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Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms

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Abstract

The products of the thermal degradation of polydimethylsiloxane (PDMS) are determined by the heating conditions, since two competing mechanisms are involved.

Cyclic oligomers are formed in the low degradation temperature range and during slow heating in programmed degradation. This involves molecular splitting of oligomers from loop conformations of the PDMS chain favoured by its flexibility, and assistance on the part of empty silicon d-orbitals.

Methane and oligomers are formed in the high temperature range and during fast heating. This shows that homolytic scission of Si–CH_3 also takes place and is followed by hydrogen abstraction. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polydimethylsiloxane; Thermal Degradation; Oligomer

1. Introduction

The mechanisms of the thermal degradation of polydimethylsiloxane (PDMS) end-blocked with (CH_3)Si-groups have been intensively studied [1,2]. Degradation in an inert atmosphere (N_2) and under vacuum results in depolymerisation and the production of cyclic oligomers [3,4]. The trimer is the most abundant product, with irregularly decreasing amounts of the tetramer, pentamer and hexamer and higher oligomers [3].

Examination of linear and cyclic PDMS has indicated that they share a common molecular depolymerisation mechanism [5]. Nielsen [6] has proposed that cationic reactions on a glass surface (borosilicate, quartz) contributes to the depolymerisation of linear PDMS, while Zeldin et al. [7] suggest that it may be catalysed by ionic impurities from the walls of Pyrex glass vessels. The small amounts of macro-cycles (>10 Si atoms) formed during the thermal degradation of PDMS have also been the subject of attention [8]. Their presence points to ionic ring-opening polymerisation reactions and formation of a distribution of cyclic species. Clarson and Semlyen [9], in fact, have demonstrated ring-opening polymerisation catalysed by ions of the surface of the glass, when the cyclic tetramer, octamethylcyclotetrasiloxane is heated at 420 °C under vacuum in a Pyrex vessel. The degradation products are consistent with subsequent formation of cyclic species from the linear high molecular mass PDMS [9].

It can be thus assumed that at temperatures below 500–600 °C, PDMS depolymerise completely in an inert atmosphere and do not form a solid residue, whereas in air their decomposition is accompanied by the formation of some white silica powder [10]. However, the products of the thermal PDMS degradation are essentially determined by the temperature and the heating rate. This question is examined in depth in the present paper.

2. Experimental

2.1. Materials

Polydimethylsiloxane end-blocked with trimethyl-siloxy-groups $(CH_3)_3$Si-containing a vinyl-methyl-siloxane unit every 1400th $-(CH_3)_2-$Si–O unit (V1400) with a viscosity of 8×10^6 mPa was supplied by Wacker–Chemie Gmbh. The effect of cross-linking involving –C=C– bonds during the thermal degradation of PDMS can be ignored owing to its very low cross-linking density.

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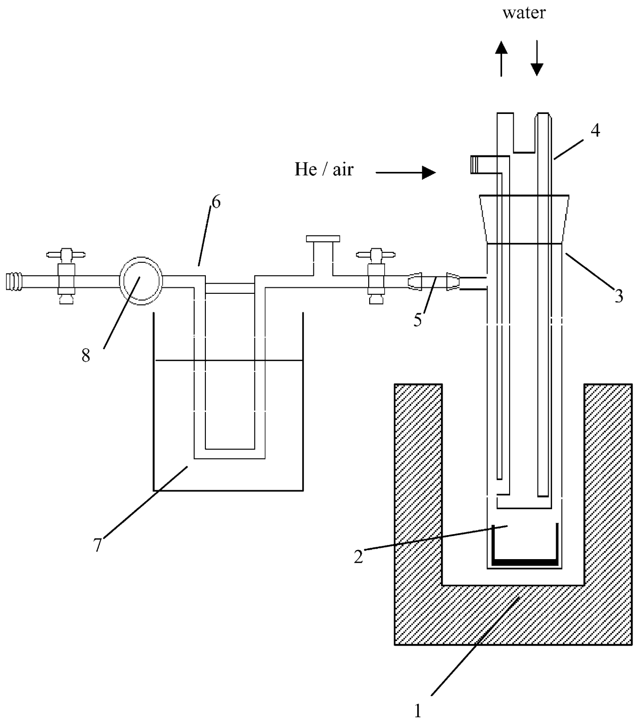


Fig. 1. Scheme of pyrolyser apparatus. 1 – furnace; 2 – quartz sample container; 3 – quartz degradation vessel; 4 – water cooled cold finger for high boiling products condensation; 5 – removal connector; 6 – U-trap for low boiling and gaseous products condensation; 7 – Dewar cooling system; 8 – KBr windows for gases IR examination.

2.2. Thermal degradation

Degradation in He or air was carried in the glass apparatus of Fig. 1. In air, methanol cooled at −78 °C was used to condense volatiles and gases in the trap and avoid oxygen condensation. In He, liquid nitrogen was used.

The ‘programmed heating’ conditions were 10°/min to 80 °C; equilibration for 1 min; 10 °C/min from 80 to 400 °C, then isothermal 1 h.

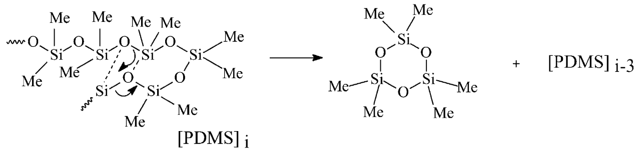
For ‘flash pyrolysis’, the samples were heated at 80°/min to 800 °C and kept at this temperature for 10 min.

The U-trap with low boiling gaseous and condensed liquid products of degradation was then removed. The gaseous products were analysed by FTIR, while the condensed liquid products were dissolved in $CHCl_3$ together with high boiling products condensed on the water-cooled cold finger and analysed using GC–MS. The solid decomposition residue was ground to a fine powder, mixed with KBr and then pressed into pellets for IR analysis.

2.3. Products analysis

IR spectra were obtained using a Perkin–Elmer 2000 Fourier transform, IR spectrophotometer: number of scans 16, gain 1.

GC–MS data were obtained with a Hewlett Packard CG 5890 A chromatograph coupled to a Hewlett Packard MSD 5970 mass spectrometer detector using a HP-5 capillary column filled with cross-linked 5% methyl-silicon (30 m). Detector temperature is 290 °C, injector temperature, 280 °C, oven maximum temperature, 280 °C, solvent delay time, 4.00 min, heating rate, 10 °C/min, and isothermal conditions, 4.00 min.



Scheme 1. PDMS molecular depolymerisation mechanism.

2.4. Thermal analysis

Thermogravimetry (TG) was performed on a Du Pont 1950 Vertical TG balance connected to a Du Pont 2100 thermal analyser, with a 100 ml/min nitrogen or air flow.

3. Results and discussion

3.1. Slow heating rate

The thermal degradation of PDMS to cyclic oligomers has been illustrated in a well-known depolymerisation diagram [10]. It has been suggested that the formation of an intramolecular, cyclic transition state is the rate-determining step [10]. Silicon d-orbital participation was postulated with siloxane bond rearrangement leading to the elimination of cyclic oligomers and shortening of the chain. The mechanism for formation of the smallest cyclic product, hexamethylcyclotrisiloxane, is illustrated in Scheme 1.

This transition state can be formed at any point of the polymer chain, and the process can take place indefinitely within a chain, until the residual linear structure is too short to cyclise.

Fig. 2 shows the gas chromatogram of the liquid degradation products of PDMS heated for 1 h under 50 ml/min. He

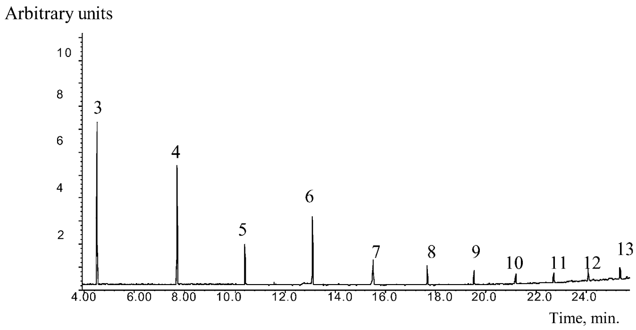


Fig. 2. Gas chromatogram of PDMS liquid degradation products (He, 400 °C), (‘programmed heating’ conditions). Figures on peaks: degree of polymerisation of cyclic oligomers (Table 1).

Table 1
GC–MS relative amounts of PDMS thermal degradation products in programmed heating conditions

Compound	Degree of polymerisation	Helium	Air
Cyclotrisiloxane, hexamethyl	3	100	100
Cyclotetrasiloxane, octamethyl	4	74	67
Cyclopentasiloxane, decamethyl	5	25	32
Cyclohexasiloxane, dodecamethyl	6	43	44
Cycloheptasiloxane, tetradecamethyl	7	16	18
Cyclooctasiloxane, hexadecamethyl	8	12	11
Cyclononasiloxane, octadecamethyl	9	9	7
Cyclodecasiloxane, eicosamethyl	10	7	10
Cycloundecasiloxane, docosamethyl	11	7	5
Cyclododecasiloxane, tetracosamethyl	12	8	4
Cyclotresdecasiloxane, esacosamethyl	13	7	4

at 400 °C reached by relatively slow programmed heating (10 °C/min). These products (Table 1) are cyclic DMS oligomers, whose yield tends to decrease as the degree of polymerisation increases. A sharp decrease is observed from trimer to heptamer with an inversion between pentamer and hexamer, whereas a comparable low yield (<10% of trimer) is found for larger oligomers. Literature data report either the trimer or the tetramer as the most abundant cyclic oligomer, with concentration of higher oligomers decreasing according to a normal distribution law [1–4].

Small oligomers (mostly trimer–tetramer) are distributed between the gas and the liquid phase in the trap of Fig. 1 as shown by GC–MS. The typical infrared spectrum of the mixture of oligomers in the gaseous phase is reported in Fig. 3 and corresponding absorption assignments are listed in Table 2.

Similar results are obtained in air (Table 1) in agreement with our preliminary data [10] showing that oxidation to SiO_2, H_2O, CO_2 mostly takes place by reaction in the gas phase between oxygen and volatile oligomers formed by thermal degradation. The IR spectrum of volatiles obtained by heating in air is dominated by absorption of water and CO_2.

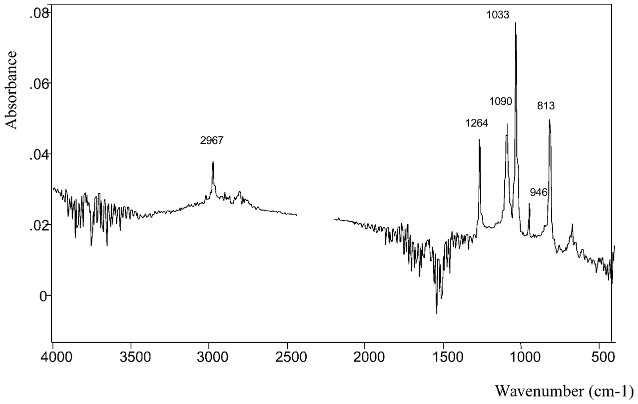


Fig. 3. FTIR spectra of gaseous phase products of PDMS thermal degradation, conditions as Fig. 2.

Table 2
Assignment of IR absorption of PDMS thermal degradation products of Fig. 3 (m, median; s, strong; w, weak)

PDMS (He)	
Wavenumber (cm^{-1})	Assignment [12]
813 m	Si–O–C
946 w	n.a.[a]
1033 s	Si–O–Si
1090 m	n.a.[a]
1264 m	C–H in $SiCH_3$
2967 w	C–H in CH_3

[a] n.a.: not assigned.

3.2. Rapid heating

Fast heating to 800 °C (flash pyrolysis) greatly alters the degradation compared to slow heating. Fig. 4 and Table 3 show that the cyclic oligomers obtained on slow heating at lower temperature are accompanied by linear DMS oligomers (e.g. 5l, Fig. 4, Table 3) or rearranged oligomeric siloxane compounds (e.g. A) formed on rapid heating to 800 °C.

A number of these other products evident in Fig. 4 have not yet been identified. Now the tetramer is the most abundant cyclic oligomer and the pentamer and hexamer are in comparable amounts, whereas the second is more abundant in Table 1.

Linear DMS oligomers, such as 5l can be accounted for by secondary reactions in the gas phase involving cyclic oligomers through glass vessel impurities catalysed ring-opening reactions, whereas, carbon–carbon and silicon–oxygen–carbon bonds, such as those in compound A of Table 3 involve an altogether different degradation mechanism, from silicon–oxygen bond scission leading to cyclic or linear DMS oligomers.

The IR spectrum of the gaseous products obtained in He (Fig. 5(a)) displays absorptions due to methane (3015 and

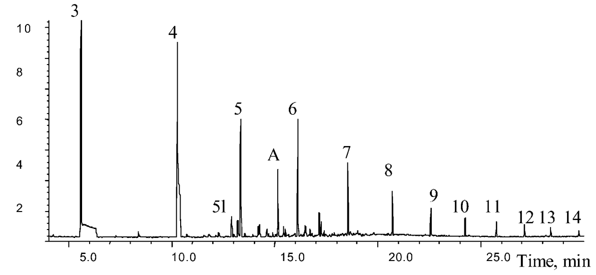


Fig. 4. Gas chromatogram of liquid PDMS degradation products (He, 800 °C), ('flash pyrolysis' conditions). Products identification, Table 3.

Table 3
GC–MS analysis of PDMS thermal degradation products in flash pyrolysis conditions

Compound	Degree of polymerisation	Helium	Air
Cyclotrisiloxane, hexamethyl	3	85	56
Cyclotetrasiloxane, octamethyl	4	100	100
Cyclopentasiloxane, decamethyl	5	37	31
Cyclohexasiloxane, dodecamethyl	6	27	23
Cycloheptasiloxane, tetradecamethyl	7	17	18
Cyclooctasiloxane, hexadecamethyl	8	12	13
Cyclononasiloxane, octadecamethyl	9	7	9
Cyclodecasiloxane, eicosamethyl	10	5	6
Cycloundecasiloxane, docosamethyl	11	5	5
Cyclododecasiloxane, tetracosamethyl	12	4	4
Cyclotresdecasiloxane, esacosamethyl	13	3	4
Cyclotetradecasiloxane, octacosamethyl	14	3	5
Linear pentasiloxane	51	11	13
Tetrasiloxane, 3,5-dietoxy-1,1,1,7,7,7-hexamethyl-3,5-bis(trimethylsiloxy)	A	5	20

1303 cm^{-1}) and silane (Si–H, 2125 cm^{-1}) [11], indicative of Si–C bond scission followed by H abstraction.

As previously observed [10], oxidation is limited during fast heating in air. This is evident from the small amount of CO_2 in Fig. 5 (2362 and 2333 cm^{-1}), whereas CO_2 and H_2O were the only evident gaseous products in oxidation during slow heating rate (shown before).

The 5% of black residue obtained in He is not visible in air owing to the overwhelming yield of white silica powder formed by oxidation of oligomers in gaseous and condensed phase [10].

Black silicon-oxycarbide is formed on thermal degradation of heavily cross-linked PDMS [12]. In our case, the radical scission mechanism may lead to cross-linking by coupling of radicals I and II of Scheme 2.

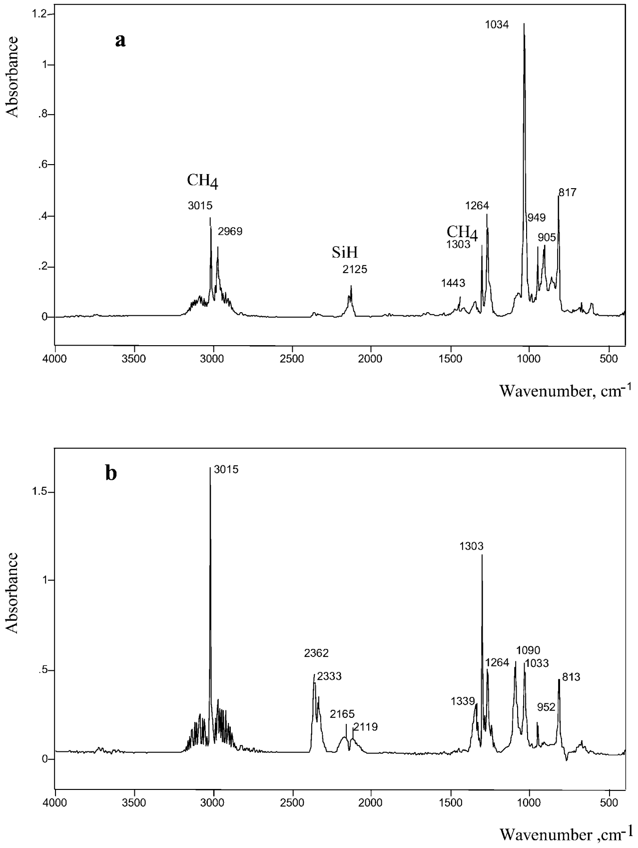
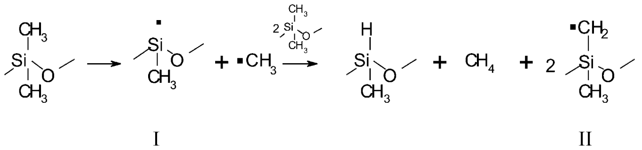


Fig. 5. FTIR spectra of gaseous phase products of PDMS thermal degradation at 800 °C, (‘flash pyrolysis’ conditions). (a) In He; (b) in air.



Scheme 2. Proposed mechanism for CH_4 formation.

4. Conclusions

Thermal degradation of PDMS occurs through two competing mechanisms. A molecular mechanism takes place with formation of cyclic oligomers. This implies Si–O bond scission, whose dissociation energy (108 kcal/mol) is lowered below that of Si–C (78 kcal/mol) by silicon d-orbitals involved in cyclic transition state favoured by chain flexibility.

A radical mechanism occurs through homolytic Si–CH_3 bonds scission. This prevails at high temperatures and leads to methane through hydrogen abstraction. Cross-linking of the macro-radicals decreases the flexibility of the PDMS chain and hinders splitting of cyclic oligomers still further. The thermal stability of the material increases and bonds reorganisation can take place with formation of ceramic silicon-oxycarbide.

Acknowledgements

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