

Solvent-induced crystallization of syndiotactic polystyrene in different liquids—sorption and diffusion phenomena

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Transport properties of different liquids inducing crystallization in syndiotactic polystyrene (sPS) were investigated at 25°C. The weight uptake kinetics in the different liquids imply Fickian behaviour, with the exclusion of n-hexane and cyclohexane for which the weight uptake starts after an induction time. The equilibrium concentration of the different liquids in sPS is a function of the solubility parameter and shows a maximum with respect to chloroform, indicating a maximum in the polymer-solvent interaction. The swollen samples are birefringent but appear substantially amorphous on the basis of the X-ray diffractograms. After drying a well developed crystalline order appears, and the diffractograms indicate the presence of solvated structures, characterized by chains in helical conformation.

(Keywords: crystallization; syndiotactic polystyrene; sorption; diffusion)

INTRODUCTION

Highly stereospecific syndiotactic polystyrene (sPS) is a recently synthesized polymer^{1,2}. Crystallization of this polymer can be achieved by several processes. Thermal-induced crystallization, both from the melt and from the glass, was the aim of the initial investigations since sPS is of great industrial interest³⁻⁸. Some evidence of strain-induced crystallization⁹ and solvent-induced crystallization (SINC) from the glass¹⁰ were also reported. In the latter, the solvent permeation lowers the glass transition temperature, T_g , inducing enhanced mobility of the chains, that may rearrange into the crystalline state.

Furthermore, since the decrease of the melting point with increasing solvent is much less pronounced than the decrease of T_g , the temperature window for crystallization becomes larger and a much higher crystallization rate can be obtained.

There are only a few systematic studies on the transport properties in systems in which the solvent induces structural rearrangements in the polymer reported in the literature¹¹⁻¹⁸. The solvent-polymer interactions differ from solvent to solvent and thus the process of SINC is dependent on the nature of the liquid. Furthermore SINC is generally controlled by the diffusion of the solvent into the polymer, leading to a diffusion-controlled process. Moreover the diffusion process is quite unique, since it involves a redistribution of free volume to accommodate penetrant molecules, as well as large-scale structural rearrangements in the polymer, and these two aspects influence each other.

The present paper reports a study of the sorption and diffusion of different liquids in films of glassy sPS, with

the aim of clarifying the phenomena leading to the crystallization of the amorphous sample.

EXPERIMENTAL

The steric purity of sPS, analysed by nuclear magnetic resonance, was 99%.

Glassy films were obtained by melting sPS powders at 300°C and pressing them into films 0.02 cm (T samples) and 0.01 cm (L samples) thick, and quickly cooling to -80°C in an acetone-dry ice bath. The films gave diffuse X-ray diffraction patterns, typical of amorphous polymers.

Different strips of the original films were immersed in various liquids at 25°C, for different times. Upon removal, the samples were blotted on filter paper to remove excess solvent from the surface and weighed in closed test tubes. Equilibrium sorption was assumed when no further weight change was observed for 24 h. Then the samples were removed from the liquids, dried for 24 h at room conditions and then for many days under high vacuum.

The liquids used are listed in *Table 1*. They were reagent grade and used without further treatment. *Table 1* also gives the solubility parameter δ , the molar volume V and the fractional polarity P .

Wide angle X-ray diffractograms of the dried films were detected at 20°C using a PW 1050/71 Philips powder diffractometer (Cu K α , Ni-filtered radiation) in the reflection mode, scanning the scattering 2θ angle in continuous mode.

For optical microscopy, samples ~40 μm thick were

Table 1 Solubility parameter, δ , molar volume, V , and fractional polarity, P , of the solvents^a

Solvent	δ (cal cm ⁻³) ^{1/2}	V (cm ³ mol ⁻¹)	P
n-Hexane	7.3	132	0.000
Cyclohexane	8.2	109	0.000
Carbon tetrachloride	8.6	97	0.000
Toluene	8.9	107	0.001
Benzene	9.2	89	0.001
Chloroform	9.3	81	0.002
Chlorobenzene	9.5	107	0.058
Dichloromethane	9.7	65	0.120
Acetone	10.0	74	0.695

^aThe fractional polarity is the fraction of total interactions that are due to dipole-dipole attractions

put in a circular cavity of a microslide with a drop of solvent, and covered with another microslide. The samples were observed with a Leitz polarizing microscope at a magnification of $\times 100$. The microscope was equipped with a photomonitor (FP800 Thermosystem-Mettler) that makes it possible to determine the brightness of the viewing field as a function of time. The intensity was reported *versus* time as the $\log(I_t/I_0)$ where I_t is the intensity at time t and I_0 is the intensity of the dry sample.

Small-angle light scattering (SALS) experiments were performed using a Spectra Physics model 162 A argon ion laser ($\lambda = 4965 \text{ \AA}$).

RESULTS AND DISCUSSION

Diffusion

The sorption of different liquids in glassy sPS is reported in *Figure 1* as a function of the square root of time, $t^{1/2}$, for T samples. For two solvents, n-hexane and cyclohexane, the increase in weight is not linear with $t^{1/2}$ (non-Fickian behaviour). The anomalous or non-Fickian diffusion processes, often noticed during the transport of liquids in glassy polymers, may show different features, for example, S-shaped or two-stage sorption curves^{19,20}. In our case an induction period is observed, followed by a linear increase in concentration with $t^{1/2}$. The induction time increases from cyclohexane (20 min) to n-hexane (1 h). A very short induction time (2 min) is also observed for carbon tetrachloride. For the other solvents, a linear increase in concentration with square root of time is observed.

Figure 2 shows the reduced sorption curves, c_t/c_{eq} , for samples of different thickness (L and T samples) in acetone, toluene, dichloromethane and chloroform, as a function of $t^{1/2}/d$, where d is the thickness of the sample. In all cases, the linear part of the curve of the thin film superimposes that of the thick film, denoting true Fickian behaviour²¹. Only near the equilibrium concentration is the appearance of maxima in the sorption curves slightly different for T and L samples. The presence of maxima (overshoot) is not unusual during SINC. When the crystallization starts, due to the mobilizing presence of penetrant molecules, the rejection of a fraction of solvent is often observed¹⁴⁻¹⁸. From the linear part of the reduced curve²¹ it is possible to calculate the diffusion coefficient \bar{D} (cm² s⁻¹) from the relation

$$\frac{c_t}{c_{eq}} = \frac{4}{d} \left(\frac{Dt}{\pi} \right)^{1/2} \quad (1)$$

The diffusion coefficients obtained are listed in *Table 2*. It is worth noting that these \bar{D} values are mean values in the explored concentration interval and are not thermodynamic parameters. To obtain the thermodynamic values D_0 , one must know the dependence of diffusion on concentration so as to extrapolate to zero concentration of penetrant.

Table 2 Diffusion coefficient \bar{D} derived from equation (1)

Solvent	\bar{D} (cm ² s ⁻¹)
n-Hexane	-
Cyclohexane	-
Toluene	6.6×10^{-8}
Chloroform	2.8×10^{-7}
Dichloromethane	4.1×10^{-7}
Acetone	5.2×10^{-8}

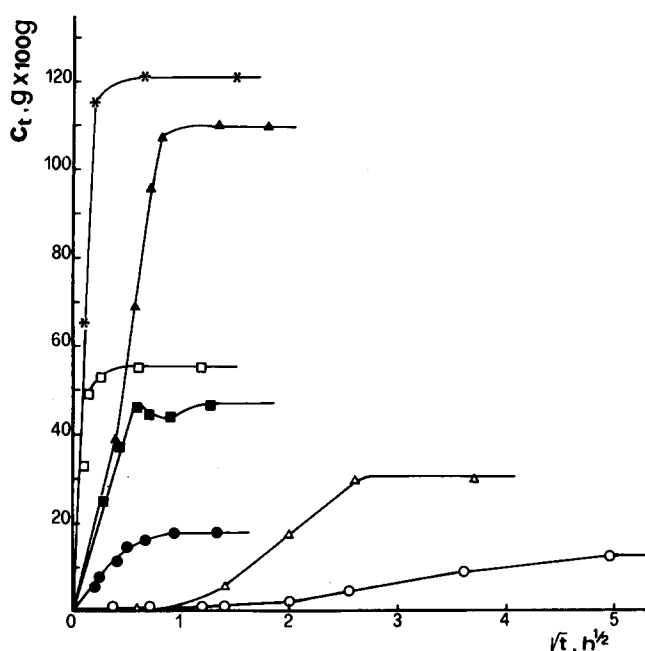


Figure 1 Absorption bulk concentration, c_t (g \times 100 g), as a function of $t^{1/2}$ for n-hexane (\circ), cyclohexane (Δ), acetone (\bullet), toluene (\blacksquare), dichloromethane (\square), carbon tetrachloride (\blacktriangle) and chloroform ($*$)

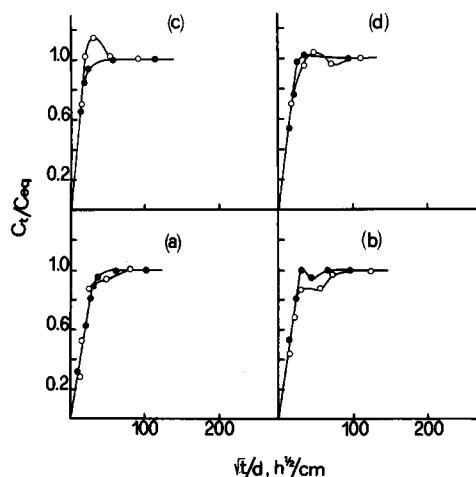


Figure 2 Reduced sorption curve, c_t/c_{eq} , as a function of $t^{1/2}/d$ ($\text{h}^{1/2} \text{ cm}^{-1}$) for T samples (\bullet) and L samples (\circ) for: (a) acetone; (b) toluene; (c) dichloromethane; (d) chloroform

We derived the D_0 parameter only in the case of dichloromethane, for which we studied the vapour sorption and diffusion as a function of concentration. We found $D_0 = 5.5 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, in good agreement with previously reported D_0 values for atactic and isotactic polystyrene^{14,22}.

The mean diffusion coefficients shown in Table 2, are mainly indicative of the polymer-solvent interaction. They are roughly related to the smallest cross-sectional area of the penetrants, being the highest for dichloromethane, with the smallest dimension. This behaviour is typical of systems with limited chain segmental mobility.

From Figure 1 it can be also observed that the sorption varies considerably among the different sPS-liquid systems. The relative solubility may be considered as a measure of the interaction between polymer and liquid. This interaction depends on many factors, such as molecular size of the penetrant, polarizability, and closeness of the solubility parameters of solvent and polymer. We have chosen liquids in the class of 'poorly hydrogen bonded' liquids, with zero or low polarizability, except acetone, which is classified as 'medium hydrogen bonded', and has the highest polarizability.

A comparison of sorption according to the solubility parameter of the liquids is reported in Figure 3. Figure 3 gives the moles of sorbed solvent on moles of polymer as a function of δ . A net maximum corresponding to chloroform ($\delta = 9.3$) is evident, and a less evident maximum corresponding to carbon tetrachloride ($\delta = 8.6$) is also observable. The solubility parameter of atactic polystyrene has been reported²³ in the range 8.7-10.6. However, the most common value is 9.1. We find that the interaction is maximum for chloroform ($\delta = 9.3$).

Therefore the observed behaviour is usual, that is the maximum of sorption is observed for the liquid having a δ value very close to that of the amorphous polymer.

Development of order during swelling

To ascertain that the ordered structure develops during the process of swelling, we detected the intensity of transmitted light, in a polarized optical microscope, during immersion of glassy sPS in toluene, acetone, dichloromethane, chloroform and n-hexane.

Figure 4 gives $\log I_t/I_0$ as a function of time for toluene, chloroform and acetone. We observe a rapid increase in the intensity, indicating that birefringence is developing during swelling. Considering that the thickness is the

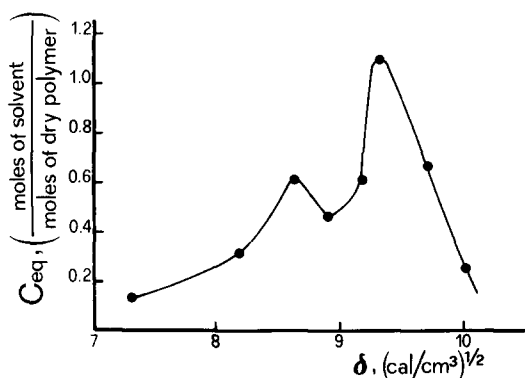


Figure 3 Equilibrium sorption, expressed as moles of sorbed solvent on moles of dry polymer, as a function of the solubility parameter δ (cal cm^{-3})^{1/2} of the solvents

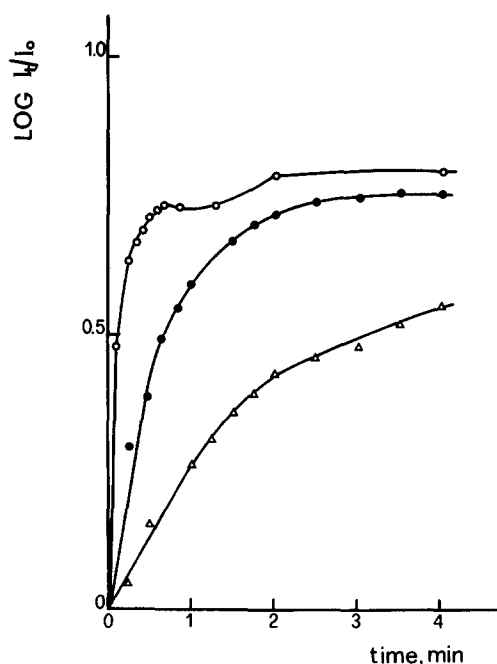


Figure 4 Intensity of transmitted light, $\log I_t/I_0$, as a function of time of immersion in acetone (Δ), chloroform (\bullet) and toluene (\circ)

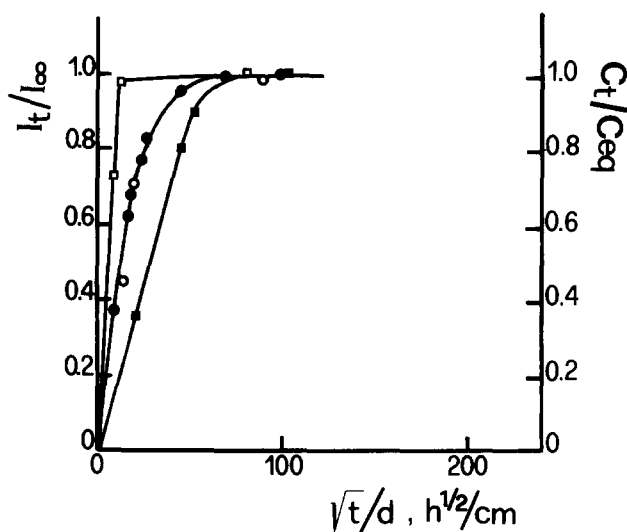


Figure 5 Reduced increase in transmitted light intensity, I_t/I_∞ , as a function of $t^{1/2}/d$ for toluene (\bullet) and chloroform (\blacksquare). The reduced sorption curve of Figure 2 is also shown for toluene (\circ) and chloroform (\square)

same for all the samples, the velocity of the process decreases going from toluene to chloroform and acetone. For dichloromethane and n-hexane, the increase in intensity (not shown) is very slow, and an appreciable effect was observed only after 24 h. The observed values of $\log I_t/I_0$ were 0.16 and 0.21, respectively.

In Figure 5 we report the increase in intensity, as I_t/I_∞ where I_∞ is the intensity after 24 h, as a function of $t^{1/2}/d$ for toluene and chloroform. The reduced increase in weight c_t/c_{eq} as a function of $t^{1/2}/d$ is also reported. It is evident that in the case of toluene the increase in intensity coincides with the increase in solvent concentration. Therefore in this case we have a diffusion-controlled process.

In the case of chloroform the increase in intensity is much slower than the increase in sorption, and the

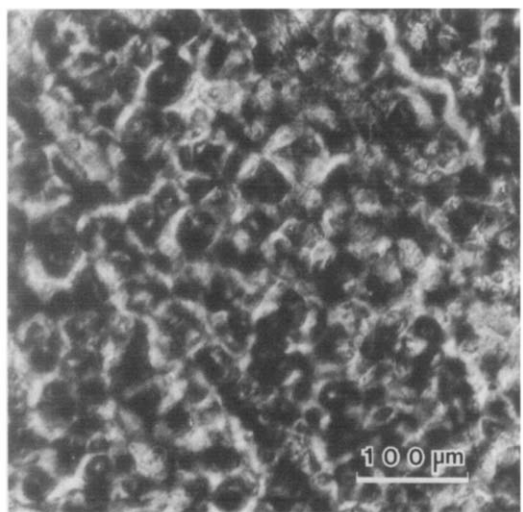


Figure 6 Micrograph in polarized light of the film swollen in acetone for 24 h

process is independent of diffusion. The same is observable for dichloromethane, n-hexane and acetone.

In *Figure 6* we show a micrograph in polarized light of the swollen film after 24 h in liquid acetone at 25°C. Similar textures were obtained for chloroform and toluene, although the dimensions of the 'black and white' regions were different for the different solvents.

The X-ray analysis of glassy sPS in the swollen state gave a diffuse scattering, indicative of very low or no crystallinity. The absence of crystalline order in the swollen samples seems to suggest that the birefringence development during swelling could be related to a mesomorphic structural organization, or simply to a molecular orientation induced by the solvent diffusion. It is interesting to note that textures like those in *Figure 6*, were often observed in lyotropic liquid crystalline systems²⁴.

Structure of the samples after solvent removal

The wide angle X-ray diffractograms of the dried samples, after SINC, are shown in *Figures 7* and *8*. In *Figure 7* the samples crystallized in toluene, chloroform and dichloromethane show the crystalline forms first recognized by Immirzi *et al.*⁵, characterized by an identity period of 7.5 Å, typical of a helical structure. It was proposed, also by other authors, that the samples crystallized in this form have solvated structures^{5,25,26}.

For the solvents presented in *Figure 7* this hypothesis is supported both by the difference in the relative intensities of the peaks, and by the high fraction of residual solvent, even after drying under vacuum at 70°C. The solvated helical structures undergo a transition at ~120°C, releasing the solvent and transforming into a different helical structure⁵. Solvated structures were suggested also for the crystalline forms obtained by SINC of isotactic polystyrene²⁷.

In *Figure 8* samples crystallized in acetone and n-hexane are shown. It is worth noting that the sample crystallized in acetone shows a different crystalline form. It corresponds to the helical structure after thermal transition occurring with expulsion of solvent, first presented by Immirzi *et al.*⁵. Therefore acetone directly induces the unsolvated helical structure; this is confirmed by the absence of residual solvent at room temperature.

Very low and poor crystallinity is induced by n-hexane (*Figure 8b*), in agreement with the low level of transmitted intensity in the optical microscope, shown before.

The dried crystalline films were also analysed by small angle light scattering (SALS). This technique, introduced by Stein for studying superstructure in polymeric solids²⁸, was utilized by Desai and Wilkes to study the morphology of poly(ethylene terephthalate) crystallized in different liquids. In many cases spherulites were observed, and their average size showed little change with different solvents¹².

In our case the SALS did not reveal any diffraction pattern typical of a spherulitic morphology and only a diffuse scattering was observable. According to the limits of the technique, the presence of spherulites having dimensions in the range of a few micrometres can be therefore excluded.

CONCLUSIONS

All the investigated liquids induce crystallization in sPS. For many solvents the weight uptake is linearly

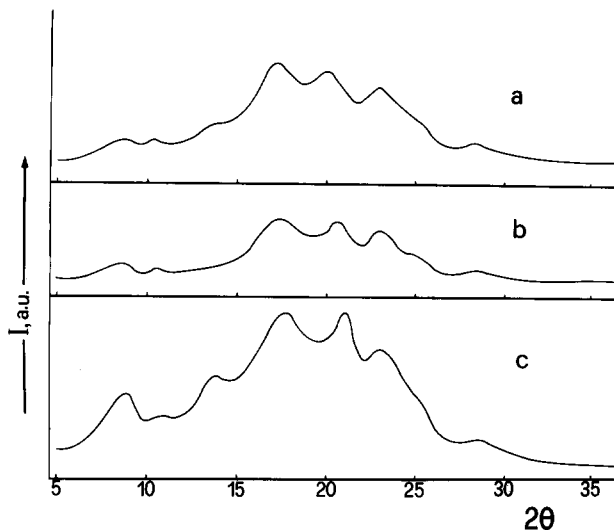


Figure 7 Wide angle X-ray diffractograms of samples immersed in the liquids for 24 h and dried at room temperature: (a) toluene; (b) chloroform; (c) dichloromethane

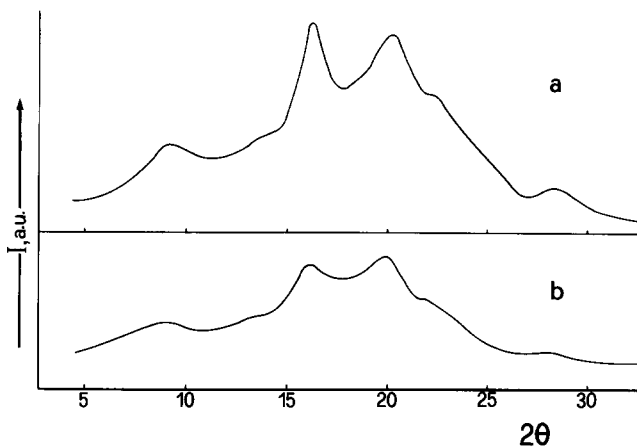


Figure 8 Wide angle X-ray diffractograms of samples immersed in the liquids for 24 h and dried at room temperature: (a) acetone; (b) n-hexane

dependent on the square root of time and the reduced curves of samples with different thickness coincide, implying Fickian diffusion behaviour. Only in the cases of n-hexane and cyclohexane does an induction period precede the linear increase in weight. The equilibrium concentration of sorbed liquids depends on the solubility parameter; the maximum of interaction has been found for chloroform, having a solubility parameter close to that reported for atactic polystyrene.

The development of order, shown by the intensity of transmitted light using a polarized optical microscope, was found to be diffusion limited in the case of toluene. In all the other cases, the ordering process occurs independently of diffusion.

The wide angle X-ray diffractograms of the swollen samples indicate that this ordering process does not lead to crystalline packing, and probably a mesomorphic order is induced. The wide angle X-ray diffractograms of the films after solvent removal show crystalline order, characterized by chains in helical conformation. This is one of the two possible conformations identified for sPS by conformational analysis²⁹.

The high level of residual solvent, and differences in the relative intensities of the peaks, suggest the formation of solvated structures. Only acetone induces the formation of an unsolvated helical structure, with a different diffractogram.

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