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Solvent induced crystallization in poly(aryl-ether-ether-ketone)

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Sorptions of methylene chloride and methylene chloride/n-heptane liquid solutions in poly(aryl-ether-ether-ketone) (PEEK) are analysed and interpreted assuming multiple transport mechanisms. The presence of the highly interacting methylene chloride is responsible for anomalous sorption behaviours. PEEK films immersed in methylene chloride poor n-heptane solutions sorb by non-ideal Fickian diffusion, while limiting Case II and diffusion controlled swelling accompany equilibration in progressively richer methylene chloride solutions. The optical microscopy observation of cryogenically fractured samples conditioned in pure liquid methylene chloride at 5, 20 and 36° C for different times, revealed the presence of a sharp moving front. Differential scanning calorimetry (DSC) indicates that the glass transition temperature of the penetrated shells was always lower than the treatment temperature. The high levels of solvent swelling and plasticization were probably responsible for the crystallinity detected in DSC thermograms and wide angle X-ray scattering (WAXS) diffractograms of the solvent treated and initially amorphous samples. The differences of WAXS diffractograms of samples crystallized by immersion in methylene chloride at 5 and 36° C for various times and by thermal treatment are discussed. Increasing levels of crystallinity were induced in the samples equilibrated in progressively richer methylene chloride solutions.

1. Introduction

The sorption of a highly interacting solvent in a polymer is generally characterized by a complex mass transfer behaviour. Several physical phenomena such as dissolution, diffusion, swelling, and relaxation, can simultaneously occur. A wide variety of sorption modes can therefore be expected depending on the mutual polymer–penetrant affinity, temperature, and penetrant activity. The description of sorption kinetics includes time-dependent boundary conditions, polymer relaxation providing the rate determining transport step, and solvent crazing of the polymer. In particular, a second limiting transport process other than exclusively driven by diffusion is often observed for glassy polymers exposed to organic solvents [1–7]. The limiting sorption modes are characterized, respectively, by smooth concentration gradient (Fickian diffusion) and by the presence of a sharp boundary between an unpenetrated glassy core and an outer solvent saturated swollen shell (Case II).

Several organic solvents [8, 9] present strong interactions with poly(aryl-ether-ether-ketone). In particular, methylene chloride, as inferred from the values of the hydrogen bonding and solubility parameters [9], can strongly interact with this polymer inducing significant swelling and plasticization. Due to these strong interactions, methylene chloride sorption has been often observed to be anomalous [9–11] in PEEK of various initial crystallinities. The sorbed solvent plasticizes the amorphous matrix to a level at which the transformation of part of the amorphous phase to lower free energy crystalline structure is favoured. This phenomenon is known as solvent induced crystallization and has been described to occur even in highly crystalline PEEK samples [9].

The investigation presented is oriented to the analysis of the sorption behaviour of the highly interactive methylene chloride as function of the temperature and activity. Wide angle X-ray scattering was used to determine the onset of solvent induced crystallization and the relationship between the swelling kinetics and degree of crystallinity.

2. Experimental details

2.1. Materials

Samples of 20 mm × 50 mm were cut from 0.25 mm thick films of amorphous (Stabar K200) and semicrystalline (Stabar XK300) PEEK produced by ICI and used as-received. The amorphous films were characterized by a crystallinity lower than 1% while in the semicrystalline samples crystallinity was of about 27%. Methylene chloride and n-heptane utilized in the

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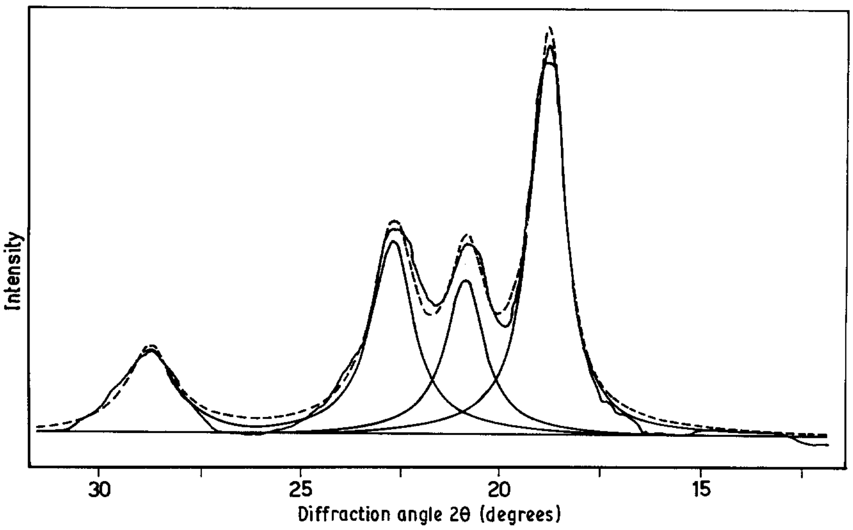

Figure 1 X-ray diffractogram of semicrystalline as received PEEK after subtraction of the amorphous halo. The dashed line represents the calculated fit of lorenzian peaks.

sorption experiments were reagent grade Merck products. The solvents were previously degassed under vacuum by multiple freeze-thaw cycles and then used in sorption experiments.

2.2. Apparatus and procedures

2.2.1. Liquid sorption experiments

The polymer samples were immersed in culture tubes containing the solvents maintained at constant temperature (±0.1°C accuracy). At determined times, the samples were rapidly removed, blotted, and then weighed using an electronic balance (Mettler AE100) with an accuracy of $\pm 10^{-4}$ g. Single samples have been used for each measurement. In order to avoid undesired desorptions during the weighing procedures of the samples conditioned at the higher temperatures, they were removed from the solvents and immediately immersed in cold water (about 0° C), then rapidly blotted and weighed. Sorptions were performed on 0.25 mm thick films immersed in liquid methylene chloride at −32, 5, 20 and 36° C and in methylene chloride/n-heptane liquid solutions at 36° C.

2.2.2. Thermal analysis

A differential scanning calorimeter (DSC) (Mettler TA 3000 System) was used to qualitatively determine the levels of crystallization and plasticization of the solvent treated samples: the absence of the cold crystallization peak in thermogram could be indicative of significant solvent induced crystallization. DSC scans performed at 20° C min^{-1} were carried out on samples saturated in pure liquid methylene chloride and in methylene chloride/n-heptane liquid solutions. Samples were allowed to desorb the solvent under vacuum at the same temperature of the sorption experiment before the thermal analysis.

2.2.3. Advancing swelling front measurements

Samples were conditioned in the liquid methylene chloride for various times and then cryogenically fractured for optical measurements of the advancement of the swelling front. An optical microscope Reichart-Jung Polyvar equipped with graduated eyepiece was used. Measurements were carried out at 5, 20 and 36° C.

2.2.4. WAXS

Wide angle X-ray diffractograms have been obtained in transmission using a powder diffractometer PW 1050 Philips. The Cu*Kα* radiation was used in the angular range 5–60°. The raw spectra were further analysed by a Graphic Mathematical Package with a Unisys 1100 mainframe computer (Istituto Guido Donegani/Unisys).

Crystallinity was calculated by subtracting the amorphous halo from the original diffractogram between 5 and 40° and calculating the respective area values by digital integration. The crystalline part of the spectrum was fitted by non-linear regression with a suitable number of lorenzian curves as indicated in Fig. 1 for an as-received semicrystalline PEEK film. Crystallinities were determined for PEEK samples immersed for various times in liquid methylene chloride at 5 and 36° C, and in methylene chloride/n-heptane solutions of different compositions at 36° C.

3. Results and discussion

3.1. CASE II behaviour

Solvent sorption can induce various levels of local swelling depending on the amount sorbed and on the intensity of the osmotic stresses generated by the solvent–polymer pair. The *osmotic stress* differs from the more common *osmotic pressure* used for dilute polymer solutions because it can be calculated through polymer partial molar quantities [5, 6]. Osmotic stresses in swollen polymers, in fact, arise from the different solvent concentration, and hence swelling, between penetrated and unpenetrated polymer and can reach, depending on the difference between experiment and polymer glass transition temperatures, values of the order of 10 MPa.

Swelling, which is initially located only at the polymer film surface, induces an osmotic tension which progressively propagates through the thickness. This limiting behaviour, indicated as "Case II" sorption, is often observed for thermoplastic polymers and is

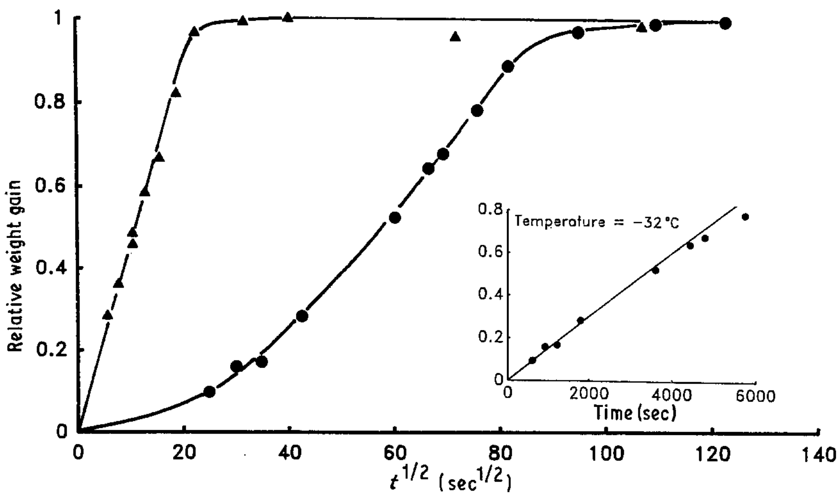

Figure 2 Liquid methylene chloride sorption curves at −32 and 36° C for 0.25 mm thick amorphous PEEK films. (●) $T = -32°$C, W.G. max = 51.7%; (▲) $T = 36°$C, W.G. max = 35.8%.

characterized by a swollen front advancing at constant rate.

The kinetic at −32° C of methylene chloride solvent uptake in an initially amorphous PEEK film is reported as function of the square root of time in Fig. 2. The methylene chloride solvent uptakes at 36° C are also reported in the same figure. While the −32° C sorption shows positive curvature, characteristic of a constant rate sorption as indicated in the reduced plot reported in the same figure, the 36° C sorption shows a trend that is linear with the square root of time. As indicated before, the rate determining step is the osmotically induced polymer relaxation at the boundary between the unpenetrated central core and the swollen outer shell. The relaxation rate remains constant as long as the penetrant concentration at the boundary stays constant, however, the diffusive control of the mass transport in the swollen shell leads to a concentration drop at the moving boundary and hence to a reduction of the relaxation rate. The change of the controlling transport mechanism with temperature reported in Fig. 2 is typical of systems exhibiting limiting Case II sorption behaviour, i.e. the temperature increase does not accelerate the less activated diffusion process as it enhances relaxation. At higher temperatures, the fast viscoelastic response to the osmotic stresses at the moving boundary is not readily followed by the slower diffusion which becomes controlling.

Solvent induced crystallization has been also observed to accompany methylene chloride sorption in PEEK at −32° C. The onset of crystallization has been confirmed by the DSC scan performed on an initially amorphous sample first equilibrated in liquid methylene chloride at −32° C and then allowed to desorb at the same temperature. The DSC thermogram does not reveal any cold crystallization peak implying that crystallization occurred during the sorption. The high solvent-polymer affinity (uptakes higher than 50%) causes significant swelling of the polymer structure depressing the glass transition temperature to a value lower than the experimental temperature leading to Case II sorption and solvent induced crystallization.

3.2. Diffusion controlled relaxations

As previously discussed, Case II limiting sorption is characterized by a sharp front advancing at constant rate through the unaffected core up to the development of a diffusion resistance in the swollen polymer which progressively reduces the penetrant concentration at the boundary and hence the osmotic stress and the penetration rate [5, 6]. The swelling rate is controlled by the penetrant diffusion in the swollen shell. Diffusion controlled relaxation has been observed in the methylene chloride sorptions at temperatures of 5, 20 and 36° C while limiting CASE II sorption occurred only at very low temperatures (−32° C). The

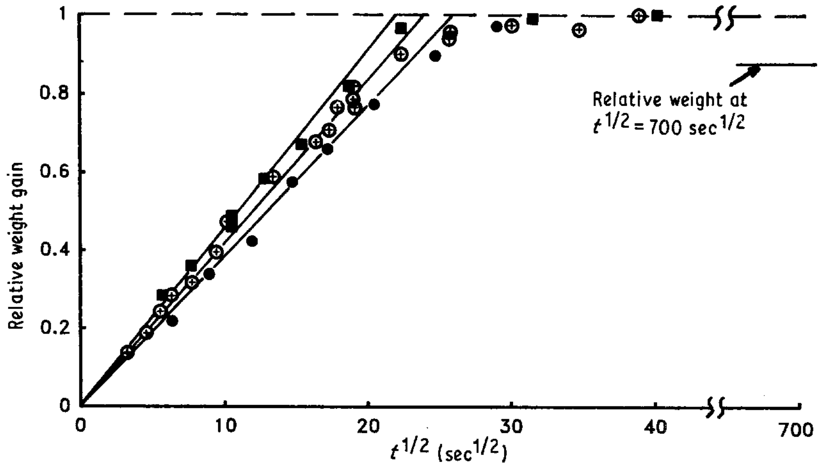

Figure 3 Liquid methylene chloride sorption curves at several temperatures for 0.25 mm thick amorphous PEEK films. (●) $T = 5°$C, W.G. max = 42.1%; ⊕ $T = 20°$C, W.G. max = 38.5%; (■) $T = 36°$C, W.G. max = 35.8%.

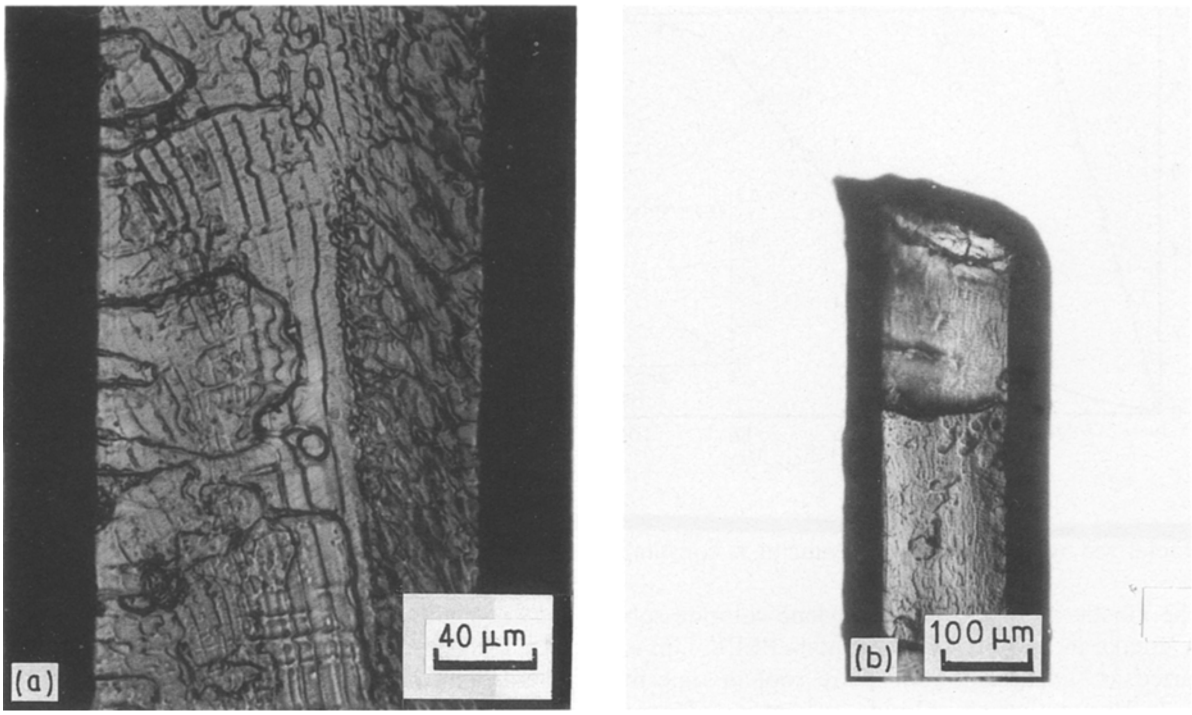

Figure 4 Optical microscope micrographs of a cryogenically fractured 0.25 mm thick sample after 40 sec immersion in liquid methylene chloride at 36° C.

change in the controlling transport mechanism with temperature has been already introduced. The penetrant uptake increases linearly with the square root of time and almost abruptly levels off when the swelling fronts meet, see Fig. 3. The existence of a sharp front was observed also in this diffusion controlled process as indicated in the photomicrograph (Fig. 4) of a sample treated in methylene chloride at 5° C and then cryogenically fractured. Diffusion controlled relaxations have been also observed at 20 and 36° C. The rate of the advancing front was determined by optical microscopy observations. The penetration depth increased linearly with the square root of time. The penetration depth was calculated as the difference between the initial thickness and the residual unaffected core. The time dependency of the relative penetration, which is the ratio between the penetration depth and the initial sample thickness, is reported in Fig. 5 for the experiments carried out at 36° C. The solvent equilibrium uptake was not achieved when the fronts met since, due to the diffusion control in the swollen shell, a non-uniform concentration profile throughout the thickness of the sample was still present.

WAXS measurements were performed on initially amorphous samples first equilibrated in methylene chloride at 5 and 36° C and then allowed to desorb. These solvent treated samples are characterized by different final crystallinity, respectively 27 and 32%, confirming the occurrence of solvent induced crystallization. WAXS measurements were also performed on samples contacted at 5° C with methylene chloride for different times. Analogous to penetration depth, the crystallinity level increases proportionally to the square root of the contacting time. A detailed analysis of the WAXS diffractograms is discussed later. The samples immersed in liquid methylene chloride at temperatures ranging from − 32 to 36° C showed an onset of opacity which has been attributed to crystallization. Several examples are reported in literature which indicate that solvent induced crystallization occurs in polyethylene-terephtalate [14–17], polyethylene-naphtalate [18] and polycarbonate [19–21]. Modelling

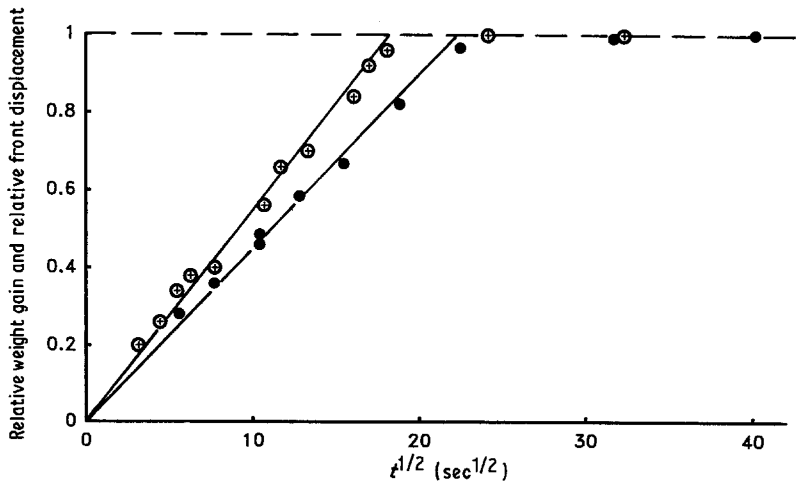

Figure 5 Penetrating front (⊕) and solvent uptake kinetics (●) for 0.25 mm thick amorphous PEEK films in liquid methylene chloride at 36° C.

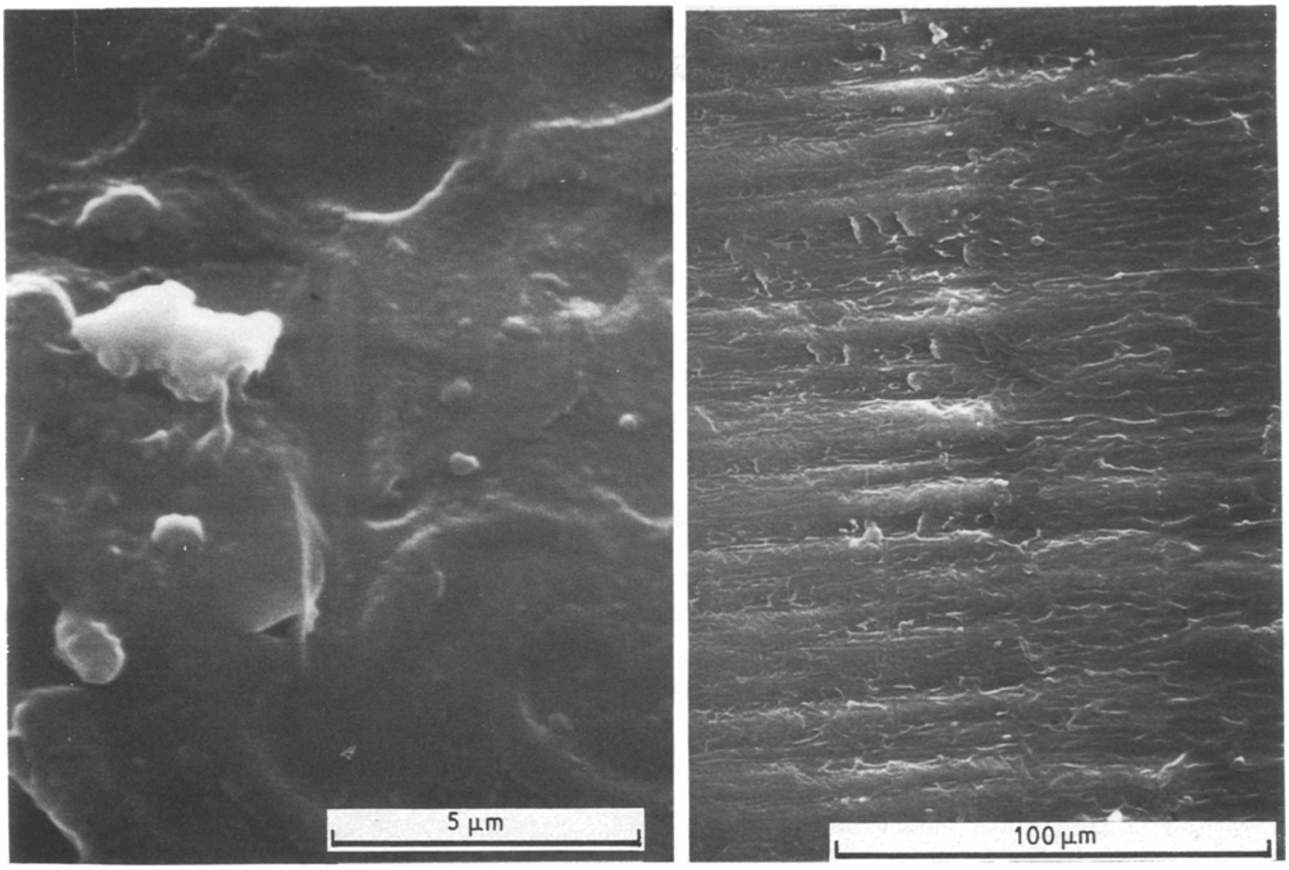

Figure 6 Scanning electron microscope micrographs of a cryogenically fractured 0.25 mm thick amorphous PEEK film after 6 h immersion in liquid methylene chloride at −32° C.

of the phenomenon has been presented by Durning and Russell [17, 22, 23] considering polymer swelling, crystallization and cavitation. Some of the events occurring in the methylene chloride/PEEK system could be explained by this model. The expulsion of solvent from developing crystallites may locally increase the solvent concentration leading to local supersaturation and then to a phase separation resulting in macrovoiding. Nevertheless, the presence of macrovoids suggested by this theory was not evident in our case as shown in the scanning electron micrograph of a sample solvent treated at −32° C (Fig. 6). Probably due to still high strength of the swollen PEEK, the macrovoid formation does not occur at this temperature even if the almost flat concentration profile, responsible of higher saturation levels, should promote macrovoiding as observed for other polymer–solvent systems at low temperatures [17]. The solvent expelled by the growing crystallites is accommodated inside the amorphous matrix, reaching concentrations higher than true equilibrium. The constrained out of equilibrium state of the polymer structure, however, induces the experimentally observed solvent desorption. This matrix relaxation and consolidation phenomena are analogous to those observed in some non-crystallizing polymer–diluent systems [24].

The complex sorption behaviour is then characterized by the cooperative methylene chloride penetration and matrix relaxation due to the supersaturation of the amorphous parts of the semicrystalline polymer.

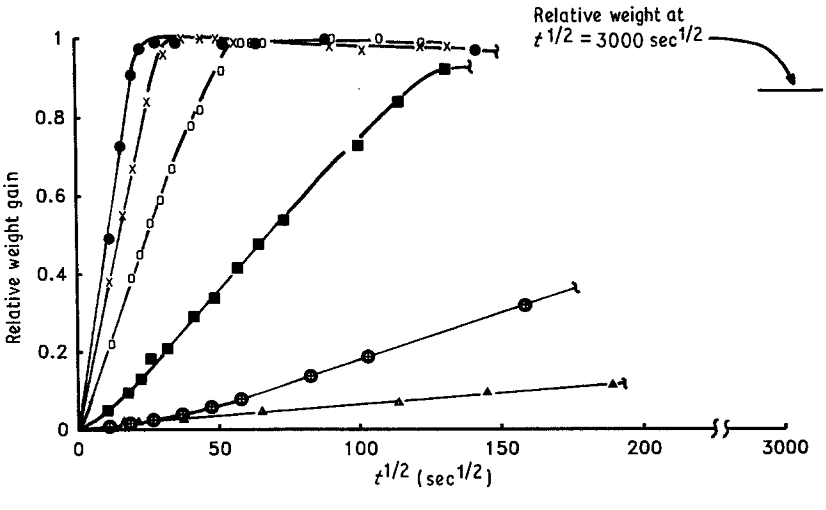

Figure 7 Methylene chloride/n-heptane solution sorption curves at different methylene chloride molar fractions (X_m) at 36° C. (▲) X_m = 0.25; (⊕) X_m = 0.40; (■) X_m = 0.50; (○) X_m = 0.65; (x) X_m = 0.80; (●) X_m = 0.95.

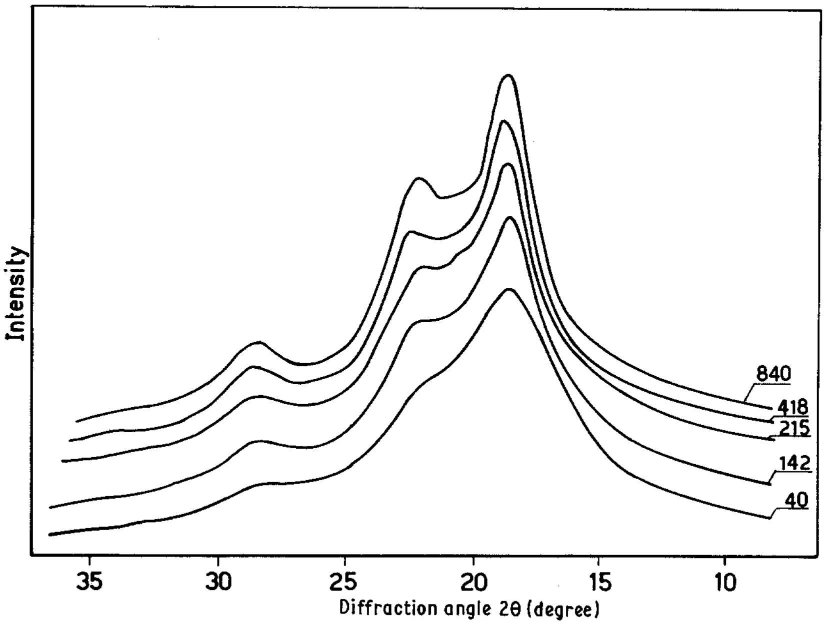

Figure 8 A sequence of X-ray diffractograms after immersion at different times (in seconds) in methylene chloride at 5° C.

As temperature decreases, diffusion is no longer controlling the process, and the concentration gradient of the diffusing penetrant is progressively reduced. The developing crystallites are then surrounded by an amorphous matrix with a super-saturated penetrant concentration higher than those attained at more elevated temperatures, leading to higher penetrant uptakes. The highest solvent uptake (51.7%) was, in fact, measured at −32° C when relaxation was controlling the sorption. At higher temperatures, the diffusive concentration gradient developed in the penetrated part presumably redistributes into the amorphous polymer the solvent expelled from the growing crystallites. Reduced super-saturation and lower penetrant uptakes are then observed. The methylene chloride uptakes at different temperatures are reported in Table I.

The assumption of rapid crystallization in the penetrated polymer is implicit in the foregoing discussion. However, the overshoot detected during the liquid methylene chloride sorption could be also attributed to crystallization times greater than the sorption times. Part of the crystallization may occur also when sorption is completed leading to the overshoot.

3.3. Sorption from methylene chloride/n-heptane solutions

Sorptions were performed at 36° C on PEEK film contacted with methylene chloride/n-heptane liquid solutions of various compositions. The methylene chloride activity, corresponding to each composition, has been calculated by means of a group contribution method [25] and is reported in Table II.

Sorption kinetics at methylene chloride activities ranging from 0.34 to 0.95 are reported in Fig. 7. As the methylene chloride activity is increased, the observed sorption behaviour passes from a *relaxation controlled diffusion* to a *diffusion controlled relaxation*. The overshoot is apparent in all cases except at the lowest activity. At moderate activity (methylene chloride molar fractions 0.40 and 0.50), relaxations are slow enough to control the first stages of the sorption up to the development of a diffusion resistance. The initial part of the curve shows an upward curvature suggesting that the sorption kinetics are initially linear with time.

WAXS measurements, performed after desorption on samples equilibrated in liquid solutions, have shown, for solution treated at methylene chloride molar fraction of 0.40, a crystallinity degree (21%) lower than those (26–28%) observed for samples immersed in solutions of molar fractions of 0.50 and higher. The sample immersed in the solution of methylene chloride molar fraction 0.25 remained in the amorphous state.

3.4. WAXS results

Figure 1 shows the X-ray reference diffractogram of an as-received thermally crystallized PEEK sample which is consistent to previously published data [13]. The amorphous halo has been determined from an amorphous reference sample.

The sequence of the diffractograms of PEEK samples

TABLE I CH_2Cl_2 maximum uptake in 0.25 mm thick PEEK films

Temperature (° C)	% uptake
−32	51.7
5	42.1
20	38.5
36	35.8

TABLE II Calculated CH_2Cl_2 activity of methylene chloride/n-heptane solutions with different methylene chloride molar fraction (X_m)

X_m	MC activity
0.05	0.076
0.08	0.120
0.23	0.345
0.25	0.375
0.40	0.524
0.50	0.623
0.65	0.747
0.80	0.850
0.95	0.955

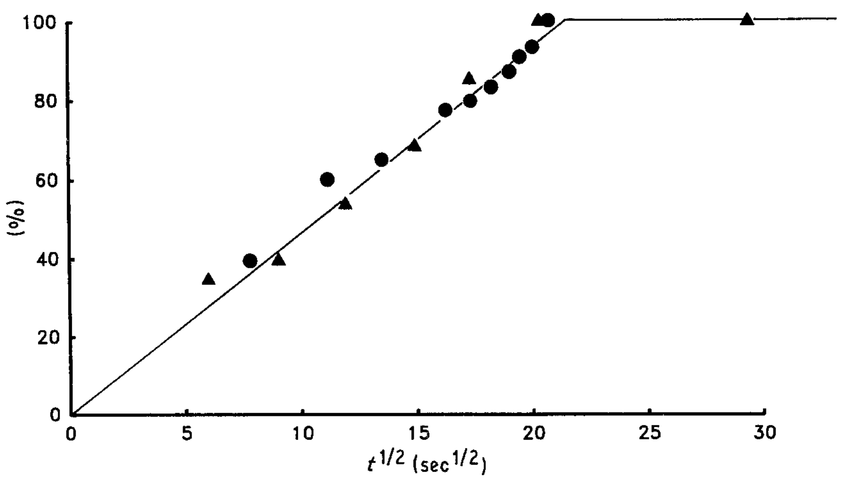

Figure 9 Crystallinity degree (▲) (in % of the maximum obtained value) and % solvent front advancement (●) as a function of square root of immersion time in methylene chloride at 5° C.

treated for various immersion times in methylene chloride at 5° C is shown in Fig. 8. A continuous transition from an amorphous-like to a semicrystalline spectrum is observed for increasing immersion times. The increase of crystallinity with time is compared in Fig. 9 to the advancement of the swollen front. The two kinetics are comparable, suggesting some correlation between swelling and crystallization.

Grayson and Wolf [26] reported that micromorphology of solvent-induced crystallization appears to be different from that induced by thermal treatment. We also noted, in fact, appreciable differences between the diffractogram relative to the solvent equilibrated sample reported in Fig. 10 and that of the thermally crystallized reference sample of Fig. 1. In particular, the peak at 20.7°, between the (1 1 0) and (2 0 0) reflections, respectively at 18.7 and 22.6°, which is attributed to (1 1 3) reflection, is missed in samples crystallized by solvent immersion. A more accurate examination of the whole diffractograms, however, revealed that some samples presented this peak of reduced intensity, while for others, even though the peak was not visible, the fitting procedure of the experimental profile with lorenzian curves gave satisfactory fit only when the (1 1 3) component was maintained. This peak, as reported in Fig. 10, appeared in all cases broadened and shifted from the standard angular position.

The crystalline structure of PEEK has been investigated by Wakelyn [12]. The diffractogram was indexed on the basis of an orthorhombic unit cell (Pbcn space group, cell parameters $a = 0.788$ nm; $b = 0.594$ nm; $c = 3.050$ nm). The variation of the intensity of the (1 1 3) reflection suggests that some disorder occurs at 1/3 of the c-axis. This position corresponds to the carboxyl group location in the structure that indeed is the less rigid part of the molecular units.

PEEK samples immersed in methylene chloride at 36° C have been also investigated. The observed sorption and crystallization behaviour are qualitatively similar to those described before. There are, however, some indications that solvent treatments at higher temperatures favour the achievement of slightly higher crystallinities (30–35%). Moreover, the intensity of the (1 1 3) reflection seems to be enhanced by protracted immersion times after the achievement of saturation. This should indicate that a more ordered situation is established, likely due to the higher mobility of the polymer chains. Since differences are small, further studies should be dedicated to this point.

4. Conclusion

Evidence has been presented for solvent induced crystallization in the case of liquid methylene chloride sorption and of different activity methylene chloride/n-heptane liquid solutions sorption. The induced crystallinity increased with the methylene chloride activity. The increase of the maximum solvent uptakes at lower temperatures and the

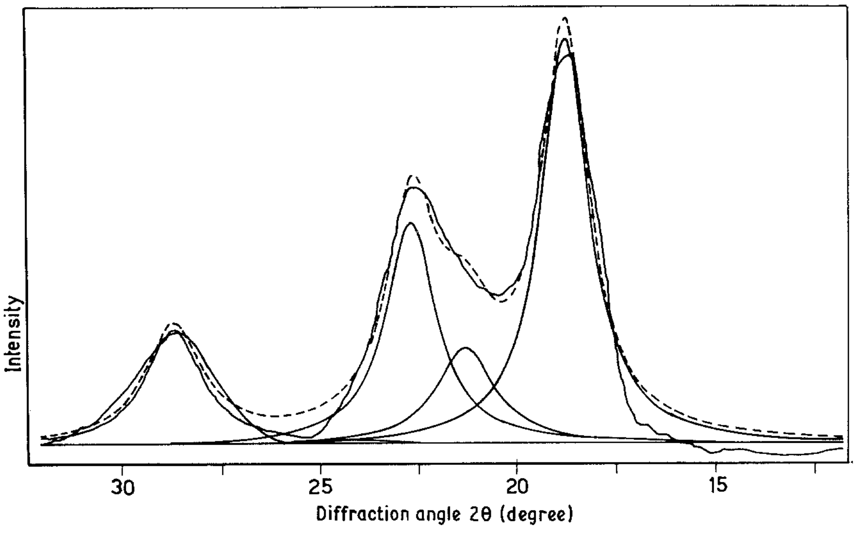

Figure 10 X-ray diffractogram of a PEEK sample after immersion in methylene chloride at 5° C for 50 min. The amorphous halo has been subtracted. The dashed line represents the calculated fit of lorenzian peaks.

presence of an overshoot in the sorption curves have been attributed to the expulsion of solvent from the growing crystallites which accommodates in the still amorphous polymer matrix leading to local supersaturation. The degree of supersaturation depends upon the concentration profile and consequently on sample thickness and experimental temperature.

WAXS measurements have shown appreciable differences between thermally-induced and solvent-induced crystallization; the latter shows a less ordered situation. There are some indications that as the solvent temperature increases the degree of solvent induced crystallinity becomes higher.

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