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Thermal characterization and crystallization of novel poly(arylene ether ether sulfide)s

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Thermal characterization has been carried out on a series of biphenol- and hydroquinone-based novel poly(arylene ether ether sulfide) polymers. Thermogravimetric analyses of the sulfide systems indicate high thermal stability in air as well as in nitrogen. X-ray studies showed the poly(ether ether sulfoxide) precursor materials to be amorphous and the poly(ether ether sulfide) materials to be semicrystalline. Based on the number-average molecular weight of the poly(ether ether sulfoxide) materials, and the glass transition temperatures determined by differential scanning calorimetry (d.s.c.), the limiting $T_{g\infty}$ has been determined for both amorphous precursors. The biphenol-based precursor sulfoxide had a $T_{g\infty}$ of 214°C and the hydroquinone-based precursor had a $T_{g\infty}$ of 179°C. D.s.c. studies showed the biphenol-based poly(ether ether sulfide) to have a T_g of 142°C and T_m of 347°C, and the hydroquinone-based poly(ether ether sulfide) to have a T_g of 100°C and a T_m of 243°C. The equilibrium melting temperature T_m° has been determined for both sulfide polymers using the Hoffman–Weeks method. The hydroquinone-based poly(ether ether sulfide) exhibited a T_m° of 278°C, and the biphenol-based poly(ether ether sulfide) showed a T_m° of 371°C. The effect of time and temperature in the melt on the subsequent crystallization behaviour of the two sulfide materials has also been investigated as a function of molecular weight.

(Keywords: poly(ether ether sulfoxide); poly(ether ether sulfide); crystallization)

INTRODUCTION

Recently, there has been considerable interest in the development of semicrystalline thermoplastic polymers for use in high-performance engineering applications. Such polymers are being developed as potential replacements for conventional thermoset materials, such as the epoxies. Advantages of the thermoplastic polymers include their longer shelf-life, their higher solvent and water resistance, and ease of processing. Owing to the semicrystalline nature of these thermoplastic resins, their final properties depend greatly on the nature and extent of crystallinity present in the matrix. In order to retain mechanical properties and solvent resistance at temperatures above T_g, the extent or degree of crystallinity must be substantial. In case the degree of crystallinity is low, the maximum service temperature is limited by the softening or glass transition temperature; a lower degree of crystallinity also lowers the solvent resistance. The nature of the crystalline morphology therefore plays a critical role in determining the performance of the polymer in any engineering application. Both the nature of the crystalline morphology as well as the degree of crystallinity depend on the processing conditions utilized, specifically the temperature and residence time in the melt.

Recent efforts have been directed towards developing semicrystalline poly(arylene ether) and poly(arylene thioether) resins. Important members in this class of polymers include commercially well established polymers like poly(ether ether ketone) (PEEK) and poly(phenylene sulfide) (PPS) respectively. Efforts in this direction have also led to the development of copolymers based on the incorporation of ketone and sulfone linkages in poly(arylene ether) and poly(arylene thioether) polymers. Recent work of Senn has dealt with the synthesis and characterization of copolymers of poly(arylene sulfide)s with sulfones and ketones[1–5].

New members in this class of polymers are the poly(arylene ether ether sulfide)s discussed in this work. The synthetic route to these polymers has been reported by Riffle *et al.*[6]. Briefly, soluble amorphous precursors, poly(arylene ether ether sulfoxide)s are prepared by nucleophilic aromatic substitution reactions between 4,4′-difluorodiphenyl sulfoxide and diphenols. The poly(ether ether sulfoxide)s are subsequently reduced to the corresponding sulfides using oxalyl chloride in conjunction with an iodide salt as shown in *Scheme 1*. The reduction results in rapid, quantitative conversion of the sulfoxides to the semicrystalline sulfides, which precipitate from solvent (tetrachloroethane) as fine particles. For simplicity, the precursor poly(ether ether sulfoxide)s derived from 4,4′-difluorodiphenyl sulfoxide and hydroquinone will be referred to as phenyl sulfoxides (**I**) and those based on biphenol as biphenyl sulfoxides (**II**). Similarly their corresponding poly(ether

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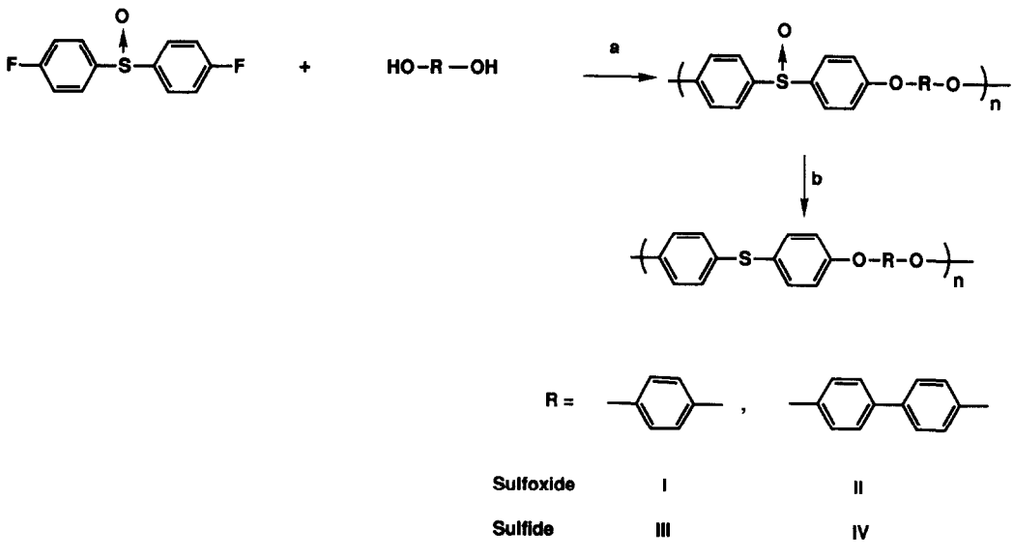

a : NMP/Toluene, K_2CO_3 (1.5), 145°C 6-12h, 185°C 36h.
b: tetrachloroethane, $(Bu)_4NI$, Oxalyl chloride

Scheme 1

ether sulfide)s will be referred to as phenyl sulfides (**III**) and biphenyl sulfides (**IV**) respectively.

It is now well known that thermal history, specifically the time and temperature in the melt, influence the crystallization behaviour of a semicrystalline polymer during isothermal and non-isothermal crystallization[7–15]. Furthermore, owing to the presence of a large distribution of crystal sizes and perfection, semicrystalline polymers do not exhibit sharp melting temperatures, but show broad melting regions. At temperatures just above the experimentally measured melting temperature, complete disordering does not occur, resulting in regions having localized order. These regions of residual order can act as nucleating agents for crystallization when the polymer is subsequently cooled[7]. This process is hence known as self-nucleation. Higher temperatures or longer times in the melt destroy the number of residual nuclei, and therefore decrease the rate of crystallization during isothermal crystallization, or decrease the maximum crystallization temperature during non-isothermal crystallization. For many polymers it has been shown that holding the polymer at temperatures above its equilibrium melting temperature for a sufficient time effectively destroys all residual nuclei. The only nuclei that survive these melt conditions are other heterogeneities such as dirt, catalyst, etc. Such behaviour has been reported for a number of materials including PEEK[8–10] and PPS[11]. However, it has also been shown that, for polar polymers such as nylon-6,6 and polytetrafluoroethylene, residual crystallinity persists even at temperatures well above the equilibrium melting temperatures, and that residence at high temperatures for very long times can still fail to destroy all the residual nuclei[12–15].

This report details the results of initial characterization studies carried out on a series of novel poly(ether ether sulfoxide)s and poly(ether ether sulfide)s, as a function of backbone structure and molecular weight, using thermogravimetric analysis (t.g.a.), differential scanning calorimetry (d.s.c.) and X-ray diffraction (x.r.d.).

EXPERIMENTAL

The phenyl sulfoxide precursors (**I**), in powder form, had number-average molecular weights ($g\,mol^{-1}$) of 8600, 21 000, 36 000 and 139 000 as determined by g.p.c. using universal calibration. Similarly the phenyl sulfide polymers (**III**) had molecular weights of 8100, 19 900 and 34 000, the difference between these values and the sulfoxide precursors being due to the chemical reduction. The biphenyl sulfoxide precursor polymers (**II**) had molecular weights (M_n) of 8200, 15 000, 20 000, 25 000, 30 000 and 42 000, and the biphenyl sulfide polymers (**IV**) had calculated molecular weights of 7800, 14 300 and 19 100. The details of the molecular weight characterization have been given elsewhere[6].

Thermogravimetric (t.g.a.) measurements were carried out on a Seiko TG/DTA on 12–14 mg of sample. The experiments were conducted on as-received powder samples at heating rates of $10°C\,min^{-1}$ under an air or nitrogen purge of $50\,ml\,min^{-1}$. Temperature calibration was based on the melting temperatures of indium and zinc. The temperatures for 5% weight loss are reported in this paper.

D.s.c. measurements were made on a Seiko DSC on 7–9 mg of sample. All the experiments were carried out at heating rates of $10°C\,min^{-1}$ under a nitrogen purge of $50\,ml\,min^{-1}$. Temperature and heat flow were calibrated using indium and zinc standards. All d.s.c. traces shown have been normalized to 1 mg. The T_g measurements on the sulfoxide materials were performed on samples that were heated to 200°C (phenyl) or 250°C (biphenyl), quenched to room temperature, and subsequently reheated at $10°C\,min^{-1}$. The temperature at the midpoint of the transition was taken to be the glass

Table 1 Temperatures for 5% weight loss by t.g.a. for poly(ether ether sulfoxide)s and poly(ether ether sulfide)s

Polymer	Molecular weight ($g\,mol^{-1}$)	Code	5% wt loss temp. (°C) Air	Nitrogen
Phenyl sulfoxide	8600	8.6K	354	354
	21000	21K	377	382
	36000	36K	367	372
Phenyl sulfide	8100	8.1K	513	509
	19900	19.9K	515	516
	34000	34K	516	513
Biphenyl sulfoxide	8200	8.2K	341	343
	15000	15K	340	341
	20000	20K	345	344
Biphenyl sulfide	7800	7.8K	531	515
	14300	14.3K	534	526
	19100	19.1K	520	526

transition temperature. Measurements on the sulfide materials involved heating the samples to 300°C (phenyl) or 400°C (biphenyl), holding for 2 min, quenching to room temperature and subsequently reheating at $10°C\,min^{-1}$. These will be referred to as the first and second heat respectively. The heating and cooling schedules involved in the melt time/temperature studies are described along with the results.

The X-ray diffraction was carried out on a Nicolet diffractometer operating at 40 kV and 30 mA and equipped with a STOE Bragg–Brentano type goniometer. Cu Kα radiation of wavelength 1.54 Å passed through a graphite monochromator before final collimation. Data were collected at 0.05° increments between angles of 5 and 60°. X-ray studies on the sulfide polymers were carried out on the as-received powders. The diffraction on the sulfoxide polymers was carried out on films that were formed by hot-pressing the sulfoxides at temperatures 30°C above their T_g for 5 min.

RESULTS AND DISCUSSION

T.g.a. studies carried out on the sulfoxide precursor polymers indicated a sharp weight loss at ca. 345°C for the biphenyl sulfoxides and ca. 370°C for the phenyl sulfoxides. *Table 1* shows the temperatures for 5% weight loss for the phenyl sulfoxide system and biphenyl sulfoxide polymers as determined by t.g.a. For the case of the phenyl sulfoxide polymers, the 8.6K polymer had a lower degradation temperature compared to the higher molecular weight polymers. For the biphenyl sulfoxide polymers, the temperature for 5% weight loss was essentially independent of molecular weight. Interestingly, changing the purge atmosphere from nitrogen to air did not appreciably change the degradation temperatures.

D.s.c. studies on the sulfoxide materials showed only an endothermic transition corresponding to the T_g and no recrystallization exotherm or melting endotherm, indicating that the sulfoxide polymers were amorphous. It is a well known fact that the T_g of a polymer increases with molecular weight and eventually reaches an asymptotic value corresponding to the glass transition at infinite molecular weight, $T_{g\infty}$. Using free-volume arguments, Fox and Flory[16] proposed the following relationship to determine the high molecular weight limit

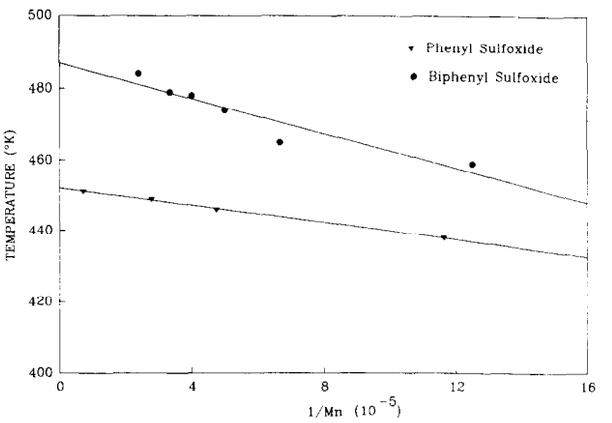

Figure 1 Plot of T_g vs. $1/M_n$ for poly(ether ether sulfoxide)s

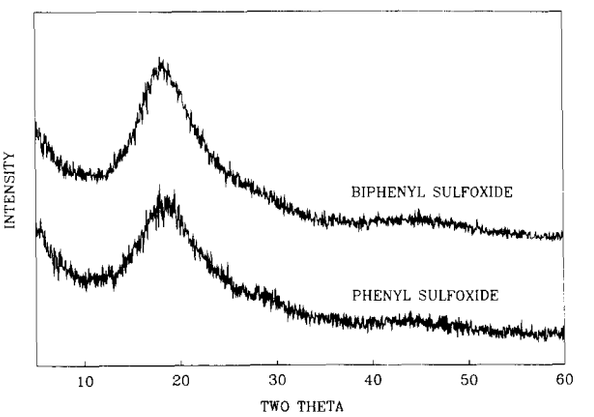

Figure 2 Wide-angle X-ray patterns for poly(ether ether sulfoxide)s

$T_{g\infty}$:

$$T_g = T_{g\infty} - K/M_n \quad (1)$$

where K is a constant for a given polymer.

As detailed in the 'Experimental' section, the T_g values of the sulfoxide polymers were determined from the midpoint of the glass transition using d.s.c. These data were plotted as a function of number-average molecular weight (*Figure 1*). A least-squares analysis of the data yielded a $T_{g\infty} = 179°C$ for the phenyl sulfoxide and $T_{g\infty} = 214°C$ for the biphenyl sulfoxide.

Wide-angle X-ray diffraction (WAXD) studies carried out on the phenyl sulfoxide (21K) and biphenyl sulfoxide (20K) films resulted in characteristic amorphous diffraction patterns (*Figure 2*). Two broad peaks corresponding to the amorphous phase are evident in *Figure 2*, supporting the conclusion obtained from the d.s.c. The features of the diffraction pattern of the biphenyl sulfoxide (20K) polymer, which was annealed at 270°C ($T_g + 70°C$) for 3 h, remained unchanged, thus reinforcing the belief that the sulfoxide system was indeed amorphous.

T.g.a. studies on the sulfide materials indicated that the polymers had good thermal stability in air as well as in nitrogen. The sulfide materials showed a 5% weight loss occurring around 510°C in air and in nitrogen. These degradation temperatures are substantially higher than the corresponding values for the sulfoxide precursors, indicating a significantly higher thermal stability for the sulfides as compared to the sulfoxides.

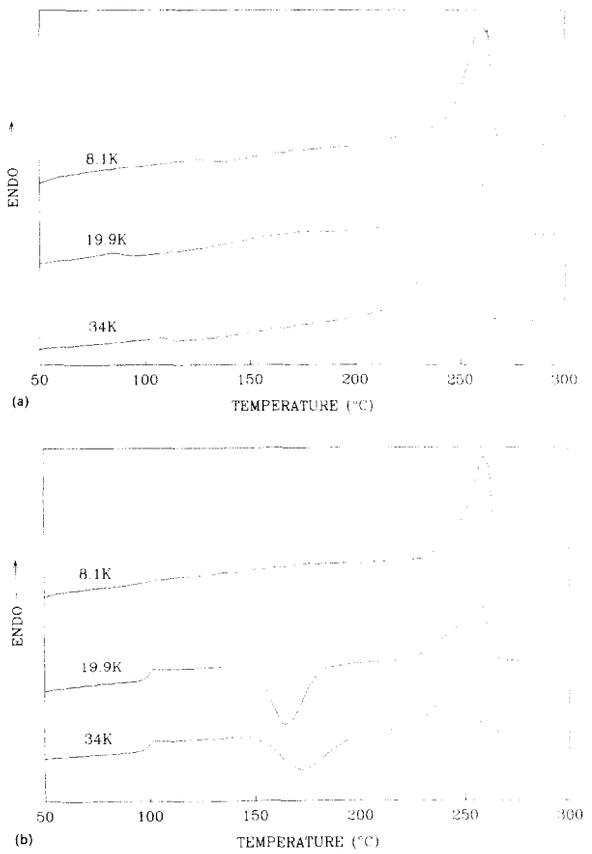

Figure 3 (a) First heat d.s.c. scan and (b) second heat d.s.c. scan for poly(phenyl ether ether sulfide)

Since the backbone chemical structures of the sulfoxides and sulfides are identical except for the presence of the S → O moiety on the chain, the lower thermal stability of the sulfoxides may well arise from an inherent thermal lability of the S → O group. *Table 1* shows the 5% weight-loss temperatures for the phenyl sulfide and biphenyl sulfide systems. It is obvious from the data that the degradation temperatures are essentially the same for both the phenyl and the biphenyl systems. The degradation temperatures also seemed to be independent of the choice of air or nitrogen as the purge gas. A critical point to be noted is that there appears to be no molecular weight dependence of degradation temperatures for either sulfide system. If the sulfoxide precursors had not been completely converted to the sulfide polymers, a weight loss would have been observed at a lower temperature corresponding to the degradation temperature of any remaining sulfoxide species. The absence of any such weight loss at lower temperatures strongly indicates complete quantitative conversion of the sulfoxides to the respective sulfides.

D.s.c. traces of the first and second heats (*Figure 3*) of the phenyl sulfide polymers yielded melting temperatures ranging from 243°C for the 34K polymer to 260°C for the 8.1K polymer. Interestingly, the values of $T_g = 100°C$ and $T_m = 245°C$ are somewhat similar to the corresponding values for the well known commercial polymer PPS ($T_g \simeq 85°C$ and $T_m = 285°C$), and poly(*p*-phenylene oxide) (PPO) ($T_g \simeq 105°C$ and $T_m = 285°C$), with PPS and PPO having slightly larger crystallization windows. The phenyl sulfide polymer can be considered a copolymer of PPS and PPO. The T_g value of 100°C for the phenyl sulfide polymer is indeed consistent with copolymer theories of the glass transition[17]. The d.s.c. traces of the phenyl sulfide system (*Figure 3*) show that the glass transition temperature was not prominent in the first heat for any molecular weight, and the T_g could be clearly observed in the second heat for the two higher molecular weight materials only. This is because the 'as-received' polymers are recovered from solvent, which leads to a high degree of crystallinity and a low amorphous fraction, resulting in a small specific heat increase across the glass transition temperature and hence a very small transition in the d.s.c. curve corresponding to T_g. At the end of the first heat, the polymers were quenched at $70°C\,min^{-1}$ to room temperature. Owing to greater mobility, the low molecular weight polymers crystallize relatively fast, resulting in crystallization during the quench process after the first heat. This again results in a low amorphous fraction and hence a very weak transition corresponding to the T_g, which could not be well resolved by the d.s.c. during the second heat. This reasoning is supported by the fact that no crystallization exotherm is observed during the second heat for the low molecular weight polymer. On the other hand, owing to lower mobility caused by higher viscosities, the higher molecular weight species cannot crystallize during the quench, resulting in essentially amorphous polymers. During the reheat, the higher molecular weight polymers exhibit prominent T_g values consistent with larger amorphous fractions. Owing to the relatively slow heating rates involved, the polymers are able to crystallize during heating, and hence exhibit exotherms corresponding to crystallization. The melting-point dependence on the molecular weight in the as-received samples can be best explained by the fact that low molecular weight polymers can form more perfect crystals than their higher molecular weight analogues, thus leading to higher melting temperatures. The molecular weight dependence of the melting point during the second heat can be explained as follows. The higher molecular weight polymers are initially amorphous, but crystallize during the heating scan, i.e. dynamic or non-isothermal crystallization. During such a process, the crystals formed are relatively unstable and hence undergo a continuous process of melting and recrystallization to form crystals of greater stability. Owing to the high viscosity and hence lower mobility, the high molecular weight polymers need longer times to form stable crystals, which, owing to the continuous heating process, is not available. It would therefore be expected that higher molecular weight polymers would form less stable crystals and hence melt at lower temperatures. *Figure 3b* also shows that the position of the crystallization peak moves to higher temperatures as molecular weight increases. This is certainly due to the higher mobility of the lower molecular weight polymers, which results in faster crystallization and hence lower peak crystallization temperatures. This observation is consistent with reports in the literature of a similar molecular-weight dependence for PEEK[18]. Comparison of the first and second heats showed the heat of fusion values to be similar, indicating that the materials do not undergo significant degradation, and that the materials crystallize during the d.s.c. scan.

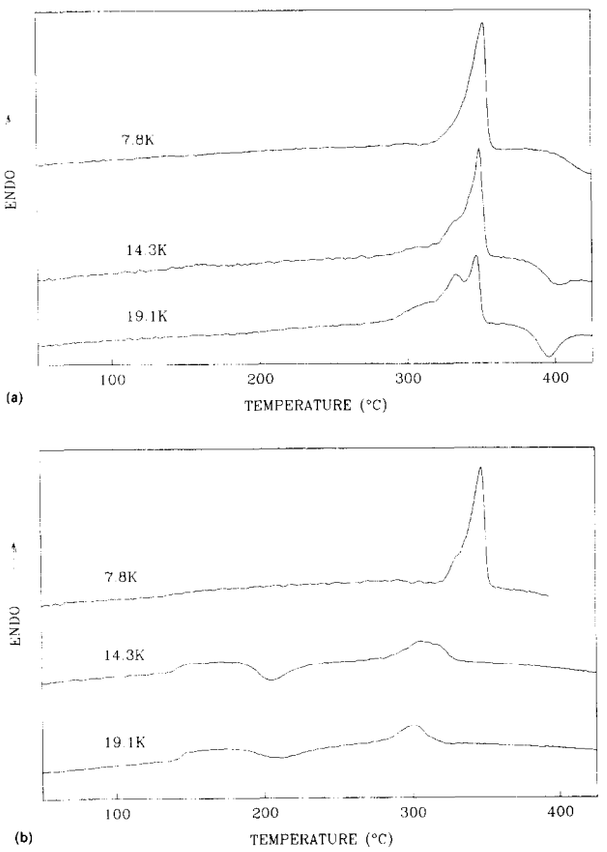

Figure 4 (a) First heat d.s.c. scan and (b) second heat d.s.c. scan for poly(biphenyl ether ether sulfide)

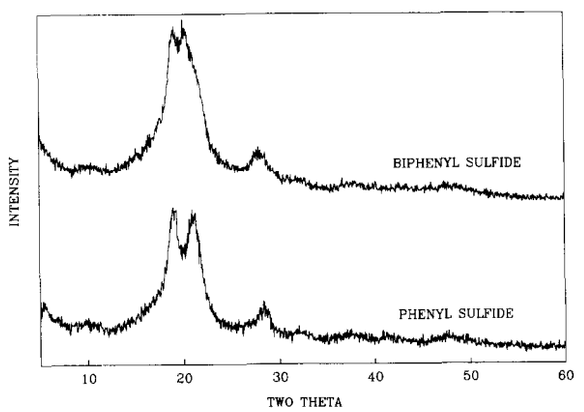

Figure 5 Wide-angle X-ray patterns for poly(ether ether sulfide)s

D.s.c. scans of the biphenyl sulfide materials (*Figure 4*) showed that these materials had a $T_g = 142°C$ and a $T_m = 347°C$. A comparison of these values with the corresponding values for the phenyl sulfide system shows that the biphenyl sulfide polymers have a substantially higher T_g and T_m than the phenyl sulfide polymers. This is undoubtedly due in part to the presence of the biphenyl linkage in the molecule (*Scheme 1*), which causes stiffening of the backbone. Other factors being equal, a stiffer chain would cause a lower entropy of fusion, which would lead to a higher T_m. An interesting observation here is the very close similarity of the values of T_g and T_m for the biphenyl sulfide system to the corresponding values for commercial PEEK ($T_g = 144°C$ and $T_m = 347°C$).

As in the case of the phenyl sulfide materials, there were no prominent glass transitions during the first heats, and the 7.8K material did not show any T_g even in the second heat. Also, no crystallization exotherm was observed for the 7.8K material during the second heat, implying that the material rapidly crystallized during quenching. Prominent glass transitions, crystallization exotherms and melting endotherms were observed for the two higher molecular weight polymers during the second heat. In contrast to the melting behaviour of the phenyl sulfides, the melting temperatures of the 'as-received' biphenyl sulfides (first heat) were essentially independent of molecular weight. As seen in the case of the phenyl sulfides, a molecular-weight dependence can be seen for the melting temperatures and peak crystallization temperatures during the second heat.

An exotherm at 400°C was prominent in the first heat d.s.c. scans of the two higher molecular weight biphenyl sulfide polymers. This may correspond to some chemical process—possibly crosslinking. The absence of this exotherm in the second heat implies that the exotherm was due to some irreversible chemical change in the material. The exotherm could be a result of some melt state curing as has been reported for PPS[19].

Comparison of the heats of fusion between the first and second heats showed no difference for the 7.8K polymer. However, for the higher molecular weight materials, the heat of fusion corresponding to the second heat was lower than that of the first heat. This could be either due to the slower crystallization rates of the higher molecular weight polymers or the result of some chemical change occurring in the polymer corresponding to the exotherm at 400°C.

A comparison of the thermal stability of the phenyl and biphenyl sulfide systems with PPS and PEEK, respectively, was carried out in air and nitrogen atmospheres. The data show that degradation temperatures for the phenyl sulfide polymers are about 30°C higher than for PPS. This may be due to the higher bond strength and hence thermal stability of the phenyl–oxygen linkage as compared to the phenyl–sulfur linkage[20]. There was no appreciable difference between the degradation temperatures of the biphenyl sulfide polymers and PEEK. The same trend was observed when air or nitrogen was used as the purge gas.

Wide-angle diffraction studies on both types of sulfide polymers showed diffraction patterns characteristic of semicrystalline polymers. *Figure 5* shows diffraction patterns for the phenyl sulfide (19.9K) and biphenyl sulfide (19.1K) polymers. The X-ray patterns are characteristic of a semicrystalline polymer with at least three prominent reflections and six other weak reflections apparent in the patterns.

As mentioned earlier, holding the polymer at a melt temperature above its equilibrium melting temperature has been found to be effective in destroying all residual nuclei. Hence, the temperature just required to destroy all residual nuclei could give an indication of the equilibrium melting temperature of the polymer[8]. The equilibrium melting temperature (T_m°) is the temperature required to melt crystals of infinite thickness and is generally obtained using extrapolative procedures. Perhaps the most common method to determine T_m° is through the Hoffman–Weeks plot[21]. This method requires one to obtain the melting temperatures (T_m) of

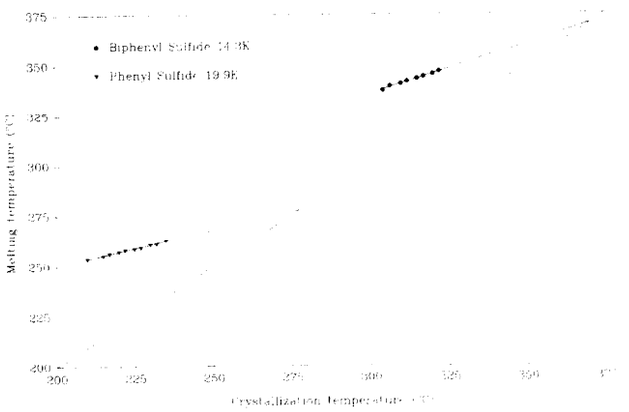

Figure 6 Hoffman–Weeks plot for poly(ether ether sulfide)s

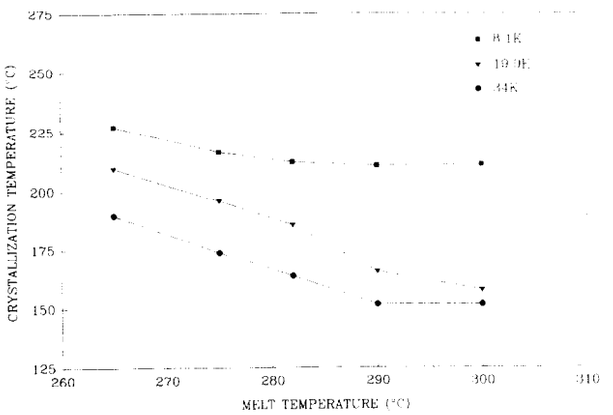

Figure 7 Effect of melt temperature on the maximum crystallization temperature for poly(phenyl ether ether sulfide). Time in the melt is 5 min

the polymer at various crystallization temperatures (T_c). In a plot of T_m vs. T_c, the line joining the points is extrapolated to the line $T_m = T_c$. The point of intersection is the equilibrium melting temperature (T_m°). An important point to be noted here is that small variations or errors in determining the crystallization temperature or melting temperature can lead to large variations in the equilibrium melting temperature owing to the extrapolative procedure used. The value of T_m° obtained from the Hoffman–Weeks plot should hence be used only as an indication of the true equilibrium melting temperature. *Figure 6* shows the Hoffman–Weeks plots of the biphenyl sulfide (14.3K) and phenyl sulfide (19.9K) polymers, from which the equilibrium melting temperatures were determined to be 371°C for the biphenyl sulfide and 278°C for the phenyl sulfide respectively.

The effect of time and temperature in the melt on the subsequent crystallization behaviour of the sulfide systems was investigated to optimize conditions for future isothermal crystallization experiments. As mentioned earlier, the melt history of the sample dictates the crystallization behaviour due to the presence of residual nuclei. During the study of isothermal crystallization kinetics, it is desirable to destroy all residual nuclei in the melt so as not to influence the nucleation mechanisms during isothermal crystallization. The absence of residual nuclei ensures that no 'self seeded nucleation' occurs. The d.s.c. heating and cooling schedules used in these experiments were as follows. The samples were

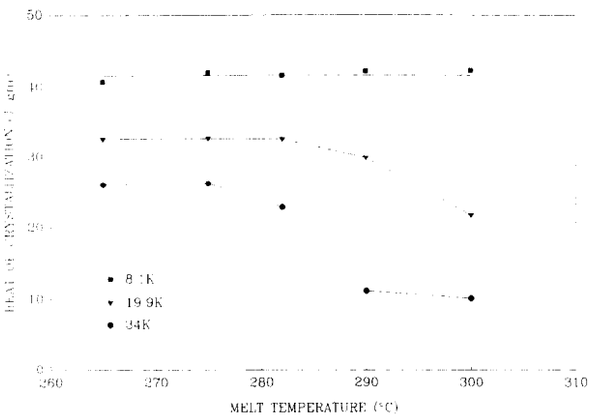

Figure 8 Effect of melt temperature on the heat of crystallization for poly(phenyl ether ether sulfide). Time in the melt is 5 min

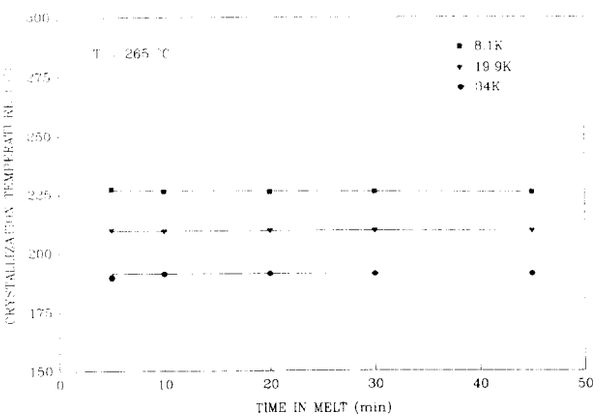

Figure 9 Effect of time in the melt on the maximum crystallization temperature for poly(phenyl ether ether sulfide)

heated at 20°C min^{-1} to various melt temperatures and held for different times. The samples were then cooled at 10°C min^{-1} to room temperature. The temperature of exothermic deviation from the baseline is taken to be the onset of crystallization. The peak of the crystallization exotherm formed during the cooling is denoted as the maximum crystallization temperature ($T_{c,max}$). The area under the crystallization exotherm is denoted as the heat of crystallization.

Figures 7–9 show the effect of time and temperature in the melt on the maximum crystallization temperature ($T_{c,max}$) and the heat of crystallization of the phenyl sulfide system. *Figure 7* shows that higher temperatures in the melt result in lower values of $T_{c,max}$, this effect being most prominent for the higher molecular weight polymers. At temperatures above 282°C, the change in $T_{c,max}$ is relatively small. The same trend was observed for the onset temperature as well. This can be explained by the fact that higher temperatures more effectively destroy any residual nuclei remaining in the material. The destruction of these nuclei causes crystallization to occur at larger supercoolings. Since the values of $T_{c,max}$ are relatively constant above 282°C, it can be concluded that the residual nuclei are effectively destroyed by residence temperatures of 282°C and above. This is consistent with the earlier observation that the equilibrium melting temperature of the phenyl sulfide polymer has been determined to be 278°C. *Figure 8* shows that the

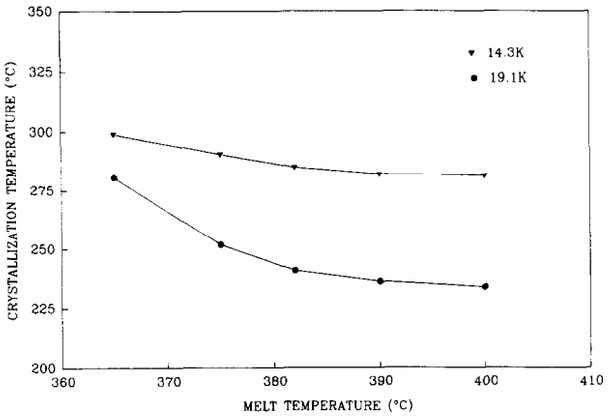

Figure 10 Effect of melt temperature on the maximum crystallization temperature for poly(biphenyl ether ether sulfide). Time in the melt is 5 min

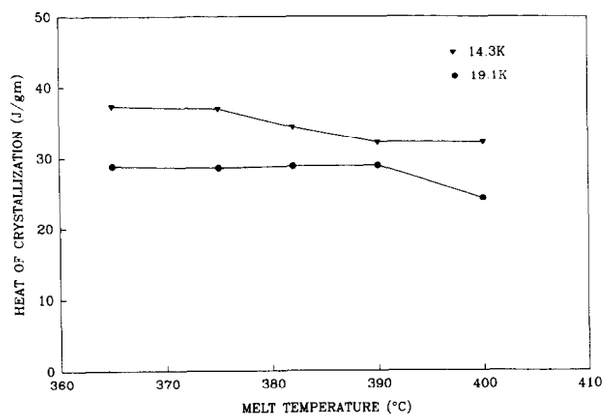

Figure 11 Effect of melt temperature on the heat of crystallization for poly(biphenyl ether ether sulfide). Time in the melt is 5 min

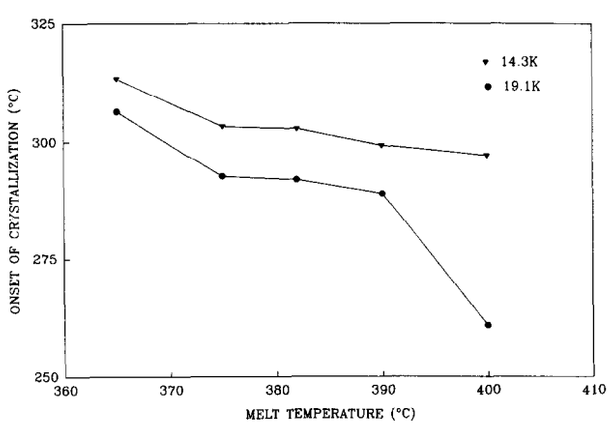

Figure 12 Effect of melt temperature on the onset of crystallization for poly(biphenyl ether ether sulfide). Time in the melt is 5 min

heat of crystallization does not change for the low molecular weight polymer and that large changes occur only at higher temperatures for the higher molecular weight polymers. T.g.a. studies of the 34K polymer annealed at 290 and 300°C showed that the degradation temperatures were the same as that of the 'as-received sample', again implying no degradation during annealing of the melt. *Figure 9* shows the effect of time in the melt at 265°C on the maximum crystallization temperature. It can be seen that the maximum crystallization temperature is essentially independent of time in the melt. The onset temperature and heat of fusion were also independent of time in the melt. The same behaviour was observed for samples annealed at 282°C for various times, implying that the crystallization behaviour was insensitive to the residence time in the melt. This independence of the crystallization behaviour on time in the melt is contrary to the behaviour observed for PEEK and PPS. Such behaviour is important from a processing point of view since a minimal residence time in the melt is sufficient to destroy residual nuclei in the material and allows for a reproducible crystallization response upon cooling.

This crystallization response to varying times in the melt can be explained as follows. Since 282°C is above the equilibrium melting temperature of the phenyl sulfide system, at this temperature we would expect all of the residual crystalline regions to be completely destroyed. Varying time hence does not affect the crystallization behaviour. However, the crystallization behaviour has been shown to be independent of time in the melt even at 265°C, which is below the equilibrium melting temperature. Lee *et al.*[8] observed that, in the case of PEEK, at low enough melt temperatures, increasing time in the melt did not substantially influence the crystallization behaviour; the time dependence of the crystallization behaviour was observed only at temperatures well above the melting temperature. For the case of the phenyl sulfide polymers, since 265°C is just 15°C above the observed melting temperature of 250°C, time in the melt does not play a significant role in affecting the crystallization behaviour.

Figures 10–14 show results of the melt studies for the biphenyl sulfide system. It can be seen in *Figure 10* that higher melt temperatures cause a decrease in the $T_{c,max}$ values. This decrease is prominent up to a temperature of 382°C, beyond which the value remains constant. The heat of crystallization variation with melt temperature is shown in *Figure 11*. For the 19.1K polymer, the heat of crystallization is a constant up to melt temperatures of 400°C, at which point the value decreases. This may be due to the exotherm seen in the first heat d.s.c. scan, which occurs at ca. 400°C. For the 14.3K polymer, there is an initial decrease beyond which the value is a constant. The onset temperature dependence on the melt temperature is shown in *Figure 12*. The decrease in the onset temperature with melt temperature is obvious from the figure. The sudden drop in the onset temperature of the 19.1K polymer at 400°C may also be due to the exothermic process occurring in the polymer. In contrast to the phenyl sulfide system, the *crystallization behaviour of the biphenyl sulfide polymers showed a strong dependence on residence time in the melt.* Before discussing the effects of time in the melt on the crystallization behaviour, a point worth mentioning is that the exotherm seen at 400°C also occurs at lower temperatures on annealing for longer times. Keeping that fact in mind, the results of time studies can be rationalized. *Figure 13* shows the effect of melt time at 365°C on the maximum crystallization temperature. It can be seen that the maximum crystallization temperature decreases with increasing time, after which it reaches a constant value. The behaviour of the onset

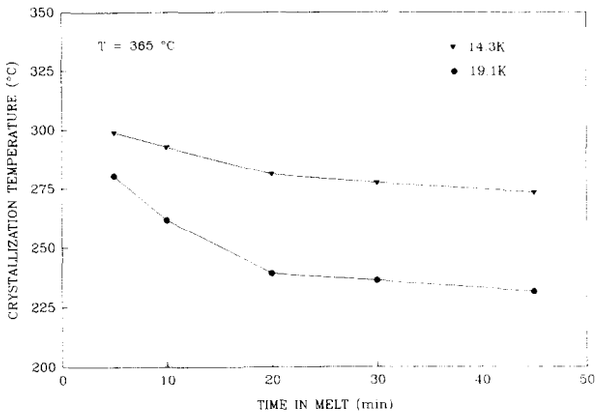

Figure 13 Effect of time in the melt on the maximum crystallization temperature for poly(biphenyl ether ether sulfide)

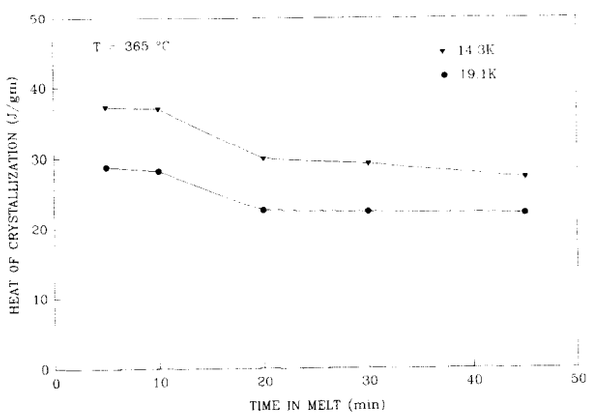

Figure 14 Effect of time in the melt on the heat of crystallization for poly(biphenyl ether ether sulfide)

temperature is qualitatively the same. From *Figure 14*, one notes that the heat of crystallization remains a constant up to the first 10 min, after which it decreases to a constant value. The effect of time in the melt at a melt temperature of 382°C was qualitatively the same as that observed at 365°C, except that the initial decrease occurred at earlier times. This follows from the experimental observation that the exotherm was observed at shorter times at higher temperatures. To confirm the irreversible effect that the exotherm had on the crystallization response, some samples were subjected to dual thermal treatments. Specifically, a sample of the biphenyl sulfide (19.1K) polymer was heated to 365°C, held for 30 min, cooled to room temperature at 10°C min^{-1}, then reheated to 365°C, held for 5 min, then cooled to room temperature at 10°C min^{-1}. The peak temperature and heat of crystallization of the exotherm developed during the second cooling step were compared to the crystallization exotherm of a sample subjected to a single thermal history at 365°C for 5 min. The peak temperature as well as the heat of crystallization of the exotherm formed after the dual thermal treatment was lower than that formed after a single thermal treatment, implying some irreversible change in the sample as a result of residence at 365°C for 30 min. Data for the 7.8K biphenyl sulfide polymer is not reported here owing to the observation of a dual exotherm on cooling from the melt.

It is obvious from the data presented above that the crystallization behaviour of these polymers shows a strong molecular weight dependence, as might be expected in this range. The onset temperatures and peak temperatures of the crystallization exotherms are higher for the lower molecular weight polymers. This is certainly due to the higher mobility of the lower molecular weight polymers, which allows for faster crystallization rates. The low molecular weight polymers also show higher heats of crystallization, implying a greater 'ease' of crystallization. This also arises due to the higher mobility and lesser number of entanglements for low molecular weight polymers.

SUMMARY AND CONCLUSIONS

This paper reports the initial characterization of a series of novel poly(arylene ether) systems. These poly(arylene ether ether sulfide)s could have potential applications as high-performance polymers. In addition, owing to the similarity of the phenyl sulfide polymer to PPS, this system could serve as a model system to study the effect of backbone structure on the crystallization behaviour of aromatic polymers. X-ray diffraction studies showed the sulfoxide precursor materials to be amorphous and the sulfide materials to be semicrystalline. T.g.a. studies indicated good thermal stability of the materials, particularly the sulfides, both in air as well as in nitrogen.

D.s.c. studies showed that higher melt temperatures or longer residence times in the melt decrease the maximum crystallization temperatures, consistent with more 'severe' thermal treatments being more effective at destroying residual nuclei in the melt. A few common features noted in this study were that the low molecular weight polymers showed higher values of onset temperature, $T_{c,max}$ and heat of crystallization as compared to the higher molecular weight polymers. Another significant fact is that the low molecular weight polymers were less affected by the melt conditions than the higher molecular weight polymers.

Based on the results of this study, isothermal and non-isothermal crystallization kinetic studies have been carried out and will be reported later.

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