Effects of Film History on Gas Transport in a Fluorinated Aromatic Polyimide

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Synopsis

The effects of film formation procedures on transport properties are reported for a rigid-chained, fluorinated, aromatic polyimide. Residual dimethylacetamide (DMAC) solvent present in films formed under certain casting protocols produces complexities in the permeation behavior of helium and carbon dioxide. Specifically, helium permeabilities are lower, while those of carbon dioxide are higher, in a film containing 8 wt% residual DMAC than in an annealed film containing < 1 wt% DMAC. Significant differences in transport properties are also observed between films prepared using two different casting techniques. These differences appear to be due to differences in organization of chain segments within films. The results of this study emphasize the considerable care needed in formation and postformation processing of these materials to ensure optimum flux/selectivity properties in such applications.

INTRODUCTION

Several families of glassy polymers have attractive characteristics for application as gas separation membranes.[1-6] Certain polyimides, polyesters, and polyamides, in particular, have been shown by Hoehn to offer unusually high permeabilities, and, especially in the case of some of the polyimides, very high selectivities as well.[2-6] Recent studies indicate the importance of both molecular structure and film history in determining gas transport properties.

Interesting and unusual effects have been observed upon the annealing of some of these polymers. In many cases, annealing has been observed to produce large increases in both the hydrogen permeability and the hydrogen/methane selectivity of these materials.[2] For example, when a fluorinated aromatic polyimide designated 1,5ND-6F** was annealed at 240°C for 6 hours after casting from dimethyl acetamide (DMAC), hydrogen permeability increased almost 100%, while hydrogen/methane selectivity increased by some 650%.[2] These results are unusual in that they do not follow the typical observation regarding annealing. In glassy polymers, sub-T_g annealing has generally been observed to result in decreased permeabilities, due to a densification of the polymer occurring upon annealing. Recent studies of the

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**Prepared from 3,4,3′,4′-diphenylhexafluoroisopropylidene tetracarboxylic dianhydride and 1,5-diaminonaphthalene.

effects of annealing on the gas transport properties of bisphenol-A poly-carbonate[7-10] and of tetramethyl bisphenol-A polycarbonate and sulfone[11,12] support the typically observed case, showing decreased permeabilities and increased selectivities upon annealing near T_g.

The effects observed in the 1,5ND-6F material could stem from the removal of moisture and/or residual solvent from the films during the heat treatment. Such moisture and/or solvent, if present in the films, might act as an antiplasticizer, causing reductions in penetrant sorption levels and mobilities as well as alterations in physical properties such as modulus and T_g.[13-18] Related phenomena demonstrating significant effects on gas transport properties have been documented for the case of various low molecular weight diluents in a variety of glassy polymers.[13-18]

The presence of condensible vapors in the feed has been seen to reduce permeabilities in polyimides[3,4] and bisphenol-A polycarbonate.[19-22] In the case of the relatively inert isopentane vapor, Koros, Chern, and co-workers[19-23] have shown that these reductions can be analyzed in terms of competition of the more condensible vapor molecules for sorption capacity, composed of molecular-scale packing defects, in the nonequilibrium glass. Such behavior, involving relatively reversible sorption/desorption phenomena with small penetrant molecules such as carbon dioxide and methane, is not typically referred to as antiplasticization if the pure component mobility coefficients of the two penetrants still apply in the mixed penetrant feed situation and only competition for sorption capacity occurs.

Additional complexity occurs when a condensible vapor can interact strongly with the polymer, as well as simply compete for sorption sites in molecular-scale packing defects. For example, water vapor is believed to act as a true antiplasticizer in Kapton® polyimide. Reductions in carbon dioxide permeabilities in Kapton® polyimide have been observed in the presence of low relative humidities. In this case, the presence of the water is believed to actually suppress sub-T_g segmental motions, thereby affecting the diffusion coefficients of other penetrants such as carbon dioxide and methane as compared to the dry polymer.[23]

Finally, the observed changes in permeabilities of the 1,5ND-6F material upon annealing could represent the effects of subtle changes in glassy-state packing known to occur as a result of the heat treatment. The rigid and bulky molecular structures of these materials are postulated to prevent close chain packing in the as-cast, unheated films.[2] Heat treatment causes a relaxation of the polymer chains, enabling more chain segments to approach a condition of efficient packing. The concomitant free volume redistribution and overall volume reduction should increase the uniformity of the free volume distribution within the glass. Such a situation could result in a medium having a free volume distribution favorable to rapid transport of small molecules and unfavorable to transport of large molecules.[2] These effects might be expected to be more pronounced for rigid, inherently packing-resistant polymers, such as are represented by 1,5ND-6F.

To study further the relative importance of the various preceding glassy state phenomena, 1,5ND-6F was synthesized, and films were prepared and heat treated following protocols similar to those used earlier by Hoehn.[2] To assess the sensitivity of the material's transport properties to the casting

protocol used, an additional film was prepared using a different casting technique. The permeabilities of the films to different gases were then measured as a function of gas pressure and film history.

EXPERIMENTAL

Consistent with earlier usage,[2-6] the fluorinated polyimide used in this study was designated as 1,5ND-6F. The polymer was prepared from 3,4,3',4'-diphenylhexafluoroisopropylidene tetracarboxylic dianhydride and 1,5-diaminonaphthalene using procedures described elsewhere,[24] and has the repeat unit structure shown below. Films of this polymer were cast using a technique similar to that used earlier.[2] A casting solution of 20 wt% 1,5ND-6F in dimethylacetamide (DMAC) was prepared. Using a doctor knife, films were cast from this solution onto a Pyrex plate heated to 100°C. After the films were drawn, they remained on the plate and were dried at 100°C for 15 minutes; drying for 5 minutes under a cover, followed by 10 minutes under a vented cover. The Pyrex plate was then removed from the hot plate and allowed to cool to room temperature. The film was then carefully removed from the plate. This process yielded films approximately 2 mils thick. One film was air-dried at room temperature for comparison to earlier as-cast samples,[2] while a second film was annealed at 240°C, under a vacuum of less than 50 μm Hg, for 6 h for comparison to earlier heat-treated samples.[2]

To assess the importance of subtle stress-induced orientation of the chains, an alternative casting procedure was also used. A dilute (5% wt) solution of the polymer in DMAC was poured inside a glass ring on a Pyrex plate at 100°C. Enough solution was used to yield a film of approximately 2 mils in thickness. After reaching apparent dryness, the film was carefully removed from the Pyrex plate and annealed in an unconstrained state, under vacuum, at 240°C for 24 h. The almost total absence of orientational stresses and the low viscosity of the casting solution were expected to allow relaxation of any flow-induced orientation occurring in the casting, giving rise to the most disordered arrangement of chains possible. Comparison of this film with the higher viscosity, knife-cast annealed film (for which a higher degree of chain organization was expected) was intended to give insight into subtle organizational effects that might result from differences in casting solution concentration and laydown procedure.

The permeation apparatus and experimental procedures have been described elsewhere.[11,25] Permeation data were taken at 35°C over a pressure

1, 5ND-6F

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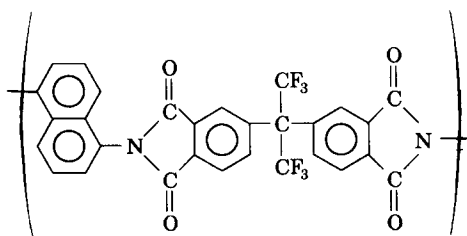
range of 1–20 atm. Helium, carbon dioxide, and methane of at least 99.99% purity were used in the study.

RESULTS AND DISCUSSION

Sorbed Diluent Effects

Figure 1 contains the pure gas permeability results for helium in an as-cast knife-drawn film and in a knife-drawn film annealed at 240°C for 6 h. Figure 2 contains the pure gas permeabilities of carbon dioxide in the same films. It is interesting to note that, in the as-cast film, the carbon dioxide permeabilities are actually higher than the helium permeabilities. Data reported previously for hydrogen and methane illustrating the beneficial effects of heat-treatment are contained in Table I.[2]
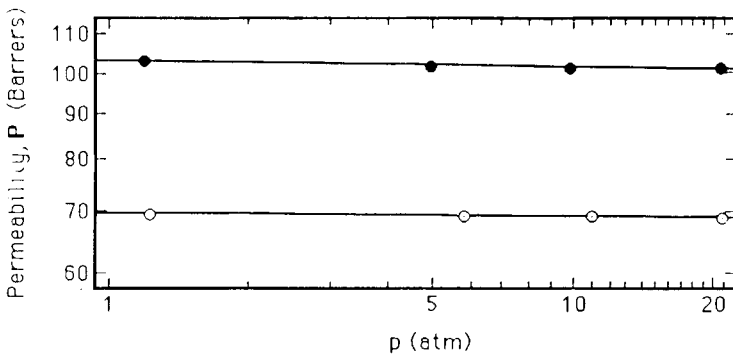
Fig. 1. Helium permeabilities in blade-cast films of 1, 5ND-6F at 35°C: (O) unannealed, (●) annealed 6 h at 240°C.
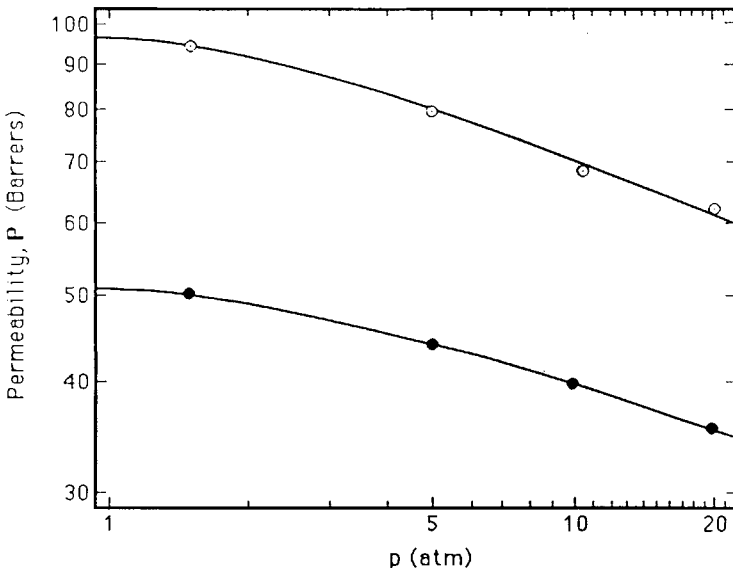
Fig. 2. Carbon dioxide permeabilities in blade-cast films of 1,5ND-6F at 35°C: (O) unannealed, (●) annealed 6 h at 240°C.

TABLE I
Hydrogen and Methane Permeabilities and Ideal Separation Factors for 1,5ND-6F[a]

| History	P_{H_2} (Barrers)	P_{CH_4} (Barrers)	α_{H_2/CH_4}
Knife-drawn, as-cast	57.6	2.34	25
Knife-drawn, annealed 6 h at 240°C	92.9	0.35	270

[a]From Ref. 2; $T = 30°C$.

The increase in helium permeability upon annealing shown in Figure 1 is similar to that previously reported for hydrogen, while the observed decrease in carbon dioxide permeability upon annealing shown in Figure 2 is similar to that observed earlier for methane.[2] In Figures 1 and 2, helium permeabilities increase by roughly 50%, while carbon dioxide permeabilities decrease by roughly 40%–50%, as a result of the 6 h annealing. In Table I, hydrogen permeabilities increase roughly 80–90%, while methane permeabilities decrease 75–80% upon annealing. To probe further the cause of these interesting results, we performed Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC) measurements on samples of the films.

FTIR measurements performed on the two knife-cast films showed a peak in the as-cast film at 2950 cm^{-1} that is not present in the 6-h annealed film, as shown in Figure 3. An IR spectrum of dimethylacetamide[26] shows a peak at 2930 cm^{-1}. Previous experiments have shown us that FTIR can detect the presence of residual DMAC solvent down to a level of about 2 wt%.

DSC scans of samples of knife-drawn films showed the presence of a broad peak in the region of 80–100°C, as shown in Figure 4. This was true for films that had been annealed, although the peak was observed to decrease in size with annealing time (also shown in Fig. 4). For each sample, after the initial heating cycle, the films were quenched and reheated through two more cycles during which no such peaks were observed. Such behavior is typical of the presence of residual solvent which is driven off in the first heating cycle. The DSC experiments are run with dry N$_2$ stream flowing past the sample. Thus, the sample is effectively exposed to a zero partial pressure of DMAC, equivalent to a vacuum in terms of DMAC removal. Hence, the devolatilization is observed at lower temperatures than the boiling point at atmospheric pressure (166°C).

Samples of the two knife-drawn films were further dried at 240°C for 48 h in a vacuum oven under a 50 μm Hg vacuum. The samples were weighed before and after being dried. The sample of the as-cast film underwent a weight loss of about 8 wt%, while the sample that had previously been annealed for 6 h lost less than 1 wt%. FTIR measurements performed on this material indicated that it had undergone complete imidization, with no residual amic acid or anhydride being present. Thus, the weight loss cannot be attributed to further imidization occurring as a result of the elevated temperature.

The observed weight losses, along with the progressive reduction of the DSC peak upon annealing, suggest that residual solvent was present in a significant amount in the air-dried film, and, to a much lesser extent, was still present in the 6-h annealed film. The FTIR results present even stronger

1,5ND-6F

as-cast

annealed at 240°C
for 6 hours

dimethylacetamide (25)
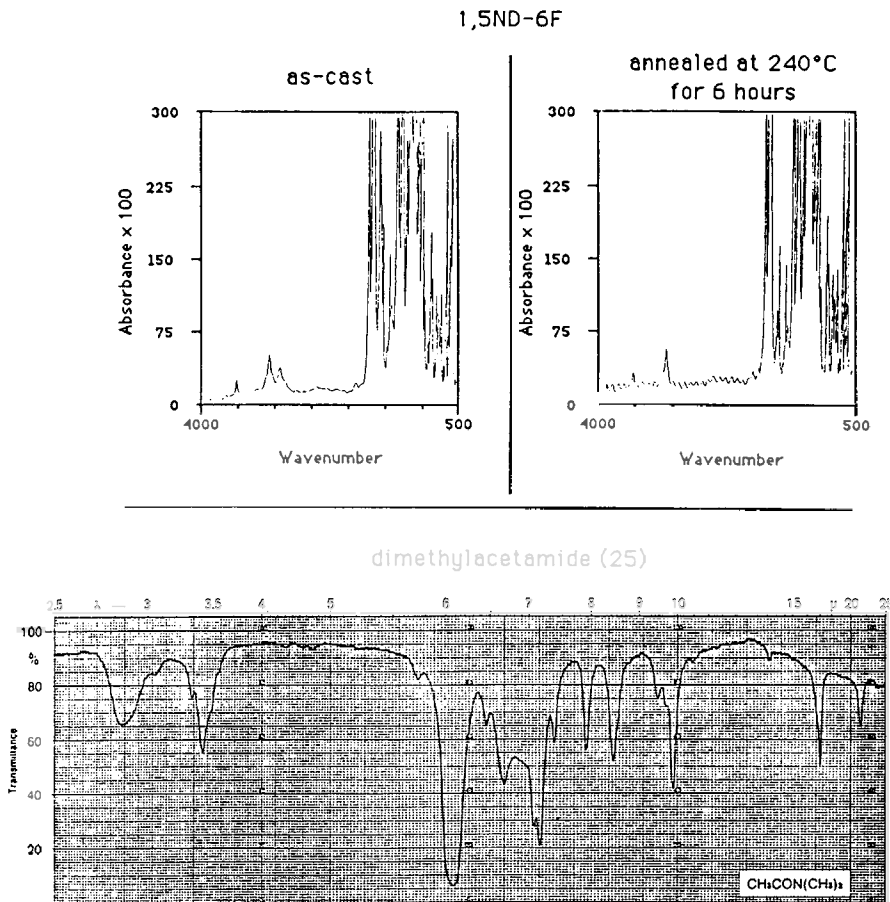
evidence of the presence of residual DMAC at a significant level in the as-cast film.

The DSC results and weight loss measurements could also be taken to indicate the presence of some moisture in the films. The films were cast at 100°C so that any moisture that might have been sorbed in preparing the casting solution would be driven off. To test how much water was likely to be absorbed from the atmosphere prior to permeation, two small film samples were prepared. After casting, each was annealed for five days at 240°C to drive off any residual solvent or moisture. One sample was then exposed to room conditions for 14 days, gaining negligible (< 1 wt%) water. The other sample was immersed in water for 14 days and gained only 1.4 wt% water. DSC scans performed on both films were essentially featureless, as shown in Figure 4. These experiments show that, if water were present in the films, it was only in trace amounts, and that the majority of the 8% weight loss during heat treatment represented the removal of residual DMAC.

The results shown in Figures 1 and 2 and those reported earlier[2] can be rationalized in terms of the effects of removing residual DMAC from the films
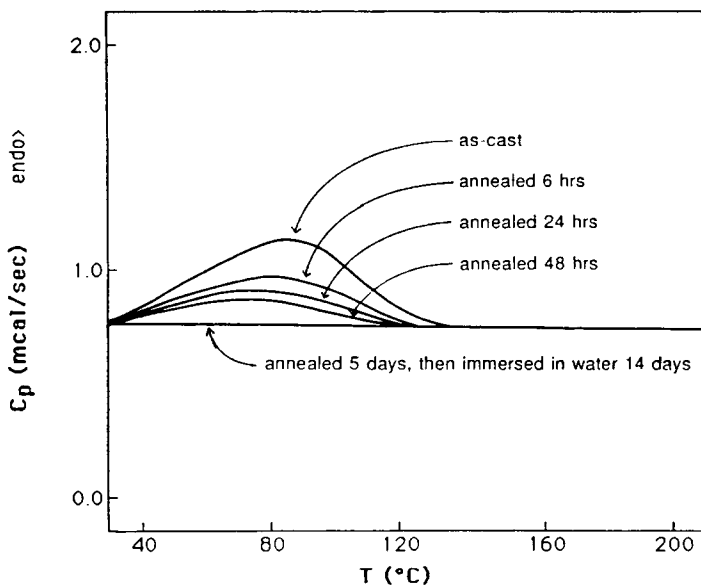
Fig. 4.   DSC scans for 1,5ND-6F samples with different thermal histories.

upon annealing. We will, however, also show data which indicate that rigid chain polymers, such as are typified by 1,5ND-6F, are unusually sensitive to casting and postcasting conditions, independent of any antiplasticization effects. These data support the idea that chain packing in these materials is particularly sensitive to processing protocols.

Several studies of the effects of low molecular weight diluents on polymer permeability have been made.[13-18] These studies have shown that diluents, when present at low but significant levels, can act as antiplasticizers; that is, they stiffen the polymer and retard segmental motions, thus reducing gas permeabilities relative to those in the pure polymer. While these diluents have been observed to decrease gas solubility, the major effect on gas permeability has been found to stem from a reduction in mobility for migration of gas molecules. This is consistent with a diminished magnitude and/or rate of main chain motions.[13, 15-18]

At higher sorbed levels, these same diluents may begin to plasticize the polymer as they force the chains farther and farther apart. In this plasticized state, the energy necessary to separate the chains is reduced, leading to an upswing in permeability with increasing concentration of the diluent. At sufficiently high levels of diluent, permeabilities may even be increased above their initial value, in some cases by as much as an order of magnitude.[14] The detailed effects can vary for a given polymer and antiplasticizing component, depending upon the size of the gas penetrant being considered.[13, 15-18]

Figure 5 illustrates the effect of different sorption levels of diluents in polysulfone (PSF) and poly(phenylene oxide) (PPO) on helium, carbon dioxide, and methane permeabilities. The trends in these figures suggest that, at a high enough concentration of diluent, the permeabilities of carbon dioxide and methane will increase to the point where they reach or exceed their values in the pure polymer. The helium permeability should ultimately turn upward also. However, because helium is less responsive to changes in diluent content
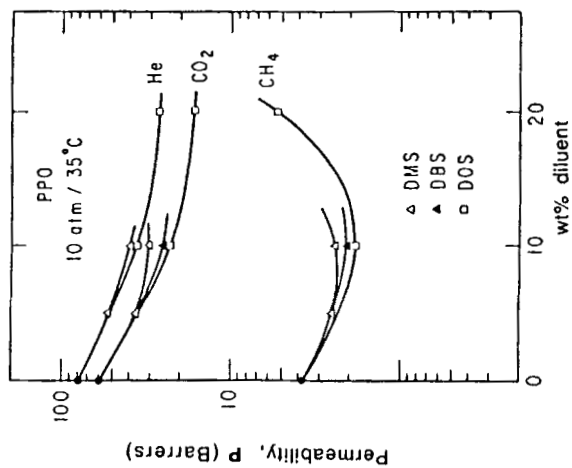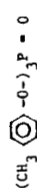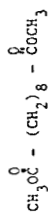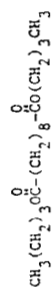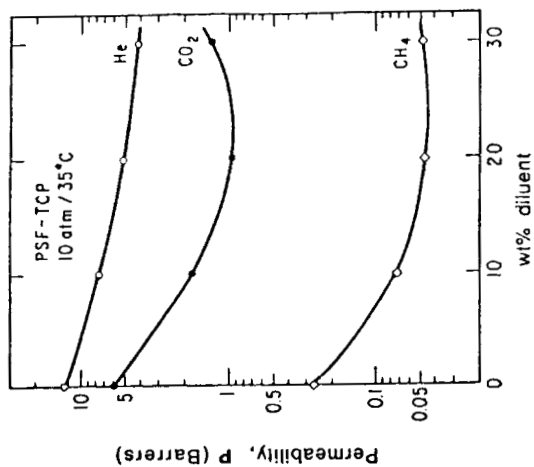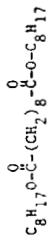
Fig. 5. (a) Effect of TCP in PSF on permeability of He, CO_2, and CH_4 at 35°C and 10 atm (13). (b) Effect of plasticizer in PPO on permeability of He, CO_2, and CH_4 at 35°C and 10 atm (13). (△) DMS; (▲) DBS; (□) Dos.

than the larger carbon dioxide and methane molecules, this upswing will not occur until much higher diluent levels are reached. If one measured helium and methane permeabilities in the DOS-loaded PPO film at a 20% diluent level and then annealed the film until essentially all of the diluent had been removed, the methane permeability would be roughly 30% *lower* and the helium permeability would be almost 200% *higher* in the annealed film than in the diluent-loaded film.

In an analogous manner, we find that, for the blade-cast films studied here, helium permeabilities are roughly 50% *higher* and carbon dioxide permeabilities are roughly 50% *lower* in the annealed film (containing < 1 wt% DMAC) than in the as-cast film (containing 8 wt% DMAC). It thus seems reasonable to conclude that an antiplasticization effect, stemming from the presence of residual solvent in the as-cast film, is responsible for the differences in permeabilities between the as-cast and annealed films. Gas permeabilities in 1,5ND-6F depend on diluent level and penetrant size in a manner similar to that of PSF and PPO.[13,15-18] These effects are presumed to be due primarily to changes in the magnitude and rate of polymer segmental motions, rather than to any specific solubility effects related to the presence or absence of the diluent.[13,15-18]

Alternatively, the behavior shown in Figure 1 could be taken to indicate that the highly condensible sorbate served to block sorption and transport pathways within the glassy matrix, as Koros, Chern, et al.[19-22] have suggested. Using a simple model for the sorption and transport of small molecules in glassy polymers, they showed that the presence of trace amounts of water or hydrocarbon vapor in the feed could lead to reductions in permeability. This is consistent with what would be expected if the vapor acted as an additional competitor for sorption and transport sites. These effects have been documented for certain polyimides.[3,4] Such an interpretation, however, cannot account for the fact that carbon dioxide and methane permeabilities are actually *higher* in the presence of sorbate than in its absence. Therefore, in this particular case, this simple physical interpretation can be ruled out as a possible source of the observed behavior.

The observed differences in the permeabilities of the knife-cast films, therefore, appear to be due to the effect of residual solvent which was present in the as-cast film, but which was driven off upon annealing. The observed behavior could, of course, represent a combination of subtle glassy-state reorganization, as suggested earlier,[2] superimposed upon the effects of the removal of the antiplasticizing sorbate. The data for the knife-cast films are, however, not sufficient to quantify the importance of any such additional subtle organizational effects that might be occurring.

Casting Condition-Induced Organizational Effects

As noted earlier, to probe further the importance of casting conditions on the resultant film's properties, we employed an additional protocol designed to minimize chain segment organization and to provide a point of comparison with the higher concentration, knife-cast material. Specifically, a film of 1,5ND-6F was cast from a 5 wt% solution in DMAC by simple pouring (rather than using a doctor knife), as described earlier. DSC scans, and weight loss
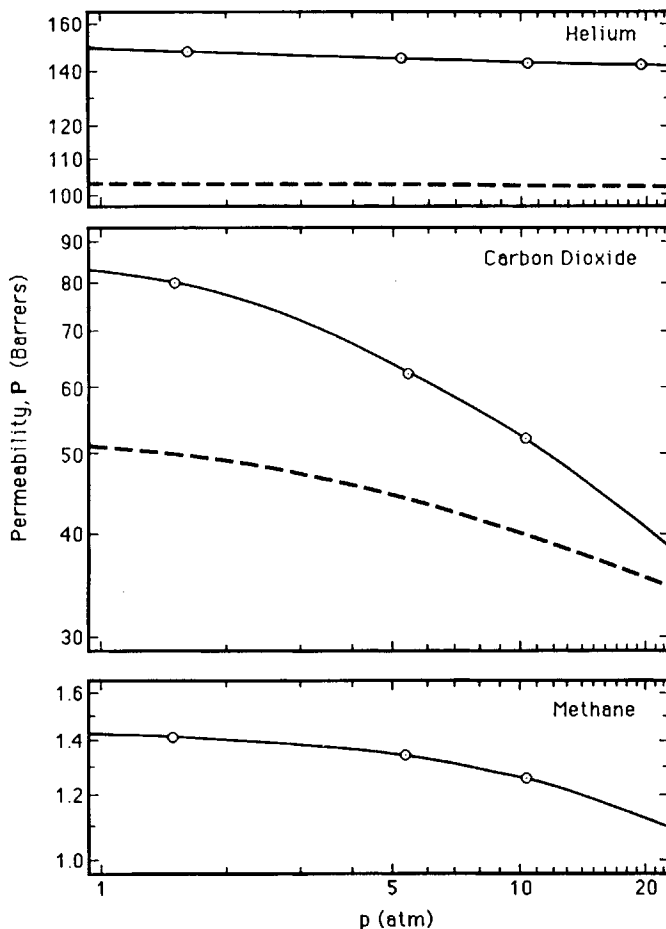
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Fig. 6. Pure gas permeabilities at 35°C in a ring-cast film of 1,5ND-6F annealed 24 h at 240°C. The dashed lines for He and CO_2 are the results for the knife-cast, 6-hour annealed film sample shown in Figures 1 and 2.

measurements, performed on samples of the film indicated that only a negligible amount (< 1%) of solvent was left in the film. The permeabilities of this film to helium, carbon dioxide, and methane are shown in Figure 6.

At one atmosphere, the helium and carbon dioxide permeabilities shown in this figure are, respectively, some 50 and 60% higher than those for the knife-cast annealed film (the dashed lines in Fig. 6). The methane permeabilities are on the order of 100 to 120% higher than those reported earlier for knife-cast annealed films.[2] The results reported here are for a temperature of 35°C, while those reported previously were for a temperature of 30°C. However, based on the determination of the activation energies of permeation in this polymer by Pye et al.,[3] the temperature difference can account for only about 5% of this difference in methane permeabilities.

Casting films with a doctor knife might produce a greater degree of orientation than would the ring-casting method. We speculate that such orientation could be responsible for the lower permeabilities observed in the
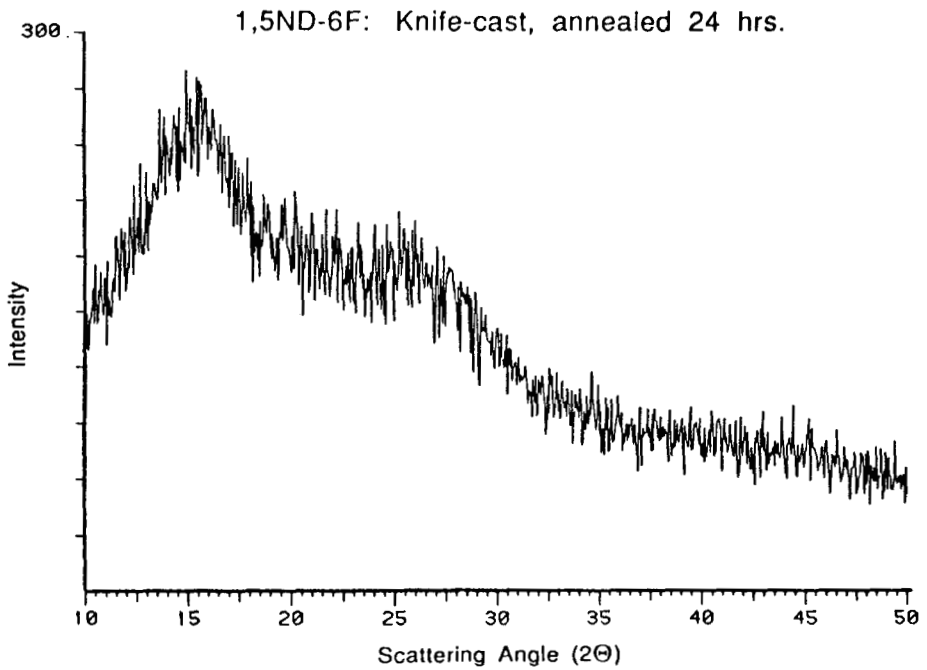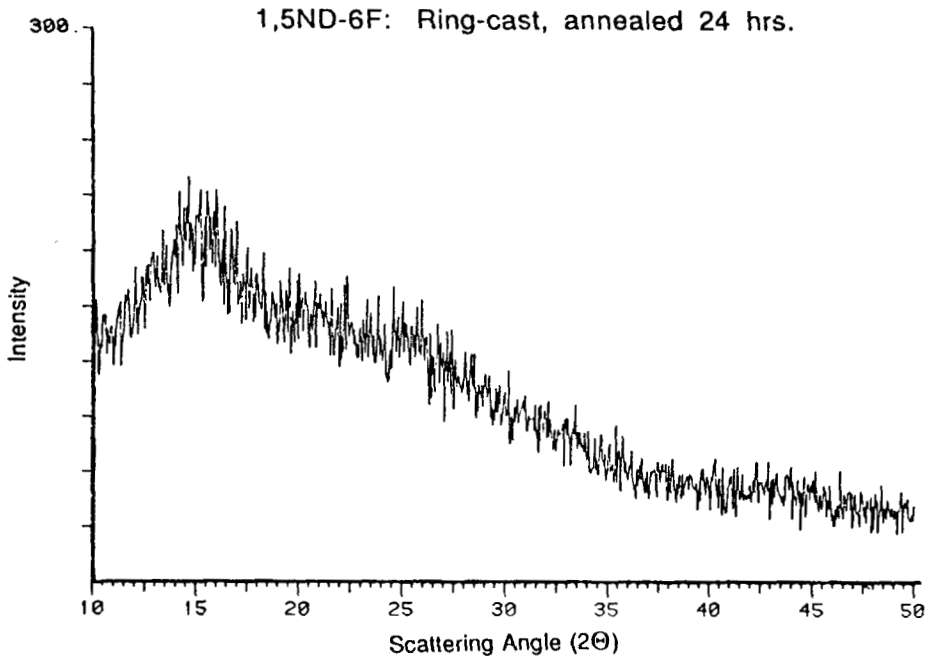
Fig. 7.   X-ray scattering for films of 1,5ND-6F prepared using different casting techniques. Top: Ring-cast, annealed 24 h; Bottom: Knife-cast, annealed 24 h.

knife-cast films. To test for any such orientation, samples of ring- and knife-cast films were examined under cross-polarizers. While no orientation was observed in the ring-cast film, orientation was clearly present in the knife-cast film. The possibility of unrecognized asymmetry in the films is negligible since the densities of all the annealed, diluent-free materials were high ($\sim$ 1.4 g/ml).

To study further the possibility that orientational and packing effects might be responsible for the observed differences in the knife-cast and ring-cast films, birefringence and X-ray diffraction measurements were performed on samples that had been annealed for 24 h to remove residual solvent. The birefringence of the ring-cast film was essentially zero, indicating a complete lack of orientation. The birefringence of the knife-cast film was determined to be 0.5×10^{-3}. This value slightly exceeds our experimental uncertainty of about $\pm 0.1 \times 10^{-3}$ and indicates a small but significant degree of orientation. This orientation was almost uniaxial in the direction of draw.

X-ray diffraction results are shown in Figure 7. Both the ring- and knife-cast films show peaks in the scattering angle (2Θ) range of 14° to 18°. However, the maxima occurs at slightly different values in each film; at 15.1° in the ring-cast film and 15.3° in the knife-cast film. Using the formula: $n\lambda = 2d \sin \Theta$, with $n = 1$ and $\lambda = 1.54$ Å, the d spacings of the ring- and knife-cast films were determined to be 5.9 and 5.8 Å, respectively.The interchain packing can thus be seen to be marginally "tighter" in the knife-cast than in the ring-cast film. The difference in d spacings was not large enough to produce a significant difference in densities between the two films, however. The densities of both films were 1.41 g/ml to within half a percent.

In addition to the smaller d spacing, the knife-cast film shows a pronounced "hump," amounting almost to a secondary peak, in the region of 20–30°. The maximum of this "hump" corresponds to a d spacing of 3.61 Å. Such a pronounced "hump" is not seen in the ring-cast film. The differences in the birefringence and X-ray results for the two films suggest that there are indeed subtle differences in orientation and packing between the two films.

It seems likely, then, that the differences in the knife-cast and ring-cast diluent-free samples stem from glassy state packing differences that are extreme manifestations of the types of phenomena whose existence was previously postulated.[2] In the present case, the casting protocols, rather than the postcasting heat treatment, appear to give rise to the differences in intersegmental packing. As noted earlier,[2] the transport properties of rigid chain polyimides, polyamides, and polyesters might be expected to show more pronounced packing-related effects than more flexible-chain materials such as the family of bisphenol-A-derived polycarbonates and polysulfones.[7-12] This expectation is consistent with the observed results.

CONCLUSIONS

The magnitudes of permeabilities measured for helium in knife-cast films were of a similar magnitude to those reported by Hoehn for hydrogen.[2] The helium permeabilities showed substantial increases upon annealing, on the order of 50% at all pressures. On the other hand, the permeabilities of the larger CO_2 molecule decreased upon annealing, on the order of 50% at one

atmosphere and 40% at 20 atmospheres. These observations are in qualitative agreement with those reported earlier showing increases in hydrogen permeability of some 80–90% and decreases in methane permeabilities of some 75–80% upon annealing for 6 h.[2] DSC and weight loss measurements showed a significant amount of solvent to be present in the as-cast film, on the order of 8 wt%. Only a small amount (less than 1 wt%) remained in the 6-h annealed film.

Results have been presented to show that the differences in permeabilities between the two knife-cast films can most plausibly be attributed to an antiplasticization effect stemming from the presence of residual solvent in the as-cast film. While the available evidence is consistent with this type of argument, the possibility of an additional aging effect cannot be ruled out as a contributing factor.

An annealed ring-cast film showed substantially higher permeabilities than did an annealed knife-cast film. The principal difference between these two films is believed to be the degree of organization in chain packing, as observed from birefringence and X-ray diffraction measurements. At one atmosphere pressure, permeabilities in the ring-cast annealed film were on the order of 50 and 60% higher than those of the knife-cast annealed film for helium and carbon dioxide, respectively. The methane permeability values in the ring-cast annealed film are also significantly higher (on the order of 120%) than values reported earlier for knife-drawn annealed films.[2] The results reported here point out the dramatic effects that casting conditions may potentially have on the transport properties of such rigid chain materials. As a practical matter, however, membrane casting solutions are not usually formulated for concentrations much below 15–20%, and some degree of orientational stress will always be present in the casting or spinning process. Constraints, therefore, exist that will minimize the likelihood of encountering the full range of solution concentration and casting stress levels explored here. Thus, the large effects seen here would not be likely to be observed in an actual membrane formation process; however, variabilities of 10–30% may be involved and these are still significant.

In addition to the antiplasticization and casting-condition effects believed to be primarily responsible for the results observed here, heat-treatment effects associated with changes in glassy state packing upon annealing may also be present. The present study has not been able to decouple such subtle effects from the more dramatic antiplasticization and casting-conditions phenomena. Systematic annealing work as a function of time with diluent-free samples would be necessary to totally resolve this issue. Such work is planned in the future.

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