Thermal Behavior and Curing Kinetics of Poly(carbosilane)

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SYNOPSIS

This study focuses on the thermal behavior and curing kinetics of a commercially available poly(carbosilane). Poly(carbosilane) is used for the production of silicon carbide (SiC) fibers by high-temperature pyrolysis. Thermal characterization studies were carried out by employing a differential scanning calorimeter and thermogravimetric analyzer. The change in the chemical structure during curing with oxygen was studied with an infrared spectrometer. It was found that the uncured poly(carbosilane) would froth under a nitrogen environment around 450°C. Curing with oxygen, which results in crosslinking at the surface, enables the sample to retain its shape during high-temperature pyrolysis. Curing was carried out at various temperatures, and the kinetics of the curing reactions were characterized.

INTRODUCTION

Manufacture of high-strength silicon-based non-oxide ceramics, which exhibit high resistance to oxidation, corrosion, and thermal shock by high-temperature pyrolysis of organometallic polymer precursors, has recently received considerable attention.[1] One example of the organometallic chemistry route commercialized by Nippon Carbon in Japan under the trade name Nicalon is the production of the SiC fiber from poly(carbosilane).[2] These fibers are principally used as reinforcements in making light, strong, and durable composite materials that can replace metals in aerospace, chemical, and auto industries. The conversion of poly(carbosilane) into silicon carbide, depicted in Figure 1, involves shaping and curing the fibers, followed by high-temperature pyrolysis, which results in the conversion of the polymer to a ceramic.

Curing in an oxygen environment results in the crosslinking of poly(carbosilane) at the surface, enabling the fiber to retain its shape during curing.[3] In addition, the curing prevents the loss of small organic volatiles during the initial stage (up to 350°C) of the pyrolysis process. The principal focus of the study here is the curing kinetics and thermal

characterization of poly(carbosilane). Such information should be useful for the processing of poly(carbosilane) fibers, as well as that of the thicker ceramic articles,[4] the porosity development aspects of which were also studied.[5]

MATERIALS

Poly(carbosilane) has the following nominal structure:[6]

$$-\begin{bmatrix} R_1 & R_3 \\ | & | \\ -Si-CH_2-Si- \\ | & | \\ R_2 & R_4 \end{bmatrix}_n -,$$
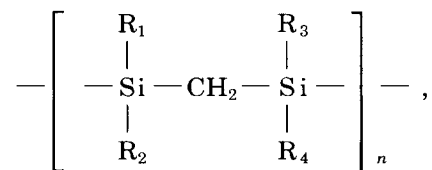
where R_1, R_2, R_3, and R_4 are hydrogen, alkyl, aryl, silyl group or a halogen.[6] The poly(carbosilane) used in our study was prepared by the conversion of monosilane to polysilane, which was then polymerized with poly(borosiloxane) at 350–500°C.[7]

The commercially available poly(carbosilane) used in the study here has a pale yellow, lumpish appearance. It is completely soluble in n-hexane and insoluble in water. Its specific gravity is 1.12 at 30°C and its mean molecular weight and melting point lie within the ranges of 1420–1450 and 200–240°C, respectively. In all the experiments here, small par-
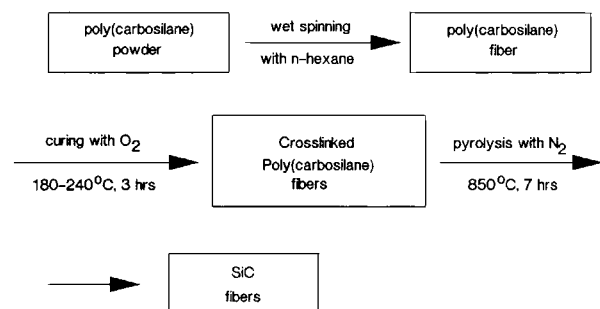

Figure 1 Schematic diagram of the conversion of poly(carbosilane) into silicon carbide.

ticles of poly(carbosilane) of approximately 300 micron range were used. The poly(carbosilane) employed in this study was designated as Nicalon and was purchased from Dow Corning Corporation.

The intrinsic viscosity was determined in our laboratories according to ASTM D-446 by employing a Ubbelohde viscometer. The solution viscosity measurements were carried out by employing n-hexane solutions of different concentrations at 25°C.[8]

The intrinsic viscosity of poly(carbosilane) was obtained at 25°C from data where reduced viscosities were obtained at different concentrations in an n-hexane solution. Figure 2 shows the plot of the reduced viscosity vs. concentration, from which the intrinsic viscosity value was calculated by extrapolation to zero concentration and was determined to be 0.0125 dl/g.

EXPERIMENTAL

Thermal Analysis with DSC

The objectives of these experiments were the determination of the curing kinetics, isothermal heat of curing and degree of curing of poly(carbosilane), determination of its specific heat, and understanding the behavior of poly(carbosilane) when it is heated in an inert atmosphere. A differential scanning calorimeter (Perkin-Elmer DSC-4) was used. This instrument is equipped with a microprocessor controller for temperature programming. Indium, which has a melting point of 156.6°C and heat of fusion of 6.8 cal/g, was used for the temperature calibration. For DSC-4, a one-point temperature calibration is satisfactory to obtain a maximum deviation of ±1°C from the true temperature in the range of 25–600°C.[9] In dynamic experiments, the temperature scanning was in the 50–500°C range with 10–40°C/min heating rate.

Specific heat measurements were conducted with DSC under a nitrogen atmosphere and at a constant heating rate of 5°C/min.

For the determination of curing kinetics and heat of curing with the DSC, an oxygen atmosphere and isothermal conditions were imposed. The oxygen pressure was set at 10 psig and the gas flow rate was kept at 10 cc/min.

Thermogravimetric Measurements

The weight change of poly(carbosilane) during heating under a nitrogen atmosphere and during curing under an atmosphere of 40% oxygen and 60% nitrogen was measured with a Perkin-Elmer TGS-2. The heating rate ranged from 10–200°C/min. For temperature calibration, Perkalloy, which has a Curie temperature of 596°C, was used.

Infrared Measurements

Chemical identification of poly(carbosilane) and chemical changes during curing were studied with a Perkin-Elmer Model PE-983 infrared spectrometer. This spectrometer uses a Nerst glower as a source of radiation and the optical material consists of a F4.2 monochromator with four gratings and nine filters. KBr pellets with 1% weight sample were prepared by compressing the mixture to 12,000 psi pressure for approximately 2 min.
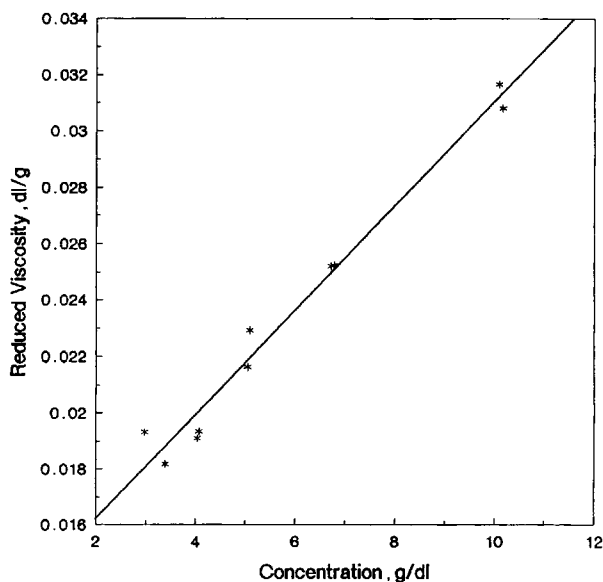

Figure 2 Reduced viscosity of poly(carbosilane) as a function of concentration.

RESULTS AND DISCUSSION

The specific heat values of poly(carbosilane) were determined under equilibrium conditions employing the DSC experiments in the 323–473°K temperature range. The results are shown in Figure 3 for a heating rate of 5°C/min. One observes a linear increase of the specific heat values with temperature. Specific heat values obtained at a heating rate of 10°C/min were found to be about 18% higher than those obtained at the heating rate of 5°C/min. These specific heat capacity values can be utilized in mathematical analysis of heat transfer for processing simulation.

Figure 4 represents a typical dynamic scanning curve obtained with the DSC from 50–550°C under a nitrogen atmosphere. After about 450°C, the sample was observed to froth and rapidly disintegrate due to the rapid escape of volatiles.

Dynamic scanning under nitrogen atmosphere was also carried out with the thermogravimetric analyzer. The results from the TG experiments are shown in Figure 5. The total weight loss was approximately 8%. The loss of weight commenced after the temperature reached about 220°C and continued up to 360°C. This is believed to be due to the vaporization of the low-molecular-weight organic molecules.[10] They should be responsible for the endothermic effect as observed in the DSC experiment shown in Figure 4. From 360–490°C, the weight of the sample did not change. However, at temperatures greater than 490°C, a weight loss of similar magnitude as in the 220–360°C range was observed.
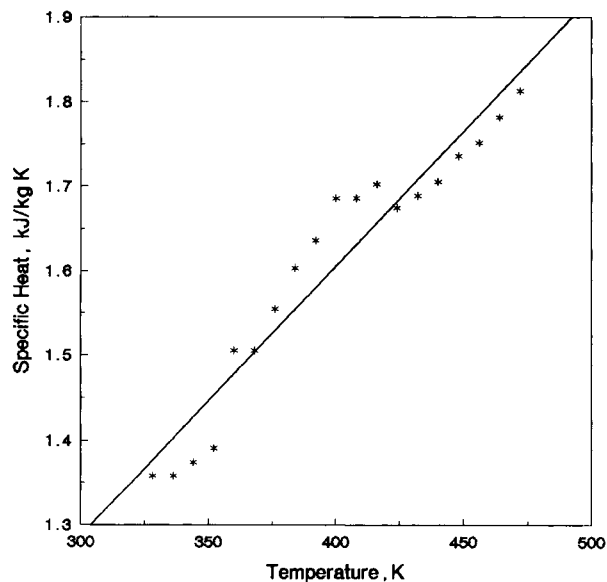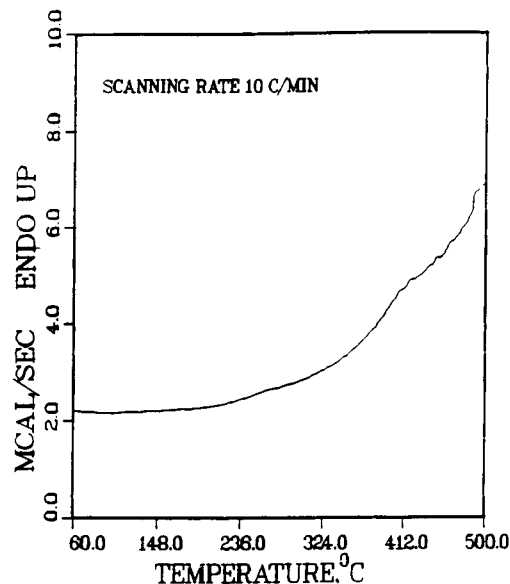

Figure 4 Dynamic scanning of poly(carbosilane) under nitrogen in the DSC.

During this phase of the dynamic scanning, the sample was found to froth and rapidly disintegrate as in the DSC experiments. Here, the associated weight loss is believed to be due to the loss of small molecules such as hydrogen and methane, which form as a result of the breakage of the Si — CH$_3$, Si — H, and C — H bonds.[10]

These results emphasize the importance of the use of an inert atmosphere during the shaping stage.

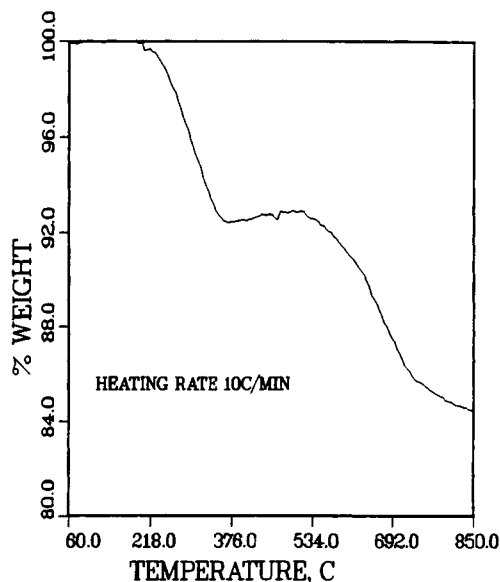**Figure 3** Specific heat of poly(carbosilane).

Figure 5 Dynamic scanning of poly(carbosilane) under nitrogen in the TGA.

The frothing temperature around 450°C sets an upper limit for the processing temperature, above which the integrity of the sample is lost. The lower limit is the melting temperature range of 200–240°C for poly(carbosilane).[4]

CURING

Prior to pyrolysis, poly(carbosilane) is cured in an oxygen environment. This process results in the crosslinking with oxygen. This enables the samples to retain their shapes during pyrolysis and to not fuse with other particles. Optimal extent of curing would confine oxidation to the exterior periphery of the sample. Otherwise, excess oxygen that would be present in the pyrolyzing sample results in the loss of strength.[10]

The curing studies for poly(carbosilane) were carried out with the DSC and TGA. Figure 6 shows the dynamic scanning of poly(carbosilane) under oxygen from 50–450°C in the DSC. From Figure 6 it is clear that the curing that results in the cross-linking of poly(carbosilane) is an exothermic process. The heat of curing calculated from Figure 6 was found to be 14,300 ± 700 cal/g. Another observation is that the frothing that occurred in the dynamic scanning of poly(carbosilane) under the nitrogen atmosphere in this temperture range did not occur with oxygen. This can be ascribed to the crosslinking process, which enables the sample to retain its integrity.
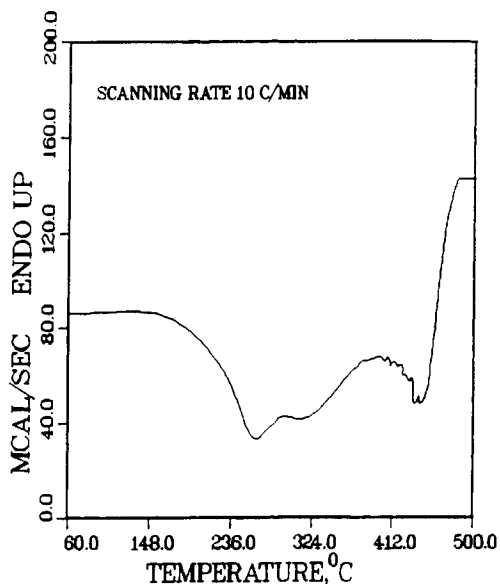

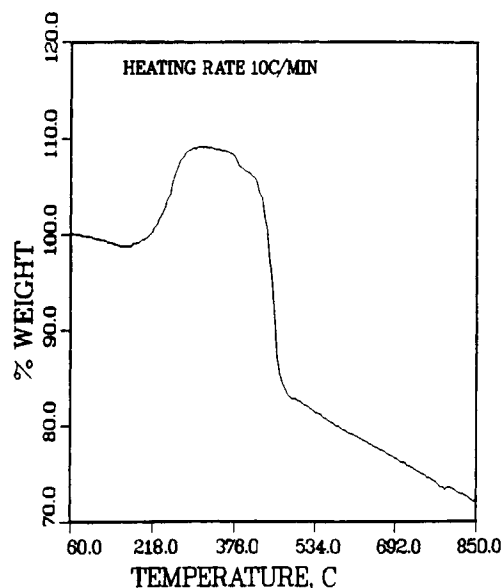**Figure 6** Dynamic scanning of poly(carbosilane) under oxygen in the DSC.

Figure 7 Dynamic scanning of poly(carbosilane) under oxygen in the TGA.

Figure 7 shows the TGA results and indicates a weight increase (due to the reaction with oxygen) starting at approximately 200°C. From this temperature to 350°C, weight loss was observed during dynamic scanning under the nitrogen atmosphere (Figure 5). One can then surmise that either the loss of low-molecular-weight organic molecules is not occurring or that this loss, if any, is more than offset by the gain in weight due to oxygen. Figure 7 also shows that after about 375°C the weight of the sample starts to decrease. From the DSC data in Figure 6, one observes that the curing is essentially completed at this phase of the dynamic scanning and that the weight loss can be ascribed to the loss of hydrogen and low-molecular-weight hydrocarbons due to dehydrogenation and dehydrocarbonation condensation reactions.[10]

Isothermal curing experiments were carried out in the temperature range of 170–450°C with the DSC. The sample was first heated to the curing temperature at a rapid heating rate of 200°C/min in a nitrogen environment. (The higher heating rate was used to prevent frothing at high temperatures, which tended to occur for slower heating rates.) After the desired curing temperature was attained, the nitrogen environment was replaced with the oxygen environment within seconds. The curing process was terminated when the isothermal curing curves leveled off. Figure 8 illustrates the DSC result for isothermal curing at 200°C.

In studying the curing kinetics the degree of curing, α, was defined as follows:
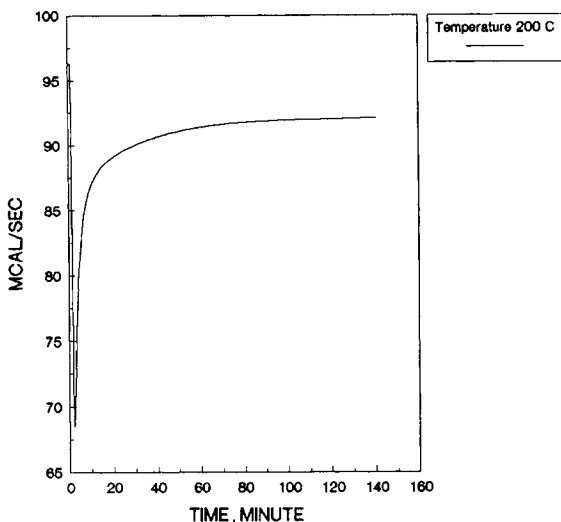
Figure 8   Isothermal curing under oxygen in the DSC.

$$\alpha = Q(t)/Q. \qquad (1)$$

Here, α is the ratio of the heat of curing at a particular time, $Q(t)$, over the total heat of curing obtained from the dynamic scanning experiments in the DSC (Q). It is assumed that the heat of curing is directly proportional to the extent of curing, with 100% curing pertaining to total heat of the curing obtained upon integration in the temperature scan up to 500°C.[11]

In the isothermal experiments, the heat of curing calculated from the DSC results (such as in Figure 8) is found to be less than the heat of curing calculated with a temperature scan. Each sample first subjected to isothermal curing was further subjected to an additional DSC scan with a heating rate of 10°C/min up to 500°C. Figure 9 shows these results upon curing in the 170–450°C temperature range. For samples cured at the lower temperatures, a significant amount of heat is released during the further temperature scan. On the other hand, it is evident that there is no additional heat of curing with the further temperature scan when the sample is cured initially at 450°C.

These results are summarized in Table I, where it is seen that the heat of curing at the lower temperatures is only a small fraction of the total heat of curing obtained with the complete temperature scan. Another observation from Table I, is the decrease in the isothermal heat of curing in the 230–300°C temperature range. Apparently, melting starts around 230°C with the accompanying change in the heat of reaction. At the higher temperatures (i.e., above 350°C), isothermal heat of curing sharply in-

creases with increasing temperature. Total heat of curing was calculated as the sum of isothermal heat of curing and the additional heat released after temperature scanning.[12]

With the exception of the 250–300°C interval, the total heat of curing does not vary significantly with temperature. The average value for the total heat of curing is 14,300 ± 700 cal/g, which is in good agreement with the 14,258 cal/g value of the heat of curing obtained from the DSC scanning shown in Figure 6.

The study of the curing kinetics by means of differential scanning calorimetry has been discussed in the literature.[13-16] In most cases, the curing re-
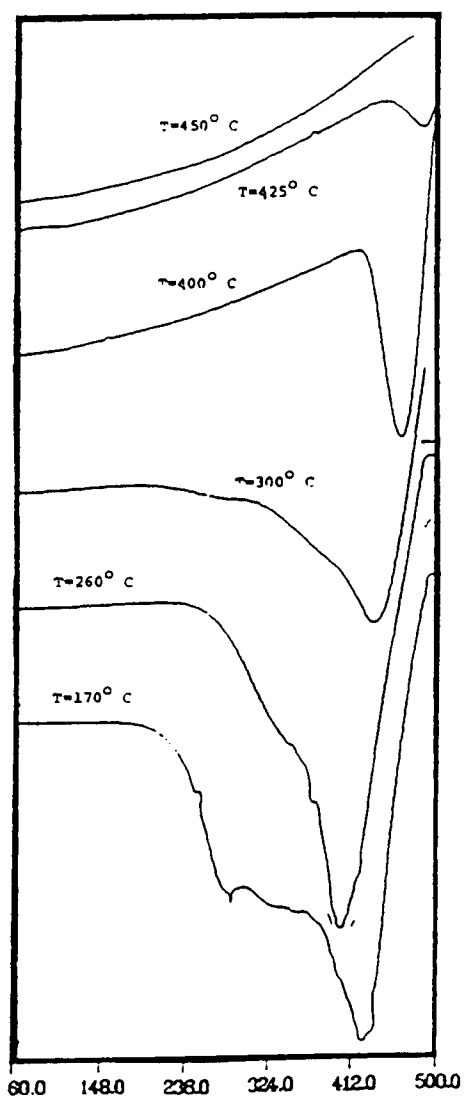

Figure 9   Dynamic scanning of poly(carbosilane) under oxygen in the DSC after curing at various temperatures, T.

Table I Isothermal Heat of Curing and the Additional Heat of Curing after Scanning as a Function of Temperature

Temp (°C)	Curing Time (min)	Isothermal Heat of Curing (cal/g)	Additional Heat After Scanning (cal/g)	Total Heat of Curing (cal/g)
170	180	1,284	13,938	15,222
180	180	1,821	12,111	13,932
190	180	3,653	8,518	12,271
200	150	3,612	10,823	14,535
210	150	4,707	9,264	13,971
220	150	6,031	9,206	15,237
230	150	6,517	8,350	14,867
240	150	5,151	8,795	13,946
250	150	3,833	6,042	9,875*
260	150	3,884	6,845	10,729*
270	240	5,538	5,970	11,508*
300	150	3,717	4,042	7,759*
350	150	13,653	1,839	15,492
400	150	13,942	596	14,088
425	150	12,987	89	13,077
450	120	13,757	—	13,757

Average heat of curing is 14,300 ± 700 cal/g (not including the 250–300°C values).
* The total heat of curing is unusually low in the 250–300°C range.

action rate has been described by means of a simple nth order kinetic expression governed by a single Arrhenius constant. There are two disadvantages of this model:

1. It cannot predict the maximum observed experimentally in the isothermal rate of reaction curve.
2. It cannot satisfy the zero initial rate of reaction, particularly evident at low temperatures.

For describing the curing kinetics, the following Kamal and Sourour equation, initially proposed for the curing of thermosetting polymers,[17] was used:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n. \qquad (2)$$

Here, K_1 and K_2 are the reaction rate constants and m and n are temperature-dependent empirical parameters. Their sum is 2.0. At a specified temperature, experimental α values were fitted based on the following equation:

$$\alpha = \sum_{i=1}^{3} a_i \cdot [1.0 - \exp(-b_i \cdot t)]. \qquad (3)$$

Here, the constants a_i and b_i were determined by using a pattern search program.[8] The kinetic parameters in eq. (2), as well as α_p and $\dot{\alpha}_p$, can be determined from isothermal curing data by following the procedures of Dutta and Ryan.[18] α_p and $\dot{\alpha}_p$ are the degree of curing and the curing rate at $t = t_p$, respectively, and t_p is the time corresponding to the maximum curing rate.

The kinetic parameters, as well as α_p and $\dot{\alpha}_p$, were evaluated from isothermal curing data in the 170–

Table II Determination of the Kinetic Parameters Based on eq. (2)

Temp (°C)	Parameters ($\times 10^{-2}$)				
	K_1 (min^{-1})	α_p	$\dot{\alpha}_p$ (min^{-1})	m	K_2 (min^{-1})
170	0.94	0.46	1.12	5.53	0.24
180	0.98	0.52	1.13	3.73	0.46
190	1.66	1.22	1.83	20.00	0.50
200	2.47	2.00	2.67	30.20	1.03
210	2.85	2.10	3.26	24.00	1.33
220	4.07	3.35	4.67	33.00	2.66
230	3.84	3.24	4.81	23.90	2.86
240	3.52	2.51	3.95	30.00	1.82

Table III Temperature Dependence of the Kinetic Parameters

Kinetic Variable	Temperature Dependence	Correlation Coefficient
K_1 (min^{-1})	$7.24 \times 10^4 \exp(-5.89 \times 10^7/RT)$	0.9393
K_2 (min^{-1})	$4.62 \times 10^6 \exp(-7.86 \times 10^7/RT)$	0.9887
α_p	$4.06 \times 10^5 \exp(-6.73 \times 10^7/RT)$	0.9553
$\overset{\circ}{\alpha}_p$ (min^{-1})	$6.80 \times 10^3 \exp(-4.93 \times 10^7/RT)$	0.9420

E_a (activation energy) in J/kmol.

240°C temperature range, and are listed in Table II. One observes that these parameters increase with temperatures up to 220°C. The decrease in the kinetic parameters at 230°C and 240°C is ascribed to the melting effect, which apparently starts around 230°C. In the 170–220°C temperature range, the kinetic parameters exhibit an Arrhenius dependence on temperature, and are listed in Table III as an Arrhenius function of temperature. Figure 10 shows the Arrhenius plots for K_1 and K_2.

The kinetic parameters listed in Table II were used to calculate $(d\alpha/dt)$ from eq. (2) and were compared to the experimental $(d\alpha/dt)$ values obtained from the DSC. The results are shown in Figure 11. Good agreement was obtained at the temperature of 200°C.

The weight gain values associated with isothermal curing obtained for the DSC and the TGA are compared in Table IV. The TGA experiments are more accurate and provided better reproducibility than the DSC as shown in Table IV. The agreement obtained with the two methods is reasonable.

Our infrared studies support the conclusion of Yajima et al.[7] that the mechanism of curing involves the crosslinking upon oxidation of Si — H and Si — CH$_3$ to produce Si — O — Si and Si — O — C. This can be seen in Figure 12, where the infrared spectra for poly(carbosilane) before curing is compared with the infrared spectra of poly(carbosilane) after it is cured at 200°C. One observes that the intensities of absorption bands at 2900 and 2950 cm^{-1} (C — H stretching of Si — CH$_3$), 2100 cm^{-1} (Si — H stretching), 1400 cm^{-1} (CH$_2$ deformation of Si — CH$_3$), 1250 cm^{-1} (Si — CH$_3$ deformation), and 820 cm^{-1} (Si — CH$_3$ rocking and Si — C stretching) are decreasing upon curing. On the other hand, the absorption band at 1710 cm^{-1}, due to C = O stretching, increases. The intensity of the band at 1100 cm^{-1} (Si — O stretching in Si — O — Si and Si — O — C) was not affected. However, after further curing by temperature scanning, the band at 1100 cm^{-1} also gained in intensity.

CONCLUSIONS

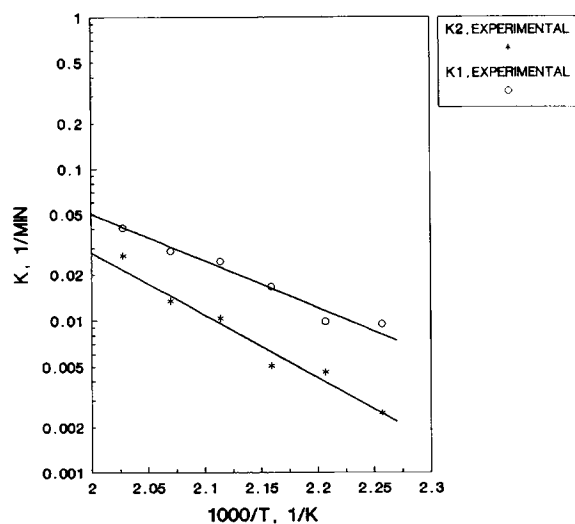Isothermal curing of poly(carbosilane) with oxygen was carried out in a differential scanning cal-

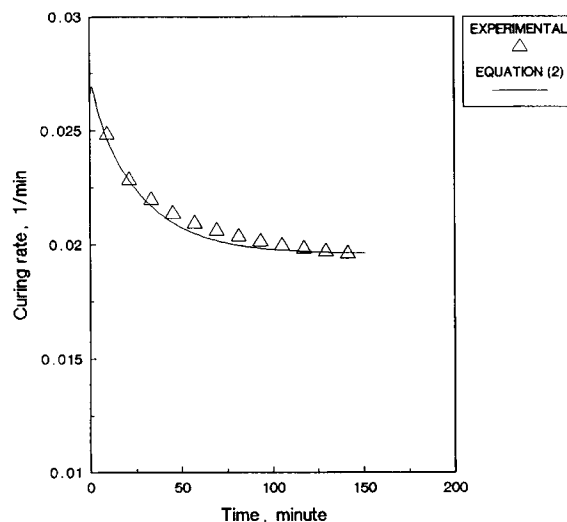**Figure 10** Variation of the parameters K_1 and K_2 with temperature.

Figure 11 Comparison of $(d\alpha/dt)$ calculated from eq. (2) with the experimental values.

Table IV   Weight Gain During the Curing Reaction in the TGA as a Function of Temperature

Temp (°C)	Curing Time (min)	Final Weight Gain (%)	
		DSC	TGA
170	180	8.12 ± 0.38	8.80 ± 0.33
180	180	10.52 ± 0.71	8.31 ± 0.31
190	180	13.85 ± 0.59	10.08 ± 0.14
200	150	16.15 ± 0.59	11.65 ± 0.42
210	150	15.35 ± 0.61	11.47 ± 0.04
220	150	14.26 ± 0.44	13.05 ± 0.25
230	150	13.92 ± 0.47	13.04 ± 0.07
240	150	12.95 ± 0.42	14.70 ± 0.33
250	150	9.32 ± 0.54	13.70 ± 0.33
260	150	9.40 ± 0.67	14.17 ± 0.28
270	150	8.95 ± 0.08	13.40 ± 0.17

orimeter and thermogravimetric analyzer. Curing is characterized as an exothermic reaction with oxygen and results in a net weight gain. Infrared studies

confirmed earlier findings[7] that the curing mechanism involves the crosslinking by oxidation, resulting in Si — O — Si and Si — O — C bonds. A kinetic expression[12] for the rate of change of the degree of curing calculated from the DSC curves satisfactorily fitted the data. Kinetic parameters were found to be Arrhenius functions of temperature.

Dynamic scanning of poly(carbosilane) under a nitrogen atmosphere in the DSC indicated significant endothermic effects starting at 350°C. Frothing occurred after 450°C as a result of the rapid loss of volatiles. Frothing was not observed when the sample was first cured or when it was subjected to dynamic scanning in an oxygen environment. Processing of poly(carbosilane) in inert environments should therefore take place at a temperature of less than 450°C but above the melting temperature of 230°C.

Overall, the presented data should facilitate a better understanding of the processability of poly(carbosilane). Shaping and curing process can thus be designed employing the reported characterization results.
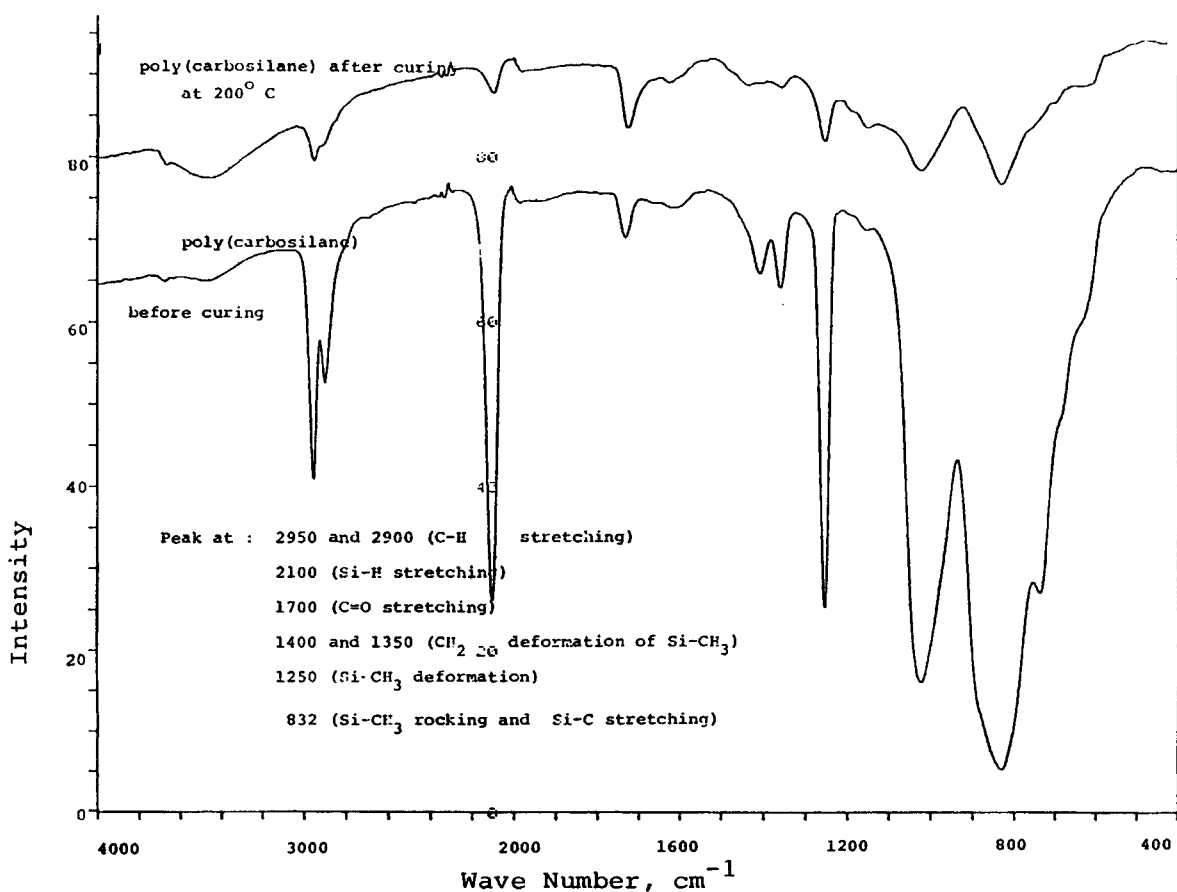
Figure 12   Infrared spectrum of poly(carbosilane) before and after curing at 200°C.

Nomenclature

α: degree of curing

α_p: degree of curing at $t = t_p$

$\dot{\alpha}_p$: $(d\alpha/dt)$, curing rate at $t = t_p$, min^{-1}

t_p: time value corresponding to the maximum curring rate, min

a_i, b_i: constants determined from pattern search in eq. (3)

K_1: reaction rate constant, min^{-1}

K_2: reaction rate constant, min^{-1}

m, n: order of reaction

Q: total heat of curing, cal/g

$Q(t)$: cumulative heat of curing from $t = 0$ to $t = t$, cal/g

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