

# Transport and Solubility of Fluids into Polyphenylene Sulfide (PPS)

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**ABSTRACT:** The solubility and transport of toluene and carbon disulfide into amorphous and crystalline polyphenylene sulfide (PPS) was investigated. The rates of sorption, desorption, and resorption of both fluids were measured as a function of temperature. The sorption of these fluids into amorphous PPS produces a semi-crystalline material by solvent induced crystallinity (SIC). Although the rate of diffusion of carbon disulfide (CS<sub>2</sub>) into crystalline PPS, (produced either thermally or by SIC), is several orders of magnitude slower than that observed in amorphous PPS, the solubility is only slightly reduced, by approximately 10%. The PPS

films exhibit highly stressed surface regions that rapidly sorb the penetrant. Thermal annealing at temperatures as high as 100°C (note  $T_g$  of PPS is 85°C) has little or no effect on the surface stress, the diffusion process or the solubility of toluene into PPS. In addition to SIC, PPS undergoes cold crystallization at 130°–140°C; however, the degree of crystallinity induced by cold crystallization is approximately 60% of that formed by cooling from the melt. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 615–625, 2003

**Key words:** diffusion; crystallization; polysulfides

## INTRODUCTION

Thermoplastic resins and resin systems have broad application in a number of commercial and engineering fields. Polyphenylene sulfide (PPS) is considered a high performance thermoplastic resin. It is reported to exhibit excellent resistance to chemical environments and is used in a variety of applications, ranging from electrical insulation to components for mechanical pumps, to components for automotive emission systems.

One practical and informative method of characterizing resin systems is a detailed study of the transport of fluids into and through the resin. PPS represents an ideal thermoplastic polymer to characterize by its transport properties; it is a commercially semi-crystalline polymer which can be obtained in either the amorphous or crystalline form. Furthermore, the amorphous material undergoes solvent induced crystallization. In this study, the transport of toluene and carbon disulfide into amorphous and crystalline PPS as a function of temperature and low temperature annealing (physical aging) was investigated in depth.

The glass transition temperature ( $T_g$ ) of the polymer is about 85°C and the polymer melts at approximately 285°C. Brady has reported that the heat of crystallization ( $H_c$ ) of the pure crystals is 80 kJ/mol.<sup>1</sup> The crys-

tallinity ranges from 50 to 65% depending on the cooling rate from the melt.<sup>2</sup> When heated above  $T_g$ , the amorphous polymer exhibits cold crystallization, at temperatures greater than 120°C. PPS has been reported to exhibit a “rigid amorphous phase,” a portion of the amorphous phase that does not relax when the polymer is heated above  $T_g$ .<sup>3</sup> Little has been reported on the transport of fluids into PPS, although the polymer has been reported to exhibit excellent resistance to organic fluids.<sup>4</sup>

We have investigated the sorption, desorption, and resorption of both carbon disulfide (CS<sub>2</sub>) and toluene into amorphous and semi-crystalline PPS as a function of temperature. Both penetrants produce solvent induced crystallinity (SIC) in amorphous PPS.

The process by which liquids penetrate polymers and resins is extremely complex and has been studied for many years. In many cases, the sorption leads to pronounced swelling, loss of mechanical properties, and ultimate failure of the polymeric material. In a film, where the thickness is much smaller than either the width or length, the rate of sorption ( $dc/dt$ ) of a penetrant as a function of time can be described in general terms by eq. 1:

$$\frac{dc}{dt} = kt^n \quad (1)$$

where  $n$  is a constant.

The diffusion processes can be classified into three categories depending on the ratio of the rate of diffusion to the rate of polymer relaxation: (a) Fickian or

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Case I diffusion,  $n = \frac{1}{2}$ , and the rate of diffusion ( $R_D$ ) is much less than the rate of relaxation ( $R_R$ ); (b) Case II diffusion,  $n = 1$  and  $R_D > R_R$ ; or (c) anomalous diffusion, where  $\frac{1}{2} \leq n < 1$  and  $R_D \sim R_R$ .<sup>5</sup>

In many studies, the transport is referred to as Fickian if the sorption is a linear function of root-time. Although this is a necessary condition for Fickian diffusion, it is not sufficient to define it. A fundamental criterion for Fickian diffusion is that the surface concentration rapidly attains its equilibrium value upon a change in conditions and remains constant throughout the sorption process. Fickian diffusion is rarely observed for the transport of a liquid through a glassy polymer (i.e., below its  $T_g$ ). In most polymers, deviations from "Fickian" diffusion arise as a consequence of the finite rates by which changes in the polymer structure occur in response to stresses imposed upon the material before and during the diffusion process. Non-Fickian behavior is so broad and general that no simple model or theoretical description can account for all of the diverse, time-dependent phenomena that have been reported. (For an excellent discussion of the mathematics of diffusion, see ref. 6.) If the sorption is linear with root time, but does not meet all of the other criteria for Fickian diffusion, it is referred to as "pseudo-Fickian."

The sorption and subsequent transport of liquids or vapors through an organic matrix are complex phenomena that consist of essentially two processes: solubility and diffusion. The solubility of a material is related to the solubility parameter, originally proposed by Hildebrand,<sup>7</sup> based on thermodynamic considerations. One can estimate the solubility parameter  $\delta$ , but it is difficult to relate  $\delta$  to the actual solubility and/or swelling and nearly impossible to predict the degree of solubility from  $\delta$ . The phenomenon of swelling is closely related to solubility except that the solution is a solid or gel rather than a liquid. As the network is swollen by the sorption of the penetrant, the network chains assume an elongated configuration and an elastic retractive force develops in opposition to the swelling process. A state of equilibrium is reached when the elastic restoring force of the network chains exactly balances the osmotic pressure driving the penetrant into the polymer. The basic theory was developed by Flory<sup>8</sup> to account for the swelling of lightly crosslinked rubber and, although useful for qualitative predictions, cannot completely account for the swelling of semi-crystalline thermoplastic resins. Thomas and Windle developed a model to characterize Case II diffusion.<sup>5,9</sup> In Case II transport, the penetrant front advances linearly with time, and a sharp demarcation exists between the swollen and non-swollen regions. The relaxation of the swollen polymer is the primary factor controlling the weight gain.

The sorption of both CS<sub>2</sub> and toluene follow anomalous diffusion, a process in which the rate of sorption is not a linear function of square root time throughout the sorption region; however, in many cases a lengthy linear region is observed. In this pseudo-Fickian region, a diffusion coefficient can be estimated. Both the sorption and the desorption processes are governed by the concentration of penetrant in the polymer, which in turn controls the  $T_g$  of the resin.

## EXPERIMENTAL

Samples of 0.25 mm thick films of amorphous PPS (<1% crystallinity, Ryton®) were obtained from the Phillips Chemical Co., Bartlesville, Oklahoma. They were either used as-received (AR) or heated in a vacuum oven at temperatures ranging from 40°C to 110°C overnight. Selected samples were crystallized at 140°C. Films approximately 60 × 6 mm were immersed in the fluid of interest contained in 2.5 × 15 cm culture tubes which were placed in a thermostatted aluminum block. At appropriate intervals, the samples were removed from the culture tubes, blotted dry, placed in a tared weighting jar and weighed on a digital electric balance (Denver Instruments Co. A200DS, ±0.1 mg). Fluid desorption was accomplished by placing the sample in a sealed culture tube filled with a mixture of a desiccant (Drierite, indicating) and dry activated charcoal (14 mesh). About 1 cm of desiccant and approximately 5 cm of activated charcoal were added to the tube. The samples were periodically removed from the desorption chamber, placed in the tared weighing jar, weighed, and returned to the chamber in less than 15 s.

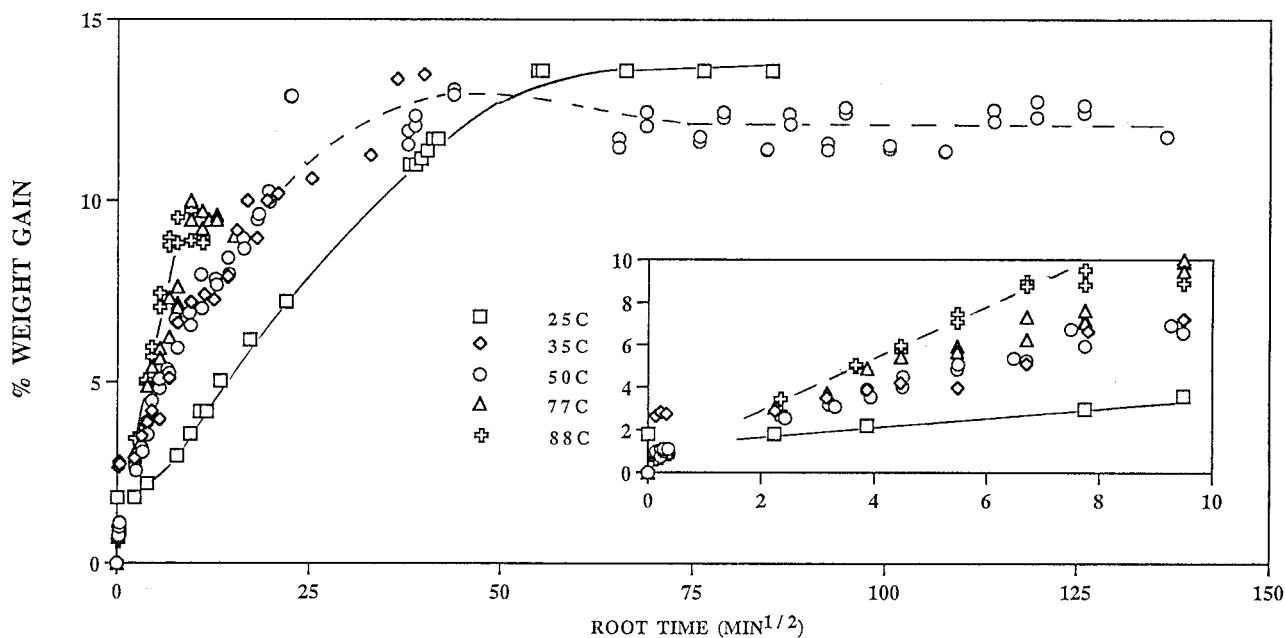
The crystallinity was evaluated by differential scanning calorimetry (DSC) in a nitrogen atmosphere at a scan rate of 10°C/min with a Thermal Analysis DSC (TA 2910 Modulated DSC).

## RESULTS AND DISCUSSION

### Toluene

The sorption of toluene into amorphous PPS as a function of temperature is shown in Figure 1. The sorption process consists of three separate regions: (1) an initial region in which 1–3 wt% is rapidly sorbed ( $S_0$ ), (2) a region that is linear with root time (pseudo-Fickian region), and (3) a maximum value ( $S_m$ ) that corresponds to the solubility. The inset, which shows the weight gain in the first 100-min sorption process, clearly illustrates both the rapid weight gain and the pseudo-Fickian regions.

The initial rapid sorption probably arises from interaction of surface stresses with the penetrant. Makarewicz and Wilkes<sup>10,11</sup> reported that the linear regions of the weight gain curves for the sorption of



**Figure 1** Sorption of toluene into amorphous PPS as a function of root-time and temperature. Insert shows expanded view of the initial sorption region.

solvents in polyethylene terephthalate do not pass through the origin when extrapolated to zero time; that is, they exhibit a rapid initial weight gain similar to that observed in this study. They attribute this rapid weight gain to surface cavitation that occurs immediately upon immersion in the solvent. The cavitation exposes a large area to the penetrant, leading to a rapid weight gain. A similar phenomenon is likely to occur in PPS, since PPS exhibits an overall morphology similar to PET, a semi-crystalline material that, when in the amorphous phase, exhibits both cold crystallization and SIC.

The second region corresponds to pseudo-Fickian sorption. The shape of the sorption curve is governed by the rate of penetration of the fluid compared to the rate of relaxation of the swollen polymer behind the advancing front. The pseudo-Fickian region, corresponding to a weight gain that is a linear function of square-root time, suggests that the rate of diffusion is greater than the rate of relaxation.<sup>12</sup> Based on a simple Arrhenius plot, and noting that the diffusion coefficient is proportional to the square of the slope of the fractional weight gain versus root-time plot, an activation energy of 46 kJ/mole (11 kcal/mol) was determined.

The data shown in Figure 1 were obtained on samples in the as-received condition. To ascertain the effect of thermal relaxation processes on the overall solubility and diffusion of toluene into PPS, the sorption at 50°C following a 16 h thermal anneal at temperatures varying from 40°C to 140°C was investigated. Typical weight gain curves, in which the percent weight gain is plotted as a function of square-root

time (Fickian form) for different annealing conditions, are summarized in Figure 2. Annealing the samples at 40°–100° has little or no effect, on either the sorption rate (slope) or the equilibrium solubility, which are the same as those observed in the AR sample. An expanded view of this graph showing the first 9 h with an insert showing the first 12 min of the sorption process is provided in Figure 3. The amount of penetrant sorbed by the AR and films annealed at or below 60°C following a one second immersion is 0.5 to 1.5 wt %; the amount sorbed in one second by the films annealed from 70° to 90°C is 1.8–3 wt %; the amount sorbed by the 100°C annealed film is about 0.5 wt %, and for those annealed at temperatures greater than 100°C it is less than 0.1 wt %.

Three different types of sorption were observed depending upon the annealing temperature: (1) for samples annealed at or below 100°C, the sorption is pseudo-Fickian (except for the rapid initial sorption); (2) the sample annealed at 110°C exhibits sigmoidal sorption and essentially no “instantaneous” weight gain curve; and (3) the sample annealed at 140°C sorbs less than 2 wt % even after several days of immersion in toluene at 50°C. Furthermore, the samples annealed at 70–100°C show a pronounced maximum in the sorption curve, and the maximum value is approximately 13 wt %, which slowly decreases to an equilibrium value of approximately 11 wt %. The maximum in the sorption curve and the subsequent decrease in amount sorbed arises because the polymer undergoes solvent induced crystallization. Small amounts of solvent are trapped inside or adjacent to the crystals, and the solvent is slowly squeezed out of the crystalline

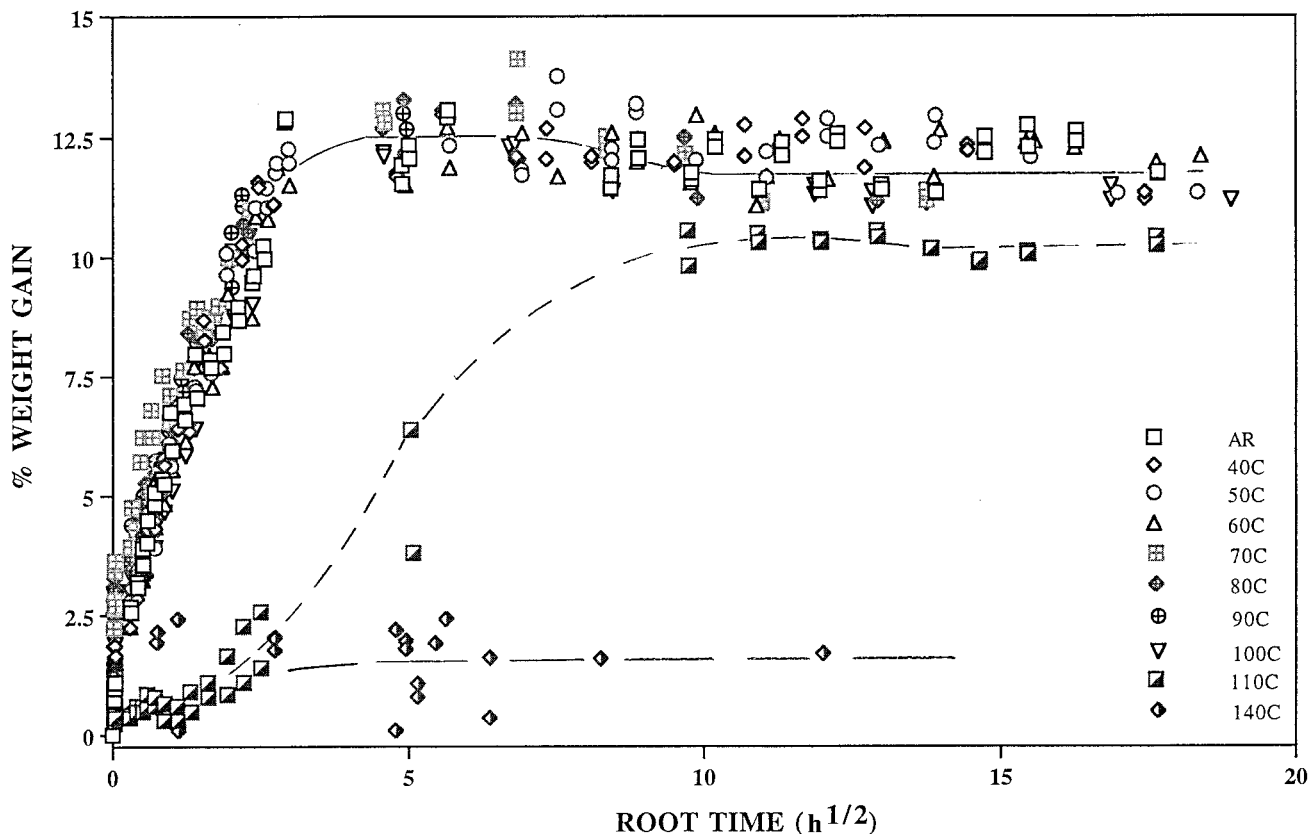


Figure 2 Sorption of toluene into PPS as a function of root-time following thermal anneal.

region as the sample slowly approaches equilibrium. The sample annealed at 110°C reaches the same equilibrium value, 11 wt %, after approximately 100 h. The rapid initial sorption does not occur in samples annealed at or above 110°C, again suggesting that the rapid sorption arises from some process that is eliminated by heating the film for 16 h at 20–25°C above its  $T_g$ . Both the solubility and the rate of diffusion of toluene at 50°C are essentially independent of the anneal process when the sample is annealed at or below 100°C. The results are summarized in Table I, where the maximum in the weight gain ( $S_{\max}$ ), the equilibrium solubility ( $S_{\text{equil}}$ ) and the diffusion coefficient for the sorption of toluene into PPS at 50°C are shown for each of the thermal conditions investigated. For thin films the diffusion coefficient is given by

$$D = \frac{\pi l^2}{16} \left[ \frac{F}{S_{\text{equil}}} \right]^2 \quad (2)$$

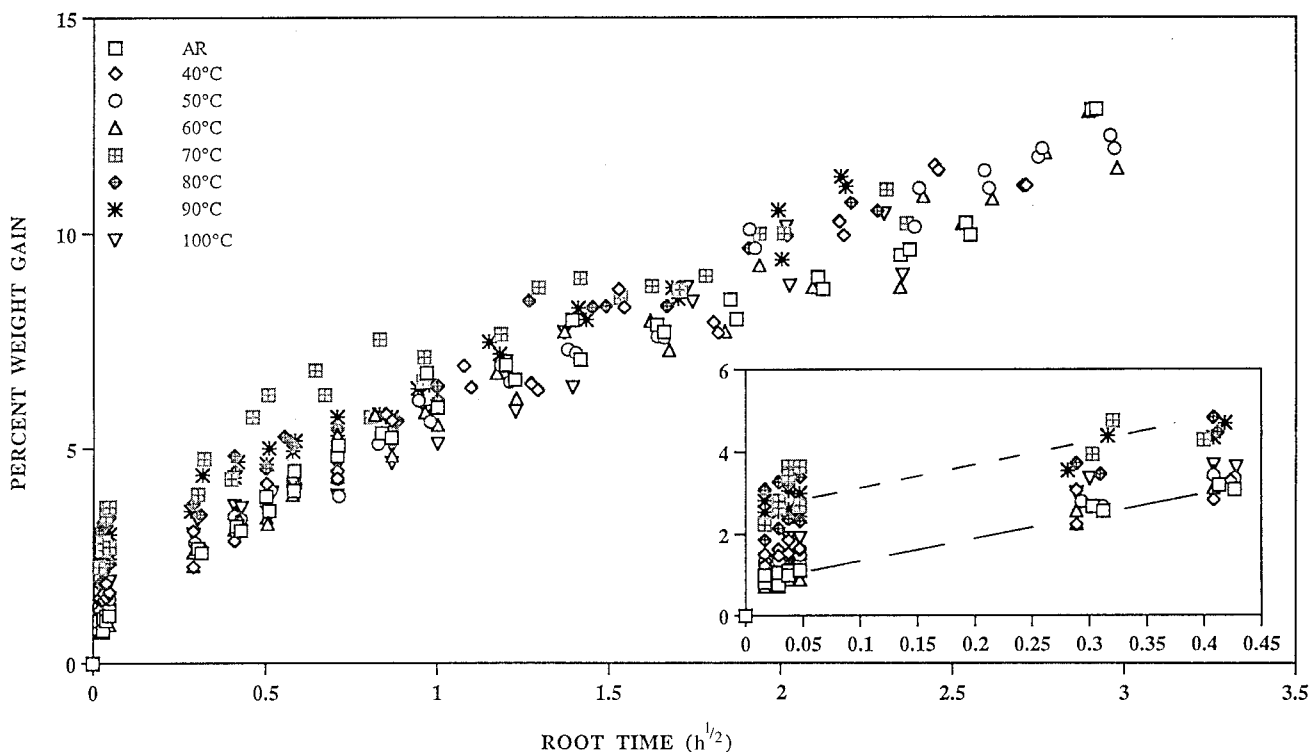
where  $l$  is the sample thickness,  $F$  is the slope of the linear region, and  $S_{\text{equil}}$  is the solubility. The average of the solubility and diffusion coefficients following thermal anneal, together with their standard deviation, are summarized in Table I.

The samples annealed at or below 60°C do not exhibit a solvent overshoot; however, those samples

annealed between 70° and 100°C show a maximum approximately 10% higher than the equilibrium value. The average of the maximum values ( $\bar{S}_{\max}$ ) is  $12.7 \pm 0.3$  wt %, while the equilibrium value in this same temperature region (70°–100°C) is  $11.5 \pm 0.2$  wt %. The average of the equilibrium values (solubility) for the samples annealed at 60°C or below is  $12.1 \pm 0.1$  wt %. The average diffusion coefficient for the samples annealed up to 100°C is essentially independent of the annealing and is  $1.90 \pm 0.44 \times 10^{-13}$  m<sup>2</sup>/s.

The effect of thermal annealing on the morphology of PPS was investigated by DSC. When amorphous PPS is heated, it can undergo two distinct changes. If heated above  $T_g$  (85–90°C), it can undergo cold crystallization, and if heated in the glassy state below  $T_g$  for extended periods of time it can undergo physical aging. (For an excellent review of physical aging see reference 12.) When a polymer is cooled from the melt through its  $T_g$  the molecular mobility and associated free volume of the amorphous phase are frozen into the glassy phase. In the glassy region, the free volume exceeds its equilibrium value and the material can slowly relax, returning to equilibrium with a loss in free volume.

Thermal annealing in the glassy state, or aging, reduces not only the free volume but also the entropy and internal energy of a polymer. When aged samples

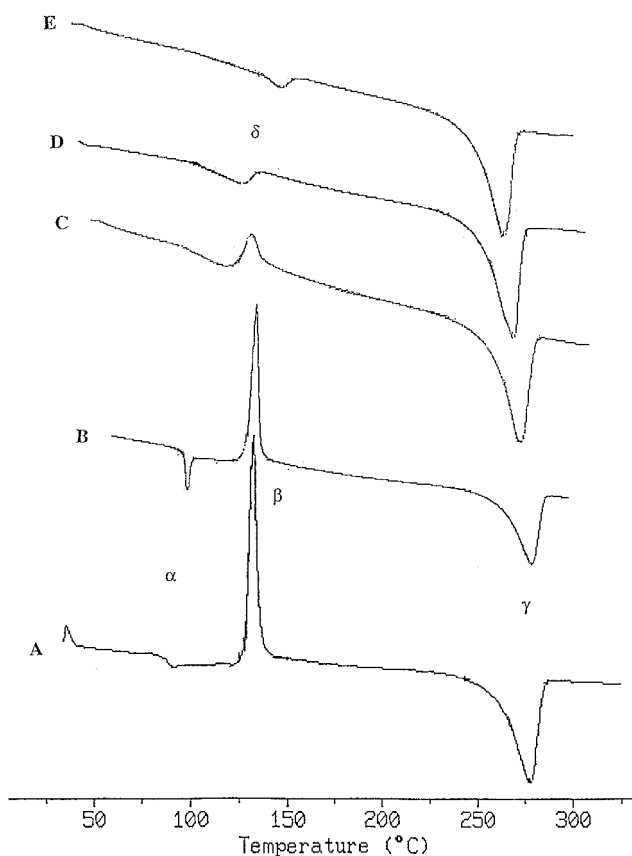


**Figure 3** Expanded view of the initial sorption period (Fig. 2) following thermal anneal. The insert shows the first 40 min of the sorption.

are heated through  $T_g$ , the sorption of heat appears as an endothermic peak in a DSC scan. A series of DSC traces following different thermal annealing cycles of PPS are shown in Figure 4. The bottom trace (A) is from the as-received polymer and the  $T_g$  (at 85°C), the cold crystallization (at 130°C), and the melting endotherm (at 270°C) are shown as  $\alpha$ ,  $\beta$ , and  $\gamma$ . Scan B is from a sample that was aged for 16 h at 70°C; the  $T_g$  has increased to 92°C and a small endothermic (physical aging) peak is observed at 92°C. The cold crystal-

**TABLE I**  
Transport Parameters for Toluene into PPS at 50°C as a Function of Pre-Sorption Annealing

Anneal Temp. (°C)	Solubility		Diffusion Coefficient ( $\times 10^{-13}$ m <sup>2</sup> /S)
	$S_{max}$ (wt %)	$S_{equil}$ (wt %)	
AR	13.0	12.1	2.05
40	13.0	12.1	1.80
50	13.4	12.1	1.63
60	12.7	12.0	1.68
$\bar{S}_{(AR-60)}$		$12.1 \pm 0.05$	
70	13.0	11.5	2.92
80	13.3	11.7	1.50
90	13.1	11.4	1.78
100	12.3	11.3	1.83
$\bar{S}_{(70-100)}$		$11.5 \pm 0.2$	
$\bar{S}_{max(70-100)}$	$12.7 \pm 0.3$		
110	10.3	10.3	0.06
$\bar{D}_{(AR-110)}$			$1.90 \pm 0.44$



**Figure 4** DSC thermograms of PPS following thermal anneal.

TABLE II  
DSC Analysis of PPS

Temperature (°C)	Cold Crystallization Exotherm (J/g)	Cold Crystallinity (%)	Melting Endotherm (J/g)	Final Crystallinity <sup>a</sup> (%)	Initial Crystallinity <sup>b</sup> (%)
AR	22.3	27.9	32.9	41.1	0.0
70	22.4	28.0	32.6	40.7	0.0
100	8.2	10.3	31.9	39.8	18
110	~0	~0	32.0	40.1	>28
130	~0	~0	31.1	38.9	>28

<sup>a</sup> Reference value: 80 kJ/kg

<sup>b</sup> Initial crystallinity = (max. % cold crystallinity) – (measured % cold crystallinity)

lization and melting peaks occur at the same temperatures as in the AR sample. The magnitude of the cold crystallization peak decreases when PPS is annealed at temperatures above 70°C. When the sample is annealed at 100°C (scan C), the cold crystallization peak is reduced to less than half of that observed in the AR sample, and, although the  $T_g$  is difficult to observe, it is approximately 92°C. When the sample is annealed at either 110°C (scan D) or 130°C (scan E), the cold crystallization peak is completely absent, but a new small endotherm ( $\delta$ ) is observed at approximately 20°C above the annealing temperature, 131 and 152°C, respectively. The DSC scan data are summarized in Table II.

According to Brady,<sup>1</sup> the heat of crystallization of 100% crystalline PPS is 80 kJ/kg. The ratio of the exotherm (at 130°C) or endotherm (at 290°C) to the heat of the crystallization gives the degree of crystallinity produced during the cold crystallization or the degree of crystallinity in the sample at the time of melting. (i.e.,  $f_c = H_M/H_C$ ), respectively.

The percent cold crystallinity produced during cold crystallization is shown in Table II. The crystallinity produced during cold crystallization is shown in Column 3. The percent cold crystallinity is the amount of crystallinity produced at low temperatures, and for amorphous PPS the maximum amount of crystallinity which is formed in this manner is approximately 28–30%. The values of the melting endotherms and their associated crystallinity are also shown in Table II. The average of all the melting endotherms,  $H_M$ , is 32.0 J/g, which corresponds to a crystallinity of about 40%. If the sample is already partially crystallized, the amount of crystallinity produced during annealing is equal to the maximum percent cold crystallinity (28%) minus the amount of cold crystallinity observed in the thermogram. The absence of the cold crystallization peaks in scans D and E (annealed at 110°C and 130°C respectively) suggests that the degree of crystallinity produced during the thermal anneal is greater than or equal to 28%. The PPS thermograms resemble the thermograms of PEEK<sup>13</sup> where the cold-crystallization exotherm is much smaller than the melting endotherm. This observation has been explained by noting

that the crystallization process in PEEK continues (after the initial cold crystallization) during the DSC scan to form more perfect crystals, which, in PEEK, melt at about 345°C.<sup>14</sup>

It is important to note that when PPS is annealed at temperatures below 100°C, annealing has little or no effect on either toluene solubility or its diffusion. The sample that was annealed at 100°C contains approximately 10% crystalline PPS; it is normally assumed that crystals are impervious to a large penetrant such as toluene. Although the diffusion coefficient is reduced by a factor greater than 300, the equilibrium solubility is only reduced by 10%.

The sorption of toluene in crystalline PPS is significantly slower than in the amorphous material. PPS was crystallized by heating at 140°C for 16 h. The sorption curve for the initially crystalline sample compared to that of an amorphous sample is shown in Figure 5. Even after time periods as long as 250 h, the total amount of toluene sorbed is less than 2.5 wt %.

### Carbon disulfide

The sorption of CS<sub>2</sub> into amorphous PPS as a function of temperature is shown in Figure 6. (Note the boiling point of CS<sub>2</sub> is 46°C and its vapor pressures at 40°, 33°, and 26°C are 633, 490, and 374 torr, respectively.) The effect of temperature on solubility is small, decreasing it from 19.6 wt % at 40°C to 17.5 wt % at 26°C. In the same temperature range, the diffusion coefficient (pseudo-Fickian) rises from 4.9 to 8.2 × 10<sup>-12</sup> m<sup>2</sup>/s.

These results are summarized in Table III, together with transport data in crystalline PPS. In addition, the transport data for the resorption of CS<sub>2</sub> from samples that were initially either amorphous or crystalline are shown. These effects are discussed later. The second and third columns of Table III show the solubility ( $S_A$ ) and pseudo-Fickian diffusion coefficient ( $D_A$ ) in the initially amorphous PPS. Based on a simple Arrhenius plot, the heat of solution ( $\Delta H_S^A$ ) and activation energy for diffusion ( $\Delta E_S^A$ ) in amorphous PPS are estimated to be -6.3 and 28.6 kJ/mol, respectively.

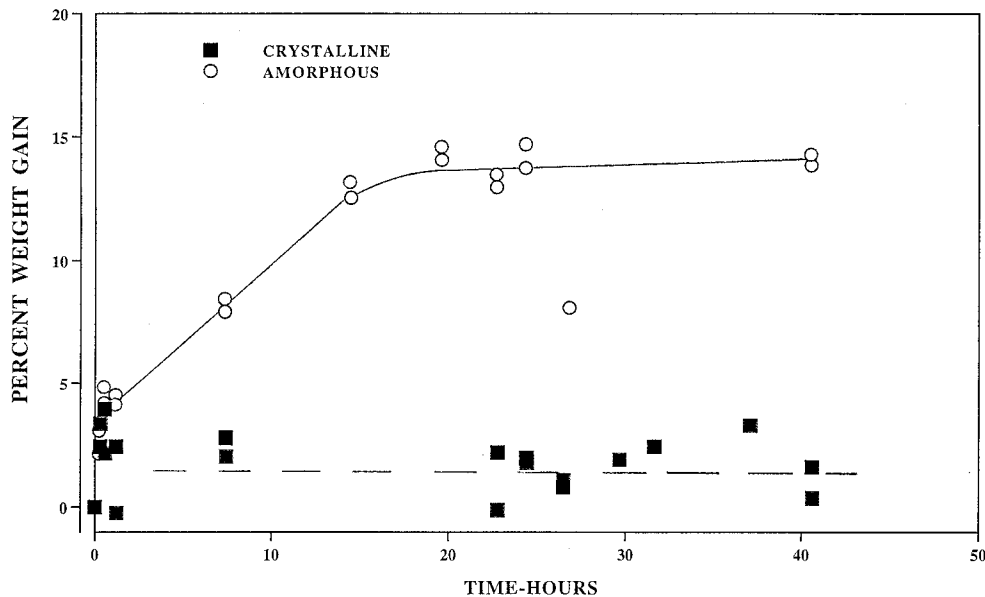


Figure 5 Sorption of toluene into amorphous and crystalline PPS.

The sorption of CS<sub>2</sub> at 24°C into crystalline PPS, compared to that into the amorphous material, is shown in Figure 7. The pronounced hump in the sorption curve, which was also observed in the toluene/PPS system, arises from the slow squeezing of penetrant from the crystalline region. The equilibrium concentration is approximately 18 wt %. The slight difference in solubility (i.e. approximately 10%) between amorphous and semi-crystalline PPS is unusual. In most polymer-penetrant systems, the difference in solubility between crystalline and semi-crystalline

material is much larger and is a direct function of the degree of crystallinity. An expanded view of the first 1.5 h of the sorption is shown in the insert. In classic Fickian diffusion, for a given thickness, the diffusion coefficient is proportional to the square of the linear region of the sorption curve (root-time curve). Here, since the solubilities are nearly the same and the slopes differ by an order of magnitude, the diffusion of CS<sub>2</sub> into amorphous PPS at 24°C is approximately 100 times faster than into the crystalline material.

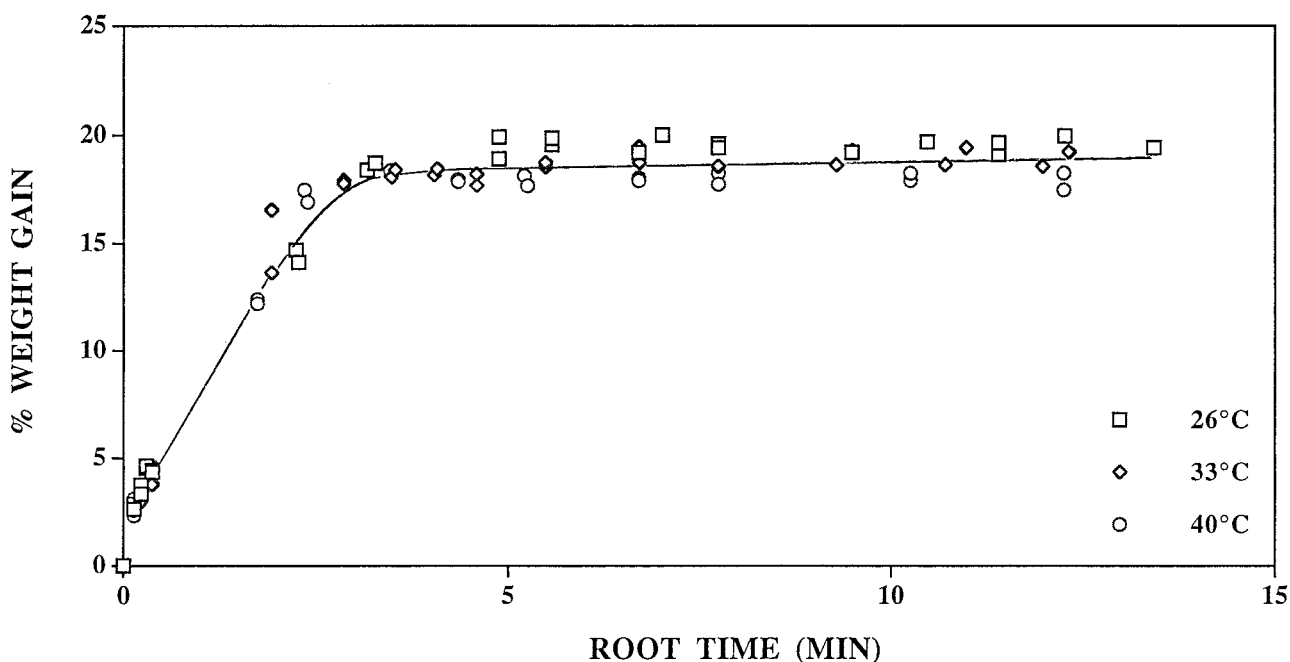


Figure 6 Sorption of carbon disulfide into amorphous PPS at different temperatures.

TABLE III  
Parameters for the Transport of CS<sub>2</sub> into PPS

Temp (°C)	Amorphous				Crystalline			
	Sorb		Resorb		Sorb		Resorb	
	S <sub>A</sub> (wt %)	D <sub>A</sub> (×10 <sup>-12</sup> m <sup>2</sup> /s)	S <sub>A</sub> <sup>R</sup> (wt %)	D <sub>A</sub> <sup>R</sup> (×10 <sup>-12</sup> m <sup>2</sup> /s)	S <sub>C</sub> (wt %)	D <sub>C</sub> (×10 <sup>-12</sup> m <sup>2</sup> /s)	S <sub>A</sub> <sup>R</sup> (wt %)	D <sub>A</sub> <sup>R</sup> (×10 <sup>-12</sup> m <sup>2</sup> /s)
26	19.6	4.9	17.6	1.6	17.7	0.2	16.8	0.2
33	18.7	6.9	16.7	2.0				
40	17.5	8.2	16.2	2.7				

### Sorption, desorption, and resorption

Of particular interest to the overall transport mechanism is the resorption of a fluid into a resin from which the initial saturating penetrant has been removed. The effect of the initial sorption on the morphology of the resin can be estimated by resorption. DSC was used to characterize the resin both before and after the initial sorption. A DSC thermogram of PPS that was saturated with CS<sub>2</sub> at 25°C and completely desorbed at 60°C (in vacuum) is shown in Figure 8, where it is compared to that of an as-received amorphous sample. The cold crystallization peak at 140°C is absent from the desorbed sample, indicating that the sample had undergone SIC in which the degree of crystallization was at least 28%.

Resorption can be used to characterize the solvent induced crystals. This particular study actually consisted of four separate experiments: resorption of CS<sub>2</sub> or toluene into a resin originally saturated with CS<sub>2</sub> or toluene. These can be abbreviated as CS<sub>2</sub>/CS<sub>2</sub>, CS<sub>2</sub>/toluene, toluene/CS<sub>2</sub> or toluene/toluene. The entire sorption and desorption process of toluene into amorphous PPS, together with the resorption of both tolu-

ene and CS<sub>2</sub>, is shown in Figure 9. The sorption and resorption were conducted at 24°C, and the desorption at 60°C in vacuum. Desorption is relatively slow, and even after 150 h approximately one-third of the initial amount sorbed remained. This is an effect similar to that observed in the toluene/PEEK system, where it is extremely difficult to remove all of the sorbed toluene.<sup>15,16</sup> The penetrant reduces the  $T_g$  of the resin system so that the resin is in the rubbery rather than the glassy region. Upon desorption, the  $T_g$  of the system increases as the penetrant desorbs and the resin passes back into the glassy region. The  $T_g$  of resin ( $T_g^R$ ) can be estimated according to the relation described by Fox<sup>15</sup>

$$\frac{1}{T_g^R} = \frac{W_p}{T_g^p} + \frac{W_s}{T_g^s} \quad (3)$$

where  $W_p$  and  $W_s$  are the weight fractions of the polymer and penetrant, respectively, and  $T_g^p$  and  $T_g^s$  are their corresponding  $T_g$  values. The  $T_g^s$  of toluene is 116 K. The amount of toluene required to lower the  $T_g$  of PPS to 60°C (the temperature of the desorption

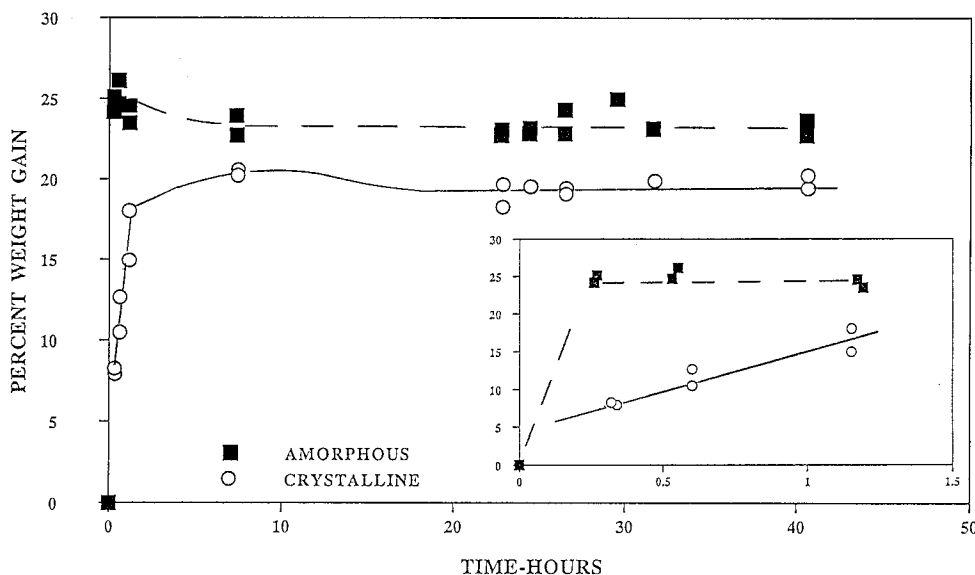
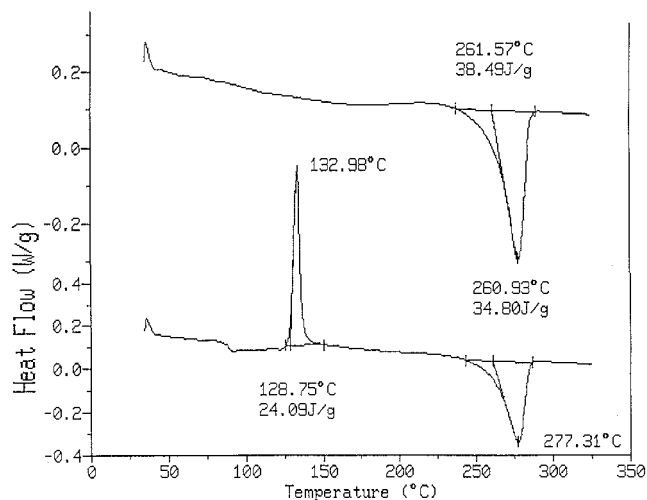


Figure 7 Sorption of carbon disulfide into amorphous and crystalline PPS at 24°C. The insert shows the first 75 min of the sorption.





**Figure 8** DSC thermograms from initially amorphous PPS (lower trace) and PPS that was saturated with carbon disulfide (25°C) and desorbed (60°C/vacuum) (upper trace).

chamber) is 3.4 wt %. This value is in fair agreement with desorption plateau value of 4.5 wt %.

When toluene is resorbed, an additional 5 wt % is sorbed, and the total concentration of toluene is about two-thirds of that initially sorbed. Interestingly, CS<sub>2</sub> is readily sorbed in the desorbed toluene material and reaches a total value similar to that observed in crystalline PPS, of 16.5 wt %. These results are summarized in Table IV.

The sorption and desorption of CS<sub>2</sub> from initially amorphous PPS, along with the resorption of toluene, are shown in Figure 10. It is of particular importance to note that CS<sub>2</sub> is completely desorbed from the saturated PPS; this is similar to the pattern observed in the CS<sub>2</sub>/PEEK system.<sup>17</sup> Toluene is resorbed slowly, reaching a maximum value of less than 2.5 wt % even after 48 h of immersion. CS<sub>2</sub>, however, is readily

**TABLE IV**  
Sorption/Desorption/Resorption

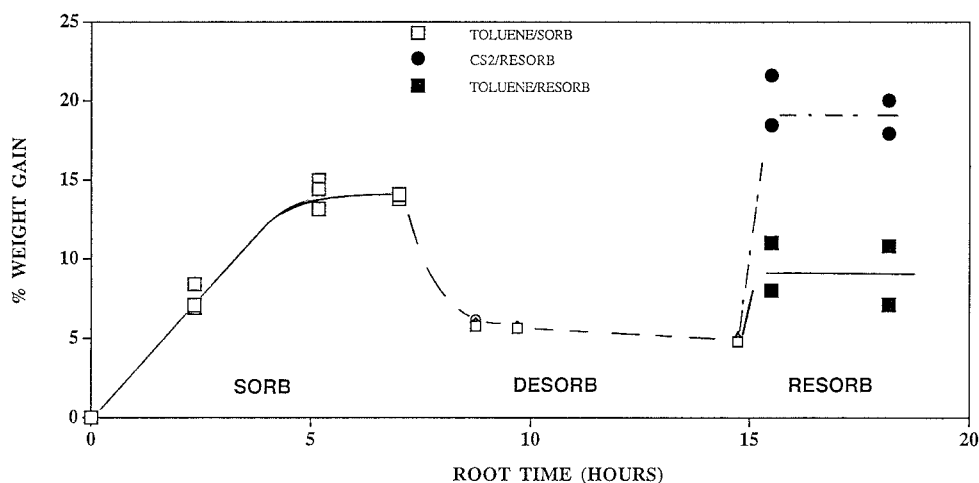
Penetrant	Temp. (°C)	Sorb (wt %)	Desorb <sup>a</sup> (%)	Resorb (wt %) <sup>b</sup>	
				Toluene	CS <sub>2</sub>
Toluene	24	13.5	67	4.6	—
Toluene	24	13.4	67	—	16.7
CS <sub>2</sub>	26	19.6	100	—	17.6
CS <sub>2</sub>	33	18.7	100	—	16.7
CS <sub>2</sub>	40	17.5	100	—	16.2
CS <sub>2</sub>	26	19.5	100	2.4	—

<sup>a</sup> (Init.wt.gain - final wt.)/Init.wt.gain × 100

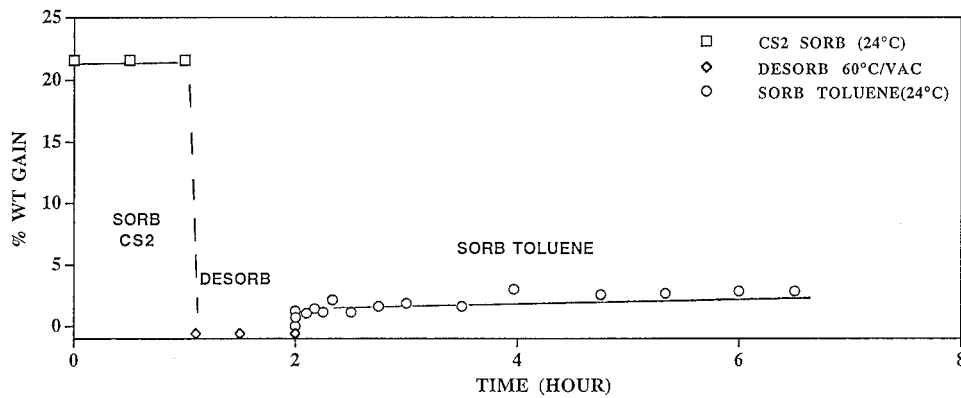
<sup>b</sup> wt% resorbed (above "desorb" wt.)

resorbed in PPS. The weight gain curves for the initial sorption compared to the curves at 26°, 33°, and 40°C are shown in Figure 11; and the solubility and diffusion coefficients obtained from this data are summarized in Table IV and are calculated according to eq. 2. The solubility at each temperature is approximately 10% less than that observed in the initially amorphous material, and, at least at 26°C, it is the same as that observed in the initially crystalline PPS. The diffusion coefficients are significantly lower than those observed in the amorphous material. The activation energy ( $\Delta E_D^R$ ), using an Arrhenius plot, is 29 kJ/mol. The diffusion coefficient in the SIC sample is approximately 10 times greater than that observed in the thermally crystallized sample,  $1.6 \times 10^{-12}$ , compared to  $0.2 \times 10^{-12}$  m<sup>2</sup>/s. Since the solubility in the two materials is essentially the same, the differences in the shape and size of the two crystals markedly affect the diffusion process. The thermal crystals are better formed and impede the transport of the penetrant more than the smaller SIC crystals.

The sorption of organic fluids into an amorphous thermoplastic resin, such as PPS, is an extremely complex process and, although extensively investi-



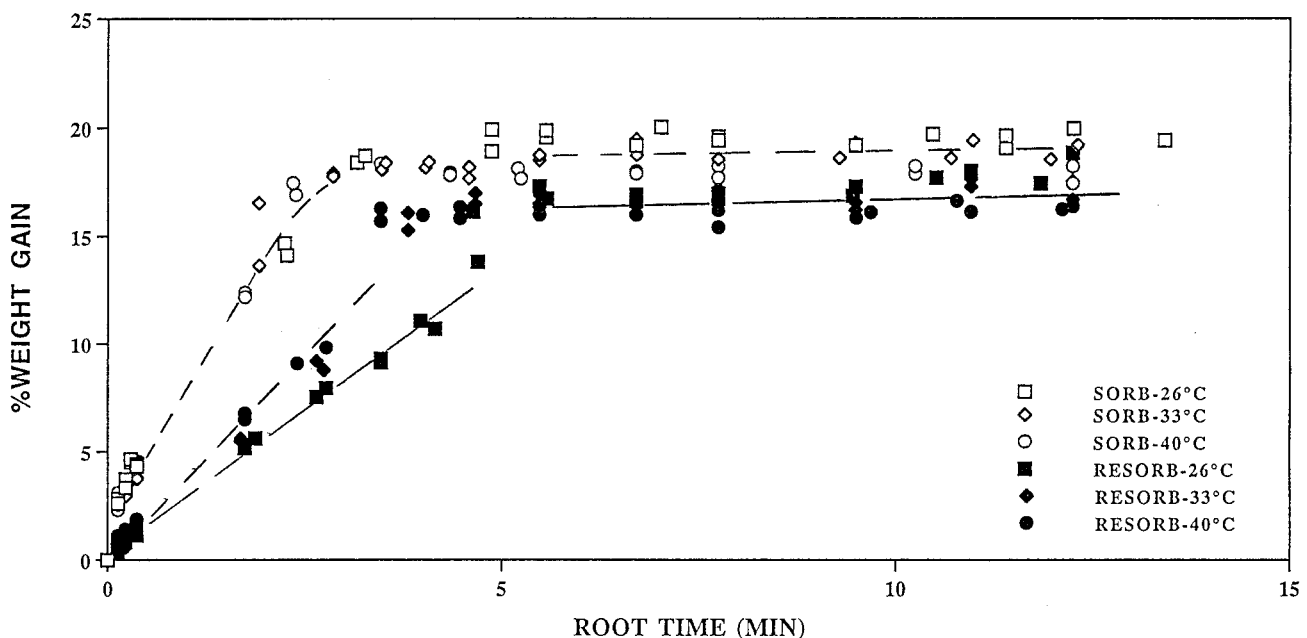
**Figure 9** Sorption (24°C) and desorption (60°C/vacuum) of toluene into PPS followed by resorption of toluene or carbon disulfide.



**Figure 10** Sorption (24°C) and desorption (60°C/vacuum) of carbon disulfide into PPS followed by resorption of toluene (24°C).

gated, is not completely understood. The primary factors that affect the transport of a nonpolar penetrant into a polymer are the thermodynamic driving forces and the internal volume available for the penetrant. The former is related to the solubility parameter, which serves a useful purpose but cannot explain the transport process. The major factors affecting the kinetics of transport are related to the internal structure of the polymer and the size and shape of the penetrating molecule. The factors affecting the internal structure of the polymer are (1) the free volume or  $T_g$  of the system (2) the degree of cross linking, and (3) the size and degree of polymer crystallization. It is normally assumed that the crystals are impervious to a penetrant molecule; the crystal structure is too tight to physically accom-

modate the molecules of the penetrant. Crosslinking, which can be either a conventional chemical branch between adjacent polymer chains or inter-chain entanglements between crystals, reduces the effective free volume of the system by reducing the chain mobility. The free volume of the polymer, especially in the glassy state, is a function of the thermal history of the material. The latter phenomenon arises when the rubbery polymer is cooled through the  $T_g$  into the glassy state. The molecules in the glassy state are not in thermodynamic equilibrium with their surroundings and slowly relax. This relaxation phenomenon is called physical aging. This physical aging is usually associated with a change in the free volume of the polymer. In principle, the transport properties of penetrant mole-



**Figure 11** Comparison of the sorption of carbon disulfide at different temperatures (open symbols) to the resorption of  $\text{CS}_2$  into the same samples following complete desorption (60°C) (closed symbols).

cules in a polymer (solubility and diffusion) can be used to examine the internal structure of the polymer.

In a crystallizable polymer, such as PPS, it is both illustrative and useful to use the similarities and differences in the transport of penetrants such as CS<sub>2</sub> and toluene to explore the morphology of the polymer. Although CS<sub>2</sub> and toluene have significantly different vapor pressures at any given temperature (the boiling points of CS<sub>2</sub> and toluene are 46°C and 110°C, respectively), their primary differences with regard to transport are their molecular size and  $T_g$ . At room temperature, the molar volumes of CS<sub>2</sub> and toluene are 58.7 and 106 cm<sup>3</sup>, respectively. The average molecular volumes of CS<sub>2</sub> and toluene were calculated and reported to be 49 and 92 Å<sup>3</sup>.<sup>14</sup> The  $T_g$  of CS<sub>2</sub> was estimated to be 60 K<sup>14</sup>, while that of toluene was 116 K. According to the Fox equation (eq. 3), a smaller amount of CS<sub>2</sub> will reduce the  $T_g$  of the resin system to that of the experimental system than required for toluene. Hence, a smaller amount of CS<sub>2</sub> is required to form a rubbery material.

A four-step process was observed for both CS<sub>2</sub> and toluene sorption. The initial sorption for samples dried at or below 100°C occurs approximately within the first 10 s. This sorption, however, is not seen for samples dried at or above 110°C, suggesting that the initial sorption is associated with the relaxation of surface stresses.

The high solubility of CS<sub>2</sub> in PPS following either solvent induced or thermal crystallization is unexpected. It is generally assumed that the penetrant is not present in the crystals but is entirely in the amorphous or the so-called rigid amorphous region (RAR), which may surround the crystals. Thus, if the penetrant is entirely restricted to the amorphous region, its concentration in that region would be greater than 30 wt %. The crystallinity of samples annealed at or above 110°C is greater than 28%. The sorption curves show a linear relationship with square root time after the initial rapid sorption, allowing pseudo-Fickian diffusion coefficients to be estimated. A marked decrease in the rate of diffusion (which is proportional to the square of the slope) for samples dried at 110°C compared to that for samples dried at or below 100°C, indicates that the molecular rearrangement that occurs at 110°C is sufficient to markedly impede the path of the diffusing toluene molecule. The overall driving force for the penetration of a fluid into a polymer is the concentration gradient across the surface, while the equilibrium solubility is obtained when the osmotic force across the boundary equals the restoring force

applied by the swelling action of the polymer chains.<sup>8</sup> The complexity of morphological changes on the transport process are illustrated by noting that the solubility of CS<sub>2</sub> is only slightly affected by the crystallization process but diffusion is markedly affected.

The DSC thermograms and transport studies show that PPS can be heated up to 90°C for periods of up to 16 h without inducing morphological changes that affect the transport process. However, the degree of crystallization for samples dried at 110°C or above show that the small morphological changes that occur at these temperatures, well below the primary cold-crystallization temperature of 130°C, do affect the diffusion process. The solubility of toluene into PPS at 50°C ranged from 10–13% (for samples dried at or below 100°C), suggesting a weak function on drying conditions. However, the greatly reduced diffusion coefficients for samples dried at or above 100°C show that diffusion is a strong function of crystallinity. The diffusion coefficient for samples dried at 110°C is about 250 times smaller than the diffusion coefficients for samples dried at 100°C and below.

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