Polymer Vol. 39 No. 3, pp. 689–695, 1998
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0032-3861/97/$17.00+0.00

PII: S0032-3861(97)00318-2

Phase behaviours of diphenylsiloxane oligomers

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(Received 19 December 1996; revised 27 February 1997)

Diphenylsiloxane oligomers (MN = 1200–4200, MW/MN < 1.3) without dimethylsiloxy end-group have been prepared and characterized. Cooling of the oligomer with a MN of 2200 or higher from the isotropic state results in the formation of the birefringent mesophase. A spherulite structure is observed upon further cooling from the mesophase. The increase of the mesophase temperature interval on the increasing molecular weight reflects that the increase of the molecular weight will improve the stability of the mesophase. Multiple melting transitions are observed from the spherulite to the mesophase for the oligomers with MN < 3800 in the d.s.c. heating scan. The end-group effect on the phase behaviours of diphenylsiloxane oligomers was revealed by comparing the phase diagram of three diphenylsiloxane oligomers with varied flexible end-groups. The phase diagram for these oligomers shows a flexible end-group effect on lowering the melting and isotropization temperature. With the increasing flexible chain-length, the critical molecular weight for mesophase formation is increased. The flexible end-group also has an effect on decreasing the endothermic heat of melting measured by d.s.c. In addition, a free-energy diagram based on thermodynamics is proposed to explain the absence of mesophase of the oligomers with MN lower than 1900. The mesophase is suggested as lamellar crystals which behave both in bright needles and plates surrounded by the isotropic melts. © 1997 Elsevier Science Ltd.

(Keywords: diphenylsiloxane oligomer; mesophase; spherulite)

INTRODUCTION

It has been established recently that a number of organic–inorganic hybrid polymers, such as polyorganosiloxanes, polyorganosilylenes and polyorganophosphazenes with symmetrical side substituents on the silicon atom show a tendency towards the formation of thermotropic mesophases. These polymers can form mesophases in spite of the absences of classical mesogenic groups in their structures[1,2]. Numerous reports in the literature have described the mesomorphic states of linear flexible poly(di-*n*-alkylsiloxanes). Poly(diethylsiloxane) (PDES) was the first observed to exhibit a mesophase between the amorphous and crystalline state[3–11]. The molecules were typically packed in a hexagonal cylinder lattice[10,11]. Moreover, an interesting feature of the mesomorphic state in PDES was the coexistence of the mesomorphic and amorphous phases[12]. Lately, the mesophases of poly(di-*n*-alkylsiloxanes) with various alkyl side groups have also been described as the hexagonal columnar mesophase[13–16]. The mesophases of polydlarylsiloxanes have only been reported in a few preliminary works[17–19]. Few reports concerning the mesophase of poly(diphenylsiloxane) (PDPhS) have been published[20,21], and these PDPhS oligomers were prepared by lithium siloxanolate-initiated ring polymerization in solution. In order to clarify the flexible end-block effect on the phase behaviours of PDPhS oligomers, our investigations are focused on the PDPhS oligomers prepared via anionic polymerization through bulk process initiated by *n*-butyl lithium instead of using lithium siloxanolate. The influence of a flexible end-group on the phase diagram and heat of melting on d.s.c. will be reported. The molecular weight effect on the phase behaviours of these diphenylsiloxane oligomers will also be discussed.

In addition, the synthesis and characterizations of diphenylsiloxane/dimethylsiloxane diblock and random copolymers with various MN and compositions have been systematically studied in our group (unpublished results). To try and reveal the phase behaviours of these copolymers and investigate the crystallizations of the copolymers with varied diphenylsiloxane monomer sequences, it is necessary to study the phase behaviours of the pure diphenylsiloxane oligomers.

EXPERIMENTAL

Materials

The hexamethylcyclotrisiloxane (P_3) monomer was kindly donated by Dow Corning Co. and used after further recrystallization in toluene. *n*-Butyl lithium in hexane (purchased from Merck) was titrated before use.

Oligomer synthesis

The diphenylsiloxane oligomers were prepared via bulk process by anionic ring-opening polymerization of the P_3 monomer in the presence of appropriate amounts of *n*-BuLi as an initiator. The following is a general procedure for the synthesis. P_3 was placed within a three-necked reactor equipped with a mechanical stirrer and a condenser under argon. The reactor was heated to 160°C and then a proper amount of *n*-BuLi in hexane was injected via syringe. After 30 min, the reaction was terminated by diphenylmethyl-

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*To whom correspondence should be addressed chlorosilane. The oligomer was obtained after precipitation from methanol. The precipitate was then dissolved in diphenyl ether and reprecipitated into methanol. The product was filtered and dried using vacuum stripping at 60°C overnight. The prepared oligomers were characterized by ^1H-NMR and gel permeation chromatography (GPC).

Measurements

Molecular weights were obtained by GPC (Kratos Model Spectroflow 400) using tetrahydrofuran (TFW) as the eluent with Shodex KF-804, KF-803, KF-802, KF-801 columns. The reported molecular weights and molecular weight distributions were calculated on the basis of the retention volumes of the oligomers relative to those of polystyrene standards. Differential scanning calorimetry (d.s.c.) scans were measured on a DuPont 9900 thermal analyser in flowing nitrogen ($100\,\mathrm{cm^3\,min^{-1}}$) at varied heating and cooling rates. Thermogravimetric analysis (TGA) was measured on a DuPont 951 thermal analyser at a heating rate of $10°\mathrm{C\,min^{-1}}$. Polarized optical microscopy (POM) was performed on an Olympus BHSP polarizing microscope equipped with a Linkam TMS92 hot stage. Examination of scanning electronic microscopy (SEM) was performed on a Hitachi S-2400.

RESULTS AND DISCUSSION

Preparation and characterization

The diphenylsiloxane oligomers used for phase investigations in this article have been prepared by ring-opening polymerization of the cyclic trimer, P_3 through bulk reaction[22]. The results of oligomer characterizations are shown in *Table 1*. The molecular weights of these oligomers synthesized through bulk polymerization, ranging from 1200 to 3800 (MW/MN < 1.3), are measured by GPC relative to polystyrene standards. Oligomer IX is insoluble in the GPC eluent THF, and thus its molecular weight is estimated according to the ratio of monomers to initiator. The melting ranges and melting peak temperatures (T_m) are recorded on d.s.c. by the following thermal treatments. These oligomers are first heated to the isotropic states in order to eliminate the previous thermal history, then cooled at a rate of $10°\mathrm{C\,min^{-1}}$ to 50°C for 10 min and subsequently heated at the same rate. The isotropization temperatures (T_i) of these oligomers are determined at the temperatures of disappearance of birefringence on heating by POM.

Differential scanning calorimetry studies

The d.s.c. second heating scans for these samples reveal complex multiple melting transitions when the molecular weight are lower than 2700. The T_m, which is assigned to the highest peak temperature in the multiple melting transitions, increases with the increasing molecular weight. Generally, increasing the MN of the oligomers ranging from 1200 to 4200 results in narrower melting range on the d.s.c. (as shown in *Table 1*).

Figure 1 shows the second heating scans of oligomers II, V and IX with MN = 1500, 2400 and 4200, respectively. Oligomer II shows a ambiguous peak around 202°C with a broad melting range. The d.s.c. scan for the oligomer V clearly shows a narrower melting range (145–230°C) and triple melting endotherms (206, 214 and 221°C). The d.s.c. curves of oligomer IX reveals a very sharp melting range (209–250°C) and a single melting peak (240°C). In addition to the peak at 240°C, another weak melting peak was also observed at 172°C. This less pronounced peak could be explained as the melting of the segregated low molecular weight fraction during the cooling of the melt–crystallization process, as will be discussed in a future report. These d.s.c. results reveal that an increase in the molecular weight results in a sharper melting range and a single endothermic peak. A similar trend in the d.s.c. profiles has been observed in the PDPhS oligomers with a flexible dimethylsiloxy segment[20]. Nevertheless, the flexible dimethylsiloxy end-group decreases the phase transition temperatures of PDPhS blocks. On cooling these oligomers from 300°C, it is observed by d.s.c. that only one exothermic transition is found, as shown in *Figure 2*. The exothermic peaks are sharper with increasing MN. The detailed study of the MN effect on the melting range of endothermic peak is currently underway.

POM observations

Phase transitions of diphenylsiloxane oligomers are also observed during the melt–crystallization and subsequent

Table 1 Characterizations of diphenylsiloxane oligmomers

Oligomer	GPC[a] MN (× 10^3)	MW/MN	d.s.c.[b] Melting range[c] (°C)	T_m[d] (°C)	POM T_i[e] (°C)	TGA T_d[f] (°C)
I	1.2	1.15	77–162	144	148	295
II	1.5	1.08	86–225	202	210	290
III	1.9	1.27	131–221	211	216	310
IV	2.2	1.30	140–230	222	265	308
V	2.4	1.20	145–230	221	335	355
VI	2.7	1.28	160–233	222	350	369
VII	3.4	1.19	187–240	224	365	380
VIII	3.8	1.30	194–245	236	380	390
IX	4.2[g]	-	209–250	240	395	384

[a] GPC were measured using TEF as eluent and polystyrenes as standards

[b] Oligomers I–V were first heated to isotropic (oligomers VI–VIII were heated to 340°C in avoidance of thermal degradation), then cooled to room temperature at a rate of $10°\mathrm{C\,min^{-1}}$ and subsequently scanned at the same rate

[c] Melting range: the temperatures from initial to final melting relative to baseline on d.s.c.

[d] T_m: the highest peak temperature in the multiple melting transitions on d.s.c.

[e] Disappearance of birefringence on the second heating; T_i of oligomers VI–VIII were recorded on the first heating

[f] T_d: the initial temperature of weight loss which were measured at a rate of $10°\mathrm{C\,min^{-1}}$ under nitrogen on TGA

[g] Estimated based on initiator/P_3 ratio

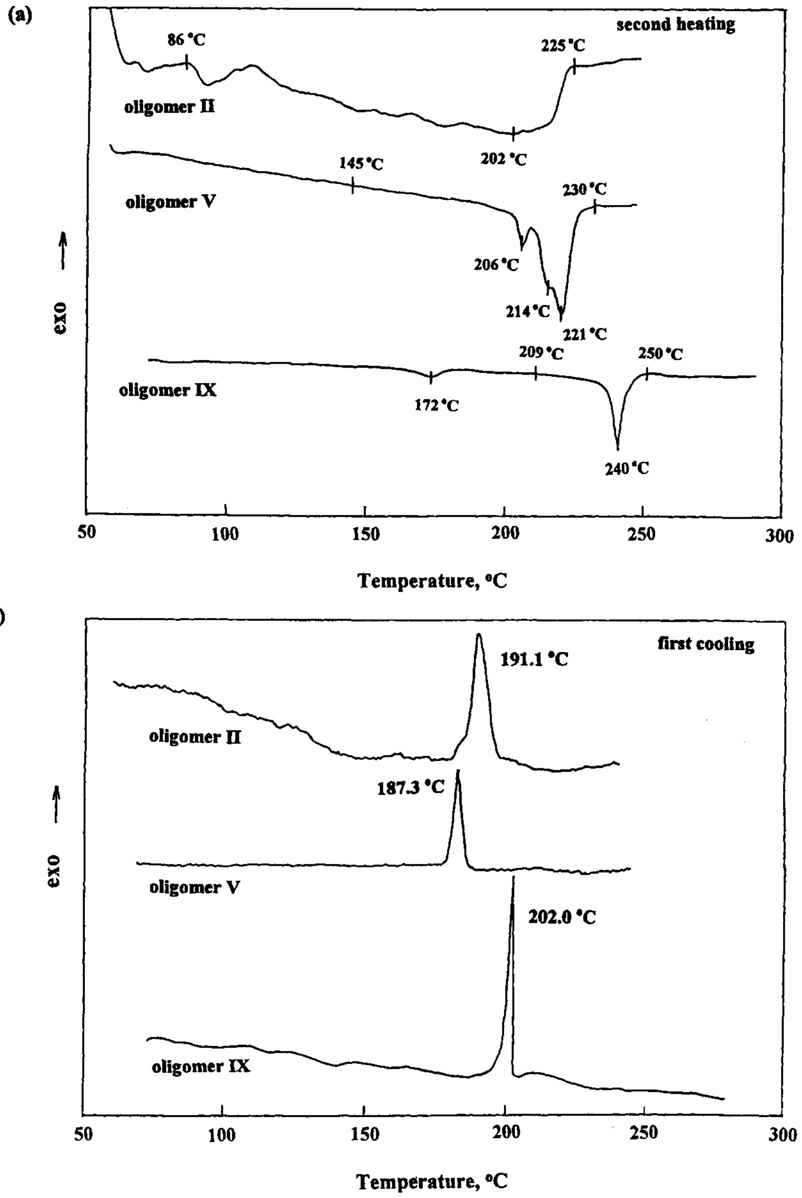


Figure 1 (a) Differential scanning calorimetry second heating scans for oligomer II, V and IX with MN = 1500, 2400 and 4200, respectively. (b) Differential scanning calorimetry first cooling scans for oligomer II, V and IX. These samples were heated to isotropic states (oligomer IX was heated to 340°C in avoidance of thermal degradation), then cooled to room temperature at a rate of 10°C min^{-1} and subsequently scanned at 10°C min^{-1}

heating process on POM. The thermal treatments on the hot-stage are parallel to that performed on the d.s.c. (10°C min^{-1} heating and cooling). Similarly, upon cooling oligomers I, II and III from their isotropic states, spherulites are observed although the degree of perfection of their spherulites in the micrographs does not appear to be high. The spherulite of oligomer I, which was developed under quenching from the isotropic state to room temperature, is shown in *Figure 2a*. A similar spherulitic pattern on POM has even been observed in the polyethylene[23]. If the crystallization is performed on a smaller supercooling (quenching from the isotropic state to 200°C) the spherulite will be more easily identified, as shown in *Figure 2b*. In addition, no mesophases are observed for oligomers with MN $\leq$ 1900. However, upon cooling the oligomers IV–IX on POM from the melt, the birefringences of the mesophase gradually appear and subsequent cooling from mesophase to the temperature below T_m results in spherulitic textures.

Figure 3a–d show the phase transitions occurred upon cooling oligomer V. Cooling from the isotropic state results in the formation of bright needles as shown in *Figure 3a* (cross-polars, photographed at 300°C after cooling from the isotropic state at a rate of 10°C min^{-1}). It is observed that both bright needles and plates appear during the cooling process. The plate was the first to be found in the PDPHS oligomers. *Figure 3b* is photographed at 300°C under parallel polars after the same thermal treatment in order to allow easier observation, because the plates are less birefringent under cross-polars. The plates can be found in the neighbourhood of bright needles. The appearance of birefringent mesophase upon cooling does not cause a detectable exothermic peak on the d.s.c. In fact, it is observed that the mesophase gradually develops over a wide temperature interval (about 150°C). *Figure 3c* (cross-polars, photographed at 250°C) shows the well-developed mesophase textures. If it is cooled further, the spherulites will appear quickly, accompanied by a d.s.c. exothermic cooling peak. *Figure 3d* (cross-polars, photographed at 170°C) shows the spherulitic textures formed under subsequent cooling and it is observed that bright needles and plates will still exist upon cooling to room temperature.

In the literature[21] it is suggested that the mesophase took

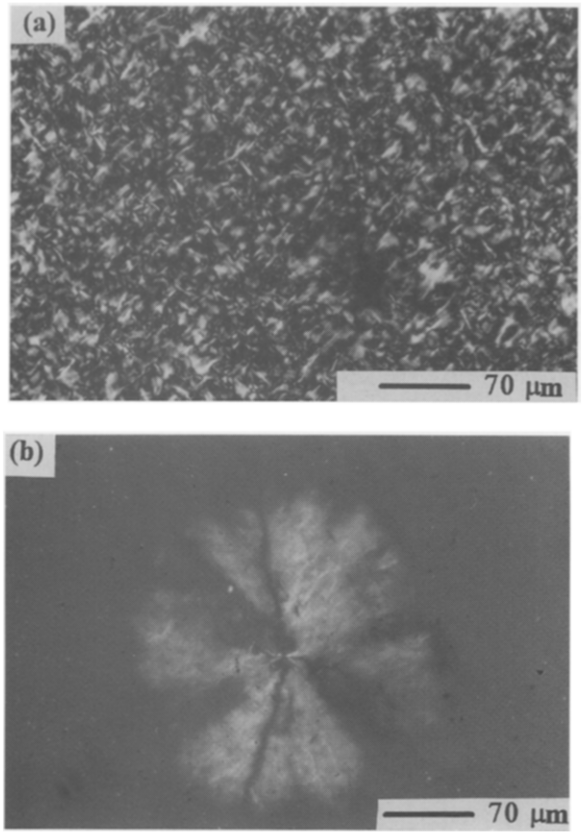
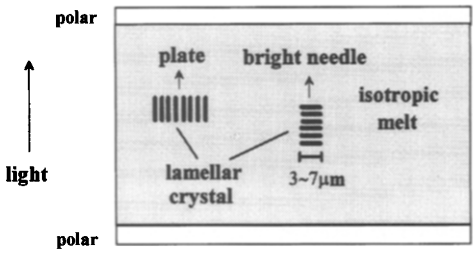


Figure 2 (a) The spherulite of oligomer I observed on POM (× 200). Samples were quenched from the isotropic state to room temperature. (b) The spherulite of oligomer II developed at 200°C for 4 min after quenching from the isotropic state



Scheme 1

the appearance of three-dimensional disk-shaped crystallites in the isotropic liquid. Although the molecular packing of the mesophase is still not clearly known at present, the POM observations imply the bright needles and plates might be the same disk-shaped crystals. In this study, the disk-shaped crystallite is suggested as a lamellar crystal. Normally, the lamellar crystal in a crystalline polymer is about 10 nm thick, such that they cannot be observed with POM. However, the PDPhS investigated here are oligomers and they can form crystals large enough to be observed optically. The nature of the mesophase is probably that of lamellar crystals surrounded by the isotropic melts. As illustrated in *Scheme 1*, the bright needles are very likely to be the lateral faces of lamellar crystals and the less birefringent plates may be the top surfaces of the lamellar crystals. Interestingly, similar bright needles have also been mentioned as the lateral faces of mesomorphic lamellae properly oriented in space in the mesophase of polydlethylsiloxanes (PDES)[9]. Nevertheless, no plate domain is observed by POM in the PDES system and it is explained by the low in-plane birefringence of PDES[9]. In this study, the appearance of a plate domain is likely to be the result of more efficient molecular packings and higher in-plane birefringence of diphenylsiloxane oligomers, in comparison to the PDES system.

As described above, the crystallization of the oligomer from the mesophase occurs with retention of the optical textures. From the microscopic point of view, the formation of spherulites proceeds as a crystal growth of both the existing lamellar crystals and the isotropic melt. This transition occurs with an single exothermic peak on d.s.c., as shown in *Figure 1b*. At the same time, viewing from the level of molecular packing, the average chain to chain distance decreases from the mesophase to the spherulitic phase during crystallization, which has been confirmed by wide angle X-ray diffraction. Although Harkness *et al.* have mentioned that there is no evidence for spherulite formation in the mesophase[20], we observed the spherulite formation in the crystalline phase.

Phase diagrams

Observation of the heatings of the oligomers on POM reveals that oligomers I–III show continuous disappearance of spherulites to isotropic states without passing through the mesomorphic states. Nevertheless, it is observed that heatings of oligomers IV–IX will result in the melting of the spherulites to the mesophases, and both bright needles and plates will be observed. Further heating will result in the gradual disappearance of birefringences and finally melt to isotropic states. In oligomers I–VII, the phase transitions observed by POM on heating and cooling are reversible. Oligomers VIII and IX are found not to be reversible on POM if they are heated to isotropization temperatures. This may be explained by thermal degradation upon heating to the isotropic state. Because the isotropization temperatures are unable to be determined by d.s.c., they are recorded on POM as the temperatures of the disappearances of the birefringences upon heating the melt–crystallized oligomers. The phase diagram on heating of the diphenylsiloxane oligomers without flexible dimethylsiloxy segments as a function of MN is shown in *Figure 4*, with the closed squares representing the T_i and the closed circles representing the T_m of the spherulites measured on the d.s.c. It is observed that the T_m of these oligomers with MN = 1500 or higher tend to rise slightly and regularly (roughly a 2.8°C increase per diphenylsiloxane unit). The regular increase of both the spherulite–isotropic transitions (oligomer II–III) and spherulite–mesophase transitions (oligomer IV–IX) implies that these two transitions have the same physical nature of the spherulitic disordering. Examinations of the isotropization temperatures of these oligomers reveal that a very steep rise of T_i is found in the critical MN range (2000–2400). However, further increase in the molecular weight results in gradual increase of T_i (roughly a 8.1°C increase per diphenylsiloxane unit). Based on the POM and the d.s.c. results, the fact that the mesophase temperature intervals increase with the increasing molecular weights of the oligomers indicates that the stability of the mesomorphic state is improved with the increase of molecular weight. The stability of mesophase could interestingly be quoted from the fact that the isotropization point of oligomer IX (395°C) is higher than the initial temperature of weight loss (384°C), as shown in *Table 1*.

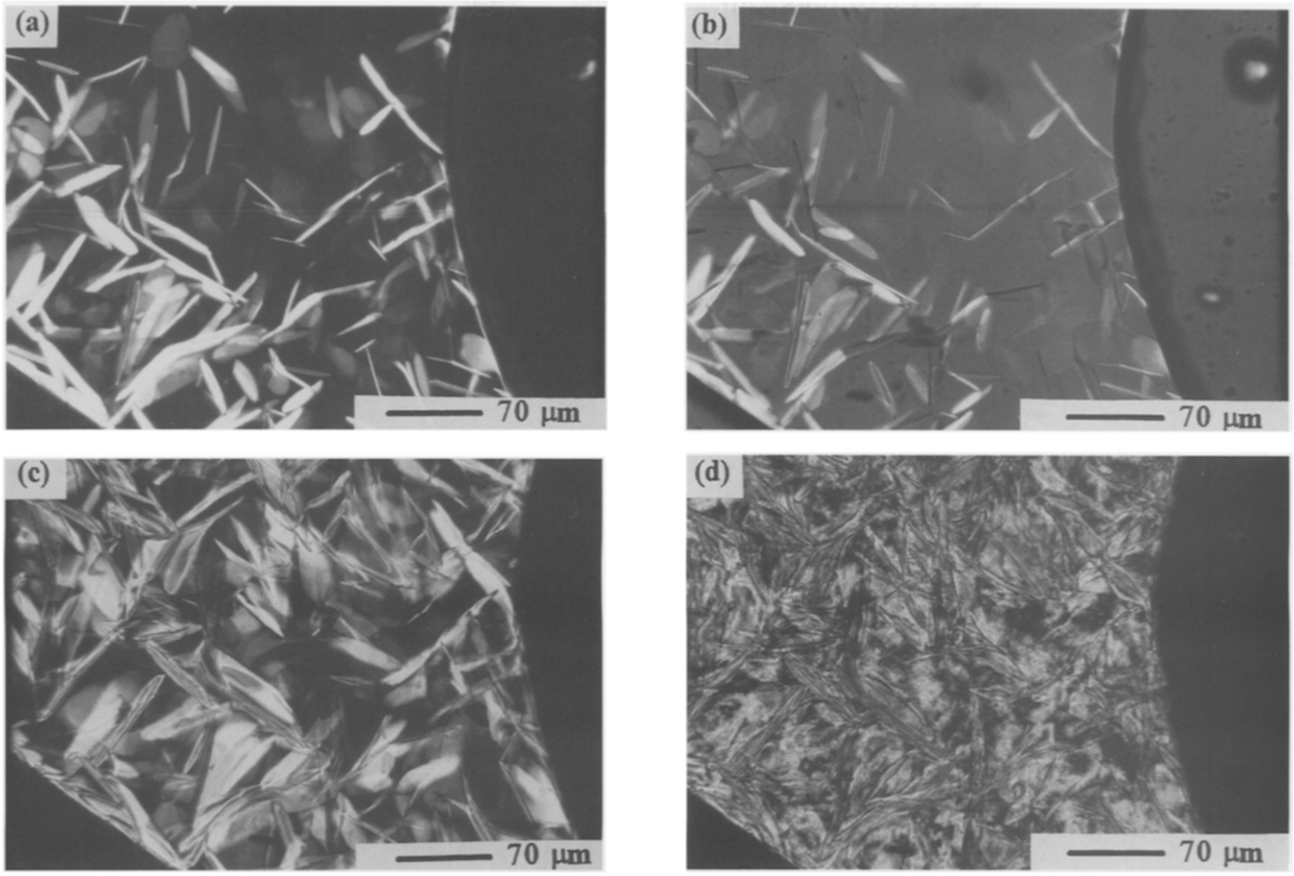


Figure 3 Optical micrographs of oligomer V. (a) Bright needles observed at 300°C after cooling from the isotropic state at a rate of 10°C min^{-1} under cross-polars. (b) Plates were found between bright needles as the arrow indicate. Photographed at 300°C and the thermal treatment is the same as (a), but under parallel polars. (c) The more developed mesophase at 250°C under cross-polars. (d) The spherulitic morphology photographed at 170°C under cross-polars

End-group effects

Figure 4 reveals the flexible end-group effect on the phase diagram. PDPHS oligomers with various flexible chain-lengths were compared. It is clearly found that the flexible end-group will affect the transition temperatures of these oligomers. The isotropization and melting temperature of the oligomer decrease with the increasing flexible chain-length. The most obvious end-group effect is the lowering of the critical molecular weight for mesophase formation. For the oligomer with MN higher than critical MN, the end-group effects on the mesophase temperature intervals are found to be less dependent on the increasing molecular weights.

The flexible end-group also introduces an effect on decreasing the endothermic heats of melting from the crystal to the mesophase. *Figure 5* shows the d.s.c. heats of melting (ΔH) of diphenylsiloxane oligomers with and without six dimethylsiloxyl units in the end-groups. The ΔH was calculated from the d.s.c. second heating scans (rate = 10°C min^{-1}). It is found that the end-group has a significant influence on decreasing the heat of melting on d.s.c. This implies the melting point depression of the diphenylsiloxane oligomers with flexible end-groups may be contributed from the decrease of melting enthalpy.

Thermodynamic considerations of mesophase formation

Another interesting phenomenon we try to explain is why the mesophase does not exist in the low molecular weight oligomers. First we consider the entropy of the isotropic states of these oligomers. In general, the amorphous entropy per repeating unit can be written using equation (1)^{24}:

$$S = S_a + (2S_e + R \ln x)/x \qquad (1)$$

where S_a is the entropy contributed from the repeating units, and the separate excess contribution from the chain ends is represented as S_e. R is the gas constant and x is the number of repeating units. From this equation, we could postulate the entropy of isotropic state increases with the decreasing molecular weight because the greater mobility of chain ends in the liquid phase would yield a greater entropy for relatively small molecules. Based on the same concept of chain ends effect, we would also expect a somewhat reduced enthalpy (H) for relatively large molecules because of the larger volume requirement of the chain ends than the chain units. Nevertheless, the enthalpy effect would be less dominant than the entropy effect here. The reason is that for the condensed phase, the system volume (V) is relatively small and, accordingly, the contribution of the item PV is less important than internal energy (U)^{24}, as the basic equation (2) in thermodynamics shows:

$$H = U + PV \qquad (2)$$

Thus, the difference in V caused by variation in molecular weight can be neglected. Free-energy diagram has been widely used to discuss the equilibrium melting, non-equilibrium melting, reorganization, recrystallization and annealing in polymers^{25}. Now we want to propose a free-energy diagram for explaining the phase transition behaviours in this oligomer system. *Figure 6* shows a schematic free-energy diagram for the oligomers. The explanation for the absence of the mesophase is based on thermodynamics

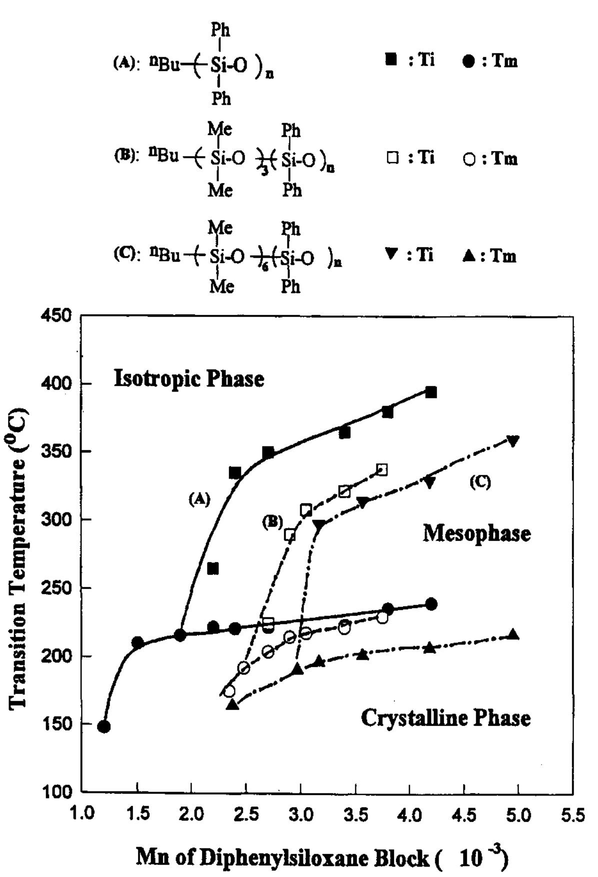


Figure 4 Phase diagram on heating for three types of diphenylsiloxane oligomers as a function of Mn. The Mn is molecular weight of the crystallizable diphenylsiloxane segment without contaoning the flexible end-segment. (a) PDPhS; (b) PDPhS with three dimethylsiloxane units, cited from Ref. [20]; (c) PDPhS with six dimethylsiloxane units (unpublished results)

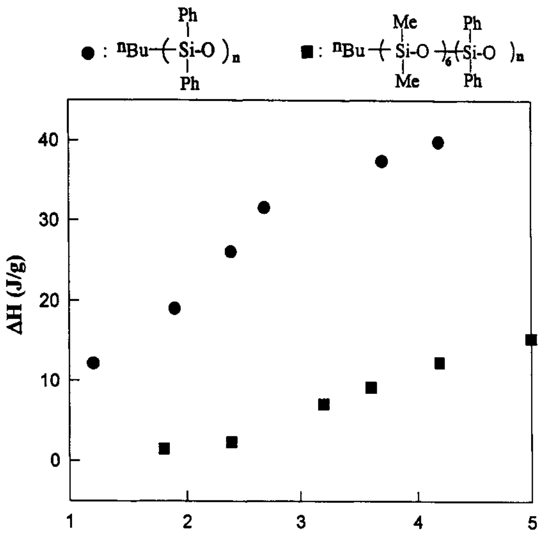


Figure 5 Heat of melting (ΔH) for the crystal to mesophase transition of the diphenylsiloxane oligomers with and without the six dimethylsiloxyl units. The ΔH was calculated from the d.s.c. second heating scans (rate = 10°C min^{-1})

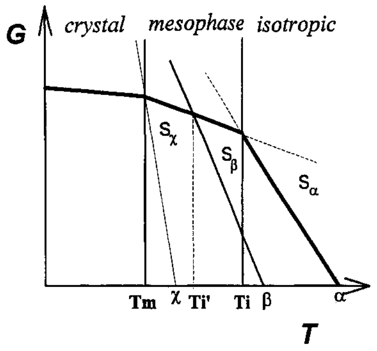


Figure 6 A schematic free-energy diagram for the explanation of the absence of the mesophase

instead of kinetics. For the purpose of simplifying the discussion, the focus is placed on the mesophase–isotropic transition which has a more obvious change than T_m with the variation of molecular weights. The equilibrium states are represented as the thickest lines in *Figure 6* and the points of intersection between various states define the temperatures of equilibrium melting point (T_m) and equilibrium isotropization point (T_i). If we assume that the entropy of the isotropic state is constant with the temperature variation, the curve in the diagram can be plotted as a line for convenience. S_α, S_β and S_χ represent the states of melting to isotropic with various molecular weights and the slopes correspond to their entropies. Line S_α is correlated to the oligomer with the highest molecular weight because it has the least slope. Line S_χ has the lowest molecular weight because it has the highest slope of the three. From the definition of free energy ($G = H - TS$), we can find the intersections of the three line with temperature axis by setting $G = 0$, thus obtaining $H = TS$. As described previously, enthalpy H could be approximately viewed as constant. Thus, the least entropy (slope of S_α) results in the highest intersection point with temperature axis (point α) and the relative positions of the three lines are reasonable in *Figure 6.*

Generally, the melting of the oligomers will pass through the least free-energy path. Thus, from the proposed diagram, the oligomer with highest molecular weight has the broadest temperature range of mesophase ($T_m \sim T_i$) and the oligomer with a intermediate molecular weight has narrower mesophase range ($T_m \sim T_i'$). It could be explained that the absence of mesophase for oligomer I–III by the line S_χ, because it does not intersect with equilibrium mesophase line.

CONCLUSIONS

The diphenylsiloxane oligomers without dimethylsiloxy end-group are prepared via bulk process by anionic ring-opening polymerization of P_3 monomer. The phase diagram of PDPhS oligomers with various flexible chain-length is compared. The flexible end-group has an effect on decreasing the melting and isotropization temperatures. The critical MN for mesophase formation is increased with the increasing chain-length of the flexible end-group. The flexible end-group also shows an effect on decreasing the heat of melting (ΔH) on d.s.c. The molecular weight effect on phase behaviours is confirmed by POM observations. The oligomer with MN equal to or lower than 1900 has only a transition of the spherulite to the isotropic state on heating. Nevertheless, oligomer with MN = 2200 or higher has a thermodynamically stable mesophase between the spherulite and the isotropic state. The bright needles and less birefringent plates are found upon cooling from the isotropic states to the mesophase. Both of them are likely to be the same lamellar crystal. Although the molecular order of the mesophase remains to be defined, the lamellar crystal and the isotropic state which coexist in the mesophase was proposed in this study according to the POM observations. A feasible scheme has also been suggested to describe the bright needles and plates. Moreover, a free-energy diagram based on thermodynamics is proposed to explain the presence of the critical MN for the mesophase formation. The investigation on the origin of multiple endotherm of this oligomeric system is now underway in our study group. It is expected that the results reported in this article will stimulate discussion on this interesting system.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by National Science Council of the Republic of China and Dow Corning Corporation, and the useful discussions for Dr Hsin-Lung Chen of the Chang Gung College of Medicine and Technology.

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