

Gas Permeabilities and Permselectivity of Photochemically Crosslinked Polyimides

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SYNOPSIS

Photosensitive polyimide BTDA-3MPDA was modified by UV irradiation. The structure of UV-irradiated polyimides was investigated by FTIR and gel fraction measurements. The results showed that longer UV exposure time resulted in a higher extent of crosslinking. The gas permeabilities of hydrogen, oxygen and nitrogen through UV-irradiated polyimides were characterized in a temperature range from 30°C to 90°C. Photocrosslinking resulted in a sharp decline in gas permeability for hydrogen, oxygen, and nitrogen through polyimide in the initial stage of photocrosslinking. Then, as the crosslinked benzophenone percentage amounted to 28–38% for hydrogen, 17–31% for oxygen and 3–28% for nitrogen, the gas permeabilities showed another sharp decline. Gas permselectivity increased significantly with the progress of photocrosslinking, and it can be adjusted in a wide range by controlling the extent of crosslinking. Arrhenius plots of gas permeability for hydrogen and oxygen through UV-irradiated polyimides are straight lines; for nitrogen, however, change in the slope of the straight line is observed and activation energies for hydrogen and oxygen permeation show abrupt increases when crosslinked benzophenone percentage amounts to about 30%. UV-irradiated polyimides with simultaneous high gas permeability and permselectivity make them ideal candidate materials for gas separation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polyimide films are well known for their excellent mechanical and insulational properties; they can be used at elevated temperatures (up to 200–250°C) and they are resistant to most solvents and chemicals. Early research on the permeabilities of polyimides to different gases showed rather poor permeability and permselectivity. For example, the permeability of Kapton film to hydrogen is only 1.5 barrer and the permselectivity of hydrogen to nitrogen is 42¹; neither is practical for use in gas separation modules. Hollow fiber polyimide gas separation modules have been prepared, the permeability to hydrogen has been enhanced to 10 barrer, and

hydrogen permselectivity to nitrogen increased to 100–150 by modification of the polyimide's chemical structure.^{2,3} Recent studies have focused on the structure–permeability relationship of polyimides.^{4–7} Introduction of bulky substituent groups to the dianhydride and/or diamine moieties (such as methyl, trifluoromethyl, halogen etc.) increases the free volume in polyimide; a series of so-called high-permeative polyimides was obtained. The value of permeability for hydrogen can be increased by one or two orders of magnitude to around 400 barrer.^{6,8} But the selectivity of hydrogen to nitrogen was shut down to 21, even less than that of polysulfone.

On the other hand, it has been reported that crosslinking of a polymer membrane can increase its permselectivity by depressing the permeability of larger-size gas molecules. So it is of interest to study the effect of crosslinking on the gas permeative behavior of polyimides. Since polyimides were considered radiation-resistant polymers, radiation crosslinking of a polyimide would require a relatively

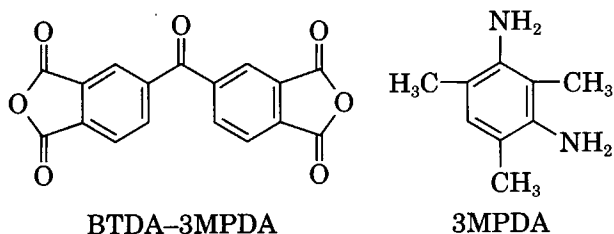
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large dose. We thus decided to use photochemical crosslinking to modify a polyimide, selecting a polyimide from benzophenone dianhydride containing a photoactive C=O group as our object in order to enhance the photocrosslinking effect. In this study, gas permeabilities through UV-irradiated polyimides prepared from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 2,4,6-trimethyl-1,3-phenylenediamine (3MPDA) are measured over a range of temperature from 30°C to 90°C. The effect of the extent of crosslinking on the gas permeability and permselectivity of polyimide and the effect of temperature on the permeabilities of photocrosslinked polyimides are investigated.

EXPERIMENTAL

Materials

The monomer structures are given below:



2,4,6-trimethyl-1,3-phenylenediamine (3MPDA) was purchased from Aldrich Chemicals (Milwaukee, WI). 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), *N*-methyl-2-pyrrolidone (NMP), acetic anhydride (Ac₂O), pyridine, and dimethylacetamide (DMF) were obtained from commercial sources. BTDA and 3MPDA were purified by vacuum sublimation and NMP was vacuum-distilled at 68°C before use.

The polyimides used were obtained by condensation of BTDA and 3MPDA in NMP for 24 h and chemical imidization with Ac₂O/pyridine for 6 h under nitrogen. The polymers were recovered by precipitation in methanol and purified by reprecipitation from DMF solution. The chemical structure of the polyimide was confirmed by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR).

Preparation of Samples

Membranes were prepared by casting a 7% solution of polyimide in DMF onto an optical flat-glass plate at 40°C to remove most of the solvent, then drying

at 200°C under vacuum for 48 h in order to remove residual DMF. The membranes were stripped from the glass plate and dried under vacuum at 100°C for 24 h. The film thickness was around 30 μm. Photocrosslinking regulation was carried out by placing the films at a distance of 8 cm from the UV source (high mercury lamp, type PRK-II, 375W, with a water-circulated cylindrical quartz filter). The extent of crosslinking was controlled by irradiation time.

Characterization of the Extent of Photocrosslinking

The extent of crosslinking was followed by FTIR, performed via Digilab FTS-TMX (USA) on 2 μm-thick film samples. In the FTIR spectrum, the 1678-cm⁻¹ band is attributed to benzophenone carboxyl stretching vibration, whose strength diminishes with the progress of the photocrosslinking reaction. The 863-cm⁻¹ band is attributed to the phenyl ring carbon-hydrogen bond, whose strength is not affected by the photocrosslinking reaction. Based on I_{1678}/I_{863} , the crosslinked benzophenone unit percentage $c = 0\%$ (r) can be calculated as below;

$$c = 0\% (r) = 1 - (I_{1678}/I_{863})_t / (I_{1678}/I_{863})_o$$

where $(I_{1678}/I_{863})_t$ for UV-irradiated samples, and $(I_{1678}/I_{863})_o$ for unirradiated samples.

Gel fraction in DMF was also determined. Unirradiated polyimide dissolved completely in DMF.

Gas Permeability Measurements

Permeability measurements of membrane samples were performed on a low-vacuum manometric apparatus⁹ at 30°C to 90°C for hydrogen, oxygen, and nitrogen whose purity is more than 99.999%.

RESULTS AND DISCUSSION

Effects of Photocrosslinking on Gas Permeability

Polyimides prepared from BTDA and alkyl-substituted aromatic diamines have been reported to crosslink on exposure to UV radiation.¹⁰ Figure 1 shows crosslinked benzophenone unit percentage and gel fraction of UV-irradiated BTDA-3MPDA as a function of irradiation time. This suggests that longer irradiation time results in a higher extent of photocrosslinking. Both the crosslinked benzophenone unit percentage and the gel fraction of UV-

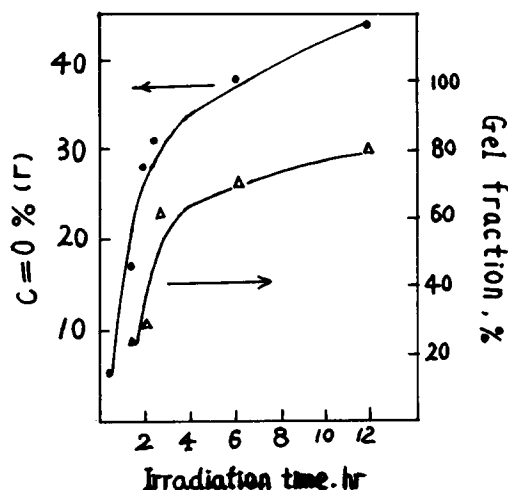


Figure 1 Change in crosslinked benzophenone unit percentage ($C=O\%$ (r)) and gel fraction on photocrosslinking of BTDA-3MPDA.

irradiated film increase sharply for the initial stage of irradiation, but start to level off after 2.5 h exposure. In the following discussion, the crosslinked benzophenone unit percentage is used as a criterion of the extent of photocrosslinking reaction.

Figure 2 shows the relationship between the relative permeabilities (P/P_0) and the crosslinked benzophenone unit percentage of UV-irradiated BTDA-3MPDA, where P_0 is the permeability of the unirradiated film.

For hydrogen, oxygen, and nitrogen, P/P_0 declines sharply when the crosslinked benzophenone unit percentage is only about 3% and the degree of permeability decrease for different gases varies in agreement with the change in their molecule diameters, i.e., hydrogen (2.73 Å) < oxygen (3.57 Å) < nitrogen (3.74 Å). P/P_0 then declines steadily but as the crosslinked benzophenone unit percentage is 28–38% for hydrogen, 17–31% for oxygen, and 3–31% for nitrogen, P/P_0 shows another sharp decline. As far as the polymer structure is concerned, changes in gas permeability result from changes in intersegmental packing and intrasegmental mobility of polymer chains.⁵ At the initial stage of photocrosslinking, intersegmental packing may become much denser and intrasegmental mobility smaller than in unirradiated polymer. So gas permeabilities decline sharply for all kinds of gases. For gases with larger molecule diameters, the effect of these polymer structure changes on their permeabilities would be larger so the degree of decrease would be higher. Then, when the extent of photocrosslinking increases to some degree, the intersegmental packing and intrasegmental mobility of polymer chains may

become even smaller for gas permeation, so gas permeability shows another abrupt decrease; for gases with smaller molecule diameters this extent of crosslinking should be higher.

The advantage of photocrosslinking can be seen by plotting gas permeability vs. permselectivity with regard to the separation of hydrogen and nitrogen. As Figure 3 shows, the effect of photocrosslinking on gas permselectivity of polyimide film is noticeable; the value of permselectivity of hydrogen to nitrogen can be adjusted over a very wide range; and, especially, the permselectivity of UV-irradiated polyimides is well above the typical tradeoff of higher permeability for lower permselectivity that is seen in many polymers, which is interesting from a membrane-separation standpoint.

Effect of Temperature on Gas Permeability

The temperature dependence of permeation coefficients of hydrogen, oxygen, and nitrogen through UV-irradiated BTDA-3MPDA from 30°C to 90°C is shown in the form of Arrhenius plots in Figure 4. For hydrogen and oxygen, a straight line is obtained for all the UV-irradiated samples. For nitrogen, a straight line is obtained when the crosslinked benzophenone unit percentage is less than 28% but

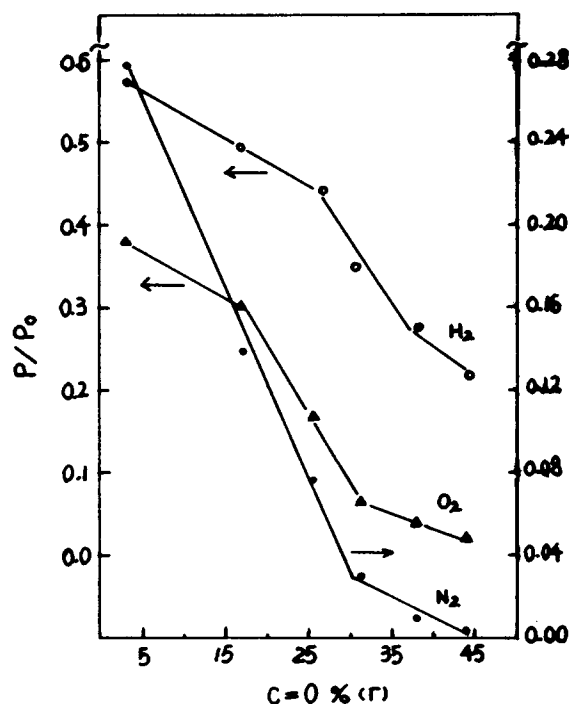


Figure 2 Effect of the extent of photocrosslinking ($C=O\%$ (r)) on the relative permeability P/P_0 of BTDA-3MPDA at 30°C.

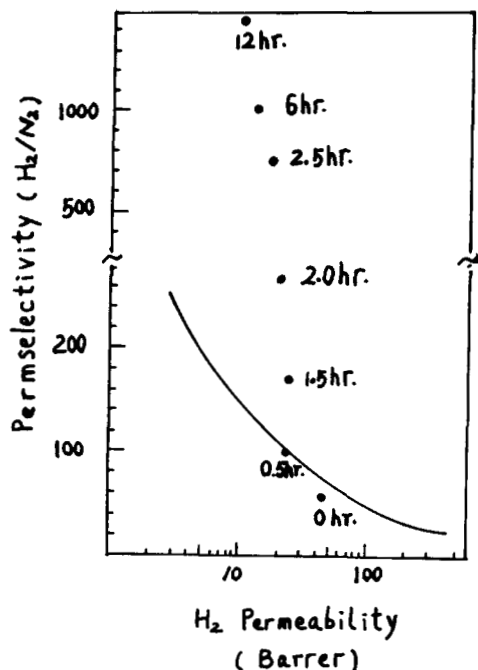


Figure 3 Tradeoff between permeability and permselectivity of photocrosslinked BTDA-3MPDA with different UV exposure times at 30°C.

abrupt slope changes in Arrhenius plots of gas permeability vs. temperature occur when that percentage is 28% or more. Such a special phenomenon may be due to its larger molecule diameter and some interaction between nitrogen molecule and polyimide.

Figure 5 shows the relationship between the relative activation energy E_p/E_{p_0} for hydrogen and oxygen permeation through UV-irradiated polyimide and its crosslinked benzophenone unit percentage, where E_{p_0} is an unirradiated sample. It can be seen from Figure 5 that the relationship between the relative activation energy and the crosslinked benzophenone unit percentage is similar to that of the relative permeability in some way, i.e., as the crosslinked benzophenone unit percentage amounts to about 30%, E_p/E_{p_0} increases sharply for hydrogen and oxygen permeation. At the initial stage of photocrosslinking, the effect of crosslinking on activation energy for permeation is small but on gas permeability is large.

As the temperature increases from 30°C to 90°C, the hydrogen-to-nitrogen gas permselectivity of UV-irradiated BTDA-3MPDA declines significantly but still remains higher as compared with other polymers. For example, at 90°C for BTDA-3MPDA with 12 h of UV exposure time, the permselectivity of hydrogen to nitrogen is 278 and gas permeability for hydrogen is 35.3 Barrer. This is still good for gas

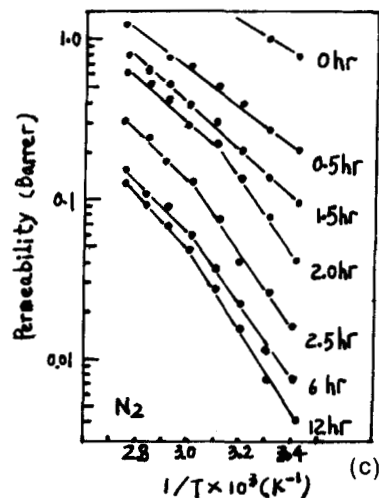
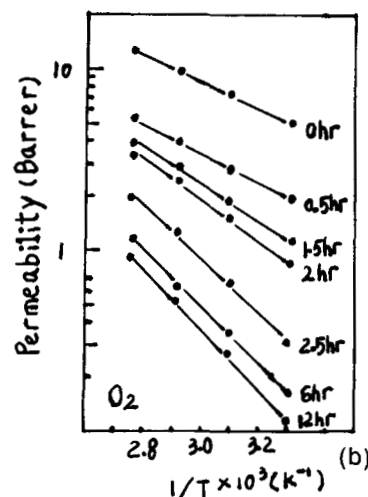
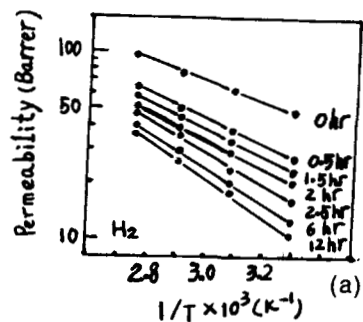


Figure 4 Arrhenius plots of permeability for different gases through photocrosslinked BTDA-3MPDA with UV exposure for different times: (a) hydrogen; (b) oxygen; (c) nitrogen.

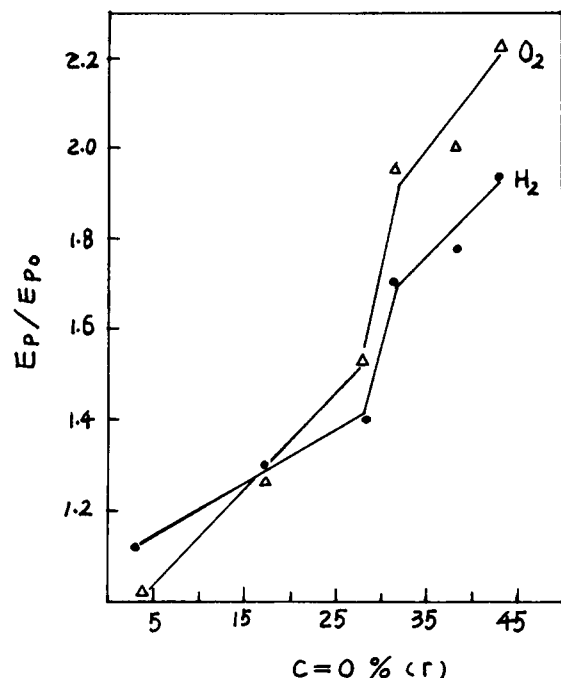


Figure 5 Effect of the extent of photocrosslinking ($C=O\%$ (r)) on the relative activation energy E_p/E_{p_0} for hydrogen and oxygen permeation through photocrosslinked BTDA-3MPDA.

separation, and with their excellent physical properties UV-irradiated polyimides can be expected to be used as membrane materials for gas separation at high temperature.

CONCLUSIONS

Photosensitive polyimides obtained from BTDA and 3MPDA are modified by UV-exposure for different lengths of time. FTIR and gel fraction measurements show that longer UV-irradiation time leads to a higher extent of crosslinking. Photocrosslinking results in a sharp decline in gas permeabilities for hydrogen, oxygen, and nitrogen at the initial stage of photocrosslinking, but such phenomena do not occur

as for activation energies for permeation. Gas permeabilities then decline steadily but show another sharp decline as the crosslinked benzophenone unit percentage reaches 28–38% for hydrogen, 17–31% for oxygen, and 3–31% for nitrogen. Activation energies for hydrogen and oxygen permeation show abrupt increases as the crosslinked benzophenone unit percentage amounts to about 30%. The relationship between gas permeability and temperature in Arrhenius plots shows a straight line for hydrogen and oxygen. For nitrogen, a straight line is observed when the crosslinked benzophenone unit percentage is less than 28%, but a change in the straight line slope in the Arrhenius plots occurs when that level is 28% or more. From a membrane separation standpoint, the overall gas separation behavior of photocrosslinked polyimides is superior to many other membrane materials that have been reported.

REFERENCES

1. H. J. Bixler and O. J. Sweeting, in *Science and Technology of Polymer Films*, Vol. 2, O. J. Sweeting, Ed., Wiley, New York, 1971.
2. A. Nakamura, M. Hotta, and K. Ninomiya, *J. Fuel Soc. Japan*, **67**, 1038 (1988).
3. R. W. Ubersax, Proceedings of ICOM'90, Chicago, August 1990, p. 798.
4. G. F. Sykes and A. K. St. Clair, *J. Appl. Polym. Sci.*, **32**, 3725 (1986).
5. T. H. Kim, W. J. Koros, and K. C. O'Brian, *J. Memb. Sci.*, **37**, 45 (1988).
6. S. A. Stern, Y. Mi, and H. Yamamoto, *J. Polym. Sci., Polym. Phys. Ed.*, **27**, 1887 (1989).
7. K. Tanaka, H. Kita, K. Okamoto, A. Nakamura, and Y. Kusuki, *J. Memb. Sci.*, **47**, 273 (1989).
8. Y. Liu, M. X. Ding, and J. P. Xu, *Chinese J. of Applied Chem.*, to appear.
9. W. Y. Liu, T. L. Chen, and J. P. Xu, *J. Memb. Sci.*, **203**, 53 (1990).
10. A. Y. Lin, V. R. Sastri, G. Tesoro, A. Reiser, and R. Eachus, *Macromolecules*, **21**, 1165 (1988).

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