

Controllably Crazed Polystyrene: Morphology and Permeability

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Synopsis

The effects of *n*-heptane and heat treatment on the structural and transport properties of polystyrene films (biaxially oriented and unoriented) were studied to determine whether these treatments improve the film as selective barriers for separation of molecules differing only slightly in size and shape. *n*-Heptane treatment of biaxially oriented polystyrene produces a sandwich structure composed of expanded, crazed, surface layers surrounding an apparently unaffected central core. The crazed layers contain a continuous network of interconnected channels. The core provides the total resistance to gas permeation, hence, the overall effect of *n*-heptane treatment is fabrication of a thinner more permeable membrane. By restricting the stress-cracking treatment to one face of the film, it should be possible to make high flux, anisotropic membranes—a type of membrane which is required for successful development of membrane separation processes. *n*-Heptane treatment of cast, annealed polystyrene results also in a crazed polymer, but the crazing is in the form of spherical voids, and the films, even with a residual uncrazed core, are too weak to be useful as separation membranes. The crazing process in both types of polymer specimens is characteristic of case II non-Fickian diffusion in which the kinetics are apparently controlled by polymer relaxation processes. Sorption of isopentane into cast, annealed polystyrene does not cause visible crazing but the kinetics are again non-Fickian. Desorption of isopentane into *n*-heptane-treated polystyrene releases the appreciable residual *n*-heptane in the film which could not be removed by long-term exposure to vacuum. Analysis of $D(0)$ values for isopentane in *n*-heptane treated films indicates that the polymer surrounding the visible voids in the film is essentially unaltered polystyrene with only a small fraction of the voids being interconnected by open channels.

INTRODUCTION

The rates of permeation, through a given polymeric membrane, of two or more molecular species differing only slightly in size, shape, or chemical nature, are found often to differ significantly in magnitude. This difference or selectivity may be exploited to provide a process for separating mixtures of two or more very similar molecular species. Although polymers as a class of materials exhibit permselectivity, modification of commercially

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available films to increase permeability or permselectivity is necessary to make membrane separation a commercially feasible process.

There are numerous citations in the literature describing attempts to alter the physical or physicochemical structure of polymer membranes to improve their properties as permselective barriers; however, almost all of these techniques involve an elaborate membrane fabrication scheme frequently employing complex casting procedures.¹⁻³ Recently, in this Department, work has been directed toward the simpler approach of solvent treating or conditioning commercially available plastic films in order to render them more permeable or more permselective. This conditioning has involved controlled swelling in suitable organic liquids for controlled times at various temperatures.^{4,5} Until this present work, the conditioning process has been used solely on microcrystalline rubbery polymers (polyolefins). Rubbery polymers do not exhibit the same degree of permselectivity as their glassy counterparts,⁶ and the relatively rapid relaxation processes peculiar to rubbery polymers, accelerated by the permeation of plasticizing molecules, may deteriorate the structural rearrangements imparted to the membrane by conditioning.

Loeb⁷ has produced a modified cellulose acetate, reverse osmosis membrane which exhibits high water flux rates and retains the same selectivity as cast cellulose acetate, presumably because it consists of a very thin, consolidated surface layer supported by a relatively permeable, expanded polymer substrate. Michaels⁸ has reported the development of similar structures based on polyelectrolyte complex resins. The demonstrated ability to prepare anisotropic, permeable, and selective films, and the stimulation of this development on the industrial exploitation of membrane separation processes, motivated this present study.

The objective of this investigation was to establish whether a glassy amorphous polymer, when subjected to controlled solvent and/or thermal treatment, would undergo changes in gas and vapor permeability and permselectivity which might be utilized in membrane separation processes. The polymer selected for study was polystyrene; treatment involved immersion in liquid *n*-heptane at controlled temperatures for specified time periods, followed by controlled *n*-heptane removal. Changes in polymer structure consequent to treatment were determined by (1) measurement of sorption, diffusion, and permeation of gases and vapors in the polymer by steady-state and unsteady-state methods; (2) measurement of polymer density by displacement methods, and (3) light microscopic examination of membrane surfaces and cross-sections.

EXPERIMENTAL

Materials

Biaxially oriented polystyrene (Trycite) was supplied by the Dow Chemical Company, Midland, Michigan, in 2, 7¹/₂, and 10 mil thicknesses. The film was used as received for studies of biaxially oriented film.

Cast films were made by dissolving Trycite in methylene chloride to produce a solution which was approximately 25 wt.-% solids. This lacquer was cast on a glass plate with a uniform gap casting bar set at 6 mils to provide unoriented, cast film. The resulting film was subsequently annealed at 110°C. for 15 min.

Argon (minimum purity 99.99%) was passed through a CaSO_4 bed and then into the gas permeation cells; 99+ mole-% *n*-heptane, isooctane, and 2-methylbutane (isopentane) were used in the course of this investigation. These liquids were subjected to repeated freeze-thaw cycles to remove dissolved gases before introducing these penetrants into the vapor sorption apparatus. *n*-Heptane is an active stress cracking agent for polystyrene at temperatures in excess of 30°C. This behavior is quite typical of normal aliphatic hydrocarbons. Conversely, branched aliphatics, including isooctane and isopentane, are more inert toward polystyrene, and the latter were chosen as the extracting liquid and the model penetrant, respectively.

Controlled Solvent Treatment of Films

A 2-mil biaxially oriented film was immersed in *n*-heptane overlaying a pool of mercury maintained at constant temperature for a specified time period. The treated films were subsequently extracted with isooctane at 0°C. for 15 min. and then allowed to dry at ambient laboratory conditions.

Similarly, cast, annealed films were treated in *n*-heptane maintained at constant temperature for a specified time period; at the end of the period, the treatment cell and contents were carefully immersed in an ice-water slurry to rapidly quench the rubbery film. The films were then immersed in isooctane at 0°C. for 15 min. and later air-dried.

Apparatus and Procedure

Argon permeability measurements were carried out in cells designed by Dr. Robert Park of the Dow Chemical Company, Midland, Michigan. The method consists of applying a static pressure drop across the supported membrane and following the consequent advance of a water slug as a function of time in a uniform bore capillary attached to the downstream side of the cell.

A quartz helical spring with a sensitivity of 1.915 mm./mg. was used to measure weight changes due to sorption or desorption of isopentane in cast, annealed polystyrene. The spring extension was measured with an Optical Reader, #184, supplied by Microchemical Specialties, Berkeley, California; the precision of the relative weight measurement, determined with this extremely sensitive cathetometer, was $\pm 2 \mu\text{g}$.

For a sorption run, an amount of isopentane sufficient to maintain a partial pressure of 500 mm. mercury was bled into the thermostatted, evacuated spring case. The consequent spring extension was measured as a function of time to determine the sorption kinetics. Similarly, for a desorption run, the spring case was rapidly evacuated and readings resumed as a function of time.

The cross-sections of *n*-heptane-treated films were observed by light-microscopic examination of microtome-sectioned films. The optical properties of film surfaces were observed by means of dark-field microscopic examination of epi-illuminated membrane surfaces.

The density of expanded cast, annealed films was determined by a water displacement technique; the film thickness was then determined by measuring the film weight and film area and dividing the calculated film volume by the film area.

RESULTS AND DISCUSSION

Biaxially Oriented Polystyrene

Crazing. Treatment of biaxially oriented polystyrene with *n*-heptane produces a white, opaque, expanded membrane characteristic of a crazed glassy polymer. Light microscopic examination of membrane cross-sections reveals that treated film is composed of striated, expanded outer surfaces surrounding an apparently unaffected central core with a sharp boundary separating the phases (Fig. 1). Treatment for longer times results first in reduction of the core thickness and then in shrinkage of the film in the plane of the sheet due to the inability of the remaining central core to support the stresses imposed by the collapsing biaxially oriented polymer network. Figure 2 indicates that the rate of advancement of the crazed polymer front on immersion in *n*-heptane is essentially constant under isothermal conditions.

These observations are consistent with those made by Alfrey et al.⁹ in a recent review of what these authors term case II diffusion in glassy polymers. Case II diffusion of a solvent into a glassy polymer results in swelling stresses being developed which are usually of such magnitude and/or duration to cause localized or complete fracture of the specimen. While the phenomenology of case II diffusion is clearly set forth in the above paper, there are a number of observations made during the course of the present work that amplify the significance of this unusual interplay of molecular diffusion and polymer mechanics.

Case II behavior was observed over the range of immersion temperatures studied (35–50°C.) The residual core was approximately 10 μ thick at the onset of shrinkage over this same temperature range. It was convenient, therefore, to consider the reciprocal of the time for the onset of shrinkage as the rate of penetrant front movement. By plotting the reciprocal time for shrinkage versus reciprocal absolute temperature (Fig. 3), it is observed that the process follows an Arrhenius type rate law with a high apparent activation energy of ca. 57 kcal./g.-mole. This is within the range of activation energies estimated for stress relaxation in polystyrene (20–300 kcal./g.-mole). The magnitude of this activation energy suggests that relaxation of the oriented polymer, initiated by swelling fracture at the advancing boundary, is the rate-limiting step of the crazing process.

Gas Permeability. The permeability of untreated, biaxially oriented

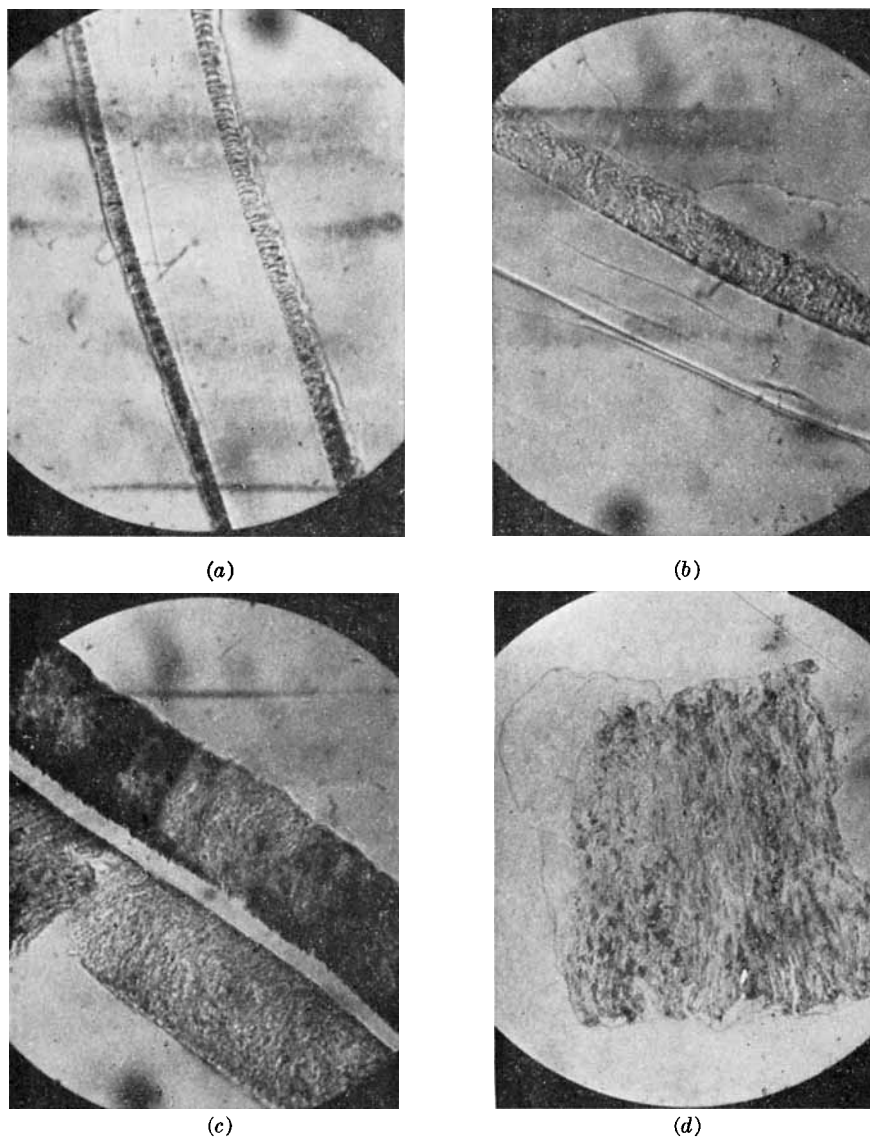


Fig. 1. Cross-sections of 2 mil Trycrite (biaxially oriented) film treated with *n*-heptane (magnification: 250 \times): (a) treated on both sides at 35°C. for 20 min.; (b) treated one side at 40°C. for 15 min.; (c) treated both sides at 35°C. for 92 min.; (d) treated on both sides at 40°C. for 25 min.

film to argon is presented in Figure 4. The scatter in the Arrhenius plot for the 2 mil Trycrite is slight, and the slope of the line corresponds to an activation energy of 3.6 ± 0.8 kcal./g.-mole at the 95% confidence level. The scatter in the data for 7 $\frac{1}{2}$ and 10 mil Trycrite is much more severe; however, the data indicate that the permeability coefficient increases with increasing film thickness. This effect of film thickness on the permeability

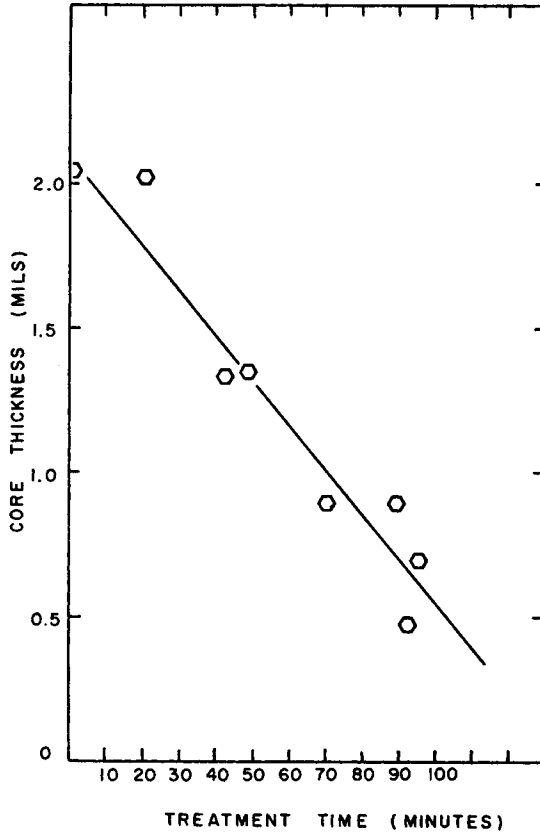


Fig. 2. Residual core thickness of 2 mil Trycrite (biaxially oriented) film as a function of immersion time in *n*-heptane maintained at 35°C.

coefficient may be a manifestation of a membrane whose surface layers offer a higher resistance to gas transport than the central core. The presence of densified surface layers in biaxially oriented film seems quite reasonable, since cooling of the freshly oriented film at the terminal stage of fabrication presumably can result in case hardening of the surfaces. During cooling, the central thermally expanded region of the film remains in tension, the contiguous surfaces are thus in compression; this compression results in a density increase (or free volume reduction) in the surface.

Figure 5 shows the graphical representation of the effect of treatment time (at constant temperature, 35°C.) on the argon permeability coefficient of treated, biaxially oriented films. These permeabilities are calculated on a basis of untreated film thickness. Two effects are striking: (1) the activation energy for permeation does not seem to be affected by the treatment; (2) increase of time of treatment results in an increased flux of penetrant across the membrane. These data suggest that the unaffected core offers the total resistance to diffusion and behaves like unmodified biaxially oriented polystyrene while the swollen, striated surface layers

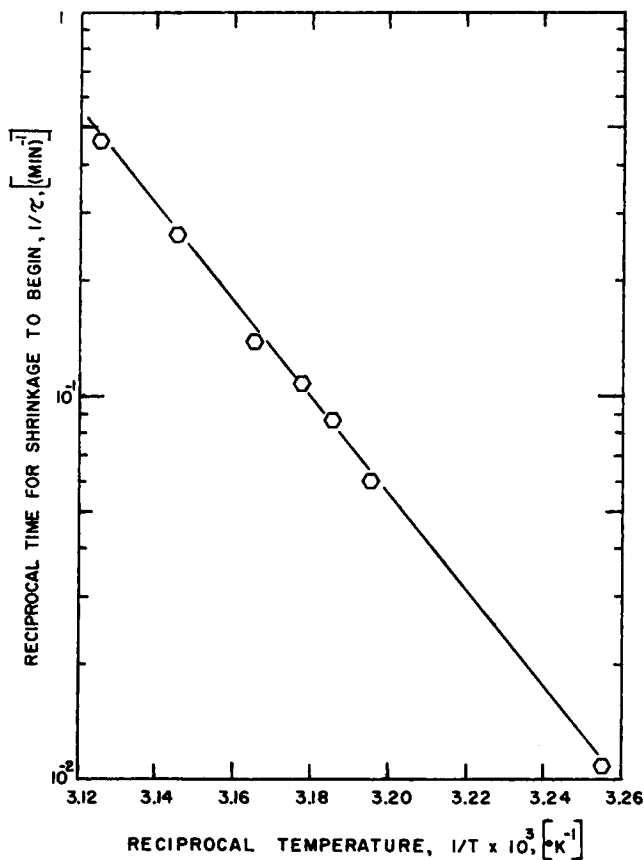


Fig. 3. Arrhenius plot of reciprocal time for incipient shrinkage of 2 mil Trycrite (biaxially oriented) film as a function of *n*-heptane temperature.

offer negligible resistance to gas transmission and are apparently composed of interconnected channels.

Further support for the idea of case-hardened surfaces on the biaxially oriented polymer is obtained from a cross plot of argon permeability coefficients versus treatment time at constant treatment and permeation temperature (Fig. 6). Between 10 and 63 min., the permeability increases monotonically with time, which is consistent with the data on core thickness versus time shown in Figure 2. Presumably, however, the rapid increase in permeability at short treatment times is indicative of the destruction of the densified, low permeability surface layers.

In summary, the data relating to treatment and gas transport in biaxially oriented polystyrene suggest that immersion of Trycrite in *n*-heptane produces a structure containing an unaffected central core surrounded by expanded, highly permeable polymer. Treatment, therefore, leads to enhanced permeability without alteration in permselectivity. The extent

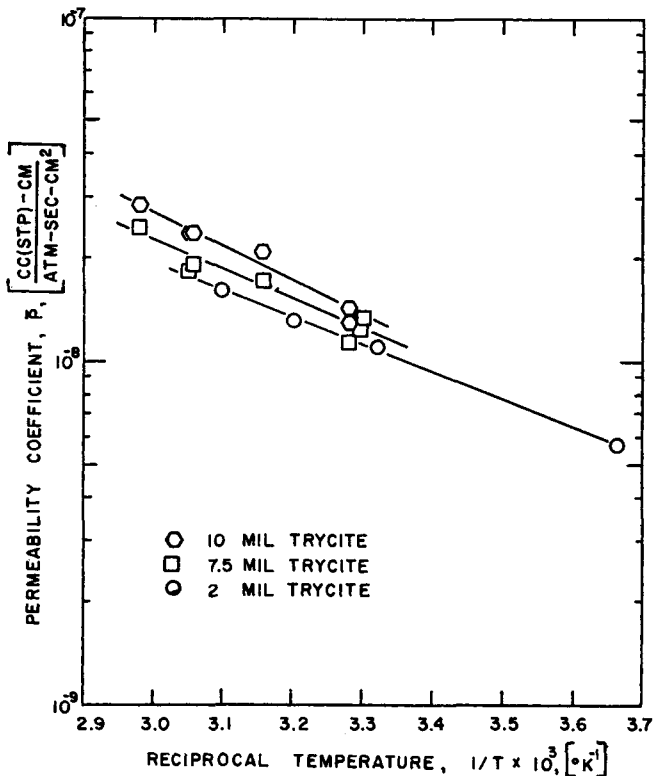


Fig. 4. Effect of film thickness of Trycite (biaxially oriented) polystyrene on permeability to argon.

to which biaxially oriented film can be treated with *n*-heptane before total collapse due to shrinkage occurs, is limited to conditions yielding a core thickness somewhat less than 10μ . This is not appreciably thinner than commercially available film, and the process does not, therefore, lead to significantly improved membranes for gas or vapor separations. However, this work does suggest that treatment with other solvents which reduce the swelling stress or alter the relaxation process could result in thinner cores remaining intact. Furthermore, treatment of the film from one side to yield a "skinned" anisotropic membrane would lead to more useful structures for a separation process.

Cast, Annealed Polystyrene

Crazing. Unoriented film, when immersed in *n*-heptane for controlled times at constant temperature (above 35°C .) becomes expanded, white, and opaque; however, at long immersion times the film does not shrink but increases in area as well as thickness. The expansion of the film is consistent with the core being under swelling tension which is not offset, in this case, by the collapse of a highly oriented polymer network. The in-

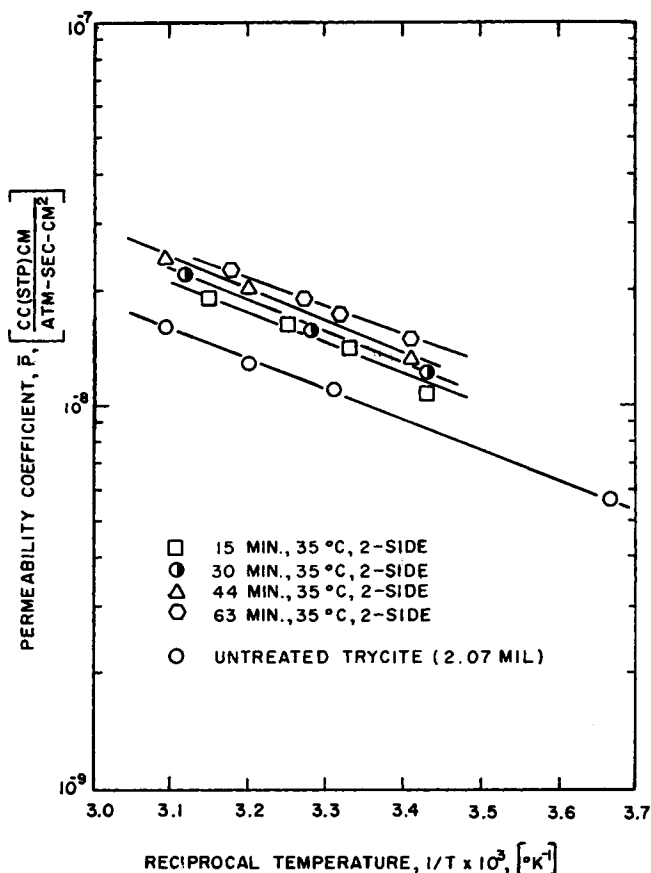


Fig. 5. Permeability of *n*-heptane-conditioned Trycrite (biaxially oriented) film to argon. Permeability values calculated from original (untreated) film thickness.

crease in film area at long treatment times is coincident with the removal of a restraining central core. The response of film density, area, and thickness to immersion in *n*-heptane at 40°C. as a function of time is presented in Figure 7. The change in film area, thickness, and density with time is qualitatively the same at temperatures above 40°C., although the rates of dimensional change are markedly accelerated with increasing temperature.

Photomicrographs of cross-sections of treated, cast, annealed films reveal that a sandwich structure is formed, similar to biaxially oriented film. However, the expanded phase is morphologically quite different from that observed with biaxially oriented material. (See Figs. 8 and 9.) The expanded phase of treated, cast, annealed polystyrene is composed of spherical microvoids (ca. 3 μ in diameter) dispersed in a continuous polymer matrix. The void formation is a consequence of localized swelling fracture of the polymer resulting from concentration gradients developed during treatment. Subsequent plasticization of the polymer surrounding a

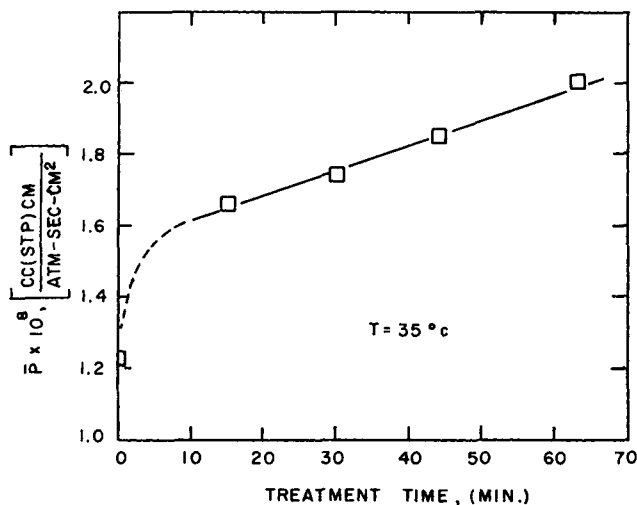


Fig. 6. Permeability of treated biaxially oriented polystyrene to argon as a function of time of *n*-heptane treatment.

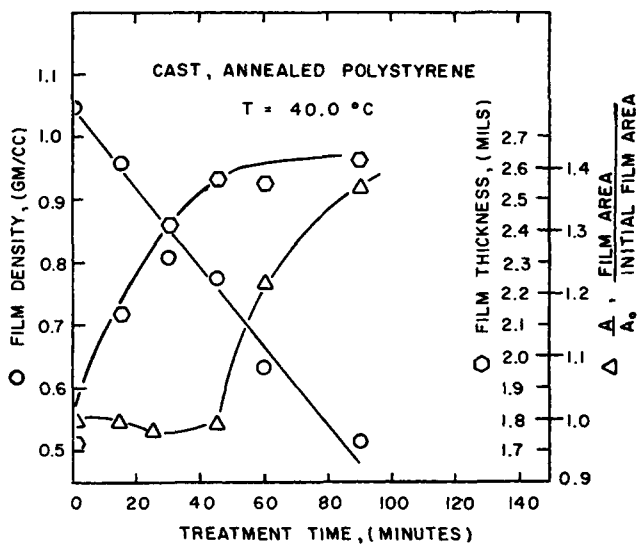


Fig. 7. Plots of (O) film bulk density, (□) thickness, and (Δ) area vs. treatment time in *n*-heptane. (Cast, annealed polystyrene; all measurements at 40°C.)

microfissure and the consequent relaxations of this polymer permit the crack to deform to its more stable spherical shape. Fragmentary quantitative data describing the kinetics of treatment of cast, annealed film suggest that the core thickness again decreases linearly with time consistent with case II diffusion.⁹ The treatment process is also again highly activated; the apparent activation energy is ca. 65 kcal./g.-mole. Thus the treatment processes in both oriented and unoriented film appear to be kinetically similar.

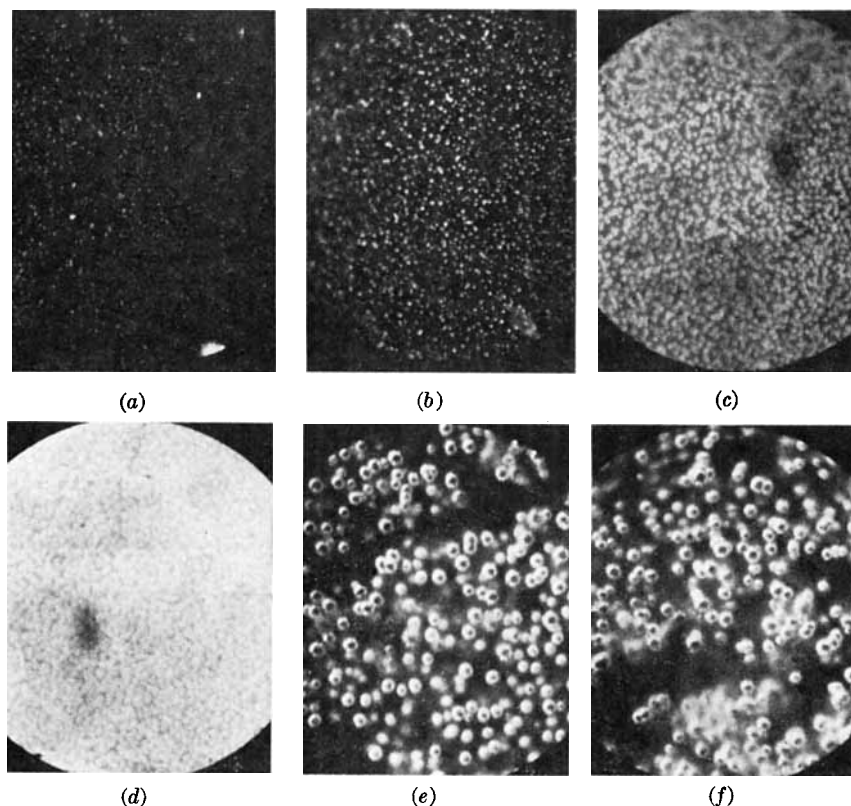


Fig. 8. Surfaces of cast, annealed polystyrene treated with *n*-heptane at 40°C. (dark field epi-illumination) at various treatment times and magnifications: (a) 5 min., 350 \times ; (b) 7 $\frac{1}{2}$ min., 350 \times ; (c) 10 min., 350 \times ; (d) 20 min., 350 \times ; (e) 20 min., 875 \times ; (f) 35 min., 875 \times .

Gas Permeability. Treated, unoriented films are mechanically weak and extremely brittle; these mechanical limitations prevented successful measurement of gas transmission properties, and indicate polystyrene in this form could not be used for preparing separation membranes.

Argon transmission measurements through untreated cast, annealed polystyrene could be made, however, and indicated that cast, annealed films were 30% less permeable than biaxially oriented films while the activation energy was not significantly different for the two films. The difference in permeability of the two films is explained by the effect of orientation as well as the effect of annealing the cast film. The biaxial orientation, followed by rapid quenching, might be responsible for relatively large interchain spacings (high free volume). Annealed films presumably have lower free volume than biaxially oriented films. A rough analogy to the experimental results reported by Craig¹ for the effect of orientation on the selectivity of cellophane dialytic membranes can be drawn. Craig found that in these membranes uniaxial orientation increased selectivity while

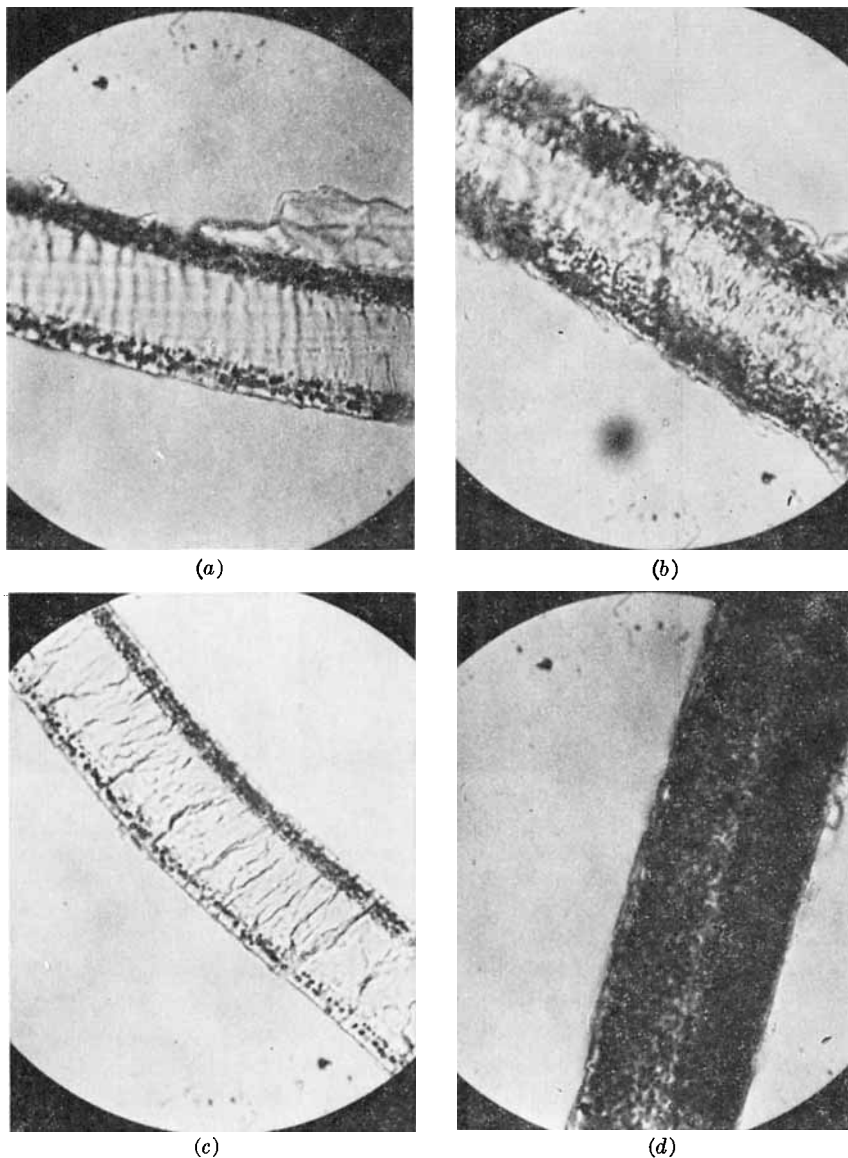


Fig. 9. Cross-sections of cast, annealed polystyrene membranes treated with *n*-heptane (magnification: $350\times$) at various treatment times and temperatures: (a) 20 min., 40°C .; (b) 35 min., 40°C .; (c) 5 min., 45°C .; (d) 25 min., 45°C .

biaxial orientation decreased selectivity relative to unoriented polymer. Craig's observations, of course, reflected changes in a much coarser scale of polymer morphology than the subtle changes in free volume suggested by these polystyrene data.

Vapor Studies. While cast, annealed polystyrene is clearly of little value as a practical permselective membrane, organic vapor sorption was

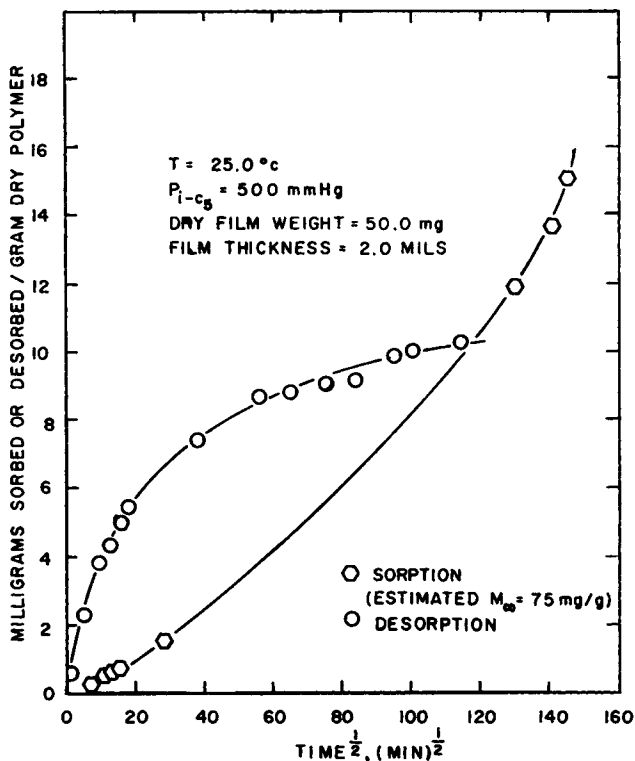


Fig. 10. Sorption and desorption of isopentane in untreated cast, annealed polystyrene.

studied in these specimens to help elucidate the unusual craze morphology noted in *n*-heptane-treated films. Isopentane was chosen as the penetrant since it did not visibly craze the film, and it was hoped it might display Fickian, though concentration-dependent, diffusion in the film. The latter was not the case, however. Had the diffusion been Fickian, the plot of weight uptake versus the square root of time in Figure 10 would have been linear at the low sorptions shown (estimated to be less than 25% of sorption equilibrium) even if the diffusion constant were strongly concentration-dependent.¹⁰ These data give a linear correlation with time to the 0.7 power, and thus, this is also not limiting case II diffusion. In the latter case, the power on time would have been 1.0.⁹ The intermediate power on time suggests that the sorption process is largely controlled by polymer relaxation processes. Isopentane is a poor solvent for polystyrene, incapable of developing appreciable swelling stresses, and the polymer-solvent system was in the vicinity of its glass temperature, thus neither crazing nor limiting case II diffusion behavior were observed.

Desorption of isopentane from the partially saturated cast, annealed film was performed, starting with the film about 25% saturated. Figure 10 shows that the initial isopentane leaving the film does so at a much faster rate than it had originally entered the film, although the process

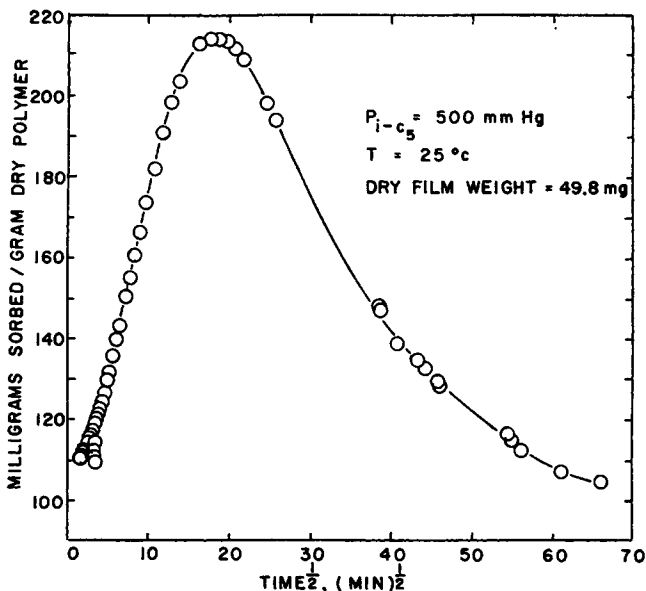


Fig. 11. Sorption of isopentane in treated, cast, annealed polystyrene (treatment conditions: *n*-heptane, 40°C., 90 min.)

slows down appreciably as desorption progresses. Visible crazing of the film during desorption was observed. Presumably the swollen interior of the polymer supports the shrinkage stresses on the outer portions of the film as desorption takes place, leading to a front of microscopically voided film being formed as desorption progresses. It is not clear at this time why the stresses on desorption are sufficient to cause crazing while on sorption crazing does not occur. This must be indicative of steeper concentration gradients existing arising during desorption than during sorption. Nevertheless, these observations are consistent with the general "blushing" of paint and varnish films during rapid desorption of modest to poor solvents, and the comments of Rosen on the fast initial desorption of vapors from polymeric glasses.¹¹⁻¹³ One might again expect this to be an example of case II diffusion with a first-power dependence of desorption on time, but the observed power dependence from the data Figure 10 is about 0.25. This may be a manifestation of the fact that desorption was started before the film sample came to sorption equilibrium so the polymer contained more isopentane near the surface than in the interior.

The sorption and desorption of isopentane was studied in films treated with *n*-heptane at 40 and 45°C.; in both cases, the films were treated sufficiently long to insure complete removal of a residual core. Analysis of sorption and diffusion in treated films is further complicated not only by the presence of spherical microvoids dispersed in a continuous polystyrene matrix, but also by the presence of approximately 10% by weight of residual *n*-heptane in the treated and "dried" films. The films were "dried" by

placing them in a vacuum chamber at 10^{-6} mm. Hg for 10 days. After this rather long desorption period the films contained more than 80% of the originally imbibed *n*-heptane. This near-zero case II diffusion velocity has been cited by Alfrey et al.⁹ as occurring at sufficiently low temperatures for a variety of solvents at unit activity, but presumably a superposition principle applies, and zero diffusion velocity would also be observed at constant temperature at a sufficiently low solvent activity.

The sorption of isopentane goes through a maximum as a function of time suggesting that the sorbing isopentane effectively "unlocks" the trapped *n*-heptane from the confines of the polymer matrix by plasticizing the polymer (Fig. 11). The above sample, thus freed of *n*-heptane, was

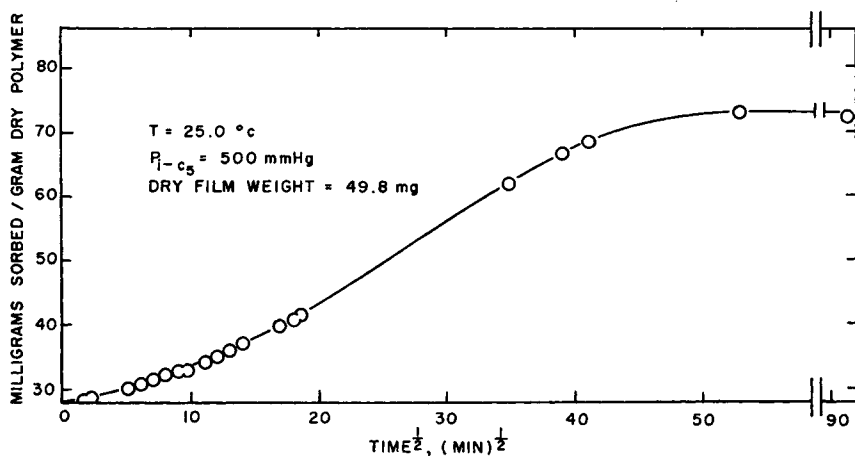


Fig. 12. Resorption of isopentane at 25°C . in treated, cast, annealed polystyrene following initial sorption/desorption run.

placed under high vacuum to desorb the penetrant from the treated polymer. Although approximately 30 mg. of isopentane/g. of polymer remained in the sample when desorption was discontinued, a subsequent resorption with isopentane was carried out until equilibrium was achieved (Fig. 12) followed by a desorption run (see Fig. 13). The resorption and subsequent desorption proceeded normally (although still showing non-Fickian behavior), and the complications which were initially caused by the residual *n*-heptane content do not play a part in the subsequent sorption-cycling.

Diffusion coefficients at zero penetrant concentration could be evaluated from the long-time desorption data¹⁴ for both treated and untreated films. These diffusion coefficients, $D(0)$, do not appear complicated by anomalous, non-Fickian or concentration-dependent effects, hence a comparison of $D(0)$ values in treated and untreated films permits a meaningful analysis of the effect of *n*-heptane treatment on the morphological factors affecting transport properties of cast, annealed films (see Table I).

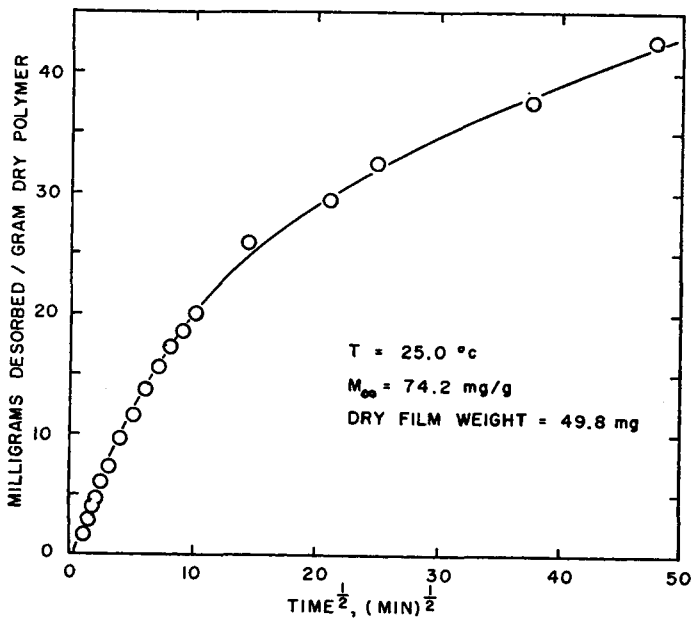


Fig. 13. Desorption of isopentane at 25.0°C. from treated, cast, annealed polystyrene after sorption in Fig. 12.

The diffusion coefficients in Table I increase with increasing void content of the film as would be expected. A theoretical analysis of the effects of the high conductivity, essentially spherical voids on the diffusion constants can be made based on Maxwell's analysis of the electrical conductivity of heterogeneous materials.¹⁵ Assuming the voids are uniform in size, the calculated diffusion constants for the treated films (based on the untreated film value) are lower than the experimental values by factors of 4-6. This may be due to the voids not being entirely monodisperse in size. It may also be due to some interconnection between the visible voids by smaller voids or cracks, but to no degree comparable to the interconnected crazing in the treated, biaxially oriented films. This analysis indicates therefore, that the polymer surrounding the voids in treated cast polystyrene is essentially indistinguishable from untreated polystyrene.

TABLE I
Isopentane Diffusion Coefficients $D(0)$ at Zero Penetrant Concentration in Treated and Untreated Films

Film treatment	Volume fraction voids ^a	$D(0) \times 10^{21}$, cm. ² /sec.
<i>n</i> -C ₇ ; 40°C.; 90 min.	0.45	6.6
<i>n</i> -C ₇ ; 45°C.; 30 min.	0.345	3.3
Untreated	0.0	0.497

^a Determined from density measurements.

The observed reduction in void content in going from *n*-heptane treatment at 40–45°C. is to be expected. Increasing the temperature decreases the swelling stresses and increases the polymer relaxation rate, and both factors would tend to suppress void formation.

CONCLUSIONS

n-Heptane treatment of polystyrene does not appear to be particularly fruitful in making improved barrier membranes for gas or vapor separation processes, although the idea of controllable stress cracking of biaxially oriented polystyrene to form "skinned" anisotropic membrane merits further investigation. The various observations presented on the morphology and kinetics of crazing biaxially oriented and cast polystyrene should help to shed light on the anomalies of diffusion of organic vapors in glassy polymers which are just beginning to be understood and studied systematically by polymer scientists.

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