

Structure-Property Relationships for Liquid Transport in Modified Polypropylene Membranes

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Synopsis

In view of the intensifying interest in the application of polymeric membranes in mixture separation processes, the permeation and permselective properties of polypropylene films toward several candidate organic liquids and vapors were investigated. Polymer films were subjected to solvent and thermal treatments, and the effects of these treatments on film morphology and transport properties were studied. Structure-property relationships for membrane permeation were then developed. Polypropylene films were found to be selective toward toluene, relative to isooctane, and *p*-xylene relative to *o*-xylene. Liquid flux rates were found to depend primarily upon the solubility of the permeants in the films and the absolute difference in the solubility parameters of the polymer-liquid pair provided a good basis for correlation of this effect. Considering liquids of closely similar solubility parameters, fluxes were found to be dependent upon the apparent molecular cross sections of the permeants. Films annealed in various organic solvents at temperatures of 60-100°C exhibited enhanced permeability, with up to fifteenfold increase relative to untreated membranes, but with reduced selectivity towards the permeants. A mechanism to account for these effects through consideration of the influence of treating solvent type on polymer morphology is proposed. It postulates the formation of more open or coarser spherulitic structures as a result of recrystallization in the presence of solvent during annealing. The enhanced flux rates in the treated films are attributed to the changes in the spherulite textures and to diminished intercrystalline tie chain constraint within the spherulitic substructure.

INTRODUCTION

Motivation and Objectives

It is well known that the composition of a liquid mixture can be altered by allowing a portion of the mixture to permeate through a polymeric membrane. This phenomenon thus provides a basis for a separation process and, as a result, has motivated a substantial amount of research and development effort which has intensified in recent years. Indeed, systems have been proposed for such diverse applications as concentration of pro-

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teins, demineralization of seawater, treatment of effluent waters and the separation of mixtures of close-boiling liquids, as discussed, for example, in the review by Li et al.¹ In many cases, the commercialization of these processes is limited by the interaction of membrane permselectivity-permeation rate. It is therefore of interest to find methods for rendering polymer structures more selective and/or permeable to components of liquid mixtures.

Studies by deFilippi² and Choo³ indicated that solvent annealing of polyethylene increases film permeability to xylene isomers and chlorocarbons. More recently, Krewinghaus⁴ demonstrated that a marked increase in permselectivity of polyethylene to benzene with respect to cyclohexane may be achieved by uniaxially cold drawing the film. Furthermore, Choo³ suggested that it might be possible to "tailor" a membrane for a given separation by properly annealing the membrane while swollen with a liquid of suitable molecular configuration.

The present investigation deals with the permeation characteristics toward organic liquids and vapors of polypropylene films subjected to various treatments. It proposes a mechanism for the process in which solvent and thermal modification of polymer films alters the permeability and selectivity of the films. Finally, the results demonstrate the use of liquid transport and sorption data in elucidation of the microstructure of semicrystalline polymers; in this case, the morphology of polypropylene films fabricated by different methods.

Theory

The steady-state activated transport of a fluid through a polymeric membrane may be described by Fick's Law:

$$J = -D(dc/dx) \quad (1)$$

where J is the mass flux of the permeant, D is the diffusion coefficient, and dc/dx is the concentration gradient of the permeant. For the case of a liquid in contact with the upstream face of a membrane (of thickness l), and with the concentration of penetrant kept negligible at the downstream face, Fick's Law may be integrated to yield:

$$Q = Jl = \int_0^{c_1} Ddc \quad (2)$$

The product, Jl , represents the flux rate normalized to unit membrane thickness and is denoted by Q .

By defining an integral diffusivity (\bar{D}) to represent the average diffusivity across the membrane, as:

$$\bar{D} = (l/c_1) \int_0^{c_1} Ddc \quad (3)$$

one obtains the following expression for Q :

$$Q = \bar{D}c_1 \quad (4)$$

This relation is of major significance, since it underlines the two primary factors which affect the steady-state permeation flux: the diffusivity of a molecule in a membrane and its equilibrium concentration (c_1), or sorption, in the polymer.

In this study, Q values were obtained from steady-state liquid permeation experiments; equilibrium vapor sorption data (at $P/P^0 = 1$) yielded c_1 values, and a combination of the two enabled calculation of integral diffusivities (\bar{D}_Q). Other estimates of diffusivity were derived from unsteady-state sorption data as described below.

As shown by Crank,⁵ the differential equation expressing Fick's second law can be solved for the conditions prevailing during the early phase of a diffusion experiment ($t \rightarrow 0$), yielding the expression:

$$M_t/M_\infty = 4(\bar{D}t/l^2\pi)^{1/2} \quad (5)$$

where M_t is the amount of permeant sorbed (or desorbed) in time t , M_∞ represents the quantity of penetrant in the film at equilibrium, \bar{D} is the integral diffusivity, and l is film thickness. The slope of a plot of M_t/M_∞ versus $t^{1/2}$, therefore, can be used to estimate the integral diffusivity during sorption, D_s , or during desorption, D_d . Crank⁵ indicates that the average of D_s and D_d (denoted by \bar{D}_{av}) for time-independent diffusion, corresponds reasonably well to the diffusivity as estimated by combining the permeation flux rate of a compound with its equilibrium concentration in the polymer ($\bar{D}_Q = Q/c_1$ under equivalent boundary conditions). Thus, \bar{D}_{av} values, representing the kinetics of sorption and desorption between the terminal states of vacuum and saturated vapor, were compared to \bar{D}_Q values.

With regard to the polymer morphological features which govern permeant transport, it is worthy of emphasis that previous studies have established that transport takes place primarily in the noncrystalline regions of polymeric membranes.⁶ A structural feature of these amorphous regions that is important in determining transport behavior is the degree of constraint of "tightness" of the amorphous polymer chain segments comprising these regions, which act as "tie-links" between crystallites.⁷ It can be readily appreciated that transport of a penetrant molecule would be more hindered when passing among stiff and immobile tie-chains (i.e., in a highly constrained matrix) than when diffusing through relatively flexible chains.

Most of the polypropylene films used in this study contain spherulites. The spherulites consist of fiberlike crystalline lamellae radially emanating from a nucleus, with the amorphous phase concentrating between or at the surface of these lamellae. As will be shown later, solvent annealing of polypropylene alters the crystalline texture of the spherulites, which in turn influences the degree of amorphous chain constraint (and thus the transport properties) of these treated films.

EXPERIMENTAL

Materials

The polypropylene film used in this study (Profax-6520F) was supplied by Hercules, Incorporated, Wilmington, Delaware. The material has reported to have a weight-average molecular weight of about 3×10^5 and to be 95% isotactic as determined by x-ray and solubility measurements.⁸ The bulk of the transport and solvent-annealing experiments were carried out with unoriented, hot-cast, 5-mil thick film ($\rho = 0.9050$ g/cc) which was fabricated by extruding polymer melt onto a casting roll kept at about 110°C. In one series of experiments, unoriented quenched polypropylene was used ($\rho = 0.8900$ g/cc); in this case the casting roll temperature was about 20°C.⁸

Reagent-grade *n*-heptane, isooctane (2,2,4-trimethylpentane), methylcyclohexane, *p*-xylene, and *o*-xylene were used in the course of this investigation. These solvents were used without further treatment, except in the case of vapor sorption experiments, when they were subjected to repeated freeze-thaw cycles to remove any dissolved gases.

Some properties of these compounds, used both as permeants and treating solvents, are given in Table I. The molecular dimensions were estimated by measuring Stuart-Briegleb molecular models of the compounds in three mutually perpendicular directions, the "diffusional cross-sectional area" being calculated from the product of the two smaller dimensions.

TABLE I
Properties of Permeating Molecules

Permeant	Permeant bp, °C	Molar volume, cc/g mole (25°C)	Cross- sectional area, (Å ²) ^a	Solubility parameter δ , (cal/cc) ^{1/2} (25°C)	Solubility parameter difference $\Delta\delta$ (WRT polypropylene)
Isooctane	99.2	167	34.0	7.1	1.0
Methylcyclohexane	100.9	129	28.2	7.8	0.3
Toluene	110.6	107	19.6	8.9	0.8
<i>p</i> -Xylene	138.4	124	20.1	8.7	0.6
<i>o</i> -Xylene	144.4	121	23.6	9.0	0.9

^a Product of two smaller dimensions as measured from Stuart-Briegleb molecular models.

Solvent Modification of Polypropylene Film

Rectangular sections (2 × 5 in.) cut from the polypropylene film roll were used for the solvent treatment of the polymer. The film was secured with clamps to a rigid aluminum frame before being immersed in the solvent bath. Temperatures in the range of 60–100°C were used in solvent treatment.

After immersion for 24 hr at constant temperature, films were removed

from the solvent and dried (in the frame), at 40°C, in either a vacuum oven or in a box through which air was continuously passed. Enough film sections were treated together (at given treatment conditions) to provide film samples for the permeation, sorption, and all other physical property studies (e.g., density, calorimetry).

Apparatus and Procedure

Liquid Permeation. Liquid permeation fluxes were determined by using the permeation cell illustrated in Figure 1. Cells were placed in a thermo-

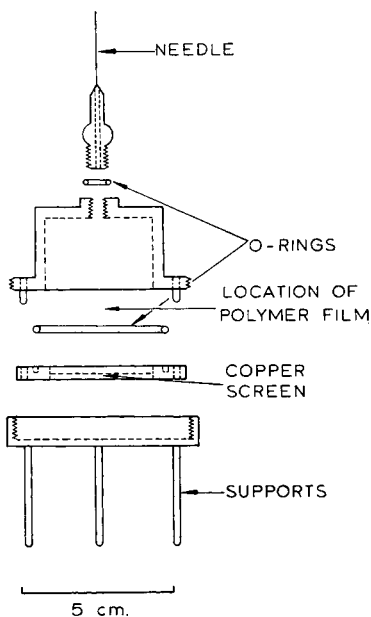


Fig. 1. Permeation cup.

stated air bath through which air was constantly blown at a rate high enough to maintain a negligible concentration of permeant at the downstream side of the films. The cells and their contents were periodically weighed on a Mettler balance (sensitivity 0.1 mg) and a normalized flux rate calculated for each period. Measurements were continued for several hours after a steady-state permeation was observed. To obtain a flux rate for a liquid through a given film, the average permeation flux as determined from two or more cells was used. The precision of the permeation flux was estimated to be $\pm 6\%$ at the 95% confidence level.

Unsteady State Vapor Sorption and Desorption. The kinetics of vapor sorption (or desorption) in polypropylene films were determined using a quartz-spring balance, enclosed in a constant temperature air bath, as shown in Figure 2. Sorption runs were started by admitting to the evacuated sorption column a given vapor, adjusting to the desired vapor pres-

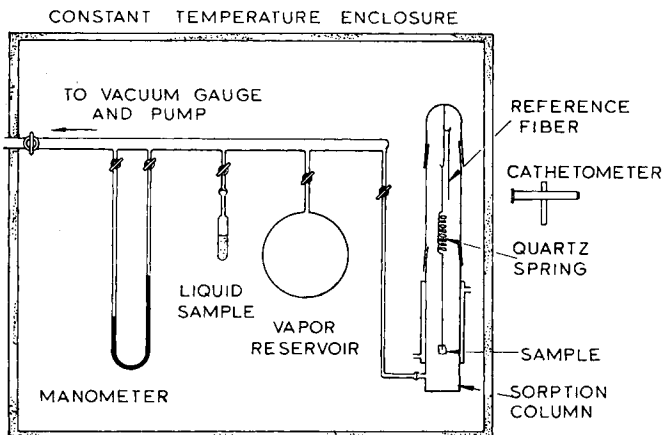


Fig. 2. Schematic diagram of quartz-spring sorption apparatus.

sure (usually saturation pressure) and following the consequent displacement of the quartz-spring using a sensitive cathetometer. For a desorption run, the spring column was rapidly evacuated and readings of spring extension as a function of time were made.

The quartz spring used was obtained from Microchemical Specialties Company (Berkeley, California) and had a sensitivity of 1.028 mm/mg. Polymer samples were usually about 50 mg. The quartz-spring system allowed detection of weight changes of the order of ± 0.03 mg compared to a total sorption usually greater than 5 mg.

Polymer Characterization. Isopropyl alcohol-water density gradient columns were used in determining film sample densities. Densities at 23°C were usually determined in triplicate and agreed to ± 0.0005 g/cc.

The amorphous volume fraction, α , was then calculated from the relationship:

$$\alpha = (\rho_c - \rho) / (\rho_e - \rho_a) \quad (6)$$

where ρ is the experimentally determined density, $\rho_c = 0.9360$ g/cc, the density of monoclinic modification of crystalline polypropylene (which is a dominant modification), and $\rho_a = 0.85$ g/cc, the amorphous phase density as reported by Natta.⁹

Optical examination of polypropylene film samples were made with a Wild M-20 microscope equipped with polarizing attachments.

For finer details of polymer morphology, the EM-75 or EM-200 Philips electron microscopes were used. Samples for microscopic examination were prepared as follows: a 2% Parlodion in acetate solution was spread on the polymer surface, specimen grids were placed on the resulting thin Parlodion film, this replicating film was then stripped with Scotch Tape and shadowed with chromium at 27° angle.

The melting behavior of various polypropylene samples was observed with the aid of a Perkin-Elmer DSC-1 differential scanning calorimeter.

RESULTS AND DISCUSSION

Properties of Untreated Polypropylene

The liquid permeation data presented in Tables II and III demonstrate the permselective nature of polypropylene films towards permeants having similar boiling points. The flux rates of methylecyclohexane and toluene are appreciably higher than the flux rate of isooctane. Similarly, *p*-xylene permeates faster than *o*-xylene in polypropylene. It is this difference in transport rate which constitutes the basis for a membrane separation process.

TABLE II
Permeation Flux in Untreated Polypropylene ($T = 40^\circ\text{C}$)

Permeant	$\Delta\delta$, (cal/cc) ^{1/2} ^a	Q, g-cm/(hr-cm ²) $\times 10^5$	
		Hot-cast film ($\rho = 0.9050$ g/cc)	Quenched film ($\rho = 0.8903$ g/cc)
Methylecyclohexane	0.3	14.3	59.5
<i>p</i> -Xylene	0.6	11.7	34.0
Toluene	0.8	15.3	44.4
<i>o</i> -Xylene	0.9	5.2	17.8
Isooctane	1.0	1.4	10.3

^a Difference in solubility parameter of polymer and solvent.

TABLE III
Selectivity of Untreated Polypropylene Films ($T = 40^\circ\text{C}$)

Permeant ^a	Selectivity (Q_i/Q_j) ^b	
	Hot-cast film ($\rho = 0.9050$ g/cc)	Quenched film ($\rho = 0.8903$ g/cc)
Tol/MCH	1.1	0.75
Tol/ <i>i</i> -Oct	11.0	4.3
MCH/ <i>i</i> -Oct	10	5.8
PX/OX	2.25	1.91

^a Permeants: Tol = toluene; MCH = methylecyclohexane; *i*-Oct = isooctane; PX = *p*-xylene; OX = *o*-xylene.

^b Ratio of pure-component permeabilities.

It should be pointed out that the selectivity values reported throughout this work are "theoretical" since they were calculated by taking a ratio of the measured permeation rates for the pure components. Although this theoretical value is indicative of the separation capacity of the films, the actual selectivity in the case of liquid mixtures would be expected to be different.⁴

The higher liquid permeation rates observed in untreated quenched polypropylene ($\rho = 0.8900$ g/cc), compared to flux rates in hot-cast film ($\rho = 0.9050$ g/cc), reflect the fact that fluid transport takes place primarily through the noncrystalline (lower density) regions of the polymer.

Independent examination of the solubility and diffusion behavior of the various permeants in polypropylene provided insight into the effect of permeant properties on transport rates (since $Q = \bar{D}c_1$). Sorption behavior is governed primarily by the relative magnitude of molecular forces acting between polymer segments and penetrant molecules; i.e., thermodynamic factors control sorption. In this study, the compatibility of a solvent and polypropylene film was expressed through the use of solubility parameters (δ), where δ equals the square root of the cohesive energy density, C.E.D. (internal energy of vaporization divided by molar volume). It is shown in Figure 3 that the degree of sorption of the fluid studied in un-

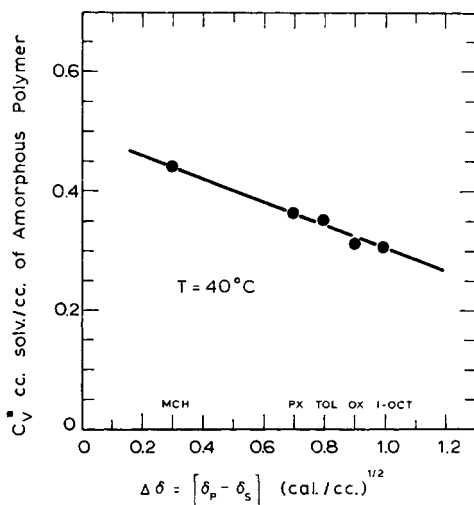


Fig. 3. Sorption as a function of the difference in the solubility parameter of polymer and solvent.

oriented polypropylene is proportional to the absolute difference in the solubility parameter of the polymer ($\delta_{PP} = 8.1$) and that of the solvent. Thus, methycyclohexane ($\Delta\delta = 0.3$) is most soluble and isooctane ($\Delta\delta = 1.0$) is least soluble in polypropylene.

The pronounced dependence of diffusivity, in untreated polypropylene film, on permeant molecular dimensions is shown in Figure 4. The data indicate a correlation between the log of the diffusion coefficient (\bar{D}_Q) and the apparent cross-sectional area of the diffusing molecules. Diffusion through the matrix of a polymer may be related to the frequency with which a dissolved molecule can find, or create, a space between adjacent polymer chains large enough to accommodate it. Thus, the higher diffusivity of a smaller molecule (e.g. toluene) may be attributed to the higher probability of finding an appropriate "gap-size" for the passage of this molecule.

Brandt¹⁰ has shown that for a polymer with limited chain segmental mobility, the activation energy for transport (and therefore diffusivity) would depend on the square of the molecular diameter of the permeant.

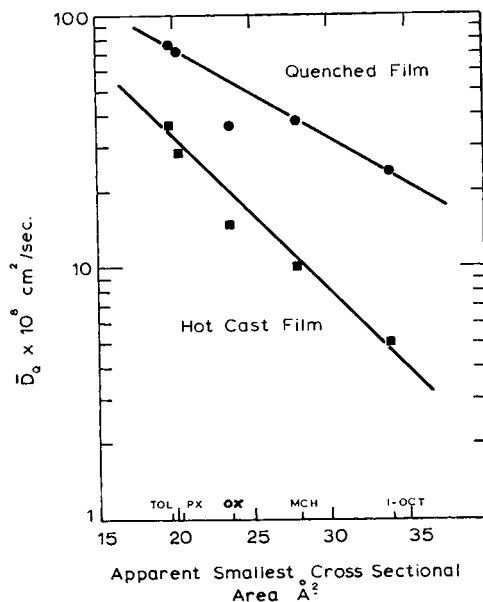


Fig. 4. Integral diffusivity as a function of molecular size in untreated polypropylene.

The apparent d^2 dependency of transport of relatively large permeants found in polypropylene is probably a reflection of the rigidity imparted to the backbone of polypropylene by the pendent methyl groups. This chain stiffness suggested by the diffusion data is also reflected in the relatively high glass transition temperature of polypropylene (263°K) compared to that of polyethylene (148°K).

Comparison with Polyethylene

The transport and selective properties of polypropylene film, with respect to *p*- and *o*-xylene, are compared to similar data in the literature for those of polyethylene film in Table IV.

TABLE IV
Comparison of Liquid Transport in Untreated Polyethylene and Polypropylene ($T = 40^\circ\text{C}$)

Film	Crystallinity, % (from density)	Q, g-cm/ (hr-cm ²) × 10 ⁵		
		Q_{PX}	Q_{OX}	Q_{PX}/Q_{OX}
Linear polyethylene	72	6.4	3.7	1.74
Linear polyethylene	60	7.0	3.6	1.95
Hot-cast polypropylene (This study)	65	11.7	5.2	2.25

The data indicate that the permeation flux of xylene isomers is higher (by about 50%) in polypropylene film than in linear polyethylene. Solu-

bilities of the xylenes in the two polymers are not expected to be appreciably different in view of the fact that the solubility parameter of polyethylene, 7.9, is quite close to that of polypropylene, 8.1. On the other hand, integral diffusivities appear to be higher in polypropylene. De Filippi² reported the diffusivities of *p*- and *o*-xylene (at 40°C, in 60% crystalline, untreated polyethylene) to be 1.8×10^{-7} cm²/sec and 1×10^{-7} cm²/sec. respectively; while the comparable values in 65% crystalline, untreated polypropylene are 2.8×10^{-7} and 1.4×10^{-7} cm²/sec. This difference in diffusivity suggests the existence of more direct diffusion paths in polypropylene, which could result from differences in the crystalline habit of these polymers. For example, narrower crystalline lamellae or the presence of lattice defects in polypropylene would shorten the tortuous path a penetrant molecule must follow in circumventing crystalline regions. Strong support for the latter hypothesis is provided by analysis of the relatively low impedance values obtained in a complementary study of permanent gas transport in polypropylene.¹¹

The flux ratios of *p*-xylene to *o*-xylene indicate that polypropylene film is more discriminating than polyethylene. The better selectivity of polypropylene can probably be attributed to the greater stiffness of its chains; i.e., less mobile chain segments are more "sensitive" to the size and shape of the permeating molecule.

Transport in Solvent-Annealed Polypropylene

Permeation. The permeation flux of several organic liquids in solvent-annealed films is appreciably higher (Table V) than in untreated hot-cast polypropylene. For example, the permeation rate of toluene through film treated in *p*-xylene at 100°C is increased by about fourfold compared to what it was in the unmodified film, whereas isooctane flux is increased by a factor of fifteen. As is shown in the following sections, the enhanced permeation rate may be related to changes in the fine structure (crystalline texture and the character of the amorphous phase) of the treated films. The enhanced permeation flux cannot be attributed to the possible formation of "voids" in the film as a result of the solvent annealing since the density of treated films was comparable or even greater than the density of the untreated films (Table VI), whereas voids would cause a reduction in density. Moreover, the activation energy for permeation in the treated membranes was found to be of the order of 10 kcal/g-mole, a value which is more representative of activated transport than pore flow through a membrane.

Sorption. The increase in permeation rates, subsequent to solvent treatment, can be partially attributed to changes in the sorptive capacity of the polymer. The data (Table VII) indicate that the volume of solvent sorbed per unit amorphous polymer, C^{\ddagger} , is generally greater in solvent-annealed polypropylene relative to the unmodified polymer.

The sorption data are quite valuable in assessing the nature of the morphological changes occurring in the film as a result of solvent treatment.

TABLE V
Permeation Rate in Polypropylene Film As a Function of Treatment
Temperature ($T = 40^\circ\text{C}$)

Permeant	$Q, \text{g-cm}/(\text{hr-cm}^2) \times 10^6$			
	Untreated	<i>p</i> -Xylene-treated (24 hr)		
		60°C	80°C	100°C
Toluene	15.3	20.6	37.2	59.4
Methylcyclohexane	14.3	16.0	28.0	46.2
Isooctane	1.4	3.2	8.7	21.2

TABLE VI
Densities and Amorphous Fraction of Poly(propylene) Films

Film	Treatment	$\rho, \text{g/cc}$ (23°C)	100 $\alpha, \%$ ^a
Quenched	None	0.8903	55.7
Hot-cast	None	0.9050	37.8
Hot-cast	PX, 60°C	0.9054	37.4
Hot-cast	PX, 80°C	0.9056	37.1
Hot-cast	PX, 100°C	0.9100	31.4
Hot-cast	<i>n</i> -Hex, 60°C	0.9055	37.2
Hot-cast	<i>i</i> -Oct, 60°C	0.9054	37.4
Hot-cast	<i>i</i> -Oct, 90°C	0.9056	37.1
Hot-cast	MCH, 60°C	0.9054	37.4

$$^a \alpha = (\rho_c - \rho)/(\rho_c - \rho_a); \rho_c = 0.9360 \text{ g/cc}, \rho_a = 0.8540 \text{ g/cc}.$$

TABLE VII
Effect of Conditioning Temperature on Sorption at 40°C (polypropylene
Treated in *p*-Xylene)

Solvent	$\Delta\delta, \text{cal/cc}^{1/2}$	C_V^* (cc solvent/cc amorphous polymer)			
		Untreated film	Film treated at:		
			60°C	80°C	100°C
Methylcyclohexane	0.3	0.45	0.47	0.51	0.70
<i>p</i> -Xylene	0.6	0.36	0.36	0.40	—
Toluene	0.8	0.35	0.32	0.37	0.49
<i>o</i> -Xylene	0.9	0.31	0.34	0.36	—
Isooctane	1.0	0.31	0.36	0.37	0.48

They enable the estimation of the degree of constraint or "tightness" of polymer chains in the amorphous regions of the polymer. The constraints are imposed by crystallites which, acting as crosslinks, exert an elastic retractive force on the tie chains due to swelling. This leads to an internal pressure on the sorbed molecules which enhances their activity. Haussein⁷ suggested that, by comparing the observed activity of a solvent ($\alpha = P/P^0$) in a semicrystalline polymer, to the activity as predicted by the Flory-Huggins equation¹² for an unrestrained polymer, an enhanced activity coefficient, γ_e , reflecting constraint may be obtained, i.e.:

$$\ln \gamma_e = \ln a_1 - (\ln v_1 + v_2 + \chi v_2^2) \quad (7)$$

where v_1 and v_2 are the volume fraction of solvent and polymer, and χ is the polymer-solvent interaction parameter.

Table VIII summarizes $\ln \gamma_e$ values calculated for *p*-xylene films treated at temperatures of 60–100°C. The lesser enhancement of solvent activity (low $\ln \gamma_e$) observed in films treated at increasing temperatures is indicative of the reduction in the amorphous phase constraints subsequent to treatment. This reduction of constraint may reflect a decrease in degree of intercrystalline bridging resulting from an increase in the degree of crystallite perfection which occurs during annealing. Reversal of the order of constraints with increasing temperature is puzzling; explanation of this phenomenon must await further experimentation.

TABLE VIII
Amorphous Phase Constraints ($\ln \gamma_e$) as a Function of Treatment Temperature
(Treating Solvent *p*-Xylene)

Polymer treatment temp, °C	$\ln \gamma_e$ at 40°C		
	Toluene	MCH	Isooctane
60	0.497	0.363	0.340
80	0.396	0.322	0.333
100	0.176	0.193	0.226

Diffusion. Solvent-annealed polypropylene films exhibited appreciably higher diffusivities than unmodified films (Table IX); with the extent of transport enhancement increasing with increasing treatment temperatures. Under conditions of reduced amorphous chain constraint, prevalent in treated samples, movement of polymer chain segments is facilitated and penetrant diffusion is enhanced. It is worth noting that chain "tightness" influences the diffusive behavior of a polymer to a greater extent than it affects the polymer's sorptive capacity. Whereas the maximum increase in sorption, subsequent to solvent treatment, was of the order of 50%, diffusivities increased by as much as 1000%. Similar behavior was observed in polyethylene⁴ where a 2 to 3-fold decrease in sorption (due to cold-drawing) was accompanied by about 100-fold decrease in the diffusivities of organic vapors.

TABLE IX
Effect of Conditioning Temperature on Diffusivity (at 40°C)

Permeant	$\bar{D}_q \times 10^7, \text{cm}^2/\text{sec}$			
	Unconditioned film	Conditioned in <i>p</i> -xylene at:		
		60°C	80°C	100°C
Toluene	3.7	5.8	9.1	12.6
Methylcyclohexane	1.1	3.4	5.5	7.0
Isooctane	0.5	1	2.7	5.9

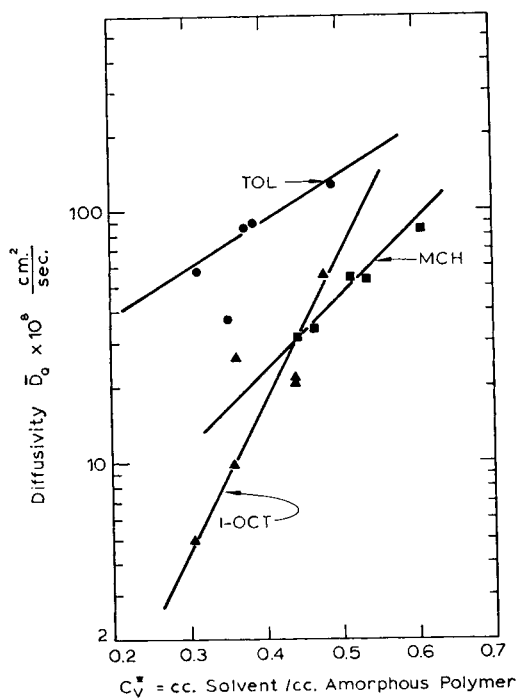


Fig. 5. Diffusion as a function of concentration.

Enhanced diffusivity in treated film can also be attributed to the higher solvent concentration in these films; Figure 5 shows that organic liquid diffusivity in polypropylene is exponentially dependent on concentration. Furthermore a more direct diffusion path may exist in treated films, resulting from either formation of defects in crystallites⁴ or changes in crystal habit¹³ which could also account for increased transport rate, as discussed further below.

Enhanced transport characteristics of polymeric membranes subjected to solvent-annealing are not confined to polypropylene systems. Choo³ has shown that the permeation rates of the xylene isomers were higher in solvent-treated polyethylene films than in untreated films. Similar results were obtained by de Filippi,² who studied the transport of xylene and acetylene dichloride isomers in various polyethylene membranes. Both Choo and de Filippi report increases of sorption and diffusivity after annealing the films in the presence of solvent. They attribute the increases to the lower number density of intercrystalline links existing in the modified membranes. More recently, Krewinghaus⁴ found that when uniaxially oriented polyethylene films are annealed, the films partially relax and values of the vapor sorptions and diffusivities increase. As in the case of polypropylene, polyethylene films treated at higher temperatures exhibit higher sorptions and transport rates than those treated at lower temperatures.

Selectivity. The changes in polymer morphology resulting from solvent treatment also influence the selectivity of the polypropylene films toward various organic liquids. Usually, the ideal permselectivity of a membrane (as reflected by the permeation flux ratio of two pure permeants) is lower in films exhibiting high flux rates. This is reasonable since low permeation rates can be related to a polymer morphology characterized by a high degree of interlamellar amorphous chain ties. In such a constrained structure, some regions may be accessible only to the smaller molecules (e.g., toluene). Solvent-annealing promotes "loosening" of the polymer matrix, and thus transport is facilitated, especially for the larger molecules (e.g., isooctane) whose size restricts their movements to a greater extent in the unmodified membrane.

The inverse relationship between flux rate and the log of selectivity is clearly demonstrated in Figure 6. As expected, variations in polymer morphology are less effective in altering the relative flux rates of molecules possessing similar structure (*o*- and *p*-xylene) than for widely dissimilar molecules (toluene and isooctane).

In considering the value of solvent modification with respect to the potential use of membranes in separation processes, the changes of both permeation flux (Q) and selectivity ($\bar{P}\bar{S}$) must be taken into account. For a given overall enrichment, the number of stages required is roughly inversely

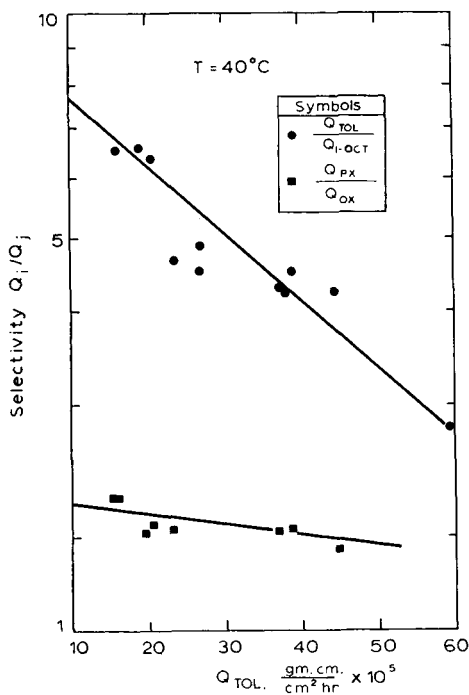


Fig. 6. Film selectivity vs. toluene flux rate.

proportional to the log of selectivity, while the area required per stage for a given throughput is inversely proportional to the permeability. Thus, if $\bar{P}\bar{S} \gg 1$, an increase in flux will always reduce area requirements even if selectivity decreases appreciably. On the other hand, if $\bar{P}\bar{S} \cong 1$, a slight loss in selectivity will be far more damaging than a large gain in permeability. In view of this, it appears that for the systems considered in this study, solvent modification may be attractive in that this would mean reduced area requirements. Determination of the optimum treatment conditions, however, would require further information concerning the details of the separation process, cost figures for the various components of the process, as well as binary mixture permeation data.

Effect of Permeation Temperature on Flux Rate and Selectivity

Organic liquid transport rates through polypropylene films are enhanced and selectivity impaired as the temperature of permeation is increased (Fig. 7). This behavior is to be expected in a system in which activated transport takes place; i.e., the higher thermal energy associated with increased temperatures facilitates the movement of the permeant molecules. However, there are other factors which also influence this behavior in polypropylene. Hausslein⁷ has shown that $\ln\gamma_e$ decreases with increasing temperature; thus, the reduction of chain segment tension would favor increased transport. The increase in the solubility of liquid hydrocarbons in

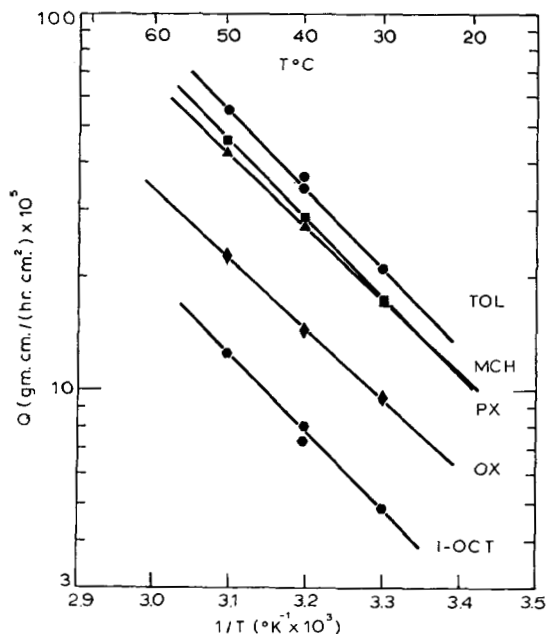


Fig. 7. Effect of temperature on liquid flux rate for polypropylene film treated in MCH at 60°C.

polypropylene at increasing temperature,¹⁴ suggests yet another reason for enhanced permeation, since fluid transport is exponentially dependent on concentration.

The decrease in selectivity with increasing temperature (e.g., from $\bar{P}\bar{S} = 7.2$ at 25°C to $\bar{P}\bar{S} = 6.2$ at 50°C for toluene–isooctane, derived from Fig. 7) is consistent with the postulated relief of constraints occurring at higher temperature, which would be expected to affect the transport rate of the larger molecule (e.g., isooctane) to a greater extent than that of a smaller one (e.g., toluene).

From the temperature dependence of flux rates, the activation energies for permeation were calculated and were found to be in the range of 7–10 kcal/mole. Not unexpectedly, the activation energies were lower in films which exhibited high transport rates, corroborating the notion that solvent-annealing promotes the “loosening” of the polymer matrix.

It is worth noting that the reported activation energy values reflect “reversible” flux-temperature behavior (i.e., the act of permeation at high temperature did not alter film structure). Such reversible behavior could not be obtained for “untreated” film (since exposure to solvent at elevated temperature modifies the film), and the apparent “activation energies” calculated for this case were higher (12–20 kcal/mol, depending on permeant molecular dimensions).

Effect of Treating Solvent Properties on the Transport Characteristics of Polypropylene

The fact that the nature of the solvent used in treatment influences the transport properties of polypropylene is clearly indicated by the data summarized in Tables X and XI. These data do not support Choo's³ sugges-

TABLE X
Effect of Treating Solvent Type on Permeation Characteristics of Polypropylene (at 40°C)

Permeant	$\Delta\delta$, (cal/cc) ^{1/2}	Untreated film	Q , g-cm/(hr-cm ²) × 10 ⁶				
			Treating solvent (at 60°C)				
			i-Oct	Tol	<i>n</i> -Hex	PX	MCH
Isooctane	1.0	1.4	2.9	5.9	5.0	3.2	8.1
<i>o</i> -Xylene	0.9	5.2	7.6	—	9.4	8.3	14.2
Toluene	0.8	15.3	19.1	26.4	23.2	20.6	37.0
<i>p</i> -Xylene	0.6	11.7	15.3	—	19.4	17.2	29.0
Methylcyclohexane	0.3	14.3	13.5	17.2	17.5	16.0	28.9
Relative values							
Isooctane		1	2.07	4.1	3.58	2.28	5.78
<i>o</i> -Xylene		1	1.46	—	1.81	1.6	2.73
Toluene		1	1.25	1.73	1.52	1.35	2.42
<i>p</i> -Xylene		1	1.31	—	1.66	1.47	2.48
Methylcyclohexane		1	0.95	1.2	1.21	1.12	2.02

TABLE XI
Effect of Treating Solvent Type on Selectivity Characteristics of
Polypropylene ($T = 40^{\circ}\text{C}$)

Permeant	Selectivity Q_i/Q_j					
	Untreated film	Treating solvent (at 60°C)				
		i-Oct	Tol	<i>n</i> -Hex	PX	MCH
MCH/i-Oct	10	4.64	2.9	3.5	4.95	3.58
Tol/MCH	1.1	1.42	1.4	1.32	1.29	1.27
Tol/i-Oct	11	6.58	4.5	4.63	6.37	4.26
PX/OX	2.25	2.08	—	2.02	2.08	2.04

tion that the solvating molecules present during annealing function as "templates" which control the intercrystalline spacing in the polymer. Polypropylene films treated with isooctane (the largest conditioning molecule used) exhibit low permeabilities to all permeants and good selectivities. Conversely, toluene-treated membranes, which according to Choo's model would have been expected to contain narrow "spacings" (due to toluene's small cross-sectional area), actually are more permeable than those modified in isooctane. The transport properties of *p*-xylene and *n*-hexane-modified films also seem to fit the inverse relationship between treating molecule size and permeability. However, solvent-annealing in methylenecyclohexane (the largest molecule next to isooctane) yields a film which is more permeable than all the other films treated at 60°C , indicating that there is at least another factor in addition to the dimensions of the treating molecule which influences the morphology of the treated film. A model is presented in the following section to explain the observed variation of polypropylene transport properties with treatment conditions.

Model for the Solvent-Annealing of Polypropylene

In arriving at a model to explain the enhanced permeation and reduced selectivity exhibited by treated polypropylene films, it has been useful to distinguish two different steps in the solvent annealing process: The first is a partial melt-out of the crystalline portion of the polymer; the second is recrystallization.

Melt-out. A portion of the crystalline phase is melted-out at the temperatures of solvent treatment (60 – 100°C) even though the melting point of polypropylene is 176°C . Several factors contribute to this melting. Small and imperfect crystallites whose high surface-free energy contributes to their melting at low temperatures (this is reflected in the broad melting region obtained in differential scanning calorimeter plots); the presence of solvent which lowers the chemical potential of the molten phase and thus establishes a lower equilibrium melting temperature; and finally, the presence of some atactic material which may further depress the melting point. Data on the dissolution temperatures of polypropylene samples immersed in various organic liquids (Table XII) demonstrate the marked reduction in

melting point (over 70°C) which occurs in the presence of solvent. These data suggest that, at the treatment temperatures which are only a few degrees below the corresponding dissolution temperatures, a substantial portion of the crystalline phase does melt out and that, during subsequent recrystallization accompanying cooling and solvent removal, the opportunity exists for significant crystalline texture modification. Of course, the higher the treatment temperature or the greater the compatibility of the modifying solvent with the polymer, the greater is the initial melt out and the greater the potential for structural changes.

TABLE XII
Dissolution Temperature of Polypropylene in Organic Solvents^a

Solvent	$ \delta_s - \delta_p $, (cal/cc) ^{1/2} ^b	$T_{\text{dissol.}}$, °C
Cyclohexane	0.1	85
Methylcyclohexane	0.3	94
<i>p</i> -Xylene	0.6	102
Toluene	0.8	105
Isooctane	1.0	100 (boil before dissolution)

^a Melting point of polypropylene 176°C.

^b δ_s = solubility parameter of solvent; δ_p = solubility parameter of polypropylene = 8.1 (cal/cc)^{1/2}.

Recrystallization. With a portion of the crystalline phase melted at a temperature below the thermodynamic melting temperature, there exists a driving force for crystallization. Crystallization in the presence of "impurities" (i.e., noncrystallizable species such as solvent or atactic molecules) is conducive to dendritic growth, since the "tip" of a growing crystal is within easier reach of crystallizing molecules, whereas the sides of the crystal are exposed to impurities (which have been rejected from growth fronts), and therefore their growth is retarded. Under these conditions a fibrous habit is established which is made up of crystalline lamellae or fibrils, which is characteristic of spherulitic structure including that of polypropylene.

It can be readily appreciated that the mobility of the impurity as it diffuses away from growth fronts, will be influential in determining the texture of the polymer. Keith and Padden¹³ have shown that spherulitic structure, characterized by a length parameter L , is related to the diffusion coefficient in the melt D and the rate of advance of a growing crystal G as follows:

$$L = D/G \quad (8)$$

L represents the width of spaces between crystalline lamellae (fibrils) and serves as a gauge of fibril diameter. Thus a fine structure is characterized by thin, highly-branched fibrils (low L), whereas a spherulite whose lamellae and spacing are relatively large is termed coarse.

The permselectivity of a fine spherulite would be expected to be different from that of a coarse one. In a fine matrix the amorphous portion of the polymer (in which sorption and diffusion occur) should be rather constrained because the proximity of adjacent fibrils increases the chances of having chains "trapped" between crystallites and thus the resulting matrix is restrained. Under these conditions fluid transport would be expected to be hindered, and the selectivity toward molecules of different dimensions would be good.⁷ On the other hand, in the coarser structure, intercrystalline bridging is less likely because of the relatively larger distances between lamellae and thus, the constraint level is lower and sorption as well as diffusion would be enhanced.

It is possible to use eq. (8) to assess the effect of the treating solvent molecule properties on the morphology of solvent-annealed films. The intrinsic crystalline growth rate of polypropylene during solvent treatment at a given temperature, in either toluene, isooctane, or *p*-xylene can be deemed approximately the same. This follows from the fact that the solubilities of these solvents in polypropylene were shown to be similar and thus the extent of supercooling should also be similar. Therefore, diffusion rate in the melt becomes the dominant factor determining L .

It was demonstrated that diffusivity is higher for molecules with smaller cross-sectional areas (Fig. 4), i.e. $\bar{D}_{\text{tol}} > \bar{D}_{\text{PX}} > \bar{D}_{\text{i.oct}}$. Thus, L would be larger (and spherulitic structure "coarser") for the film annealed in the more mobile solvent (since $L = D/G$). Relating this to the permselective properties of treated films, one would anticipate a more permeable, less discriminating structure for toluene-modified films compared to either *p*-xylene or isooctane-treated films. Transport data shown in Table X support this contention.

The high flux rates exhibited by methylenecyclohexane-treated films (at 60°C) can be explained, in spite of the relatively large dimensions of this solvent, if one notes the high solubility of methylenecyclohexane in polypropylene which can promote the development of coarse spherulites. At higher solvent concentrations diffusivity is higher. Moreover, Keith and Padden indicate that in the presence of solvent, polypropylene spherulitic growth rate is inhibited;¹³ both these factors contribute to a large value of L .

The high selectivity and low flux rates exhibited by the "original" untreated hot-cast film may be attributed to a fine spherulitic structure which results, in part, from the presence of impurities (i.e., atactic and low molecular weight polymer molecules) whose diffusion coefficient is low. During solvent annealing the smaller interfibrillar crystallites (which contribute most to amorphous phase constraint) melt out and recrystallize in a configuration which yielded a coarse structure.

Time-Dependent Vapor Transport in Polypropylene

Although steady-state liquid transport in polypropylene is ostensibly normal, vapor transport through polypropylene film at 40°C was found to be non-Fickian, i.e., diffusivity was time-dependent. Evidence suggesting

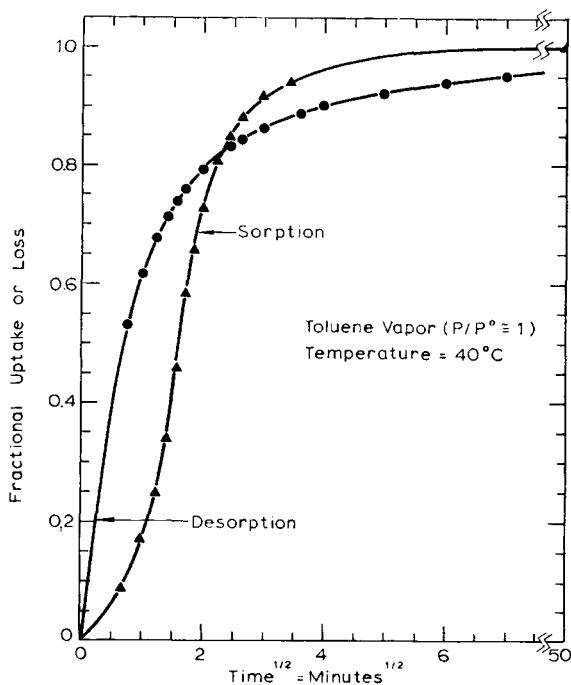


Fig. 8. Typical sorption in hot-cast polypropylene.

this is presented in Figure 8, which depicts a typical plot of vapor sorption and desorption in polypropylene. Contrary to what occurs in systems which are not time-dependent, desorption is shown to be faster than sorption; the sorption and desorption curves intersect, and the sorption curve has a sigmoidal shape. Furthermore, integral diffusivities as estimated from steady-state measurements (\bar{D}_Q) were found to be higher than values calculated from transient methods (\bar{D}_{av}) (Table XIII).

TABLE XIII
Integral Diffusivity in Polypropylene as Determined By Two Different Methods (40°C)

Permeant	Steady-state method ($\bar{D}_Q = Q_c/C \times 10^7$) ^a			Transient Method $\bar{D}_{Av} = 1/2(\bar{D}_s + \bar{D}_d) \times 10^7$		
	Untreated	PX ₈₀	PX ₁₀₀	Untreated	PX ₈₀	PX ₁₀₀
Toluene	3.7	9.1	12.6	1.4	3	3.3
Methylcyclohexane	3.1	5.5	8.2	1.1	1.6	2.4
Isooctane	0.5	2.7	5.9	0.6	1	1.6

^a Where C denotes sorption at vapor saturation ($a = 1$).

Time-dependent diffusion has usually been reported for permeation of solvating molecules in a polymer below its glass transition temperature.¹⁵ In polypropylene all the measurements were made at 40°C, which is above

the glass transition temperature, yet the observed time dependency is similar to that in glassy polymers. It is probable that the restraining nature of the crystallites in the polymer is responsible for this behavior.

Two mechanisms are prevalent in explaining time-dependent transport.¹⁶ One involves changes in polymer morphology occurring over a finite time interval, the other relates to the establishment and relaxation of an internal stress set up in the polymer as a result of the asymmetric swelling of the matrix at the solvated polymer-dry polymer interface.

It is thought that, in the case of polypropylene, the mechanism of stress relaxation is more appropriate in explaining the data obtained. The fact that time effects do occur in solvent-annealed samples in which significant further morphological changes are unlikely to occur at the temperature of diffusion, suggests that a "permeation-treatment mechanism" cannot be of primary importance in this case.

The measured diffusivity represents the equilibrium diffusivity only if the time necessary for determining the diffusion constant is large compared to the time needed for molecular relaxation to occur. Several factors are important in establishing if the calculated diffusivity does indeed represent the true steady state value. It has been shown¹⁶ that time-dependent diffusion is more likely to be manifested in systems in which thin membranes are used; the magnitude of the diffusivity is high, and there exists an exponential dependence of diffusivity on concentration. It may be that the observation of time dependent diffusion during this research was due to the fact that these conditions existed, to various extents, in the polypropylene systems studied. Film thickness was usually less than 5 mil and the exponential concentration-diffusivity relationship is shown in Figure 8. As can be seen in the data presented in Table XIII, when diffusivity was low, as with isooctane in untreated films, time effects are not appreciable ($D_Q = D_{av}$). On the other hand, for higher diffusivity values obtained with either toluene and *p*-xylene or in the case of treated films, $D_Q \neq D_{av}$, indicating time-dependent diffusion.

In summary, it has been found that polypropylene membranes exhibit inherent selectivity for methylecyclohexane and toluene over isooctane and for *p*-xylene over *o*-xylene. Hot cast polypropylene film ($\rho = 0.9050$ g/cc) is more permeable and selective than linear polyethylene toward the xylene isomers.

Concerning the separate components, diffusion and sorption, of the permeation flux Q , there is a logarithmic dependence of diffusion coefficient in polypropylene on the cross-sectional area of the penetrant. Sorption in the polymer increases as the absolute difference in the solubility parameter of the polymer and solvent decreases. Considering permeation fluxes per se, a marked enhancement (up to 15-fold) of permeation rate through polypropylene may be achieved by solvent-annealing films at temperatures of 60–100°C. Increased permeation, however, is usually accompanied by reduced permselectivity of the film toward the organic liquids studied.

These results are explained by the alteration of the polymer micro-

structure subsequent to solvent-annealing, resulting from an initial partial melt-out of the crystalline phase of the polymer followed by recrystallization in the presence of solvent. Crystallization in presence of more mobile treating molecules (e.g. toluene) produces a coarse spherulite (e.g., a spherulite with wide interfibrillar spacings), which is more permeable but not as selective as those present in a film obtained by treatment with a less mobile impurity such as isooctane.

The diffusion of organic vapors in polypropylene film at 40°C is time-dependent, as evidenced by the unsteady-state kinetic data obtained. The time effects are believed to be a manifestation of slow relaxation processes taking place within the polymer microstructure in response to swelling stresses.

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References

1. N. N. Li, R. B. Long, and E. J. Henley, *Ind. Eng. Chem.*, **57**, 18 (1965).
2. R. P. de Filippi, Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1962.
3. C. Y. Choo, Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1959.
4. A. B. Krewinghaus, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1966.
5. J. Crank, *The Mathematics of Diffusion*, Oxford Univ. Press, London, 1956.
6. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 393 (1961).
7. R. W. Hausslein, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1964.
8. E. P. Moore, Jr. (Hercules Inc., Wilmington, Delaware, personal communication (August 26, 1965)).
9. G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Amer. Chem. Soc.*, **77**, 1708 (1955).
10. W. W. Brandt, *J. Phys. Chem.*, **63**, 1080 (1959).
11. W. Wuerth, Sc.D. Thesis, Massachusetts Institute of Technology, Department of Chemical Engineering, Cambridge, Massachusetts, December 1967.
12. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953.
13. H. D. Keith and F. J. Padden, Jr., *J. Appl. Phys.*, **35**, 1270, 1286 (1964).
14. R. B. Long, *Ind. Eng. Chem. Fundamentals*, **4**, 445 (1965).
15. G. S. Park, *Trans. Faraday Soc.*, **48**, 11 (1952).
16. J. Crank, *J. Polym. Sci.*, **11**, 151 (1953).

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