Mesomorphic Behavior in Poly(diphenylsiloxane). 2. An Examination of Diphenylsiloxane Oligomers

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ABSTRACT: Oligomers of diphenylsiloxane with number average molecular weights ranging from approximately 2200 to 3450 have been prepared and characterized. Samples with an M_n above a critical value of approximately 2400 form a mesomorphic phase similar to that formed by poly(diphenylsiloxane), when heated above the melting point of the crystalline phase. Above this critical molecular weight, the highly birefringent mesomorphic phase formed by the oligomers transforms completely to the isotropic state at a temperature that rises sharply with increasing molecular weight. Slow cooling of the molten isotropic phase results in the development of the mesophase as three-dimensional crystallites in the surrounding isotropic melt. The experimental evidence suggests that the PDPhS mesophase is a disordered crystalline phase in which the constituent oligomers have a degree of dynamic conformational disorder within the confines of a three-dimensional lattice structure.

Introduction

Poly(diphenylsiloxane) (PDPhS) has been reported to form a mesomorphic phase (a phase intermediate between crystalline and liquid states) above its melting temperature of 260 °C.[1-5] According to an X-ray study by Tsvankin and co-workers,[3] above its so-called melting transition, the diffraction pattern for PDPhS is greatly simplified, showing only a single intense reflection in the small angle region ($2\theta = 8.8°$) and a broad halo in the wide angle region ($2\theta \sim 15-25°$). The simplicity of this pattern is suggestive of a type of mesomorphic structure. For PDPhS, the transition from this mesomorphic state to the isotropic state has been reported to occur above 500 °C,[5] a temperature that is above the onset of thermal decomposition of the polymer (>400 °C[6]) and a temperature that is exceedingly high to microscopically observe the development of microscopic textures as the mesophase evolves upon cooling of the isotropic melt. Such observations may offer valuable information concerning the state of order within the mesomorphic phase.

In addition to PDPhS, the cyclic tetramer of diphenylsiloxane, octaphenylcyclotetrasiloxane (OPCTS) has been reported to form a disordered phase on heating above its melting point of 188 °C.[7,8] With continued heating, this phase transforms to the isotropic liquid at 205 °C. The results of these studies have suggested that the disordered phase of OPCTS is plastic crystalline.

In a recent communication, it has been shown that oligomers of diphenylsiloxane with degrees of polymerization of less than 30 can be prepared by anionic ring-opening polymerization of hexaphenylcyclotrisiloxane.[9] The resultant oligomers show significantly improved solubility in organic solvents relative to the high molecular weight material, which is only soluble in high boiling solvents at temperatures greater than 150 °C. In addition, the oligomers also melt completely to the isotropic state at greatly reduced temperatures relative to the high molecular weight polymer. In an example, an oligomer with a number average molecular weight of 3600 was found to melt completely at 330 °C. On cooling from the melt, the birefringent mesomorphic state appeared at 300 °C with subsequent crystallization at 184 °C. The X-ray diffraction patterns for the mesomorphic phases of both the oligomer and high molecular weight PDPhS were found to be essentially the same. Microscopic observation of mesophase formation from the oligomer melt showed that the mesophase actually appears in the form of distinct three-dimensional crystallites with a disklike geometry in the surrounding isotropic phase, thus suggesting that the mesophase is crystal-like as opposed to liquid crystalline.

The formation of a stable mesomorphic phase by low molecular weight oligomers of diphenylsiloxane is unique given that the alkyl-substituted analogs, poly(diethylsiloxane) (PDES) and poly(dipropylsiloxane) (PDPrS), require significantly higher molecular weights for their respective mesophases to form. PDES in the crystalline state can assume two different polymorphic modifications α and β that melt at 7 and 17 °C, respectively, to give a mesomorphic phase that in turn gradually converts to the isotropic liquid over the temperature range 27–47 °C;[1,2,10-13] however the critical molecular weight for mesophase formation has not yet been evaluated.[10] PDPrS forms a mesophase 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;[14,15] significantly broader than the approximately 40 deg range of stability for the PDES mesophase. The temperature for transition to the isotropic state was found to be sensitive to molecular weight; however, a sample with a weight average molecular weight of 8000 (DP ~ 61) reportedly failed to form a mesomorphic phase[14] but instead melted directly to an isotropic fluid, whereas the mesophase was reportedly stable for molecular weights greater than 27000. Substituting longer alkyl side chains such as butyl, pentyl, and hexyl onto the siloxane backbone results in a further increase in mesophase stability with the hexyl-substituted polymer showing a crystal to mesophase transition at 23 °C and a mesophase to isotropic transition at 330 °C, for a 307 °C range of stability.[16] Further increases in side chain length appear to have a destabilizing effect on the mesophase. For polysiloxanes with longer alkyl side chains, no data have been given for the critical molecular weight for mesophase formation. In addition to the

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Table 1

initiator: Ph_2SiO ratio	solvent	wt % P_3 in solvent	polymerization time (min) (temp (°C))	yield (%)	M_n
1:8	*p*-xylene	45	90 (reflux)	40	2200
1:10	*p*-xylene	42	105 (reflux)	74	2400
1:12	*p*-xylene	42	105 (reflux)	81	2600
1:14	diphenyl ether	50	40 (160 °C)	71	2900
1:16	diphenyl ether	50	40 (160 °C)	66	3000
1:18	diphenyl ether	50	40 (160 °C)	82	3300
1:20	diphenyl ether	50	40 (160 °C)	79	3450

nature of the side group and molecular weight, molecular weight distribution and cyclic impurities present in the polymer have also been implicated as factors influencing the temperature for conversion of the mesophase to the isotropic state and the breadth of this transition. To date, no theories have been proposed to account for how these factors influence the mesomorphic properties of siloxane-based polymers.

In this paper we would like to describe in more detail some of our results concerning the preparation and characterization of diphenylsiloxane oligomers and their mesomorphic properties with the goal of identifying the type of order present in the mesophase.

Experimental Section

In an earlier communication,[9] diphenylsiloxane oligomers were prepared using an initiating dimethylsiloxane trimer unit. In this work the initiating segment length has been reduced to one unit in an attempt to decrease end-group effects on the thermal transitions. As a result some slight variations between the data reported in this report and those in the earlier report can be expected.

Preparation of Oligomers. (The following is a representative example for the case in which the ratio of initiator to diphenylsiloxane unit is 1:10.) To a 10 mL round bottom flask equipped with a magnetic stir bar was added 0.5 mL of tetrahydrofuran and 0.75 g of hexamethylcyclotrisiloxane (D_3). The atmosphere was replaced with nitrogen, and 5.52 mL of a 1.83 M solution of *n*-butyllithium in hexanes was added with constant stirring at 0 °C. The initiator mixture was allowed to warm to room temperature and stirred for 5 min. In a separate 100 mL three-neck round bottom flask equipped with a mechanical stirrer and condenser, 10 g of hexaphenylcyclotrisiloxane (P_3) was dissolved in 15 mL of dry xylene, under nitrogen, at reflux. After complete dissolution, 3.64 mL of the initiator solution was added to the P_3 solution, that was then allowed to stir at reflux for 1 h and 45 min. To terminate the polymerization, 1 mL of phenyldimethylchlorosilane was added to the reaction mixture. After stirring for 10 min, the reaction was cooled to room temperature, resulting in the precipitation of the oligomer. The precipitate was washed twice with a 50:50 mixture of acetone and methanol and filtered. The precipitate was then dissolved in hot xylene and reprecipitated into methanol. The product was filtered and dried to yield 8 g of oligomer.

The above procedure describes the preparation of oligomers with a ratio of initiator to diphenylsiloxane unit of 1:12 or less. Variations in the conditions and the yields are listed in Table 1. To prepare higher molecular weight oligomers, a higher boiling solvent, diphenyl ether, was required to prevent precipitation of the oligomer during the polymerization process. These conditions are also listed in Table 1.

Preparation of High Molecular Weight Poly(diphenylsiloxane).[5] Into a 200 mL round bottom flask equipped with a condenser, mechanical stirrer, and septum was added 30 g of hexaphenylcyclotrisiloxane and 95 g of dry diphenyl ether. The flask was purged with argon and heated to 180 °C with an oil bath. To a separate 30 mL round bottom flask was added 2 mL of dry tetrahydrofuran and 0.42 g of hexamethylcyclotrisiloxane under argon. To the stirring mixture was then added 1.9×10^{-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 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 resulting in the precipitation of the polymer. The precipitate was then washed with 500 mL of methanol followed by several washings with acetone to remove residual cyclic material. The final yield of polymer was 57%.

General Experimental Considerations

The purities, molecular weights, and molecular weight distributions of the oligomers were measured with a TOSOH HLC-8020 gel permeation chromatograph with toluene as the eluting solvent. The molecular weights and molecular weight distributions were calculated on the basis of the retention times of the oligomers relative to those of polystyrene oligomeric standards, and as such, the values for the molecular weights in this report are relative values. ^{29}Si NMR spectra were recorded with a Bruker APC300 NMR spectrometer at a frequency of 59.6 MHz for samples dissolved in chloroform-*d*. DSC scans were recorded with a Rigaku TAS 200-DSC830D thermal analysis system. DSC scans were performed under a nitrogen atmosphere with a heating/cooling rate of 10 °C/min. The DSC scan for poly(diphenylsiloxane) was recorded after ten consecutive heating and slow cooling cycles to 300 °C.[6] 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. Heating and cooling rates were 5 °C/min. X-ray diffraction patterns were obtained with a JEOL JDX-3530 X-ray diffractometer system.

Results and Discussion

Oligomer Preparation. High molecular weight poly(diphenylsiloxane) has traditionally been prepared by ring-opening polymerization of the cyclic trimer, hexaphenylcyclotrisiloxane (P_3), under nonequilibrium reaction conditions. The natural tendency for diphenylsiloxane to form the more thermodynamically stable cyclic tetramer, octaphenylcyclotrisiloxane (P_4), precludes the possibility of producing polymer under equilibrium conditions, as is the case for polydimethylsiloxane. At present, the route of choice for preparing high molecular weight PDPhS is the kinetically controlled solution ring-opening polymerization of hexaphenylcyclotrisiloxane using a lithium silanolate as the polymerization initiator.[4,5] This procedure also requires the addition of a small amount of a polymerization promoter such as tetrahydrofuran or dimethyl sulfoxide to the reaction mixture. To obtain high molecular weight polymer, it is necessary to conduct the polymerization in a high boiling solvent such as diphenyl ether at a high temperature (150−190 °C) to avoid the 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 changes in the concentrations of the cyclic trimer and tetramer must be carefully monitored as the polymerization proceeds. Under these controlled conditions, it has been reported that high molecular weight poly(diphenylsiloxane) with a relatively narrow molecular weight distribution can be obtained.[4] Although this

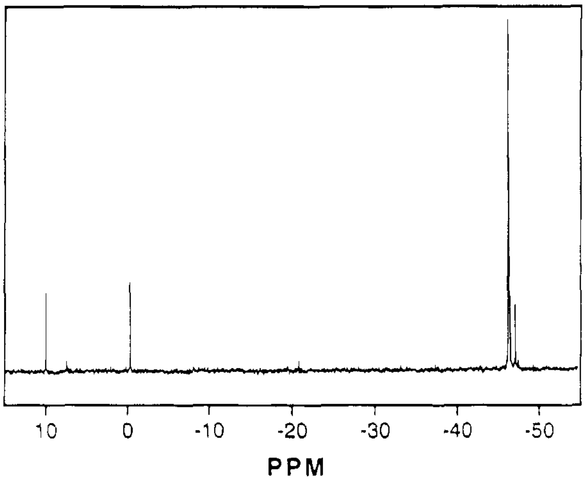

Figure 1. ^{29}Si NMR spectrum for a diphenylsiloxane oligomer with a number average molecular weight of approximately 2400 dissolved in chloroform-*d*.

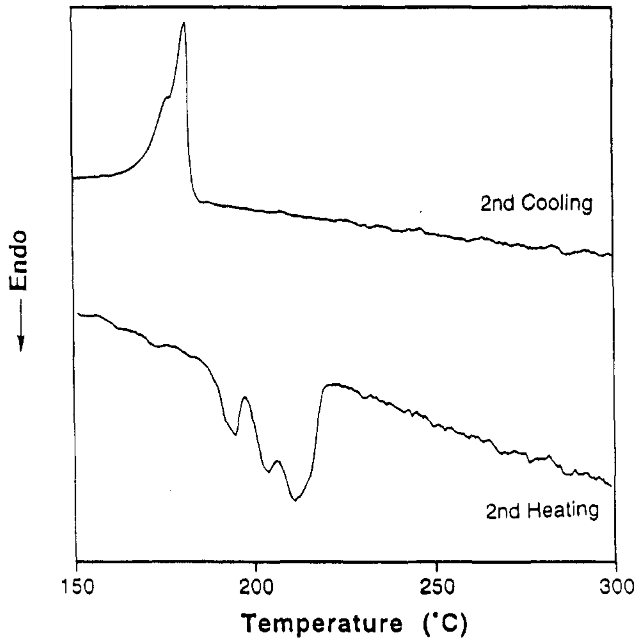

Figure 2. DSC second heating and second cooling scans for a diphenylsiloxane oligomer with a number average molecular weight of approximately 3000 (rate = 10 °C/min).

method has proven to be successful for the preparation of high molecular weight material, its application for preparing short chain oligomers has not been explored. We have utilized a modification of this method to prepare oligomers with degrees of polymerization of less than 30 and having narrow molecular weight distributions. In a typical preparation, the cyclic trimer P$_3$ is dissolved in refluxing anhydrous *p*-xylene or hot diphenyl ether at a concentration of approximately 50% solids. The polymerization initiator, prepared by the reaction of a 1:3 molar ratio of hexamethylcyclotrisiloxane (D$_3$) to *n*-butyllithium (in a previous communication[9] the molar ratio of the *n*-butyllithium to D$_3$ was 1:1; in this case the molar ratio has been adjusted to reduce the length of the initiating segment to one unit in order to decrease end-group effects), is then added with a small amount of promoter (tetrahydrofuran), to the hexaphenylcyclotrisiloxane (P$_3$) solution. The degree of polymerization of the resultant oligomer can be controlled by adjusting the ratio of initiator to diphenylsiloxane unit (in this study ratios of 1:8, 1:10, 1:12, 1:14, 1:16, 1:18, and 1:20 were chosen). The polymerization process was terminated by adding dimethylphenylchlorosilane after a suitable time at reflux. The oligomers were purified by twice washing with a 50:50 mixture of acetone and methanol, which effectively removed low molecular weight oligomers and residual cyclic species, as confirmed by GPC. The yield of oligomer after purification was in the range of 40–80%, with lower yields generally obtained for low molecular weight materials. The oligomers were sufficiently soluble in toluene and chloroform to be examined by GPC and ^{29}Si NMR spectroscopy. The individual GPC traces showed a smooth distribution of molecular weights, with a gradual increase in M_n as the ratio of initiator to diphenylsiloxane unit was decreased. The smoothness of the curves implied that there is some redistribution of the oligomer during preparation else one would expect chain growth as multiples of three, thus conferring some structure to the curves. The number average molecular weight of the oligomers was found to range from 2200 to 3450 (degree of polymerization of approximately 11–17) relative to polystyrene standards. The ^{29}Si NMR spectrum for the oligomer with a molecular weight of 2400 is shown in Figure 1. The strong signal at −46.7 ppm corresponds to the Si atoms of the diphenylsiloxane units with a small peak at −47.3 ppm that may be attributable to diphenylsiloxane units adjacent to the end groups. The dimethylsiloxane initiating segment shows a peak at 10 ppm with minor peaks at +8 and −22 ppm that likely result from a small amount of a dimethylsiloxane dimer species present in the initiator solution that became incorporated into the oligomer. The peak at −0.3 ppm can be assigned to the dimethylphenyl group used to terminate the polymerization reaction and end-block the oligomer.

DSC Studies. The second heating and second cooling scans for a diphenylsiloxane oligomer with an M_n of 3000 are shown in Figure 2. On heating at a rate of 10 °C/min, a rather complicated melting process takes place with three distinct peak maxima distinguishable at 198, 210, and 214 °C. Continued heating of the sample above the melting transitions failed to show any additional peaks that might be indicative of transitions at higher temperatures. On cooling from 300 °C, a sharp exothermic transition corresponding to the crystallization of the oligomer appears at 180 °C, with a small shoulder at a slightly lower temperature (combined peaks: $\Delta H \sim 3.1$ kJ/mol; $\Delta S \sim 6.8$ J/(K·mol)). These transitions are completely reversible in the rapidly equilibrated oligomeric samples; however for the high molecular weight polymer, prior to equilibration by annealing, repeated thermal cycling through the crystal–mesophase transition results in a gradual increase in the enthalpies and sharpness of the transitions.[6] On heating the equilibrated high molecular weight polymer, the transition to the mesophase appears as a single peak in the DSC around 260 °C with crystallization on cooling at 215 °C ($\Delta H \sim 7$ kJ/mol; $\Delta S \sim 14$ J/(K·mol)) (Figure 3). The complex melting process observed for the oligomers on heating may be due to the mixture of molecular weights in the individual samples, leading to melting point variations. The possibility of polymorphism must also be considered as a possible explanation for this behavior. It has been observed that as the molecular weight of the oligomer is gradually increased, the appearance of the DSC trace approaches that of the high molecular weight polymer, as shown in the DSC heating traces recorded for samples with molecular weights of 2400, 2900, and 3450, respectively (Figure

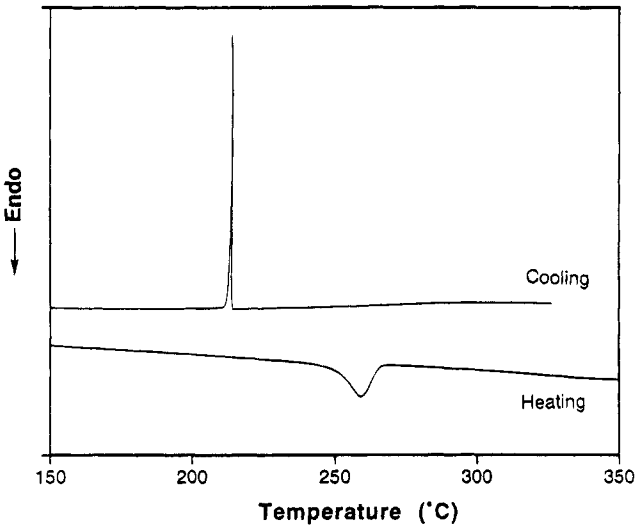

Figure 3. DSC heating and cooling scans for thermally equilibrated high molecular weight poly(diphenylsiloxane) (rate = 10 °C/min).

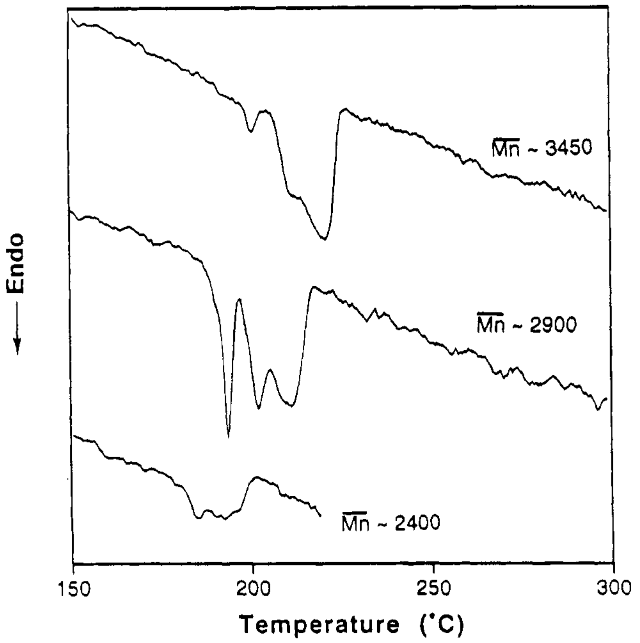

Figure 4. DSC second heating scans for diphenylsiloxane oligomers with number average molecular weights of approximately 2400, 2900, and 3450, respectively (rate = 10 °C/min).

4). The scan for the lowest molecular weight oligomer shows only a very weak endothermic peak around 180 °C, within which it is quite difficult to resolve individual transitions. The DSC scan for an oligomer with a slightly higher molecular weight (2900) clearly shows the three-peak pattern. A further increase in the molecular weight to 3450 results in a reduction in the intensity of the two lower temperature transitions and an increase in the intensity of the high-temperature transition. In addition to the changes in the appearance of the melting transition in the DSC scan, there is also a gradual shift in the melting point toward that of the high molecular weight polymer (260 °C). A similar trend in the DSC profiles has also been observed in a separate set of oligomers with an initiating dimethylsiloxane timer segment.

Microscopic Observations. With the DSC data as a guide, the changes in the appearance of the oligomers on heating through the melting of the crystalline phase to the isotropic melt were observed by polarized optical microscopy as a function of molecular weight. Two of the oligomers with the lowest average molecular weights (2200 and 2400) were found to melt directly from the crystalline state to the isotropic phase, with subsequent loss of birefringence when heated to 161 and 181 °C, respectively. These temperatures correspond well with the melting points for the oligomers as measured by DSC. The other higher molecular weight oligomers failed to melt to the isotropic state at the melting points identified by DSC and remained birefringent to higher temperatures. The actual transition to the isotropic melt appeared to take place gradually as the sample was heated above the crystalline melting point, with the temperature required for complete isotropization being very sensitive to the average molecular weight of the sample. The phase diagram on heating for the diphenylsiloxane oligomers as a function of average molecular weight is shown in Figure 5, with the open squares representing the temperature at which the sample became completely isotropic (no birefringence as observed by polarized optical microscopy) and the closed diamonds representing the melting points of the crystalline phase as measured by DSC. It is evident that there is a very steep rise in the temperature required for complete isotropization as the molecular weight is increased above the apparent critical molecular weight for mesophase formation of approximately 2400. It appears that in this regime the addition of as few as one or two diphenylsiloxane units greatly enhances the stability of the mesophase (a roughly 46 °C increase in stability per additional diphenylsiloxane unit as based upon the initial slope of the curve). In spite of this spectacular rise in the isotropization temperature as a function of molecular weight, the same does not hold true for the crystal–mesophase transition temperature. In fact, the difference between the transition temperatures for the lowest and highest molecular weight samples was less than 30 °C. For the oligomers with molecular weights of less than 2400, the formation of the crystalline phase eliminates the possibility of observing the transformation to the mesomorphic phase.

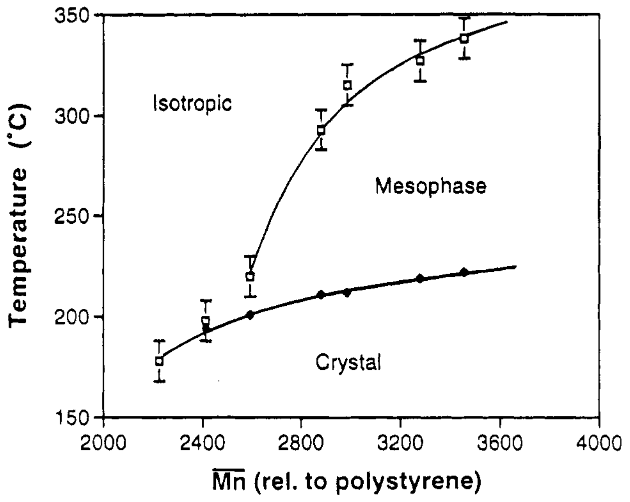

Figure 5. Phase diagram on heating for the diphenylsiloxane oligomers.

The steep rise in the isotropization temperature with only small increases in the average molecular weight may help to explain why no peak is observed in the DSC scan for the transition from the mesophase to the isotropic melt. Since the polydispersity index of the oligomers is greater than 1 (approximately 1.2) and the

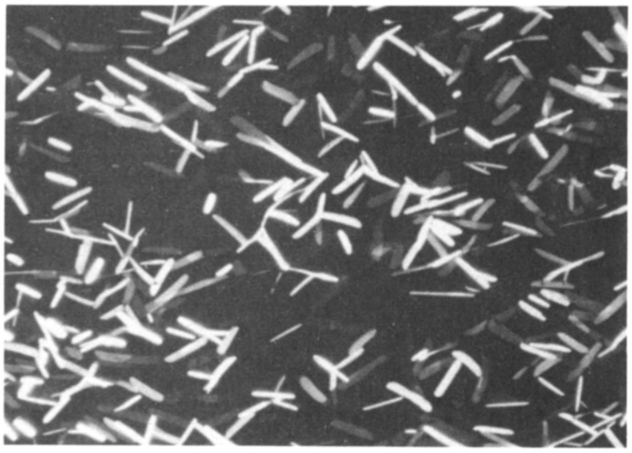

Figure 6. Formation of the mesomorphic phase from a diphenylsiloxane oligomer with a number average molecular weight of approximately 2600 on slow cooling (1 °C/min) to 214 °C from the isotropic melt.

molecular weight dependence for this transition very high, these oligomeric samples can be expected to undergo isotropization over a rather broad temperature range. This was confirmed by optical microscopy which showed a gradual reduction in the birefringence as the samples were heated through the mesomorphic region to the isotropic state. In addition, since the enthalpies associated with the isotropization of PDES and PDPrS from the mesophase were found to be low,[1] if it can be assumed that this is true for PDPhS, detection becomes even more difficult. The phase diagram for the oligomers cooled from the isotropic melt is quite similar to the phase diagram observed on heating, with the exception that the transition temperatures on cooling were depressed by a few degrees due to supercooling.

Compared to PDES and PDPrS, the critical molecular weight for mesophase formation by PDPhS is very low. As discussed earlier, there is not a clear explanation as to why the phenyl side groups offer more stability to the mesophase relative to ethyl and propyl side groups. If this difference can be attributed to a more rigid backbone for PDPhS compared to the other siloxanes is not known since the chain stiffness of PDPhS has yet to be determined. Other factors such as differences in inter- and intrachain interactions must also be considered as factors that may influence the stability of the mesophase.

The ability of diphenylsiloxane oligomers to show three distinct phases on heating (crystalline, mesomorphic, and isotropic) has made it possible to observe the formation of the mesomorphic phase by slow cooling of the isotropic melt. As the melt is gradually cooled (1 °C/min) to a temperature below the critical temperature for mesophase formation, the mesophase begins to slowly appear as three-dimensional disk-shaped crystallites in the dark isotropic liquid (Figure 6). There is no evidence for the formation of spherulitic structures or microscopic textures that would be indicative of the formation of a liquid crystalline phase. According to the photograph in Figure 6, the resultant crystallites appear to have a variety of shapes; however this is due to variations in the orientation of the crystallites relative to the angle of observation. The crystallites are highly birefringent when observed on edge and show minimum birefringence when observed perpendicular to the face of the disk. Continued slow cooling of the sample results in a gradual growth in the number of crystallites which may result in microfractionation of the oligomer sample into the mesophase (given the strong molecular weight dependence of the transition). The partially developed mesophase between the glass plates was subject to a sudden shear by fixing the position of the bottom slide while simultaneously shifting the position of the top slide and observing the change in the sample by optical microscopy. The result was no significant change in the birefringence or shape of the crystallites nor was there induced birefringence in the isotropic phase. This implies that the oligomers in the isotropic state cannot attain a state of preferred orientation. Within the crystalline entities, the lack of deformation on shear is indicative of the rigid nature of these crystallites that precludes the possibility of shear flow. Further cooling results in the increased development of the mesophase up to the point of complete crystallization.

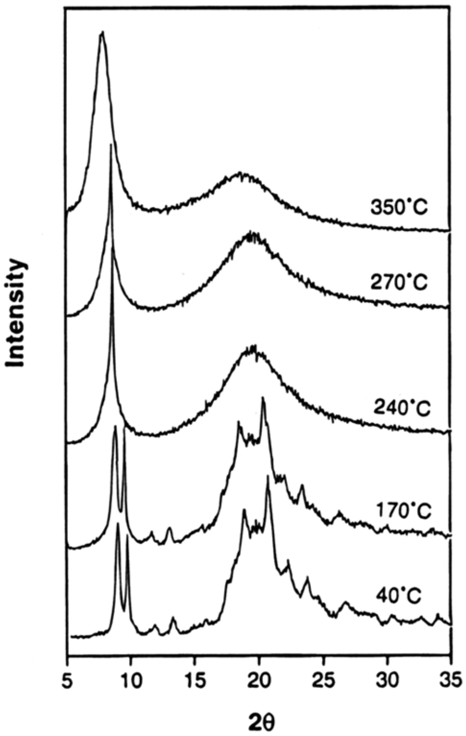

Figure 7. X-ray diffraction patterns for a diphenylsiloxane oligomer with a number average molecular weight of approximately 3000 as a function of temperature.

X-ray Diffraction Analysis. As discussed earlier, poly(diphenylsiloxane) in the mesomorphic state shows a very simple X-ray diffraction pattern consisting of a sharp intense small angle reflection and a broad halo in the wide angle region. The diffraction pattern profile for an oligomer with an average molecular weight of 3000 is shown in Figure 7. The diffraction pattern for the crystalline phase of the oligomers is similar to that of the high molecular weight polymer with the exception that the intensity of the sharp small angle reflection indexed as 200 ($d = 9.7$ Å) appears to be reduced relative to the other reflections in the scan. This may be due to crystalline defects resulting from the high concentration of chain ends or to polymorphism, as hinted by the DSC scan. Heating the oligomer above the melting point of 205 °C results in the loss of the crystalline reflections with the exception of the sharp small angle reflection with a Bragg spacing of 10.2 Å, corresponding to the intramolecular spacing between the chains, and in the wide angle region a broad halo around $2\theta = 20°$. There is no indication of reflections with spacings of $d/\sqrt{3}$ and $d/2$ that might suggest a hexagonal columnar arrangement of the chain in the mesophase. Heating the oligomer under nitrogen to 350 °C, a temperature at which the sample is completely isotropic (no birefringence nor shear-induced birefringence), as determined by optical microscopy, gives a diffraction pattern consisting of two broad reflections. The first appears in the small angle region centered at $2\theta = 8°$ and is shifted to smaller angles and is broad relative to the small angle reflection observed in the mesomorphic state; a second broad reflection appears at $2\theta = 20°$. Similar diffraction patterns consisting of two amorphous halos, with the small angle region peak being more intense than that in the wide angle region have been reported for the isotropic melts of PDES and PDPrS and appear to be a general phenomenon for polysiloxanes.[1]

Conclusions

Oligomers of diphenylsiloxane have been prepared by the anionic ring opening polymerization of hexaphenylcyclotrisiloxane in refluxing xylene or diphenyl ether. Samples with number average molecular weights ranging from 2200 to 3450 relative to polystyrene standards and a polydispersity index (M_w/M_n) of approximately 1.2 have been prepared. An examination of these oligomers by DSC and polarized optical microscopy has revealed that the critical number average molecular weight for mesophase formation is approximately 2400, with lower molecular weight materials showing only two phases (crystalline and isotropic). The higher molecular weight oligomers show a birefringent mesomorphic phase above the melting point of the crystalline phase; the isotropization temperature of which increases sharply with small increases in the molecular weight. Cooling of the molten isotropic phase below the isotropization temperature results in the slow development of the mesophase as three-dimensional crystalline entities in the surrounding isotropic melt. The system behaves in a fashion similar to that expected for the growth of crystallites from a melt and does not appear to show the textures or birefringence that might be expected from a thermotropic liquid crystalline phase. The nature of the molecular order in the mesophase remains to be adequately defined; however two different postulates have been presented in the literature. The first proposes that the mesophase formed by dialkylsiloxanes is a conformationally disordered crystalline phase ("condis crystal"), defined as a crystalline phase in which there is a degree of dynamic conformational disorder of the polymer chains.[1,17] Alternatively, it has been suggested that the mesophase of dialkylsiloxanes is a hexagonal columnar liquid crystalline phase with order in two dimensions.[16,18] For PDPhS the evidence tends to support the hypothesis that the PDPhS mesophase is a disordered crystalline phase since it has a degree of disorder as shown by X-ray analysis yet appears in the form of three-dimensional crystallites with three-dimensional ordering of the oligomers. The conclusion that the mesomorphic phase of PDPhS is a conformationally disordered phase is also supported by a study of the properties of the high molecular weight polymer, as will be discussed in a future report.[6]

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