④

OFFICE OF NAVAL RESEARCH
Contract N00014-91-J-1045
R&T Code 4132047---02-1

TECHNICAL REPORT NO. 9

Selectivity and Permeability of Microporous Block Copolymer Membranes

by

D.H. Rein, R.F. Baddour and R.E. Cohen
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139-4037

April 16, 1993

Reproduction in whole or in part is permitted for any purpose of the U.S. government.

This document has been approved for public release and sale; its distribution is unlimited.

15P

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
April 16, 1993

3. REPORT TYPE AND DATES COVERED
Technical Report

4. TITLE AND SUBTITLE
Selectivity and Permeability of Microporous Block Copolymer Membranes

5. FUNDING NUMBERS
N00014-91-J-1045

6. AUTHOR(S)
D. H. Rein, R. F. Baddour, R. E. Cohen

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
MIT Department of Chemical Engineering
Cambridge, MA 02139

8. PERFORMING ORGANIZATION REPORT NUMBER
9

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
—

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any purpose of the U.S. Government.

This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A selective solvent was used to develop a uniform microporous structure in a polystyrene-polymethylmethacrylate block copolymer. Pore diameters in the range of 200-500Å were produced. Gas permeation measurements demonstrated a dramatic, five order of magnitude, increase in permeability coefficient associated with the throughgoing microporous structure. These high-flux membranes retained some selectivity for certain gas pairs as expected for transport based on Knudsen diffusion in the porous materials.

14. SUBJECT TERMS
Microporous membranes
Knudsen Diffusion
Gas Separations
Block Copolymers

15. NUMBER OF PAGES
14

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
unclassified	unclassified	unclassified	UL

NOTE

Selectivity and Permeability of Microporous Block Copolymer Membranes

D.H. Rein, R.F. Baddour and R.E. Cohen*
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

Abstract

A selective solvent was used to develop a uniform microporous structure in a polystyrene-polymethylmethacrylate block copolymer. Pore diameters in the range of 200-500Å were produced. Gas permeation measurements demonstrated a dramatic, five order of magnitude, increase in permeability coefficient associated with the throughgoing microporous structure. These high-flux membranes retained some selectivity for certain gas pairs as expected for transport based on Knudsen diffusion in the porous materials.

Engineering of polymeric materials at the molecular level [1-7] for the purpose of modifying gas transport properties has led to improved gas separation membranes and certain levels of understanding of the relative importance of chain packing and chain segment mobility [3]. Morphological engineering is another method used to influence gas transport in polymers; skin layers [8] and morphology orientation [9] can lead to membranes with advantageous gas barrier and selectivity properties. In all of these examples the materials are nonporous and the gas transport occurs by a solution-diffusion mechanism in the bulk polymer; selectivity for the permeation of one gas versus another depends on both a 'solubility selectivity' and a 'mobility (diffusivity) selectivity'.

The separation properties of a polymer membrane can also be altered by changing the mechanism of gas transport. Flow through a porous membrane could be used to separate gases instead of the solution - diffusion process of dense polymers. If the mean free path of a gas molecule is much larger than the pore diameter, the gas flux is limited by the wall 'resistance' and not by molecular collisions. This porous flow regime is known as Knudsen diffusion [10]; the separation characteristics of a porous membrane through which gas transport is controlled by Knudsen diffusion can be estimated from the kinetic theory of gases. The Knudsen diffusion coefficient in a straight cylindrical pore can be expressed as [9]:

$$D_k = 9700 * r_e * (T/M)^{0.5} \qquad (1)$$

with r_e = pore radius, T = temperature, M = molecular weight of the diffusing gas, and D_k is the Knudsen diffusion coefficient. When the flux is controlled by Knudsen diffusion, selectivity becomes independent of the flux and depends on the inverse ratio of the square root of the molecular weights of the two gases.

This note describes the changes in gas transport associated with the formation of a microporous polymer structure which we have generated from a heterogeneous glassy block copolymer. The morphology of the microporous structure is characterized using SEM, bubble point analysis and BET N_2 absorption. Changes in the ideal separation factor are measured for several gas pairs at various stages of perfection of the microporous structure; a transition to Knudsen diffusion is identified and correlated with changes in the morphology.

Block Copolymer Synthesis

The high vacuum and inert gas system previously described [11] were used for the reagent purification and anionic synthesis. Standard methods were employed for the purification of the styrene and methyl methacrylate monomers and the tetrahydrofuran solvent. The sequential anionic block copolymer synthesis involved the polymerization of the styrene block in THF at -78 °C using *n*-BuLi as the initiator. After complete conversion, 1,1-diphenylethylene was added to the chain ends to reduce the nucleophilicity of the styrene carbanion [12]. Then, methyl methacrylate monomer was added to the living chains at -78 °C, polymerized to completion and terminated with methanol. The molecular weight of the polystyrene block, determined by gel permeation chromatography, was 150,000 and the polydispersity of the polystyrene-polymethylmethacrylate block copolymer (PS-b-PMMA) was 1.2. Proton NMR (250 MHz) of PS-b-PMMA revealed a molar composition of 31% PMMA.

Formation of Microporous Membranes

Thin films (0.2 mm) of PS-b-PMMA were produced by casting a 5% (w/w) solution in THF onto a flat polytetrafluoroethylene surface and slowly evaporating the solvent under a N_2 purge. The static cast films were annealed in vacuum for 24 hours at 100 °C to remove any solvent and stresses remaining from the casting process. Transmission electron microscopy [13] of microtomed samples revealed a microphase separated morphology of PMMA cylinders with a diameter of 200 Å in a continuous matrix of PS. Staining was not necessary to achieve contrast in the TEM since the PMMA selectively degrades in the electron beam.

A PMMA-selective solvent crazing process was employed in the production of the microporous structure. The process required a solvent for PMMA which was a nonsolvent for PS. Mixtures of alcohols and water satisfy this criterion [14]; a mixture of 90% isopropanol, 10% water was chosen for our work. PS-b-PMMA films were immersed in the isopropanol/water mixture at 70°C for various periods of time. As the solvent treatment proceeded, the brittle, transparent PS-b-PMMA films exhibited remarkable changes in physical appearance and properties; they became opaque, increased in weight and size and became quite flexible, resembling ordinary filter paper. The weight and thickness of the film both increase rapidly at early exposure times (Figure 1) and eventually level off. The extent of solvent treatment will hereafter be referred to as a percentage of weight gain, % W = 100 * $((W_t - Wo)/W_\infty - Wo)$ where W_t is the weight of the film at a specified time after immersion in the solvent, Wo is the initial weight and W_∞ is the final weight. Solvent treated films attained a final weight uptake corresponding to 2.7 times Wo. This absorbed solvent could be completely removed by exposure to vacuum for 24 hours at room temperature leaving a porous polymer film of weight Wo; these films remained in the expanded state at room temperature, but they readily collapsed to the original thickness upon annealing for 4 hours at 100°C.

Dramatic morphological changes were observed in SEM of the surface (Figure 2) and edge (Figure 3) views of a PS-b-PMMA film solvent treated to 100% W. The edge view was taken from a sample frozen and fractured in liquid N_2. These micrographs suggest a relatively narrow size distribution of voids incorporated during the solvent treatment; the voids appear to be about 500 Å-1000 Å in diameter. The pores were also characterized using bubble point analysis with isopropanol as the wetting fluid, and these results indicated a diameter between 200 - 500 Å ± 10%. The size of the limiting constriction through the film which is probed by the bubble point fluid is therefore smaller than the pore size observed in the SEM.

The surface area of the pores in the solvent treated block copolymers can be calculated knowing the volume fraction of the pores and assuming a pore diameter. Choosing a pore diameter of 1000 Å and estimating the pore volume fraction from the increase in film dimensions with solvent treatment yields a, the pore surface area of 11.2 m^2/g. This is significantly smaller than the specific surface area of 41.2 m^2/g measured directly using the N_2 BET. A uniform pore diameter of 270 Å would be required to match the calculated and measured surface areas; the discrepancy suggests that there are voids in the films smaller than those visible in the SEM which are accessible by N_2 in the BET measurement.

The mechanism for the formation of the porous morphology involves an advancing sharp front in the early stages of the solvent treatment. The front is clearly visible in optical micrographs of edge views of films solvent treated to various extents [13]. The SEM edge view of Figure 4 delineates the advancing front between the porous and nonporous material. The velocity of the advancing front under the present treatment conditions, estimated from a series of optical micrographs, is about 300 nm/minute; penetration to the center of the film occurs at a solvent treatment near 25% W. Solvent absorption past 25% W involves an expansion of the porous structure ultimately attaining the structure seen in Figure 3. The solvent treatment which occurs prior to the penetration of the front through to the film center results primarily in the formation of new pores, while subsequent solvent treatment primarily involves the growth and coalescence of the existing pores.

Gas Transport

Gas permeability coefficients (P) for He, Ar, CO_2, and CH_4 were measured as a function of solvent treatment at 25 °C using a variable-volume permeation apparatus [15]. Figure 5 displays the permeability coefficients for Ar and CO_2 as a function of solvent treatment. There is a large increase in permeability for all gases at a treatment level of 10% W, and by 45% W the permeability coefficients increased five orders of magnitude beyond the values for untreated bulk films. Table I shows the ideal separation factors for He/Ar and CO_2/Ar as a function of solvent treatment as well as those predicted assuming gas transport by Knudsen diffusion. Based on these selectivity results, the mechanism governing the gas permeation changes from transport through the polymer to flow through the pores near a solvent treatment of 10% W.

To summarize, controlled solvent crazing of a microphase separated block copolymer was used to form microporous membranes in which the size and size distribution of the pores reflects the nature of the starting morphology. Bubble point analysis determined the final pore size to be 200-500 Å in diameter. Gas permeation measurements on the porous block copolymer displayed a five order of magnitude increase in the permeability coefficient, and a transition to a selectivity based on Knudsen diffusion. The solvent treatment produces membranes which lose some but not all of the selectivity of the bulk film (e.g. a reduction from about 15 for He/Ar in bulk to about 3 for the fully porous material). However there is a very favorable increase of more than five orders of magnitude in the overall flux (permeability) which accompanies this selectivity reduction.

Acknowledgements

This research was supported by the Office of Naval Research and by the DuPont (RFB) and the Miles (REC) professorships in chemical engineering at MIT.

References

1. Koros, W. J.; Story, B. J.; Jordan, S. M.; O'Brian, K.; Husk, G. *Polym. Eng. Sci.* **1987**, *27*, 603.

2. Moe, M. B.; Koros, W. J.; Paul, D. R. *J. Polym. Sci. Polym. Phys.* **1988**, *26*, 1931.

3. Coleman, M. R.; Koros, W. J. *J. Mem. Sci.* **1990**, *50*, 285.

4. Kim, T. H.; Koros, W. J.; Husk, G. R.; O'Brian, K. C. *J. Mem. Sci.* **1988**, *37*, 45.

5. Puleo, A. C.; Muruganandam, N.; Paul, D. R. *J. Polym. Sci., Polym. Phys.* **1989**, *27*, 2385.

6. Chern, R. T.; Sheu, F. R.; Jia, L. Stannett, V. T.; Hopfenberg, H. B. *J. Mem. Sci.* **1987**, *35*, 103.

7. Chern, R. T.; Jia, L.; Shimoda, S.; Hopfenberg, H. B. *J. Mem. Sci.* **1990**, *48*, 333.

8. Anand, M.; Costello, C. A.; Keith, D. U.S. Patent 5 013 338, 1991.

9. Csernica, J.; Baddour, R.F.; Cohen, R.E.; *Macromolecules*, **1990**, *23*, 1429.

10. Satterfield, C. N. *Heterogeneous Catalysis in Practice:* McGraw Hill, New York, 1980.

11. Cazzaniga, L.; Cohen, R. E. *Macromolecules*, **1991**, *24*, 5817.

12. Rempp, P.; Merrill, E. W. *Polymer Synthesis*: Huthig & Wepf, New York, 1986.

13. Rein, D. H. Ph.D. Thesis, Massachusetts Institute of Technology, October, 1991.

14. Cowie, J. M. G.; Mohsin, M. A.; McEwen, I. J. *Polymer*, **1987**, *28*, 1569.

15. ASTM D-1434, *American Society for Testing and Materials*: Philadelphia, 1984.

Table I

Ideal Separation in Solvent Treated PSPMMA

	Measured		Knudsen	
Solvent treatment %W	$\frac{P(He)}{P(Ar)}$	$\frac{P(CO2)}{P(Ar)}$	$\frac{P(He)}{P(Ar)}$	$\frac{P(CO2)}{P(Ar)}$
0	15	8.0	3.2	0.6
7	20	5.1	3.2	0.6
10	3.2	0.9	3.2	0.6
25	2.5	0.9	3.2	0.6
45	3.1	0.9	3.2	0.6

Figures

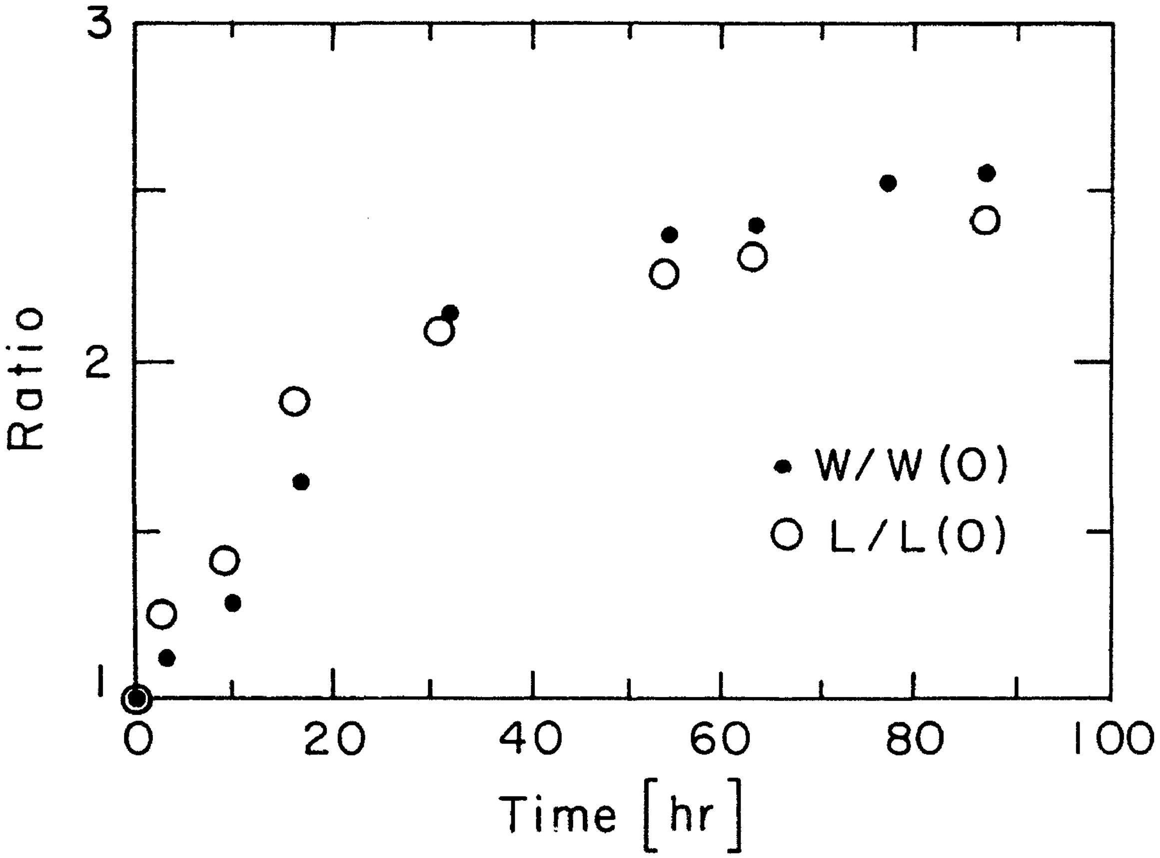
1. Dependence of the normalized weight gain, W/W(o), and thickness increase, L/L(o), as a function of solvent treatment time. Lateral dimensions remained essentially uncharged.

2. Scanning electron micrograph of the surface of a film treated to 100%W. Scale bar corresponds to 5μm.

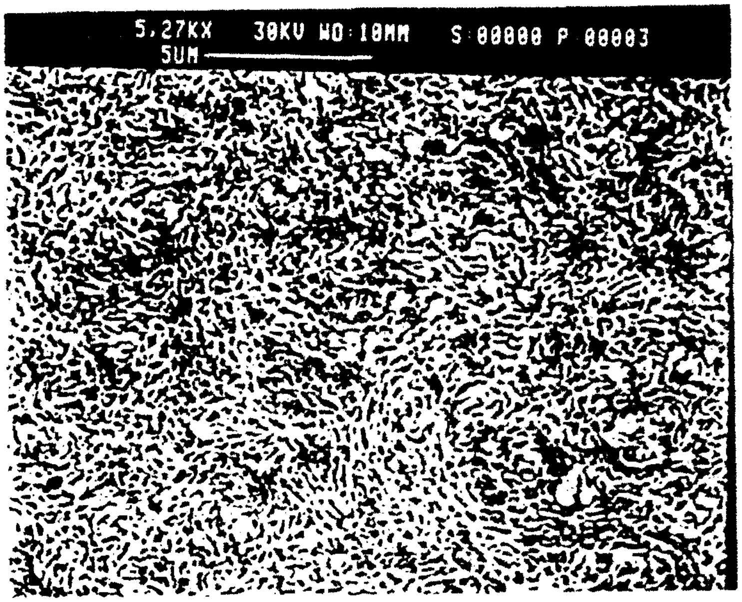
3. Scanning elecgron micrograph of a cryo-fracture surface, of a film treated to 100%W. View is perpendicular to that of Figure 2. Scale bar corresponds to 1μm.

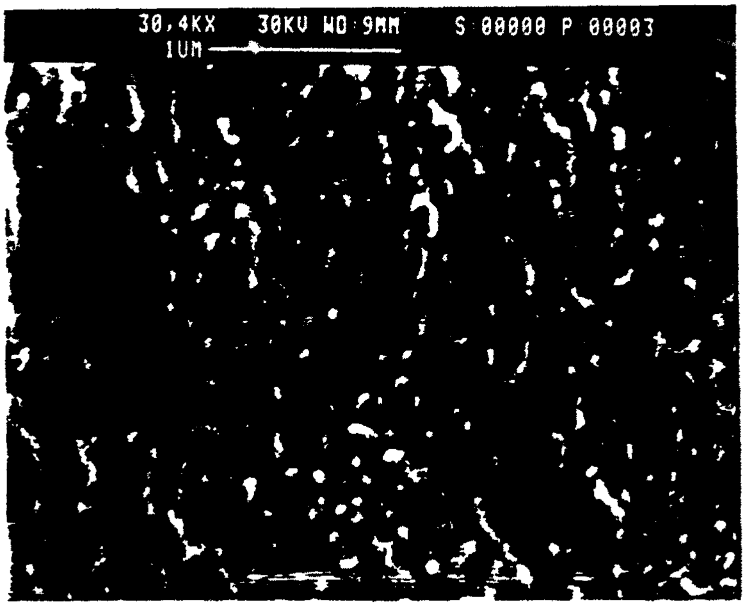
4. SEM of a cryo-fracture surface similar to Figure 3. Film treatment is less than 25%W. The advancing front between porous (right) and bulk (left) material is visible near the center of the micrograph.

5. Dependence of gas permeability on solvent treatment for argon and carbon dioxide.



FIG


5,27KX 30KV WD:10MM S:00000 P:00003
5UM


30,4KX 30KV WD:9MM S:00000 P:00003
1UM

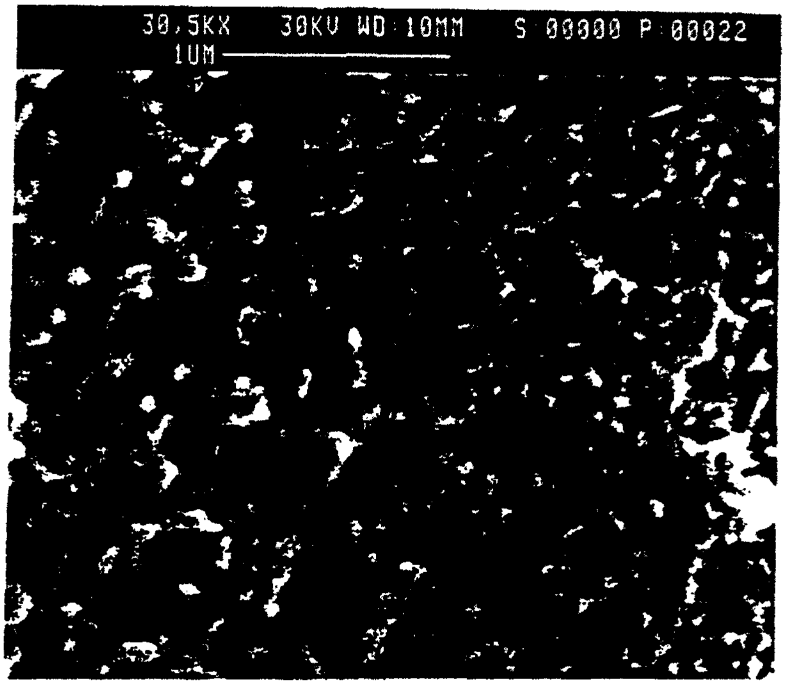


Fig 7

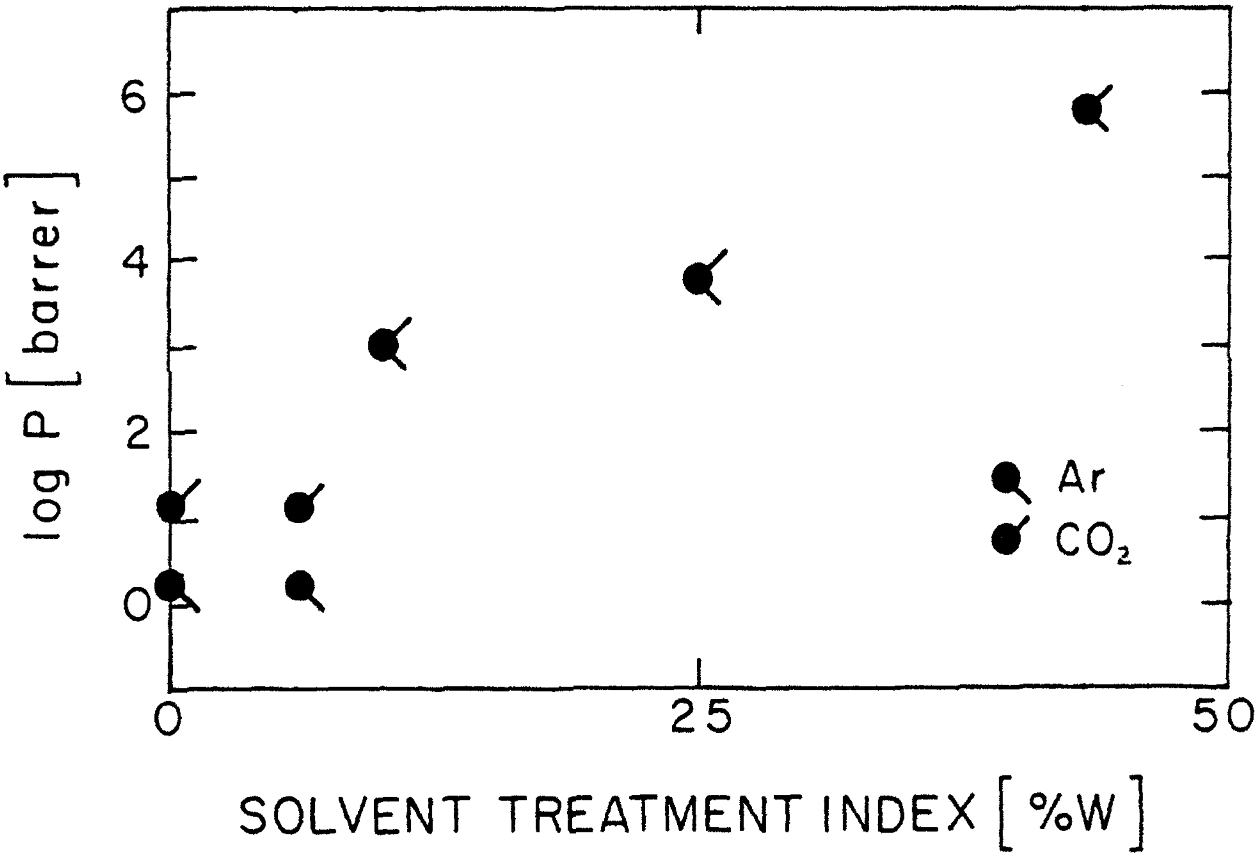


FIG 5