Supercooling of Polydimethylsiloxane

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Synopsis

This study was undertaken to determine the quenching rates necessary to supercool polydimethylsiloxane. A technique was developed that allowed controlled quenching rates up to 52°C/sec and a modified DTA apparatus was used to obtain thermograms during the warm-up cycle. No supercooling was observed for a cooling rate of 1.6°C/sec; 56% supercooling was found for a 9.6°C/sec cooling rate; 65% for 10.6°C/sec and 85% for a 52°C/sec cooling rate. Evidence was also presented showing that the crystals in polydimethylsiloxane consist of two forms.

INTRODUCTION

A number of published papers[1-7] deal with low temperature behavior of siloxane polymers, copolymers, and elastomers thereof. Polmanteer and Hunter[6] used an experimental quenching method in conjunction with a Gehman Flex Apparatus, which allowed the study of supercooling effects in certain copolymers of dimethylsiloxane and phenylmethylsiloxane. However, they were unable to observe supercooling of polydimethylsiloxane elastomers using their experimental method. Bacon Ke[8] showed experimental evidence for the supercooling of a polydimethylsiloxane elastomer using a DTA (Differential Thermal Analysis) apparatus. This present study was designed to determine the quenching rates necessary to supercool polydimethylsiloxane. A DTA method was used with appropriate experimental modifications to allow variable quenching rates. Thermograms obtained during the warm-up cycle then provided excellent data relating areas of the crystallization exotherms and crystal melting endotherms with quenching rates. The data also showed how the extent of supercooling influenced the size of the discontinuity in the thermograms at Tg (glass temperature).

EXPERIMENTAL METHOD AND RESULTS

A linear polydimethylsiloxane free of polymerization catalyst and equilibrium cyclics, and having a weight average molecular weight of 450,000 was used in this study. Five milligrams of this polymer were placed in a glass vial having a wall thickness of 0.01 in., and an outisde diameter of 0.07 in. The polymer was allowed to flow for 24 hr under

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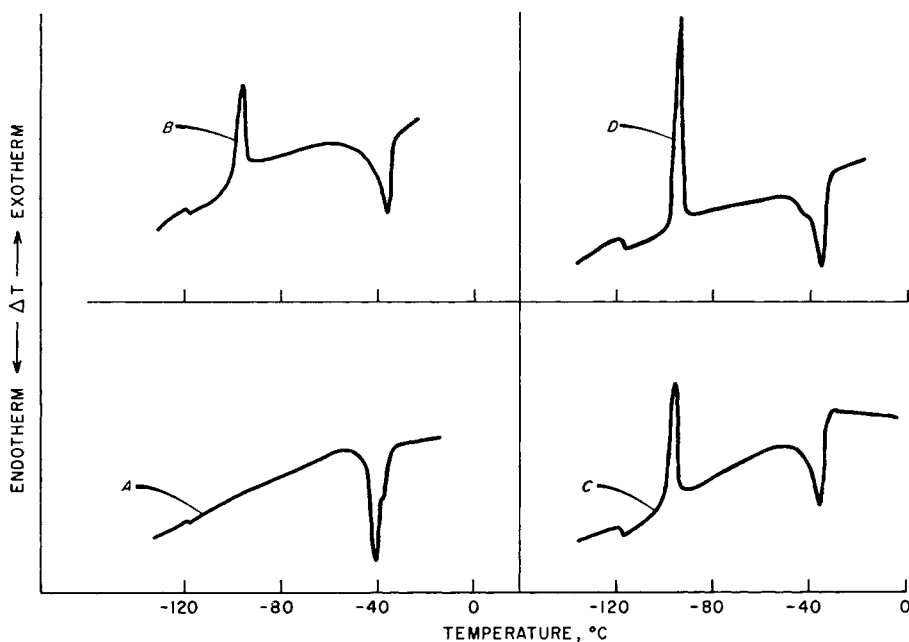* Present address: Battelle Memorial Inst., Columbus, Ohio.

Fig. 1. Warming cycle DTA thermograms for polydimethylsiloxane, Curve A, cooling rate = 1.6°C/sec, heating rate = 10°C/min; Curve B, cooling rate = 9.6°C/sec, heating rate = 10°C/min; Curve C, cooling rate = 10.6°C/sec, heating rate 10°C/min, Curve D, cooling rate = 52°C/sec, heating rate = 10°C/min.

vacuum to remove entrapped air. A Chromel-Alumel thermocouple was inserted into the polymer within the sample vial. The response rate of the thermocouple was measured in a preliminary experiment using an iso-prene-liquid nitrogen slurry and found to be 1960°C/sec. This thermo-couple response rate was many fold greater than the quenching rates used for the polymer, hence the quenching rates measured for the polymer were considered accurate.

Since very fast cooling rates were used, it was convenient to use a cathode ray oscilloscope to follow the rate of cooling. This was done by connecting the thermocouple leads to the DC vertical amplifier and the calibrated horizontal sweep was used to determine the systems response. Response measurements were made by photographing the oscilloscope trace.

A du Pont 900 DTA instrument was used in this study. Since this in-strument was designed to be programmed for cooling rates between 1 and 30°C/min, it was necessary to modify the instrument to allow much faster cooling rates. After considerable experimentation procedures were de-veloped that allowed uniform cooling rates between 1.6 and 52.0°C/sec. The cooling rates were constant within the temperature interval of −30 and −120°C which adequately encompasses crystallization temperatures

possible for unstrained polydimethylsiloxane. The cooling rates were changed by altering the mass of the assembly to be cooled. It is important to point out that the same sample, sample vial, and thermocouple were used in each experiment. In each case the sample vial assembly was held at room temperature for 40 min before quenching at the indicated measured rate to $-196°C$. Care was taken in handling the sample vial assembly (sample, sample vial, thermocouple) so that its configuration would not be altered. As a result of these precautions, the areas under the crystalline melting endotherms (corrected for nonlinearity of the Chromel-Alumel thermocouple) agreed to within six per cent for the different experiments. The thermograms given in Figure 1 are for the warmup cycles, each recorded at the same heating rate of $10°C/min$.

DISCUSSION

This study resulted in data that clearly showed the effect of quenching rate on degree of supercooling. Curve D shown in Figure 1 relates to the sample which was first cooled to $-196°C$ at a rate of $52°C/sec$. A large discontinuity in the base line can be observed at $-119°C$ which corresponds to Tg, the glass temperature. A large sharp exotherm caused by crystallization was initiated at $-102°C$ and peaked at $-94°C$. At this cooling rate of $52°C/sec$, time was insufficient for the potential maximum of crystal formation and growth to occur before Tg was reached. Once the sample temperature was below Tg, further crystal growth was impossible. A crystalline melting endotherm started at $-58°C$, peaked at $-36°C$ and was complete at $-32°C$. The melting endotherm was broader and lower in peak height than the crystallization exotherm of the supercooled polymer, indicating that the rate of crystallization was greater than the rate of melting. Note that the endotherm consisted of two peaks. This will be discussed in greater detail later. The areas under the peaks are related to the heat involved in each respective process. The exotherm had an area of 0.60 sq in. as compared with 0.71 sq in. for the endotherm. This indicates that 85% of the total crystallization occurred during the heating cycle. Since the heat change of melting was greater than the heat change during crystallization of the supercooled polymer, the remaining 15% of the potential maximum crystallization occurred during the rapid cooling cycle.

The sample after remaining at room temperature for 40 min was cooled a second time, but at a rate of $10.6°C/sec$. The thermogram for the subsequent $10°C/min$ heating cycle is shown as curve C in Figure 1. The same general thermogram trace may be observed here as in the previous case. Note the decrease in peak height and smaller area under the crystallization exotherm as compared to curve D. The discontinuity at $-119°C$ was also decreased, but within experimental error, the melting endotherm area was the same.

Again the sample was cooled to $-196°C$, but at a rate of $9.6°C/sec$. The same trends outlined above were observed as illustrated by curve B

TABLE I
DTA Thermogram Peak Areas and Temperatures

Curve	Cooling rate, °C/sec	Cryst peak[a] area of supercooled polymer, in.²	Melting[b] peak area, in.²	Calc cryst.[c] peak area during cooling, in.²	Relative[d] crystallization, per cent	Major peak melting temp, °C	Minor peak melting temp, °C	Cryst peak temp of supercooled polymer °C	Tg, °C
A	1.6	None	0.71	0.71	100	−41	−37	None	−119
B	9.6	0.38	0.68	0.30	44	−36	−42	−96	−120
C	10.6	0.47	0.72	0.25	35	−36	−42	−96	−119
D	52	0.60	0.71	0.11	15	−36	−43	−94	−119

[a] Area of crystallization exotherm during warming.
[b] Area of melting endotherm during warming.
[c] Area equal to (b − a).
[d] Relative crystallization that occurred during cooling cycle.

in Figure 1. Finally, the sample was cooled at a rate of 1.6°C/sec to −196°C. The heating cycle thermogram for this experiment was recorded and shown as curve A in Figure 1. In this case, no supercooling was observed. The discontinuity at Tg was the smallest of the four thermograms, and the melting endotherm, although the same area as in the other experiments, took on a new shape. In each of the four experiments the endotherm is composed of two peaks of different relative peak heights. The temperatures of these peaks, referred to as major and minor peak temperatures in Table I, were 36–37°C and 41–43°C. The relative magnitude of the peaks depended on the rate of quenching. The faster quenching rates followed by heating at 10°C/min favored the higher temperature for the major melting peak, while the slowest quenching rate resulted in the lower temperature for the major melting peak. This double melting peak phenomena is not without precedent. Bacon Ke[9] summarized studies by Kingdon and Suchance[11] that demonstrated identical behavior. Their findings were interpreted as resulting from two crystalline forms. It seems likely that the same is true for polydimethylsiloxane. Warrick[5] determined from crystallization kinetic data on unstretched and stretched polydimethylsiloxane filled elastomers that spherulitic growth was favored for the unstretched sample and aciform growth was favored for the stretched sample. His data showed further that the rate of crystal growth of the aciform crystals was considerably greater than for spherulitic growth and crystallization took place at a higher temperature. Although in our experiments the polymer was not strained by externally applied forces, there would be strains set up by the crystallization and growth process itself. It seems likely that these strains in combination with the different rates of quenching could lead to different forms and combinations of crystal growth. The faster quenching rates in combination with higher temperatures for the major endotherm peak are consistent with Warrick's[5] data for aciform growth.

The data showed that the size of the discontinuity at Tg varied directly with the rate of cooling. In related studies Bacon Ke[10] attributed changes in magnitude of the Tg discontinuity to differences in level of internal strain. The differences in relative degree of crystallinity occurring in the polymer in the different experiments of the present study, while going down in temperature below Tg, could equally well be used to explain the magnitude of the discontinuity. This would follow since the discontinuity size should be proportional to the volume fraction of amorphous polymer present while passing through Tg.

With regard to supercooling effects, the data of this study showed that if cooling rates of 1.6°C/sec or less were used for polydimethylsiloxane, no supercooling was achieved and maximum potential crystallization took place during cooling. As the quenching rate was increased to 52°C/sec, the polymer was 85% supercooled or 15% of the maximum potential amount of crystallization occurred during this rate of cooling. It was not

found possible in these studies to cool the polydimethylsiloxane rapidly enough to completely preclude crystallization.

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