

Gas Sorption and Transport in UV-Irradiated Poly(2,6-dimethyl-1,4-phenylene oxide) Films

C. T. WRIGHT, D. R. PAUL

Department of Chemical Engineering and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712

Received 24 March 1997; accepted 27 July 1997

ABSTRACT: Gas sorption and transport properties at 35°C have been reported for a series of UV-irradiated films of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). UV irradiation induced crosslinking in all films. The gas permeability was reduced upon crosslinking while significant increases in gas permselectivity were observed. The addition of benzophenone to the PPO films did not result in marked improvements in crosslinking or the resulting gas transport properties of the film. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 875–883, 1998

Key words: poly(phenylene oxide); crosslinking; gases; permeation; ultraviolet irradiation

INTRODUCTION

Previous studies of crosslinked polyimides demonstrate that with appropriate structural tailoring of the polymer, crosslinking can be used to advantageously improve polymer permeability and selectivity characteristics.^{1–3} It is of interest to know whether similar types of improvements in gas transport properties can be achieved for other polymer families. Crosslinking of polymethacrylates and polyarylates failed to achieve improvements comparable to those reported for the polyimides.^{4–6} As a continuation of this approach, this article examines the gas transport properties of UV-irradiated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) films. PPO is a well studied engineering thermoplastic that has been shown to crosslink upon exposure to ultraviolet light.

EXPERIMENTAL

PPO ($M_n = 22,600$, $M_w = 34,000$, $M_z = 57,200$) was provided as a gift from General Electric Com-

pany and was used as received. The polymer structure was verified through nuclear magnetic resonance; two lines were observed at $\tau = 6.49$ ppm and $\tau = 2.14$ ppm with integration of 3 : 1. Dense films were solution cast from chloroform into metal rings on glass plates heated to $\sim 45^\circ\text{C}$. The films of PPO containing benzophenone were cast in the dark. After the solvent had evaporated, the films were dried in a vacuum oven at 50°C for 1 day, 100°C for 1 day, and then at 150°C for at least a week. The films were then air quenched to room temperature and removed from the glass by immersion in water. To reduce loss of benzophenone, the films of PPO containing benzophenone were irradiated prior to drying. When the ratio of benzophenone in the PPO films was greater than 1 mol per 4 mol of PPO repeat unit (28 wt %), the films appeared cloudy after casting and were not used further. All other films were clear and differential scanning calorimetry (DSC) confirmed the absence of crystallization. Thermogravimetric analysis was used to ensure that solvent removal was complete. Unless otherwise noted, the films used were ~ 3 mils thick.

Some of the polymer films were irradiated in air with a 100-W high-intensity, longwave mercury arc lamp (UVP B-100A Blak-Ray). The inten-

Correspondence to: D. R. Paul.

Journal of Applied Polymer Science, Vol. 67, 875–883 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/050875-09

sity of the lamp was found to vary with sample position and hours of lamp use. To ensure consistent irradiation conditions, the intensity was measured before each irradiation with a UV intensity meter (JBA Model 100B), which can measure light output at 310 nm or 365 nm. Although the samples in this study were irradiated with polychromatic light, the intensity at 365 nm is provided for comparison purposes.

An effort was made to characterize the extent of crosslinking by swelling ratio and gel fraction measurements. However, upon immersion in chloroform, the films broke into small, highly swollen strands. These small strands were difficult to handle, and accurate quantitative analysis of crosslinking was not possible.

A Perkin–Elmer differential scanning calorimeter was used to measure the glass transition temperature, T_g , of the polymers at a heating rate of 20°C/min. The T_g was taken as the onset of the heat capacity step change during the second scan. The polymer density was determined at 30°C by use of a density gradient column filled with an aqueous calcium nitrate solution. The fractional free volume (FFV) was calculated from the specific volume, V , and the occupied volume, V_o , as follows:

$$\text{FFV} = \frac{V - V_o}{V} \quad (1)$$

The method of Bondi⁷ was used to calculate V_o from the van der Waals volume, V_w .

$$V_o = 1.3 V_w \quad (2)$$

The van der Waals volumes of the polymers were estimated from a group contribution method.⁸

A pressure-rise permeation cell was used to measure the pure gas permeability coefficients at 35°C for the polymer films to He, H₂, O₂, N₂, CH₄, and CO₂.⁹ Due to the brittleness of the films, the upstream driving pressure was not raised above 10 atm. The ideal selectivity was calculated from

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (3)$$

where P_A and P_B are the permeabilities of pure gases A and B.

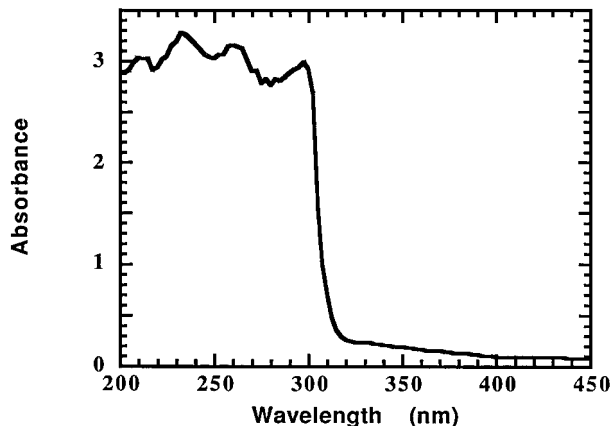


Figure 1 UV spectra for a poly(2,6-dimethyl-1,4-phenylene oxide) film (1.7 mil).

UV RESPONSE OF POLYMERS

The UV spectrum of PPO is shown in Figure 1. PPO shows a high absorbance for wavelengths below 300 nm and a significantly lower absorbance at higher wavelengths. In an electron resonance study (ESR) of PPO, Tsuji and Seiki observed free radicals in the polymer after 45 s of irradiation at all incident wavelengths between 250 and 460 nm; higher radical concentrations were observed at lower wavelengths.¹⁰ Photooxidation studies of PPO have also shown that PPO responds to a broad range of wavelengths throughout the UV and visible regions of the spectrum.¹¹ In the current study, PPO was irradiated with polychromatic light that extended well into the visible region. Light below 300 nm was filtered out by the borosilicate bulb. During the irradiation of PPO, Rivaton and Morel showed that the absorbance of PPO increases, especially at wavelengths around 340 nm, due to the chemical changes occurring within the polymer.¹¹

The FTIR spectra of PPO before and after 4 h of UV irradiation, shown in Figure 2, is consistent with the results observed by others. These spectra can be used to identify general changes in the PPO chemical structure upon UV irradiation; a detailed analysis of a PPO FTIR spectrum can be found elsewhere.¹² A small broad band developed $\sim 3530 \text{ cm}^{-1}$ after irradiation and is due to hydroxyl group formation. Another broad band in the carbonyl region, centered around 1720 cm^{-1} , also developed. Bands in the ether region were found to increase or decrease upon irradiation. The bands observed around 2350 cm^{-1} are negligible, as they are the result of atmospheric CO₂.

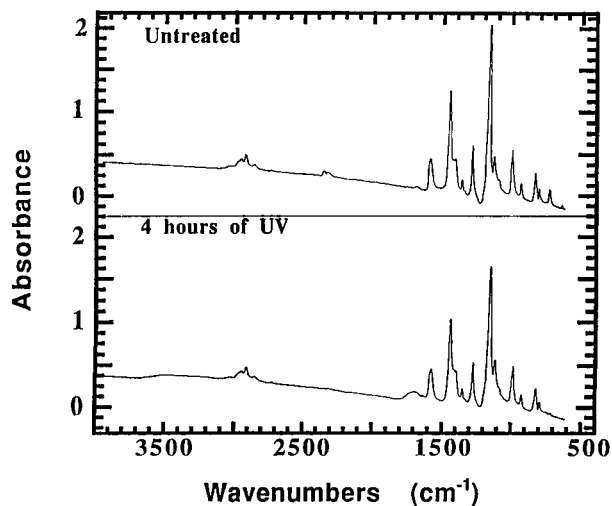


Figure 2 FTIR spectra of untreated PPO (top) and a sample irradiated for 4 h (bottom).

Although the response of PPO to ultraviolet light has been studied extensively,^{10–18} the resulting reaction mechanisms are not fully understood. However, most studies have shown that both crosslinking and chain scission result from UV exposure and are enhanced in the presence of oxygen. The crosslinking reaction has even been postulated by some to be initiated by the chain scission reaction.¹¹ The expected crosslinking reaction mechanism is shown in Figure 3. A benzylic hydrogen is abstracted from a methyl substituent and the resulting radicals may combine by scheme A or B as shown. Alternately, the chain scission mechanism results from cleavage of the polymer backbone and formation of poly(2,6-dimethylphenoxy) (PDMP) radicals (see Fig. 4). The addition of benzophenone to the polymer is expected to enhance the crosslinking reaction. Upon irradiation with ultraviolet light, benzophenone is excited to its singlet state followed by intersystem crossing to the triplet state. It will then abstract a benzylic

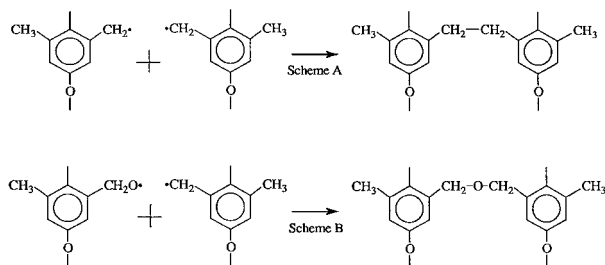


Figure 3 Expected crosslinking reaction mechanism for PPO.

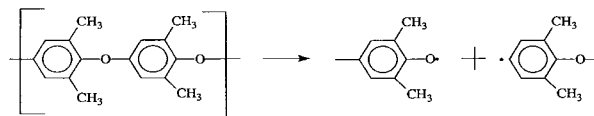


Figure 4 Expected chain scission reaction mechanism for PPO.

hydrogen from a methyl group and crosslinking can proceed as shown in Figure 3. The resulting benzophenone radical may react in several ways. Two benzophenone radicals may combine with each other to form benzopinacol.¹⁹ The benzophenone radical may react with the methyl substituent and attach to the polymer. Finally, the benzophenone radical may react with other radicals generated during the chain scission process.

PHYSICAL CHARACTERIZATION

The physical properties of the PPO-based polymers used in this study are given in Table I. The polymers formed clear, transparent films and turned yellow and brittle upon UV irradiation. Crosslinking was confirmed in the irradiated polymers by their incomplete dissolution in a known solvent for the uncrosslinked copolymer. The T_g of the PPO films did not change significantly when irradiated with UV light. This was not expected, as crosslinking typically causes an increase in T_g . Addition of benzophenone to the PPO films resulted in a lowering of the T_g by $\sim 30^\circ\text{C}$. The T_g of miscible polymer–plasticizer systems usually decreases linearly as the plasticizer content increases. The FFV of PPO is reduced both by irradiation and by the addition of benzophenone to the polymer.

The thermal stability of PPO was evaluated using thermogravimetric analysis (TGA). Figure 5 shows the TGA scan at a heating rate of $20^\circ\text{C}/\text{min}$ for an untreated PPO sample and one irradiated for 2 h. Both scans are similar; decomposition begins at $\sim 440^\circ\text{C}$ and char formation is observed. The thermal stability of PPO is not significantly altered by UV irradiation.

GAS TRANSPORT

The gas permeabilities and ideal selectivities are given in Tables II–IV. Figures 6 and 7 show the effect of UV intensity and time on the gas permeability coefficients of PPO. The permeability is reduced as irradiation time and intensity increase

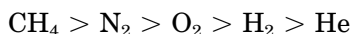
Table I Physical Properties of UV-Irradiated Poly(2,6-dimethyl-1,4-phenylene oxide)

Polymer (wt %)	Benzophenone (wt %)	Irradiation		T_g (°C)	Density (g/mL)	FFV
		Time (h)	Intensity ^a (mW/cm ²)			
100	0	0	0	206	1.070	0.197
100	0	0.5	190	207	1.076	0.193
100	0	1.1	129	207	1.076	0.193
100	0	4	36	204	1.077	0.192
100	0	4	129	202	1.077	0.192
100	0	4	190	202	1.086	0.186
88	12	4	36	174	1.111	0.172
88	12	4	36 ^b	174	1.105	0.176
88	12	4	129	178	1.110	0.172

^a The samples were irradiated with polychromatic light. For comparison purposes, intensity at 365 nm is given.

^b This sample was irradiated with light primarily at 365 nm.

and, with the exception of CO₂, this effect is greater for gases with larger molecular diameters, i.e.,



The effects of UV intensity and exposure time on the ideal permselectivity of PPO films are shown in Figures 8 and 9. Again, the UV-induced changes are dependent on the sizes of the gas molecules. The He/CH₄ selectivity of PPO increased by > 900%, the O₂/N₂ selectivity by 17%, the CO₂/CH₄ selectivity by 23%, and the He/H₂ selectivity by 100% after 4 h of irradiation with an intensity at 365 nm of 190 mW/cm².

A simplistic point of view would suggest that the UV-induced changes in PPO should be propor-

tional to the total energy, i.e., the product of time and intensity of irradiation, of the incident light. This implies that the results of a long-time, low-intensity irradiation should be the same as that of a short-time, high-intensity irradiation. A comparison of the PPO samples irradiated for 1.1 h, 129 mW/cm² and for 4 h, 36 mW/cm² shows that this reciprocity is not obeyed. Long-time, low-intensity light results in lower permeability and higher permselectivity than short-time, high-intensity light. The ESR study of PPO published by Tsuji and Seiki showed that the rate of formation of phenoxy radicals, a product of the chain scission reaction, was dependent on light intensity.¹⁰ Higher intensity light produced more phenoxy radicals. An increase in the chain scission reactions may reduce the extent of crosslinking and result in the smaller changes in the gas transport properties of PPO observed at higher light intensities.

After irradiation for 4 h at 36 mW/cm², the PPO films containing benzophenone had lower permeabilities and permselectivities than the PPO without benzophenone. The gas transport properties of the PPO films containing benzophenone do not change much with higher intensity incident light. Since benzophenone has a strong absorbance at 365 nm, the sample irradiated with light primarily at 365 nm provides the best indication of any changes induced by benzophenone. This polymer film has slightly higher gas permeabilities, due to a higher FFV, and slightly lower permselectivities than an analogous sample irradiated with polychromatic light.

The intensity of UV energy diminishes with

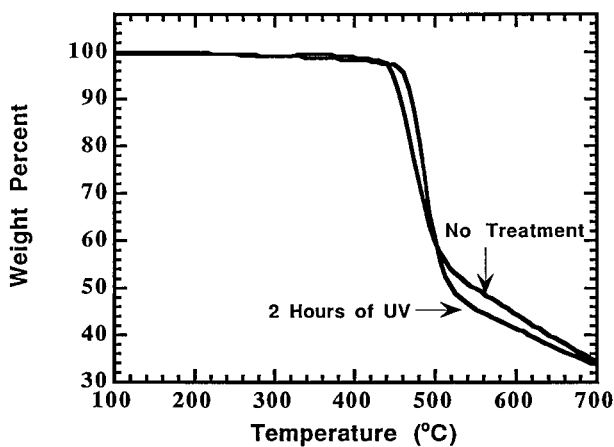


Figure 5 Thermogravimetric analysis of PPO before and after UV irradiation. Heating rate is 20°C/min.

Table II Helium Permeabilities and Ideal Selectivities for UV-Irradiated PPO at 2 atm and 35°C

Polymer (wt %)	Benzophenone (wt %)	Irradiation		P(He) Barrers	P(He)/P(CH ₄)	P(He)/P(H ₂)
		Time (h)	Intensity ^a (mW/cm ²)			
100	0	0	0	90	23	0.70
100	0	0.5	190	80	27	0.73
100	0	1.1	129	76	28	0.73
100	0	4	36	73	52	0.79
100	0	4	129	64	95	0.99
100	0	4	190	49	240	1.5
88	12	4	36	40	45	0.83
88	12	4	36 ^b	43	39	0.81
88	12	4	129	41	50	0.83

^a The samples were irradiated with polychromatic light. For comparison purposes, intensity at 365 nm is given.

^b This sample was irradiated with light primarily at 365 nm.

depth through the film due to absorption. The UV profile can often be described quite adequately by analyses such as the Beer–Lambert law

$$I = I_0 \times 10^{-ECD} \quad (4)$$

where I is the intensity at a point within 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. However, for PPO the absorption spectra vary with time due to the chemical changes arising in the polymer and the yellowing of the films. This greatly complicates absorption analysis as the profile of intensity cannot be estimated without a thorough understanding of this changing absorp-

tion behavior. However, it is known that the UV intensity, and hence crosslinking, is greater near the surface of the film. This suggests that more substantial changes in gas transport properties with irradiation might be obtained for thinner films. Table V reports the gas transport properties for PPO films of varying thicknesses irradiated for 4 h (I at 365 nm = 129 mW/cm²). The thinner film, 1.8 mil, has the lowest gas permeabilities and highest He/CH₄ and O₂/N₂ selectivities. Much thinner PPO films in the form of composite membranes were prepared by a spin coating technique described previously.²⁰ Gas transport properties for the O₂/N₂ gas pair were measured and found to be consistent with those of dense films. After UV irradiation, both the gas permeabilities

Table III O₂/N₂ Permselectivity Characteristics for UV Irradiated PPO at 2 atm and 35°C

Polymer (wt %)	Benzophenone (wt %)	Irradiation		P(O ₂) (Barrers)	P(O ₂)/ P(N ₂)	D(O ₂) × 10 ⁸ (cm ² /s)	D(O ₂)/ D(N ₂)	S(O ₂) [cm ³ (STP) cm ⁻³ atm ⁻¹]	S(O ₂)/ S(N ₂)
		Time (h)	Intensity ^a (mW/cm ²)						
100	0	0	0	17	4.7	17	3.3	0.76	1.4
100	0	0.5	190	13	5.0	17	3.5	0.58	1.4
100	0	1.1	129	12	5.0	16	3.1	0.61	1.6
100	0	4	36	8.7	5.6	12	3.6	0.57	1.6
100	0	4	129	4.1	5.6	11	3.3	0.28	1.7
100	0	4	190	1.0	5.5	5.7	3.4	0.14	1.6
88	12	4	36	4.7	5.4	7.0	3.5	0.51	1.5
88	12	4	36 ^b	5.5	5.3	8.1	3.6	0.52	1.5
88	12	4	129	4.6	5.6	6.8	3.3	0.52	1.7

^a The samples were irradiated with polychromatic light. For comparison purposes, intensity at 365 nm is given.

^b This sample was irradiated with light primarily at 365 nm.

Table IV CO₂/CH₄ Permselectivity Characteristics for UV-Irradiated PPO at 2 atm and 35°C

Polymer (wt %)	Benzophenone (wt %)	Irradiation		P(CO ₂) (Barrers)	P(CO ₂)/P(CH ₄)	D(CO ₂) × 10 ⁸ (cm ² /s)	D(CO ₂)/D(CH ₄)	S(CO ₂)	
		Time (h)	Intensity ^a (mW/cm ²)					[cm ³ (STP) cm ⁻³ atm ⁻¹]	S(CO ₂)/S(CH ₄)
100	0	0	0	70	17	8.4	5.9	6.4	2.9
100	0	0.5	190	54	18	7.8	6.4	5.3	2.8
100	0	1.1	129	53	19	7.3	6.7	5.5	2.9
100	0	4	36	34	24	5.3	6.5	4.9	3.7
100	0	4	129	16	23	5.8	6.2	2.0	3.7
100	0	4	190	4.0	21	3.2	7.0	0.97	3.0
88	12	4	36	19	21	3.1	6.8	4.6	3.1
88	12	4	36 ^b	22	20	3.7	6.5	4.5	3.1
88	12	4	129	18	23	2.9	6.9	4.7	3.3

^a The samples were irradiated with polychromatic light. For comparison purposes, intensity at 365 nm is given.

^b This sample was irradiated with light primarily at 365 nm.

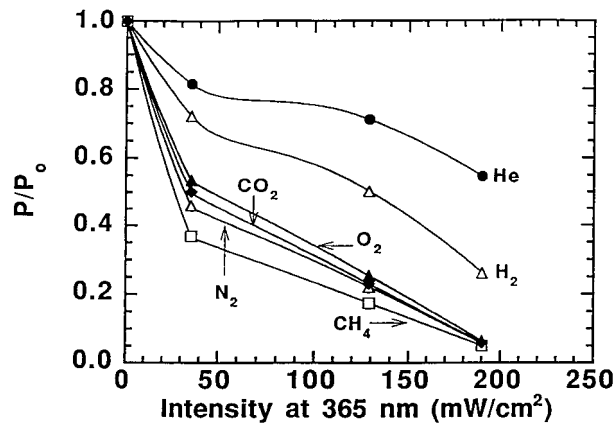


Figure 6 Effect of UV intensity on the gas permeability coefficients of PPO at 2 atm and 35°C; P_0 is the permeability coefficient of the film prior to UV irradiation for each gas. The films were irradiated for 4 h.

and selectivities decreased; the permselectivity values represented those typically observed for Knudsen diffusion. Defects in the polymer selective layer of the composite membrane, however, were not observable by scanning electron microscopy.

COMPARISON TO BENZOPHENONE-CONTAINING POLYIMIDES

Crosslinked polyimides prepared from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 2,4,6-trimethyl-1,3-phenylenediamine (TMPD) have been described recently.² A comparison of the gas transport properties of these cross-

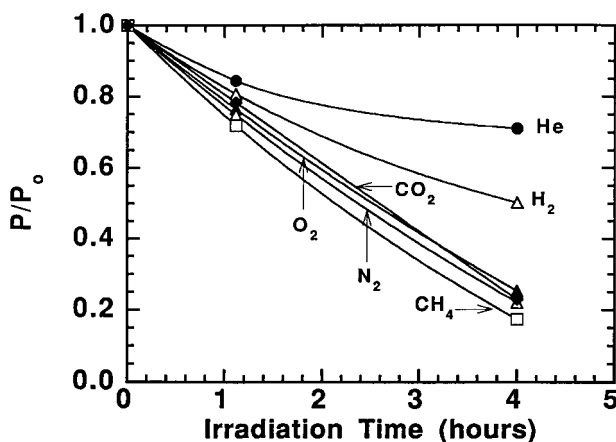


Figure 7 Effect of UV irradiation time on the gas permeability coefficients of PPO at 2 atm and 35°C. The UV intensity at 365 nm was 129 mW/cm².

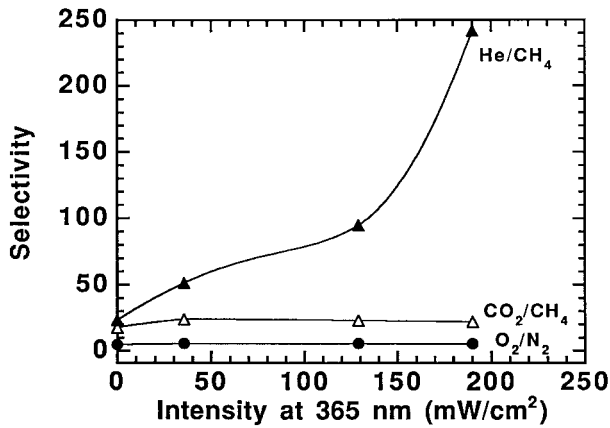


Figure 8 Effect of UV intensity on the permselectivity coefficients of PPO at 2 atm and 35°C. The films were irradiated for 4 h.

linked polyimides and the crosslinked PPO polymers of this study is shown in Figures 10–13. The different points represent various irradiation conditions and sample thicknesses. The solid line represents an “upper bound” proposed by Robeson above which no polymers are currently known to exist.²¹ The He/CH₄ selectivity increased quite dramatically with very little loss in He permeability. The polyimide study did not examine the He/CH₄ gas pair. The increase in selectivity for the H₂/CH₄ gas pair was also very large, although a larger decrease in H₂ permeability was observed. The O₂/N₂ data tend to lie very close to the upper bound; the polyimides cross the upper bound at very low O₂ permeabilities. Neither the PPO nor the polyimides exceed the CO₂/CH₄ upper bound; however, the polyimides have a better balance of selectivity and productivity for CO₂/CH₄ separations. These plots of ideal selectivity versus permeability indicate that UV-induced crosslinking of PPO and BTDA/TMPD polyimide result in quite similar changes in gas transport properties.

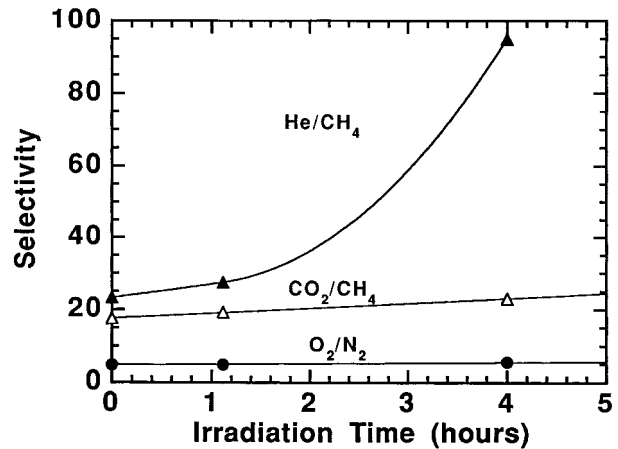


Figure 9 Effect of UV irradiation time on the permselectivity coefficients of PPO at 2 atm and 35°C. The UV intensity at 365 nm was 129 mW/cm².

SORPTION

The gas permeability coefficient can be represented as the product of a solubility term and a diffusivity term

$$P = D \times S \quad (5)$$

An apparent diffusion coefficient, D , can be calculated from

$$D = \frac{l^2}{6\Theta} \quad (6)$$

where l is the film thickness and Θ is the diffusion time lag. The solubility, S , is then calculated from the ratio of permeability and diffusivity. The ideal selectivity can likewise be factored into solubility and diffusivity terms

Table V Effect of Film Thickness on the Gas Transport Properties of UV-Irradiated PPO

Polymer Thickness ^a (mil)	P(He) ^b (Barrers)	P(He)/P(CH ₄)	P(O ₂) (Barrers)	P(O ₂)/P(N ₂)	P(CO ₂) (Barrers)	P(CO ₂)/P(CH ₄)
1.8	53	340	1.3	7.2	4.5	29
2.6	58	190	2.9	6.9	10	33
3.3	64	95	4.1	5.6	16	23

^a The films were irradiated for 4 h. The intensity at 365 nm was 129 mW/cm².

^b All data reported at 35°C and 2 atm.

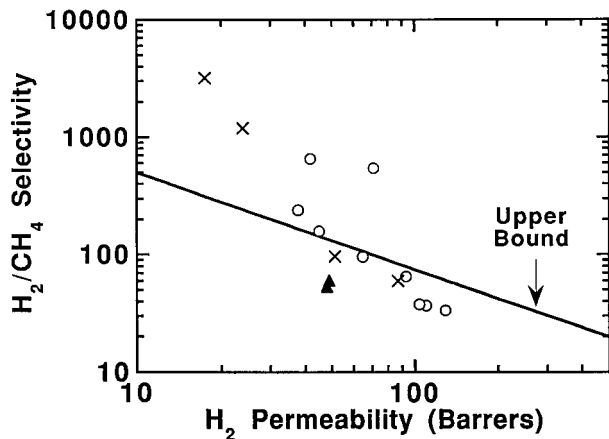


Figure 10 Comparison of the effect of UV irradiation on hydrogen/methane permselectivity characteristics for the current PPO (○) and PPO containing benzophenone (▲) films with BTDA-TMPD polyimides (×). The PPO data were obtained at 2 atm and 35°C while the polyimide data were obtained at 10 atm and 35°C.

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \cdot \left(\frac{S_A}{S_B} \right) \quad (7)$$

The diffusion and solubility coefficients are shown in Tables III–IV. There is a decrease in both the O_2 and CO_2 solubility and diffusivity coefficients with UV irradiation. Kita et al. found that the permeability changes resulted from changes in diffusivity coefficients but not solubility coefficients.² However, there was a significant amount

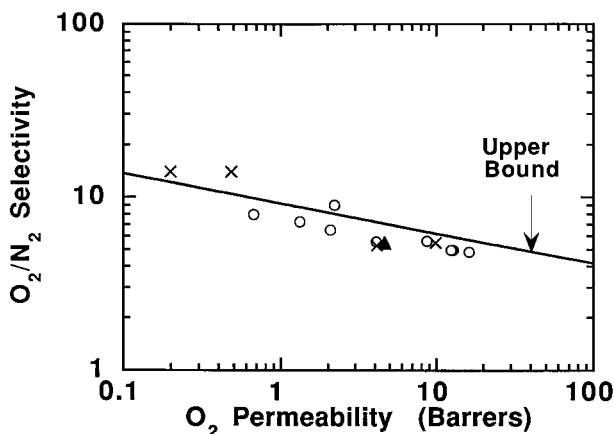


Figure 11 Comparison of the effect of UV irradiation on oxygen/nitrogen permselectivity characteristics for the current PPO (○) and PPO containing benzophenone (▲) films with BTDA-TMPD polyimides (×). The PPO data were obtained at 2 atm and 35°C while the polyimide data were obtained at 10 atm and 35°C.

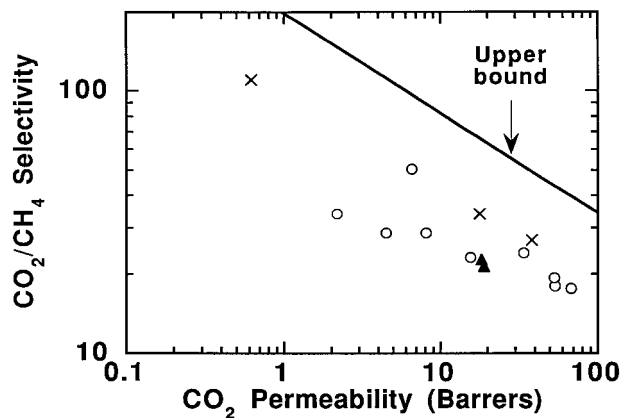


Figure 12 Comparison of the effect of UV irradiation on carbon dioxide/methane permselectivity characteristics for the current PPO (○) and PPO containing benzophenone (▲) films with BTDA-TMPD polyimides (×). The PPO data were obtained at 2 atm and 35°C while the polyimide data were obtained at 10 atm and 35°C.

of scatter in their solubility coefficient data, as much as 40% in some cases. The films of PPO containing benzophenone have even lower diffusivity coefficients; the solubility coefficients are lower for the sample irradiated 4 h, 36 mW/cm² but not 4 h, 129 mW/cm². There is some variability in the diffusivity and solubility selectivity coefficients; however, the increases in permselectivity seem to be the result of changes in both the solubility and diffusivity selectivities.

CONCLUSIONS

Gas sorption and transport properties at 35°C are reported here for a series of PPO films crosslinked

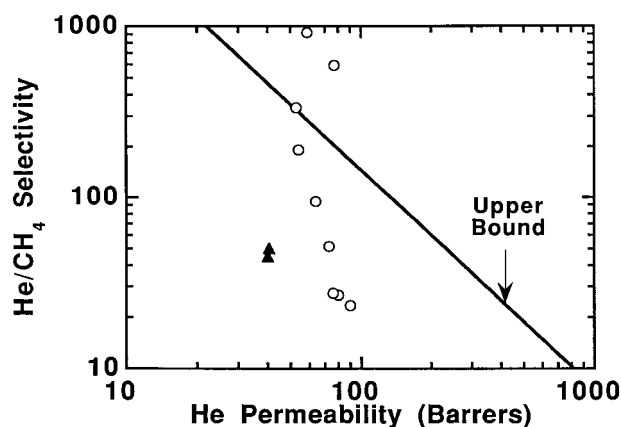


Figure 13 Helium/methane permselectivity characteristics for the current PPO (○) and PPO containing benzophenone (▲) films. Data were obtained at 2 atm and 35°C.

by UV irradiation. Solubility characterization of these films suggests that crosslinking was limited to the upper surface of the films. This theory is further supported by the fact that thinner films resulted in larger changes in gas transport properties upon irradiation.

Crosslinking reduces the gas permeability and increases the ideal permselectivity. These changes are greater for the larger gases. The permeability reduction results from decreases in both the diffusion and solubility coefficients, primarily due to free volume, or reduced chain packing efficiency, caused by crosslinking. The addition of benzophenone to the polymer did not lead to further improvements in the gas transport properties of the crosslinked PPO. The gas transport properties of the current crosslinked PPO polymers are quite comparable with those in the literature for crosslinked polyimides.

In this article, UV irradiation was carried out in air and, thus, involves some degree of photooxidation.²² A more in-depth study of the reactions that occur when this polymer is UV-irradiated in the presence and in the absence of oxygen might provide useful insights for improved modification. The presence of oxygen has been shown to cause a small inhibition effect on the similar crosslinking of polyimides²³; however, the role of oxygen may be quite different in the present case.

Another issue that needs to be better understood is the extent that the reactions induced by UV irradiation vary throughout the thickness of these films. The separating layer in practical gas separation membranes is very thin ($<1\ \mu\text{m}$) and results obtained with the thick films used here will not accurately model the productivity versus selectivity balance for thin layers if the extent of reaction varies greatly with thickness.

This research was supported by the Separations Research Program at The University of Texas at Austin. C.T.W. gratefully acknowledges the National Science Foundation and the College of Engineering at The University of Texas at Austin for fellowship support. The

authors express their appreciation to L. M. Robeson for helpful discussions.

REFERENCES

1. R. A. Hayes, U.S. Pat. 4,717,393, January 5, 1988.
2. H. Kita, T. Inada, K. Tanaka, and K.-i. Okamoto, *J. Membr. Sci.*, **87**, 139 (1994).
3. Y. Liu, M. Ding, and J. Xu, *J. Appl. Polym. Sci.*, **58**, 485 (1995).
4. C. T. Wright and D. R. Paul, *J. Membr. Sci.*, to appear.
5. C. T. Wright and D. R. Paul, *Polymer*, to appear.
6. C. T. Wright and D. R. Paul, *J. Membr. Sci.*, submitted.
7. A. Bondi, *Physical Properties of Molecular Crystals, Liquids, and Glasses*, John Wiley and Sons, Inc., New York, 1968.
8. D. W. V. Krevelen, *Properties of Polymers*, Elsevier, New York, 1990.
9. W. J. Koros, D. R. Paul, and A. A. Rocha, *J. Polym. Sci.: Polym. Phys. Ed.*, **14**, 687 (1976).
10. K. Tsuji and T. Seiki, *Polym. J.*, **4**, 589 (1973).
11. A. Rivaton and P. Morel, *Polym. Degrad. Stab.*, **35**, 131 (1992).
12. M. Scoponi, F. Pradella, H. Kaczmarek, R. Amadelli, and V. Carassiti, *Polymer*, **37**, 903 (1996).
13. R. A. Jerussi, *J. Polym. Sci.: Part A-1*, **9**, 2009 (1971).
14. P. G. Kelleher, L. B. Jassie, and B. D. Gesner, *J. Appl. Polym. Sci.*, **11**, 137 (1967).
15. J. Petruj and Z. Slama, *Makromol. Chem.*, **180**, 2461 (1980).
16. J. E. Pickett, *Amer. Chem. Soc. Polym. Preprints*, **25**, 48 (1984).
17. S. Schneider, J. Harrer, F. Richter, R. Weib, and J. Koch, *Polym. Degrad. Stab.*, **50**, 211 (1995).
18. Z. Slama, E. Svejdoва, and J. Majer, *Makromol. Chem.*, **180**, 2449 (1980).
19. R. Wycisk, P. N. Pintauro, W. Wang, and S. O'Connor, *J. Appl. Polym. Sci.*, **59**, 1607 (1996).
20. J. D. Le Roux, D. R. Paul, J. Kampa, and R. J. Lagow, *J. Membr. Sci.*, **90**, 21 (1994).
21. L. M. Robeson, *J. Membr. Sci.*, **62**, 165 (1991).
22. C. T. Wright, Ph.D. dissertation, The University of Texas at Austin, 1997.
23. A. A. Lin, V. R. Sastri, G. Tesoro, A. Reiser, and R. Eachus, *Macromolecules*, **21**, 1165 (1988).