Polymer Bulletin 16, 201-207 (1986)

Polymer Bulletin

Anomalous penetrant transport in glassy polymers

VII. Overshoots in cyclohexane uptake in crosslinked polystyrene

Nikolaos A. Peppas[1] **and Kent G. Urdahl**[2]

School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA

Summary

Transport of liquid cyclohexane through well characterized, initially glassy, crosslinked polystyrene slabs was investigated as a function of time at 20, 30, 40, and 50 ° C. The samples used were produced by bulk polymerization of styrene and divinyl benzene using benzoyl peroxide as an initiator at 90 ° C for 48 hrs. The samples tested had initial crosslinking ratios, X, between 0.005 and 0.0250 mol DVB/mol styrene, their thickness varied from 0.025 to 0.180 cm, and the aspect ratio was maintained above 10 to achieve one-dimensional transport. A cyclohexane uptake overshoot was observed as a function of time. This overshoot was analyzed as a function of crosslinking ratio and geometric characteristics of the samples and it was attributed to molecular changes of polystyrene during swelling.

Introduction

Penetrant transport in glassy polymers is known to proceed by Fickian or non-Fickian (anomalous) mechanisms depending on the penetrant activity, experimental temperature, degree of crosslinking, diffusion coefficient, relaxation time and geometric characteristics of the samples studied (1-5). The limiting mechanisms of this phenomenon are Fickian diffusion, where the penetrant uptake is proportional to $t^{0.5}$ in the early transport period, and Case-II transport, where the penetrant uptake is proportional to t (6,7). Vrentas and Duda (8) have used the diffusional Deborah number De, the ratio of the characteristic relaxation to the characteristic diffusion times, as an indicator of Fickian diffusion or Case-II transport behavior.

An interesting observation in penetrant transport in thin slabs of glassy polymers is the appearance of a penetrant overshoot, that is an increase of the normalized quantity of penetrant up to a "pseudo-equilibrium" value, followed by apparent exudation of a portion of the polymer-sorbed penetrant. This phenomenon has been analyzed by Vrentas et al., (9) and Smith and Peppas (10) for selected polymer systems.

Here we offer further evidence of the existence of this penetrant overshoot for cyclohexane transport in divinyl benzene (DVB)-crosslinked polystyrene slabs and we analyze various structural and other parameters which influence its magnitude.

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[1] Author to whom correspondence should be addressed

[2] Present address: IBM Products Development, Lexington, KY 40502, USA

Experimental Part

To 10 ml of vacuum-distilled styrene there was added DVB as a comonomer and crosslinking agent, and 1.2 mol % benzoyl peroxide as an initiator. The amount of DVB was calculated to produced polystyrene samples with crosslinking ratio, X, of 0.00525, 0.00797, 0.0107, 0.0126, 0.0155, 0.0206 and 0.0258 mol DVB/mol styrene. The copolymerization/crosslinking reaction was carried out at 90 ° C for 48 hrs and the ensuing films were cut with a heated surgical knife in square slabs of 1.7 or 2.5 cm length and 0.025 to 0.180 cm thickness.

The number average molecular weight between crosslinks, $\overline{M}_c$, and the equilibrium polymer volume fraction, v_2, of the samples were determined by equilibrium swelling experiments as reported before by Smith and Peppas (10). Dynamic swelling experiments were performed in cyclohexane at 20, 30, 40 and 50 ± 0.5 ° C. During the transport (swelling) experiments the weight of the samples was recorded.

Effect of Crosslinking Ratio on Cyclohexane Overshoot

Typical cyclohexane uptake data for samples of the same thickness but varying crosslinking ratio, X, are shown in Figure 1. In all situations, an overshoot was observed in the cyclohexane transport, followed by exudation of a portion of the penetrant and attainment of the true equilibrium. Figure 1 serves as an excellent example of the relationship of the degree of crosslinking to the amount of a penetrant uptake overshoot observed. The most loosely crosslinked sample shows a significant difference in the maximum and equilibrium penetrant uptake values, whereas the more highly crosslinked sample shows little or no difference in these two values. The same phenomenon was observed in almost all the other samples studied, which can be found in Urdahl (11).

The magnitude of the penetrant overshoot was analyzed by calculating the normalized overshoot parameter, $(M_m - M_e)/M_e$, and plotting the data versus various polymer structural parameters. Here, M_m is the maximum in penetrant uptake and M_e is the equilibrium penetrant uptake. The normalized overshoots for the sorption data of various samples are reported in Table 1. Similar behavior was observed at 30, 40 and 50 ° C.

Table 1 Values of v_2 for Polystyrene Slabs Swollen in Cyclohexane at 20 ° C

Crosslinking Ratio X, mol DVB/mol styrene	Equilibrium Polym. Vol. Fr. v_2	Normalized Overshoot, $(M_m-M_e)/M_e$	Standard Deviation, $s \cdot 10^3$
0.00525	0.429	0.7891	2.3
0.0107	0.486	0.1416	1.6
0.0155	0.532	0.02248	1.5
0.0155	0.555	0.05289	2.5
0.0206	0.574	0.003011	2.3

These results indicate that as the crosslinking density and the equilibrium polymer volume fraction of the samples decreased, the magnitude of the observed overshoot increased. Overshoots of this type have been noted by Jenkel and Nogay (12).

Kambour et al. (13), Titow et al. (14), and Overbergh et al. (15) have also observed maxima in sorption curves for penetrant transport in various polymers. However, they attributed the overshoots to crystallization brought about by the presence of the penetrant. They stated that the ordered regions formed during the transport process reject the penetrant which was sorbed before the ordered regions existed. Since crosslinked polystyrene does not crystallize to any substantial degree, this explanation is not feasible for the systems we studied.

We note that the characteristic diffusion times of highly crosslinked samples were significantly larger than those for loosely crosslinked samples. This observation was partially explained by the fewer barriers to penetrant diffusion inherent in the loosely crosslinked polystyrene samples. It is also true that the mobility and length of macromolecule chain segments are also greater in loosely crosslinked samples. In terms of the diffusional Deborah number these samples have a smaller characteristic relaxation time of the macromolecular chains. This greater mobility of the macromolecular chains also tends to enhance the transport process since the mobility of the penetrant molecules in the swollen regions of the polymer increases as the rate of relaxation of the macromolecular chains increase. In terms of free volume theory this is equivalent to a free volume which increases at a much faster rate in loosely crosslinked polystyrene samples than in highly crosslinked samples.

Figure 1 indicates that the cyclohexane overshoot depends on time, since the time required for the dynamically swollen samples to reach an equilibrium is substantial compared to the time of initial sorption. This change in solubility can be

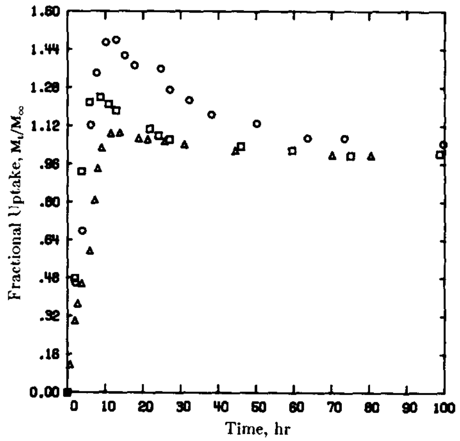

Figure 1: Fractional cyclohexane uptake, M_t/M_∞, versus diffusion time t, at 40 °C for DVB-crosslinked polystyrene slabs with initial thickness $\delta_0=0.0965$ cm. Crosslinking ratios, X, of 0.008 (○), 0.010 (□) and 0.015 (Δ) mol DVB/mol styrene.

explained as a slow reordering of the macromolecular chains and chain segments; it occurs on a much longer time scale than the transport process and results in the rejection of some of the sorbed cyclohexane. For samples with a relatively high crosslinking density, the transport process occurs on a comparable time scale as that for the reordering of the macromolecular chains and chain segments. The amount of cyclohexane rejected by the polymer is dependent on the ability of the macromolecules to rearrange themselves, and the relative difference in the time scales of the transport process and the bulk relaxation process.

The macromolecular mobility can also be explained if data such as those reported in Figure 1 are plotted as penetrant uptake, M_t/M_p, i.e. g cyclohexane/g polystyrene, versus time, as in Figure 2. A large change in the penetrant solubility in the continuously swelling polymer occurs during the swelling process. To understand the effect of the penetrant solubility, the equilibrium polymer volume fractions, v_2, of all samples tested were determined as in Smith and Peppas (10), and some of them are also reported in Table 1. Clearly, the equilibrium polymer volume fractions, v_2, increased with increasing crosslinking ratio, or alternatively, the final equilibrium values, M_t/M_p, decreased with increasing crosslinking. Since the macromolecular chains are by nature more contrained in highly crosslinked systems, their ability to accommodate the penetrant us lower than in loosely crosslinked systems, and, therefore, the overshoot is much smaller in this case.

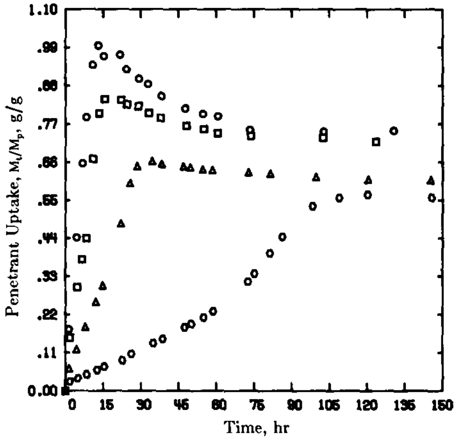

Figure 2: Cyclohexane uptake per polymer weight, M_t/M_p, versus diffusion time, t, at 30 ° C for DVB-crosslinked polystyrene slabs with initial thickness δ_o=0.10 cm. Crosslinking ratios, X, of 0.0077 (○), 0.0126 (□), 0.0176 (Δ), and 0.0257 (∘) mol DVB/mol styrene.

Effect of Initial Thickness on Cyclohexane Overshoot

Differences in the characteristic transport time are effectively gained by altering the thickness of the samples while holding the degree of crosslinking and therefore the penetrant diffusion coefficient constant. A comparison of the transport data presented in Figure 3 shows this to be true. The magnitude of the overshoots observed in these curves is dependent on time of transport, and therefore on the thickness of the crosslinked polystyrene.

Figure 4 shows the normalized overshoots determined from the transport in samples of various thicknesses and crosslinking ratios. In each case, the normalized overshoot decreases with increasing thickness. This observation substantiates the idea that the ordering process of the macromolecular network occurs along a different time scale than penetrant transport. Comparatively, the longer time of sorption in thicker samples results in achievement of the relaxed state by the macromolecular chains present in the outer rubbery regions. Similar observations have been made by Vrentas et al. (9) in their work with vapor sorption of ethylbenzene in poly(ethyl methacrylate). They were able to how that at vapor pressures lower than 300 mm Hg a larger overshoot was observed for the thinnest sample (0.025 cm thickness) than for the thickest sample (0.050 cm thickness) they studied. However, as they increased the vapor pressure to 402 mm Hg, the difference in magnitude of the overshoots decreased.

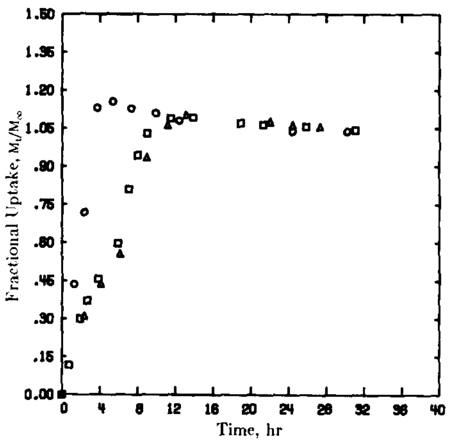

Figure 3: Fractional cyclohexane uptake, M_t/M_∞, versus diffusion time, t, at 40 °C for DVB crosslinked polystyrene slabs with crosslinking ratio X=0.0154 mol DVB/mol styrene. Initial thickness, δ_0, of 0.059 (○), 0.100 (□) and 0.123 (Δ) cm.

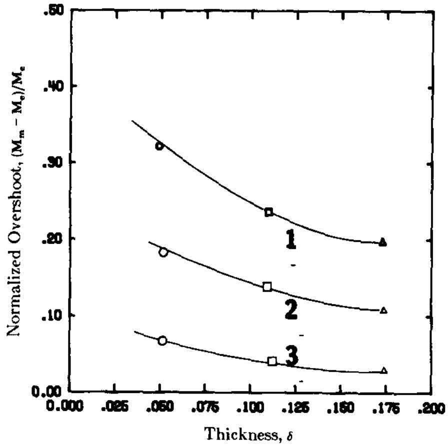

Figure 4: Normalized cyclohexane overshoot versus thickness for cyclohexane transport in DVB-crosslinked polystyrene slabs. Crosslinking ratios, X, of 0.0107 (curve 1), 0.0155 (curve 2) and 0.0204 mol DVB/mol styrene (curve 3).

Conclusions

A penetrant uptake overshoot is observed in almost all the studies performed in this work. This overshoot is real (not the result of some experimental error), and we have proven that it is affected mainly by the thickness of the slabs and the degree of crosslinking, and to a lesser extent by the temperature of experimentation (at least in the range of temperature used in this study). The explanation offered here for this overshoot is that it is related to a relaxational process of the macromolecular chains occurring in the polymer after the material has become rubbery, but before the real equilibrium has been attained.

Acknowledgments

This work was supported by a grant from the National Science Foundation of the USA (No. CPE-82-07381).

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Accepted August 4, 1986 *C*