

Anomalous Penetrant Transport in Glassy Polymers V. Cyclohexane Transport in Polystyrene

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Synopsis

Transport of liquid cyclohexane through well characterized, initially glassy, crosslinked polystyrene slabs was investigated. The samples were produced by bulk polymerization of styrene and divinyl benzene using benzoyl peroxide as an initiator at 90°C for 48 h; they had initial crosslinking ratios, X , between 0.005 and 0.025 mol DVB/mol styrene, initial thickness of 0.25 mm to 1.80 mm, and the aspect ratio was maintained above 10 to achieve one-dimensional transport. The results of cyclohexane uptake as a function of time were used to elucidate the effects of degree of crosslinking and sample geometry on the mechanisms of penetrant transport. These results were interpreted in terms of relaxational and diffusional mechanisms.

INTRODUCTION

The study of penetrant transport in glassy polymers has received considerable attention over the past thirty years. The incorporation of a penetrant in an initially glassy polymer can often lead to a transition to its rubbery state, depending upon the thermodynamic compatibility of the penetrant for the polymer.

An understanding of this transition on a molecular level has long been sought. Fox and Flory^{1,2} attempted to describe the glass transition phenomenon in terms of the free volume of the polymer. They associated a critical free volume with the point where the macromolecular chains become "frozen" into a matrix at the glass transition temperature, T_g . Below T_g the free volume and its distribution become constant,¹ whereas above T_g the free volume increases with temperature and penetrant concentration. Free volume theories can also be used to describe the transport of penetrants in glassy polymers. The increase in free volume during transport can be attributed in part to the penetrant, which typically contains more free volume than the polymer, and to the added free volume brought about by the increased mobility of the polymer chains. This enhanced mobility also tends to increase the transport of penetrant molecules,³ which is indicative of a concentration-dependent diffusion coefficient.

Vrentas, Duda, and their collaborators^{3,4} have developed this theory to the extent that the concentration and temperature dependence of the penetrant

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self-diffusion coefficient in concentrated polymer solutions can be predicted. The fact that a polymer molecule may be entangled within the polymer matrix was also considered in Bueche's⁵ theory of entanglement friction.

The swelling of a glassy polymer by a thermodynamically compatible penetrant is one of the possible structural changes that can accompany the transport of the penetrant. Astarita and Nicolais⁶ recognized microcavity formation, and primary and secondary phase transitions also as products of penetrant transport. Naturally these structural changes require a rearrangement of polymer chains, and are processes which can dominate the kinetic behavior. Because of these phenomena, the transport behavior observed may be controlled either by a relaxation process, or the transport of the penetrant itself, or a coupling of the two.

Transport processes that can be described by Fick's law are called Case I transport. This is one of the limiting cases of transport behavior, the other being Case II transport.⁷⁻⁹ Alfrey et al.^{8,10} were the first to designate conditions necessary for Case II transport, including a linear relationship between penetrant uptake and time, and the existence of a sharp front separating the glassy and rubbery states which progresses at a constant velocity. Transport processes which fall between these two limiting cases are termed anomalous. Processes which have the penetrant uptake increasing with time have also been noted and termed Super Case II transport.^{7,11}

The modeling of penetrant transport which cannot be described by Fick's law has received considerable attention. One of the earliest models was that by Frisch et al.,¹² who included an extra term, vc , in the diffusion equation, to account for the movement of the penetration front. This model has been very successful in describing Case II transport,^{7,13} although the ambiguity of the added term does not help in achieving a better understanding of the transport process. Peterlin¹⁴⁻¹⁶ suggested that the velocity of the front was a function of the material itself, not a consequence of the diffusing species. He attributed time-dependent rupture and disentanglement of polymer chains as the controlling mechanisms for transport.

Peppas and Sinclair et al.^{13,17} approached this problem by dividing the polymer/penetrant system into two regions, one rubbery and one glassy, and used the Frisch equation to describe the transport process. This method provided a convenient way of accounting for the discontinuity present at the penetration front through the use of diffusion coefficients and concentrations indicative of the regions involved. Several investigators have expressed the penetrant front position, X_1 , as

$$X_1 = \alpha t^{1/2} + vt \quad (1)$$

where α is a constant. The importance of Eq. (1) is that it separates out the contributions of limiting transport behavior. If the first term is negligible, Case II transport can be predicted, whereas if the second term is negligible Case I or Fickian diffusion prevails. When both terms are important this model suggests anomalous transport as the defining behavior.

A model that attempted to incorporate the role of stresses in the diffusion process was that proposed by Petropoulos and Roussis.¹⁸ Thomas and Windle^{7,9,19} also attempted to describe the transport process in terms of a

mechanical response. They proposed that the determining factor for transport was the time-dependent viscous response of a swelling element of glass to the osmotic pressure of the penetrant. They considered this process as primarily a local one, occurring at the swelling front, and controlled by the glassy network. This approach assumes that the activity of penetrant behind the front is the same as the medium in which the sample was placed. This results in the existence of a sharp change in concentration across the front, which is indicative of Case II transport.

Perhaps the most important analysis relevant to the present work was that developed by Vrentas, Duda, and their collaborators.²⁰⁻²² They defined a diffusional Deborah number as a means of classifying the sorption behavior present in polymer/penetrant systems. This dimensionless group is defined as the ratio of a characteristic relaxation time, λ , of the system to the characteristic diffusion time, θ , of the process:

$$De = \frac{\lambda}{\theta} \quad (2)$$

This ratio is a representation of the relative importance of the rate of diffusion to the rate of rearrangement of polymer chains in the diffusion process. A large De is indicative of a diffusional process where there is essentially no relaxational variation of the polymeric structure and the transport is Fickian. A small Deborah number is indicative of a fast relaxation process relative to diffusion and can also be considered Fickian. It is only when the diffusive transport and relaxation processes are of the same order of magnitude that anomalous transport can be expected. The diffusional Deborah number is dependent on concentration, temperature, pressure, and polymer molecular weight.²¹ Since each finite element of a polymer sample experiences a spectrum of concentrations during the transport process, a De number may be defined for each composition. Therefore, if the concentration of penetrant changes markedly during the transport process, a single De may not adequately describe the whole process. Calculation of diffusional Deborah numbers can be a lengthy and difficult task. Work by Davidson and Peppas^{23,24} with poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) copolymers swollen by water would serve as a good example for the calculations involved.

An interesting form of Eq. (2) is obtained by substitution of the characteristic diffusion time in this equation to obtain

$$De = \frac{\lambda D}{\delta^2} \quad (3)$$

This equation illustrates the importance of the characteristic length of the polymer sample, δ , in defining the transport behavior and implies that by changing this parameter alone different behavior may be observed. This is an important concept and is a major consideration of this work. Although not explicitly appearing in Eq. (3), temperature and the degree of crosslinking can also affect the diffusional Deborah number through λ and D . These parameters will be examined in light of their effect on the observed diffusional behavior.

A common means of defining the type of transport *in a slab geometry* involves fitting transport data to the heuristic expression:

$$\frac{M_t}{M_\infty} = kt^n \quad (4)$$

Here, M_t is the mass of penetrant sorbed at time t , M_∞ is the mass sorbed at long times, and k a constant indicative of the system. A value of n of 0.50 implies Fickian diffusion, a value of n of 1.00 implies Case II transport, and for values of n of $0.50 < n < 1.00$ anomalous transport is observed. Values of n greater than 1.0 define Super Case II transport. It is usually stipulated that this equation is only valid for short times and $M_t/M_\infty < 0.60$.^{25,26} All these conclusions apply only to planar geometry. This equation, therefore, should reflect the importance of thickness, temperature, and degree of crosslinking as suggested by the definition of the diffusional Deborah number.

EXPERIMENTAL

Preparation of Crosslinked Polystyrene

Styrene (Aldrich Chemical Co., Milwaukee, WI) was vacuum-distilled through a Vigreux column at 40°C/15 mmHg. To 10 mL of distilled styrene there was added a desirable amount of divinyl benzene (DVB) (Polysciences Inc., Warrington, PA) and 1.2 mol% benzoyl peroxide as an initiator (Aldrich Chemical Co). These samples were reacted in a nitrogen atmosphere at 90°C for 48 h. Square samples were cut from the films produced using a template and a hot surgical knife.

The final samples had thickness ranging from 0.25 mm to 1.80 mm and length of approximately 17 mm or 25 mm. All the samples prepared had aspect ratios (length over thickness) of 10 or greater in order to achieve one-dimensional penetrant diffusion. The crosslinking ratios, X (mol of DVB per mol of styrene), were 0.0050, 0.0075, 0.010, 0.013, 0.015, 0.020, and 0.025.

Swelling Experiments

Dynamic swelling experiments were performed in liquid cyclohexane at 20°C, 30°C, 40°C, and 50°C ± 0.5°C. The samples were periodically removed from their swelling containers, weighed, and the thicknesses and lengths measured. Equilibrium swelling studies were performed to examine if any residual monomer had remained in the samples during the polymerization process. It was found that the unreacted monomer, extracted during the swelling process, was less than 0.1 wt% in all cases, a result further supported by the recent theoretical conclusions of Mikos et al.²⁷

Studies of Crazing Phenomenon

Samples having crosslinking ratios, X , of 0.00525, 0.0107, 0.0155, 0.0206, and 0.0258 were placed in vials containing liquid cyclohexane. The temperature was maintained at 30°C ± 0.5°C in a water bath. The samples were periodi-

cally removed from their vials, the lengths and thicknesses measured, and photographs under polarized light taken.

RESULTS AND DISCUSSION

Effect of Crosslinking on Penetrant Transport Behavior

The diffusional Deborah number implies that by changing either the relaxational or the diffusional times, or both, while keeping the sample thickness constant, the observed transport behavior may be altered. Experimentally this can be achieved by using samples of different degrees of crosslinking (as expressed by a wide range of crosslinking ratios) since both λ and D are strongly dependent on the degree of crosslinking. The effect of the degree of crosslinking of a polymer on penetrant transport has not been studied before except for the preliminary work of Smith and Peppas,²⁸ and the work of Robert et al.²⁹ and Dušek.³⁰

Figures 1 and 2 show typical results of the fractional uptake of cyclohexane, M_t/M_∞ , as a function of diffusion time at 30°C for polystyrene samples crosslinked at different levels (as indicated by the various values of X) and having the same thickness. Comparison of these plots shows that as the nominal crosslinking ratio, X , decreases from 0.0257 mol/mol to 0.00525 mol/mol the penetrant transport becomes significantly faster. It must be noted that other studies of penetrant uptake in crosslinked polystyrene (one specific degree of crosslinking, usually not cited) have been published by

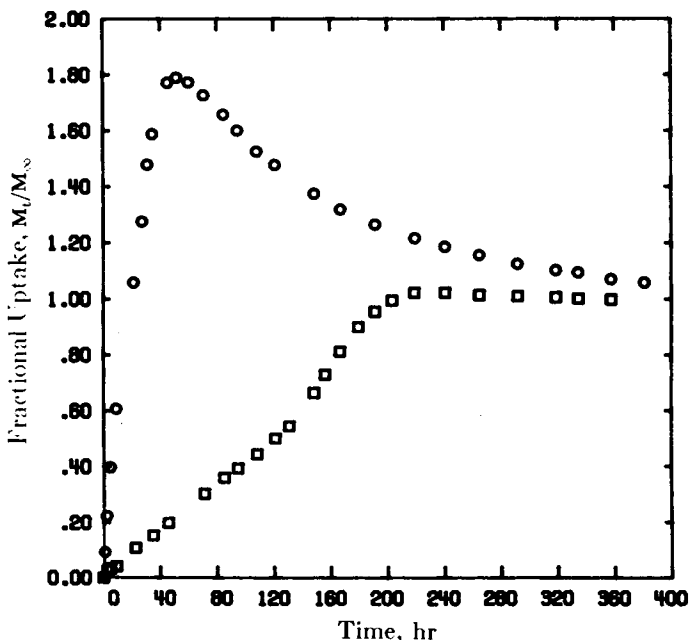


Fig. 1. Fractional uptake of cyclohexane, M_t/M_∞ , versus diffusion time, t , at 20°C for crosslinked polystyrene slabs No. 1Ya (\circ) ($\delta_o = 0.120$ cm and $X = 0.00525$ mol/mol) and No. 3Ya (\square) ($\delta_o = 0.123$ cm and $X = 0.0155$ mol/mol).

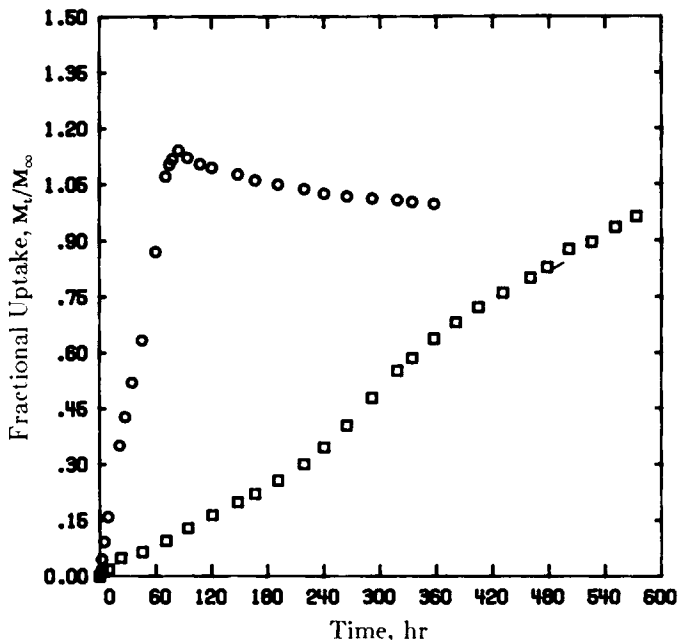


Fig. 2. Fractional uptake of cyclohexane, M_t/M_∞ , versus diffusion time, t , at 20°C for crosslinked polystyrene slabs No. 2Ya (\circ) ($\delta_o = 0.105$ cm and $X = 0.0107$ mol/mol) and No. 4Ya (\square) ($\delta_o = 0.0962$ cm and $X = 0.0204$ mol/mol).

Hopfenberg³¹ for *n*-hexane, *n*-heptane, and *n*-pentane in thin films, and by Enscore et al.³⁵ and Berens and Hopfenberg³²⁻³⁴ for microspheres. In addition, Dušek³⁰ has studied the swelling of crosslinked polystyrene in toluene and has found similar dependence of its swelling characteristics on the crosslinking ratio.

A comparison of the initial slopes of these curves shows that the most loosely crosslinked samples absorb penetrant within 40 h. This observation is a direct result of the fact that the penetrant diffusion coefficient is significantly higher for loosely crosslinked polystyrene than for highly crosslinked polystyrene. The characteristic diffusion time, θ , of Eq. (2) increases with increasing X . In fact, preliminary swelling experiments done by Smith and Peppas²⁸ with crosslinked polystyrene samples at 30°C with relatively high degrees of crosslinking (0.060 mol/mol) showed little or no uptake of penetrant. This is probably due to the highly crosslinked network structure that cannot accommodate the penetrant by relaxation of its chain segments.

The penetrant uptake versus time curves of some of the dynamic swelling experiments exhibited a "burst" effect, that is, an abrupt and fast initial uptake (see Figs. 3 and 4). This was especially true of transport in the highly crosslinked polymers. Burst effects have been reported by Korsmeyer and Peppas³⁶ for water penetration in P(HEMA-co-NVP) copolymers, and others, including some (but not all) of the studies of Hopfenberg and associates.

Berens³⁷ studied the sorption of gaseous *n*-alkanes in poly(vinyl chloride) (PVC) powder at 30°C and noted the same burst effect. He attributed this rapid weight gain to surface adsorption of the *n*-alkanes. In order to analyze

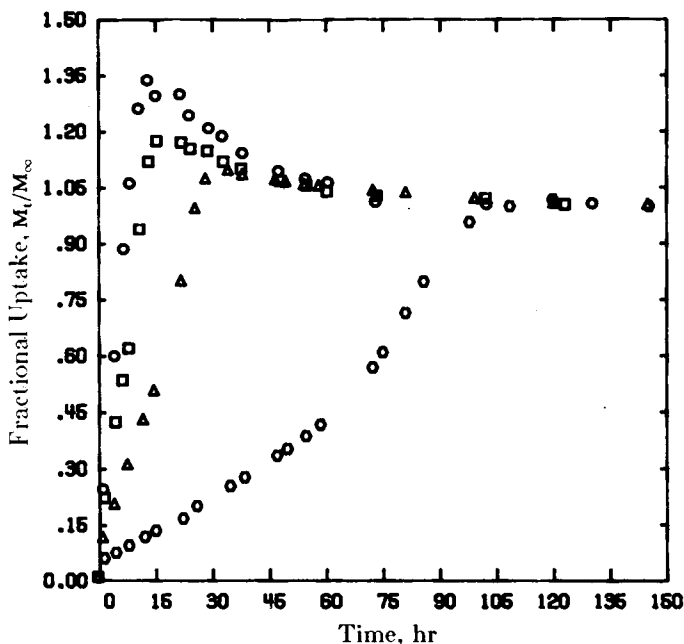


Fig. 3. Fractional uptake of cyclohexane, M_t/M_∞ , versus diffusion time, t , at 30°C for crosslinked polystyrene slabs No. 2Vb (○) ($\delta_o = 0.105$ cm and $X = 0.00771$ mol/mol), No. 4Vb (□) ($\delta_o = 0.100$ cm and $X = 0.0126$ mol/mol), No. 6Vb (△) ($\delta_o = 0.0966$ cm and $X = 0.0176$ mol/mol), and No. 8Vc (○) ($\delta_o = 0.101$ cm and $X = 0.0257$ mol/mol).

these data, he essentially shifted each of his plots upward based upon the magnitude of the burst effect apparent in each of his plots. Using Eq. (5) this shifting of the fitting curve can be expressed as

$$\frac{M_t}{M_\infty} - \alpha = kt^n \quad (5)$$

where α is a shift factor indicative of the initial burst effect during sorption. The values of α , k , and n are determined by fitting the experimental data to Eq. (5). This equation was used in this work, with the same stipulations as for Eq. (4), and only for the transport data of those samples with crosslinking ratios, X , of 0.0200 and above.

Table I shows the values of n , k , and 95% confidence intervals obtained from the fitting of the data to Eq. (5) for the experiments performed at 30°C. The data for highly crosslinked samples give values of n of nearly 1.0, which corresponds to Case II transport. This is interesting since the diffusion times for penetrant transport in these samples are significantly different and it implies that the characteristic relaxation times must change substantially in order to give the same type of observed transport behavior. Values of n for the penetrant transport in polystyrene have been reported by Hopfenberg et al.³³ for the transport of n -alkanes. Specifically, the transport of n -pentane at 30°C was characterized by values of n between 0.8 and 1.0 progressively changing with solvent vapor activity.

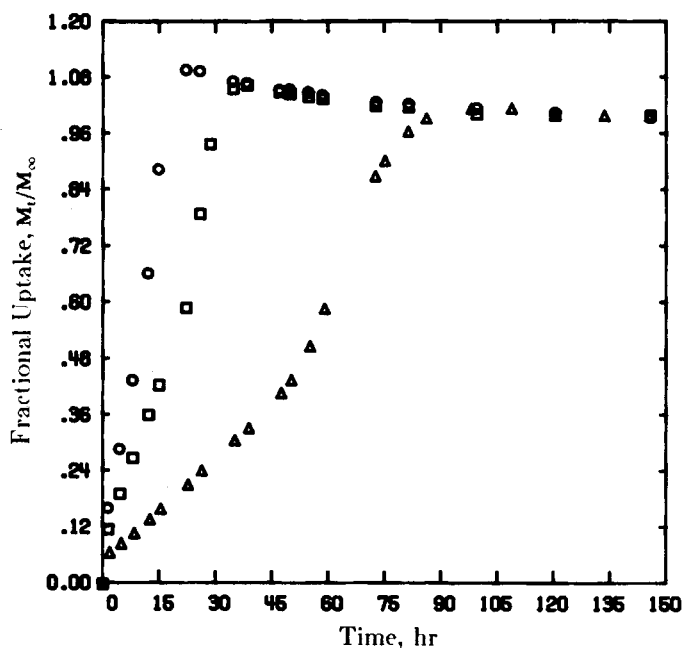


Fig. 4. Fractional uptake of cyclohexane, M_t/M_∞ , versus diffusion time, t , at 30°C for crosslinked polystyrene slabs No. 6Va (○) ($\delta_o = 0.0807$ cm and $X = 0.0176$ mol/mol), No. 7Vc (□) ($\delta_o = 0.0835$ cm and $X = 0.0207$ mol/mol), and No. 8Va (△) ($\delta_o = 0.0828$ cm and $X = 0.0257$ mol/mol).

A few quantitative statements can be made concerning Figures 1 and 2. First, most transport experiments exhibited an overshoot, a maximum in penetrant uptake followed by a decrease to an equilibrium value. This penetrant uptake overshoot is a function of the crosslinking ratio of the polymer and it is characteristic of the relative importance of diffusion and relaxation phenomena and related to geometrical factors such as thickness of the sample. Overshoots in the penetrant uptake curves have been observed by Vrentas et al.,³⁸ Franson and Peppas,³⁹ Smith and Peppas,²⁸ and Davidson and Peppas.^{23,24}

Another interesting phenomenon is the apparent sudden change in slope in the penetrant uptake versus time plots of some of the more highly crosslinked samples. This change is often indicative of Super Case II transport.⁷

TABLE I
Analysis of Penetrant Transport at 20°C

Crosslinking ratio, X , mol/mol	k $g/(g \cdot h^n) \cdot 10^2$	Exponent, n	95% Confidence interval	
			Lower limit	Upper limit
0.0052	10.4	0.785	0.642	0.928
0.0107	1.42	1.03	0.890	1.18
0.0155	0.888	0.827	0.755	0.899
0.0204	0.150	0.979	0.946	1.01

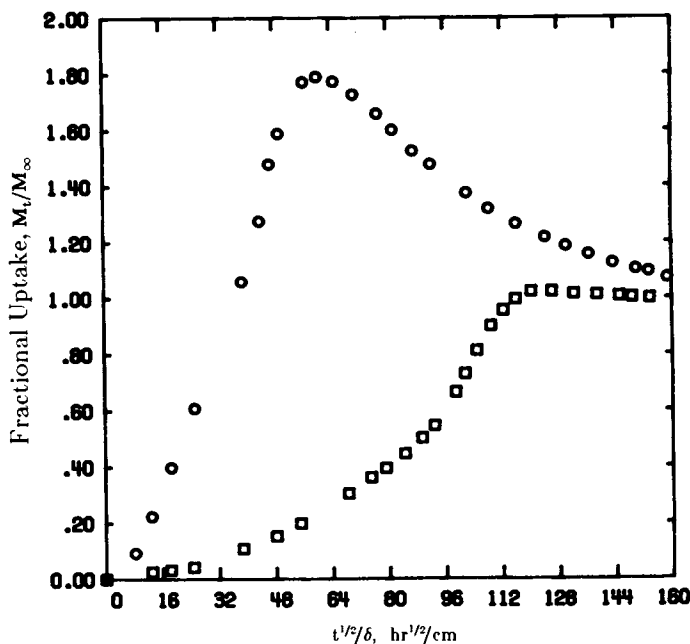


Fig. 5. Fractional uptake of cyclohexane, M_t/M_∞ , versus $t^{1/2}/\delta$ at 20°C for crosslinked polystyrene slabs No. 1Ya (\circ) ($\delta_0 = 0.120$ cm and $X = 0.00525$ mol/mol) and No. 3Ya (\square) ($\delta_0 = 0.123$ cm and $X = 0.0155$ mol/mol).

The data may be also replotted using a normalized parameter, $t^{1/2}/\delta$, thereby achieving a representation of the transport data that avoids differentiation of the thickness of the samples. A typical graph is shown as Figure 5. Plotting the data in such a manner is also useful in that it clearly shows any deviations of the transport mechanism from the lower limiting case of transport behavior, Case I transport or Fickian diffusion, which corresponds to an n of 0.5 under the conditions of Eq. (4). For samples with the same crosslinking ratio X , the term $t^{1/2}/\delta$ can be helpful when comparing samples of the same thickness but different crosslinking ratios since, although the diffusion coefficients are unknown, their relative magnitudes are reflected as a deviation in the penetrant uptake curves.

Determination of Penetrant Front Velocity

The dynamic swelling of crosslinked polystyrene by cyclohexane is characterized by the formation of a front which separates the glassy and rubbery regions. This front moves at a velocity indicative of the transport mechanism defining the sorption process. The penetrant front position, X_1 , can be described by Eq. (1). In order to obtain penetrant front velocities, a set of crosslinked polystyrene samples were swollen by cyclohexane at 30°C and photographed under polarized light at various time intervals during the process.

Figure 6 shows typical results for the position of the penetrant front separating the rubbery layer from the unswollen glassy core, X_1 , and the external front, X_2 , as a function of time. Analysis of these results with Eq. (1)

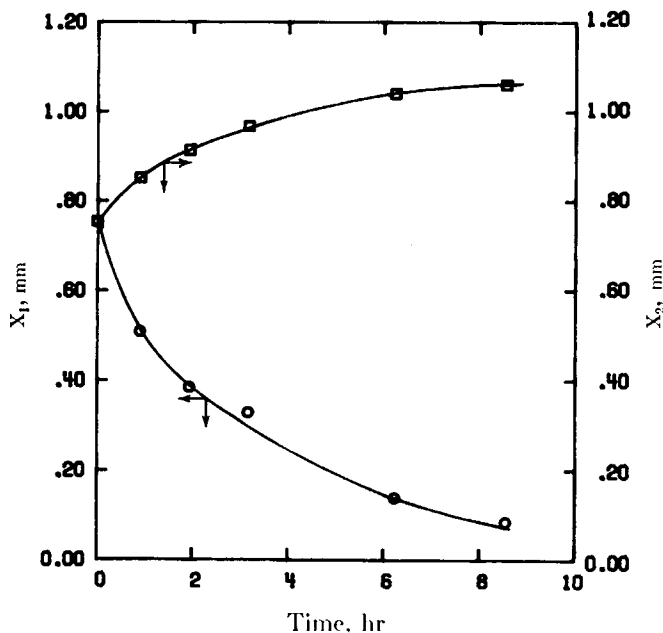


Fig. 6. X_1 (\circ) and X_2 (\square) versus diffusion time, t , at 30°C for crosslinked polystyrene slab No. 1Yf ($\delta_o = 0.151$ cm and $X = 0.00525$).

indicates that the Fickian term, $\alpha t^{1/2}$ is more important than the Case II term, νt . This type of observation appears to be consistent with the value of n obtained from the fitting of the sorption data to Eq. (4) ($n = 0.678$). Figure 6 also shows that the distance of the outer or moving boundary from the center of the slab increases at a much slower rate than the progression of the penetrant front inwards. From these data values of the initial velocity, ν_1 , for the penetrant front were obtained as shown in Table II. The penetrant front position, X_1 , is often nonlinear with respect to diffusion time. The value of ν_1 obtained in this manner is characteristic of the crosslinking density of the polymer and applies only to the initial portions of the sorption process. Naturally this approximation of ν_1 becomes more meaningful as the transport behavior approaches Case II transport, since Eq. (1) implies that the penetrant front position should become linear with diffusion time. The velocity, ν_2 , of the moving boundary (given as X_2), was also determined in a similar manner.

TABLE II
Velocities of Penetrant Front and Moving Boundary

Crosslinking ratio, X , mol/mol	Initial velocity, ν_1 cm/s $\cdot 10^7$	Initial velocity, ν_2 cm/s $\cdot 10^7$	Exponent, n from Eq. (4)
0.00525	76.0	30.0	0.678
0.0107	43.0	9.1	0.674
0.0155	13.0	3.8	0.815
0.0206	3.1	1.1	0.918
0.0257	1.1	0.32	1.03

The values of both these velocities are reported in Table II along with the value of n obtained from the fitting of the sorption data to Eq. (4).

Effect of Thickness on Penetrant Transport Behavior

The sample thickness is an important parameter in defining the transport process, since the diffusional Deborah number [Eq. (3)] is a function of characteristic diffusion and characteristic relaxation times, and the characteristic diffusion time is related to thickness. In our studies the decoupling of relaxation and diffusion was achieved by dynamically swelling polystyrene samples with the same crosslinking density, but with different thicknesses. Morphologically, there was no difference in these samples, and therefore the characteristic relaxation time and the penetrant diffusion coefficient should be the same regardless of thickness.

Figures 7 and 8 show the fractional uptake of cyclohexane, M_t/M_∞ , as a function of transport time for samples with the same crosslinking density and different initial thicknesses at 30°C. Figure 7 shows the transport data of the samples coded 2Yc, 2Yb, and 2Yf, with thicknesses of approximately 0.05 cm, 0.11 cm, and 0.17 cm, respectively. Comparison of the initial portions of these curves reveals the differences in time required to swell these samples to equilibrium. Sample 2Yf, which is the thickest of the samples whose transport data are represented in Figure 7, takes the longest time to swell (approximately 40 h). Samples 2Yb and 2Yc, exhibit swelling times of approximately

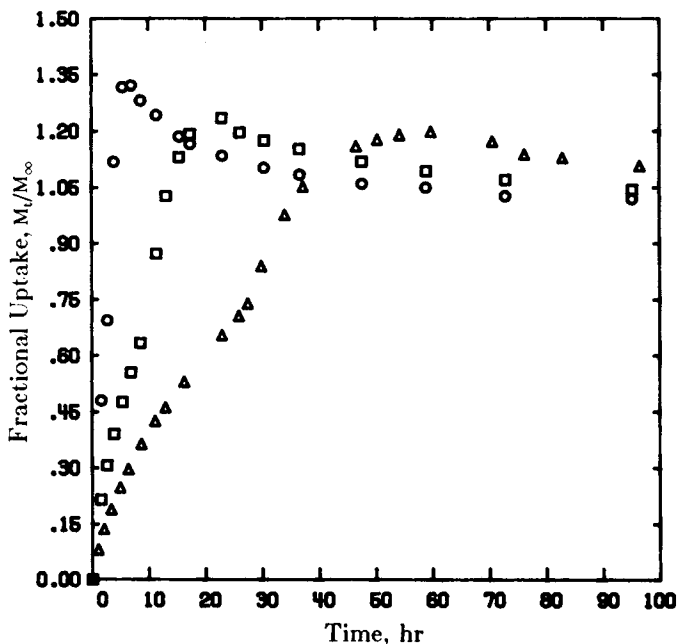


Fig. 7. Fractional uptake of cyclohexane, M_t/M_∞ , versus diffusion time, t , at 30°C for crosslinked polystyrene slabs No. 2Yc (○) ($\delta_0 = 0.0490$ cm and $X = 0.0107$ mol/mol), No. 2Yb (□) ($\delta_0 = 0.108$ cm and $X = 0.107$ mol/mol), and No. 2Yf (△) ($\delta_0 = 0.173$ cm and $X = 0.0107$ mol/mol).

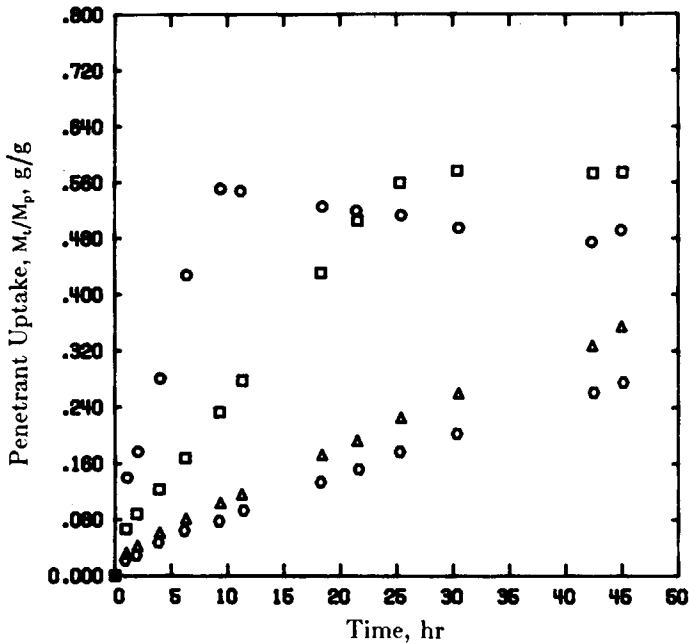


Fig. 8. Penetrant uptake of cyclohexane, M_t/M_p , versus diffusion time, t , at 30°C for crosslinked polystyrene slabs No. 4Ta (○) ($\delta_o = 0.0465$ cm and $X = 0.0205$ mol/mol), No. 4Tc (□) ($\delta_o = 0.0725$ cm and $X = 0.0205$ mol/mol), No. 4Tb (△) ($\delta_o = 0.135$ cm and $X = 0.0205$ mol/mol), and No. 4Td (◇) ($\delta_o = 0.162$ cm and $X = 0.0205$ mol/mol).

20 h and 10 hs respectively. This progression of diffusion times is expected, since Eq. (2) shows that the diffusion time should increase with increasing thickness. This observation implies that the diffusional Deborah should change, and therefore the transport behavior we observe in the dynamic swelling of these samples should be varied.

TABLE III
Analysis of Penetrant Transport at 30°C

Sample code no.	Crosslinking ratio, X , mol/mol	Initial thickness, δ_o , (cm)	k $g/(g \cdot h^n) \cdot 10^2$	Exponent, n	95% Confidence interval		
					Lower limit	Upper limit	No. of points
2Yb	0.0107	0.108	16.9	0.619	0.608	0.631	6
2Yf	0.0107	0.173	8.30	0.674	0.647	0.701	11
3Yd	0.0155	0.062	13.9	0.775	0.725	0.824	5
3Yc	0.0155	0.124	7.82	0.737	0.714	0.760	10
3Yf	0.0155	0.181	3.34	0.803	0.767	0.838	14
4Yd	0.0206	0.096	3.93	0.857	0.838	0.877	7
4Yf	0.0206	0.135	1.18	0.918	0.912	0.925	10
4Tb	0.0205	0.135	—	0.833	0.816	0.850	11
4Tc	0.0205	0.072	10.8	0.581	0.460	0.701	6
4Td	0.0205	0.162	—	0.837	0.816	0.857	12

The utility of Eq. (4) as a means of defining the observed transport behavior can be of great help here, since the values of n obtained from the fitting of the transport data to Eqs. (4) or (5) should indicate differences in the observed transport behavior. These values of n , along with their standard deviations, appear in Table III. Although the range of these values is relatively small, the values of n obtained from the analysis of the sorption data from the two thickest samples are significant, since their respective confidence intervals do not overlap. This dependence of the defining transport behavior on thickness is supported by Hopfenberg,³¹ who observed a similar dependence in his studies with n -hexane vapor absorption in polystyrene at 35°C.

Effect of Length on the Transport Process

Geometrical factors can be important in describing the transport behavior of penetrants in polymers. It has been noted^{23,24,36} that the transport process in various polymers is often characterized by a rather large change in the sample thickness. In order to better understand how this and other geometric factors such as sample length are affected during the transport process, these parameters were monitored during the cyclohexane sorption experiment.

Cyclohexane transport in crosslinked polystyrene can be modeled as a one-dimensional process as long as the aspect ratio (the length of the sample over its thickness) is kept greater than 10. To study the effect of the aspect ratio on penetrant transport, square samples with the same thickness but different length were swollen by cyclohexane at various temperatures.

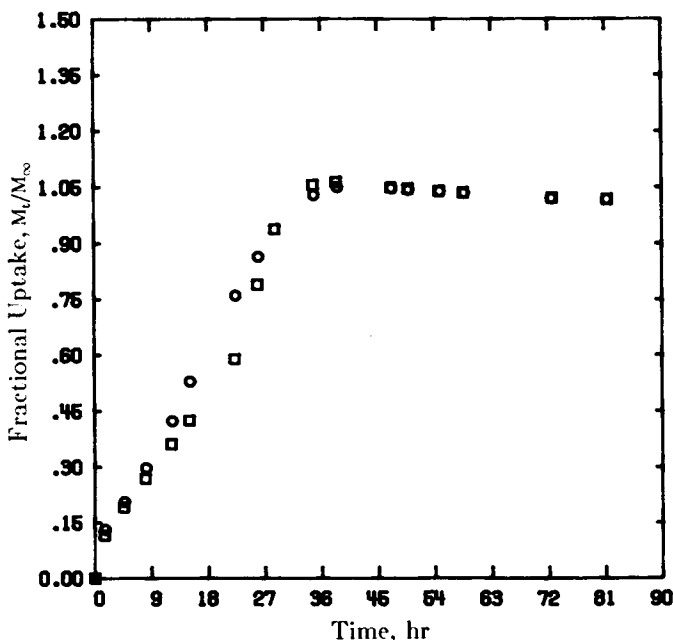


Fig. 9. Fractional uptake of cyclohexane, M_t/M_∞ , versus diffusion time, t , at 30°C for crosslinked polystyrene slabs No. 7Va (\circ) ($\delta_o = 0.0753$ cm, $L_o = 2.44$ cm and $X = 0.0207$ mol/mol) and No. 7Vc (\square) ($\delta_o = 0.0835$ cm, $L_o = 1.71$ cm and $X = 0.0207$ mol/mol).

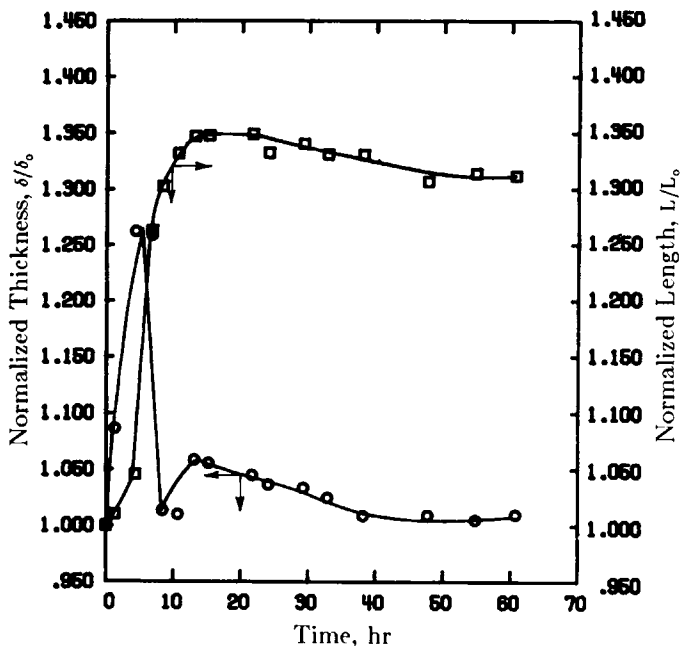


Fig. 10. Normalized thickness (\circ) and normalized length (\square) versus diffusion time, t , at 30°C for crosslinked polystyrene slab No. 2Vb ($\delta_0 = 0.105$ cm and $X = 0.00771$ mol/mol).

Some of the results of these experiments are given in Figure 9 as M_t/M_∞ versus time of transport for samples with lengths of 1.71 cm and 2.44 cm. The plots show a near collapse of the transport data, even though the lengths of the samples differed by a factor of 1.5. Also, since these experiments were performed at two different temperatures and with samples of different crosslinking densities, this curve collapse is independent of these parameters.

Dimensional Changes During the Transport Process

The transport of cyclohexane into a crosslinked polystyrene slab is characterized by the formation of a penetrant front which moves inward and separates the glassy and rubbery regions. The ability of various crosslinked polystyrene slabs to swell, and the degree to which they swell, is dependent upon how constrained the macromolecular structure is. Since the mobility of the macromolecular chains is dependent on concentration and temperature as well, the rate at which the polymer dimensions change should also be affected.

Figure 10 shows the normalized thickness, δ/δ_0 , and normalized length, L/L_0 , as a function of transport time for a sample whose transport data are depicted in Figure 3. The thickness of the sample increases to a maximum and then decreases, whereas the length slowly increases, then rather rapidly increases to a nearly constant value. This behavior can be explained in terms of the state transition during the swelling process. As the penetrant diffuses into the polymer, the glassy outer regions become rubbery due to the in-

creased mobility of the macromolecular chains and the presence of the penetrant. This swelling of the outer regions, however, is restricted by the central glassy core so that expansion occurs only in the direction normal to the face of the polymer slab. As the glassy core disappears, it no longer constrains the swelling of the polymer in the direction normal to the face, and therefore a change in both the thickness and length is observed. This maximum in sample thickness does not correspond to the maximum in penetrant uptake. The sample with the lowest crosslinking density reached a maximum value in thickness faster than the other samples. The time required to reach a maximum value in thickness increases with sample crosslinking density. This observation is consistent with the information given in Figure 3, which shows that the time of cyclohexane transport in these samples increases monotonically with crosslinking density. Therefore, the time required for the penetrant to reach the center of the polymer slab also increases with crosslinking density.

In Figure 10 the maximum value in sample thickness is followed by a very rapid decrease. This is followed by a substantially smaller increase to a maximum, followed by a decrease to a time-invariant sample thickness. Comparison of this behavior to that given in Figure 3 shows that the second maximum in sample thickness during the transport process mirrors the observed penetrant uptake overshoot. Also, as the crosslinking density of the sample increases, there is an increase in the rate at which the thickness decreases during the transport process. This suggests that the mobility of the macromolecules is significantly different in the highly crosslinked samples than in the loosely crosslinked samples. The region following the maximum value in sample thickness is normally where the entire crosslinked polymer is in a rubbery state.

The transport data of the last sample depicted in Figure 3 (sample 8Vc) show typical Super Case II transport behavior. The sorption process is essentially linear with respect to time until a point is reached where the uptake of penetrant begins to increase at a more rapid rate with respect to time. A further comparison of these transport data with the normalized thickness and length changes during transport shows that the maximum value in sample thickness corresponds to the point where the rate of transport begins to increase. Thus, the presence of the glassy core suppresses the sorption of penetrant at earlier times.

Our studies also show that the rate at which the length changes during the swelling process is related not only to the degree of crosslinking, but also to the sample thickness. These plots show that initially the length of the sample during the swelling process changes very little. However, after the maximum in sample thickness has occurred, the length increases at a usually rapid rate, indicative of the crosslinking density of the sample. The reason for this behavior can be attributed in part to the disappearance of the glassy core which allows the sample to swell in the direction parallel to face of the sample. The data show that this change in length is essentially a step function, since it occurs so suddenly. Comparatively, this transition is much slower for the highly crosslinked sample and supports the idea that this is a much more constrained system than the previous one. Also, since the length

and thickness change fairly significantly shortly after the maximum in thickness has been reached during the transport process, it is suggested that a considerable amount of force has built up during this time.

Fractional Area Changes During the Transport Process

In order to compare how various crosslinked polystyrene samples respond to the uptake of cyclohexane, plots of fractional area increase, $\Delta A_t/\Delta A_\infty$, versus fractional uptake, M_t/M_∞ were constructed. As described by Durning and Rebenfeld,⁴⁰ this graphical analysis gives curves characteristic of the system's mechanical constants. A perfectly elastic polymer, with a concentration-independent modulus, has $\Delta A_t/\Delta A_\infty$ equal to M_t/M_∞ throughout the swelling process. If the fractional area increase is lower than the fractional uptake, this is an indication that the polymer is viscoelastic with a characteristic relaxation time comparable to the characteristic diffusion time.

Figure 11 shows typical data of the fractional uptake versus fractional area increase for one of the samples with $X = 0.0257$ mol/mol. The straight line drawn specifies the equality of $\Delta A_t/\Delta A_\infty$ and M_t/M_∞ . This and similar figures for other samples have several interesting features. The first is that the fractional area shows a curvature only for M_t/M_∞ less than approximately 0.60. Beyond this point the crosslinked polymer behaves similarly to a perfectly elastic medium since the points fall on the line specifying equality of fractional uptake and fractional area increase. This is an indication that the polymer behaves as two separate media during the swelling process, an elastic

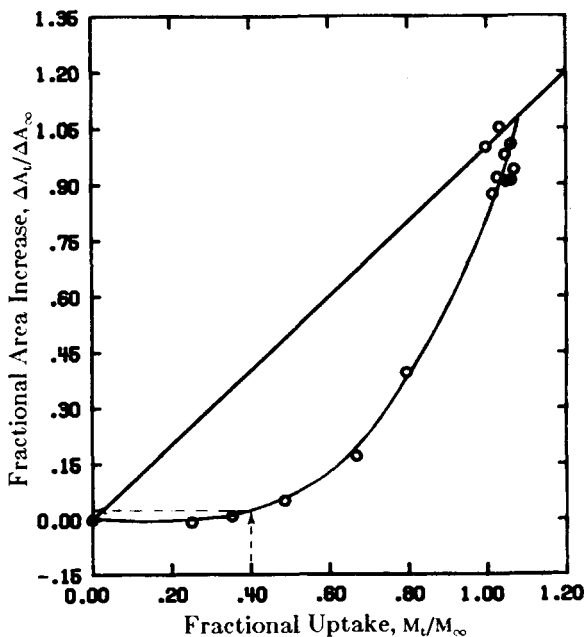


Fig. 11. Fractional area increase versus fractional uptake at 30°C for crosslinked polystyrene slab No. 8Vb ($\delta_0 = 0.0385$ cm and $X = 0.0257$ mol/mol).

and a viscoelastic medium. The transition point is when the glassy core no longer affects the uptake of cyclohexane, that is when the glassy core disappears.

In the analysis of swelling data with Eq. (5), the highest value of M_t/M_∞ used was the one corresponding to the maximum in sample thickness. The reason for this now becomes obvious. Due to the change in sorption behavior when the polymer becomes totally rubbery, an analysis using Eq. (5) as usually specified ($M_t/M_\infty < 0.60$) could have resulted in the inclusion of points not characteristic of the early, defining transport process. Since the maximum value in M_t/M_∞ corresponding to the maximum in sample thickness during the sorption process usually never exceeds the value of 0.60 to any large degree, it is assumed that no great violation of the principles of this equation has occurred.

Figure 12 shows the experimental data obtained from a sample with the same crosslinking density but larger thicknesses. This figure shows some very interesting behavior concerning the importance of thickness on the fractional area increase. As the initial sample thickness increases the fractional area increase increases. This can be explained in terms of the forces existing between the rubbery and glassy regions. The ability of the glassy core to compress the very outer rubbery regions depends on distance, for the farther away the outer edge, the less force it can exert. Therefore, during the transport process, thicker samples deform more than thinner samples along the respective outer edge. This deformation tends to increase as the penetrant front moves inward.

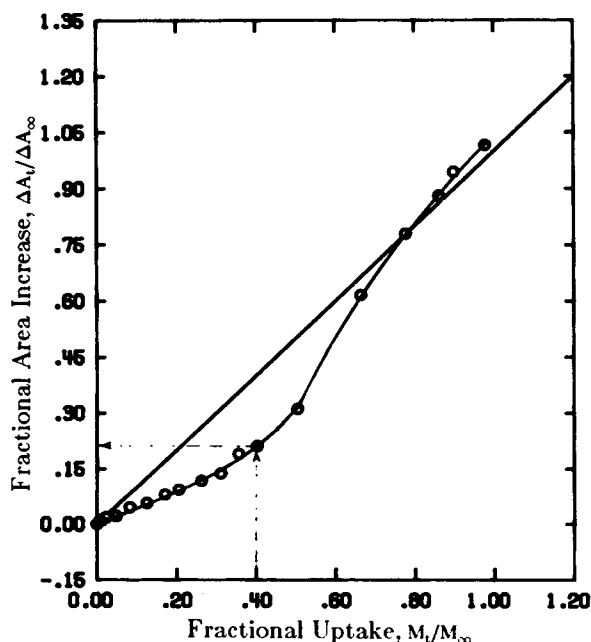


Fig. 12. Fractional area increase versus fractional uptake at 30°C for crosslinked polystyrene slab No. 5Yf ($\delta_0 = 0.119$ cm and $X = 0.0258$ mol/mol).

CONCLUSIONS

Using cyclohexane transport in thin films of DVB-crosslinked polystyrene at 20°C and 30°C we have shown that penetrant transport in glassy polymers is influenced by the crosslinking ratio and the thickness of the samples. The other dimensions do not seem to influence the transport mechanism as long as the aspect ratio is kept above 10.

In general, more crosslinked systems exhibit an anomalous cyclohexane transport behavior of ten leading to Case II transport. The penetrant front position is dependent on time. A penetrant uptake overshoot is observed for most polystyrene samples. Other phenomena related to the glassy/rubbery transition and associated with the total change of polystyrene into a rubbery material include the abrupt change of the normalized thickness as a function of time and the sudden increase of the length.

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References

1. G. E. Roberts and E. F. T. White, in *The Physics of Glassy Polymers*, R. N. Haward, ed., Halsted Press, New York, 1973.
2. T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).
3. J. S. Vrentas, J. L. Duda, and L. W. Ni, *Macromolecules*, **16**, 261 (1983).
4. J. S. Vrentas and J. L. Duda, *Macromolecules*, **9**, 785 (1976).
5. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962.
6. G. Astarita and L. Nicolais, *Pure and Appl. Chem.*, **55**, 727, (1983).
7. A. H. Windle, in *Polymer Permeability*, J. Comyn, ed., Elsevier, London, 1985.
8. T. Alfrey, *Chem. Eng. News*, **43**, 64 (1965).
9. N. L. Thomas and A. H. Windle, *Polymer*, **23**, 529 (1982).
10. T. Alfrey, E. F. Gurnee, and W. G. Lloyd, *J. Polym. Sci.*, **12**, 249 (1966).
11. C. H. M. Jacques, H. B. Hopfenberg, and V. T. Stannett, in *Permeability of Plastic Films*, H. B. Hopfenberg, ed., Plenum, New York, 1974.
12. H. L. Frisch, T. T. Wang, and T. K. Kwei, *J. Polym. Sci.*, **7**, 879 (1982).
13. N. A. Peppas, J. L. Sinclair, M. J. Smith, and J. G. Mounts, in *Advances in Rheology*, Vol. 3, *Polymers*, B. Mena, A. Garcia-Rejon, and C. Rangel-Nafaile, eds., 290, UNAM, Mexico City, 1984.
14. A. Peterlin, *Makrom. Chem.*, **124**, 136 (1969).
15. A. J. Peterlin, *Polym. Eng. Sci.*, **17**, 183 (1977).
16. A. J. Peterlin, *J. Polym. Sci., Polym. Phys.*, **17**, 1741 (1979).
17. N. A. Peppas and J. L. Sinclair, *Coll. Polym. Sci.*, **261**, 404 (1983).
18. J. H. Petropoulos and P. P. Roussis, *J. Membr. Sci.*, **3**, 343 (1978).
19. N. L. Thomas and A. H. Windle, *Polymer*, **21**, 60 (1980).
20. J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys.*, **15**, 441 (1977).
21. J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Polym. Phys.*, **15**, 403 (1977).
22. J. S. Vrentas, C. M. Jarzebski, and J. L. Duda, *AIChE J.*, **21**, 894 (1975).
23. G. W. R. Davidson and N. A. Peppas, *J. Contr. Rel.*, **3**, 243 (1986).
24. G. W. R. Davidson and N. A. Peppas, *J. Contr. Rel.*, **3**, 259 (1986).
25. N. A. Peppas, *Pharm. Acta Helv.*, **60**, 110 (1985).
26. G. W. Sinclair and N. A. Peppas, *J. Membr. Sci.*, **17**, 329 (1984).
27. A. G. Mikos, C. G. Takoudis, and N. A. Peppas, *Macromolecules*, **19**, 2174 (1986).
28. M. J. Smith and N. A. Peppas, *Polymer*, **26**, 569 (1985).
29. C. C. R. Robert, P. A. Buri, and N. A. Peppas, *J. Appl. Polym. Sci.*, **30**, 301 (1985).
30. K. Dušek, *Chemický Průmysl*, **13**, 436, (1963).
31. H. B. Hopfenberg, *J. Membr. Sci.*, **3**, 215 (1978).
32. A. R. Berens and H. B. Hopfenberg, *Polymer*, **18**, 793 (1977).

33. H. B. Hopfenberg, R. H. Holley, and V. Stannett, *Polym. Eng. Sci.*, **9**, 242 (1969).
34. A. R. Berens and H. B. Hopfenberg, *Polymer*, **19**, 489 (1978).
35. D. J. Ensore, H. B. Hopfenberg, and V. T. Stannett, *Polym. Eng. Sci.*, **20**, 102 (1980).
36. R. W. Korsmeyer and N. A. Peppas, *J. Contr. Rel.*, **1**, 89 (1984).
37. A. R. Berens, *J. Vinyl Tech*, **1**, 8 (1979).
38. J. S. Vrentas, J. L. Duda, and A. C. Hou, *J. Appl. Polym. Sci.*, **29**, 399 (1984).
39. N. M. Franson and N. A. Peppas, *J. Appl. Polym. Sci.*, **28**, 1299 (1983).
40. C. J. Durning and L. Rebenfeld, *J. Appl. Polym. Sci.*, **29**, 3197 (1984).

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