Effect of the degree of crosslinking on penetrant transport in polystyrene

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The effect of the degree of crosslinking of glassy polymers on the transport mechanism of penetrants was investigated using a series of divinyl benzene (DVB)-crosslinked polystyrenes of nominal crosslinking ratio X from 0.00138 to 0.060 mol DVB/mol styrene. The number average molecular weight between crosslinks, $\bar{M}_c$, was determined from equilibrium swelling experiments in cyclohexane. Dynamic swelling experiments with cyclohexane at 30°C showed that the mechanism of penetrant transport was anomalous. An overshoot in the penetrant uptake was observed, characteristic of macromolecular relaxations and of changing solubility of the cyclohexane in the continuously swelling polystyrene. Photographs of various samples during the swelling process showed that solvent crazing occurred predominantly in loosely crosslinked samples.

INTRODUCTION

Transport of penetrants in glassy polymers has been the subject of considerable research work over the past twenty years. It is now known that in most cases of penetrant transport associated with transition from the glassy to the rubbery state, macromolecular relaxations are observed at and behind the penetration front separating the inner glassy core from the outer rubbery layer. These relaxations are important in the transport process and may be the controlling step of the transport mechanism[1-12]. In a recent review, Astarita and Nicolais[13] offer a complete analysis of our knowledge on this subject.

Several years ago Vrentas et al.[14,15] proposed the diffusional Deborah number, De, as a means of classifying the mechanisms of transport processes of penetrants in glassy polymers. This dimensionless number, defined as the ratio of the characteristic relaxation time of the penetrant–polymer system to the characteristic diffusion time of the penetrant in the polymer, is instrumental in the development of the general relaxation-controlled transport models of Astarita and his collaborators[12,13,16,17]. In fact, in these contributions the reciprocal square root of the Deborah number, ϕ, is used. For values of De much greater or smaller than one, Fickian diffusion is the predominant transport mechanism. However, for values of De of the order of one, non-Fickian transport is observed where diffusion and relaxation mechanisms are coupled. The exact constitutive equation of this type of penetrant transport is not yet known, although Wang et al.[5] have proposed a simplified equation which can, in certain cases, predict experimental results[18].

Since the characteristic diffusion time, appearing in the definition of the Deborah number, depends on the size of the polymer sample, it is possible to observe the relaxation/diffusion coupling by changing the size of the polymer samples, as discussed by Hopfenberg and his collaborators[10,19].

The early studies of Hartley[20] with penetrant transport in cellulose acetate were instrumental in establishing some important peculiarities of anomalous transport in terms of observed penetrant fronts and their movement in the glassy zone. Most recent experimental studies have been performed using polystyrene and poly(methyl methacrylate), two easily prepared and widely used polymers, and a variety of penetrants including alcohols, aliphatic and aromatic hydrocarbons, etc.

Since relaxation and diffusion coupling may be observed by changing the relative magnitude of the relaxation time with respect to diffusion time, it was our intention to vary the degree of crosslinking of polystyrene, thus potentially achieving conditions of non-Fickian, anomalous or even Case-II transport. For our studies, cyclohexane was selected as the penetrant due to previous knowledge of its thermodynamic interaction with polystyrene at different temperatures[21].

Penetrant transport, especially of aliphatic hydrocarbons in linear polystyrene has been the subject of extensive research by Hopfenberg, Nicolais, Drioli and their collaborators[19,22-26]. In particular, there have been extensive studies of the penetrant uptake in films[22-25]. Their analysis has shown that, under certain conditions, the limiting case of anomalous transport, i.e. Case-II transport, can be achieved[25]. Recently Nicolais et al.[27] have also found that as the temperature increases transport of n-hexane in polystyrene becomes Fickian. Also Berens and Hopfenberg[28] have studied the effect of characteristic length of the sample on the penetrant transport.

In other studies Hopfenberg et al.[22] and Nicolais et al.[25] have examined crazing as a result of hydrocarbon penetration in glassy polymers. In this respect, the studies of Kambour et al.[29,30] and Narisawa[31] offer a more complete analysis of solvent crazing as a function of thermodynamic interactions of the penetrant.

In view of the recent studies on this subject, here we also examine the penetrant transport and solvent-crazing of polystyrene, for samples of a wide range of crosslinking densities.

EXPERIMENTAL

Polymer preparation and characterization

Polystyrene films were prepared by a bulk copolymerization/crosslinking technique using styrene and divinyl benzene (DVB) which also acts as the crosslinking agent. Styrene (Aldrich Chemical Co., Milwaukee, Wisconsin) was vacuum-distilled at 45°C/15 mm Hg. To this 0.14–0.44 mol% DVB (Polysciences, Warrington, Pennsylvania) were added along with 1.2 mol% benzoyl peroxide as an initiator. According to the manufacturer's specifications, the commercial DVB contained 58.1 wt% DVB, 38.8 wt% ethyl vinyl benzene and 3.1 wt% diethyl benzene. It was used as received, but all calculations henceforth refer to the pure component DVB. Reaction mixtures were prepared with nominal crosslinking ratios of $X = 0.00138$, 0.00280, 0.00360, 0.00385, 0.00410, 0.00445 and 0.060 mol pure DVB/mol styrene.

The copolymerization/crosslinking reaction was carried out in Petri dishes at $40 \pm 1°C$ or $70 \pm 1°C$ for 24 h. The resulting glassy polystyrene samples were cut into rectangular slabs (films) and each thickness was measured with a micrometer (precision $\pm 12.5 \ \mu m$).

Thin samples of the products of initial weight W_a were swollen in cyclohexane at $30 \pm 0.5°C$ to thermodynamic equilibrium. At that point, their weights in air, W_a', and in water, W_w', were determined, and they were subsequently dried to constant weight, W_p. These values were used to calculate the number average molecular weight between crosslinks, $\bar{M}_c$, of each sample.

Dynamic swelling studies

All previously prepared samples (usually in dimensions of 1.3 cm × 1.6 cm with thickness varying from 3 to 3.5 mm in one set of experiments and 4.3 to 4.6 mm in another) were swollen in cyclohexane at $30 \pm 0.5°C$. Values of their weight, thickness, and volume were obtained periodically and until reaching thermodynamic equilibrium. This was attained in about 1100 to 1200 h depending on the degree of crosslinking. A number of dynamic swelling experiments were also performed in n-hexane at $30 \pm 0.5°C$.

Selected samples were observed under polarized light to determine the velocity of the cyclohexane penetration front and other structural and geometric changes of the slabs. Pictures were taken of the penetrant process as a function of time.

RESULTS AND DISCUSSION

Characterization of crosslinked structure

The equilibrium swelling data of the samples prepared are shown in *Table 1* as a function of the crosslinking ratio. These data were obtained with cyclohexane at 30°C, a penetrant for which the values of the Flory interaction parameter, χ, with polystyrene are known at different temperatures from the work of Cantow and Schuster[21].

From the values of the weights of the samples in air and water in the swollen polymer, the equilibrium volume degree of swelling, Q, and the polymer volume fraction in the swollen polymer, v_2, were calculated from equation (1),

$$v_2 = Q^{-1} = \frac{W_a' - W_w'}{\rho_w} \tag{1}$$

where ρ_w is the density of water at 25°C.

The number average molecular weight between crosslinks, $\bar{M}_c$, was determined using equation (1), which was obtained from the application of the modified Gaussian distribution theory of Lucht and Peppas[32] to the swelling behaviour of highly crosslinked networks, as discussed by Peppas et al.[23].

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{\bar{v}[\ln(1-v_2) + v_2 + \chi v_2^2][1 - v_2^{2/3}/N]^3}{V_1[v_2^{1/3} - 0.5v_2][1 + v_2^{1/3}/N]^2} \tag{2}$$

$$N = \frac{\bar{M}_c}{M_r} \tag{3}$$

In these equations, $\bar{M}_n$ is the number average molecular weight of the uncrosslinked polystyrene, $\bar{v}$ is the specific volume of polystyrene in the amorphous state ($\bar{v} = 0.95 \ cm^3/g$), V_1 is the molar volume of cyclohexane ($V_1 = 108.1 \ cm^3 \ mol^{-1}$), v_2 is the equilibrium polystyrene volume fraction in the swollen gel, χ is the Flory interaction parameter for polystyrene/cyclohexane, and M_r is the molecular weight of the repeating unit ($M_r = 104.1$). The χ factor is given[21] by equation (4)

$$\chi = 0.4433v_2^2 + 0.2308v_2 + 0.507 \tag{4}$$

Using the values of v_2 for the different samples, shown in *Table 1*, $\bar{M}_c$ could be determined by an iterative, simultaneous solution of equations (2) and (3). The value of M_n used in equation (2) requires some discussion, since the reaction of the two monomers produces crosslinked polystyrene and consequently M_n for uncrosslinked polystyrene is not immediately known. $\bar{M}_n$ was determined from equation (5) which applies to the kinetics of free

Table 1 Characteristics of crosslinked polystyrene samples swollen in cyclohexane at 30° C

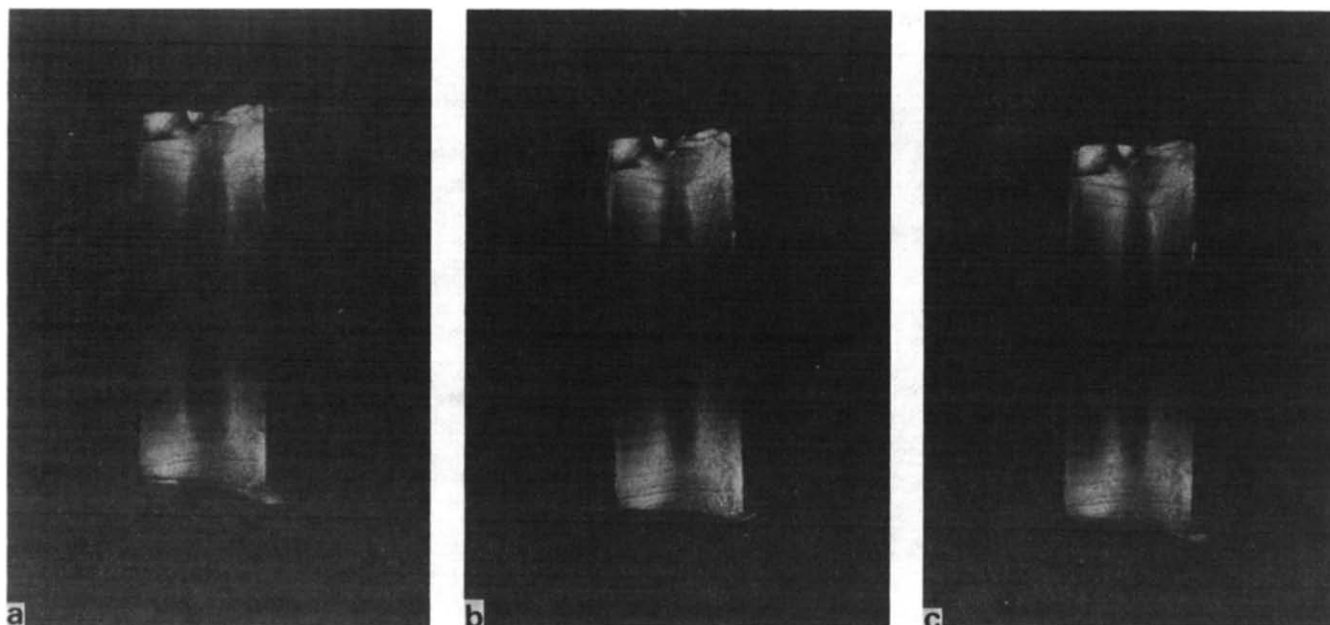| Nominal crosslinking ratio, X (mol/mol)	Equil. polymer volume fraction v_2	Equil. degree of swelling in cyclohexane Q	Experimental $\bar{M}_c$
0.00138	0.288	3.47	7150
0.00280	0.317	3.15	6975
0.00360	0.323	3.09	6250
0.00385	0.349	2.86	6200
0.00410	0.373	2.68	5950
0.00445	0.3853	2.53	5800

Figure 1 Lateral movement of cyclohexane penetration front at 30°C in a film of polystyrene of original thickness of 3.3 mm with $\bar{M}_c$=5.950. (a) 23 h; (b) 29 h; (c) 32 h

radical polymerization of styrene.

$$\bar{M}_n = \frac{k_p[M]}{(fk_dk_t[I])^{1/2}}M_r \qquad (5)$$

Here the initiation, propagation and termination kinetic constants are[34] $k_d = 4.7 \times 10^{-5} \, s^{-1}$, $k_p = 145 \, l/mol \, s^{-1}$ and $k_t = 2.9 \times 10^7 \, l \, mol^{-1} \, s^{-1}$, respectively, the initiator efficiency is 0.5, and [M] and [I] are the monomer and initiator concentrations used in the reaction in mol l^{-1}. Using these values, $\bar{M}_n$ was calculated as 15 550.

The calculated values of $\bar{M}_c$ ranged from 5800 to 7150 and increased with decreasing nominal crosslinking ratio, X, as expected. The equilibrium uptake of cyclohexane in the polystyrene samples was also a function of X as judged by the values of the equilibrium polymer volume fraction in the swollen samples, v_2, which increased from 0.288 to 0.395 as the crosslinking ratio increased from 0.00138 to 0.00445.

However, highly crosslinked polystyrene prepared at a crosslinking ratio of $X = 0.06$ mol/mol showed a very small penetrant uptake at equilibrium ($v_2 = 0.99$) probably indicative of major changes in the polystyrene structure upon incorporation of larger amounts of DVB. The equilibrium values for this last sample could not be used to determine $\bar{M}_c$.

Similar equilibrium swelling studies performed with highly crosslinked samples in n-hexane at 30°C showed again a negligible amount of penetrant uptake. However, the studies of Hopfenberg et al.[22] with the same system at lower degrees of crosslinking had shown a significant penetrant uptake.

Penetration front

The motion of the cyclohexane penetration front in the polymers was measured by polarized photography. The moving front was clearly observed in all three directions. *Figures 1* and *2* show a sequence of seven pictures of a film with $\bar{M}_c = 5950$. *Figure 1a, 1b* and *1c* show the lateral movement of the front of cyclohexane at 23, 29 and 32 h, when the two fronts have almost met. This transport process is associated with considerable expansion of the film volume and change of its thickness. A sequence of photographs of penetrant front motion in the sides of the same sample at 23, 29, 32 and 48 h is shown in *Figures 2a–2d*. Regions of significant stresses built in the slab are shown as interference fringes in the four corners of the sample.

However, similar observations with a film with $\bar{M}_c = 11\,200$ (and with similar samples of lower degree of crosslinking) showed the development of a number of crazes in the film. *Figure 3* shows a film with $\bar{M}_c = 11\,200$ swollen in cyclohexane after 72 h. These studies show the importance of the degree of crosslinking in solvent-crazing. At low degrees of crosslinking, as the penetration front moves towards the glassy core, the outer rubber (gel-like) layer swells considerably than it would be for highly crosslinked polystyrene. Consequently, the internal stresses formed at and behind the penetration front are considerably higher for loosely than for highly cross-linked samples, and the former appear to craze much faster than the latter.

Additional information concerning the penetrant transport may be obtained from these photographs by calculating the front position, X_1, and the position of the rubbery state/penetrant interface, X_2. From these values the average penetration front velocity was determined as $v = 0.158$ mm/h for a sample with $\bar{M}_c = 5950$ $v = 0.25$ mm/h for a sample with $\bar{M}_c = 6200$ and $v = 0.336$ mm/h for a sample with $\bar{M}_c = 7150$. Within the limits of statistical analysis ($r^2 > 0.97$), all reported values of the front velocity were constant throughout the cyclohexane transport process.

Dynamic swelling studies

Dynamic swelling studies of polystyrene samples with different $\bar{M}_c$ were performed at 30 ± 0.5°C. The cyclohexane weight uptake was determined for all samples as a
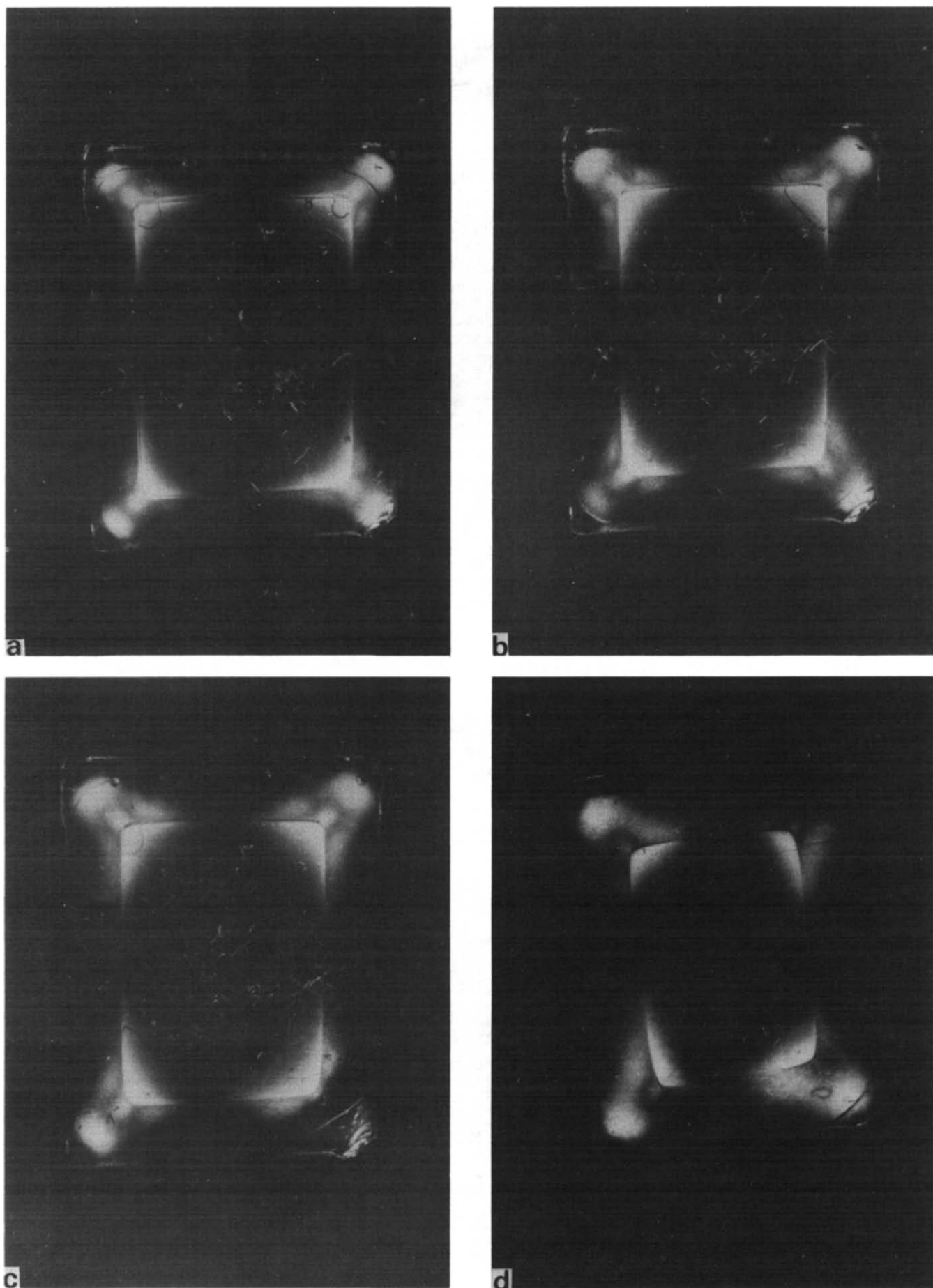
Figure 2 Polarized micrographs of cylohexane front in a film of polystyrene with $\bar{M}_c = 5.950$. (a) 23 h; (b) 29 h; (c) 32 h; and (d) 48 h

function of time and the normalized weights with respect to the final dry weight of the polymer are plotted in *Figures 4* and *5*. Thus, any small, unreacted quantities of monomers which might have been included in the glassy polymer, were leached out during the early stage of swelling and are not taken in consideration in these plots.

These results show an initial fast uptake of cyclohexane to about 200 h followed by a characteristic overshoot and loss of penetrant over a period of 500 h. Eventually, an equilibrium value of penetrant uptake is attained. The overshoot is characteristic of macromolecular relaxations[35] due to the rapid penetrant uptake which leads to a change in the solubility of cyclohexane in the swollen polystyrene. The maximum, M_m, and equilibrium, M_e, cyclohexane uptake (in g cyclohexane per g dry polystyrene) are reported in *Table 2*.

To investigate the effect of crosslinking on the re-

laxation overshoot, the normalized overshoot uptake, $(M_m - M_e)/M_e$ was plotted as a function of $\bar{M}_e$ in *Figure 6*. It can be seen that as the degree of crosslinking increases, the overshoot decreases. Since the equilibrium cyclohexane volume fraction decreases with increasing degree of crosslinking, the normalized overshoot uptake is a monotonically increasing function of the cyclohexane content in this region of thicknesses of samples.
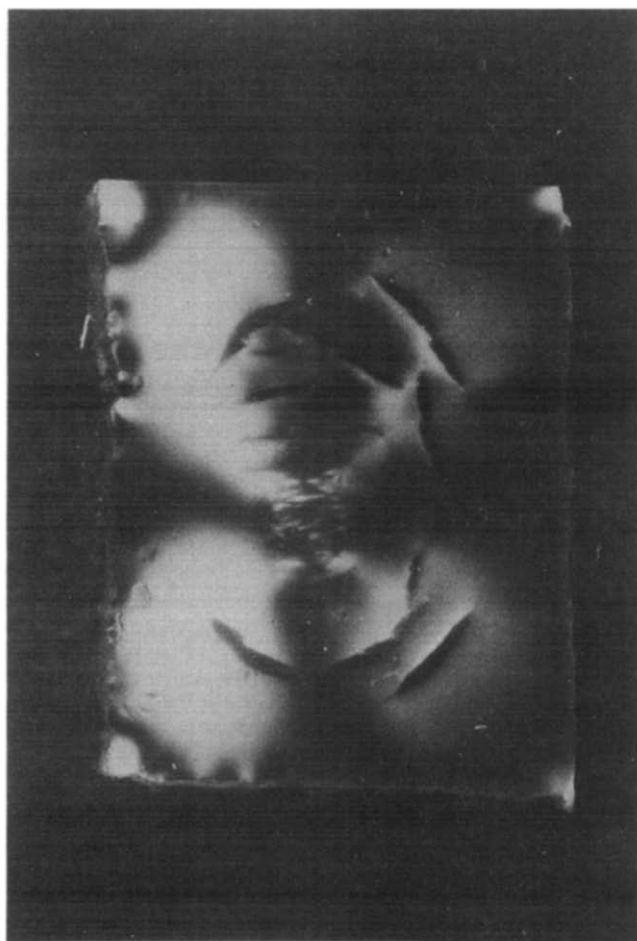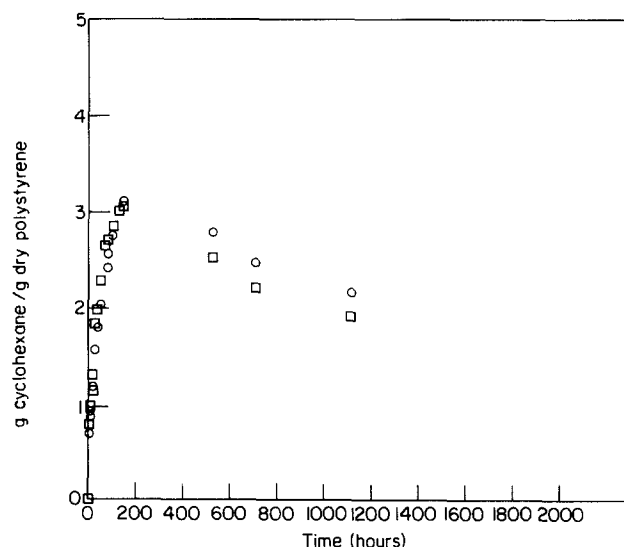

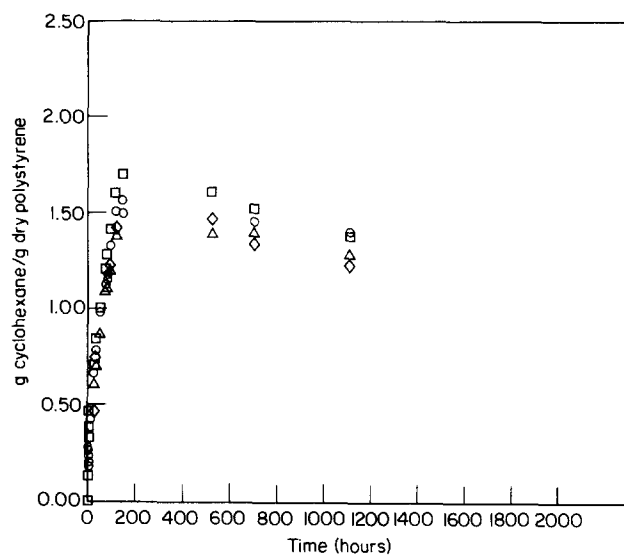**Figure 4** Cyclohexane uptake in polystyrene at 30°C. Sample (O) $M_c = 7150$; (□) $M_c = 6975$

Figure 5 Cyclohexane uptake in polystyrene at 30°C. Samples: (O) $M_c = 6250$; (□) $M_c = 6200$; (△) $M_c = 5950$; (◇) $M_c = 5800$

Figure 3 Sheet of polystyrene with $\bar{M}_c = 11\ 200$ observed under polarized light 72 h after immersion in cyclohexane at 30°C

Table 2 Dynamic swelling characteristics of polystyrene samples in cyclohexane

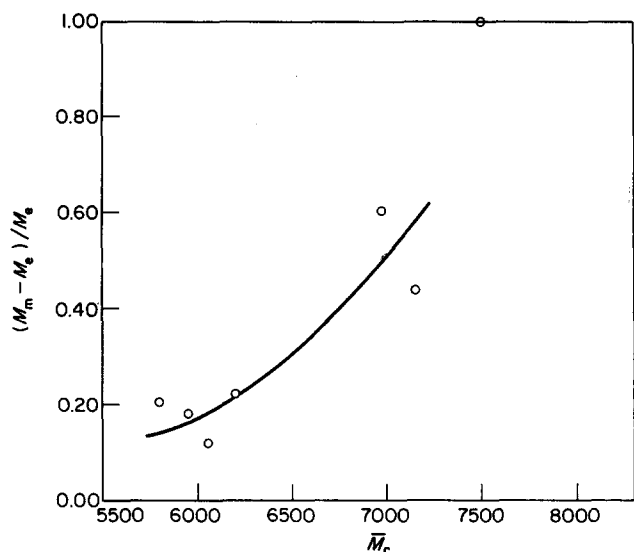| $\bar{M}_c$	Maximum uptake M_m (g/g)	Equil. uptake M_e (g/g)	Swelling time of M_m, t_m (hours)
7150	3.100	2.157	147
6975	3.057	1.907	146.5
6250	1.560	1.396	146.5
6200	1.688	1.381	146.5
5950	1.507	1.278	146.5
5800	1.488	1.237	147

Figure 6 Effect of number of average molecular weight between crosslinks. M_c on the cyclohexane uptake overshoot
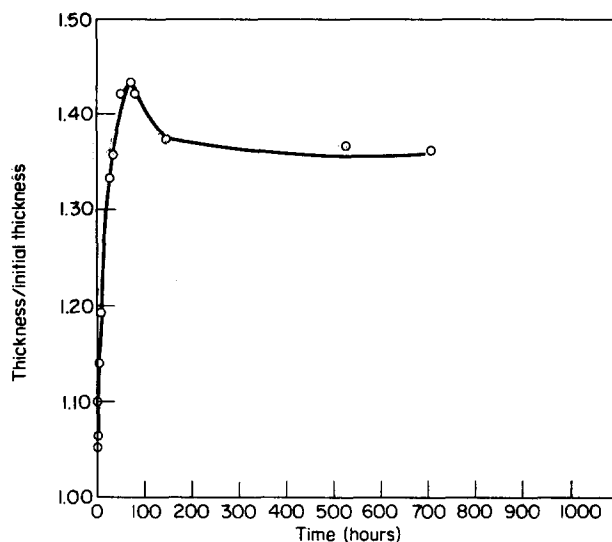

Figure 7 Normalized thickness of a polystyrene sample with $M_c = 6200$ swollen in cyclohexane at 30°C as a function of swelling time

The observed anomalous transport is clearly influenced by the slow relaxation process in the polymer/penetrant system, a process which is strongly affected by the degree of crosslinking. Usually the penetrant enters the macromolecular chains due to thermodynamic interactions before these chains can relax and rearrange. Upon rearrangement of the chains, partial exudation of penetrant is observed which is more pronounced when diffusion is faster than the relaxation rate, as for example in the case of decreasing degree of crosslinking, i.e. increasing values of $\bar{M}_c$.

The anomalous transport of cyclohexane in polystyrene was further observed by following the thickness change of the samples as a function of time. At about 147 h when the maximum in penetrant uptake is observed, the thickness decreases significantly due to the relaxation process (*Figure 7*). The thickness change is also a function of the degree of crosslinking, being more prominent for the loosely crosslinked systems.

CONCLUSIONS

Anomalous transport of cyclohexane in crosslinked polystyrene samples is affected by the degree of crosslinking. The transport is characterized by an overshoot in the dynamic cyclohexane uptake which depends on the relative ratio of diffusional and relaxational times. Solvent crazing is induced at low degrees of crosslinking, due to the relatively high swelling stresses in the gel region.

ACKNOWLEDGEMENTS

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