Pyrolysis Kinetics of Highly Crosslinked Polymethylsiloxane by TGA

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SYNOPSIS

The pyrolysis kinetics of highly crosslinked polymethylsiloxane (PMS) was investigated by thermogravimetric analysis (TGA) under both isothermal and elevated temperature conditions with several environmental gases, such as oxygen, nitrogen, air, and helium. A non-chain-scission mechanism composed of initiation, propagation, and termination was proposed to interpret the thermal degradation of highly crosslinked PMS. The mechanism was verified by the experimental results under isothermal conditions. The activation energy of initiation, E_i, was about 20–30 kcal/mol and the activation energy of propagation, E_p, was about 4–6 kcal/mol. These activation energies were found to be different for different gases. The activation energy of initiation for PMS in an aggressive atmosphere, such as oxygen, was lower than that in an inert atmosphere, such as nitrogen. But the activation energy of propagation for PMS was higher in an active environment than in an inert one. There were no direct conclusions about the thermal degradation of highly crosslinked PMS at elevated temperature. Based on thermogravimetric experiments, it is suggested that a pyrolysis process be conducted with a rate of temperature increase less than $10°C/min$ for preparing the silicon base inorganic membrane.

INTRODUCTION

Pyrolysis is a very important step in the polymerization–pyrolysis process for preparing silicon base inorganic membranes.[1,2] This process has been used to produce inorganic membranes which are excellent candidates for membrane gas separation at high temperature.[3] There have been some studies[4–19] on the thermal degradation characteristics of commercially interesting cyclic and linear polydimethylsiloxanes (PDMS), which have very low or even zero crosslinking degree as shown in Figure 1. Due to its intrinsic nature, pyrolysis of PDMS produces mainly cyclic molecules such as $[(CH_3)_2SiO]_3$ and $[(CH_3)_2SiO]_4$ and traces of H_2 and CH_4. Bannister and Semlyen[12] used the concept of the siloxane bond interchange process to interpret the result of the thermal degradation of cyclic as well as linear PDMS. However, to our knowledge, there is nothing in the literature dealing with the thermal degrada-

tion characteristics of a 3-dimensional polymethylsiloxane (PMS), which is the intermediate product of silicone base inorganic membranes as shown in Figure 2. This kind of polymer itself is not industrially interesting. This insoluble and unmelted PMS has more than 50% crosslinking degree. PMS has, furthermore, the $Si — O — Si$ crosslinking bonds (which are formed in the polymerization) instead of the $Si — CH_2 — CH_2 — Si$ crosslinking bond (which is formed in vulcanization of PDMS by coupling the polymer radicals). Due to the reasons mentioned above, PMS probably follows a mechanism different from that followed by PDMS in thermal degradation.

Thermal decomposition of a polymer is probably one of the oldest techniques still being used to study the nature and structure of a polymer undergoing pyrolysis. The present study, however, is more concerned with the final product of the pyrolysis. For instance, the pyrolysis kinetics of poly(vinyl chloride)s and poly(vinylidene chloride)s have been extensively studied by several investigators[20–24] in order to elucidate how the carbon molecular sieve was produced by pyrolizing the poly(vinyl chloride)s. The investigation of the pyrolysis kinetics

$$\begin{array}{c}
\underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\\
-Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}\\
\underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_2}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\\[4pt]
\underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_2}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\\
-Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}\\
\underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}
\end{array}$$

Figure 1 Structure of PDMS.

$$\begin{array}{c}
\underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\\
-Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}\\
\underset{\mid}{O}\quad \underset{\mid}{O}\quad \underset{\mid}{O}\quad \underset{\mid}{O}\quad \underset{\mid}{O}\\
-Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}\\
\underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}\quad \underset{\mid}{CH_3}
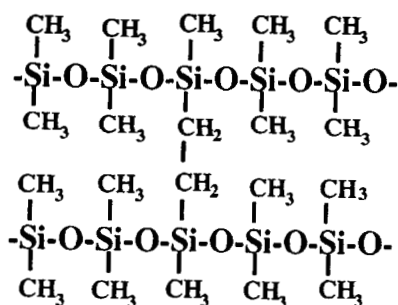\end{array}$$

Figure 2 Structure of PMS.

of PMS will be of great value in understanding the underlying mechanism involved as well as in finding the activation energy of the reaction. Furthermore, this study will also be useful in simulating the pyrolysis process which will allow us to control the final membrane properties.

MODEL

The basic idea of the pyrolysis step is that, under suitable conditions, a 3-dimensional PMS (which has been polymerized inside of the pores of a porous support material) will bring about a scission reaction involving its substituted group while the main chain itself remains intact. This kind of decomposition is called non-chain-scission reaction, or side group decomposition. This idea comes from the analysis of the covalent bond energy of the silicon and other different atoms in the PMS, such as oxygen, carbon, and hydrogen. From the set of data listed in Table I,[25] it is easy to observe that the siloxane bond, Si—O, is not the weakest bond in highly crosslinked PMS molecules. This leads to a breakdown of the Si—C bond and the formation of a rigid inorganic framework with open pores, which had originally been occupied by the substituted groups. For instance, at temperatures above 400°C, the PMS may oxidize, presumably by the following reactions:
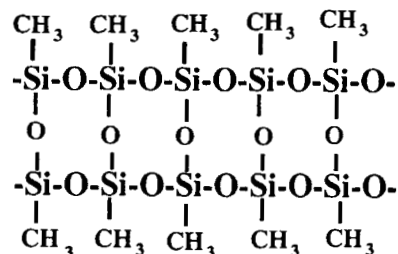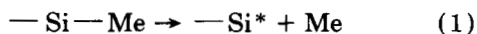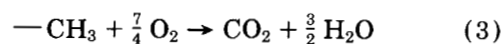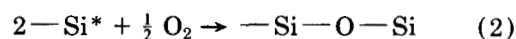
$$-Si-Me \rightarrow -Si^* + Me \qquad (1)$$

Here the superscript * means that the atom or group are in an activated state:

$$2-Si^* + \tfrac{1}{2}O_2 \rightarrow -Si-O-Si \qquad (2)$$

$$-CH_3 + \tfrac{7}{4}O_2 \rightarrow CO_2 + \tfrac{3}{2}H_2O \qquad (3)$$

These three reactions convert the PMS to silica.

It is assumed that reaction (1) is the rate-controlling reaction: As soon as the activated silicon and methyl groups are formed, silicon will react immediately, according to eq. (2), to form silica, and the methyl group will either evaporate or burn to give carbon dioxide and water, according to eq. (3). Since the volatile molecules evaporate under the operating conditions (high temperature and high flow rate of carrying gas), a directly measurable quantity for these reactions is the residual weight of the sample.

Theoretical treatments for thermal decomposition of polymers are generally classified into two categories: random decomposition and chain decomposition.[26,27] These divisions are closely analogous to the two distinct mechanisms of polymerization, i.e., step polymerization and chain polymerization. In the thermal decomposition of polymer, however, the initiation conditions are different, where one starts with polymers with finite initial size. A non-chain-scission mechanism is proposed for the thermal decomposition of PMS, which implies a scission reaction involving a substituted group, with the main chain itself remaining intact. The mechanism, similar to that of poly(vinyl chlo-

Table I   Approximate Bond Dissociation Energies (D) and Bond Lengths (r) for Si—X and C—X

| Bond	Compound	D/KJMO	n (nm)	Bond	D/KJMO	r (nm)
Si—C	Me$_4$Si	318	0.189	C—C	334	0.153
Si—H	Me$_3$Si	339	0.148	C—H	420	0.109
Si—O	Me$_3$SiOMe	531	0.163	C—O	340	0.141
Si—N	(Me$_3$Si)$_2$N	320	0.174	C—N	335	0.147

ride) and poly(vinyl acetate),[21-24] may be adopted here for chain-type decomposition in the propagation step.

The primary steps in the chain-type decomposition are composed of initiation, propagation, and termination. The mechanism may be represented by the following series of equations:

Initiation:

$$P \rightarrow D_1 + Me \qquad (4)$$

Propagation:

$$D_1 \rightarrow D_2 + Me$$
$$\vdots$$
$$D_n \rightarrow D_{n+1} + Me \qquad (5)$$
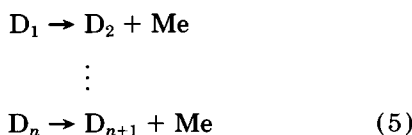
where P represents a degradable end of a PMS polymer, which has a degradable ends concentration of [P], D_n represents a PMS chain in which n number of bonds between silicon and carbon have been broken in conjugation, and Me represents the methyl group.

The propagation steps can be illustrated as shown in Figure 3, which shows that propagation occurs at the Si — C bond conjugating with the activated silicon atom. It is assumed that the propagation rate constants, K_p, for the removal of each methyl group after a chain is initiated, are all equal. The scission rate of methyl group is the sum of propagation and initiation rates. Termination occurs when the non-chain-scission reaction has propagated to the end of a chain or to some point of structural imperfection, such as the polymer connecting to the support material which blocks further methyl group scission. For initiation,

$$\frac{d[Me]}{dt} = K_i[P] \qquad (6)$$

For propagation,

$$\frac{d[Me]}{dt} = K_p \sum_{r=1}^{n-1} [D_{r+1}] = K_p K_i[P]t \qquad (7)$$

So, total scission rate of methyl group is

$$\frac{d[Me]}{dt} = K_p K_i[P]t + K_i[P] \qquad (8)$$

If $K_i[P]$ is negligible compared with $K_p K_i[P]t$, then

$$\frac{d[Me]}{dt} \cong K_p K_i[P]t \qquad (9)$$

Assuming [P] remains approximately constant at the early stage, the following result is obtained by integrating eq. (9):

$$[Me] \cong \tfrac{1}{2} K_p K_i[P]t^2 \qquad (10)$$

Thus, a plot of $d[Me]/dt$ vs. time will result in a straight line in the early stages of pyrolysis. In other words, the amount of methyl group produced will be linearly proportional to the reaction time squared.
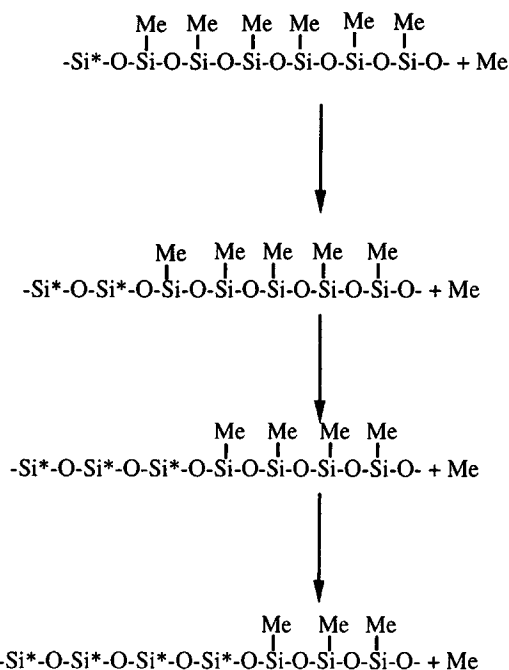
According to the proposed mechanism, a maximum rate of reaction will occur when the initiation rate equals the termination rate, which is usually called the stationary state. This condition will give a relationship to evaluate the propagation rate constant K_p. The average time taken for each successive methyl group to be evolved from an initiated chain is $1/K_p$ s. The initiated chain has N units (number average between the degradable end and the end of a chain, or between the degradable end and the imperfect structure which prevents further propagation). The first initiated chain will, therefore, be terminated in N/K_p s. Consequently, the time taken for the maximum rate of the reaction to occur will be the lifetime of the kinetic chain. Then,

$$N/K_p = t_{max} \qquad (11)$$

EXPERIMENTS

Instrument

A TGA 7 thermogravimeter (Perkin-Elmer) was used to follow the weight loss due to pyrolysis. The instrument permits temperature programing, data recording, and calculation using the accompanying PE 7500 professional computer. The temperature scale of the thermogravimetric balance has been calibrated prior to its use. A given environment (inert or active) is maintained by flowing the desired gas at a constant rate about 60 cm³/min through the balance. This flow rate is adequate to overcome the thermal fluctuation. The sample is placed in a platinum crucible and directly weighed by the balance. At the end of each experiment, the resulting thermograms are either transferred to a plotter or read out from the computer screen.

Me Me Me Me Me Me
 | | | | | |
-Si*-O-Si-O-Si-O-Si-O-Si-O-Si-O- + Me

↓

Me Me Me Me Me
 | | | | |
-Si*-O-Si*-O-Si-O-Si-O-Si-O-Si-O- + Me

↓

Me Me Me Me
 | | | |
-Si*-O-Si*-O-Si*-O-Si-O-Si-O-Si-O- + Me

↓

Me Me Me
 | | |
-Si*-O-Si*-O-Si*-O-Si*-O-Si-O-Si-O- + Me

Figure 3   Propagation steps of highly crosslinked PMS thermal degradation.

Measurement of Weight Loss

The weight of sample is continuously monitored as a function of time or temperature, which is programmed into two stages:

The Degassing Stage

The temperature is increased from 30°C to the degassing temperature, 250°C, at the rate of 40°C/min, and then held steady for 30 min. During this time, no chemical reaction occurs except the evaporation of water and other gases adsorbed in the sample.

The Pyrolyzing Stage

Isothermal Condition. The temperature is increased from the degassing temperature, 250°C, to the desired temperature at the rate of 40°C/min, and then held steady for 600 min. During this time, the pyrolysis reaction takes place. The pyrolysis of PMS at isothermal condition is conducted in oxygen, nitrogen, helium, and air.

Elevated Temperature Condition. The temperature is increased from the degassing temperature, 250°C, at a constant rate of 10°C/min up to 900°C, and then stopped. During this time the pyrolysis reaction takes place. The pyrolysis of PMS at nonisothermal condition is also conducted in oxygen, nitrogen, helium, and air.

Identification of Pyrolysis Products

Some preliminary experiments have been conducted to qualitatively identify the residue of pyrolysis product by FTIR. The experimental results did prove that the methyl groups were lost during pyrolysis.

Reference

In order to avoid the biases in a programmed process, a reference has to be run. In the reference operation, 30 mg of the blank Vycor porous glass powder (which is the typical quantity of a sample) is placed in a sample holder. The data for this run is recorded as the reference for the very next sample run at the same programmed process conditions. In this way, any difference in the rate between the sample run and the reference run should be directly induced by the pyrolysis of the PMS. Experimentally, the plot of the reference run is almost a horizontal straight line, which means that the Vycor porous glass can be treated as an inert material at these tested temperatures.

Sample

The PMS–Vycor glass membranes used in this work are all prepared at the same condition (temperature, catalyst, and monomer concentration), so that physical properties such as the average molecular weight and the concentration of degradable ends of the polymer may be assumed to be the same without further verification.

Pyrolysis Gas

All gases used were ultrahigh purity grade (99.9 mol %) from the Linde Division of Union Carbide Corp.

THEORETICAL DATA TREATMENT

The thermogravimetric data of residual weight versus time and/or temperature are recorded for kinetic analysis. The empirical active weight fraction h is generally defined as[28]

$$-h = \frac{W_0 - W}{W_0 - W_\infty} \qquad (12)$$

where W_0 is the initial sample weight before pyrolysis, W_∞ is the final residual weight, and W is the weight of residue remaining at any time and/or

temperature during pyrolysis. If the measured data for the sample run and corresponding reference run are recorded at the same temperature or time, the real empirical active weight fraction h is redefined by

$$-h = \frac{(W_{0s} - W_{0r}) - (W_s - W_r)}{(W_{0s} - W_{0r}) - (W_{\infty s} - W_{\infty r})} \quad (13)$$

where the subscripts s and r denote the sample and reference values, respectively.

The rate equation can be conveniently written as:

$$-\frac{dh}{dt} = kf(h) \quad (14)$$

where k is the apparent specific rate constant and the particular form of $f(h)$ depends on the type of kinetic process.

Isothermal Condition

If reaction (1) is the controlling step, then the formation rate of methyl group at isothermal conditions, $d[\mathrm{Me}]/dt$, is proportional to the rate of change of empirical active weight fraction. By multiplying by a proportionality factor F, the following equation results:

$$\frac{d[\mathrm{Me}]}{dt} = -\frac{dh}{dt} F \quad (15)$$

Substituting eq. (15) into eq. (9) yields

$$-\frac{dh}{dt} F \cong K_p K_i [\mathrm{P}] t \quad (16)$$

The dependency of the reaction rate on temperature is usually expressed by the Arrhenius law:

$$k = A \exp(-E/RT) \quad (17)$$

where k, E, and A are the apparent specific rate constant, Arrhenius activation energy, and frequency, respectively.

Nonisothermal Condition

For the case of constant rate of temperature increase, the temperature can be expressed as

$$dT = B \, dt \quad (18)$$

or

$$T = T^0 + Bt \quad (19)$$

where T^0 is the initial temperature at the begining of pyrolysis, B is the rate of temperature increase, and t is the time.

Substituting eq. (18) into eq. (8) yields

$$\frac{d[\mathrm{Me}]}{dT} B = K_p K_i [\mathrm{P}] t + K_i [\mathrm{P}] \quad (20)$$

If $K_i[P]$ is negligible compared with $K_p K_i[\mathrm{P}]t$ at elevated temperature conditions, and if [P] remains approximately constant at the early stage of pyrolysis, according to eqs. (17) and (15), eq. (20) can be written as

$$\frac{-dh}{dT} \frac{1}{t} = \frac{A_i A_p}{BF} [\mathrm{P}] \exp\left[\frac{-(E_i + E_p)}{RT}\right] \quad (21)$$

RESULTS AND DISCUSSIONS

If the non-chain-scission mechanism proposed for the thermal degradation of PMS is correct in the early stages of the isothermal reaction, the plot of the rate of empirical active weight fraction vs. time will be a straight line according to eq. (16), and then will approach a maximum as shown in Figure 4. Figures 4–6 show the experimental kinetic data of a PMS–Vycor glass membrane pyrolizing in oxygen at different temperatures. These experimental observations seem to substantiate the theoretical treatment presented above. The experimental results for the other three gases, nitrogen, air, and helium, show similar trends. Figure 4 shows a tendency that as the isothermal pyrolysis temperature increases, the maximum point in the rate curve will shift to the left, and the dh/dt value at the maximum point will increase. Using the data shown in Figures 4 and 6, the specific rate constants of initiation and propagation for oxygen at different temperatures can be calculated. These results together with similar data for the other gases are listed in Table II. Then the activation energy of initiation and propagation can also be calculated from Figures 7 and 8. These results are listed in Table III.

From the specific rate data listed in Table II, one can observe that the rate of propagation is much faster than the rate of initiation. Thus, it is reasonable to assume that the formation rate of methyl group is primarily due to propagation. Comparing
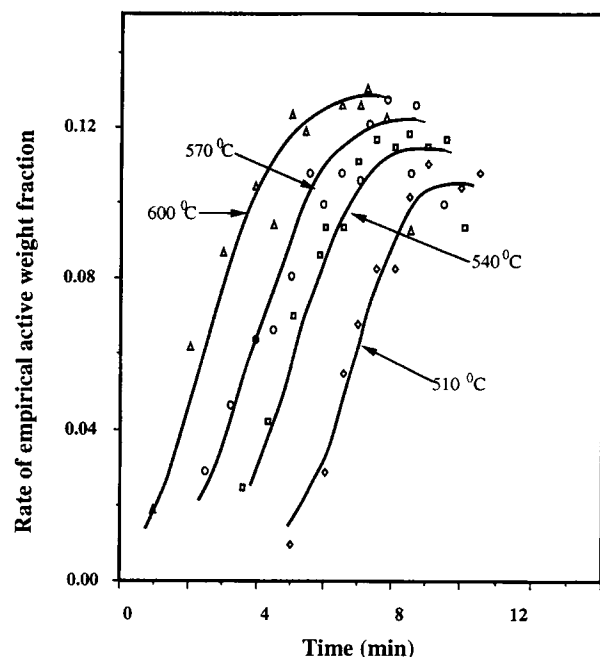
Figure 4 t_{max} for thermal degradation of PMS in oxygen.

Table II   Specific Rate Constants of Initiation and Propagation at Different Temperature for Different Atmosphere

Gas	Temperature (°C)	$K_i[P]N/F$ (min^{-1})	K_p/N (min^{-1})
O$_2$	510	0.02149	0.1124
O$_2$	540	0.03956	0.1264
O$_2$	570	0.05850	0.1349
O$_2$	600	0.08409	0.1645
N$_2$	510	0.0165	0.1158
N$_2$	540	0.02987	0.1207
N$_2$	570	0.06366	0.1332
N$_2$	600	0.1046	0.1517
He	510	0.01983	0.1071
He	540	0.04787	0.1215
He	570	0.07371	0.1243
He	600	0.11277	0.1368
Air	510	0.02006	0.1118
Air	540	0.04784	0.1154
Air	570	0.06263	0.1271
Air	600	0.08318	0.1696

the activation energy data for initiation, E_i, and propagation, E_p, listed in Table III, one may conclude that the propagation step is much easier than the initiation step since E_i is higher, for every gas, than E_p.

The experiments on pyrolysis conducted with different gases give a good opportunity to inspect the effects of environment on the process. Since the experimental data for all gases show a maximum value in the rate curve and a linear relation in the early stage, it is logical to infer that the pyrolysis of PMS in different gases follows the same proposed non-chain-scission mechanism.

It should be pointed out that the activation energy of initiation is lower for an aggressive gas, such as oxygen or air, than that for an inert one, such as nitrogen or helium. It is possible that the active environment, acting as catalyst, can reduce the energy required for silicon atom to become activated. Consequently, the initiation of PMS is less sensitive to the temperature change of an active environment than to that of an inert one. The activation energy of propagation is higher, however, in an active atmosphere than in an inert one.

It is expected that the activation energies, E_i and E_p, for oxygen and for air are very close. If the PMS reacts independently with nitrogen and oxygen, both being the main portion of air, then the activation energy of initiation, E_i, for air will presumably be lower than that for nitrogen, but much higher than

that for oxygen. It appears that the PMS responds only to the oxygen in the air. This phenomenon can be related with the thermodynamic equilibrium of silica and silicon nitride at 800 K^{29} as shown below:

$$Si_3N_4(c) = 3\ Si(l) + 2\ N_2(g),\quad \log K_p = 31.350$$

$$SiO_2(c) = Si(l) + O_2(g),\qquad \log K_p = 49.912$$
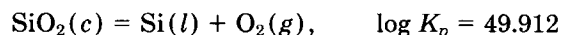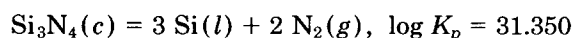
Based on the difference in the values of the equilibrium constants for the two reactions, the formation of silica predominates when PMS is pyrolized in air.

The experimental data of PMS pyrolizing at an elevated temperature for different gases are shown in Figure 9. The data from Figure 9 may also be plotted by using eq. (21), as shown in Figure 10. No evidence is available to prove that, in the early stage of pyrolysis, the plotting of $\ln[(-dh/dT)(1/t)]$ vs. $1/T$ (Fig. 10) is a straight line with the slope equal

Table III   The Activation Energy of Initiation and Propagation for Different Atmosphere

Gas	$-E_i$ (kcal/mol)	$-E_p$ (kcal/mol)
Oxygen	20.4	5.4
Nitrogen	28.5	4.1
Helium	25.7	3.4
Air	20.7	6.0
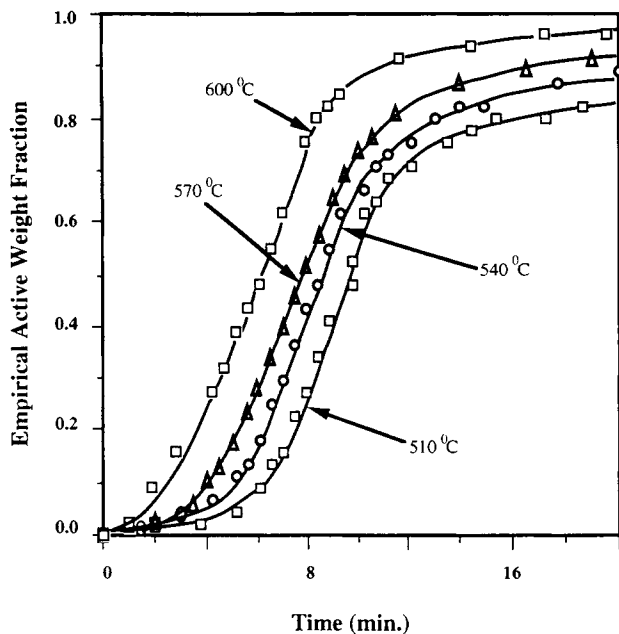
Figure 5 Thermal degradation of PMS in oxygen.

Figure 7 ln K_i vs. $1/T$ for different gases.

to $(E_i + E_p)$. For a constant heating rate thermo-gravimetric analysis, the experimental results may suggest that either the assumption of [P] remaining approximately constant at the early stage, or, the simplification by neglecting K_i[P] in eq. (8) no longer holds under the circumstances. Consequently, the total rate equation can no longer be represented
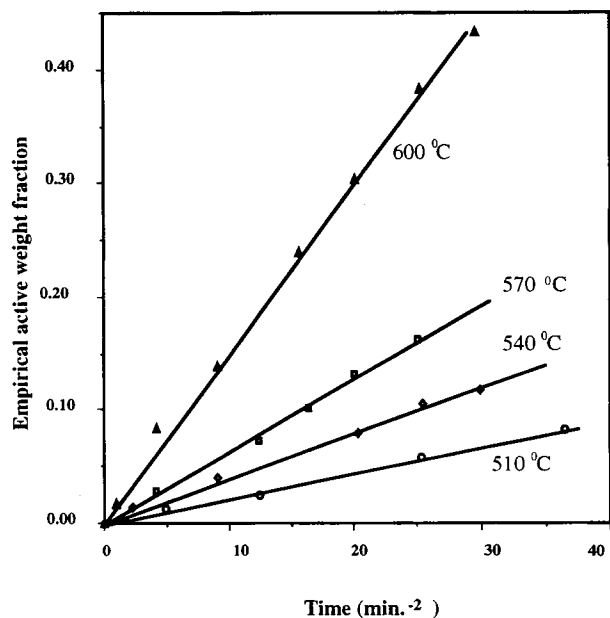
by eq. (9). Another difficulty of correlating the thermogravimetric data at an elevated temperature may also be attributed to the buoyance effect. It is suggested that a pyrolysis process which has a temperature increase rate above $10°C/min$ may be avoided in preparing the silicon base inorganic membrane.

Figure 6 Square root relationship for thermal degradation of PMS in oxygen.
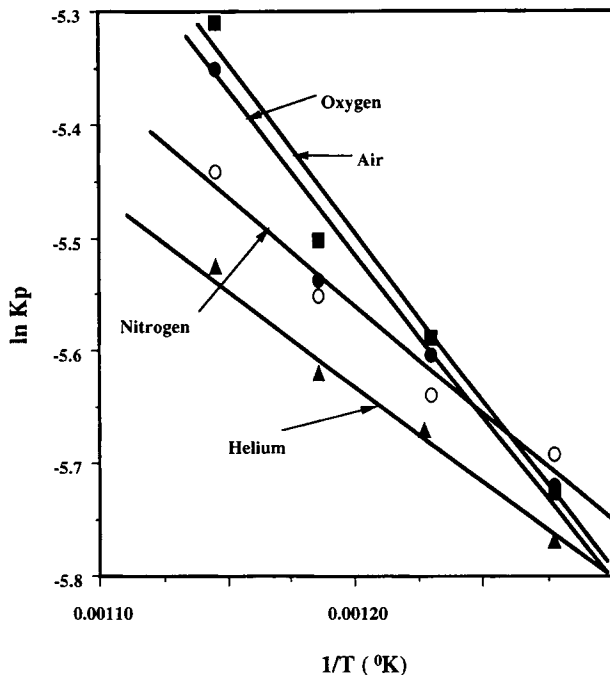

**Figure 8** ln K_p vs. $1/T$ for different gases.

CONCLUSIONS

The present investigation provides several conclusions. The thermal degradation of highly crosslinked polymethylsiloxane seems to follow a non-chain-scission mechanism consisting of initiation, propagation, and termination under isothermal conditions. According to this mechanism, a linear relationship between the rate of change of empirical active weight fraction and time would be observed in the early stage of pyrolysis; then it would approach a maximum. The initiation step of polymethylsiloxane for all gases used in this investigation, had a higher activation energy than the propagation step. The initiation step of polymethylsiloxane had a lower activation energy in an aggressive atmosphere, such as oxygen, than in an inert atmosphere, such as nitrogen. But the propagation step had a higher activation energy in an active environment than in an inert one. More efforts are needed to interpret the elevated temperature thermogravimetry of highly crosslinked poly(methylsiloxane).

NOMENCLATURE

A	frequency: initiation, A_i; propagation, A_p
B	temperature increasing rate constant
$[D_r]$	concentration of PMS chain in which r number of bonds between silicon and carbon have been broken in conjugation
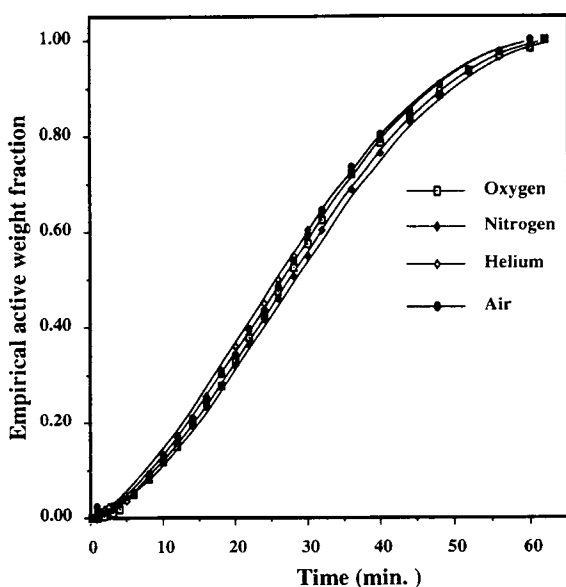
Figure 9   The empirical active weight fraction of PMS thermal degradation in different gases at elevated temperature.
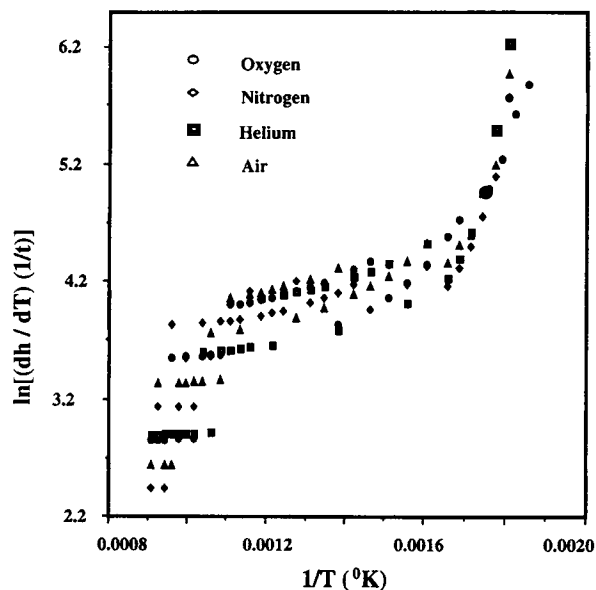
Figure 10   The plot of $\ln[(-dh/dT)(1/t)]$ vs. $1/T$.

E	activation energy: initiation, E_i; propagation, E_p
F	Proportionality factor
h	Empirical active weight fraction, defined by eq. (12)
K	Specific rate constant: initiation, K_i; propagation, K_p
$[Me]$	Concentration of methyl group
n	Number of monomer units in a species (n-mer) produced by decomposition
N	number of monomer units in the original molecular
$[P]$	concentration of degradable ends
R	gas constant
t	time
T	temperature
W	species weight: initial sample weight before pyrolysis, W_0; final residual weight, W_∞; weight of residue remaining at any time and/or temperature during pyrolysis, W

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