



# The application of heating rate to studies of polysiloxanes with cyanoethyl substituents and silazane polymers

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## Abstract

Thermal behaviour of polysiloxanes containing cyanoethyl side groups was studied by differential scanning calorimetry (DSC). Samples were quenched to  $-165\text{ }^{\circ}\text{C}$  and then reheated at different heating rates. The glass transition, an exothermal crystalline formation (cold crystallization) and endothermal melting of crystalline formations were detected. A broad cold crystallization peak and a melting peak were observed at a heating rate of 20 K/min. However, the samples gave a sharp cold crystallization peak and three endothermal peaks using a heating rate of 5 K/min. The DSC traces obtained were thus sensitive to heating rates. Thermal degradation of silazane polymers was studied by a thermogravimetric method. Three stages of degradation occur in the course of thermal decomposition. It was shown that the yields of pyrolytic product increased with the heating rate decreasing.

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## 1. Introduction

Thermoanalytical techniques are much used in research laboratories. Examples of such techniques are thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). They have been widely applied to the study and characterization of polymeric materials. Orrah et al. [1] investigated the low temperature behaviour of cyclic and linear polydimethylsiloxanes (PDMS) and indicated that DSC was used with cooling (49 K/min) and heating (10 K/min) rates

that are quite suitable for studying glass transition temperature but not for investigating crystallization behaviour. At the same time, they reported the results of DSC measurements using slower heating and cooling rates (2 K/min). Friedrich and Rabolt [2] used DSC to study low and high molecular weight polydimethylsiloxane samples. DSC traces of PDMS were obtained at a heating rate of 10 K/min. An obvious difference observed between the low and high molecular weight samples occurs in the shape of the traces.

In recent years, Si–C–N ceramic materials have gained particular interest because of their excellent properties [3–9]. This kind of ceramics which consists mainly of SiC and Si<sub>3</sub>N<sub>4</sub> can be manufactured as fibers, plates, and shaped products, and have high strength and high modulus of elasticity. Silazane

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polymers can be used as precursors for preparing such ceramic materials.

The present work involves a study of the low temperature thermal behaviour of polysiloxanes containing cyanoethyl groups, and the pyrolytic decomposition of silazane polymers, using varying heating rates. Both DSC and TG were applied.

## 2. Experimental

### 2.1. Materials

Octamethylcyclotetrasiloxane (D<sub>4</sub>), hexamethyldisiloxane (MM) (Shietsu Chemical Co., Japan), 2-cyanoethylheptamethylcyclotetrasiloxane (it was synthesized in our laboratory). Silazane polymers (molecular weight 2300) were provided by F. Meng.

Polysiloxanes with cyanoethyl groups were prepared by coequilibration of D<sub>4</sub>, MM, and 2-cyanoethylheptamethylcyclotetrasiloxane [10]. The polysiloxanes used in this study had a molecular weight of 5100 and cyano groups are 2.6 wt. %.

### 2.2. Differential scanning calorimetry

A Rheometric Scientific DSC-SP differential scanning calorimeter interfaced to a RSI ORCHESTRATOR microprocessor was used for this investigation. The temperature scale of the instrument was checked and effects due to thermal lag in the system were corrected by regular calibration using indium and zinc fusion standards. To assure a consistent thermal history in each case, the following conditions were employed throughout the experiments. The DSC cell containing the sample and reference was rapidly cooled to  $-165^{\circ}\text{C}$  at a rate of 49 K/min and held at this temperature for 3 min to allow the system to attain thermal equilibrium. The cell was then heated to  $20^{\circ}\text{C}$  at different heating rates under a high-grade N<sub>2</sub> purge. The thermal events over the temperature range scanned were recorded by the microprocessor.

### 2.3. Thermogravimetry

A Rheometric Scientific TGA 1500 was used for this study. An atmosphere of high-grade nitrogen was

maintained. The samples were placed in platinum crucibles and they were weighted directly on the thermogravimetric balance. The mass of the sample used was typically 10.0 mg, and was heated at different heating rates over the temperature range of  $20\text{--}1000^{\circ}\text{C}$ .

## 3. Results and discussion

The shape of the DSC curves depends on many factors. Some of these are heating rate, heat of reaction, furnace atmosphere, amount of sample, nature of sample container, particle size, etc. Thermal behaviour of polysiloxanes containing cyanoethyl side groups was studied using DSC. The samples were quenched to  $-165^{\circ}\text{C}$  and reheated at different heating rates under a N<sub>2</sub> purge. The results are shown in Fig. 1. The glass transition, an exothermal crystalline formation (cold crystallization) and endothermal melting of crystalline formations were detected. The DSC traces obtained were sensitive to heating rates. Fig. 1 contrasts the effect of fast and slow heating rates for the samples. A broad cold crystallization peak and only a melting peak were detected at a heating rate of 20 K/min. However, the sample gave a sharp cold crystallization peak and three endothermal peaks when subjected to a heating rate of 5 K/min. The slower heating rate (e.g. 5 K/min) is good for studying crystallization behaviour. The glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_c$ ) and crystalline melting temperature ( $T_m$ ) of the samples are shown in Table 1. Because of the thermal lag,  $T_g$ ,  $T_c$  and  $T_m$  increase as the heating rate is increasing.

The thermal degradation of silazane polymers, which are often used to prepare Si–C–N ceramic materials, was also studied by a thermogravimetric method. The results are given in Fig. 2. There is no significant weight loss below  $200^{\circ}\text{C}$ , and three stages of degradation occur in the course of thermal decomposition of silazane polymers. The first stage occurs

Table 1  
 $T_g$ ,  $T_c$  and  $T_m$  of polysiloxanes with cyanoethyl substituents

Heating rate (K/min)	$T_g$ ( $^{\circ}\text{C}$ )	$T_c$ ( $^{\circ}\text{C}$ )	$T_{m1}$ ( $^{\circ}\text{C}$ )	$T_{m2}$ ( $^{\circ}\text{C}$ )	$T_{m3}$ ( $^{\circ}\text{C}$ )
5	-127	-84	-49	-41	-17
20	-125	-71	-45		

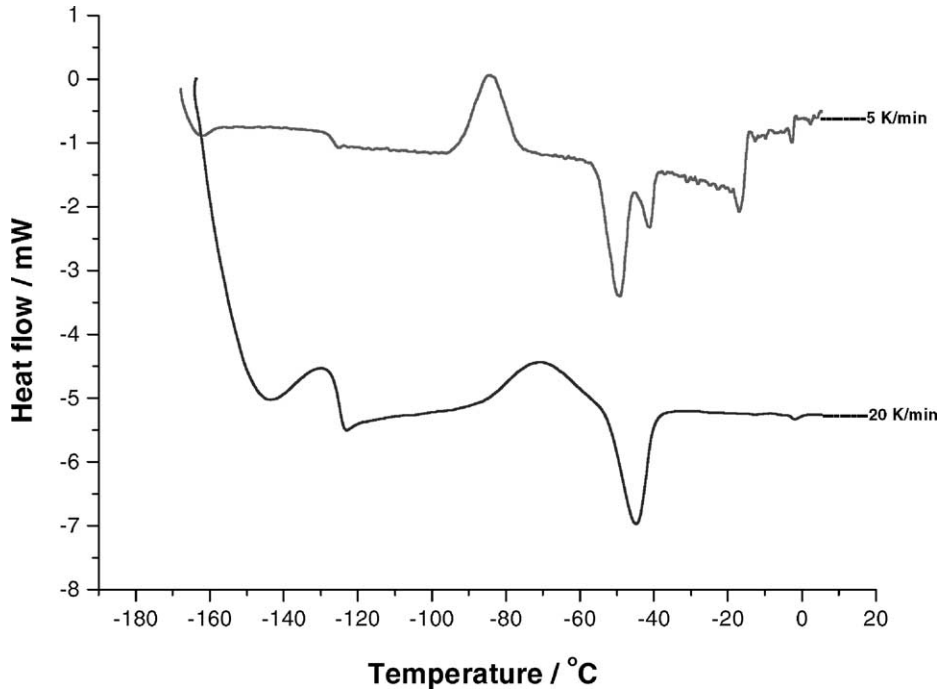


Fig. 1. DSC curves of polysiloxanes with cyanoethyl substituents.

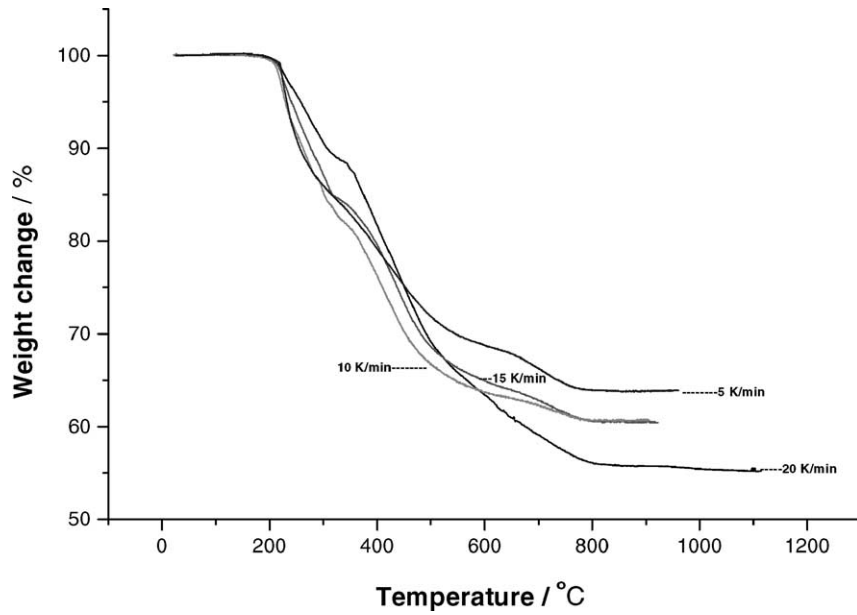


Fig. 2. TGA curves of silazane polymers.

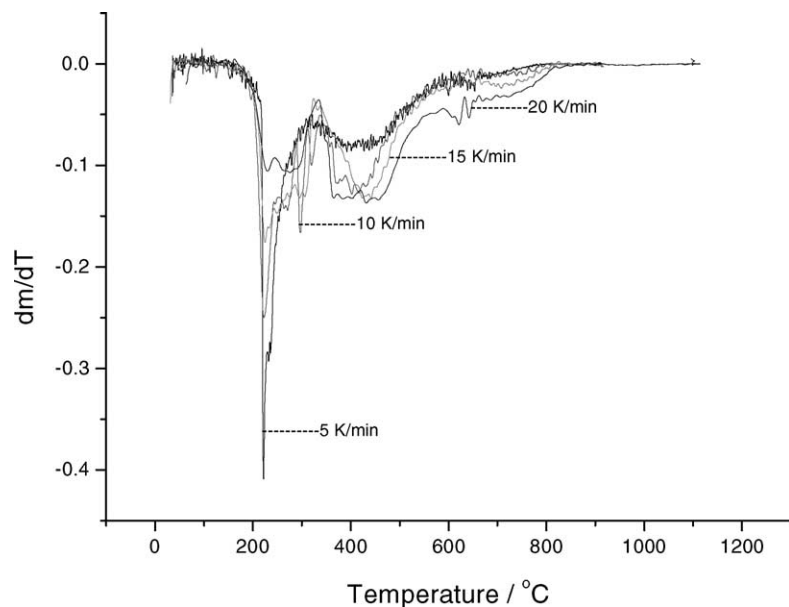


Fig. 3. DTG curves of silazane polymers.

in the range of 0.0–12.4% weight loss. TGA curves indicate that the thermal lag took place in this stage. However, the initial degradation temperatures at different heating rates are the same. In the third stage that occurs in the temperature range of 525–850 °C,

the different yields of pyrolytic product are shown. The yields of pyrolytic product (Si–C–N ceramic materials) increased with the heating rate decreasing, see Table 2. The second stage is between the first and the third stage. The curve of 5 K/min is different

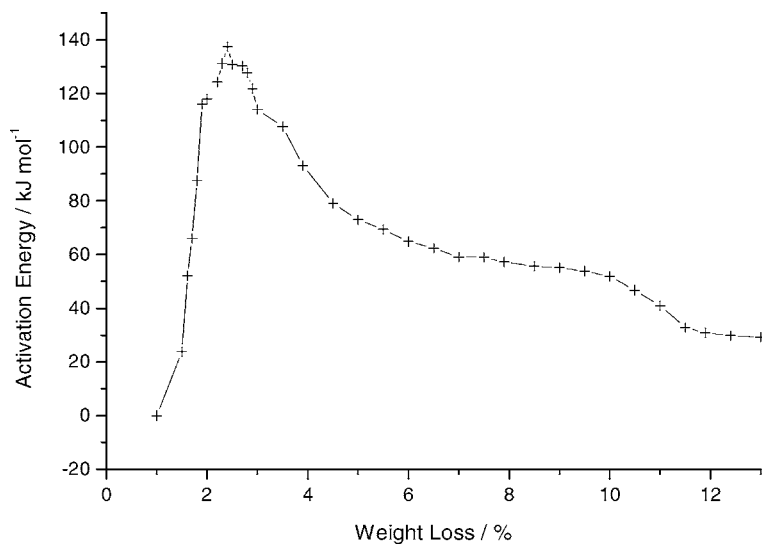


Fig. 4. Activation energies of silazane polymer degradation process vs. weight loss.

Table 2  
Yields of pyrolytic product at different heating rates

Heating rate (K/min)	Yield (%)
5	36.1
10	39.4
15	39.5
20	44.3

from the other three curves in this stage. This suggests that the mechanism of thermal degradation of silazane polymers is not the same at different heating rates. This was also clearly revealed in Fig. 3. The differential thermogravimetry (DTG) curves illustrate different regions of weight loss rates. On increasing of the heating rate, the size of the peak below 300 °C decreases while the peak above 300 °C increases. Activation energies of the first degradation stage were calculated using the Flynn and Wall method. Fig. 4 displays the change of activation energies of silazane polymers degradation. Activation energy ( $E$ ) increases in the initial conversion and the maximum value of  $E$  was at 2.5% weight loss. The results

show broad variation of activation energies with the degree of weight loss. This suggests that thermal degradation of silazane polymers is a very complex process.

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