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Communications to the Editor

Mesomorphic Behavior in Poly(diphenylsiloxane). 1. A Preliminary Examination of Diphenylsiloxane Oligomers

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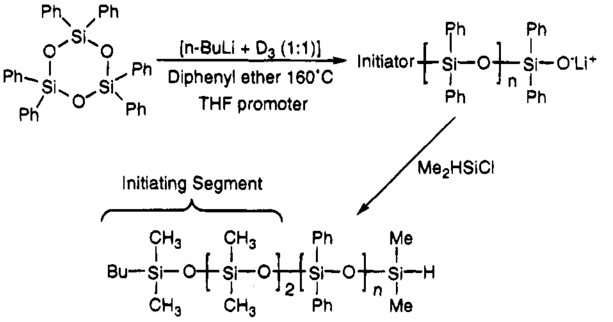
Introduction. Numerous reports in the literature have described the formation of a liquidlike ordered phase that appears upon melting of the crystalline phase of certain flexible poly(dialkylsiloxanes).[1] The first such observation was made by Beatty and coworkers,[2] who described a phase "intermediate between amorphous and crystalline states" when poly(diethylsiloxane) (PDES) was heated to a temperature just above its melting point of −3 °C. Recently, more detailed work has shown that PDES in the crystalline state can assume two different polymorphic modifications α and β that melt at 7 and 17 °C, respectively, to give the mesophase, which has been denoted as the μ or α_m phase.[1,3−6] Slow heating of the mesophase results in its gradual transformation to the isotropic liquid over the temperature range of 27−47 °C, the enthalpy of which (12.6 cal/g) is approximately 15% that of the heat of fusion of the α_2 and β_2 forms.

Poly(dipropylsiloxane) (PDPrS) has also been observed to form a mesophase[7,8] upon melting of the crystalline phase at 57 °C, but in this case the mesophase is stable to a maximum temperature of 207 °C for a total temperature interval of 150 °C. A clear rationale for this approximately 3-fold increase in the thermal range relative to PDES has yet to be demonstrated, although it has been suggested that chain rigidity may play a role. For both PDES and PDPrS the molecular weight distribution and cyclic impurities present in the polymer have been implicated as factors influencing the temperature for both conversion of the mesophase to the isotropic state and the breadth of the transition. PDES, for example, will only form a mesophase if the molecular weight of the polymer is very high. For PDPrS, the temperature for transition to the isotropic melt was found to be very sensitive to molecular weight, in fact no mesophase was observed for a sample with a weight-average molecular weight of 8000 (DP ~ 61).

In addition to PDES and PDPrS, poly(diphenylsiloxane) (PDPhS) has also been reported to form a mesophase above its melting temperature of 260 °C.[1,9,10] The X-ray diffraction pattern for PDPhS has been examined by Tsvankin and co-workers,[11] from which it was found that below the melting transition the pattern is characteristic of a crystalline sample but upon melting the crystalline reflections disappear with the exception of an intense reflection in the small-angle region (2θ = 8.8°) and a broad halo that appears in the wide-angle region (2θ ~ 15−25°). The diffraction pattern for the PDPhS mesophase is very similar to those recorded from the mesomorphic phases of PDES and PDPrS. The transition from the mesomorphic to the isotropic state for PDPhS has been reported to occur above 500 °C.[9,10] With the exception of only a few reports,[1,9−11] the mesomorphic properties of PDPhS remain essentially unexplored. This can be attributed to problems associated with preparing the polymer combined with its high melting point and intractability at temperatures below 150 °C[10,12] that make it difficult to characterize the material by traditional methods. In addition, the high isotropization temperature (T > 500 °C) makes it virtually impossible to observe the changes in the optical properties that accompany the transition from the mesophase to the melt and vice versa. In an attempt to circumvent these problems, we have been examining methods for preparing oligomers of diphenylsiloxane and evaluating their properties. By preparing shorter segments, it was hoped that the material will display lower transition temperatures and be sufficiently tractable to allow traditional methods of polymer characterization. In this paper we describe some of our preliminary results concerning the preparation, characterization, and physical properties of diphenylsiloxane oligomers.

Scheme 1



Results and Discussion. A synthetic methodology for the preparation of diphenylsiloxane oligomers with a narrow molecular weight distribution is not available in the literature. However, it has been reported that the solution ring-opening polymerization of hexaphenylcyclotrisiloxane, using a lithium silanolate as initiator in combination with a polymerization promoter, yields a high molecular weight polymer with a narrow molecular weight distribution.[9,10] We utilized a modification of this technique for preparing diphenylsiloxane oligomers as illustrated in Scheme 1. Initially, hexaphenylcyclotrisiloxane is dissolved in hot diphenyl ether (160 °C), while maintaining anhydrous conditions. The polymerization initiator was prepared by reacting a 1:1 molar ratio of hexamethylcyclotrisiloxane and n-butyllithium. The degree of polymerization of the oligomer is controlled by adjusting the ratio of initiator to diphenylsiloxane unit. To terminate the polymerization and prevent potential depolymerization processes, dimethylchlorosilane was added after an appropriate time interval (~40 min).[13]

The DSC first cooling and second heating scans for a diphenylsiloxane oligomer with a number-average mo-

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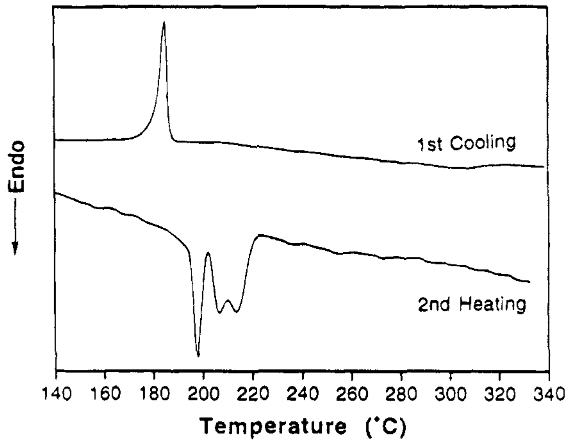

Figure 1. DSC first cooling and second heating scans for a diphenylsiloxane oligomer with a number-average molecular weight of 3600 relative to polystyrene standards (rate = 10 °C/min).

lecular weight of 3600 (relative to polystyrene standards) is shown in Figure 1. On heating at 10 °C/min, a rather complicated melting process consisting of three distinct transitions at 198, 208, and 214 °C was observed. High molecular weight poly(diphenylsiloxane) shows a single broad melting peak around 260 °C,[13,14] that corresponds to melting to the mesomorphic state. Whether the complex melting process observed in the oligomer is due to a polymorphic crystalline structure or other factors is not known. An examination of a series of oligomeric samples with number-average molecular weights ranging from 2200 to 4000 has revealed that, as the molecular weight of the oligomers is increased, the melting transitions shift to higher temperatures, with the lower temperature peak gradually disappearing and the two higher temperature transitions appearing to coalesce to give a single peak.[13] On cooling the oligomer ($M_n \sim 3600$; Figure 1), a single sharp peak resulting from the crystallization of the sample appears in the DSC trace at 184 °C, with a heat of fusion of 5 cal/g. This behavior on cooling is similar to that for poly(diphenylsiloxane) with the exception that the crystallization temperature for the polymer appears at a higher temperature (approximately 215 °C) and the enthalpy of fusion is larger (approximately 8.5 cal/g for an equilibrated sample).[13] In all cases, the transitions observed on heating and cooling are completely reversible.

On heating the diphenylsiloxane oligomer ($M_n \sim 3600$) above 214 °C, optical microscopic observations revealed that the sample remains highly birefringent to a temperature of about 330 °C, at which point a transition to the isotropic state is completed. In spite of this observed transition, no peaks were observed in the corresponding DSC heating scan. Similarly, on cooling from the isotropic liquid, a birefringent phase began to appear around 300 °C; however, again no transition was observed in the DSC scan. It has already been shown for PDES and PDPrS that the enthalpy for the mesomorphic to isotropic phase transition is very small relative to the enthalpy of fusion. We have also observed that there is a very strong molecular weight dependence for the mesophase to isotropic phase transition in the molecular weight region between 2200 and 4000.[13] Thus the strong molecular weight dependence of the isotropization temperature combined with the polydispersity of the oligomeric sample ($M_w/M_n = 1.15$ in this case) likely functions to spread the transition over a broad temperature range.[13] In fact, on cooling the oligomer from the melt, it was observed by optical microscopy that, rather than appear suddenly, the mesophase formed gradually over a very wide temperature interval.

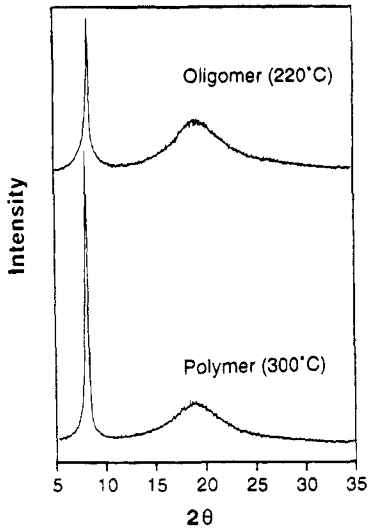

Figure 2. X-ray diffraction patterns for the mesomorphic phase of a diphenylsiloxane oligomer and for high molecular weight poly(diphenylsiloxane) at 220 and 300 °C, respectively.

The appearance of a birefringent phase above the melting point of the oligomers implies that there is an ordered phase between the crystalline phase and the appearance of the isotropic state. The X-ray diffraction pattern for the diphenylsiloxane oligomer at 220 °C, just above the melting point of the crystalline phase, is shown in Figure 2. In addition, the X-ray diffraction pattern for high molecular weight poly(diphenylsiloxane) in the mesomorphic state at 300 °C is also shown. The pattern for the polymer is very simple with only a single sharp maximum at $2\theta = 8.08°$ and a broad wide-angle reflection between 15 and 25°. The oligomer at 220 °C shows the same pattern with a sharp small-angle reflection at $2\theta = 8.44°$ and a broad reflection between 15 and 25°. The corresponding d spacings for the sharp small-angle reflections are 10.9 and 10.5 Å for the polymer and oligomer, respectively, and correspond to the spacing between the molecular chains. The similarity between the two diffraction patterns strongly suggests that the mesomorphic state observed in the polymer at high temperatures is also present in the oligomer above its melting point of 214 °C. In addition, both diffraction patterns are very similar to the diffraction patterns observed for PDES and PDPrS in the mesomorphic states, which may imply that each of these materials adopts a similar mesomorphic structure. Another interesting point concerning the appearance of the mesomorphic phase in the diphenylsiloxane oligomers is that this phase appears even in very low molecular weight material. Our studies have indicated that the mesophase begins to appear above a critical degree of polymerization of approximately 12 diphenylsiloxane units.[13] This is significantly lower than the critical degrees of polymerization reported for PDES and PDPrS. We can speculate that this increased stability is due either to a more rigid PDPhS chain or to electronic effects. The possibility that the mesomorphic phase of PDPhS is different from that of PDES and PDPrS must also be considered.

The classification of the mesophases formed by PDES and PDPrS remains somewhat controversial, with some

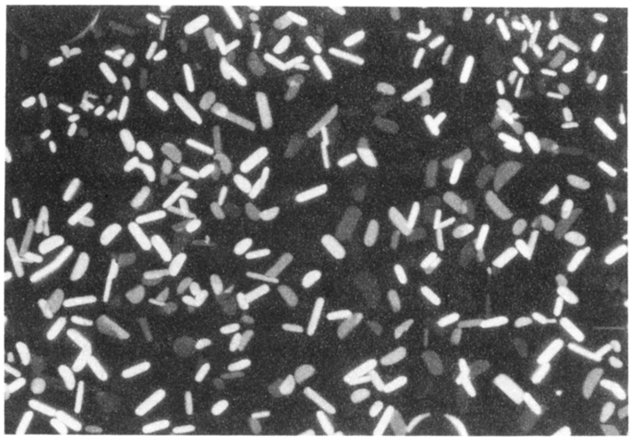

Figure 3. Appearance of the mesophase from the isotropic melt for a diphenylsiloxane oligomer ($M_n \sim 2700$ relative to polystyrene standards) heated to the isotropic melt and then slowly cooled to 234 °C.

reports suggesting that the phase is a conformationally disordered phase or "condis crystal" with three-dimensional order as defined by Wunderlich and co-workers[14] or a hexagonal columnar liquid crystalline phase with two-dimensional order.[15] A technique often used to classify the type of liquid crystalline order in mesomorphic materials has been to examine the microscopic texture that appears on cooling the material from the isotropic melt. This is impossible to do with high molecular weight PDPhS due to its very high isotropization temperature (>500 °C). Diphenylsiloxane oligomers, however, show both the mesomorphic phase and a mesophase to isotropic phase transition at much lower temperatures. The photograph shown in Figure 3 was obtained from a diphenylsiloxane oligomer ($M_n \sim 2700$) that was first heated to the isotropic melt and then slowly cooled to 234 °C, a temperature that marks the appearance of the mesomorphic phase. Rather than assume a liquid crystalline texture, the mesophase, as observed between crossed polarizers, appears as three-dimensional crystallites in the surrounding dark isotropic phase (the lengths of the crystallites range from 20 to 70 μm and appear to be a function of the growth rate). While it appears from the photograph that these apparently crystalline structures have a variety of shapes, this is due to the orientation of the crystals relative to the viewing angle. Subjecting the partially developed mesophase to a slight shear does not result in a major change in appearance, with the exception that some of the crystallites are set into rotation about their long axis from which a disklike geometry was confirmed. The birefringence of the disks reached a maximum when observed on edge and a minimum when observed perpendicular to the plane of the disk, perhaps suggesting a lamellar type of structure with the chain axis oriented perpendicular to the face of the disks, but how this might be possible with short chains is not known. The formation of small crystals does not appear to support the hypothesis that PDPhS forms a liquid crystalline phase; for example, there is no evidence for spherulite formation, and, as shown in Figure 3, there is no molecular ordering around the edge of air bubbles present in the sample nor is there shear-induced orientation.

These preliminary data have shown that the mesomorphic phase of diphenylsiloxane oligomers and likely poly(diphenylsiloxane) is one in which the molecular chains occupy positions within a three-dimensional crystalline structure. The mesophase is found to occur even in low molecular weight diphenylsiloxane oligomers and has a very strong molecular weight dependence. The nature of the molecular order within the mesophase remains to be defined but according to X-ray diffraction data may be similar to that of PDES and PDPrS mesophases.

Although a thorough examination of the diphenylsiloxane mesophase is far from complete, it is hoped that this new information will help stimulate fruitful discussion concerning the properties and structures of these unusual systems.

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