

Polydimethylsiloxane thermal degradation

Part 1. Kinetic aspects

G. Camino^{a,*}, S.M. Lomakin^b, M. Lazzari^a

^aDipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali dell'Università, Via P. Giuria 7, 10125 Torino, Italy

^bGuest researcher from the Institute of Biochemical Physics of Russian Academy of Sciences, 117978, Kosygin 4, Moscow, Russian Federation

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Abstract

A combination of traditional kinetic formal treatments and computer simulation has been made to analyze polydimethylsiloxane (PDMS) thermal degradation. It was shown that PDMS thermally decomposes to cyclic oligomers through Si–O bond scission in a chain-folded cyclic conformation energetically favored by overlapping of empty silicon d-orbitals with orbitals of oxygen and carbon atoms. Kinetic treatment shows that PDMS thermal volatilization, as rate of heating increases, becomes dominated by rate of diffusion and evaporation of oligomers produced on its decomposition. At high heating rate (e.g. 100°C min⁻¹) thermal decomposition in nitrogen and in air tend to overlap because the rate of reaction between the material and oxygen is strongly reduced by low-oxygen solubility and high-thermal degradation rate. In nitrogen a small black residue is formed (silicon oxycarbide) which is produced by an alternative decomposition path leading to cyclic oligomers, made possible at high heating rate. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Depolymerization of polysiloxanes; Kinetics of depolymerization; Thermal degradation

1. Introduction

Kinetics of thermal degradation — depolymerization of end-blocked with (CH₃)₃Si– groups polydimethylsiloxane (PDMS) has been widely studied for a period of over 50 years [1–4]. It is well known that the thermal degradation of PDMS in inert atmosphere and under vacuum results in depolymerization over the range of 400–650°C to produce cyclic oligomers [3,4]. The trimer is reported to be the most abundant product, with decreasing amounts (although not regularly) of tetramer, pentamer, hexamer and higher oligomers [3].

Formal and informal attempts of kinetic consideration have been made to analyze the kinetics of this phenomenon in a wide range of heating rates (in nitrogen and in air). In this paper we have tried to reveal some new aspects of kinetic analysis with the ultimate goal of disclosing the nature of the solid residue formed during PDMS thermal degradation in order to predict its dependency on heating conditions.

2. Experimental

2.1. Materials

Polydimethylsiloxane endblocked with trimethylsiloxy-groups (CH₃)₃Si– containing a vinyl-methylsiloxan unit every 1400–(CH₃)₂–Si–O units (V1400) with a viscosity of 8 × 10⁶ mPa was supplied by Wacker-Chemie GmbH. Crosslinking mechanism involving –C=C– bonds during PDMS thermal degradation can be neglected due to very low crosslinking density of the polymer.

2.2. Thermal analysis

The following instruments were used to obtain weight loss data (TG) for the PDMS thermal degradation: TA INSTRUMENTS Hi-Resolution TGA 2950 Thermogravimetric analyzer and SDT 2960 Simultaneous TG-DTA (Differential Thermal Analysis). Constant heating rates of 1, 3, 4, 5, 7, 10, 50 and 100°C min⁻¹ were used. For the thermal degradative runs, the samples were purged with nitrogen gas or air at a flow rate of 60 cm³ min⁻¹. The sample weights were approximately 10 mg.

* Corresponding author. Tel.: +39-011-670-7557; fax: +39-011-670-7855.

E-mail address: camino@ch.unito.it (G. Camino).

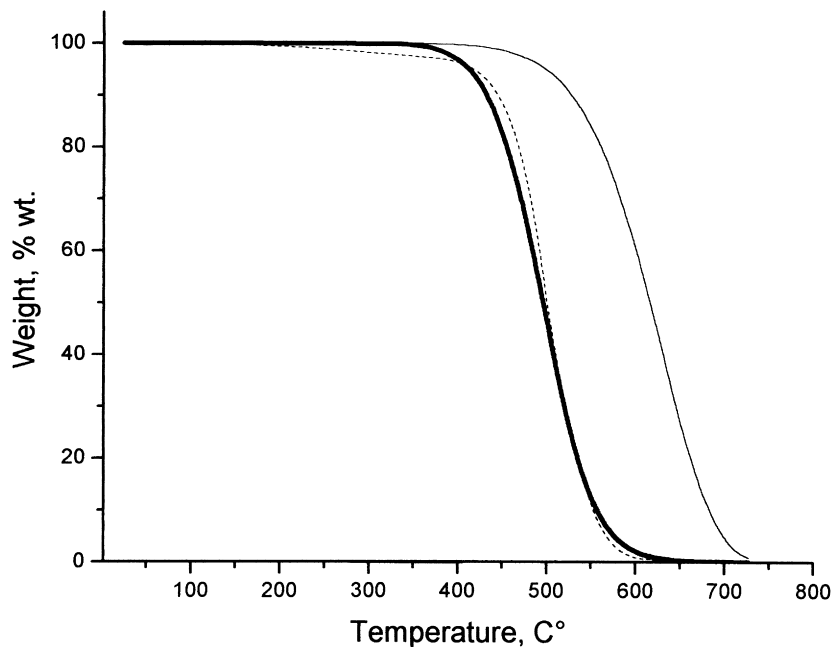


Fig. 1. TGA curves of PDMS (N_2 , $10^\circ \text{ min}^{-1}$). Experimental data: solid thick line; simulated: solid thin line, $A = 0.50 \times 10^6 \text{ s}^{-1}$, $E = 26.76 \text{ kcal mol}^{-1}$. Simulated-optimized: dashed line, $A = 0.25 \times 10^7 \text{ s}^{-1}$, $E = 25.11 \text{ kcal mol}^{-1}$.

3. Results and discussion

3.1. Kinetic approach

Since PDMS thermogravimetry carried out in inert atmosphere shows a single weight loss step (Fig. 1, experimental curve), we can assume that PDMS undergoes a thermal degradation reaction which is described by a one-step Arrhenius reaction term.

Therefore, assuming that the sample temperature is uniform, the thermogravimetric experiment may be expressed in a differential form by

$$dc/dt = (1 - c)^n A \exp(-E/RT), \quad (1)$$

where n is generally called the order of reaction, in analogy with chemical kinetics; A the pre-exponential factor and E the energy of activation. In the case where the change of temperature of specimen with

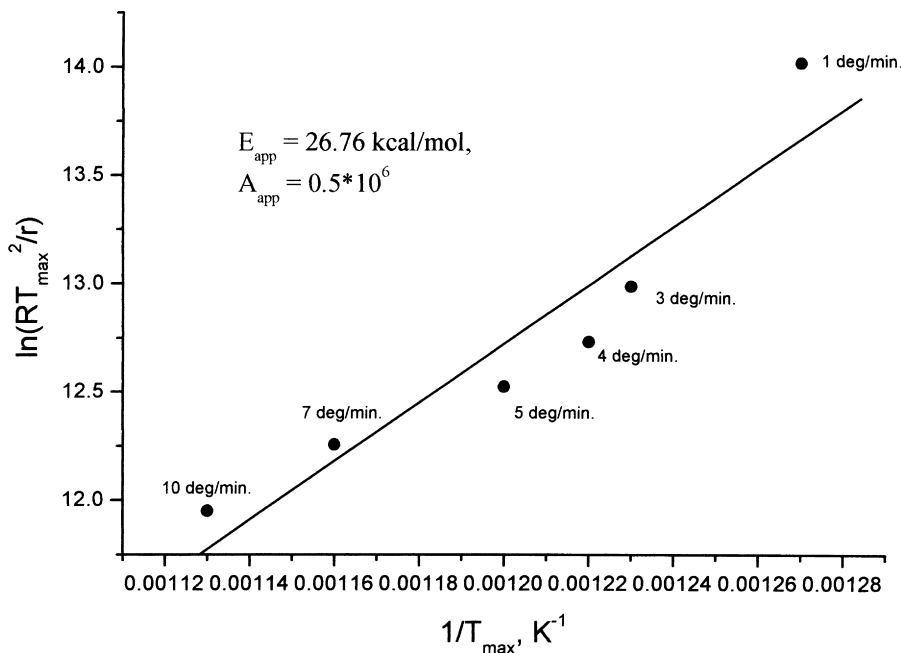


Fig. 2. Plot showing first-order thermal degradation of PDMS in N_2 ($1 < r < 10$).

Table 1
Temperature of maximum weight loss rate from PDMS TG under nitrogen

r ($^{\circ}\text{min}^{-1}$)	T_{max} ($^{\circ}\text{C}$)
1	514
3	532
4	540
5	560
7	589
10	611

time is $r = dT/dt$, we have

$$dc/dt = r(dc/dT) = (1 - c)^n A \exp(-E/RT), \quad (2)$$

with initial conditions

$$(1 - c)_{t=0} = 1; \quad T_{t=0} = T_a \quad (3)$$

where T_a is ambient temperature (K).

For a given ramping rate (r) a material may be characterized by the temperature, T_{max} , at which the mass flux from solid to gas is a maximum. Particularly, when the rate of change of mass flux with time is zero

$$d^2(1 - c)/dt^2 = 0 \quad (4)$$

For the system comprising the ordinary differential equations (1) and (2) and the initial conditions given by Eq. (3) the maximum temperature, T_{max} is given by Eq. (5) (Kissinger method [5,6]).

$$A/r = E/RT_{\text{max}}^2 \exp(-E/RT_{\text{max}}) \quad (5)$$

Following Eq. (5), $\ln(RT_{\text{max}}^2/r)$ should be linearly related to $1/T_{\text{max}}$. Fig. 2 shows the data from the experiments carried out at heating rates between 1 and $10^{\circ}\text{C min}^{-1}$. (Table 1) interpolated by the best fitting straight line which gives the apparent kinetic parameters $E_{\text{app}} = 27 \text{ kcal mol}^{-1}$, and $A_{\text{app}} = 0.5 \times 10^6$. A better fitting is obtained if experimental data encompassing smaller temperature intervals are considered. In this case, however the calculated apparent kinetic parameters depend on the temperature range (Table 2). Apparent A and E values in Table 2 are correlated with r , both decreasing with an increasing rate of heating as shown for E in Fig. 2. This suggests that in terms of formal kinetics at the heating rates of $10^{\circ}\text{min}^{-1}$ and above, we are measuring the ‘diffusion-limited kinetics’ of PDMS thermal degradation which can be ultimately described by means of

Table 2
Experimental values of apparent activation energy and pre-exponential factor in different intervals of heating rate for PDMS in nitrogen

r , interval ($^{\circ}\text{min}^{-1}$)	E_{app} (kcal mol^{-1})	A_{app} (s^{-1})
1–4	51.09	0.32×10^{12}
1–5	44.00	0.64×10^{10}
1–7	31.30	0.60×10^7
1–10	26.76	0.50×10^6
5–10	20.60	1.60×10^5

evaporation rates of the degradation products. Among the cyclic products of PDMS thermal degradation the smallest and the most abundant is hexamethylcyclotrisiloxane, with an enthalpy of evaporation of $13.2 \text{ kcal mol}^{-1}$ [7]. This can therefore be considered to be the lowest limit of the apparent energy of activation of diffusion/evaporation to PDMS degradation products (Fig. 3).

In the region of r being $1\text{--}4^{\circ}\text{min}^{-1}$ the value of the activation energy is approaching the upper limit, which may have a real value of the kinetic-limiting reaction. The comparatively high order of the pre-exponential factor (12, Table 2), and the similarity between the highest estimated E_{app} (51 kcal mol^{-1}) and the calculated value for the transitional state in PDMS cycles splitting thermal degradation ($61.2 \text{ kcal mol}^{-1}$, see below) supports this idea. At the heating rates between the two, the overall value of E , $26.76 \text{ kcal mol}^{-1}$, ($1 < r < 10$) suggests that the process of thermal degradation of PDMS takes place in a mixed diffusion-kinetic controlled zone.

This can be expressed by the proposed semi-empirical equation:

$$E_{\text{app}} = (D + \Delta H_v)/(1 + e^{-(r-a)/b}) \quad (6)$$

where D (dissociation) and ΔH_v (evaporation) combine to a ratio depending on the heating rate (Fig. 3).

3.2. Thermogravimetry simulation

The classical kinetic approach used to describe and predict PDMS thermogravimetric behavior at practically relevant heating rates ($>5^{\circ}\text{C min}^{-1}$) is therefore worthless because of the mixed bond scission products and diffusion regime.

Whereas the use of parameters calculated by Chemical Kinetics Simulator (CKS), IBM Co. software, allows a most useful and reliable prediction [8,9].

The CKS allows us to program the reaction temperature conditions to follow either a *linear program* or an arbitrary *external profile* (experimental TG analysis). Following a *linear program* allows us to set linear time-dependence of the temperature in the form of the first-order equation:

$$T(t) = T_i + b(t) \quad (7)$$

where $T(t)$ is the instantaneous temperature, T_i the initial temperature, b the slope, and t is the time.

The simulation is carried out under variable volume conditions since the solid sample undergoes marked changes during the reaction. This allows the concentrations to be continuously recalculated as thermolysis proceeds, and ensures that any rate constant extracted from the simulations are consistent. The rate constants can be checked by comparison of experiment and simulations for several heating rates, and by isothermal decomposition conditions.

The outputs of the simulation are amounts vs. time and temperature, and volume vs. temperature. For a

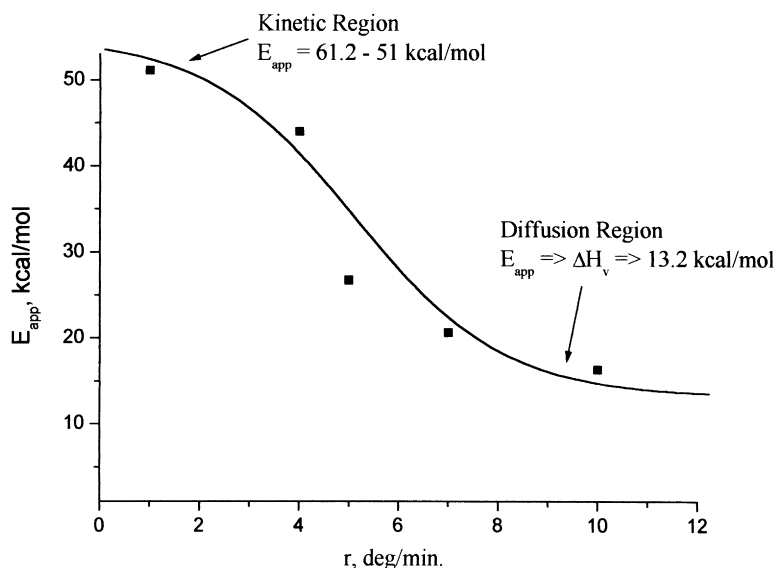


Fig. 3. Semi-empirical equation of E_{app} vs. r : $E_{app} = (D + \Delta H_v)/(1 + \exp(-r - a)/b))$; $a = 5.2 \pm 0.3$, $b = -1.1 \pm 0.2$, $D = 61$.

direct comparison to the thermogravimetric data, the simulation results have to be exported to a spreadsheet for the calculation of weight as a function of time and temperature. Initial values for the iterative procedure of CKS software can be selected on the basis of any suitable procedure.

However, the best fit for $r = 10^\circ\text{C min}^{-1}$ is obtained when Kissinger A and E data are used as starting values for optimizations that are simultaneously adjusted (simulated-optimized curve, Fig. 1): $E_{app} = 25.11 \text{ kcal mol}^{-1} \pm 1.16 (4.5\%) - 105.0 \text{ kJ mol}^{-1}$

$$\ln(A_{app}) = 14.73 \pm 1.15 (8.0\%); A_{app} = 0.25 \times 10^7 \text{ s}^{-1}$$

Whereas fitting failed when one Kissinger parameter was kept constant in the adjusting procedure (simulated curve, Fig. 1) or when the guess starting values were used.

3.3. Mechanism of PDMS thermal degradation

Similarity of the results obtained here and those of the literature referring to linear PDMS, indicates that the cross-linking density of our PDMS is too low to affect the thermal degradation path. The thermally weakest bond in PDMS is the C–Si bond (78 kcal mol^{-1}) [10], however the cyclic oligomers formed by its decomposition suggest that the Si–O bond ($108 \text{ kcal mol}^{-1}$) [10] should break instead.

This fact suggests that the depolymerization of PDMS could be governed mainly by the molecular structure and kinetic consideration, and not by bond energies.

In early studies, it has been found that the formation of intramolecular, cyclic transition state as the rate-determining step in PDMS thermal degradation required an activation energy about 40 kcal mol^{-1} [11]. Silicon d orbital participation is postulated with siloxane bond rearrangement leading to

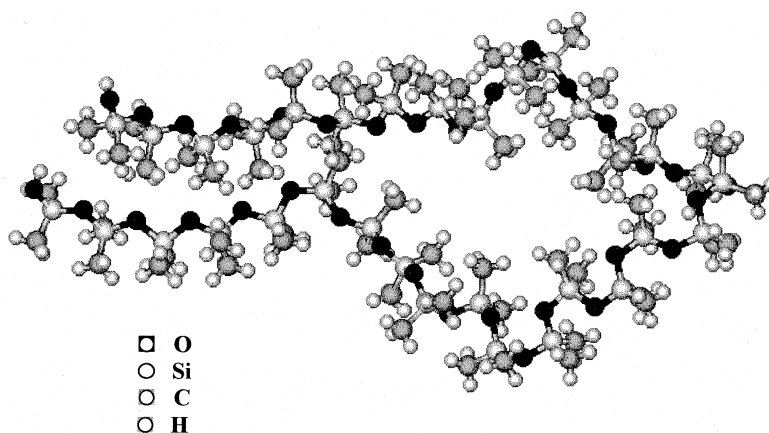


Fig. 4. A model of PDMS (m.w. = 2432) geometrically optimized using the Polak–Ribiere Algorithm (HYPERCHEM 5.0).

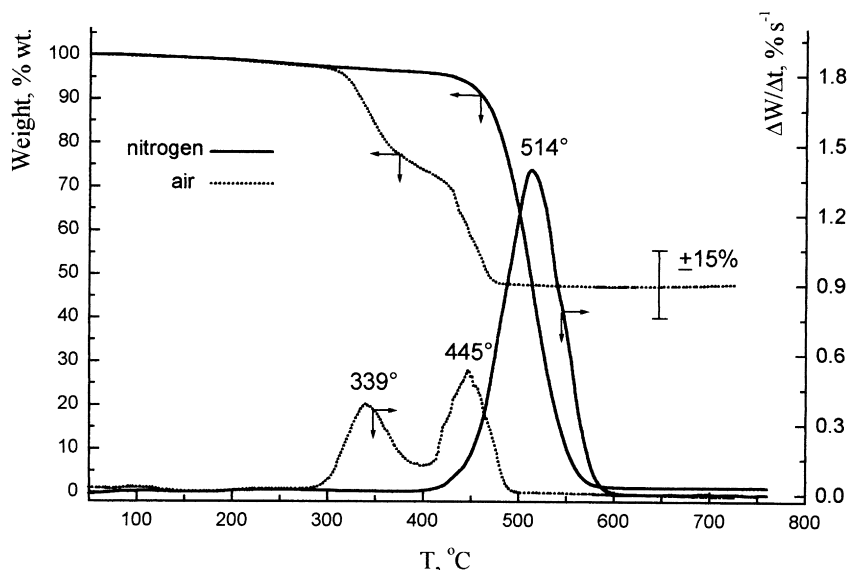
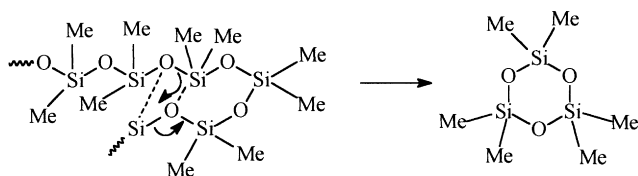


Fig. 5. TG and DTG curves of PDMS in nitrogen (solid line) and in air (dotted line) at a heating rate of $1^{\circ} \text{min}^{-1}$.

the elimination of cyclic dimethylsiloxane and the shortening of the residual chain length. This mechanism can be illustrated for the formation of the smallest cyclic product, hexamethylcyclotrisiloxane.



This transition state can be formed at any point of the polymer chain, as shown by the model chain fragment of PDMS (Fig. 4, m.w. = 2432, 32 monomer units) optimized using Polak–Ribiere Algorithm (HYPERCHEM 5.0 software, Hypercube) which allows to calculate and display the structure for a molecule in conformation with the minimum energy and minimal atomic forces (Fig. 4).

Assuming that the elementary reaction of PDMS leads to the formation of hexamethylcyclotrisiloxane and of a PDMS shorter molecule with 29 monomer units the calculated energy of the transitional state is $\Delta E^{\ddagger} = 61.2 \text{ kcal mol}^{-1}$.

This value is probably higher than it may be expected because of model limitation to only one cyclic monomer unit-hexamethylcyclotrisiloxane. A more complete model should describe the formation of 4, 5, 6 and higher-members cyclic fragments. The calculated value ($61.2 \text{ kcal mol}^{-1}$) compares however well with that obtained by application of kinetic treatments in the range of heating rate where kinetic control operates ($51.0 \text{ kcal mol}^{-1}$, Fig. 3).

It should be pointed out that this mechanism only operates

in completely trimethylsilylated end-capped PDMS and that in molecules containing some terminal hydroxyl groups, there may be some contribution from end-initiated mechanism.

The above cyclic oligomers splitting process from PDMS

chains will proceed until the residual linear structure is too short to cyclize and/or the evaporation of the shortened chain fragments favorably competes with cyclization.

3.4. Thermal oxidative degradation of PDMS

Thermal oxidative degradation of PDMS in the presence of air gives results much different from the degradation in nitrogen. It has been found that there are, at least, two stages of degradation. At low heating rate ($1^{\circ} \text{C min}^{-1}$, Fig. 5) the first stage takes place at a much lower temperature in air ($T_{\text{max}}^1 = 339^{\circ} \text{C}$) than in nitrogen ($T_{\text{max}} = 51.4^{\circ} \text{C}$), whereas the second begins at a comparable temperature ($T^2 = 400^{\circ} \text{C}$). In both steps the major degradation products are a similar mixture of oligomers as in nitrogen with additional CO_2 and water. Oxidation takes place also on oligomers in the gas phase as shown by a very fine powder observed floating in the carrier gas above 400°C . The residue left at 500°C is shown to be silica by infrared which

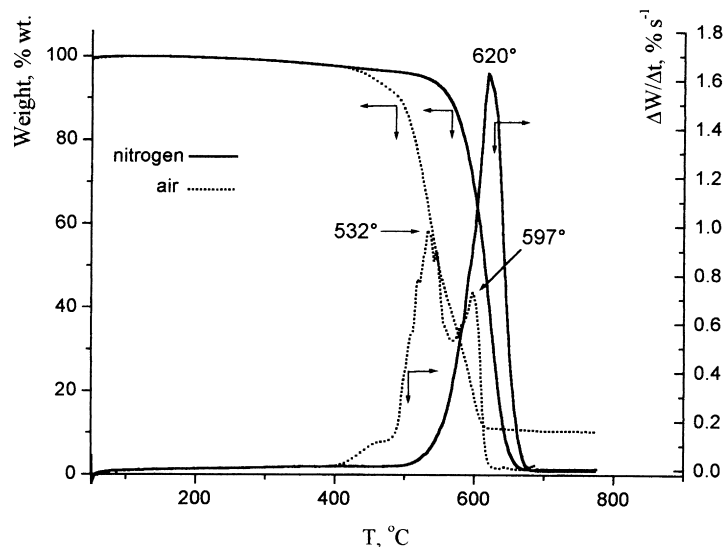
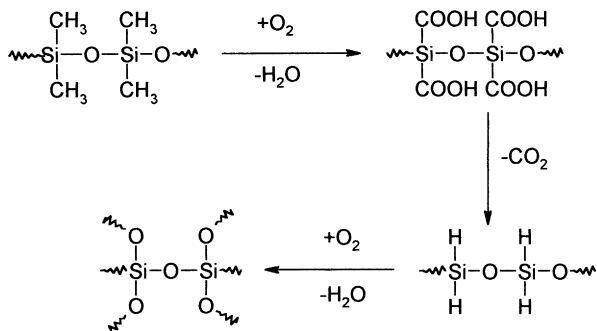


Fig. 6. TG and DTG curves of PDMS in nitrogen (solid line) and in air (dotted line) at a heating rate of 50° min⁻¹.

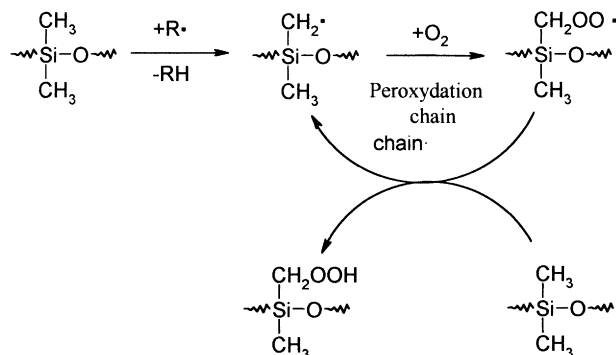
is non reproducible, varying by ±15%, around the average 47%. This is due to the fact that silica from gas phase oxidation randomly falls on the sample pan or on the weighting arm of the balance, adding weight to the silica formed by oxidation in the condensed phase.

The two steps feature of the process can be explained assuming that oxygen catalyses the depolymerization reaction of PDMS to volatile cyclic oligomers, leading to a lower temperature for beginning of weight loss (290°C) than in nitrogen (400°C). However, the fact that lower temperature volatilization is slowed down at about 20–25% weight loss can be explained by condensed phase oxidation of PDMS leading to further tight crosslinking of the polymer with increasing thermal stability:

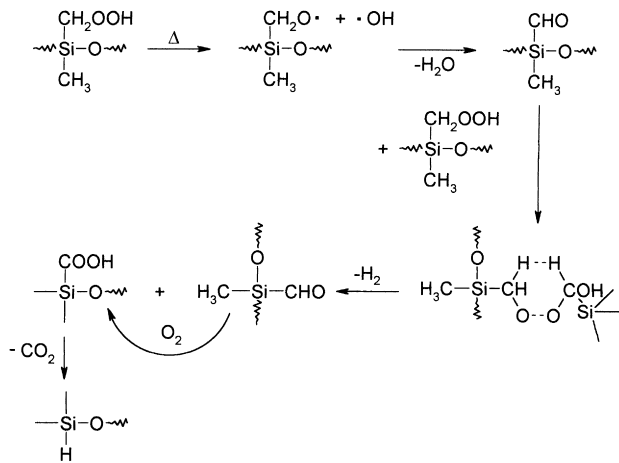


Oxidation is likely to proceed through peroxydation mechanism initiated by adventitious radicals R· (e.g. ‘weak links’ or impurities scission) that gives primary

hydroperoxides:



which as reported in the literature [12] decompose eliminating hydrogen:



Radicals created in the peroxydation chain may also

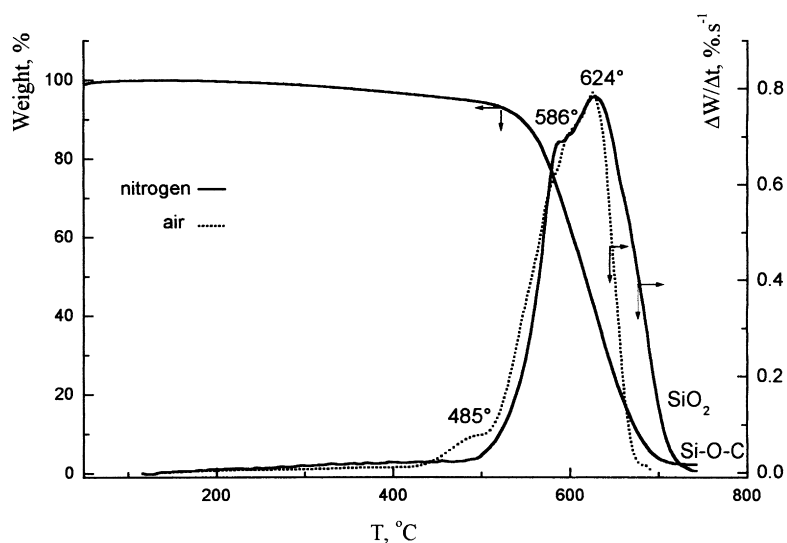


Fig. 7. TG and DTG curves of PDMS in nitrogen (solid line) and in air (dotted line) at a heating rate of $100^{\circ}\text{C min}^{-1}$.

further crosslink by addition to unreacted residual vinyl double bonds. Besides thermal stabilization by oxidative crosslinking also physical oxygen scavenging action of the silica type crosslinked polymer surface might contribute to slow down the weight loss at the end of first step volatilization. The infrared of the residue of this step can not give evidence of the crosslinking Si–O bonds because they exist in the original PDMS structure.

Above 400°C breakdown of the crosslinked structure takes place as for virgin PDMS in nitrogen by molecular splitting of cyclic oligomers with however a higher rate probably due to competing oxidation.

4. Thermal behavior of PDMS at high heating rates

By increasing the heating rate to $50^{\circ}\text{C min}^{-1}$, weight loss shifts to a higher temperature both in nitrogen and in air (Fig. 6) as-expected. However, the first step of weight loss in air overlaps with the second while stabilization due to oxidative crosslinking taking place at a larger weight loss (60%) and the final silica residue decreases to 10% (Fig. 6). Interaction of oxygen with the degrading condensed phase depends on a complex competition between oxygen diffusion and solubility on one side and degradation reaction and products evaporation on the other. On increasing the heating rate, chemical reactions occur at a higher temperature where the solubility of oxygen in the condensed phase decreases and the rate of thermal degradation reactions increases, making the heterogeneous phase reaction of active species with oxygen of air that stabilize the material in the first step, less probable.

At $100^{\circ}\text{C min}^{-1}$ the thermal degradation behavior of PDMS is clearly modified, since the weight loss in nitrogen is now the result of two overlapping processes (DTG: shoulder ($T_s = 586^{\circ}\text{C}$), peak ($T_p = 624^{\circ}\text{C}$)) (Fig. 7).

Moreover, a black residue is left at $700\text{--}800^{\circ}\text{C}$ although small (4%). This indicates that in this condition, the increase in the degradation temperature due to the high heating rate, exposes PDMS and/or slowly diffusing oligomers resulting from depolymerization, to a temperature ($>600\text{--}700^{\circ}\text{C}$) at which a new decomposition process can take place, producing a very stable black solid phase (e.g. silicon carbide or oxycarbide [13–15]).

In air, at $100^{\circ}\text{C min}^{-1}$ the first degradation process is suppressed and the TG curves becomes similar to that obtained in nitrogen (Fig. 7). In this condition the direct reaction of oxygen with the condensed phase either does not take place or it does at a limited extent. The residue (18%) is however larger than that obtained at $50^{\circ}\text{C min}^{-1}$ (10%, Fig. 6) possibly because silica is now formed mostly by gas phase oxidation which is more effective at higher temperatures. On the other hand, the process leading to the black stable residue observed in nitrogen should also occur in air but it is difficult to detect, being finely dispersed in an overwhelming amount of white silica.

5. Conclusions

It is shown that PDMS thermally decomposes to cyclic oligomers through Si–O bond scission in a chain folded cyclic conformation energetically favored by the overlapping of empty silicon d-orbitals with orbitals of oxygen and carbon atoms.

A combination of traditional kinetic formal treatments and computer simulation supplies a method to predict the weight loss of PDMS in any condition.

Kinetic treatment shows that PDMS thermal volatilization, as rate of heating increases, becomes dominated by the rate of diffusion and evaporation of oligomers produced on decomposition.

Thermal oxidation of PDMS catalyses decomposition to cyclic oligomers which occurs at a lower temperature than in nitrogen. This process competes with oxidative crosslinking which stabilizes the material. Further decomposition to cyclic oligomers occurs above 400°C as in nitrogen which is however accelerated by competing oxidation.

At high heating rate (e.g. 100°C min⁻¹) thermal decomposition in nitrogen and in air tend to overlap because rate of reaction between the material and oxygen is strongly reduced by low oxygen solubility and high thermal degradation rate. In nitrogen a small black residue is formed (silicon oxycarbide) which is produced by alternative decomposition path to that leading to cyclic oligomers, that becomes possible at a high heating rate.

Acknowledgements

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