Thermal Degradation of Poly(dimethylsilylene) and Poly(tetramethyldisilylene-*co*-styrene)

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ABSTRACT: Thermal degradation of poly(dimethylsilylene) homopolymer (PDMS) and poly(tetramethyldisilylene-*co*-styrene) copolymer (PTMDSS) was investigated by pyrolysis-gas chromatography and thermogravimetry (TG). PDMS decomposes by depolymerization, producing linear and cyclic oligomeric products, whereas PTMDSS decomposes by random degradation along the chain resulting in each monomeric product and various other combination products. The homopolymer was found to be much less stable than the copolymer. The decomposition mechanisms leading to the formation of various products are shown. The kinetic parameters of thermal degradation were evaluated by different integral methods using TG data. The activation energies of decomposition (*E*) for the homopolymer and the copolymer are found to be 122 and 181 kJ/mol, respectively, and the corresponding values of order of reaction are 1 and 1.5. The observed difference in the thermal stability and the values of the kinetic parameters for decomposition of these polymers are explained in relation with the mechanism of decomposition. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2679–2686, 2006

Key words: polysilanes; pyrolysis; thermogravimetric analysis (TGA)

INTRODUCTION

Even though polysilane polymer was known much earlier,[1] interest in polysilanes was aroused in 1975 with the discovery by Yajima and Hayashi that the permethyl polymer $(Me_2Si)_n$ or its cyclic oligomer $(Me_2Si)_6$ could be transformed into silicon carbide by heating to high temperatures.[2,3] Since then pyrolysis of various organosilicon polymers has been developed as a major method to produce ceramic fibers.[4–8] Therefore, characterization of the pyrolysis process and the mechanism of degradation of the polymer provide valuable inputs for the production process.

Thermal degradation of polydimethylsilane in an autoclave under pressure and inert atmosphere at temperatures above 450°C produces polycarbosilane, which is converted to SiC fiber by heating to temperatures above 1000°C.[9] Mechanisms shown for the formation of polycarbosilane from polydimethylsilane include cleavage of the Si—Si bond, followed by rearrangement involving insertion of methylene groups in the polysilane backbone; and polymerization by methylene insertion reaction of the monomer (dimethylsilylene) formed from PDMS. Pyrolysis process of polycarbosilane has been well characterized.[10,11] Thermo-gravimetry of PDMS has been reported.[9] Although there have been several studies on photodegradation of permethylated linear and cyclic polysilanes,[12–18] literature shows no detailed studies on thermal degradation of PDMS. Pyrolysis of PDMS may produce cyclic oligomers as major products, similar to the pyrolysis behavior of polydimethylsiloxane reported earlier.[19–21] The cyclic peralkylsilane oligomers could also form polycarbosilane, as it is formed from $(Me_2Si)_6$.

Presence of comonomers in the polymer chain usually modifies the thermal properties and mechanism of degradation. The combined data from pyrolysis GC and thermogravimetry would provide a wealth of information for characterization of thermal degradation of polymers, as shown in our earlier studies.[19,22–25] Thermal properties and kinetics of degradation of poly(methylvinylsilylene) and its styrene copolymer were investigated in the previous studies.[26,27] In this article, thermal degradation of PDMS and its styrene copolymer is reported.

EXPERIMENTAL

Materials

Poly(dimethylsilylene) (PDMS)

The homopolymer PDMS has been synthesized by dechlorination of dimethyldichlorosilane (DMDCS) using sodium in toluene, as per known procedure.[28]
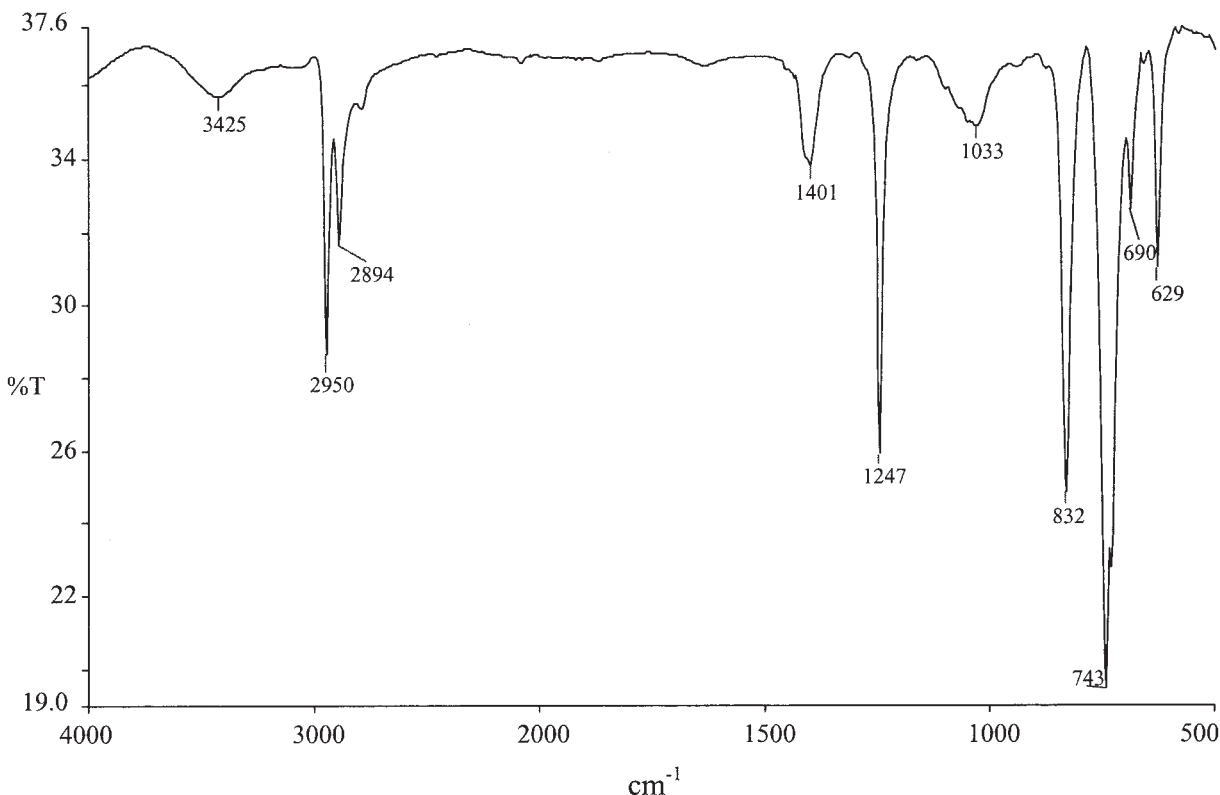
Figure 1 IR spectrum of PDMS.

Poly(tetramethyldisilylene-*co*-styrene) (PTMDSS)

The copolymer has been synthesized by the dechlorination of dimethyldichlorosilane, using sodium in the presence of styrene with a monomer ratio of 1 : 0.5. The synthesis is reported elsewhere.[29]

Pyrolysis-gas chromatography (PGC)

PGC experiments were carried out using a CDS 100 Pyroprobe interfaced with Fisons HRGC MEGA 2 gas chromatograph equipped with a digital temperature programmer and a flame ionization detector (FID). About 0.5–1 mg of the sample was taken in a quartz sample boat 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 700°C for 20 s. The volatile degradation products were separated using SP-2100 and OV-101 columns connected in series. The column temperature was programmed from 50 to 220°C at a heating rate of 20°C/min. The injector and the detector were maintained at 250°C. The carrier gas (helium) flow rate was 40 mL/min. The pyrograms were recorded using Fisons Chromcard GC software.

FTIR analysis

Infra red spectra were recorded using Perkin–Elmer Spectrum GX A FTIR specrometer with a resolution of 4 cm^{-1}. The spectrum of the homopolymer (powder) was recorded using KBr pellet. As the copolymer was some what rubbery in nature, the spectrum was recorded using a thin film (prepared by wetting with chloroform) between two NaCl plates.

Thermogravimetric studies

Dynamic thermogravimetric (TG) experiments were performed in dry N_2 (50 mL/min flow) on a DuPont 951 Thermal Analyzer in conjunction with a DuPont Thermal Analyzer 2000. About 10 mg of the sample was heated in a platinum crucible from ambient temperature to 600°C at a heating rate of 10°C/min. The fractional conversion (α) and the corresponding temperatures were evaluated using the General Analysis software version V4.0D. The onset temperature of decomposition was evaluated based on inflection point on extrapolation of the initial base line of the TG curves.

RESULTS AND DISCUSSION

Structure of the polymers

PDMS

IR spectrum of the homopolymer PDMS is shown in Figure 1. The spectrum is identical to the IR spectrum of PDMS reported by Yajima et al.[9] The C—H absorp-
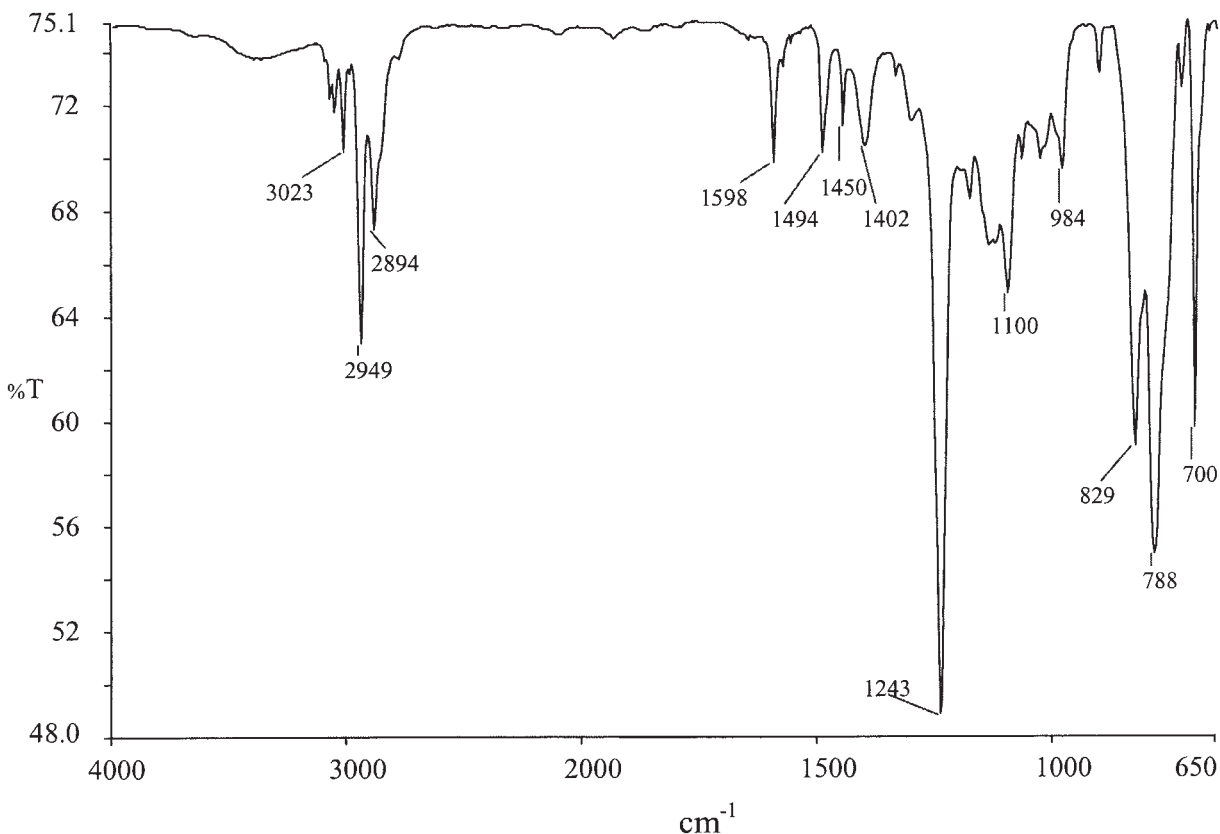
Figure 2 IR spectrum of PTMDSS.

tions appear at 2950, 2894, and 1401 cm^{-1} and Si—Me absorptions are seen at 1247, 832, 743, 690, and 629 cm^{-1}.[30] Si—O absorptions appear between 1000 and 1100 cm^{-1} and OH absorption between 3200 and 3600 cm^{-1}. Hence the structure of the polymer is identified as HO—[Si(Me$_2$)]$_n$—OH. The polymer backbone contains only polysilyl linkages in the homopolymer.

PTMDSS

Dechlorination of DMDCS in the presence of styrene results in copolymers containing tetramethyldisilylene and styryl moieties as repeating units. The synthesis of the copolymer and characterization based on ^{1}H, ^{13}C, and ^{29}Si-NMR are reported elsewhere.[29] When DM-DCS to styrene feed ratio used in the reaction is 1:0.5, the structure of the copolymer obtained is found to be — [Si(Me$_2$)—Si(Me$_2$)—CH$_2$—CH(Ph)]$_n$—, containing very little polysilyl or polystyryl blocks. The copolymer has disilyl and disilyl–styryl linkages in the polymer chain. The IR spectrum of the polymer is shown in Figure 2. Incorporation of styrene in the polymer was seen from the peaks at 1599, 1492, and 1451 cm^{-1} because of aromatic moiety of styrene.[26,31] Absorption due to silahydrocarbon is seen at 1100 cm^{-1}.[32]

Pyrolysis GC studies

The homopolymer and the copolymer were subjected to flash pyrolysis at 700°C under helium gas flow using CDS 100 pyrolyser, with a view for understanding their thermal degradation characteristics. The degradation products were separated by GC and the pyrograms obtained are shown in Figures 3 and 4. Though the structures of individual products are not identified, since an integrated PGC-MS system was not available, the nature of the products may be assigned as follows.

The Si—Si linkage in PDMS is weak and readily undergoes homolytic cleavage on pyrolysis. This can lead to depolymerization of the linear chain, resulting in the formation of oligomeric products. The pyrogram of PDMS (Fig. 3) shows a regular pattern characteristic of a series of oligomers produced by depolymerization. Production of dimethylsilylene by cleavage of Si—Si bond is the initial step in the reaction mechanism shown for the synthesis of polycarbosilane from PDMS by Yajima et al.[9] The major reactions in photodegradation by UV light are homolysis to give silyl radicals and elimination of dimethylsilylene.[13,15,17,18] Since dimethylsilylene (monomer unit) is unstable, the first main peak (M) in the pyrogram can be assigned to be the product derived from it. The
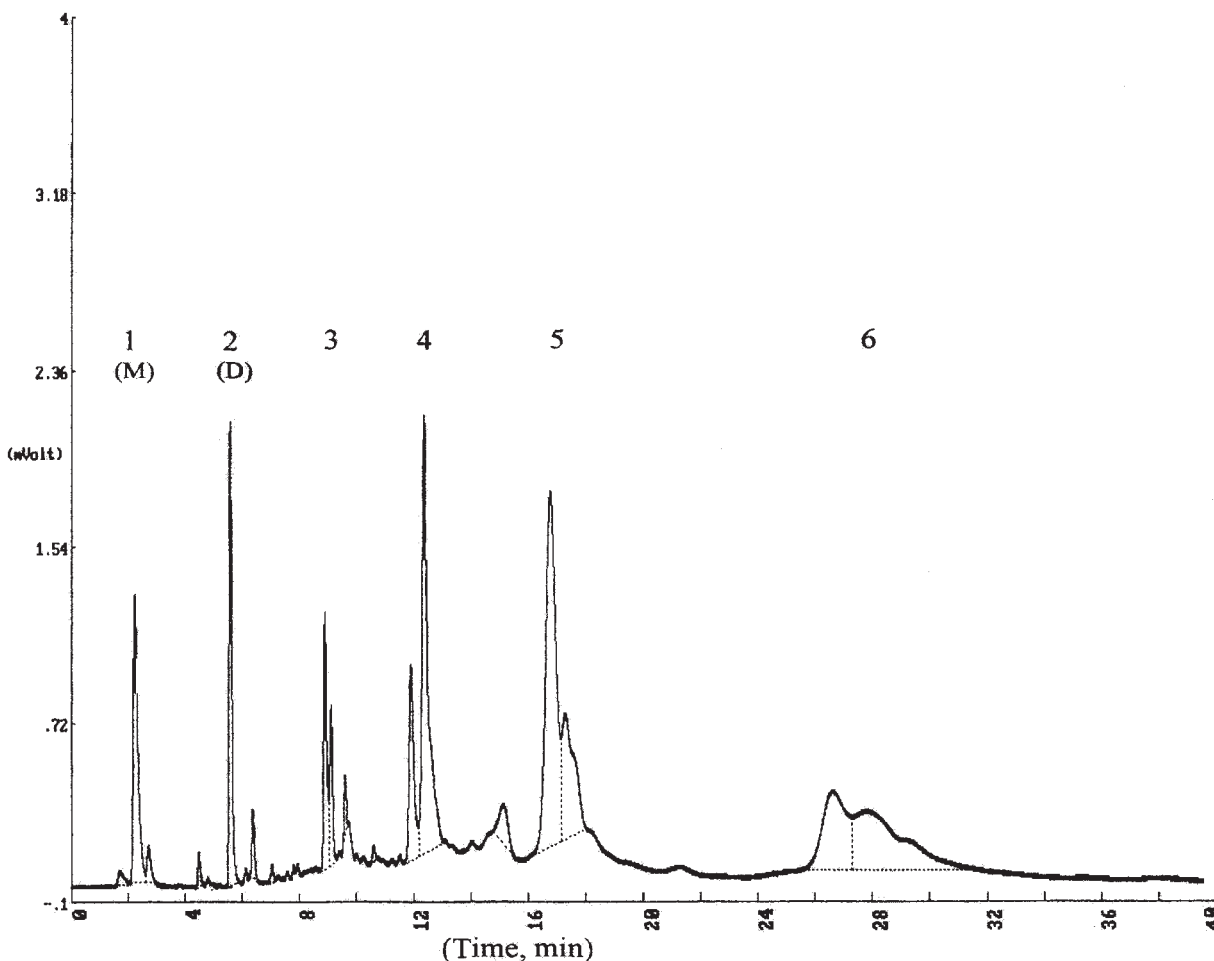
Figure 3 Pyrogram of PDMS at 700°C.

dimer unit tetramethyldisilene is also unstable and the second peak (D) is assigned to be the product derived from it. Radical cleavage of Si—Si bond can lead to depolymerization of the polysilane chain by elimination of cyclic oligomers. Depolymerization can also take place by kinetically favored bond rearrangement reactions involving cyclic transition state, in a manner similar to the pyrolysis process of polydimethylsiloxane,[19–21] resulting in extrusion of the cyclic oligomers from trimer onwards. H-abstraction by silyl radical can result in the production of linear oligomeric products. Hence, cyclic and linear oligomers are expected in the products. Pairs of peaks are found from third peak and are assigned to be the cyclic and linear oligomeric products from trimer to hexamer (peaks 3–6). Minor products arising from other possible reactions are also seen in the pyrogram.

Pyrogram of the copolymer, PTMDSS, is shown in Figure 4. The polymer chain contains alternating disilyl and styryl units, and hence, disilyl (Si—Si) and silyl–styryl [Si—CH₂CH(Ph)] linkages. Incorporation of styrene hinders degradation by depolymerization and favors random degradation of the polymer along the chain. Therefore, pyrolysis is expected to produce various products containing silyl, disilyl, and styryl units. The first two main peaks (M and D), as expected, are found to be the same monomeric and dimeric products from PDMS. The third main peak (S) is identified as styrene by comparing with the styrene peak in the pyrogram of polystyrene[26] under identical conditions. The pyrogram shows peaks due to various other combination products. The high intensity of styrene peak in the pyrogram suggests that in addition to the cleavage of Si—Si bond, cleavage of silyl–styryl bond also is a preferred mode of decomposition. Thermogravimetric analysis further substantiates that the copolymer degrades by competing reactions, as discussed later.

Thermal properties

To evaluate the thermal properties and kinetics of degradation of the polymers, dynamic thermogravimetric analysis (TG) was carried out from ambient temperature to 600°C at a heating rate of 10°C/min. The thermograms (TG) and the derivative thermo-
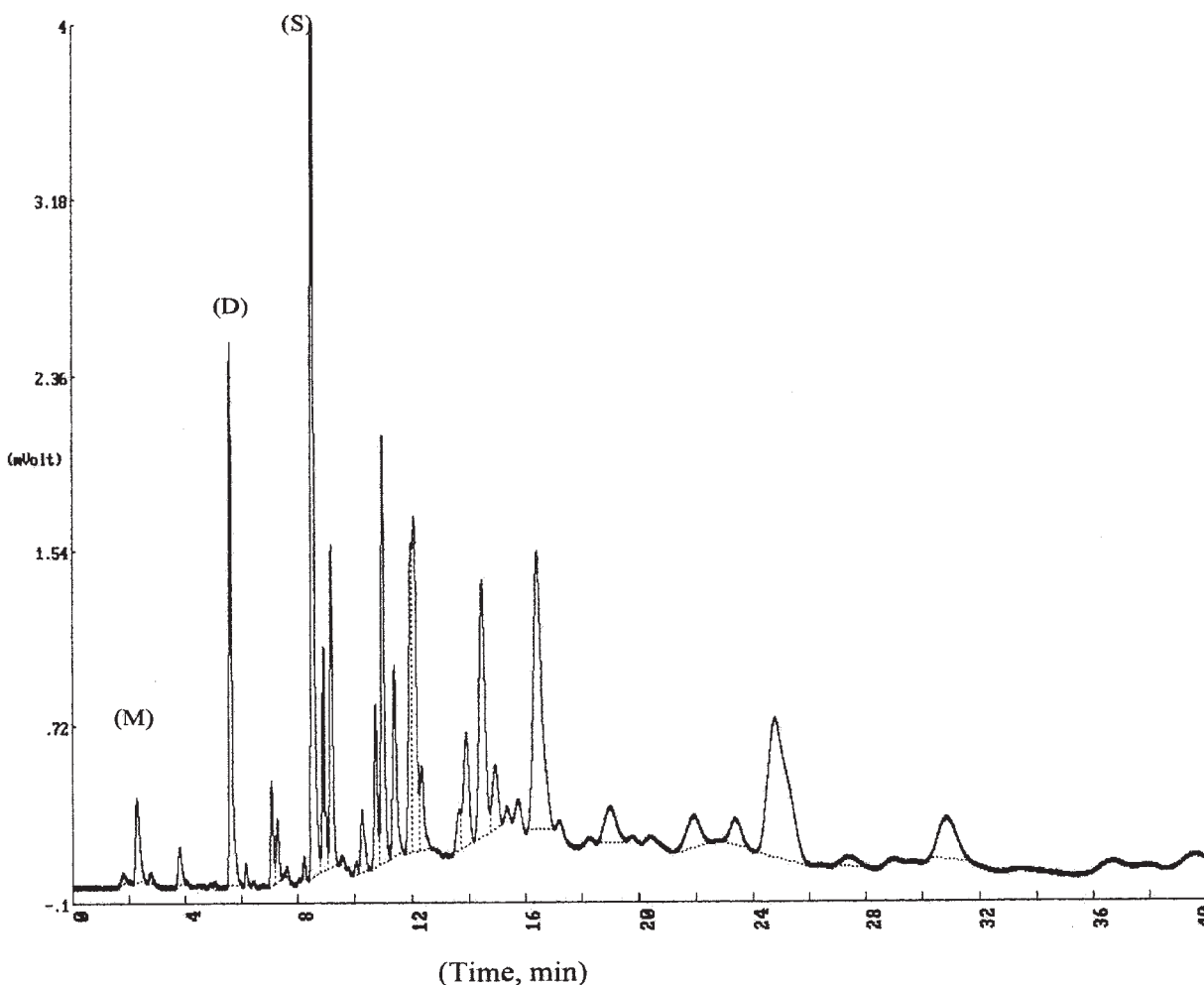
Figure 4 Pyrogram of PTMDSS at 700°C.

grams (DTG) of the homopolymer and the copolymer are shown in Figure 5. A comparison of the TG and DTG curves of the polymers shows that there is a considerable difference in the thermal stability of these polymers. PDMS starts decomposing at a much lower temperature compared to PTMDSS. The weight loss from PDMS begins around 250°C and the decomposition is almost complete by about 460°C, whereas the corresponding temperatures for PTMDSS are 320 and 520°C, respectively. Similarly, temperature corresponding to the maximum rate of weight-loss for PDMS is 421°C, while the corresponding temperature for PTMDSS is 435°C. Both the polymers degrade completely into volatile products without leaving behind any significant amount of residue. The char residue left behind at 600°C is only 1.5 and 0.2%, respectively, for PDMS and PTMDSS.

Si—Si bond (222 kJ/mol) is relatively unstable when compared to Si—C bond (318 kJ/mol), Si—H bond (314 kJ/mol), and C—H bond (414 kJ/mol).[33] The poor thermal stability of PDMS is due to repeating Si—Si linkages of the polymer backbone, which can readily undergo homolytic radical cleavage. This is facilitated by depolymerization leading to volatile oligomeric products, as evident from PGC studies. Moreover, PDMS can depolymerize by cyclization reactions as discussed earlier. TG curve shows that the weight loss is gradual in the initial stage of decomposition. This could be due to the formation of non-volatile cyclic products as well at lower temperatures, which subsequently decompose into smaller volatile products at higher temperatures. The slow rise of the derivative peak and minute shoulders in the initial stage of the DTG curve also indicates this behavior. Permethylcyclosilanes containing up to 35 silicon atoms or higher have been reported.[34,35] Differential thermal analysis reported by Yajima et al.[9] showed exothermic as well as endothermic reactions during the initial stages of thermal degradation of PDMS. This further supports the occurance of cyclization reactions in addition to the decomposition.

Polycarbosilane was synthesized by thermal decomposition of polydimethylsilane under pressure in an autoclave at temperatures above 450°C.[9] Formation of
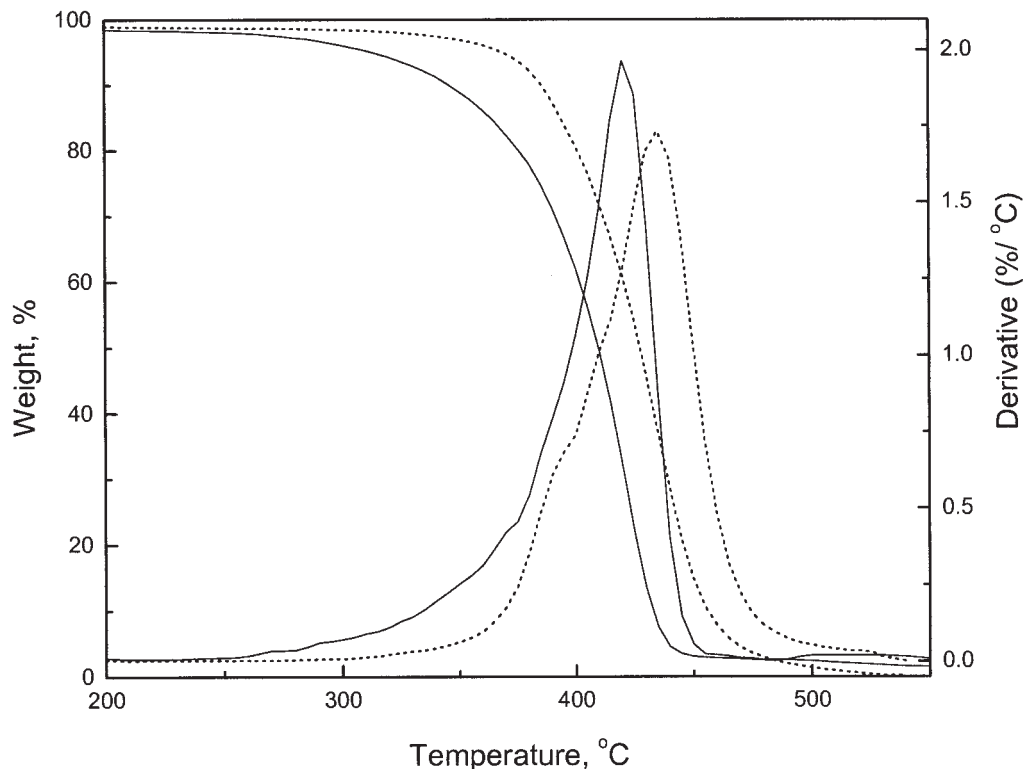
Figure 5 TG and DTG of PDMS (solid curves) and PTMDSS (dotted curves).

polycarbosilane involves cleavage of Si-Si bond in PDMS, followed by rearrangement involving insertion of methylene groups in the polysilane chain. TG of polycarbosilane in nitrogen showed very high residue, about 61% at 850°C and 54% at the final tempetrature of 1300°C.[10,11] Since TG of polydimethylsilane shows only a negligible amount of residue (1.5%) at 600°C, it is evident that methylene insertion reactions resulting in the formation of polycarbosilane do not occur under the present conditions.

Incorporation of styrene in the polymer backbone hinders depolymerization process and hence the copolymer stability is expected to be higher. The TG curve of PTMDSS is considerably shifted to higher temperature as expected. The steady weight loss from the start of decomposition in the case of the copolymer reveals degradation resulting in volatile products. The derivative curve (DTG) shows an unresolved shoulder peak before the main peak, indicating competing decomposition reactions. This suggests cleavage of Si—Si linkages as well as disilyl–styryl linkages, leading to various products as inferred from PGC studies.

Mechanism of degradation

Decomposition of PDMS results in the production of linear and cyclic oligomeric products, as discussed earlier. Further, methylene insertion reactions resulting in the formation of polycarbosilane are found to be

absent. Hence, the degradation paths and the major products can be predicted based on a depolymerization mechanism as shown later. The disproportionation reaction resulting in —SH and —Si=CH$_2$ ends has been shown in photodegradation of polysilanes.[36]

The cyclic products can be formed by either a radical mechanism or a molecular mechanism as shown below. However, the kinetically favored low activation energy process involving a cyclic transition intermediate may be the preferred mode of decomposition, similar to the decomposition mechanism of polydimethylsiloxane. This is further supported by the fact that the activation energy of decomposition for PDMS (122 kJ/mol) was found to be much less compared to that for PTMDSS (181 kJ/mol).

Radical cleavage and hydrogen abstraction (Scheme 1) lead to the formation of linear oligomeric products while cyclization reactions (Scheme 2) resulted in the production of cyclic oligomers.

PTMDSS decomposes by random degradation along the chain, resulting in various products containing silyl, disilyl, and styryl units. The mechanism of degradation may be represented as follows (Scheme 3).

As styrene is a major product, in addition to the breakage of Si-Si bond, cleavage of silyl–styryl linkage is also a preferred mode of degradation resulting in various products containing both monomeric units. Cleavage of silyl–styryl linkage is favored by the for-

$$R \quad R \quad R \quad R \quad R$$
$$Si-Si-Si-Si-Si\sim \quad \rightarrow \quad \sim Si-Si. \quad + \quad .Si-Si-Si\sim$$
$$R \quad R \quad R \quad R \quad R$$

(R = CH₃)

$$:Si< \; + \; >Si=Si< \; + \; .Si-Si$$

$$\sim Si-Si. \; + \; .Si-Si-Si\sim \quad \rightarrow \quad \sim Si-Si-SiH \; + \; CH_2=Si-Si\sim$$

$$CH_2=Si-(Si)_n-SiH$$

Scheme 1

$$Si-Si-CH_2-CH(Ph)-Si-Si-CH_2-CH(Ph)\sim \quad \rightarrow$$

$$\sim Si-Si-CH_2-CH(Ph). \; + \; .Si-SiCH_2-CH(Ph)\sim$$

$$Si-Si-CH_2-CH(Ph). \quad \rightarrow \quad CH_2=CH(Ph) \; + \; \sim CH_2-CH(Ph)-Si-Si.$$

$$:Si< , \; >Si=Si< , \; \text{products formed by H-abstraction}$$

$$.Si-Si-CH_2-CH(Ph)\sim \quad \rightarrow \quad :Si< \; + \; .Si-CH_2-CH(Ph)\sim$$

products formed by H-abstraction

Scheme 3

mation of a secondary radical. Hydrogen abstraction will lead to the formation of various products.

Thermal decomposition kinetics

PGC studies and thermal analysis reveal the difference in the thermal degradation characteristics of the homopolymer and the copolymer. Incorporation of styrene in the polysilane backbone increases the thermal stability, and the degradation process is modified as discussed earlier. This difference is expected to be reflected in the kinetics of degradation of these polymers. Hence, TG data were used to evaluate the kinetic parameters, using the following four integral methods: Coats–Redfern method (C–R),[37] Mac Callum–Tanner method (M–T),[38] Horowitz–Metzger method (H–M),[39] and Madhusudhanan–Krishnan–Ninan method (MKN).[40] Activation energy of decomposition (E) and pre-exponential factor (A) were determined employing reaction order values n from 0 to 3 by varying the value in 0.1 increments, using a computer program. The best fit values of n, E, and A for the overall reaction for both the polymers and the correlation coefficient (r) obtained are shown in Table I. The values obtained by different methods are in good agreement with each other, except H–M method, and the correlation coefficient is high in all the cases. The higher values obtained in the case of H–M method may be due to the approximations made in deriving the integral equation. Similar observation was made in earlier studies also.[27,41,42]

$$Si-Si-Si-Si-Si\sim \rightarrow \sim Si-Si. \; + \; .Si-Si-Si\sim \rightarrow \overset{Si}{\underset{Si}{|}})(Si)_n \; + \; .Si-Si-Si\sim$$

$$Si-Si-Si-Si-Si-Si\sim \rightarrow \overset{\sim Si-Si-Si}{\underset{\sim Si-Si}{|}})(Si)_n \rightarrow \overset{Si}{\underset{Si}{|}})(Si)_n \; + \; \sim Si-Si-Si\sim$$

Scheme 2

The activation energy obtained for PDMS (average, 122 kJ/mol) is much less compared to that for PTMDSS (average, 181 kJ/mol). This is as expected because degradation by depolymerization usually requires less activation than that required for random degradation. Further, decomposition by molecular mechanism involving cyclic transition state is a kinetically favored path requiring much less activation energy.[19,20] This further supports the degradation mechanisms of the polymers discussed in the previous sections. The order of reaction for the decomposition of the homopolymer PDMS is found to be 1. The copolymer backbone has disilyl–styryl linkages also in addition to the Si—Si bonds, and decomposition reactions involve cleavage of both the linkages. Therefore, the change in the order of reaction from 1 to 1.5 in the case of the copolymer is in accordance with the competing reactions involved in the decomposition.

CONCLUSIONS

Pyrolysis GC and thermogravimetric studies reveal that the homopolymer PDMS decomposes by depoly-

TABLE I
Kinetic Parameters for the Thermal Degradation of PDMS Homopolymer and PTMDSS Copolymer

Kinetic parameters[a]	Kinetic equations			
	C-R	M-T	H-M	MKN
PDMS				
E	121	123	158	121
A	8.51×10^6	1.58×10^7	7.08×10^9	9.77×10^6
n	1.0	1.0	1.0	1.0
r	0.979	0.982	0.979	0.980
PTMDSS				
E	180	184	207	180
A	1.82×10^{11}	3.98×10^{11}	1.58×10^{13}	1.99×10^{11}
n	1.5	1.5	1.5	1.5
r	0.998	0.998	0.997	0.998

[a] E, activation energy (kJ/mol); A, pre-exponential factor (s⁻¹); n, order of reaction; r, correlation coefficient.

merization, resulting in the production of linear and cyclic oligomeric products. The linear products are formed by homolytic cleavage of the Si—Si bond and hydrogen abstraction by the silyl radicals, and the cyclic products are formed mainly by kinetically favored molecular mechanism involving cyclic intermediates. Methylene insertion reactions resulting in the formation of polycarbosilane do not occur under flash pyrolysis and the TG conditions employed. Incorporation of styrene in the polymer backbone hinders degradation by depolymerization. The copolymer PTMDSS decomposes by random degradation along the chain. Cleavage of disilyl bond and disilyl–styryl bond produces each monomeric product and various combination products. The lower thermal stability and activation energy for decomposition of the homopolymer compared to those of the copolymer are in agreement with their degradation mechanisms. The activation energy (E) and the order of reaction (n) for thermal decomposition of PDMS are 122 kJ/mol and 1, respectively. The corresponding values for PTMDSS are 181 kJ/mol and 1.5.

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