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Effect of UV crosslinking and physical aging on the gas permeability of thin glassy polyarylate films

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Abstract

The effect of crosslinking by UV irradiation on the gas permeation properties of thin films (thickness $\leq 1\ \mu m$) made from two benzophenone-based polyarylates were examined. In addition to the permeation response to UV crosslinking in these two polymers, the effects of crosslinking on the rate of physical aging was also explored. The sequence of physical aging and crosslinking, as well as reversal of the aging process was studied in order to separate the similar effects of aging and crosslinking. The results show that crosslinking very thin films can greatly improve the long-term performance of membranes when compared to noncrosslinked films of similar thickness. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Benzophenone-based polyacrylates; UV cross-linking; Physical aging

1. Introduction

High permeability and high selectivity are fundamental characteristics required of polymeric membranes for improved gas separation processes [1–10]; maintaining this performance over the life of the membrane is essential. Membrane performance can be improved by the synthesis of new polymers, by modification of existing polymers, or by a combination of the two. There are some indications from the literature that crosslinking of polymeric membranes with high performance gas separation properties may be a useful way to change the balance between intrinsic permeability and selectivity in a beneficial manner [11–14]. This paper explores this issue using a UV crosslinking strategy. To achieve high fluxes in practical applications, it is necessary to make the membrane as thin as possible; thicknesses on the order of 100 nm are typical. Owing to the high absorbance of UV irradiation, it turns out that membranes of thicknesses comparable to those used in practice must be employed to obtain uniform crosslinking throughout the thickness. Recent studies have shown that such thin, glassy polymer films undergo an accelerated physical aging process, relative to macroscopic specimens of glassy polymers, manifested as a significant decline in permeability or gas flux [15–23]. Thus, an assessment of the effects of crosslinking on separation performance of thin films must consider the issue of physical aging. A side benefit of crosslinking might be to ameliorate to some extent the permeability loss due to physical aging.

In this article, the time-dependent gas transport properties of thin polyarylate films crosslinked by UV irradiation are examined. The effect of the sequence of aging and UV exposure was studied to separate and further understand the effects of both physical aging and crosslinking. Reversal of the physical aging process in crosslinked films by heating above the glass transition temperature was also demonstrated.

2. Background

2.1. Strategy

This article examines the effect of crosslinking and physical aging on the permeation properties of two polyarylates based on benzophenone dicarboxylic acid, designated by the acronyms TMBPA-BnzDCA and TMHFBP-BnzDCA. The structures and physical properties of these polymers are shown in Table 1. The benzophenone dicarboxylic acid (BnzDCA) structural unit was chosen because it contains a chromophore (carbonyl between aromatic rings) which is useful for UV crosslinking of these homopolyarylates. A benzophenone bisphenol was used to crosslink polyarylates in a previous study by Wright and Paul

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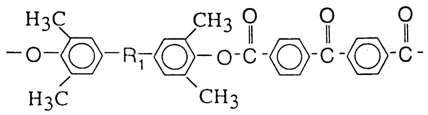
Table 1
Polymer structure and physical properties

Structure[a] R_1	Polymer abbreviation	T_g (°C)	Density (g/cm^3)	FFV_{bulk}[b]
$-C(CH_3)_2-$	TMBPA-BnzDCA	237	1.148	0.164
$-C(CF_3)_2-$	TMHFBP-BnzDCA	247	1.263	0.199

[a] The general polymer structure is as follows:



[b] FFV calculated by Bondi method.

[14], but the extent of crosslinking was not high enough to cause a significant gain in selectivity. The bisphenol monomers tetramethyl bisphenol-A (TMBPA) and tetramethylhexaflouro bisphenol (TMHFBP) were chosen because they are a source of benzylic hydrogens which are necessary for this type of UV crosslinking. Additionally, TMBPA and TMHFBP lead to a higher free volume and, hence, gas permeability than use of monomers like unsubstituted bisphenol-A.

The use of very thin polymer films is necessary to achieve uniform crosslinking throughout the membranes thickness; the latter is essential for making meaningful intrinsic property comparisons with uncrosslinked polymers and with widely accepted performance standards, such as the Robeson [24] trade-off curves. Robeson has compared selectivity versus permeability for an extensive database of different homogeneous polymers and has proposed an "upper bound" trade-off relationship above which no polymers are currently known to exist. The thickness levels required to assure UV crosslinking that is essentially uniform throughout the film is in the range where high rates of physical aging are observed; i.e. relatively large changes in permeability are observed with time [18,25]. Thus, it is necessary to factor physical aging time into the study of changes in gas permeability caused by UV crosslinking of thin films.

2.2. Prior work on crosslinking

One of the first indications that UV crosslinking could improve the performance of gas separation membranes came from claims in the patent literature [26]. Since then other studies have appeared in the scientific literature concerning the effect of UV crosslinking on the gas permeation properties of polyimide films [11,12,27]. Kita et al. [11] demonstrated significant gains in selectivity caused by UV irradiation of thick polyimide films, especially for H_2/CH_4 separation. However, it is not possible to compare these results with the intrinsic properties of homogeneous polymers because the films were undoubtedly not uniformly crosslinked for the following reason. The extent of crosslinking at any point in the film is dependent on the intensity of the UV irradiation at that point and the duration of the exposure. The intensity of UV light decreases with depth through the film due to absorption; the intensity profile can

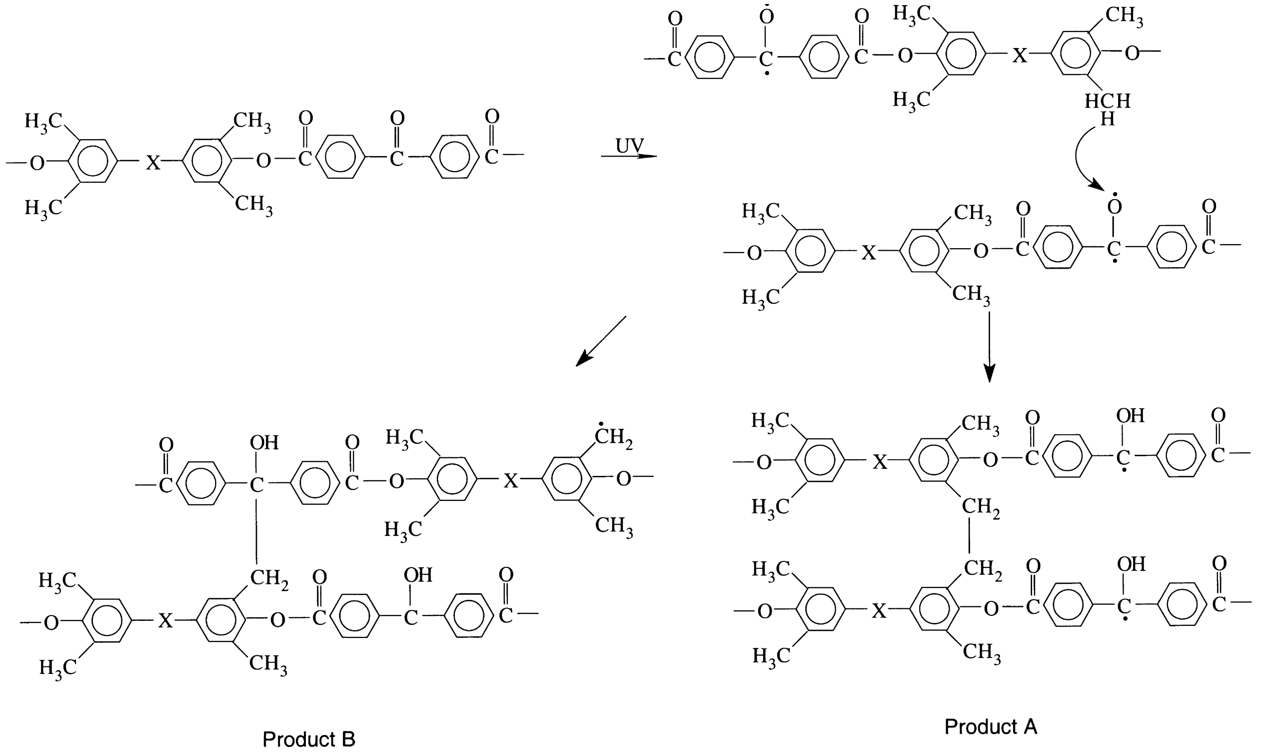
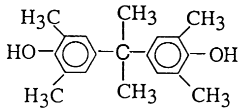
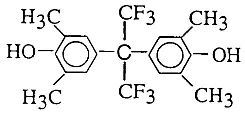
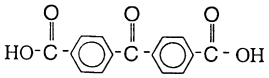


Fig. 1. The proposed UV crosslinking scheme for a BnzDCA-based polyarylate where X is the connector group: $C(CH_3)_2$, $C(CF_3)_2$ or fluorene.

Table 2
Monomer sources and purification

Monomer	Source	Purification	Melting point (°C)
Tetramethylbisphenol-A (TMBPA) 	Aldrich	None	165–167
Tetramethylhexaflourobisphenol (TMHFBP) 	Polysciences Inc.	Sublimation	218–219
Benzophenone dicarboxylic acid (BnzDCA) 	Nihon Nohyaku	None	—[a]

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[a] Decomposes at 260°C before melting.

be described by the Beer–Lambert law

$$I = I_0 \times 10^{-ECD} \tag{1}$$

where I is the intensity at any point in the film, I_0 is the incident intensity, E is the extinction coefficient, C is the concentration of the photoactive species and D is the path length in the film. Thus, thick films are expected to have a gradient of crosslinking, and their permeation properties cannot be directly compared with homogeneous materials. Based on the expected values for E and C and the thickness of the films ($\ell \approx 15\ \mu m$) used by Kita et al., the UV irradiated membranes would have a crosslinking gradient in spite of the fact that they exposed the films on both sides. However, they showed that UV crosslinking can produce significant improvement in selectivity with only a modest loss in permeability.

Wright and Paul [14] explored UV crosslinking of polyarylate films, but the results were complicated by a photo-Fries rearrangement [28] that competed with the crosslinking reaction; the reaction occurred because their material had unsubstituted sites *ortho* to the ester group on the bisphenol linkage. This limited the extent of crosslinking, and, thereby reduced the effect of UV irradiation on the gas transport properties of the polyarylate used in that study.

2.3. Crosslinking mechanism

The crosslinking reactions initiated by UV irradiation of polymers containing a benzophenone unit have been studied extensively. Hydrogen abstraction via an excited benzophenone unit is a classic reaction in organic photochemistry [29–31]. The accepted mechanism for crosslinking involves hydrogen abstraction from benzylic hydrogen donor groups by triplet benzophenone and subsequent radical coupling [11,12,14,31,32]. This mechanism of crosslinking polyarylates is outlined in Fig. 1, where a general polyarylate structure is shown with X representing possible connector groups: $C(CH_3)_2$, $C(CF_3)_2$ or fluorene. The polyarylate is exposed to UV light and the benzophenone carbonyl bond is cleaved yielding an oxygen radical and a carbon radical. The oxygen radical abstracts a benzylic hydrogen from a nearby source, thereby creating another carbon radical. The carbon radicals can then couple causing crosslinks between the polymer chains. The most likely scenario for crosslinking is the coupling of radical pendant groups (product A), but this has not been proven. Steric interactions as revealed by CPK models of the crosslinked polymers probably limit the formation of crosslinked product B. The positions *ortho* to the ester linkage on the bisphenol segment are occupied with methyl groups which effectively block photo-Fries rearrangement as demonstrated by Lo et al. [28]. The progress of the reaction can be tracked by Fourier transform infrared (FTIR) spectroscopy as the benzophenone carbonyl peak ($1678\ cm^{-1}$) [33] decreases due to increased UV exposure.

2.4. Physical aging of thin glassy polymer films

Physical aging, or volume relaxation, is a well-known phenomenon in glassy polymers which would be expected to lead to a decrease in gas permeability as a result of the loss in free volume [15–18,20–22,25]. For macroscopic specimens of glassy polymers, the rate of volume relaxation, and hence the expected change in gas permeability, is extremely slow except just below the glass transition

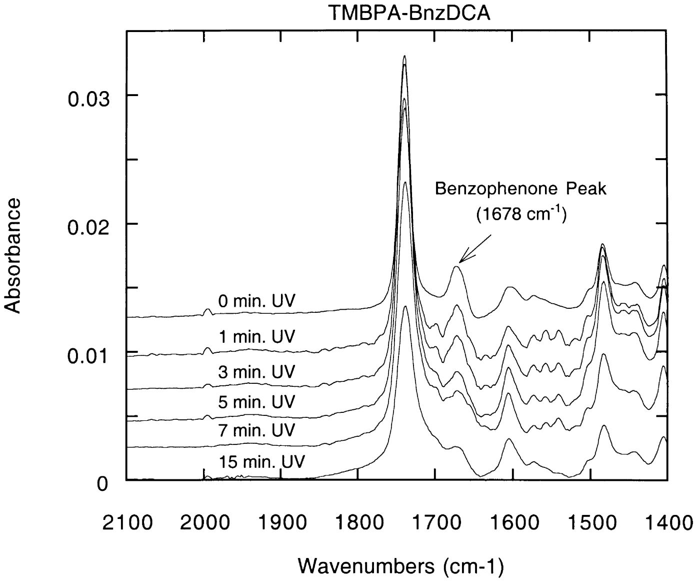

Fig. 2. FTIR analysis of the benzophenone peak decay resulting from increased UV irradiation for TMBPA-BnzDCA.

temperature. However, there is strong evidence that physical aging occurs much more rapidly for very thin films of glassy polymers. Pfromm and Koros [15] and Rezac et al. [16,17] reported that thin polyimide films showed substantial reduction in gas permeation rates with time that were attributed to physical aging. McCaig and Paul [18] documented similar changes in gas permeability for a polyarylate membrane over a wide range of thicknesses; this study utilized two methods for accurately determining the thickness of thin films so that absolute permeability coefficients could be reported.

3. Materials and methods

The monomers used to synthesize the two polyarylates studied here are described in Table 2. Both polymers were synthesized by an interfacial polymerization method described by Morgan [34]. The tetramethylbisphenol A (TMBPA) was used as received from Aldrich Chemical while the tetramethylhexafluoro-bisphenol (TMHFBP) was purified by vacuum sublimation. The benzophenone dicarboxylic acid (BnzDCA), graciously donated by Nihon Nohyaku, was refluxed with excess thionyl chloride and purified by vacuum distillation to yield the diacid chloride [6]. The polymer structures and physical characteristics are listed in Table 1. The polymers were reprecipitated twice from chloroform into ethanol and then vacuum dried to remove residual solvent.

To approach uniformity of crosslinking throughout the film thickness, a practical but arbitrary criteria of at least 90% transmittance of light at 365 nm was adopted. A Hewlett Packard UV–vis 8452 A Diode Array Spectrophotometer was used to measure the transmission of light as a function of film thickness for both polymers. Films of TMBPA-BnzDCA thinner than 0.9 μm and of TMHFBP-BnzDCA thinner than 1.1 μm were found to transmit 90% or more of incident UV irradiation.

Such thin films were solution cast from methylene chloride onto silicon wafers inside metal casting rings, and their thicknesses determined using procedures described in a previous paper [18]. Solution concentration was adjusted to obtain film thicknesses ranging from 0.25 to 33 μm. The thick films ($\ell > 2.5$ μm) were removed from the wafer and vacuum dried at room temperature for 24 h and then at 150°C for five days according to the standard procedures established in this laboratory for film preparation prior to permeation testing. Thermogravimetric analysis (TGA) using a Perkin–Elmer TGA-7 was used to confirm the complete removal of solvent. The thin films ($\ell > 2.5$ μm) were floated off the casting surface with water and then lifted onto porous ceramic supports. To ensure solvent removal, the procedures established by Pfromm [15] were used: the thin films were allowed to air dry overnight, then dried at 100°C for 24 h and finally heated at 20°C above their respective glass transition temperatures. In addition to ensuring the removal of solvent, heating the polymers above their T_g and quenching them according to a procedure described in a previous article [18] establishes the beginning of the aging process ($t = 0$).

Film thickness was measured by a micrometer for thick films while a scanning electron microscope (SEM) procedure was used for films thinner than 2.5 μm. Following completion of the permeation measurements, the composite membranes were cooled in liquid nitrogen and fractured to yield a polymer/ceramic cross-section; photomicrographs using a JEOL JSM-35c SEM microscope were then taken of an edge view of the polymer/ceramic composite membrane. The SEM technique compares a secondary electron image to a backscattered electron image during a single

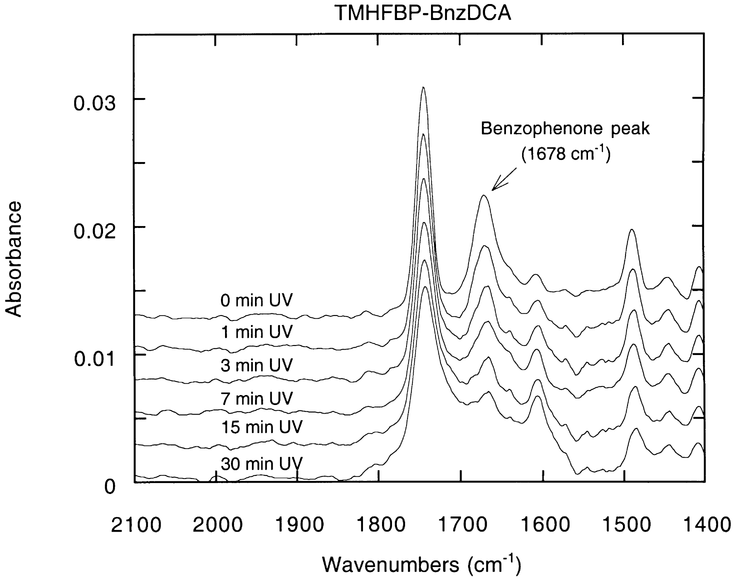

Fig. 3. FTIR analysis of the benzophenone peak decay resulting from increased UV irradiation for TMHFBP-BnzDCA.

scan; the former shows both the polymer and ceramic, while in the latter only the ceramic support is visible due to its higher atomic mass. It is important to obtain an accurate measurement of the film thickness, ℓ, so that the absolute permeability coefficient (P) can be calculated rather than simply reporting the observed permeance, P/ℓ, as is done in most studies of such thin films.

Crosslinking was performed by irradiating the samples at a distance of 2.5 cm from the UV lamp for various exposure times with a 100 W high pressure mercury arc lamp (BLAK-RAY® Longwave Ultraviolet Lamp Model B-100 A) equipped with a 365 nm filter. A nitrogen purge was used to minimize the possibility of peroxide formation during the crosslinking reaction; Wright and Paul [14] and Lin et al. [31] showed that UV irradiation in nitrogen of polymers containing benzophenone groups had a slightly positive effect on the extent of crosslinking. The intensity of the lamp was monitored with a JBA Model 100B UV meter and the bulbs were changed frequently.

The glass transition temperature, T_g, of each polymer was measured using a Perkin–Elmer DSC-7 differential scanning calorimeter at a heating rate of 20°C/min. The polymer samples were heated twice, and the T_g was evaluated as the onset of the transition during the second scan. Both polymers appear to be amorphous due to their clarity and the absence of a crystalline melting point. The density of each polymer was measured at 30°C in a density gradient column based on aqueous calcium nitrate solutions.

Table 3
Permeability and selectivity for O_2/N_2 and H_2/CH_4 separation based on thick film (bulk) data

Polymer	P_{O_2} (Barrers)	α_{O_2}/N_2	P_{H_2} (Barrers)	α_{H_2}/CH_4
TMBPA-BnzDCA	4.85	5.3	41.9	47.0
TMHFBP-BNzDCA	12.9	4.5	78.7	35.2

The FTIR spectra of the virgin and crosslinked polymers were obtained using a Nicolet 550 Magna-IR™ spectrometer with a nitrogen purge. Thin polymer films were spun on NaCl disks for FTIR analysis.

Pure gas permeability coefficients were evaluated at 35°C for O_2, N_2, H_2 and CH_4 using a standard pressure-rise type permeation cell following standard procedures employed in this laboratory [6]. The gas permeability coefficients were measured at an upstream driving pressure of 2 atm for O_2, N_2, and H_2. The permeability coefficients for CH_4 are normally reported at 10 atm, but the crosslinked membranes were quite brittle so the upstream driving pressure was never raised above 5 atm. Liquid nitrogen traps were used on all permeation equipment and vacuum ovens to eliminate possible contamination of the samples by pump oil.

4. Characterization of UV irradiated films

The extent of crosslinking is usually documented by measurement of the extent of swelling and the amount of polymer extracted, or conversely the gel fraction, after exposure to a good solvent. As the current films were extremely thin (<1 μm), it was difficult to make quantitative measurements of this kind. The shortest UV exposure time (1 min) resulted in no visible polymer swelling in chloroform; this suggests that the degree of crosslinking is very high and that likely there is no extractable material.

The progress of the crosslinking reaction (see Fig. 1) can be tracked by observing the reduction in the benzophenone carbonyl infrared peak (1678 cm^{-1}) [33] as a function of UV exposure time. Figs. 2 and 3 show the FTIR spectra for TMBPA-BnzDCA and TMHFBP-BnzDCA as a

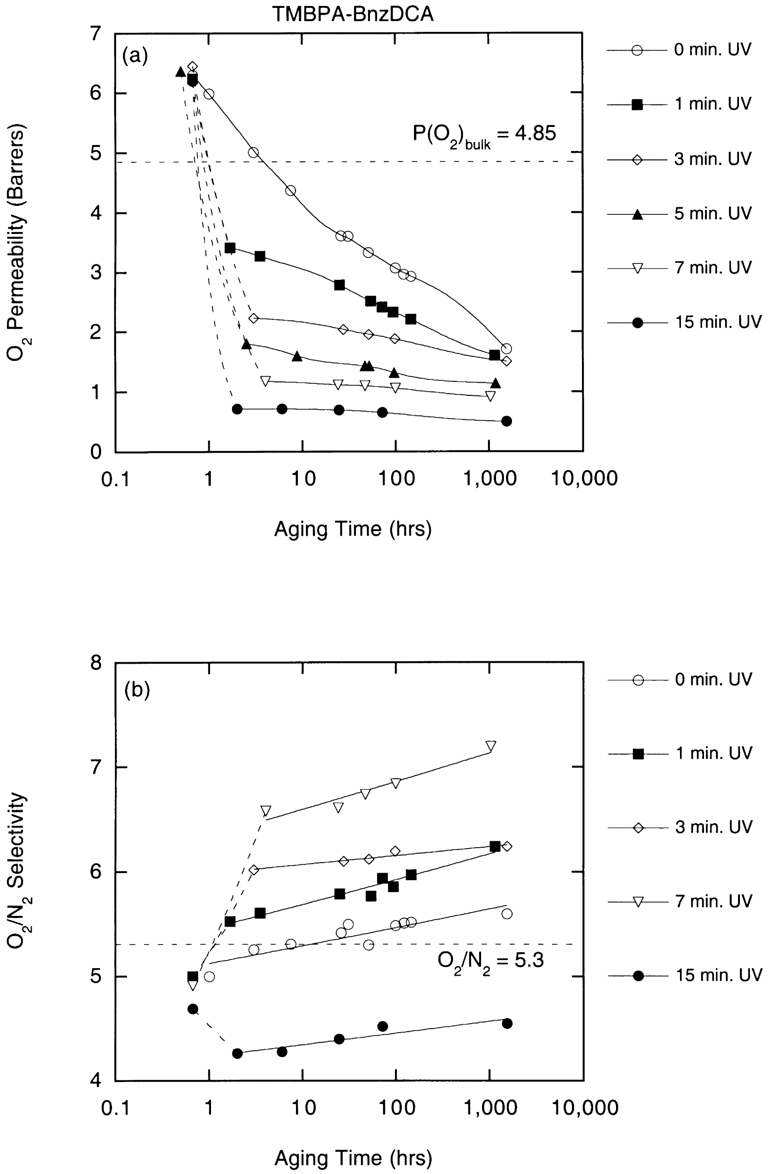

Fig. 4. Effect of UV exposure on the aging response of (a) oxygen permeability and (b) the O_2/N_2 selectivity coefficients for TMBPA-BnzDCA for the exposure times: (○) 0 min, (□) 1 min, (◇) 3 min, (▲) 5 min, (▽) 7 min, (●) 15 min.

function of UV exposure times over the range corresponding to those used in the gas transport study to be discussed subsequently. The benzophenone peak effectively disappears after 15 min of UV exposure for TMBPA-BnzDCA. The UV dose required to yield the same effect for TMHFBP-BnzDCA is larger, as the benzophenone peak is still visible at 30 min.

UV irradiation significantly alters both the physical and chemical properties of BnzDCA-based polymers; for both polymers the results indicate that the crosslinking reaction proceeds rapidly. The disappearance of the benzophenone peak after short irradiation times is consistent with the proposed crosslinking mechanism. The differences in rates for the two polymers could be due to steric inhibition of mobility needed for radical coupling or screening effects of bulky structural groups.

5. UV irradiation prior to long-term aging

The permeation properties measured at 35°C for thick films (“bulk” values) are shown in Table 3 and on the figures as a dashed horizontal line for the two new polymers, TMBPA-BnzDCA and TMHFBP-BnzDCA, synthesized here. “Bulk” values are defined here as gas transport coefficients measured on very thick films ($\ell > 25$ μm) according to standard procedures established in this laboratory [18]. The gas transport properties were measured at 2 atm for O_2, N_2 and H_2 and 5 atm for CH_4. For consistency, time zero for

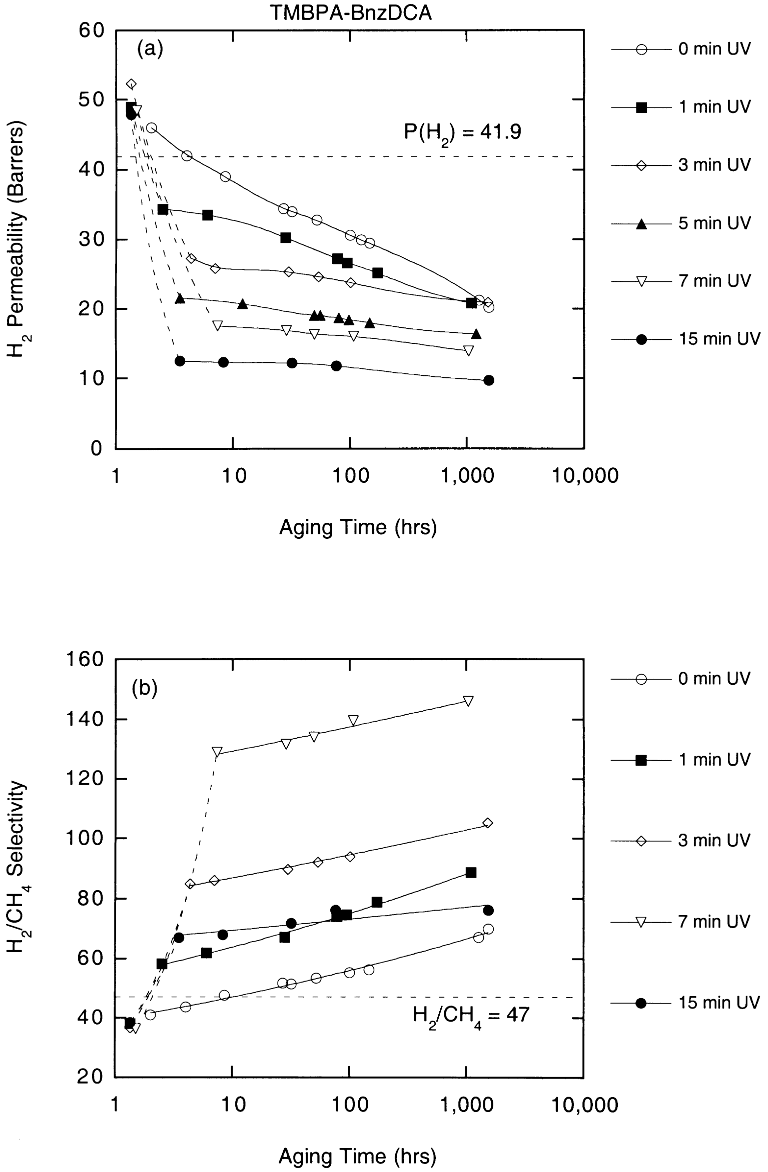

Fig. 5. Effect of UV exposure on the aging response of (a) hydrogen permeability and (b) the H_2/CH_4 selectivity coefficients for TMBPA-BnzDCA for the exposure times: (○) 0 min, (■) 1 min, (◇) 3 min, (▲) 5 min, (▽) 7 min, (●) 15 min.

physical aging was defined as when the membranes were removed from the vacuum oven where they were heated above T_g. Permeability reduction due to physical aging in thin glassy films has been shown to have a strong thickness dependence [15–18,25]. Ideally, the films in this study should all have the same thickness, but this was not possible due to the nature of the casting process and the difficulty in obtaining defect-free films. However, for the range of thicknesses used here (0.38–0.86 μm) for TMBPA-BnzDCA and (0.48–1.04 μm) for TMHFBP-BnzDCA, no attempt is made to normalize the aging time for any thickness dependence, e.g. t/ℓ^2 as suggested previously [18,25], because the effect of crosslinking was such that any differences in the rate of physical aging due to thickness were relatively insignificant when compared to the effects due to UV irradiation. With this in mind, simple comparisons of permeability and selectivity versus aging time were deemed more informative.

5.1. TMBPA-BnzDCA

Fig. 4 shows the effect of the duration of the UV irradiation exposure and the subsequent effect of the time for physical aging on the oxygen permeability coefficients and O_2/N_2 selectivity values for TMBPA-BnzDCA. The first data point for each sample corresponds to the O_2 permeability coefficient observed after about 1 h of physical aging but prior to UV exposure. The dotted lines connect these points to curves that represent the gas permeability or selectivity after UV crosslinking and the subsequent physical aging

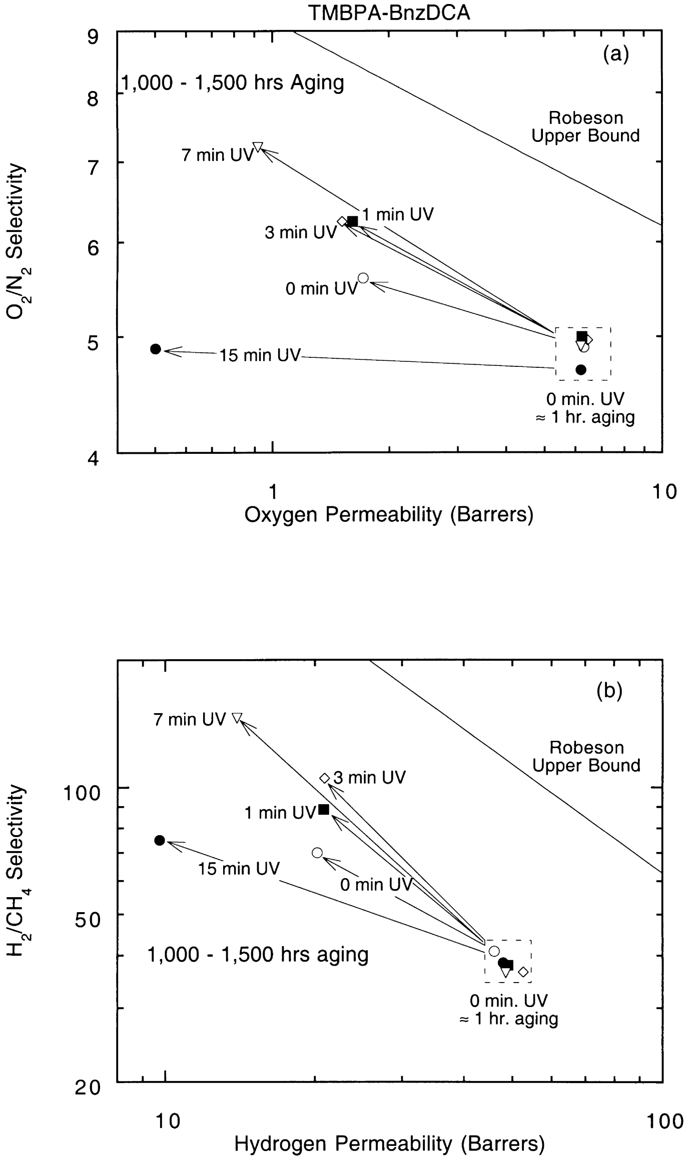

Fig. 6. Effect of crosslinking and long aging times (1000–1500 h) on (a) oxygen permeability and oxygen/nitrogen selectivity at 2 atm and 35°C and (b) hydrogen permeability and hydrogen/methane selectivity at 5 atm and 35°C for TMBPA-BnzDCA for the exposure times: (○) 0 min, (■) 1 min, (◇) 3 min, (▽) 7 min, (●) 15 min. The solid line on both plots is the "upper bound" proposed by Robeson [24].

that occurs. One film was allowed to age without UV exposure to show the effect of physical aging in the absence of crosslinking on membrane performance. This uncrosslinked film shows a gradual decay in permeability over time and its absolute oxygen permeability approaches the range observed for the crosslinked films; the oxygen permeability coefficient for this control film is reduced by a factor of 3.5 after 1500 h of aging from its initial value obtained at 1 h of aging time. It is interesting to note that the absolute permeability coefficients for these thin films begin above the "bulk" value observed for a thick film of this material (see Table 3) while the selectivity values of the thin films begin below the bulk selectivity value; this issue has been discussed in detail by McCaig and Paul [18]. The loss in permeability due to UV exposure is much greater than that expected from physical aging for the same time interval. The longer the UV exposure, the greater the reduction in oxygen permeability. Significant increases in O_2/N_2 selectivity are caused by crosslinking these polymer films as shown in Fig. 4(b). Although the selectivity for the control increases slightly due to physical aging, the increases in selectivity resulting from exposure to UV irradiation are much greater. The film crosslinked for 15 min is an exception; irradiation appears to cause a reduction in selectivity in this case. Similar trends are shown in Fig. 5 for the H_2/CH_4 gas pair; for the unirradiated film, the hydrogen permeability coefficient following 1500 h of aging is reduced by a factor of 2.3 from its initial value obtained at 2 h of aging time. For H_2/CH_4, the selectivity gain following 7 min of UV exposure is even more pronounced than for O_2/N_2.

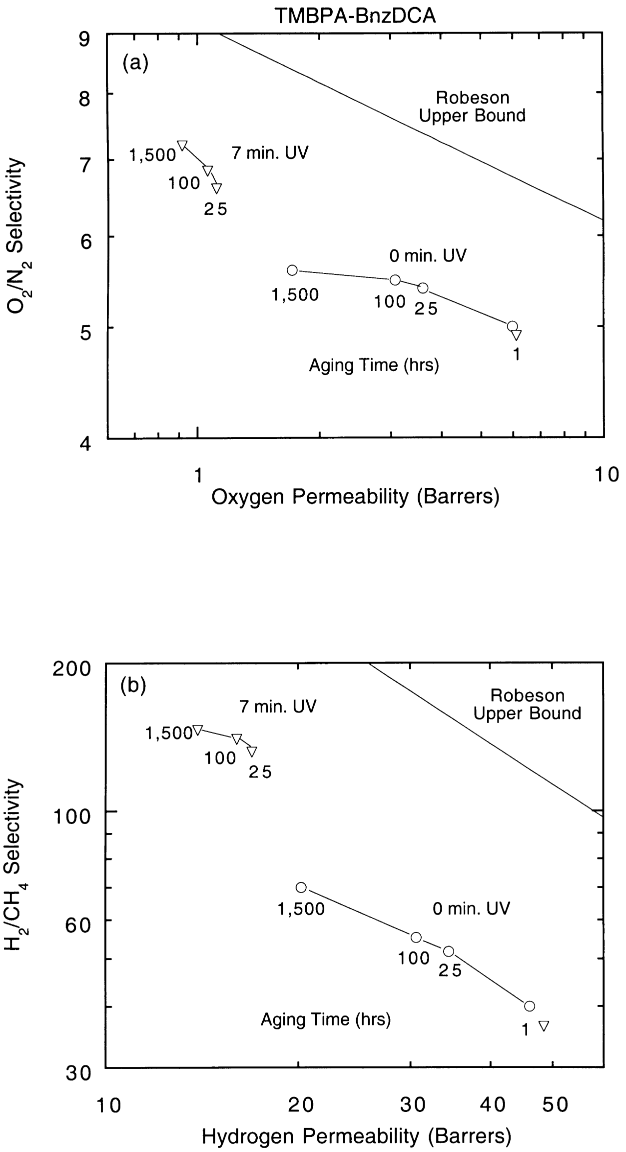

Fig. 7. Effect of crosslinking and aging time (1, 25, 100 and 1500 h) on (a) oxygen permeability and oxygen/nitrogen selectivity at 2 atm and 35°C and (b) hydrogen permeability and hydrogen/methane selectivity at 5 atm and 35°C for TMBPA-BnzDCA for the exposure times: (○) 0 min, (▽) 7 min. The solid line on both plots depicts the "upper bound" proposed by Robeson.

As seen in Figs. 4(a) and 5(a), the slopes of the curves of permeability versus aging time decrease as the duration of UV exposure increases. The rate of permeability loss due to physical aging is significant for the film irradiated for only 1 min, but for the films irradiated for 7 and 15 min, the curves are nearly flat. Conversely, the modest rate of increase in selectivity following crosslinking due to physical aging (Figs. 4(b) and 5(b)) does not seem to be a function of UV exposure time. The increase in selectivity due to crosslinking is dependent on the UV exposure time, but the increase due to aging is not. These trends are evident for both gas pairs.

As the thin films used in this study are uniformly crosslinked throughout their thickness, it is appropriate to compare them to other homogeneous materials. Fig. 6(a) and (b) show plots of selectivity versus permeability for the O_2/N_2 and H_2/CH_4 gas pairs; the position of the crosslinked and uncrosslinked TMBPA-BnzDCA films can be compared to the Robeson "upper bound" lines. The values for films with no UV exposure after approximately 1 h of aging appear at the lower right corner for both figures and are shown to serve as a reference for the combined effects of physical aging and crosslinking. The remaining data are for thin films exposed to UV irradiation for different periods of time and then aged for 1000 to 1500 h; this range of aging times was selected since this provides a good indication of how crosslinking affects long term membrane performance. Physical aging without crosslinking in the thin control film causes an increase in selectivity and a decrease in permeability such that the performance parallels the Robeson upper bound curves for O_2/N_2 and for H_2/CH_4. UV exposure times from 1 to 7 min move the long term performance closer to the O_2/N_2 "upper bound" compared to the unirradiated control; they have higher levels of selectivity and only slightly lower permeability values. The film exposed for 7 min exhibits the best performance. Fifteen minutes of UV exposure causes a significant decrease in both permeability and selectivity; clearly this level of exposure is detrimental to performance as noted earlier. Fig. 6(b) shows similar results for the H_2/CH_4 gas pair. UV exposures for 1 and 3 min lead to higher hydrogen permeability coefficients and higher H_2/CH_4 selectivity values. Seven minutes of exposure causes a further increase in selectivity but a significant loss in permeability compared to the uncrosslinked film. Again, 15 min of UV exposure is not beneficial.

To better understand the separate effects of physical aging and crosslinking, results for the film irradiated for 7 min and the control film are shown in Fig. 7(a) and (b) after 1, 25, 100 and 1500 h of aging. As aging time increases, the uncrosslinked film moves away from the Robeson upper bound curve; the permeability loss due to physical aging is not matched by a large enough selectivity gain to move parallel to or towards the upper bound for either gas pair. Conversely, 7 min of UV irradiation significantly increases the selectivity and decreases the permeability so that the performance approaches the upper bound curves for both gas pairs and, if anything, aging subsequent to the crosslinking slightly improves the performance when compared to the uncrosslinked film.

5.2. TMHFBP-BnzDCA

Owing to the presence of fluorine substituents on the isopropylidene connector group, TMHFBP-BnzDCA has a higher free volume than TMBPA-BnzDCA, FFV = 0.199 vs. 0.164 in the "bulk" glassy state. Comparison of these two polymers should provide some insights about the role of chain packing and stiffness on the effects of crosslinking and

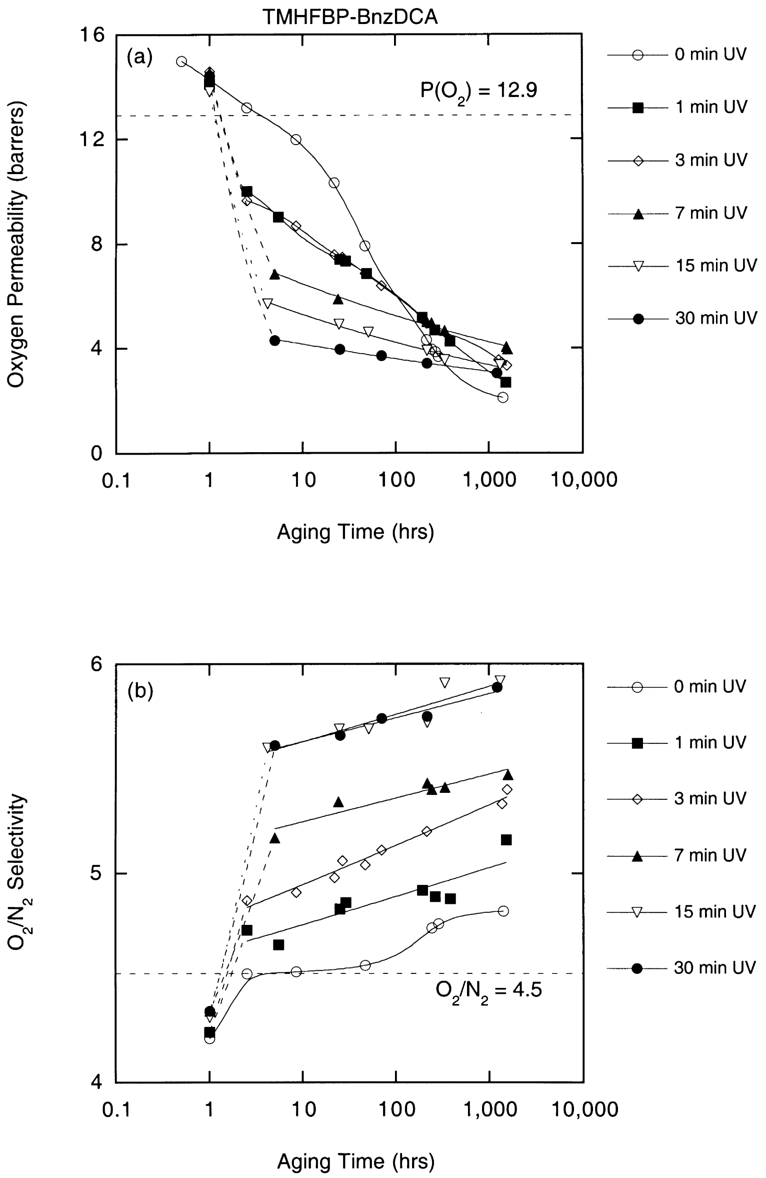

Fig. 8. Effect of UV exposure on the aging response of (a) oxygen permeability and (b) the O_2/N_2 selectivity coefficients for TMHFBP-BnzDCA for the exposure times: (○) 0 min, (■) 1 min, (◇) 3 min, (▲) 7 min, (▽) 15 min, (●) 30 min.

physical aging. As seen in Fig. 8(a), the absolute oxygen permeability values for the thin TMHFBP-BnzDCA films begin above the bulk value and decay dramatically due to physical aging. The oxygen permeability coefficient after 1400 h of aging is reduced by a factor of 6.8 from the initial value obtained at 1 h of aging; this reduction is almost twice the value of 3.5 observed for the uncrosslinked TMBPA-BnzDCA control film. The O_2 permeability values after 1 and 3 min of UV exposure are nearly identical and exhibit considerable permeability losses due to physical aging. For longer UV exposure times (7, 15 and 30 min), the permeability values are all correspondingly lower and the slopes of the aging curves decrease as exposure time is increased. At the end of the aging period studied here, the oxygen permeability values for all of the UV irradiated specimens are higher than that of the unirradiated control. Significant gains in O_2/N_2 selectivity due to UV crosslinking are shown in Fig. 8(b); these gains are similar to those observed for TMBPA-BnzDCA in Fig. 5(b). There is a modest increase in selectivity due to physical aging, but UV exposure causes even greater increases in selectivity. The O_2/N_2 selectivity levels at 15 and 30 min of UV exposure were the highest and nearly identical. Similar trends for hydrogen permeability and H_2/CH_4 selectivity are seen in Fig. 9(a) and (b). For an unirradiated film, the hydrogen permeability coefficient is lower by a factor of 4.4 after almost 1500 h of aging than the initial value obtained after 2 h of aging; once again the reduction factor is almost twice the value of 2.3 observed for the uncrosslinked TMBPA-BnzDCA control film. For H_2/CH_4 separation, 15 min of UV exposure leads to the

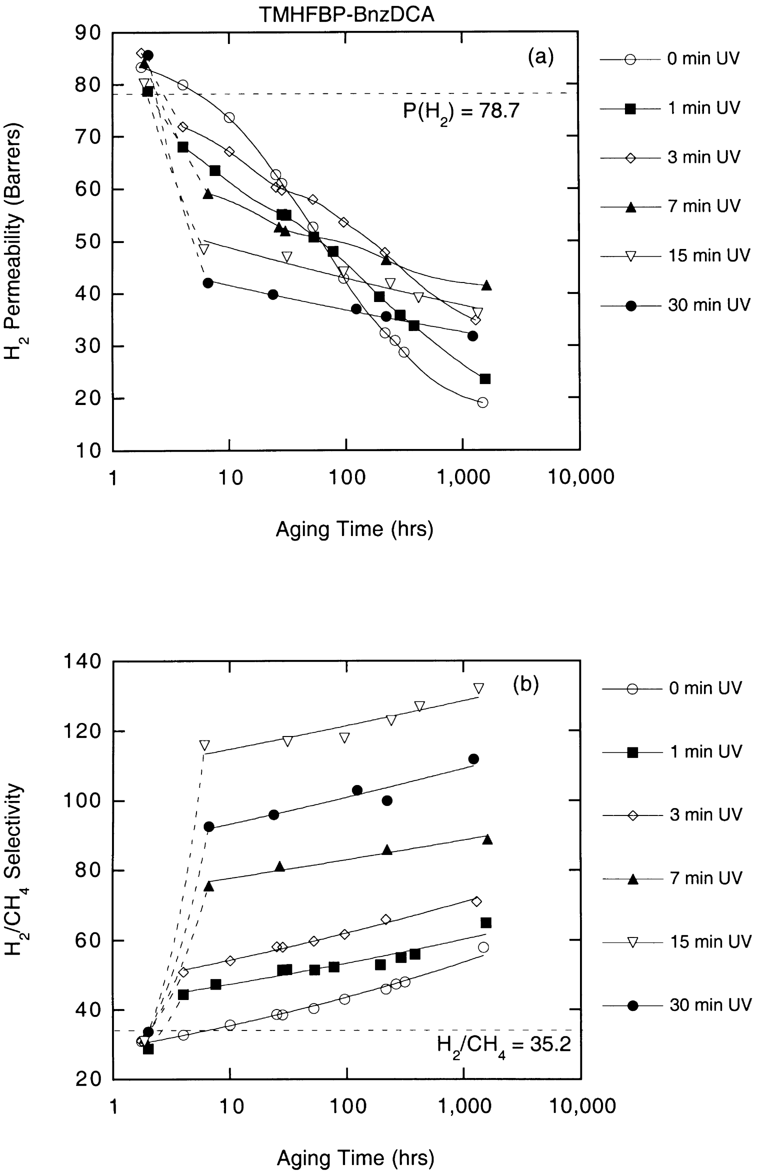

Fig. 9. Effect of UV exposure on the aging response of (a) hydrogen permeability and (b) the H_2/CH_4 selectivity coefficients for TMHFBP-BnzDCA for the exposure times: (○) 0 min, (■) 1 min, (◇) 3 min, (▲) 7 min, (▽) 15 min, (●) 30 min.

highest level of selectivity and the second highest value of hydrogen permeability at the end of the aging period examined here.

Crosslinking of a TMHFBP-BnzDCA film moves the balance of selectivity versus permeability closer to the Robeson “upper bound” curves (after long term aging on the order of 1200 to 1500 h) than that of the noncrosslinked film at similar aging times as seen in Fig. 10. The improvement in performance due to crosslinking is such that all the irradiated specimens have higher permeability values and higher levels of selectivity at this long aging time compared to the aged but unirradiated control. Physical aging of a film that was not exposed to UV irradiation film causes it to move away from the O_2/N_2 and H_2/CH_4 “upper bound” (see Fig. 11). After long-term aging (1500 h), the H_2/CH_4 performance of the film crosslinked for 15 min is very near the “upper bound” curve.

Fig. 11(a) and (b) show in more detail the effect of aging time on the membrane performance for films exposed to UV irradiation for various times. As seen before, the changes in the gas permeation performance of the crosslinked films are much smaller than those of the aged but uncrosslinked film at comparable aging times for both gas pairs.

Physical aging in the absence of irradiation, as tracked by oxygen and hydrogen permeability loss, is significant in the thin films tested for both polymers and results in large permeability losses and modest selectivity gains. Of the two polymers studied, the aging rate is greater for the polymer with the higher level of free volume (TMHFBP-BnzDCA) as evidenced by larger losses in relative

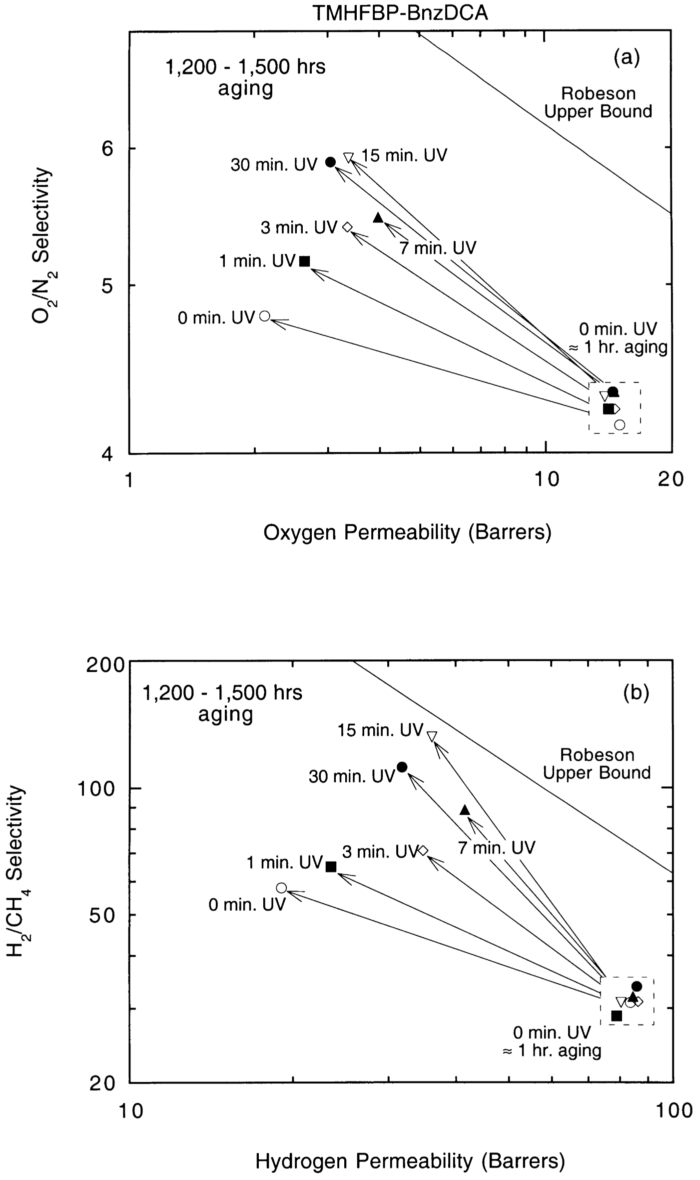

Fig. 10. Effect of crosslinking and long aging times (1200–1500 h) on the (a) oxygen permeability and oxygen/nitrogen selectivity at 2 atm and 35°C and (b) hydrogen permeability and hydrogen/methane selectivity at 5 atm and 35°C for TMHFBP-BnzDCA for the exposure times: (○) 0 min, (■) 1 min, (◇) 3 min, (▲) 7 min, (▽) 15 min, (●) 30 min. The solid line on both plots is the "upper bound" proposed by Robeson.

permeability over similar time scales. Physical aging of these thin glassy membranes causes their gas transport performance values to move away from the Robeson "upper bound" tradeoff curves.

Crosslinking slows the rate of physical aging (decrease in slope of permeability versus aging time) as seen in Figs. 4(a), 5(a), 8(a) and 9(a) compared to the uncrosslinked control film. The crosslinked films also exhibit much higher selectivity values for both O_2/N_2 and H_2/CH_4 separations. The combination of slower aging rates and higher selectivity values, both due to crosslinking, lead to greatly improved gas transport performance as seen in Figs. 6, 7, 10 and 11. In some cases, the improvement is such that both the permeability and selectivity values are higher than those of the uncrosslinked film at comparable aging times. The similarity in slope of the selectivity versus aging time curves for all the films (crosslinked and uncrosslinked) indicates that some physical aging continues after substantial crosslinking has taken place.

6. UV irradiation after long-term physical aging

Both physical aging and UV crosslinking cause significant permeability losses. The mechanistic details of the permeability reduction are too complicated to be addressed fully, but physical aging has been shown to lead to a decrease in free volume and crosslinking may do the

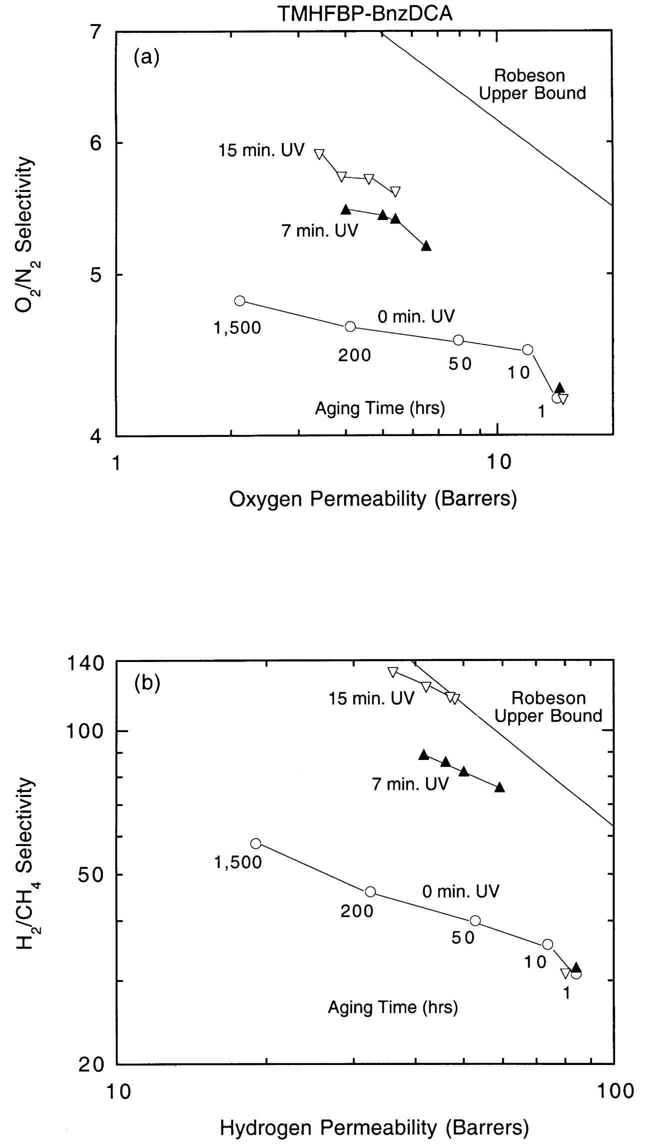

Fig. 11. Effect of crosslinking and aging time (1, 10, 50, 200 and 1500 h) on (a) oxygen permeability and oxygen/nitrogen selectivity at 2 atm and 35°C and (b) hydrogen permeability and hydrogen/methane selectivity at 5 atm and 35°C for TMHFBP-BnzDCA for the exposure times: (○) 0 min, (▲) 7 min, (▽) 15 min. The solid line on both plots depicts the “upper bound” proposed by Robeson.

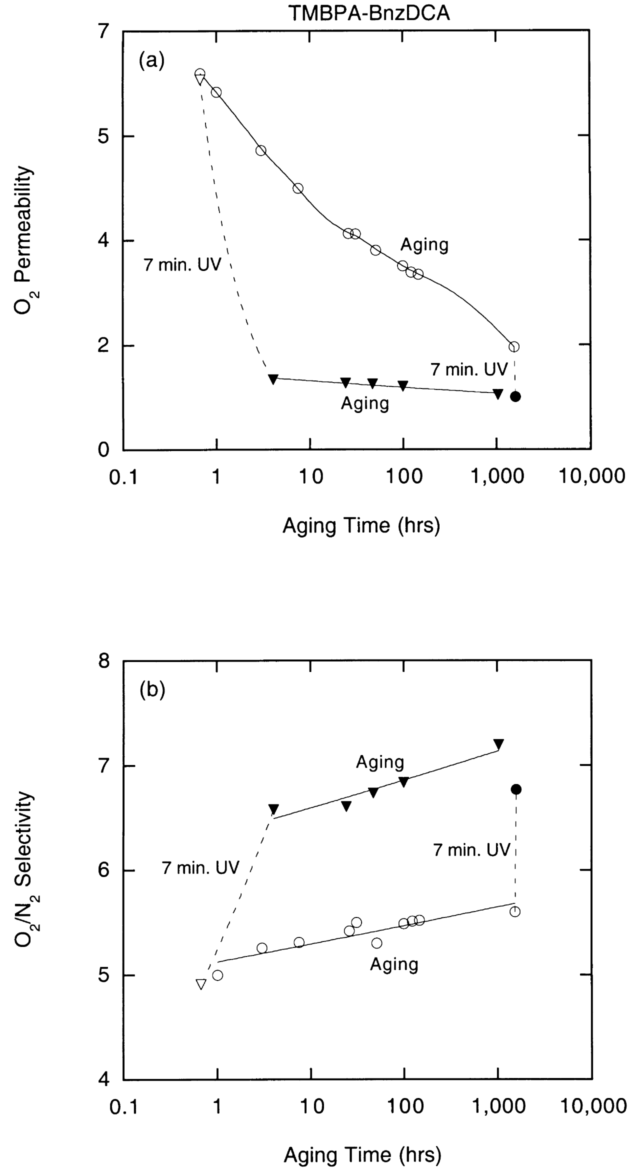

Fig. 12. Effect of sequence of UV exposure and aging on (a) oxygen permeability and (b) O_2/N_2 selectivity coefficients for two TMBPA-BnzDCA films: open symbols (○) and (▽) are for films prior to irradiation and closed symbols (●) and (▼) are for the films following 7 min of UV irradiation.

same; additionally crosslinking produces a structural modification that causes a significant increase in selectivity. The effect of the sequence of crosslinking and aging was explored by comparing the permeability reduction in two films; one film was aged and then crosslinked, while the other was crosslinked and then aged. This comparison for TMBPA-BnzDCA is shown for O_2 permeability and O_2/N_2 selectivity in Fig. 12; both films were irradiated for 7 min and the open symbols represent the data before irradiation and the closed symbols represent the data after irradiation. The final permeability and selectivity are nearly identical regardless of the sequence of physical aging and UV exposure. The same trends are evident in Fig. 13 for the H_2/CH_4 gas pair. Figs. 14 and 15 show similar results for TMHFBP-BnzDCA using a 15-min UV exposure time. After long-term physical aging, the oxygen and hydrogen permeability coefficients for the unirradiated TMHFBP-BnzDCA film are lower than those of the crosslinked film; thus, irradiating the aged film did not have a large effect on its permeability to gases. However, the O_2/N_2 and H_2/CH_4 selectivities are very similar for films that were crosslinked then aged as found for the reverse protocol.

The sequence of physical aging and crosslinking does not have much of an effect on selectivity, but since crosslinking seems to inhibit the rate of permeability loss, the sequence can have a significant effect on the permeability values at

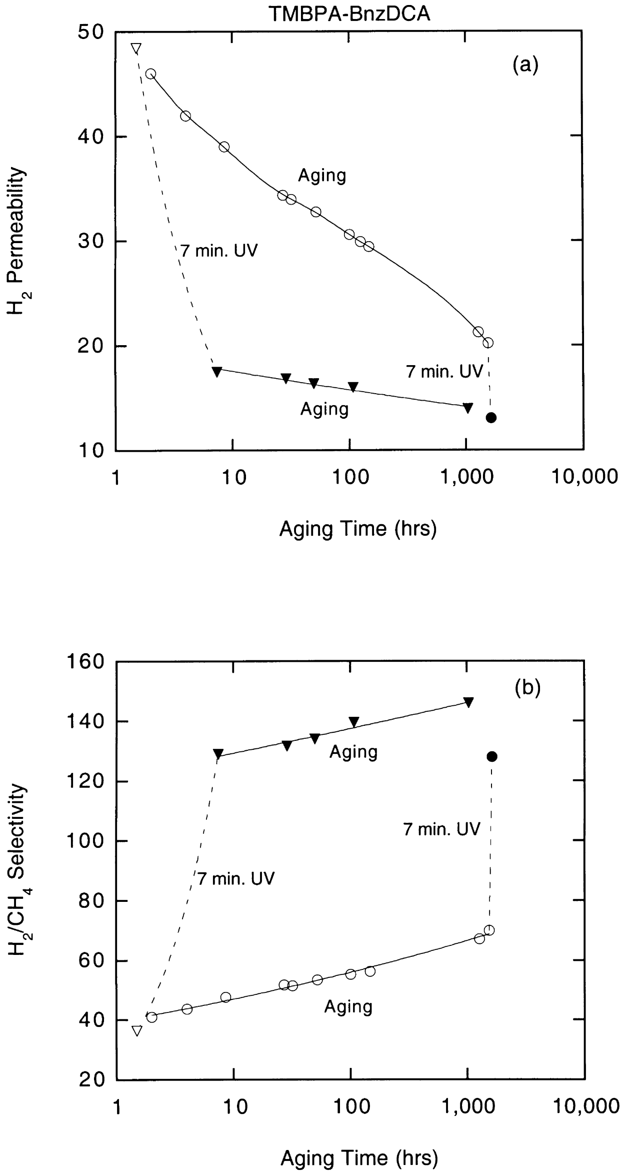

Fig. 13. Effect of sequence of UV exposure and aging on (a) hydrogen permeability and (b) H_2/CH_4 selectivity coefficients for two TMBPA-BnzDCA films: open symbols (○) and (▽) are for films prior to irradiation and closed symbols (●) and (▼) are for the films following 7 min of UV irradiation.

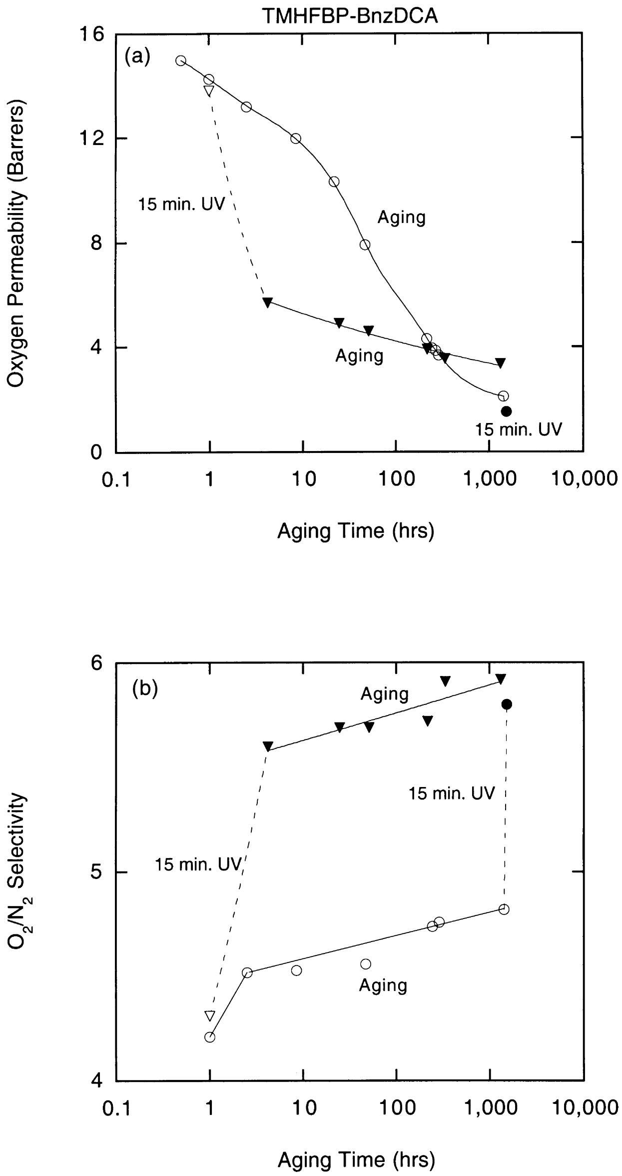

Fig. 14. Effect of sequence of UV exposure and aging on (a) oxygen permeability and (b) O_2/N_2 selectivity coefficients for two TMHFBP-BnzDCA films: open symbols (○) and (▽) are for films prior to irradiation and closed symbols (●) and (▼) are for the films following 15 min of UV irradiation.

long aging times. If a film is allowed to age before it is crosslinked, then the benefit of slowing the rate of permeability loss by crosslinking is not realized. These results indicate that the separation performance can be enhanced by crosslinking the films before extensive aging takes place.

7. Reversal of the effects of physical aging for crosslinked polymers

Reversing the effects of physical aging by heating above the glass transition temperature has been demonstrated in many studies [18,25,35–40]. In a recent study detailing the effects of physical aging on the gas permeation properties of a glassy polymer similar to those described here, McCaig and Paul [18] showed that the permeability of an aged sample could be restored to its initial value by heating above T_g for short times. This was attempted here for the TMBPA-BnzDCA and TMHFBP-BnzDCA films that had been irradiated for 1 min and aged for over 1500 h. The results of these experiments for the O_2/N_2 and H_2/CH_4 gas pairs are shown in Figs. 16–19. The shape and magnitude of the permeability and selectivity curves for the second aging cycle are all similar to those of the original films. The selectivity values during the second aging cycle all seem to be slightly lower than the original values. This ability to

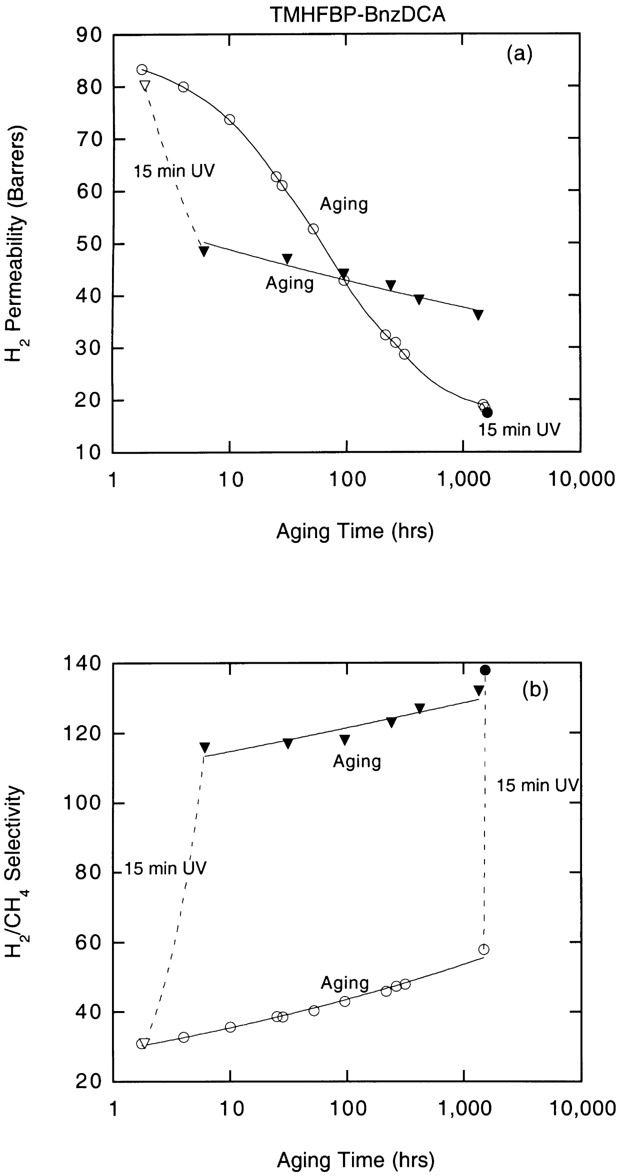

Fig. 15. Effect of sequence of UV exposure and aging on (a) hydrogen permeability and (b) H_2/CH_4 selectivity coefficients for two TMHFBP-BnzDCA films: open symbols (○) and (▽) are for films prior to irradiation and closed symbols (●) and (▼) are for the films following 15 min of UV irradiation.

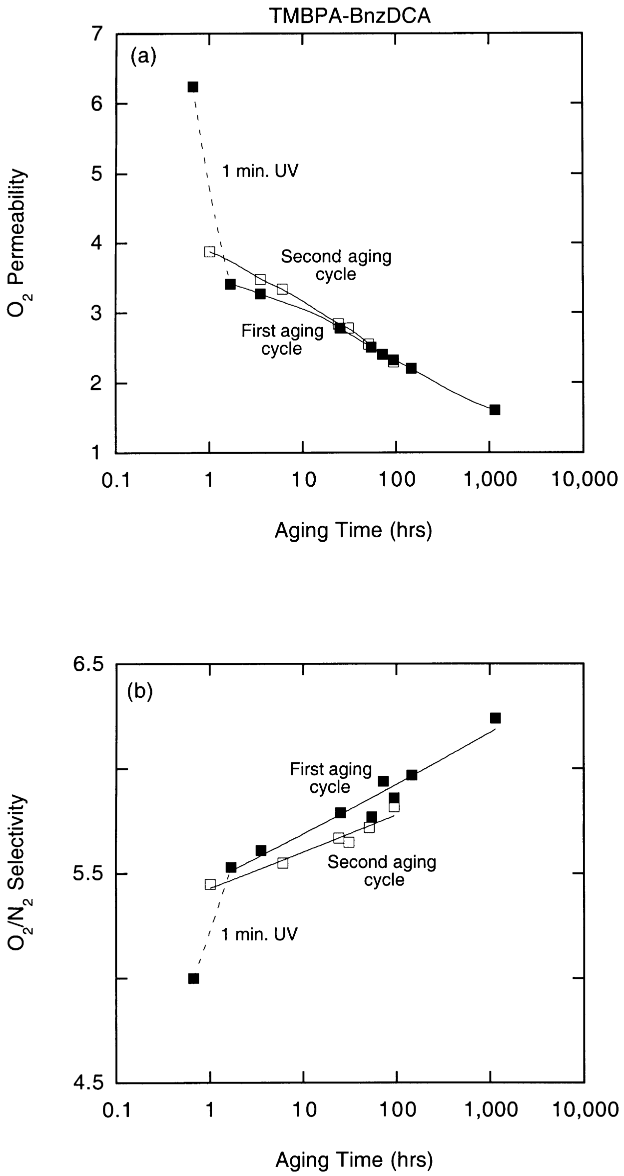

Fig. 16. Reversal of the aging response of (a) oxygen permeability and (b) O_2/N_2 selectivity coefficients for TMBPA-BnzDCA by heating above the T_g again. The first aging cycle following 1 min of UV irradiation (■) and the second aging cycle (□).

reverse only the effects of the aging part of the permeability loss by heating above T_g shows that the changes due to crosslinking are irreversible and further validates the conclusion of the previous studies [18,25] that physical aging in thin films causes a reversible loss of free volume and, therefore, permeability.

8. Summary and conclusions

The effect of UV crosslinking on the gas permeation performance of two thin glassy polyarylate films was studied here. Additionally, the aging response of crosslinked films was investigated to gain insight into the mechanisms responsible for permeability loss due to physical aging and crosslinking. The importance of the sequence of physical aging and crosslinking on gas transport properties was also studied, and the reversal of the permeability loss due to aging in crosslinked films by heating above T_g was demonstrated.

To fully explore the effects of UV irradiation on the gas transport properties of polyarylates, uniform crosslinking throughout the membrane thickness is required; this necessitated the use of very thin films due to the high absorbance of UV irradiation by the polymers studied here. Glassy

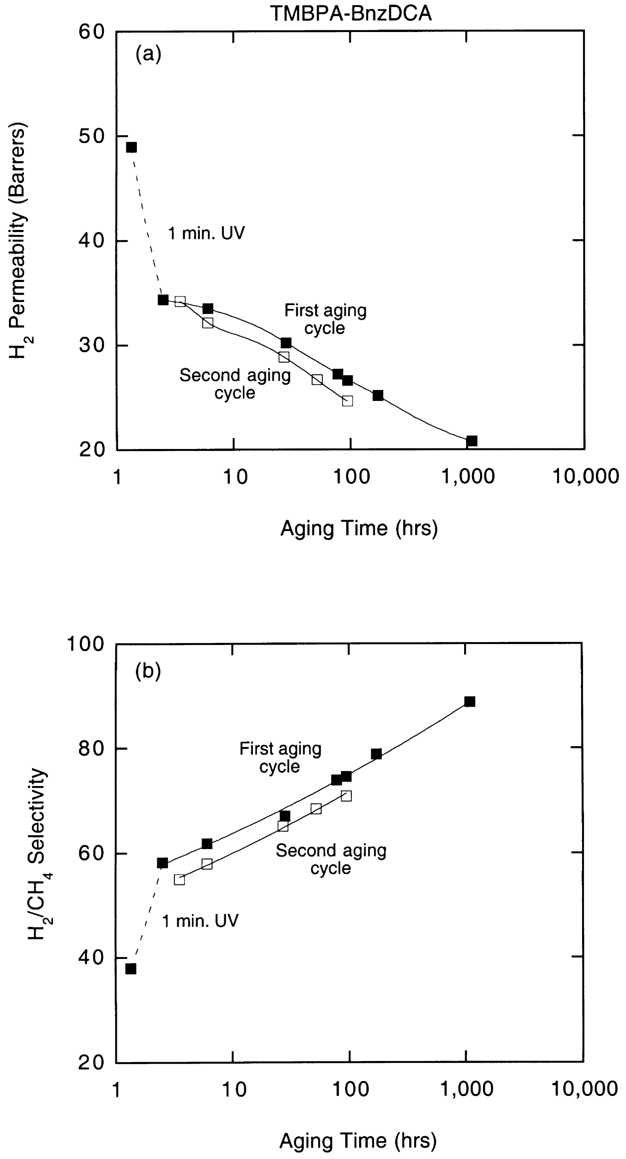

Fig. 17. Reversal of the aging response of (a) hydrogen permeability and (b) H_2/CH_4 selectivity coefficients for TMBPA-BnzDCA by heating above the T_g again. The first aging cycle following 1 min of UV irradiation (■) and the second aging cycle (□).

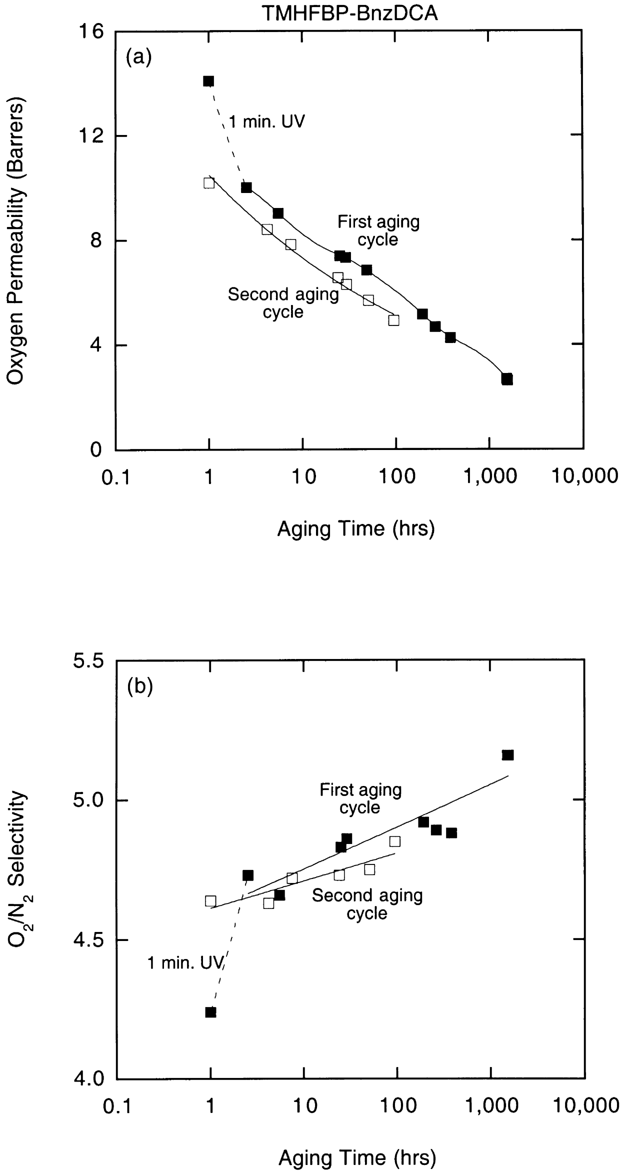

Fig. 18. Reversal of the aging response of (a) oxygen permeability and (b) O_2/N_2 selectivity coefficients for TMHFBP-BnzDCA by heating above the T_g again. The first aging cycle following 1 min of UV irradiation (■) and the second aging cycle (□).

polymer films with thicknesses on the order of those used here have been shown to exhibit significant permeability losses as a function of time; therefore, any study of the effects of UV irradiation on thin films must also include an analysis of the effects of physical aging on the gas transport properties.

Both crosslinking and physical aging cause a significant loss in gas permeability, but only crosslinking leads to a substantial gain in selectivity. Crosslinking slowed the rate of physical aging significantly but did not completely stop the aging process. The combination of higher levels of selectivity and a decreased rate of physical aging resulting from crosslinking yields greatly improved membrane performance when compared to noncrosslinked thin films. Crosslinking a high free volume polymer such as TMHFBP-BnzDCA may lead to membrane performance that approaches the upper bound for hydrogen/methane separation. This is due to the ability to optimize the extent of crosslinking by varying the UV exposure time to increase the size selective nature of the crosslinked matrix. The sequence of aging and crosslinking is important in maintaining gas transport performance. Crosslinking immediately after quenching will lead to the highest possible permeability values and comparable selectivity values when compared to films crosslinked after a significant aging time.

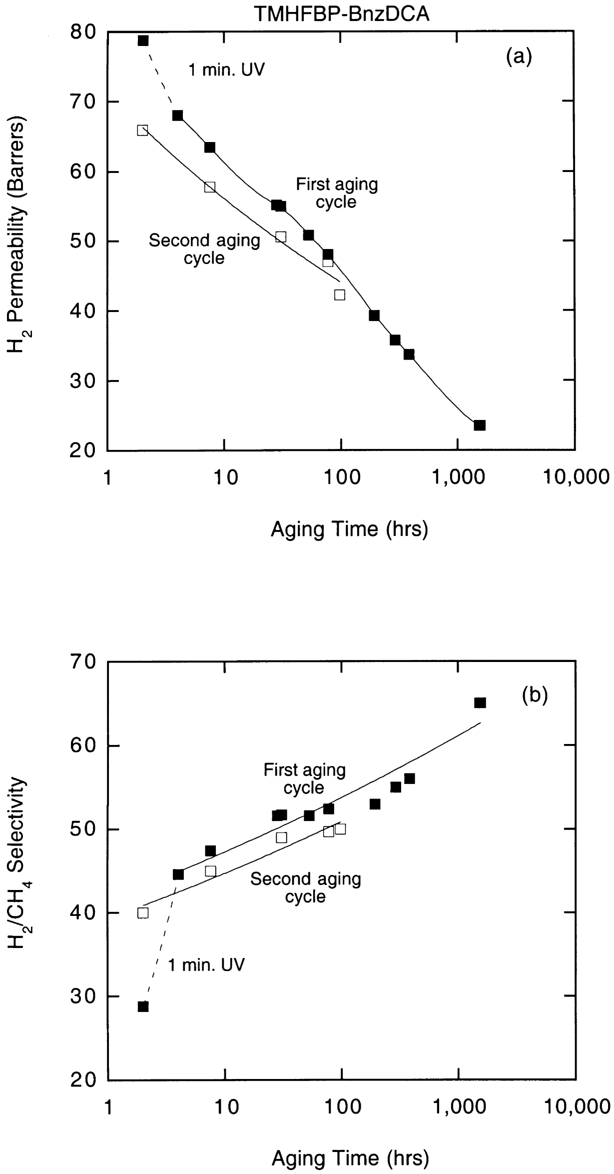

Fig. 19. Reversal of the aging response of (a) hydrogen permeability and (b) H_2/CH_4 selectivity coefficients for TMHFBP-BnzDCA by heating above the T_g again. The first aging cycle following 1 min of UV irradiation (■) and the second aging cycle (□).

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