

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Photocontrol of Gas Separation Properties

Dale E. Hauenstein^{ab}; David G. Rethwisch^a

^a Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa ^b Dow-Corning Corporation, Midland, MI

To cite this Article Hauenstein, Dale E. and Rethwisch, David G.(1990) 'Photocontrol of Gas Separation Properties', Separation Science and Technology, 25: 13, 1441 — 1453

To link to this Article: DOI: 10.1080/01496399008050402

URL: <http://dx.doi.org/10.1080/01496399008050402>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PHOTOCONTROL OF GAS SEPARATION PROPERTIES

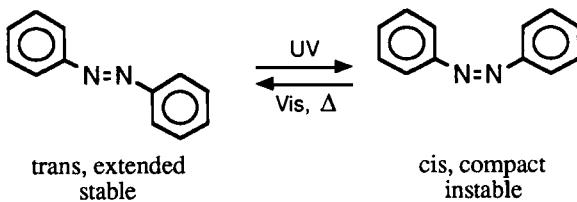
Dale E. Hauenstein^a and David G. Rethwisch^b
Department of Chemical and Biochemical Engineering
University of Iowa
Iowa City, Iowa 52242

ABSTRACT

Incorporation of photoresponsive moieties (phenylazobenzene) into a polymer (ethyl cellulose) has been shown to provide a method to reversibly modify the diffusivity of a non-porous membrane for gas separations. The diffusivity of N₂ decreased by up to 18% upon exposure to UV light. No changes were observed for the other gases in this study (Ar, He, H₂, CO, CO₂, and O₂). The anomalous behavior of N₂ is explained in terms of an interaction between the N₂ and cis-azobenzene.

INTRODUCTION

In azoaromatic compounds, ultraviolet (UV) irradiation ($310 < \lambda < 400$ nm) induces a reversible trans-cis isomerization. The cis-trans reverse isomerization occurs in darkness or is stimulated by visible light ($410 < \lambda < 440$ nm) or heating.



^aCurrent address: Dow-Corning Corporation, Midland, MI

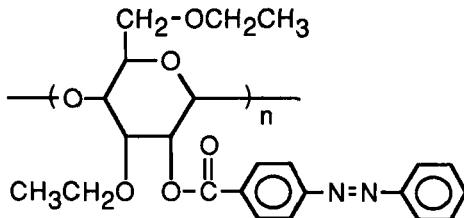
^bAuthor to whom all correspondence should be addressed.

Incorporation of these photoresponsive molecules into polymers allows reversible control of polymer properties (e.g., viscosity, solubility, and length [1-8]). This study deals with the use of these photoresponsive polymers to develop systems capable of selectively controlling the separation of gases.

Several methods have been reported for controlling membrane properties in real-time. Most of these methods involve porous membranes using a polymer with a "chemical valve" function. In these membranes, a mechano-chemical contractive force is used to enlarge and contract membrane pores reversibly resulting in controlled permeability for the separation of macromolecular solutes. This valving action is controlled by use of temperature [9], magnetic fields [10], electrical fields [11], changes in pH or ionic concentration of the medium [12,13], or by chemical complexing agents [14]. While these control mechanisms are readily implemented in liquid systems, they are difficult to use for gas separation membranes. For example, pH, ionic concentration, and chemical complexing agents require the presence of liquids as solvents or electrolytes.

Recent studies have suggested that membrane properties can be controlled by incorporating photoresponsive molecules such as azobenzene into membranes. The most significant development in the photocontrol of membrane separation properties was reported by Ishihara and Shinohara [6]. A swollen membrane of poly(2-hydroxyethyl methacrylate) (pHEMA) containing 2 mole% p-phenylazobenzoyl (PAB) sidegroups displayed a 50-80% reduction in permeability when irradiated with UV light (350 ± 50 nm). Larger reductions were observed for the higher molecular weight substrates. Indeed, following irradiation, lysozyme and chymotrypsin no longer permeated through the membrane.

In this study, the use of photoresponsive polymers as membranes is expanded to use as controllable gas separation membranes. In particular, we studied the ability to use UV irradiation to reversibly modify the permeability and diffusivity of gases through nonporous membranes made of ethyl cellulose (EC) modified with 18-46% p-phenylazobenzoyl chloride (PAB/EC).



EXPERIMENTAL METHODS

Sample Preparation

The modification of EC proceeded by a two-step esterification similar to that described by Crowther, et. al (15). Briefly, ethyl cellulose (Dow Chemical, Ethocel, 49% ethoxy content) was dissolved in toluene, and butyllithium (1.6 M solution in

hexanes) was added over a 10 min period, producing a clear, turbid solution. The reaction proceeded for 15 min under a N₂ purge. P-phenylazobenzoyl chloride (PABC) in a 50/50 (v/v) mixture of anhydrous ethyl ether and toluene was added, and the reaction continued for 20 h. Then 5 ml of distilled water was added to the mixture to quench the reaction, resulting in a slight precipitation. The solution was rotovapped to dryness, producing a reddish product.

To purify the resulting polymer and remove unreacted azobenzene, the product was washed 3 times with 0.2 M aqueous sodium chloride solution, followed by 5 washes with warm (ca. 310 K) distilled water. After drying, the product was redissolved in THF and precipitated in distilled water (twice) and dried at 335 K in a drying oven. The resulting PAB/EC samples were uniform in color, with sample color ranging from orange-red for the lowest PAB concentration (18 mol%) to dark red for the highest PAB concentration (46 mol%). Samples were insoluble in water, but were soluble (ca. 0.1 g polymer/ml solvent at 298 K) in acetone, chloroform, ethyl ether, DMF, MEK, THF, and toluene. Analysis with UV, IR, and NMR spectroscopies verified the successful attachment of the PAB groups.

Sample Characterization

The dye concentration and the trans-cis ratio in the films were determined spectrophotometrically at a wavelength of 334 nm. The mole percent of PAB incorporated into the ethyl cellulose (PAB/EC) ranged from 18% to 46%. Sample names were derived from the sample composition. For example, 46 PAB/EC indicates a sample in which 46 mol% of the free hydroxyl groups in EC (51% hydroxy content) had been reacted with PABC. The density of each sample was determined using the displacement method. The molecular weights of the PAB/EC samples were determined using gel permeation chromatography. A DuPont Zorbax PSM Bimodal-S column was used, having a molecular weight range from 10² to 10⁶ g/mole. The mobile phase was degassed HPLC-grade THF. Differential scanning calorimetry (DSC) was kindly run by the Polymer Research Group at the University of Wisconsin-Madison. A Perkin-Elmer DSC-II instrument was used with a scan rate of 20 K/min from 150-490 K.

The PAB/EC samples were used to prepare non-porous membranes. An 8% (w/v) solution of PAB/EC in MEK was filtered through a 70-100 μ m fritted-glass filter (Ace Glass), cast in an aluminum weighing pan, and the solvent evaporated over 5 days, producing a reddish membrane. The resulting membrane was dried in a drying oven at 335 K for 4 days, evacuated at 298 K for 4 days, and stored in a desiccator until use.

The "time-lag" method of Daynes and Barrer was used for measuring the permeability and diffusion coefficients (16,17). The units used throughout this investigation were Barrer (cm³(STP)-cm/sec-cm²-cmHg) for permeability and cm²/sec for the diffusion coefficient. For these measurements, we used an upstream pressure of 1275 Torr and an initial downstream pressure of 10⁻³ Torr. The diffusion cell was specially constructed with a quartz window to allow the entire membrane to be irradiated during permeability measurements. A detailed description of this apparatus is given elsewhere (18). The UV source was a BlackRay[®] longwave ultraviolet lamp consisting of a 115 volt transformer, 100 watt bulb, and a 365 nm filter. The filtered lamp provided wavelengths from 365 to 367 nm. The light intensity of the lamp was rated for 7000 mwatt/cm² at a distance of 38 cm.

Before permeability measurements, the membrane (40 mm OD x 0.1-0.3 mm thick) was sealed in the permeability apparatus and preconditioned by treating for 48 h at ca. 10^{-3} Torr during which the membrane was annealed by cycling the temperature twice from 300 K to 350 K. Between runs the membrane was degassed by evacuation for 1-8 h. The required evacuation times to obtain reproducible results varied with each gas. For example, consistency in data was established with evacuation times of 1.5 h for He and H₂; 3 h for CO₂; 4 h for O₂; and 8 h for Ar, CO, and N₂. When changing gases the system was evacuated for at least 12 h, exposed to 1275 Torr of the new gas, then evacuated for 24 h prior to measurements. The uncertainty associated with these values was $\pm 4\%$.

For runs in which UV illumination was used, the film was irradiated with the UV source at a distance of 16 cm from the sample surface for 1 h prior to the run and continued during measurements.

Gases

Ar (99.995% pure), He (99.995% pure), H₂ (99.995% pure), CO (98% pure), CO₂ (99.8% pure), N₂ (99.995% pure), and O₂ (99.995% pure) were obtained from Air Products, and were used without further purification.

RESULTS

The temperature dependence of the permeability and diffusion data for 46 PAB/EC are shown in Figures 1 and 2 and summarized in Table 1. The results for EC, and 18, 27, and 46 PAB/EC, were all qualitatively similar. The temperature dependence of the permeability and diffusion data for pure EC compared well with reported literature values (19,20). The plots of log P versus 1/T and log D versus 1/T are linear. A discontinuity in the permeability and diffusivity data was evident at about 320 K for all gases (Figures 1 and 2) and is consistent with the transition temperatures observed in DSC measurements (see below). Increasing the PAB content increased the sample density resulting in a decrease in the permeability and diffusion coefficients (Table 1).

No changes in any of the separation parameters were observed upon UV irradiation of the pure EC membrane. Indeed, for the majority of gases in this study (Ar, He, H₂, CO, CO₂, and O₂) irradiation of the PAB/EC membrane caused no significant changes in permeation properties. However, for N₂ the diffusivity during UV irradiation decreased by as much as 18% relative to the non-irradiated membrane (see Figure 3). The percent change in diffusivity increased with increasing PAB loading. These decreases were completely reversible, and the diffusivity returned to its preirradiated value upon letting the membrane sit for 12 or more hours in darkness at 308 K.

The effect of UV irradiation on diffusivity increased as the temperature was increased from 303 to 323 K, but above 323 K there was no observable change in the diffusivity (Figure 3). For example, for 46 PAB/EC the diffusion coefficient was decreased by 8.5% at 303 K, 18.3% at 323 K, and 0% at 333 K. This behavior is also evident in Figure 4 for the apparent solubility (P/D). UV irradiation increased the apparent solubility of N₂ in PAB/EC. This increase was maximized at ca. 310 K, while above 323 K UV irradiation had no measurable effect.

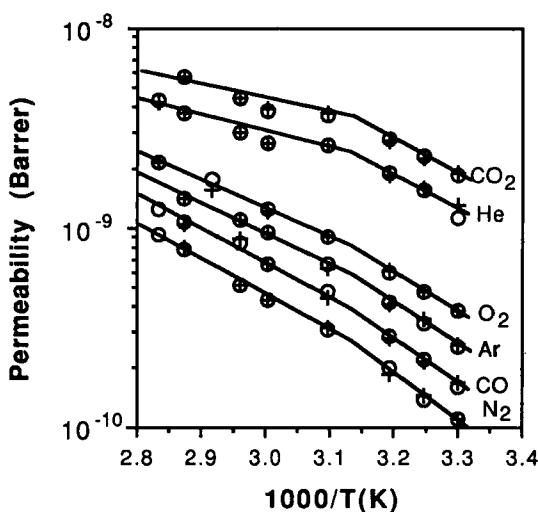


Figure 1. Permeability of several gases (CO_2 , He, O_2 , Ar, CO, and N_2) through 46 PAB/EC as a function of temperature. The open circles are the nonirradiated measurements and the crosses are measurements taken during UV irradiation.

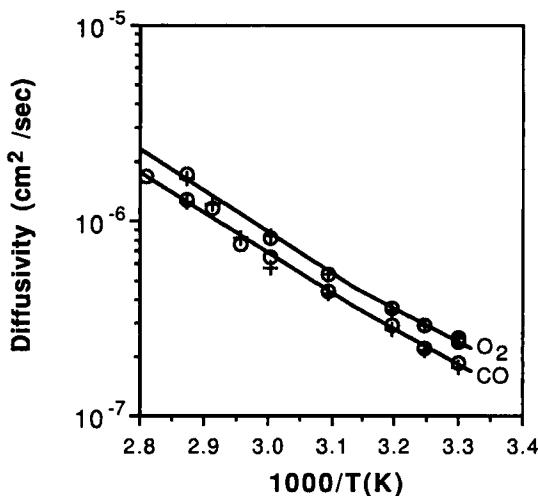


Figure 2. Diffusivity of CO and O_2 through 46 PAB/EC as a function of temperature. The open circles are the nonirradiated measurements and the crosses are measurements taken during UV irradiation.

Table 1. Permeability (P), Diffusion Coefficient (D), and Apparent Solubility (P/D) of a number of gases through ethyl cellulose and PAB/EC at 313 K.

	P ($\times 10^{-9}$) (Barrer)		D ($\times 10^{-7}$) (cm 2 /sec)		P/D ($\times 10^{-4}$) (scc/cm 3 -cmHg)	
	non	irr ^a	non	irr ^a	non	irr ^a
Ethyl Cellulose^b						
CO ₂	7.16	-	3.66	-	195	-
He ^c	4.68	-	-	-	-	-
CO	0.704	-	5.30	-	13.3	-
N ₂	0.523	-	5.70	-	9.16	-
18 PAB/EC						
CO ₂	3.67	3.66	4.00	3.97	91.7	92.0
He ^c	2.87	2.86	-	-	-	-
CO	0.357	0.345	4.71	4.53	7.56	7.63
N ₂	0.245	0.248	4.76	4.82	5.15	5.15
27 PAB/EC						
CO ₂	2.52	2.54	2.63	2.60	95.8	98.0
He ^c	1.81	1.77	-	-	-	-
CO	0.258	0.265	4.45	4.69	5.80	5.65
N ₂	0.145	1.47	4.04	3.57	3.59	4.12
46 PAB/EC						
CO ₂	2.77	2.74	2.78	2.74	99.6	100
He ^c	1.90	1.85	-	-	-	-
O ₂	0.601	0.608	3.60	3.52	16.7	17.3
Ar	0.426	0.410	3.44	3.50	12.4	11.7
CO	0.284	0.283	2.95	2.79	9.62	10.2
N ₂	0.200	0.185	2.73	2.23	7.26	8.30
(16 h after irr.)	0.195	-	2.69	-	7.25	-

- a. Membrane UV irradiated for 1 h prior to measurement and irradiated during measurement.
- b. No P, D, or P/D data are available for irradiated ethyl cellulose at 313 K; however, measurements during irradiation at 308 and 328 K showed no appreciable changes.
- c. The lag times for helium were too short to measure reliably.

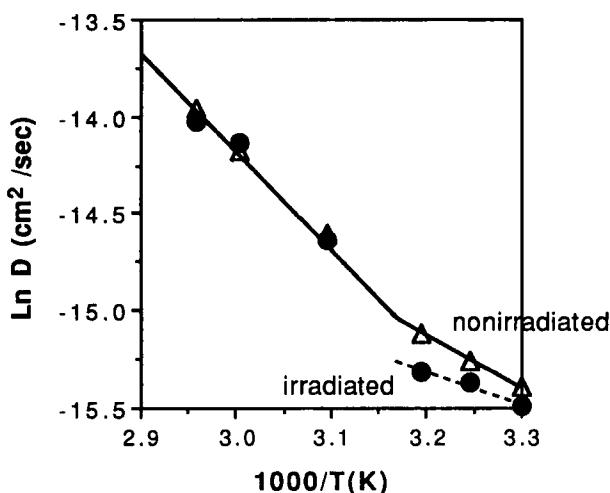


Figure 3. Diffusivity of N₂ through 46 PAB/EC as a function of temperature. The open triangles are the nonirradiated measurements and the closed circles are measurements taken during UV irradiation.

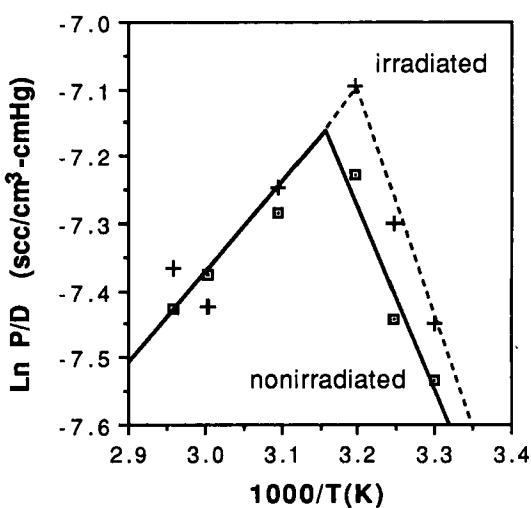


Figure 4. Apparent solubility (P/D) of N₂ through 46 PAB/EC as a function of temperature. The open squares are the nonirradiated measurements and the crosses are measurements taken during UV irradiation.

To determine if UV irradiation had an appreciable effect on the membrane temperature in the permeation cell, a thermocouple was embedded in a membrane of 46 PAB/EC. The highest PAB loading was selected because it should show the largest temperature fluctuation upon irradiation. At a cell temperature of 303 K, 1 h of irradiation raised the membrane temperature 5 K; while at a cell temperature of 308 K, irradiation increased the membrane temperature only 2 K. No measurable differences between the cell and membrane temperatures were observed at cell temperatures above 313 K. This behavior is attributed to the absorption of UV radiation by the azo chromophores.

UV/vis spectra showing the effect of UV irradiation on the cis-trans ratio of the 46 PAB/EC membrane at 303 K are presented in Figure 5. Photoisomerization of the azo bond is indicated by the decrease in area of the trans peak (370 nm) and the increase in area of the cis peak (440 nm) upon irradiation with UV light (365 nm) for 1 h. The decrease in the trans peak indicates that 19% of the material is in the cis state following irradiation. The cis fraction increased to a maximum of 30% at 313 K, then decreased to 11% at 323 K. Similar behavior has been observed for other polymer-azoaromatic systems (8).

The percent decrease in the diffusivity of N_2 for 27 and 46 PAB/EC, and the fraction of the PAB groups in 46 PAB/EC which were in the cis state during irradiation are plotted versus temperature in Figure 6. All three curves increased to a maximum at 313 K, then decreased as the temperature was increased further. The parallel behavior of these curves taken with the indication that the change in diffusivity of N_2 was directly proportional to PAB content strongly suggests that the decrease in diffusivity was directly related to the concentration of cis azobenzene moieties in the membrane.

DSC results indicated thermal transition temperatures of 330, 323, and 319 K for 18, 27, and 46 PAB/EC, respectively. This transition temperature was assigned to an increase in side chain (PAB) mobility. This temperature corresponds closely to that observed for the discontinuity in the permeability and diffusivity and the maximum conversion to cis-PAB. This suggests that the lack of observable changes above this transition temperature may be caused in part by a decrease in the energy barrier for isomerization to the trans form. However, Mita *et. al* (8) reported that the maximum conversion to cis-PAB was at ca. 320 K for a physical mixtures of PAB in several glassy polymers (i.e., polycarbonate and polymethylmethacrylate). This suggests that the maximum conversion to cis-PAB at ca. 320 K may be inherent in the isomerization kinetics of PAB.

Results of the size exclusion chromatography (GPC) measurements are listed in Table 2. The number-average molecular weight (M_n) increased from 10200 for EC to 13000, 14300, and 16800 g/mole for 18, 27, and 46 PAB/EC, respectively. These are in good agreement with the predicted values of M_n assuming the incorporation of PAB as side chains (Table 2). Similarly, M_w increased from 45700 for EC to 61600, 69300, and 84700 g/mole for 18, 27, and 46 PAB/EC, respectively. The polydispersity index was essentially constant for all samples at ca. 4.7. Density measurements indicate that the density increased with increasing PAB content. For example, the density of the 46 PAB/EC sample was 1.6% higher than that for pure EC. No measurable changes in density were observed upon UV irradiation.

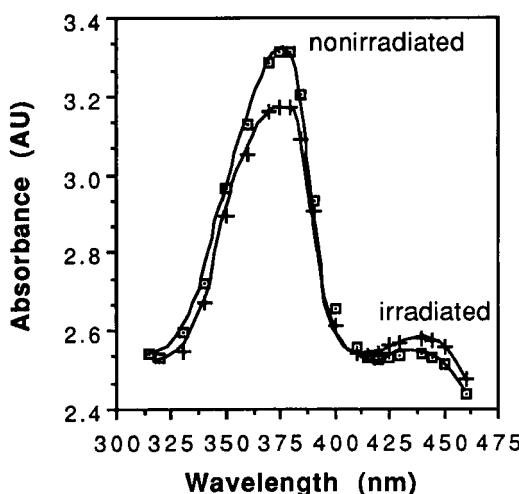


Figure 5. UV/visible spectrum 46 PAB/EC. The open squares are the nonirradiated measurements and the crosses are measurements taken during UV irradiation.

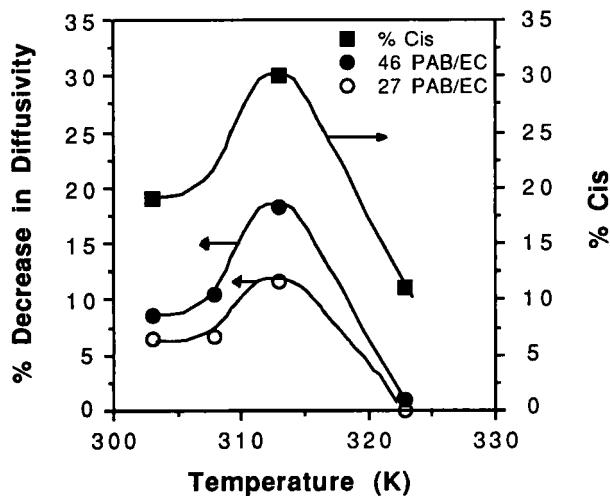


Figure 6. Decrease in diffusivity of N_2 in PAB/EC and fraction of PAB in cis state in PAB/EC as a function of temperature.

Table 2. Molecular weights measured by GPC for ethyl cellulose and PAB/ethyl cellulose samples

Sample	\bar{M}_n	Predicted	\bar{M}_w	\bar{M}_w/\bar{M}_n
	(g/mole)	\bar{M}_n	(g/mole)	
Ethyl cellulose	10200		45700	4.5
18 PAB/EC	13000	13000	61600	4.7
27 PAB/EC	14300	14400	69300	4.8
46 PAB/EC	16800	17400	84700	5.0

DISCUSSION

Incorporation of photoresponsive moieties into a polymer provided a reversible method to modify diffusivity of N_2 in a gas separation membrane. However, no changes in diffusivity were observed for the remaining gases in this study (Ar, He, H_2 , CO, CO_2 , and O_2). This is particularly surprising because N_2 and CO are similar in size and isoelectronic, and yet no change in diffusivity was observed for CO. Potential causes for the anomalous behavior of N_2 are discussed below.

There are several models which we will consider to explain the observed decrease in N_2 diffusivity during UV irradiation. In these models we will consider thermal effects due to absorption of UV light, crosslinking of the polymer by UV light, changes in polarity and geometric structure of the membrane caused by trans-cis isomerization, and interactions between nitrogen and the cis-azo moiety. Each model is discussed briefly below.

As discussed above, UV irradiation increased the membrane temperature by 2 and 5 K at 308 and 303 K, respectively, and had no effect on membrane temperature above 308 K. This suggests that thermal effects may have been partially responsible for the observed behavior. However, increasing the membrane temperature was shown to increase the diffusivity of N_2 (Figure 2); while, UV irradiation decreased N_2 diffusivity. In addition, increasing the temperature should affect all gases, not just N_2 . Yet, no significant changes in diffusivity were observed for any of the other gases. Therefore, the observed decrease in the diffusivity of N_2 cannot be explained by thermal effects.

The decrease in diffusivity of N_2 cannot be explained by UV-induced crosslinking of the PAB/EC membranes. The UV light source was filtered to minimize UV damage to the membrane. Indeed, minimal crosslinking was evident in samples as no changes in the solubility, viscosity, or molecular weight of the polymers were observed before or after irradiation. However, the primary argument against crosslinking effects is that crosslinking is irreversible, but the observed diffusivity changes were completely reversible.

The trans to cis isomerization of the azo group causes large conformational changes in the azo structure and increases the polarity. This will in turn modify the properties of polymers containing these species (PAB/EC). Irradiation of polymer samples containing these dyes has been reported to cause sample shrinkage (density increase). Increasing the polymer density reduces the free volume of the membrane. Diffusion in non-porous membranes occurs through the free volume of the membrane; therefore, UV irradiation should decrease the diffusivity.

While this model is appealing, it leaves a major question unanswered. Why was N₂ the only gas for which the diffusivity was significantly affected? Diffusivity and permeability are dependent on the volume of the permeant molecule. Typically, a decrease in the diffusivity and permeability is observed with an increase in molecular size of the gas molecule. This suggests that all gas molecules of comparable size would be affected equally by free volume changes. However, upon irradiation the diffusivity of N₂ decreased, while that of CO (which is comparable in size) was unaffected, and there were no measurable changes in polymer density upon irradiation. In addition, the change in polarity of the PAB moiety should have a larger effect on more polar gases such as CO, but again CO showed no change while N₂, a nonpolar gas, showed the only effects. Thus, this model does not explain the observed results.

The magnitude of the decrease in N₂ diffusivity was directly proportional to the concentration of azo groups in the polymer, and the percentage of azo groups isomerized from the trans to the cis state (Figures 5 and 7). This suggests that the observed photobehavior is caused by a direct interaction of the N₂ molecule with the azo group. This interaction would retard the N₂, thus, reducing the diffusivity while increasing the apparent solubility (P/D). In this model, the interaction must be stronger with the cis-azobenzene than with trans-azobenzene to explain the observed reversibility of the interaction. If the N₂ molecule must closely approach the azobenzene, a weaker interaction with trans-azobenzene is expected due to steric hindrance.

The bond lengths for N₂ and CO are 1.09 and 1.13 Å, respectively; whereas, the bond length in the azo group is 1.23 Å [21]. Thus, both N₂ and CO are of the correct size to overlap and perhaps interact with the azo group. This interaction could be a chemical bond or a weaker interaction such as London forces. Nitrogen and CO are isoelectronic and have no orbitals appropriate for bonding with the azo group; therefore, a chemical bond is unlikely. If the interaction were due to dipole-dipole or dipole-induced dipole interactions, CO (a dipole) would be expected to show the larger effect. Yet, N₂ not CO was affected.

At this time the exact nature of the anomalous interaction of N₂ with azobenzene is unclear; however, the interaction should be detectable using other methods. Future work on this project is directed at determining the exact nature of the interaction between nitrogen and the azobenzene group. Infrared and UV/visible spectroscopies will be used to probe for any perturbations of the spectra of these species. For example, if the interaction is sufficiently strong the symmetry of N₂ should be distorted and IR absorption bands would become visible. Shifts in the absorption bands for the azo group are also expected if the species are interacting with N₂. The proposed interaction of N₂ with the azobenzene suggests the use of azobenzene as a carrier molecule in liquid membrane studies. If the proposed interaction is real, cis-azobenzene should increase the permeability of N₂ with respect to trans-azobenzene. Thus, these studies should provide further insight into this anomalous behavior.

CONCLUSIONS

Incorporation of phenylazobenzene into ethyl cellulose has been shown to provide a method to reversibly modify the diffusivity of a non-porous membrane for gas separations. The only significant changes were observed for the diffusivity of N_2 ; decreasing diffusivity (up to ca. 20%) was observed upon exposure to UV light. No changes were observed for the other gases in this study (Ar, He, H_2 , CO, CO_2 , and O_2). The extent of the photoresponse was found to be directly related to the concentration of PAB groups attached to the polymer, and the percentage of PAB groups isomerized to the cis state. The anomalous behavior of N_2 is explained in terms of an interaction between the N_2 and cis-azobenzene. The extent of the photoresponse was found to be directly related to the concentration of PAB groups attached to the polymer, and the percentage of PAB groups isomerized to the cis state. Near 323 K, the cis to trans reaction rate became significant, causing a reduction in the percentage of PAB groups isomerized to the cis state. This resulted in the subsequent lack of photoresponse at temperatures above 323 K.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the National Science Foundation under grant number CBT-8707927 and the National Institutes of Health through a Biomedical Research Support Grant.

REFERENCES

1. Guillet, J. "Polymer Photophysics and Photochemistry," Cambridge Univ. Press, New York (1985).
2. Matejka, L.; Ilavsky, M.; Dusek, K.; Wichterte, O. *Polymer* **22**, 1511 (1981).
3. Vilanove, R.; Hervet, H.; Gruler, H.; Rondolez, F. *Macromolecules* **16**, 825 (1983).
4. Smets, G. *Adv. Polym. Sci.* **50**, 17 (1983).
5. I. Cabrera, F. Shvartsman, O. Veinberg and V. Krongauz, *Science* **226** (1984) 341.
6. K. Ishihara, N. Hamada, S. Kato and I. Shinohara, *J. Polym. Sci.-Polym. Chem. Ed.* **22** (1984) 121.
7. M. Irie, T. Iwayanagi and Y. Taniguchi, *Macromolecules* **18** (1985) 2418.
8. I. Mita, K. Horie and K. Hirao, *Macromolecules* **22** (1989) 558.
9. Mahadger, Y.; Tobolsky, A. V.; Kwei, T. K. *Macromolecules* **7**, 924 (1974).

10. Langer, R.; Folkman, J.; Hsieh, D. S. T. Proc. Natl. Acad. Sci. U.S.A. **78**, 1863 (1981).
11. Bhaskar, R. K.; Sparer, R. V.; Himmelstein, K. J. J. Membr. Sci. **24**, 83 (1985).
12. Minoura, N.; Aiba, S.; Fujiwara, Y. J. Appl. Polym. Sci. **31**, 1935 (1986).
13. Ishihara, K.; Muramoto, N.; Fujii, H.; Shinohara, I. J. Polym. Sci.: Polym. Chem. Ed. **23**, 2841 (1985).
14. Osada, Y.; Takeuchi, Y. Polym. J. **15**, 279 (1983).
15. Crowther, G. P.; Kaiser, E. M.; Woodruff, R. A.; Hauser, C. R. Org. Syn. **51**, 96 (1971).
16. Daynes, H.A. Proc. Royal. Soc. A **97**, 286 (1920).
17. Barrer, R.M. Trans. Farad. Soc. **35**, 628 (1939).
18. Hauenstein, Dale E., Ph.D. Thesis, University of Iowa, (1989).
19. Hsieh, P. Y. J. Appl. Polym. Sci. **7**, 1743 (1963).
20. Roberts, R. W.; Kammermeyer, K. J. Appl. Polym. Sci. **7**, 2183 (1963).
21. Sutton, L. E. "Tables of Interatomic Distances and Configurations in Molecules and Ions"; The Chemical Society; Burlington House: London (1958).