  and rate (R) of decomposition, rate constant (k), and activation energy  $(E_{\alpha})$  for thermal degradation of polymers can be evaluated from sequential and repeated pyrolysis-GC data, as indicated below.

In sequential pyrolysis, about 1 mg of sample is pyrolyzed for a given time (t, 20 s), at different temperatures in a number of steps (n) of 50°C, and the chromatograms are recorded at each temperature of pyrolysis. If  $AT_i$  represents the sum of the areas of all peaks in the chromatogram at pyrolysis temperature  $T_i$ , and n is the total number of steps, then



**Figure 2** Pyrograms of polydimethylsiloxanes at 950°C: (a) PS; (b) PS-V.

$T_{i}$		$\alpha_{:}$	W.	$R_{\star}  imes 10^2$	$k_z  imes 10^3$
(°C)	$AT_i^{-1}$	(%)	(%)	$(s^{-1})$	$(s^{-1})$
		PD	MS Sample: PS		
500	1263	0.42	99.58	0.021	0.21
550	2701	0.90	98.68	0.045	0.45
600	11314	3.77	94.91	0.189	1.91
650	47695	15.89	79.02	0.795	8.37
700	104875	34.94	44.08	1.747	22.11
750	97732	32.56	11.52	1.628	36.93
800	33228	11.07	0.45	0.554	48.05
850	1351	0.45	0.00	—	—
		PDN	IS Sample: PS-V		
500	100	0.14	99.86	0.007	0.07
550	251	0.36	99.50	0.018	0.18
600	1262	1.82	97.68	0.091	0.91
650	6124	8.82	88.86	0.441	4.51
700	19803	28.52	60.34	1.426	16.05
750	32485	46.78	13.56	2.339	38.76
800	7895	11.37	2.19	0.569	41.92
850	1245	1.94	0.25	0.097	44.29
900	173	0.25	0.00	—	_

Table I Computation of Kinetic Parameters from Sequential Pyrolysis-GC

Pyrolysis time, t = 20 s.  $AT_i$  = total area count of all the peaks in the chromatogram at pyrolysis temperature  $T_i$ .  $\alpha_i$  = fraction of sample decomposed and  $w_i$  = the amount of sample left undecomposed at  $T_i$ .  $R_i$  = rate and  $k_i$  = rate constant at  $T_i$ .

Total amount of sample decomposed  $(W_o) \propto \sum_{1}^{n} AT_i$ 

Fraction of sample decomposed  $(\alpha_i)$ 

at 
$$T_i = \frac{AT_i}{\sum\limits_{1}^{n} AT_i}$$

Fraction of sample left undecomposed  $(w_i)$ 

at 
$$T_i = 1 - \sum_{1}^{i} \alpha_i$$

The values of  $AT_i$ ,  $\alpha_i$ , and  $w_i$  obtained for sequential pyrolysis of PS and PS-V in the temperature range 500–900°C are shown in Table I.

Therefore, a pyrothermogram (PTG) that represents mass versus temperature of decomposition can be constructed and is shown in Figure 3 for polymers PS and PS-V. These pyrothermograms are similar to mass loss-temperature curves recorded in thermogravimetry (TG), and kinetic parameters can be derived therefrom. As-

suming the order of reaction for decomposition is 1, as is generally the case with polymer degradation and shown to be so for PDMS,<sup>10</sup> Coats-Redfern method<sup>25</sup> was used to derive activation energy ( $E_a$ ) of decomposition based on the first-order expression

$$\ln[-\ln(1-\alpha)/T^2]$$
$$= \ln[AR/\beta E(1-2RT/E)] - E/RT$$



**Figure 3** Pyrothermograms (PTG) of PS (solid curve, ■) and PS-V (dotted curve, ▲).

The activation energy values calculated for the decomposition of PS and PS-V from 550 to 750°C ( $\alpha = \sim 0.5-0.9$ ) were 39.7 ± 2 and 46.5 ± 2 kcal mole<sup>-1</sup>, respectively.

Furthermore, because pyrolysis was carried out at very high heating rate (~ 1000°C s<sup>-1</sup>), the rate of decomposition may be approximated equal to the fraction decomposed in unit time; that is, rate of decomposition  $(R_i)$  at  $T_i = \alpha_i/t$ ; where, t= time for which the sample is pyrolyzed. For a first-order reaction, rate and rate constant are related by the equation  $R_i = k_i$ .  $W_i$  at a given temperature; therefore,

$$k_i = rac{R_i}{W_i} = rac{lpha_i}{t} imes rac{1}{1-\sum\limits_{i=1}^{i-1}lpha_i}$$

Thus, rates  $(R_i)$  and rate constants  $(k_i)$  can be calculated from sequential pyrolysis data, and the results obtained are shown in Table I. Arrhenius plot of log k versus 1/T (Figure 4) provides the activation energy  $E_a$ , and the values obtained for the decomposition of PS and PS-V from 550 to 750°C were 40.6  $\pm$  2 and 45.8  $\pm$  2 kcal mol<sup>-1</sup>, respectively. These values are in excellent agreement with the values derived from pyrothermograms using Coats–Redfern method. Datapoints above 750°C were not used for computation of  $E_a$ because additional degradation reactions were involved, as discussed later.

The above method was further confirmed from repeated pyrolysis for PS polymer at 650°C. In this method, the sample is pyrolyzed repeatedly at the same temperature over a period of time. The extent of decomposition was evaluated in the same manner as described above in the case of sequential pyrolysis, and an isothermal weight loss-time curve was constructed and is shown in Figure 5a. The rate of weight loss R derived therefrom was plotted against  $(1 - \alpha)$  for initial convertions of  $\alpha < 0.4$  (Figure 5b), and the rate constant k was evaluated from the slope of the plot. The very satisfactory agreement between the rate constants derived from sequential pyrolysis ( $k = 8.4 \times 10^{-3}$ , s<sup>-1</sup>) and repeated pyrolysis  $(k = 10.2 \times 10^{-3}, s^{-1})$  validates the evaluation of kinetic parameters from pyrolysis-GC data. The validity of the methodology adopted here is further confirmed by comparing the  $E_a$  values obtained from thermogravimetry and available literature data (cf. Table II).



**Figure 4** Arrhenius plots for PS ( $\blacksquare$ ) and PS-V ( $\blacktriangle$ ).

#### **Thermogravimetic Studies**

The TG and DTG curves at a heating rate of 10°C min<sup>-1</sup> of PS and PS-V samples are shown in Figure 6. The derivatives showed initial inflections on the rising side, although they were not resolved noticeably in the weight-loss curves. This can not be attributed to the volatilization of low molecular weight cyclic oligomers that may be present, because this is expected to occur at much lower temperature and was reported to be below 250°C by Thomas and Kendric.<sup>10</sup> These are attributed to low temperature decomposition processes attributable to the presence of ionic impurities or residual polymerization catalysts before the main depolymerization process begins. The role played by these impurities in catalyzing the decomposition of PDMS has been shown in several studies.<sup>7,8,26–31</sup> The temperature corresponding to the initial shoulder peak in the derivative thermogram of PS-V is around 455°C, which is very close to the peak temperature 460°C of DTG of PS. Hence, this may be attributed to the decomposition of small amount of silanol terminated PDMS present in the PS-V sample. The indication of hydroxyl group in the FTIR spectrum of PS-V supports this inference.

The kinetic parameters for the thermal degradation are evaluated using Coats-Redfern



**Figure 5** Isothermal weight-loss curve (a) and rate versus conversion plot (b) for PS at 650°C.

method. The first-order activation energy, for the main process of decomposition from 460 to 610°C, obtained for vinyl terminated PDMS is 42  $\pm$  2 kcal mol<sup>-1</sup>. This agrees closely with the value of 43  $\pm$  3 kcal mol<sup>-1</sup> for the depolymerization of methyl end-blocked catalyst-free PDMS determined from TG using Coats–Redfern method by Thomas and Kendrik.<sup>10</sup> Similar values are reported by Shulman<sup>32</sup> and Nelsen<sup>33</sup> (cf. Table II). The corresponding activation energy of decomposition obtained for PS in the temperature range from 400 to 540°C is 37  $\pm$  2 kcal mol<sup>-1</sup>.

It is gratifying to note that the values obtained from PGC data are similar to those obtained from TG studies, and this validates the treatment of PGC data for obtaining the kinetic parameters. The slightly higher  $E_a$  values obtained from PGC studies can be attributed to small contribution

Table II	Activation Energies $E_a$ for the
Thermal	Decomposition of
Polydime	ethylsiloxanes

		$E_a \; (\mathrm{kcal} \; \mathrm{mol}^{-1})$	
		PGC	ļ
PDMS	TG	Coats-Redfern	Arrhenius
PS PS-V PS-M <sup>a</sup>	$\begin{array}{rrrr} 37 & \pm \ 2 \\ 42 & \pm \ 2 \\ 43 & \pm \ 3^{10} \\ 43.5 & \pm \ 1^{32,33} \end{array}$	$39.7 \pm 2$ $46.5 \pm 2$	$\begin{array}{c} 40.6\pm2\\ 45.8\pm2\end{array}$

 $E_a$  values shown for PS-M are from literature.

<sup>a</sup> PS-M = methyl end-blocked polydimethylsiloxane.

from cleavage of Si—C bonds at the elevated temperatures, as discussed later.

#### **Thermal Stability**

A comparison of the TG and DTG curves of PS and PS-V (Figure 6) shows that there is a considerable difference in the thermal stability of these polymers. PS starts decomposing at a much lower temperature as compared to PS-V. The weight loss from PS begins around 315°C, and the decomposition is complete by 540°C; whereas, the respective temperatures for PS-V are 365 and 615°C. Similarly, the temperature corresponding to the weight-loss rate-maximum for PS-V is 525°C, which is about 65°C higher than that of PS. The pyrothermograms and the derivative



**Figure 6** Thermograms of PS (solid curve) and PS-V (dotted curve).

	Weight % of Products								
Temperature (°C)	$CH_4$	$D_3$	$\mathrm{D}_4$	$\mathrm{D}_5$	$D_6$	$D_7$	$D_8$	$D_9$	D <sub>10</sub>
			PDMS	S Sample:	$\mathbf{PS}$				
600	< 0.05	45.4	15.6	6.7	8.4	9.1	7.7	4.3	_
650	0.05	45.7	18.4	7.8	10.5	9.1	4.2	2.0	1.2
750	0.07	46.3	20.3	8.9	11.1	8.3	3.3	1.3	0.6
800	0.15	46.8	19.8	8.9	11.3	8.1	2.9	1.2	0.4
850	0.2	50.6	20.4	8.3	9.9	6.7	2.3	1.0	0.2
950	0.7	50.8	20.6	8.6	9.3	6.1	2.1	0.9	0.1
			PDM	S Sample:	PS-V				
600	0.1	37.2	13.5	6.9	14.8	13.8	8.4	3.8	
650	0.2	42.4	15.1	7.5	15.4	11.5	5.2	2.3	1.3
750	0.4	46.3	18.5	8.1	12.3	8.6	3.1	1.1	0.8
800	0.9	49.1	17.2	8.0	11.6	8.0	2.9	1.1	0.5
850	1.1	51.4	18.8	8.0	10.0	6.6	2.3	0.9	0.2
950	3.0	51.3	19.8	8.5	8.1	5.3	2.0	0.8	0.1

Table III Composition of Principal Decomposition Products of PDMS at Various PyrolysisTemperatures

curves (Figure 3) also show similar results. The curves of PS-V are shifted to higher temperatures as compared to those of PS. The temperature of rate-maximum for PS-V is about 20°C higher than that of PS. These results show that hydroxyl end group lowers the thermal stability of PDMS considerably. This agrees with the results of earlier studies that replacement of hydroxyl end group with methyl group enhances thermal stability of PDMS considerably.<sup>7,8,12,17,20</sup> This suggests that degradation from chain ends involving terminal hydroxyl group is thermally more facile than random degradation of PDMS with methyl or vinyl end groups.

## **Pyrolysis at Different Temperatures**

To study the product distribution with respect to pyrolysis temperature and to get a better insight into the mechanism of degradation, PS and PS-V were pyrolyzed at various temperatures from 600 to 950°C and the results are shown in Table III. Similarly, sequential pyrolysis was carried out from 600 to 900°C at 100°C interval, and the product composition at each temperature is given in Table 4. The pyrolysis behavior with respect to variation of product composition with temperature was similar in both experiments. Assuming degradation of PS mainly from chain end and

The second se	Weight % of Products								
(°C)	$\mathrm{CH}_4$	$D_3$	$D_4$	$\mathrm{D}_5$	$D_6$	$D_7$	$D_8$	$D_9$	
			PDMS Sar	mple: PS					
600	$<\!0.05$	45.4	15.6	6.7	8.4	9.1	7.7	4.3	
700	0.05	46.8	19.8	8.4	11.6	8.8	3.4	1.2	
800	0.1	48.7	19.4	8.7	11.0	7.9	3.0	1.1	
900	0.3	53.1	19.3	8.2	9.8	6.7	2.5	0.8	
			PDMS Sar	mple: PS-V					
600	0.1	37.6	14.1	7.2	15.2	14.4	8.7	2.9	
700	0.3	46.6	16.7	7.9	13.9	10.2	3.3	1.0	
800	0.6	50.6	17.4	8.0	11.4	7.7	2.6	0.8	
900	2.2	55.4	18.4	7.3	9.0	5.8	1.9	0.9	

Table IV Composition of Principal Decomposition Products of PDMS on Sequential Pyrolysis

random degradation for PS-V, the results in Tables III and IV can be rationalized as follows.

First, at lower temperatures of pyrolysis, PS produced more  $D_3$  as compared to PS-V. This indicates that depolymerization from chain ends causes liberation of larger amounts of  $D_3$  as compared to random degradation.

Second, the amount of  $D_3$  produced from PS was almost constant at lower temperatures; whereas, it varied continuously with temperature from 37 to 51% in the case of PS-V. This suggests that relative concentration of  $D_3$  in the products does not vary much with temperature for endinitiated degradation, whereas, random degradation is characterized by an increase in the amount of  $D_3$  produced as the temperature is increased. However, the concentration of  $D_3$  varied for PS at higher temperatures, and, finally, the product composition of PS approached that of PS-V. This clearly indicates a significant contribution of random degradation also for PS, the contribution of which increases with temperature.

Third, the amount of  $D_6$  formed was more in the case of PS-V compared to PS. Furthermore,  $D_6$  steadily decreased with temperature for PS-V; whereas, in the case of PS  $D_6$  increased initially and then decreased at higher temperatures. This, again, suggests the increasing contribution of random degradation at higher temperatures in the case of PS.

Fourth, for both the polymers, the relative amounts of lower oligomers ( $D_3$  to  $D_5$ ) increased with temperature; whereas, the amounts of higher oligomers, particularly  $D_8$  onward, decreased. This is the general behavior of random degradation, again, supporting the contribution of random degradation for PS.

From the above discussions, it can be concluded that, although PS-V depolymerizes by random degradation along the chain, PS depolymerizes mainly from chain ends with an appreciable contribution of random degradation as well, and the extent of random degradation increases with temperature.

The concentration of methane in the products was found to increase with increase in pyrolysis temperature, especially at higher temperatures above 750°C. The production of  $CH_4$  indicates that, in addition to the siloxane rearrangement leading to the formation of cyclic oligomers, random cleavage of Si—CH<sub>3</sub> bonds is also involved, the contribution of which increases significantly at elevated temperatures.

## Mechanism of Degradation

Although the Si—C bond is thermodynamically less stable than the Si—O bond, thermal degradation of PDMS occurs by depolymerization through siloxane rearrangement via kinetically favored paths, requiring much less activation energy as compared to the high siloxane Si—O bond energy of 108 kcal mol<sup>-1</sup>, leading to production of cyclic oligomers. Depolymerization from chain ends is suggested for hydroxyl terminated PDMS<sup>7,8,12,17,19</sup>; whereas, random degradation along the chain is proposed for methyl end-blocked polymer.<sup>10,12,15,17</sup> Unzipping by catalyst participation eqs. (1a<sup>7,8</sup> and b<sup>15</sup>) and molecular mechanisms eqs. (2a<sup>12,17,19</sup> and b<sup>10,12,17</sup>), have been postulated for the depolymerization by different groups of authors.

$$\begin{array}{cccc} & \text{Me Me Me Me Me} \\ & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & &$$





PGC results show although PS-V decomposes by random degradation along the chain, PS decomposes from chain end as well as by random process, as discussed before. Furthermore, the activation energy for the end-initiated depolymerization is expected to be much less as compared to that for random degradation along the chain. The  $E_a$  calculated by Rode et al<sup>17</sup> based on the principle of additivity of bond energies for the endinitiated mechanism eq. (2a) is about half (14 kcal  $mol^{-1}$ ) of that for random degradation mechanism eq. (2b) (32 kcal mol<sup>-1</sup>). However, the activation energy values obtained for PS and PS-V are not so different. This suggests a significant contribution of random degradation for PS. The pyrothermograms (Fig. 3) also indicate this. The PTG curve of PS comes closer to that of PS-V toward higher temperature region. The increased molecular motion and chain mobility at higher temperatures may facilitate random degradation by mechanism (2b). The contribution of mechanism (2b) for the degradation of hydroxyl terminated PDMS has been shown by Rode et al<sup>17</sup> also from an increase in  $E_a$  values as molecular weight increased.

Degradation by mechanism (2) shortens the residual chain length progressively with the extent of degradation, and volatile linear oligomers are formed at higher conversions. Hence, the concentration of linear products in the volatile products is expected to increase with conversion. However, the pyrograms of PS and PS-V show the presence of linear products initially itself, and their concentration was not found to increase significantly with conversion either in sequential pyrolysis or repeated pyrolysis studies. This suggests that the unzipping mechanisms involving catalyst also contribute to the depolymerization consistent with the commercial nature of the samples. The initial inflection in DTG of these samples inferred as attributable to catalysis/ionic process also supports this theory.

Hence, it can be concluded that PS degrades mainly by end initiation at lower temperatures; whereas, at higher temperatures, random degradation also is significant. Both molecular mechanism and unzipping by catalysis contribute to the depolymerization. Similarly, PS-V degrades by random initiation by molecular mechanism as well as by catalyst participation. The relative contribution of each process to depolymerization depends on sample history and pyrolysis conditions. This can account for most of the disagreements in the results of earlier studies. Nielsen<sup>13</sup> also has pointed out the contribution of all these mechanisms for degradation of commercial PDMS.

In addition to depolymerization by siloxane rearrangements, cleavage of Si-C bond also occurs, the extent of which increases with increase in temperature, as discussed earlier. This may result in formation of thermally more stable crosslinked products in the residue that decompose at elevated temperatures as inferred from repeated pyrolysis studies. The sample was repeatedly pyrolyzed at 650°C, initially for 10 s each time and later for 20 s as the rate decreased very much (cf. Fig. 5a), until no more decomposition products were detected by GC. The residue remaining in the sample boat was further subjected to repeated pyrolysis at the higher temperature of 850°C. Substantial amounts of products were formed by decomposition of the residue that remained after repeated pyrolysis at 650°C. This clearly indicates the formation of stable crosslinked products in the residue at lower temperatures of pyrolysis, which decompose at elevated pyrolysis temperatures.

The random cleavage of Si— $CH_3$  bond leading to the formation of methane with the resultant crosslinking of the PDMS can be represented as follows.



### **CONCLUSIONS**

The important conclusions drawn from the present study are the following. First, the decomposition products of silanol-terminated and vinyl-terminated polydimethylsiloxanes at elevated temperatures are principally the cyclic oligomers, with small amounts of methane and traces of linear oligomers. Second, such kinetic parameters as k and  $E_a$  can be evaluated from sequential and repeated pyrolysis-GC data. Third, vinyl-terminated PDMS depolymerize by random decomposition along the chain; whereas, hydroxyl-terminated PDMS depolymerize from chain end as well as by random decomposition, and the contribution

of random decomposition increases at elevated temperature. Fourth, random cleavage of  $Si-CH_3$  bond also is significant at elevated temperatures.

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