

Crystallinity of Siloxane Polymers

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I. INTRODUCTION

A new experimental approach for studying crystallinity in pure siloxane polymers has been developed. Prior work has emphasized crystallinity investigations in fumed silica-filled vulcanizates.

Rather than give a chronological review of the past investigations in polysiloxane crystallinity behavior, two major divisions will be discussed: first, qualitative measurements which record the initial crystallinity behavior; second, quantitative measurements which determine the degree or extent of crystallinity.

Qualitative measurements based on the use of specific volume as a function of temperature have been made by Polmanteer and Hunter¹ and Warrick.² These measurements show the existence of a crystallinity temperature by a change in slope of the specific volume-temperature plot. Warrick also measured rates of crystallization in vulcanized polydimethylsiloxane by changes in specific volume as a function of time. His kinetic analysis of these data gives constants which are indicative of crystal growth type. They imply spherulite growth in the unstretched vulcanizate and acicular growth in the elongated vulcanizate.

Measurements of tensile strength as a function of temperature by Warrick² and Polmanteer and Hunter¹ have shown the initial crystallinity behavior of stretched and unstretched polysiloxane vulcanizates. In every case a characteristic increase in tensile strength was observed when crystallinity was initiated. In some of these experiments the initial crystallinity temperatures were studied as a function of elongation. These results showed that the highest temperature at which crystallinity could be achieved was 0°C.

Another major approach to qualitatively determining crystallinity effects was made with a Gehman Flex apparatus. This work of Polmanteer and Hunter¹ shows the specific effect of copolymer composition on the crystallinity behavior. The dimethylsiloxane-phenylmethylsiloxane copolymer

system has a crystallinity phase diagram similar to that of a binary eutectic system. The minimum point on this phase diagram is actually a second-order transition temperature rather than a true eutectic temperature.

Quantitative measurements on the extent of crystallinity in filled polysiloxanes have been published by Ohlberg, Alexander, and Warrick,³ who have conducted an extensive analysis on x-ray diffraction patterns of polysiloxane vulcanizates as a function of temperature and elongation. In each measurement the amount of amorphous material was calculated in order to obtain the remaining amount of the crystalline phase; thus, a quantitative measure of the extent of crystallinity was obtained.

II. NEW TECHNIQUE OF STUDYING POLYMERS

This technique involves a qualitative measurement of crystallinity based on the existence of birefringence in the crystalline phase. This birefringence is observed under a microscope with the aid of crossed nicols.

Since polydimethylsiloxane crystallized below room temperature, a cold stage had to be designed for the microscope. The essential features of this stage are given in Figure 1. The sample was placed between two glass disks. A thermocouple was placed directly into the sample and positioned so that it could be seen in the field of view of the microscope. The sample rested on the ledge of a thick transite cylinder. Directly behind this cylinder was a hollow cooling chamber. Four layers of material insulated this hollow chamber from outside heat sources.

The temperature of the sample was controlled by the accessories diagrammed in Figure 2. Air, cooled by evaporation of liquid nitrogen, flows into the hollow chamber surrounding the transite cylinder which holds the sample. The flow of air is controlled primarily by a solenoid valve actuated by a Wheelco temperature regulator whose thermo-

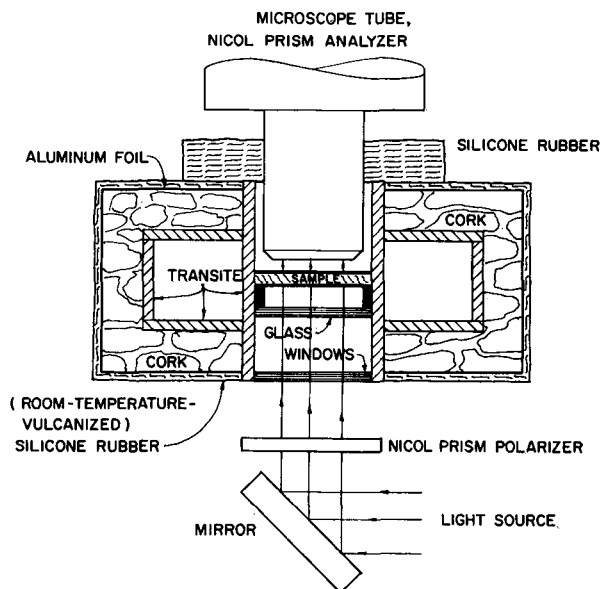


Fig. 1. Cold stage.

couple is placed at the cool air exit of the cold stage. The temperature of the air in the cold chamber varies; however, this variation decreases throughout the inner Transite cylinder surrounding the sample so that little if any temperature fluctuation is observed within the sample. At -60°C . the temperature could be controlled to $\pm 0.05^{\circ}\text{C}$. Such temperature monitoring was necessary for good control over crystal growth.

The thermal capacity of the sample is very small as compared to that of the inner Transite chamber upon which it is mounted. Furthermore, the sample is very thin (approximately 11 mils) so that thermal conductivity is not a problem and is limited only by that of the glass disks which enclose the sample.

Two terms will be used in discussing the observations of freezing and melting inherent in this technique. The first, incipient crystallinity temperature (ICT) is defined as the temperature at which crystallinity first appears. The second, melting point temperature (MPT) is defined as that temperature at which the last crystal melts.

The previous thermal history of the polymer influences the ICT. This fact is not unique for polysiloxanes. However, in order to know the extent of this influence, the ICT and MPT were studied as functions of the rate of temperature change during cooling and melting of a polydimethylsiloxane. (These initial studies were conducted on a high molecular weight linear polysiloxane from which the low molecular weight materials had been

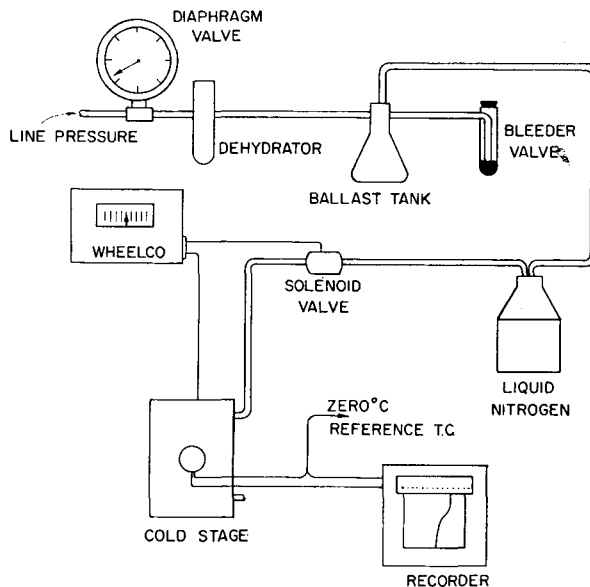


Fig. 2. Accessories to cold stage.

removed.) Figure 3 presents these data. These results show the ICT to be sensitive to the rate of temperature change, thus eliminating the ICT as a characteristic of the polymer. The MPT is less influenced.

In order to eliminate the sensitivity of the ICT to the rate of temperature change, the effect of nucleation inhibition and rate should first be minimized. When this is done, the crystal growth rate is isolated as the only remaining factor.

The ability to minimize nucleation inhibition and rate effects is shown in Figure 4. This experiment involves reducing the temperature at a constant rate until crystallization is observed. Then the rate of temperature change is reversed until the

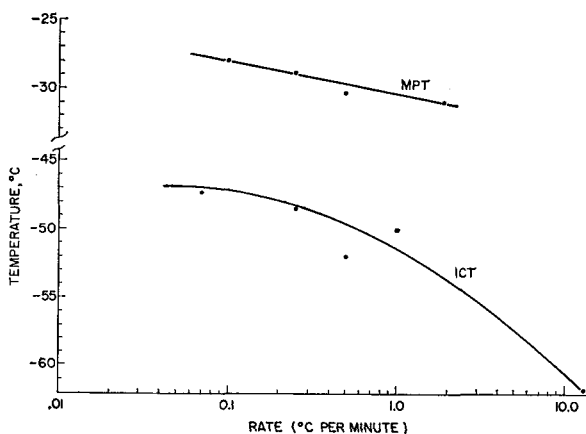


Fig. 3. Effect of rate of temperature change on ICT and MPT.

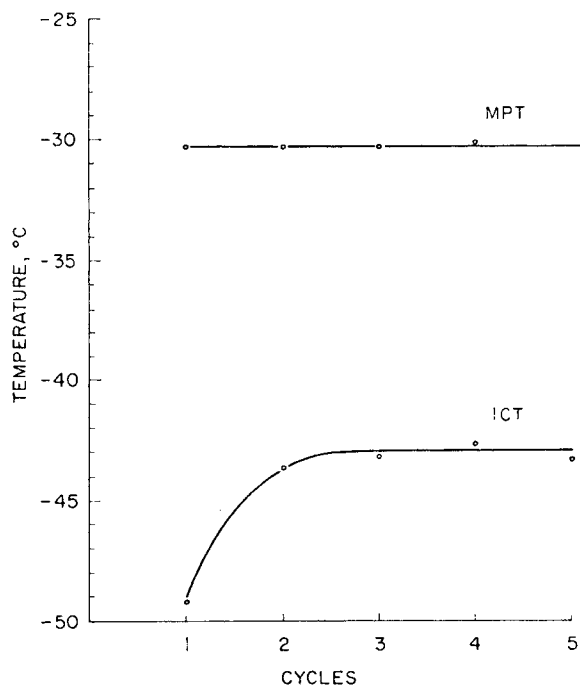


Fig. 4. Cycling at a constant rate of temperature change ($0.4^{\circ}\text{C./min.}$) between the ICT and MPT.

last spherulite was melted. After this, the complete cycle is immediately repeated. By cycling at this constant rate of temperature change between the ICT and MPT, a steady state is obtained. Perhaps it may seem obvious, but it should be pointed out that the spherulite growth obtained during this cycling took place in the same nucleated points that existed in the previous cycle. This experimental procedure gives a close approximation to ideal equilibrium freezing and melting.

A specific consideration of these results leads to the recommendation that the average of the stabilized ICT and MPT obtained upon cycling is a true characteristic temperature of the polymer, perhaps a pseudoequilibrium freezing-melting temperature. Rates of cycling between 0.08 and $0.5^{\circ}\text{C./min.}$ had little if any effect on this temperature, even though the stabilized ICT and MPT values had a slight tendency to be further apart for the faster rates.

In order to further justify the existence of this pseudo-equilibrium crystallinity temperature (PECT), an additional experiment was conducted. A polydimethylsiloxane was cooled at a very low rate of temperature change ($0.08^{\circ}\text{C./min.}$) until spherulite formation was observed. At this point the temperature change was reversed at a controlled rate and a spherulite count was made at a

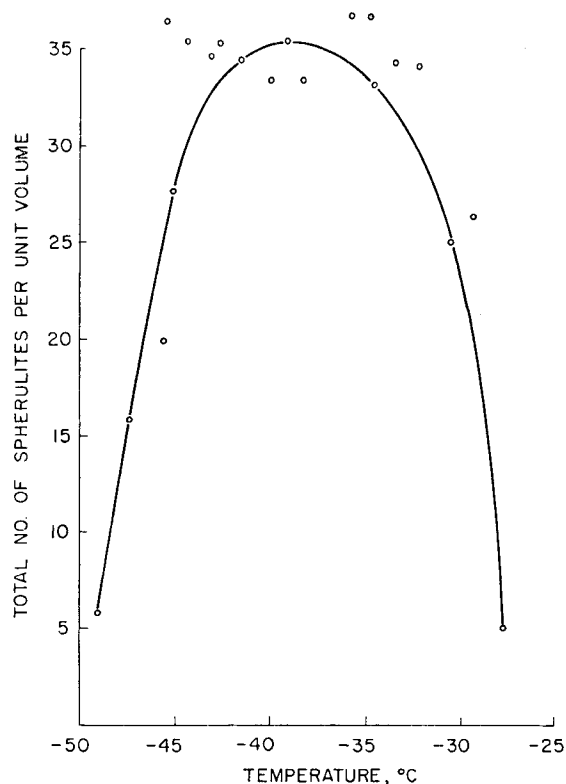


Fig. 5. Spherulite count as a function of temperature. Rate of change is $0.08^{\circ}\text{C./min.}$

function of temperature. These results are shown in Figure 5. At approximately -43°C. the nucleation rate appears to be zero, since the total number of spherulites remains constant. This is the same temperature at which the ICT stabilized during the cycling process. In addition, a decrease in the number of spherulites is observed above -33°C. , which is slightly higher than value (-36.5°C.) proposed as the pseudocrystallinity temperature for this polymer.

This spherulite count experiment points out the existence of a temperature range over which the nucleation rate is zero and the crystal growth rate remains as the only variable. This range is the same as that obtained using the cycling technique. Therefore, if the crystal growth and melting rates can be considered comparable at equivalent distances from the true equilibrium freezing-melting point, the average of the stabilized ICT and MPT is a good characteristic crystallinity temperature for the polymer.

III. EXPERIMENTAL RESULTS

Several polysiloxane homopolymers and copolymers were characterized by means of this

TABLE I
The Effect of Soluble, Low Molecular Weight Impurities on the Pseudoequilibrium Crystallinity Temperature

Cycle	With soluble impurities			Without soluble impurities		
	ICT, °C.	MPT, °C.	PECT, °C.	ICT, °C.	MPT, °C.	PECT, °C.
1	-49.40	-32.07		-47.90	-29.03	
2	-44.67	-32.07		-42.20	-28.92	
3	-45.08	-32.14		-42.22	-29.03	
Final values	-44.9	-32.1	-38.5	-42.2	-29.0	-35.6

technique. In addition to inherent pseudoequilibrium crystallinity temperature (PECT) for the polymers, several additional variables which may affect their values were investigated.

The effect of soluble impurities or low molecular weight fractions on the PECT of the polymer is of practical interest, since ordinary polymerization techniques leave appreciable amounts of low molecular weight cyclics. The presence of 11% low molecular weight cyclics in a linear polydimethylsiloxane lowered the pseudocrystallinity temperature by 3°C. (Table I). This result is consistent with the normal effect of soluble impurities.

The value of -35.6°C. for this linear polydimethylsiloxane is the highest value obtained during testing a series of samples whose low molecular weight fragments had been removed. The lowest value which was obtained on the specific polymer used in developing the complete technique was -36.5°C.

The pseudoequilibrium crystallinity temperatures of polydimethylsiloxanes having molecular weights of 50,000 and 350,000 were determined. The temperatures were identical (-38.5°C.), indicating that no effect of molecular weight existed within this range.

The third variable studied was the effect of vinyl end-blocking (Table II). The PECT's of a dimethylhydroxysilyl and dimethylvinylsilyl end-blocked dimethylsiloxane polymer with the low molecular weight impurities removed were found to be essentially equal.

TABLE II
Effect of Vinyl End-Blocking

Polydimethylsiloxane	Impurities removed, %	PECT, °C.
Dimethylhydroxysilyl	11	-35.6
Dimethylvinylsilyl	12	-35.7

Since the vinyl end-blocking showed no effect, another polymer, branched and dimethylvinylsilyl

end-blocked, was studied to see if branching would lower the PECT. Branching existed in one out of every 2140 siloxane units. Table III shows that similar values of the PECT were obtained when this polymer, with and without its low molecular weight impurities, was compared with a normal linear polydimethylsiloxane. This is very significant, especially since the plasticity of the branched polymer was 2.5 and the recovery 16 times that of the linear dimethylhydroxysilyl end-blocked polymer. (ASTM, D-926-56).

TABLE III
Effect of Branching in Polydimethylsiloxane

Polymer	Volatiles removed, %	PECT, °C.
Dimethylhydroxysilyl		
End-blocked	0	-38.5
Branched and vinyl end-blocked	0	-38.7
Dimethylhydroxysilyl		
End-blocked	11	-35.6
Branched and vinyl end-blocked	12	-36.3

The pseudoequilibrium crystallinity temperature was then determined for phenylmethylsiloxane and diphenylsiloxane homopolymers. The value for the phenylmethyl polymer was -35.4°C., which is slightly above that of the dimethyl siloxane polymer (-38.5°C.). The determination for the diphenyl polymer (molecular weight distribution not known) gave a high value of +367°C.

An investigation on poly- γ , γ , γ -trifluoropropylmethylsiloxane failed to reveal any birefringent crystallites under a variety of cooling conditions. These conditions included seeding with polydimethyl siloxane and phenylmethylsiloxane crystallites. These results may have two interpretations: either the polymer goes directly to its second-order transition, or its crystalline phase is not birefringent.

The values for the PECT obtained on the phenylmethylsiloxane, diphenylsiloxane, and di-

TABLE IV
Phenylmethylsiloxane-Dimethylsiloxane Copolymer Systems

Polymer composition		
Me ₂ SiO, mole-%	PhMeSiO, mole-%	PECT, °C.
0	99.5 ^a	-35.4
70	30	^a
92.5	7.5	^b
100	0	-38.5

^a Crystals present, but precise PECT hard to determine.

^b No crystallization.

^c Plus 0.5 mole-% MeViSiO units.

methylsiloxane homopolymers can be considered as base points for looking at the crystallinity behavior of their copolymer systems.

Since Polmanteer and Hunter¹ have studied silica-filled vulcanizates of the phenylmethylsiloxane-dimethylsiloxane copolymer system in detail, experimentation with this new technique was limited to critical copolymer compositions for confirmation of similar crystallinity behavior in the pure copolymer system. The data obtained by this new technique (Table IV) do indicate a similar type of liquid-solid equilibrium for the pure copolymer system.

Figure 6 and Table V present the characteristic liquid-solid equilibria for the phenylmethylsiloxane-

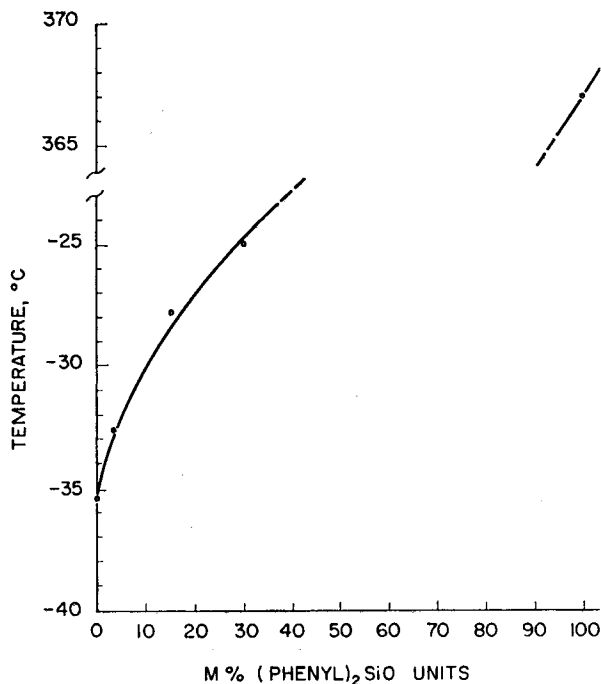


Fig. 6. Crystallinity in diphenylsiloxane and phenylmethylsiloxane homopolymers and copolymers.

TABLE V
Crystallinity in Phenylmethylsiloxane-Diphenylsiloxane-Methylvinylsiloxane System

Polymer composition			
Ph ₂ SiO, mole-%	PhMeSiO, mole-%	MeViSiO, mole-%	PECT, °C.
0	99.5	0.5	-35.4
3	96.5	0.5	-32.5
10	89.5	0.5	-28.1
15	84.5	0.5	-27.8
30	69.5	0.5	-25.0
100	0	0	+367

ane-diphenylsiloxane-methylvinylsiloxane system as determined by this new technique. These results are distinctly different from those observed in the phenylmethylsiloxane-dimethylsiloxane system. In this case the presence of increasing amounts of diphenylsiloxane units raises the pseudo-equilibrium crystallinity temperature.

IV. DISCUSSION

This work shows the inherent crystallinity characteristics of siloxane polymers and therefore provides a basis for studying the specific effects of filler and crosslinking. Qualitative conclusions with respect to these two effects might be attempted from existing data (Table VI). These conclusions, however, must be qualified, since the previous thermal histories of the pure polymers and filled vulcanizates are not exactly the same. If we can assume that the Gehman twist and PECT measurements are characteristic of the same phenomena, the general conclusion may be drawn that the presence of filler and crosslinks in the polyphenylsiloxane raises the characteristic crystallinity temperature of the polymer, while a similar effect does not appear to exist in the polydimethylsiloxane system.

The difference in behavior of the diphenylsiloxane-phenylmethylsiloxane-methylvinylsiloxane system from that of the phenylmethylsiloxane-dimethyl siloxane copolymer system is very significant.

TABLE VI
Comparison of Crystallinity Temperatures in Polymers and Filled Vulcanizates

Type of data	Crystallinity temperature, °C.	
	Me ₂ SiO	PhMeSiO
Gehman twist data ^a	-38	-26.7
PECT (pure polymer)	-38.5	-35.4

^a Data of Polmanteer and Hunter.¹

cant. Previously, Polmanteer and Hunter¹ showed that the presence of the bulky phenyl group in low concentrations in the phenylmethylsiloxane-dimethylsiloxane copolymer system sterically hindered crystallization. This situation does not exist in the phenylmethylsiloxane-diphenylsiloxane-methylvinylsiloxane system, so crystallization does not appear to be impeded. Thus, the liquid-solid equilibrium of this latter polymer system takes on a form similar to that of a binary solid solution.

V. SUMMARY

Birefringence exists in the crystallites of dimethyl, phenylmethyl and diphenyl polymers and many of their copolymers.

The existence of this birefringence allows the use of a new technique for studying inherent crystallinity behavior of siloxane polymers. This new technique involves minimizing nucleation effects so that crystal growth and melting rates can be balanced to allow calculation of a pseudoequilibrium crystallinity temperature (PECT) for the polymer. PECT's were obtained on each of the polymers and copolymers with two exceptions: polymers that go directly to their second-order transition and polymers which do not exhibit a birefringent crystalline phase.

The type of crystallinity in silica-filled vulcanizates of the phenylmethylsiloxane-dimethylsiloxane copolymer system of Polmanteer and Hunter¹ was found to also exist in the pure copolymer system.

The observations of spherulite formation support the earlier work of Warrick² that this type of growth takes place in unstretched polysiloxane vulcanizates.

The results for the diphenylsiloxane-phenylmethylsiloxane-methylvinylsiloxane polymer system indicate that the presence of diphenylsiloxane units does not contribute enough relative steric hindrance to impede crystallization. The volume of these groups integrates quite well into the crystalline structure to give a phase diagram of the solid-solution type.

The author wishes to express his thanks to John Saylor (Physical Chemistry Research) and Tom Talcott (Silastic Development) of the Dow Corning Corporation for their special synthesis of these polymers.

References

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Synopsis

Four homopolymers (dimethyl-, phenylmethyl-, diphenyl-, and trifluoropropylmethylpolysiloxanes) and two copolymer systems (dimethylsiloxane-phenylmethylsiloxane and phenylmethylsiloxane-diphenylsiloxane) have been studied by observing spherulite nucleation, growth, and melting. A characteristic crystallization temperature is proposed which can be considered representative of the equilibrium freezing-melting point. This work isolates the crystallinity characteristics of pure siloxane polymer and copolymer systems.

Résumé

Quatre homopolymères (diméthyl-, phénylméthyl-, diphényl- et trifluoropropylméthylpolysiloxanes) et deux systèmes de copolymères (diméthylsiloxane-phénylméthylsiloxane et phénylméthylsiloxane-diphénylsiloxane) ont été étudiés par l'observation de la formation de noyaux de sphérulites, de la croissance et de la fusion. Une température de cristallisation caractéristique, qui peut être considérée comme représentative du point de l'équilibre solide-liquide, est proposée. Ce travail indique les caractéristiques de cristallinité des polymères de siloxane purs et des systèmes de copolymères.

Zusammenfassung

An vier Homopolymeren (Dimethyl-, Phenylmethyl-, Diphenyl- und Trifluorpropylmethylpolysiloxan) und zwei Copolymersystemen (Dimethylsiloxan-Phenylmethyl und Phenylmethylsiloxane-Diphenyl) wurden Beobachtungen über Sphärolitkeimbildung, -wachstum und -schmelzen gemacht. Es wird eine charakteristische Kristallisationstemperatur angegeben, die den Gleichgewichtsschmelzpunkt repräsentiert. Die vorliegende Arbeit stellt eine Kristallinitätscharakteristik für reines Siloxanpolymeres und für Copolymersysteme auf.

Received October 28, 1960