

# Mesomorphic Behavior in Polydiphenylsiloxane. 3. An Examination of High Molecular Weight Polydiphenylsiloxane

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Polydiphenylsiloxane (PDPhS) has been prepared by solution ring opening polymerization of hexaphenylcyclotrisiloxane and characterized by <sup>29</sup>Si solid-state NMR spectroscopy. The thermal characteristics of the polymer have been examined by DSC, dynamic mechanical thermal analysis, linear expansion and X-ray diffraction analysis, and polarized optical microscopy in an attempt to elucidate the nature of the high-temperature mesomorphic phase and understand the high-temperature processing difficulties associated with the material. The results were indicative of a partially ordered molecular structure in the mesomorphic region that is not capable of viscous flow and cannot be ordered by shear. The absence of purely crystalline or purely liquid crystalline behavior is suggestive of a type of intermediate structure for mesomorphic PDPhS.

## Introduction

An evaluation of the literature with regard to polysiloxanes reveals a wealth of information concerning the phase transitions of polydialkylsiloxanes with several reports focusing on the mesomorphic behavior of polydialkylsiloxanes with *n*-alkyl side groups.<sup>1,2</sup> An additional member of the siloxane family whose morphology and phase transition behavior has received relatively little attention is polydiphenylsiloxane (PDPhS). Presumably this is due to difficulties in synthesizing the high molecular weight polymer, combined with its high crystallinity and intractability that make this particular siloxane especially difficult to characterize.<sup>3–11</sup> Dissolution of high molecular weight PDPhS only occurs in high-boiling solvents such as diphenyl ether at temperatures above 150 °C. This greatly limits the evaluation of even the basic properties of the material such as molecular weight and solution properties. In

an attempt to overcome some of these difficulties, PDPhS has been prepared in which some or all of the phenyl side groups were replaced with tolyl substituents.<sup>3,11,12</sup> This modification has the effect of reducing the thermal transition temperatures of the polymer and increasing its solubility in organic solvents, making these materials amenable to solution-state characterization. For pure PDPhS, however, most of the work conducted to date has focused on its bulk properties, yet even these remain to be thoroughly examined. An aspect of PDPhS that has been addressed in some detail in prior reports is its crystalline structure. On the basis of X-ray diffraction data of oriented films prepared from tolylated siloxanes, combined with diffraction data obtained from nonoriented PDPhS, Dubchak and co-workers have suggested that the chains of PDPhS assume a 4<sub>1</sub> helical structure with two chains occupying a rhombic unit cell in the crystalline phase.<sup>7</sup> Recently the structure has been redefined, and it is now postulated that the chains assume a quasi-planar rather than helical conformation.<sup>13</sup> High-temperature X-ray diffraction analysis of PDPhS has been reported to show an unusual temperature-dependent change in the diffraction pattern<sup>8</sup> above the melting point of 230 °C. The transition results in the disappearance of all of the crystalline reflections with the exception of an intense small angle reflection at  $2\theta = 8.8^\circ$  and a broad halo at  $2\theta = 20^\circ$ . That the  $2\theta = 8.8^\circ$  reflection remained and actually increased in intensity on heating combined with the simplicity of the diffraction pattern suggested a possible transition to a mesomorphic state upon melting. Similar X-ray diffraction patterns have also been recorded above the crystalline melting points of polydi-

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ethylsiloxane (PDES) and polydipropylsiloxane (PDPrS).<sup>14</sup>

That certain flexible polydialkylsiloxanes form a mesomorphic state above the melting point of the crystalline phase is well-known; however, the state of order of the flexible chains in the mesomorphic structure has been the focus of some debate. Early reports have referred to the mesophase formed by dialkylsiloxanes as a conformationally disordered crystal or "condensed crystal", which is defined as a crystalline structure in which the flexible chains experience a degree of dynamic conformational mobility within the confines of a three-dimensional crystalline lattice.<sup>15</sup> Alternatively, it has been suggested that the mesophase formed by polydialkylsiloxanes is a hexagonal columnar liquid crystalline phase with positional order in only two dimensions.<sup>16</sup> The state of order for PDPhS has not been examined in detail, although a recent report has proposed that the high-temperature phase of PDPhS is a nematic liquid crystal on the basis of its microscopic textures and X-ray diffraction pattern.<sup>11</sup> A recent study of oligomers of diphenylsiloxane has shown that even at low molecular weight ( $M_n < 4000$ ) PDPhS is capable of forming a mesophase.<sup>17,18</sup> A consequence of reducing the molecular weight was that an isotropic melt of the polymer could be obtained at temperatures below 300 °C; hence, the formation of the mesophase from the isotropic melt could be observed. According to this study, the mesophase appears from the melt in the form of three-dimensional crystal-like entities, which suggested that the mesophase has much more crystalline character rather than liquid character. To support this conclusion, information regarding the properties of the mesophase derived from the high molecular weight polymer are required. In this work, the thermal transitions and mesomorphic properties of high molecular weight PDPhS have been examined by X-ray diffraction analysis, DSC, dynamic mechanical analysis, and optical microscopy. It is hoped that these results will cast some light on the state of molecular order in the mesomorphic phase.

## Experimental Section

**Preparation of High Molecular Weight Polydiphenylsiloxane.**<sup>11</sup> Into a 200 mL round-bottom flask equipped with a condenser, mechanical stirrer, and septum were added 30 g of hexaphenylcyclotrisiloxane and 95 g of dry diphenyl ether. The flask was then purged with argon and heated to 180 °C with an oil bath. In a separate 30 mL round-bottom flask were added 2 mL of dry tetrahydrofuran and 0.42 g of hexamethylcyclotrisiloxane under argon. To this stirring mixture was then added  $1.9 \times 10^{-3}$  mol of *n*-butyllithium in hexanes. After 5 min exactly one-fifth of the total volume of the initiating solution was extracted from the 30 mL flask and added to the hexaphenylcyclotrisiloxane/diphenyl ether solution (ratio of initiator:diphenylsiloxane unit of 1:400). An additional 3 mL of tetrahydrofuran was added to the polymerization reaction to act as the reaction promoter. The polymerization was

allowed to proceed at 180 °C for 2.5 h, following which a 5-fold molar excess of diphenylmethylchlorosilane was added to the flask to terminate the polymerization. After 10 min the flask was allowed to cool to room temperature, which resulted in the precipitation of the polymer. The precipitate was then washed with 500 mL of methanol followed by three washings with 500 mL of acetone to remove residual cyclic material. The final yield of polymer was 57%.

**General Procedures.** <sup>29</sup>Si solid-state NMR spectra were recorded with a Varian Unity Plus NMR spectrometer at a frequency of 79.403 MHz. The solid samples were measured in a 7 mm silicon nitride rotor spinning at 5 kHz in a Varian wide-bore multinuclear magic angle spinning probe. Samples for <sup>29</sup>Si solid state NMR evaluation were prepared by compression molding PDPhS in a press at a temperature of 300 °C under a pressure of 100 kg/cm<sup>2</sup>. The sample was then pulverized with a mortar and pestle prior to NMR examination. DSC, TGA, and linear expansion coefficient determinations were performed with Rigaku TAS 200-DSC830D, TG8101D, and TMA 8140C thermal analysis systems, respectively. DSC scans were conducted under a nitrogen atmosphere at the heating/cooling rates specified in the text. The thermally equilibrated sample for DSC was prepared by heating the polymer 10 times to 300 °C, followed by slow cooling to room temperature while being held in the slow cooling platens of a press. The nonequilibrated sample was obtained by dissolving the polymer in hot 1-methyl-2-pyrrolidone and rapidly quenching the solution in cold water. The powdery sample was then washed several times with methanol and dried under vacuum prior to analysis. Dynamic mechanical thermal analysis was performed on a sample of PDPhS (previously compression molded at 300 °C) using a Rheometrics II Dynamic Mechanical Analyzer. The initial strain was set to 0.06% and the sample heated at a rate of 4 °C to a maximum temperature of 400 °C. The flexural 3 point bend was measured at room temperature using an Instron Tester. Optical microscopic observations were made with an Olympus BH-2 polarizing microscope equipped with a Mettler PF98 hotstage attached to a Mettler PF90 central processor. Samples were placed as powders between glass plates prior to heating. X-ray diffraction patterns were obtained with a JEOL JDX-3530 X-ray diffractometer system with the sample maintained under nitrogen for the high temperature analysis.

## Results and Discussion

### Preparation of Polymer and Characterization.

Polydiphenylsiloxane is generally prepared by ring-opening polymerization of hexaphenylcyclotrisiloxane under nonequilibrium reaction conditions in the bulk or solution state using an alkyllithium or a lithium silanolate as the polymerization initiator. Under kinetic control the polymerization is driven to high molecular weight by the energy gain associated with the ring opening of the strained cyclic trimer. If equilibration of the mixture is allowed, the more thermodynamically favored cyclic tetramer, octaphenylcyclotetrasiloxane, forms as the major product. The preferred route for preparing PDPhS is the high-temperature solution polymerization of hexaphenylcyclotrisiloxane with an alkyllithium or lithium silanolate as the polymerization initiator and a small amount of a polymerization promoter such as tetrahydrofuran or dimethyl sulfoxide added to the reaction.<sup>11</sup> To obtain high molecular weight polymer the polymerization must be conducted in a high-boiling solvent such as diphenyl ether at a sufficiently high temperature (150–190 °C) to avoid phase separation and precipitation of the growing polymer chain. Care must also be taken to minimize depolymerization processes that lead to the formation of the stable cyclic tetramer; hence, the concentrations

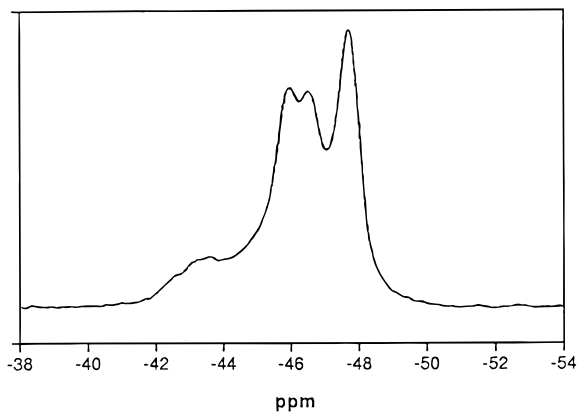
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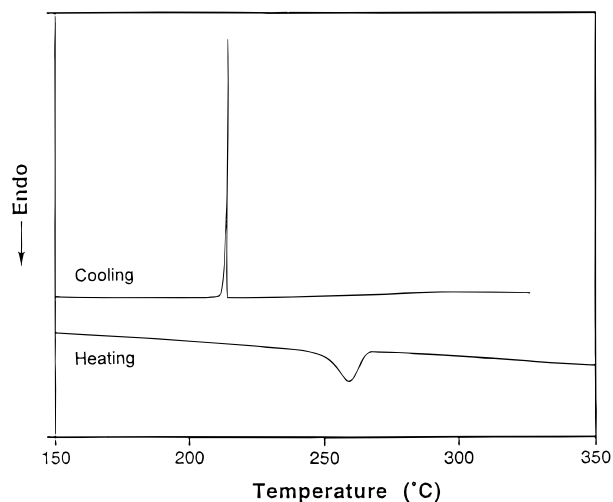


**Figure 1.**  $^{29}\text{Si}$  solid-state NMR spectrum for thermally equilibrated high molecular weight PDPHS.

of the cyclic trimer and tetramer must be carefully monitored to optimize polymer formation. For this study polydiphenylsiloxane was prepared using an initiator to diphenylsiloxane unit ratio of 1:400. An extensive examination of several solvents and solvent combinations failed to reveal a system capable of forming a stable polymer solution at ambient temperature, thus making it impossible to determine its molecular weight and polydispersity. Hence characterization of the polymer structure was limited to solid-state  $^{29}\text{Si}$  NMR spectroscopy and IR spectroscopy.

The  $^{29}\text{Si}$  solid-state NMR spectrum for thermally equilibrated PDPHS is shown in Figure 1, as prepared by compression molding at 300 °C and slow cooling to room temperature. At a frequency of 79.4 MHz, three main  $^{29}\text{Si}$  resonances can be observed with chemical shift values of -45.97, -46.55, and -47.72 ppm. A weak signal can also be observed at -43.60 ppm. The corresponding spectra for pure hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane showed resonances at -33.76 and -42.70 ppm, respectively. Their absence in the spectrum for PDPHS illustrates the effectiveness of the process utilized for purifying the polymer; however, this does not eliminate the possibility of larger diphenylsiloxane macrocycles being present. The four resonances in the NMR spectrum appear in the region expected for the diphenylsiloxane unit (-46.9 ppm) as observed in the dilute solution  $^{29}\text{Si}$  NMR spectrum for oligomeric diphenylsiloxane.<sup>17</sup> The shift of the signals to higher field relative to the cyclic analogues reflects the more relaxed conformation of the chain in the linear polymer. The presence of three strong distinct resonances for the diphenylsiloxane unit in the NMR spectrum indicates that at the given level of resolution the backbone Si atoms are perturbed by a minimum of three distinct electronic environments in the crystalline state, although these remain to be defined. The broad weak resonance centered at -43.60 may be due to impurities such as larger macrocycles or to amorphous polymer in the highly crystalline sample.

**TGA and DSC Studies.** The thermal stability of the PDPHS sample was evaluated by TG-DTA under an air atmosphere, from which it was determined that the onset of thermal decomposition begins in the vicinity of 400 °C with subsequent 10% weight loss at approximately 510 °C (heating rate of 10 °C/min). As a result of this evaluation, all subsequent analyses of the sample were performed at temperatures below 400 °C

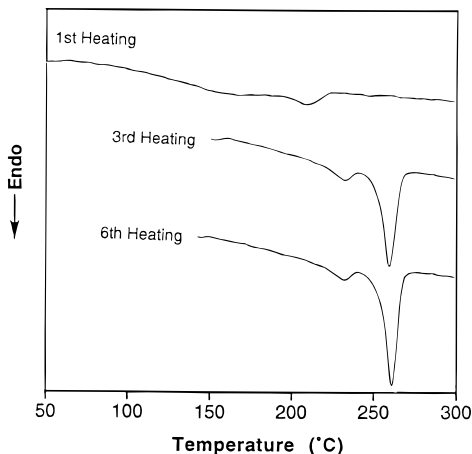


**Figure 2.** DSC heating and cooling scans for thermally equilibrated PDPHS (rate = 10 °C/min).

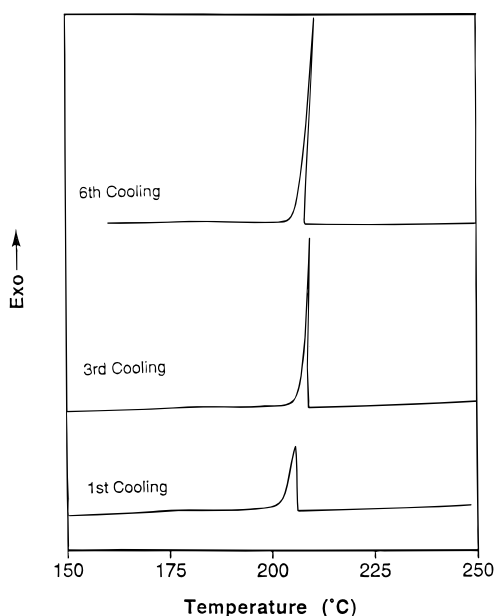
to limit polymer decomposition; however, this does not preclude the possibility of some thermal equilibration of the sample at temperatures approaching 400 °C.

The DSC heating and cooling scans for a thermally equilibrated sample of PDPHS are shown in Figure 2. The sample for analysis was prepared by heat cycling 10 times to 300 °C in a hot press followed each time by slow air cooling of the platens. According to the DSC, on heating from room temperature at rate of 10 °C/min, the transition from the crystalline phase to the mesophase appears as a broad peak with a maximum at 260 °C. Continued heating to 400 °C revealed no additional transitions. There was no evidence in the DSC for a glass transition, which might be expected since PDPHS is a highly crystalline polymer with only a small amorphous component. On cooling, the transition from the mesophase to the crystalline phase appears as a sharp peak at 218 °C ( $\Delta H = 7$  kJ/mol,  $\Delta S = 14$  J/K mol). The sharpness of the mesophase to crystal transition on cooling is due to supercooling of the sample.

A nonequibrated sample of PDPHS was prepared by dissolving a small amount of polymer into hot 1-methyl-2-pyrrolidone and quickly quenching the solution in cold water. The powdery sample was filtered and washed several times with methanol to remove residual solvent and dried under vacuum prior to analysis. As expected, the appearance of the DSC trace was considerably different from that of the equilibrated sample shown in Figure 2. Figure 3 shows the DSC traces for the first, third, and sixth heating scans for the quenched polymer subjected to heating and cooling cycles between 350 and 150 °C at a rate of 10 °C/min. On the first heating, the transition to the mesophase is suppressed to lower temperatures and over a broad temperature range. On the third heating the crystal to mesophase transition is similar to that observed for the equilibrated sample with the exception of a reduced enthalpy and a small endotherm that appears at a slightly lower temperature. Further heat cycling results in an increase in the transition enthalpy and a move of the peak maximum to that approaching the equilibrated PDPHS sample. An interesting observation made during the course of the DSC investigation was the gradual increase in the transition enthalpy over the series of heating and

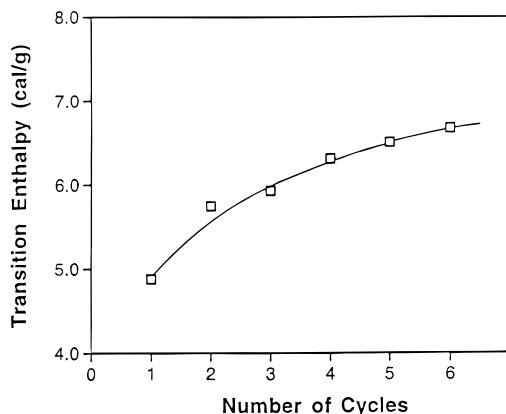


**Figure 3.** DSC first, third, and sixth heating scans for nonequilibrated PDPHS (rate = 10 °C/min).

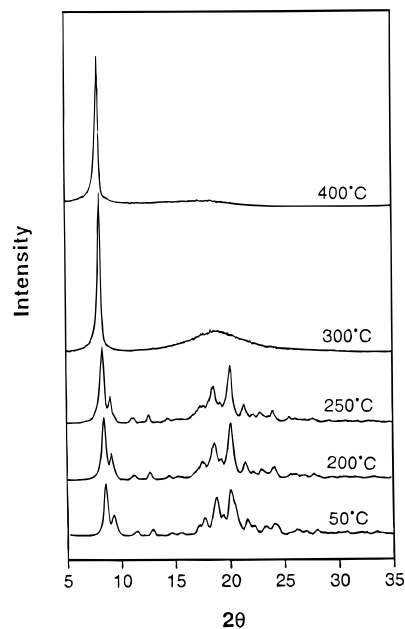


**Figure 4.** DSC first, third, and sixth cooling scans for nonequilibrated PDPHS (rate = 10 °C/min).

cooling cycles. This is also apparent in the DSC cooling scans for the nonequilibrated sample as it was cycled between 150 and 350 °C (Figure 4), although on cooling the peaks corresponding to the transition to the crystalline phase are considerably sharper than the reverse transition observed on heating. Figure 5 graphically illustrates the gradual increase in the enthalpy of the mesophase to crystal phase transition as a function of the number of thermal cycles. That the enthalpy continues to rise as a function of heat cycling implies that an equilibrium morphology is not reached despite heating the material to a temperature that greatly exceeds the crystal to mesophase transition temperature of 260 °C. Hence under the above conditions of temperature and time, PDPHS is able to retain some memory of its prior thermal history when heated above 260 °C. This implies that under these conditions of time and temperature the polymer chains do not have sufficient mobility to assume an equilibrium morphology on cooling and does not lend support to the thesis that the mesophase is as free flowing as a liquid crystalline phase.

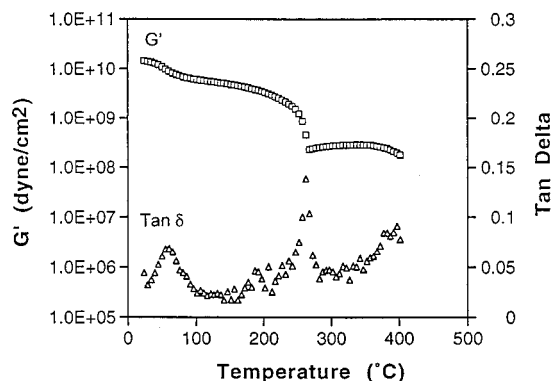


**Figure 5.** Mesophase to crystal transition enthalpy for nonequilibrated PDPHS as a function of DSC heating and cooling cycles to 350 °C (rate = 10 °C/min).



**Figure 6.** X-ray diffraction pattern for thermally equilibrated PDPHS as a function of temperature.

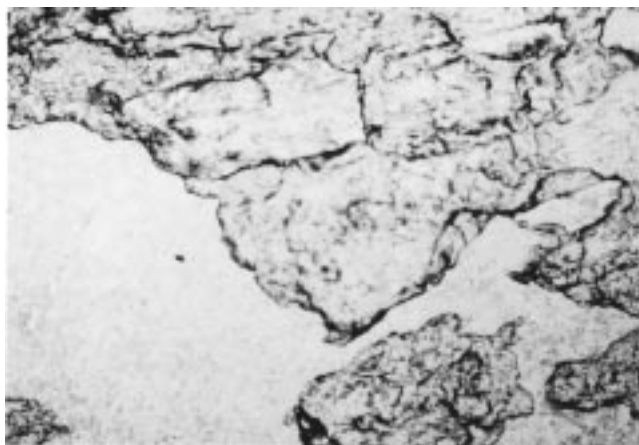
**X-ray Diffraction Analysis.** The X-ray powder pattern profile as a function of temperature for PDPHS is shown in Figure 6. At temperatures below 250 °C, the diffraction pattern is characteristic of crystalline PDPHS with little indication of an amorphous component. An increase in the temperature of the crystalline phase to 250 °C results in only a small increase ( $1.0 \times 10^{-3} \text{ \AA}/^\circ\text{C}$ ) in the Bragg spacing for the small angle 200 reflection at  $2\theta = 8.5^\circ$ . The linear thermal expansion coefficient measured for PDPHS compression molded into a block was approximately  $85 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  over the same temperature range. Heating through the transition temperature resulted in a sharp rise in the linear thermal expansion coefficient to a maximum value of  $450 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , before decreasing to approximately  $112 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  above the transition temperature. Over the same temperature range there is also a corresponding large jump in the Bragg spacing for the 200 reflection, as has been reported previously by Tsvankin and co-workers.<sup>8</sup> The X-ray diffraction pattern above the crystal to mesophase transition is greatly simplified relative to that for the crystalline state. The pattern includes only a sharp small angle reflection at  $2\theta = 8.0^\circ$



**Figure 7.**  $\tan \delta$  and storage modulus ( $G'$ ) for thermally equilibrated PDPHS as a function of temperature (rate = 4 °C/min.).

and a broad diffuse halo centered around  $2\theta = 18^\circ$ . There are no additional reflections with spacings of  $d/\sqrt{3}$  and  $d/2$  that might be suggestive of a hexagonal columnar arrangement of the polymer chains in the mesophase. Above the transition temperature there is a definite sharpening and increase in intensity of the small angle 200 reflection. Increasing the temperature above 300 °C results in a further gradual increase in the Bragg spacing of the 200 reflection ( $2.2 \times 10^{-3} \text{ \AA}/^\circ\text{C}$ ) to a value of 11.21 Å at 400 °C. Accompanying this change is a relative decrease in the intensity of the wide angle amorphous halo.

**Mechanical Properties.** To prepare samples for mechanical testing the polymer was compression molded into flat plates in a press at a temperature of 300 °C. Even under these conditions it was apparent that the material did not flow smoothly. The resultant plates, which resembled a fused solid more than a molded polymer, were quite brittle. The flexural modulus was high (4.2 GPa), but the flexural strength was low (24 MPa), which could be the result of a high level of defects. For dynamic mechanical thermal analysis the polymer plates were cut with a saw and sanded to achieve the necessary sample dimensions. The temperature profile for the storage modulus ( $G'$ ) and  $\tan \delta$  for PDPHS are shown in Figure 7. On heating, the glass transition ( $T_g$ ) of the polymer appears as a small drop in the modulus to  $9.1 \times 10^9 \text{ dyn/cm}^2$  between 55 and 60 °C, with a corresponding maximum in  $\tan \delta$ . This value for  $T_g$  is only slightly higher than the value of 49 °C reported by Ibemesi and co-workers for the diphenylsiloxane component in poly(diphenylsiloxane–dimethylsiloxane) block copolymers.<sup>6</sup> As the temperature of PDPHS is increased above  $T_g$ , the crystal to mesophase transition is reflected in a fall in the modulus, by about an order of magnitude to a value of  $2.3 \times 10^8 \text{ dyn/cm}^2$ , with a corresponding maximum in  $\tan \delta$  at 265 °C. The decrease in the storage modulus is significantly less than expected for a transition from a crystalline phase to a free-flowing liquid crystalline phase. Interestingly, above the crystal to mesophase transition temperature the leather-like polymer is easily cut with a knife without brittle fracture. As the polymer is further heated to 400 °C, there is little change in the value of the storage modulus with perhaps the exception of some slight tailing at the highest temperatures that might represent the onset of a high temperature transition, perhaps the onset of melting to the isotropic state. A point of concern



**Figure 8.** Microscopic texture of the PDPHS mesophase at 360 °C following shear.

regarding the plateau for the storage modulus in the mesomorphous region was whether thermally induced physical cross-linking might be responsible. To prove that this was not the case, a small piece of PDPHS compression molded at 330 °C was placed in diphenyl ether solvent and heated to 235 °C. Clean dissolution of the polymer in the solvent confirmed the absence of any substantial cross-linking of the material to 330 °C.

**Microscopic Observations.** The optical texture of PDPHS was examined by placing a small amount of the powdered polymer between two glass slides and heating in a hot-stage to a temperature of 360 °C. The hot stage was then quickly opened and the two glass plates compressed to obtain a sample with a uniform thickness. The sample was then allowed to equilibrate for a few minutes and then observed through crossed polarizers. The material was birefringent but did not display a texture that could be readily interpreted as being liquid crystalline. Another observation was the presence of a small amount of molten material on the periphery of the sample that likely appears as the result of some lower molecular weight, lower melting polymer present in the sample. The same sample was then subjected to shear by moving the two glass slides in opposite directions over a distance of approximately 1 mm. A photograph of the resultant texture is shown in Figure 8. The rough contours of the sheared sample clearly demonstrate the reluctance of the polymer to flow even at such high temperatures. In addition, rotation of the sample between the crossed-polars failed to show significant shear-induced birefringence, indicating a failure to align the polymer molecules in the direction of the shear force.

## Conclusions

The objective of this work has been to improve our understanding of the thermal behavior of polydiphenylsiloxane and discern the nature of the mesomorphic state that exists above the so-called melting point of crystalline PDPHS at 260 °C. Evaluation of the polymer in the mesomorphic state by X-ray diffraction analysis revealed a simple pattern with only a single intense small angle reflection and a broad halo in the wide angle region that is reminiscent of liquid crystalline type ordering of the polymer chains. DSC and dynamic mechanical thermal analysis of the polymer, however,

show the mesophase to be highly viscous, with no viscous flow at temperatures up to 400 °C. This is also confirmed by optical observations of the mesomorphic polymer which failed to show any significant molecular reorientation when subject to a shear force. This behavior is in agreement with earlier reports<sup>17,18</sup> that describe the properties of the mesophase formed by diphenylsiloxane oligomers with degrees of polymerization less than 20. For these systems the transition from the isotropic phase to the mesophase could be observed given the lower melting points of the oligomers relative to high molecular weight PDPhS. The observed result was the formation of the mesophase as three-dimensional plate-like structures in the slowly cooling

melt. Although it is not possible to make a similar observation for PDPhS due the very high temperatures required to reach the isotropic state, it is likely that a similar type of molecular organization is also taking place.

These experimental results are indicative of a partially ordered molecular structure in the mesomorphic region that is not capable of viscous flow and cannot be ordered by shear. The absence of purely crystalline or purely liquid crystalline behavior is suggestive of a type of intermediate structure for mesomorphic PDPhS.

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