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# Structure/Permeability Relationships of Silicon-Containing Polyimides

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STRUCTURE/PERMEABILITY RELATIONSHIPS OF  
SILICON-CONTAINING POLYIMIDES

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SUMMARY

The permeability to  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO_2$ , and  $CH_4$  of (1) three silicone-polyimide random copolymers, and (2) two polyimides containing silicon atoms in their backbone chains, was determined at 35.0°C and at pressures up to about 120 psig (~8.2 atm). The copolymers contained different amounts of BPADA-*m*-PDA and amine-terminated poly(dimethyl siloxane), and also had different numbers of siloxane linkages in their silicone component. The polyimides containing silicon atoms ("silicon-modified polyimides") were SiDA-4,4'-ODA and SiDA-*p*-PDA. The gas permeability and selectivity of the copolymers are more similar to those of their silicone component than of the polyimide component. By contrast, the permeability and selectivity of the silicon-modified polyimides are more similar to those of their parent polyimides, PMDA-4,4'-ODA and SiDA-*p*-PDA. The substitution of SiDA for the PMDA moiety in a polyimide appears to result in a significant increase in gas permeability, without a correspondingly large decrease in selectivity. The potential usefulness of the above polymers and copolymers as gas separation membranes is discussed.

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INTRODUCTION

A study has been in progress for several years at Syracuse University on the relationships between the chemical structure of polymers and their permeability and selectivity to different gases. A better understanding of these relationships is of great importance for the development of new processes for the separation of gases by selective permeation through polymer membranes. Two classes of polymers have been investigated up to now for this purpose, namely silicone polymers [poly(organosiloxanes)] and polyimides (1-5). Therefore, it was of interest also to study the structure/permeability relationships of silicon-containing polyimides. Accordingly, the following types of polymers were used in this study: (1) silicone-polyimide copolymers, and (2) "silicon-modified polyimides", i.e., polyimides containing silicon atoms in the backbone chains. These polymers were employed in the form of thin, nonporous membranes, and their permeability to  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO_2$ , and  $CH_4$  was determined at 35.0°C and at pressures up to about 120 psig (~ 8.2 atm.). The results of the study are discussed below.

## EXPERIMENTAL TECHNIQUE

### 1) Apparatus and Procedure

Gases permeate through nonporous polymer membranes, such as used in membrane separation processes, by a "solution-diffusion" mechanism (6-9). The gas permeability of polymer membranes is characterized by a mean permeability coefficient,  $\bar{P}$ , which is defined by the isothermal relation:

$$\bar{P} = J_s \cdot \delta / (p_h - p_l), \quad (1)$$

where  $J_s$  is the steady-state rate of gas permeation through unit area of a membrane of thickness  $\delta$ , when the gas pressures  $p_h$  and  $p_l$  ( $< p_h$ ) are maintained at the two membrane interfaces, respectively (1,6-9).  $J_s = G_s/A$ , where  $G_s$  is the total rate of gas permeation, and  $A$  is the effective membrane area. In the present study,  $p_h$  was varied whereas  $p_l$  was always near atmospheric pressure. The membrane area  $A$  was 3 in.<sup>2</sup> (19.35 cm<sup>2</sup>). The apparatus and experimental procedure used to measure  $G_s$  have been described elsewhere (1).

### 2) Polymers

#### (a) Silicone-Polyimide Copolymers

Three silicone-polyimide copolymers (designated as A, B, and C) were studied in the form of 5-7 mil (~127-178  $\mu$ m)-thick membranes. These materials, whose compositions are shown in Figure 1, were synthesized by the Silicone Products Division of General Electric Co., Waterford, NY. Copolymers A, B, and C differ in the relative amounts of *m*-phenylenediamine and amine-terminated poly(dimethyl siloxane) used in the copolymerization with 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA). In addition, copolymer C differs from A and B in the number of siloxane linkages in the amine-terminated poly(dimethyl siloxane).

(b) Silicon-Modified Polyimides

Two types of silicon-modified polyimides, SiDA-4,4'-ODA and SiDA-*p*-PDA, whose structures are shown in Figure 2, were used in the form of 1-3 mil (~25-76  $\mu\text{m}$ )- thick membranes. These polyimides were synthesized as follows (10). Poly(amic acid) solutions were prepared by reacting bis(3,4-dicarboxyphenyl)-dimethylsilane (SiDA) (10) with 4,4'-oxydianiline (4,4'-ODA) and paraphenylenediamine (*p*-PDA). Stoichiometric amounts of the diamine and dianhydride were magnetically stirred in a vaccine bottle overnight at a concentration of 15-20% solids in N,N-dimethylacetamide (DMAc). Membranes were cast onto soda-lime glass plates that had been very lightly sprayed with Frekote 33<sup>R</sup> and then wiped with ethanol. After drying tack-free overnight in a low-humidity clean box, the films were imidized 1 h each at 100°, 200°, and 300°C in air. The membranes were removed from the glass plate by soaking in hot water and dried. PMDA-4,4'-ODA (Kapton<sup>R</sup> -like) membranes were also prepared in-house. Poly(dimethyl siloxane) (PDMS) membranes were supplied by Dow Corning Corp. of Midland, MI.

The inherent viscosity ( $\eta_{\text{inh}}$ ) of the poly(amic acid) precursors was determined with a Cannon-Ubbelohde viscometer at 0.5% wt./vol. in DMAc at 35°C. Values obtained for SiDA-4,4'-ODA and SiDA-*p*-PDA were 1.54 and 2.04 dl/g, respectively.

All membranes were stored in a desiccator prior to use. Table 1 lists the glass transition temperature ( $T_g$ ), the density, and the mean intersegmental separation of the polymers. The  $T_g$  values were determined by differential scanning calorimetry, and the densities were measured with a density-gradient column. The mean intersegmental distance was taken to be represented by the "d"-spacing obtained from maxima in wide-angle x-ray diffraction spectra, as suggested by Koros

et al. (11).

It is interesting to note that copolymers A, B, and C exhibited two second order transition temperatures. These materials were prepared as random copolymers but appeared to have undergone some microphase separation (12). Therefore, three transitions should have been observed in each of the copolymers: two for the phase separated domains of the copolymer (i.e., for the component homopolymers) and one for the mixed phase domains. However, the DSC measurements were made only at temperatures above 25°C, and, consequently, the T<sub>g</sub> of the silicone component was not observed. In the case of the silicon-modified membranes, Table I reports their glass transition temperatures.

### 3) Gases

The penetrant gases, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>, were obtained from the Linde Division of Union Carbide Corp. The gases were represented as having a minimum purity of 99.5-mol-% and were used without further purification.

## EXPERIMENTAL RESULTS

### 1. Silicone-Polyimide Copolymers

The permeability of the silicone-polyimide copolymers to H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> at 35.0°C is reported in Figures 3-5 in the form of semilogarithmic plots of the permeability coefficients,  $\bar{P}$ , versus the pressure difference,  $\Delta p$ , across the copolymer membranes. It is seen from these figures that the permeability coefficients for H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub> are either independent of  $\Delta p$  or decrease slightly as  $\Delta p$  is increased.  $\bar{P}(\text{CO}_2)$  increases slightly with increasing  $\Delta p$  for all three copolymers studied. This indicates that the copolymers were plasticized by CO<sub>2</sub>, very likely because the solubility of CO<sub>2</sub> in polymers is commonly much higher than that of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>.

The plots in Figures 3-5 can be represented by the relation:

$$\log \bar{P} = n + m \cdot \Delta p, \quad (2)$$

where  $n$  [ $= \log P(\Delta p = 0)$ ] and  $m$  are constants at a given temperature. Values of  $n$  and  $m$  for the gas/copolymer systems studied are listed in Table II. These values were obtained from least-squares fits of eqn. (2) to the experimental data. The experimental error in  $\bar{P}$  has been estimated to be  $\pm 8\%$ . The slightly negative slopes of some of the plots in Figures 3-5 are within the experimental error.

## 2. Silicon-Modified Polyimides

The permeability of SiDA-4,4'-ODA and SiDA-*p*-PDA membranes to H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> at 35.0°C is reported in Figures 6 and 7 in the form of semilogarithmic plots of  $\bar{P}$  versus  $\Delta p$ . These data can also be represented by eqn. (2), and pertinent values of the constants  $n$  and  $m$  are listed in Table III.

Permeability coefficients for the above gases in SiDA-*p*-PDA were measured again six months after the first measurements. The values of  $\bar{P}$  were found to have decreased by 20-35%, depending on the penetrant gas. However, the selectivity of SiDA-*p*-PDA toward any two penetrant gases remained essentially unchanged. The selectivity of a polymer to a gas A relative to another gas B is characterized by an ideal separation factor,  $\alpha^*$ , which is defined by the relation (12):

$$\alpha^*(A/B) \equiv \bar{P}(A) / \bar{P}(B), \quad (3)$$

where the permeability coefficients  $\bar{P}(A)$  and  $\bar{P}(B)$  must be taken at the same temperature and pressures.

## DISCUSSION OF RESULTS

### 1. Silicone-Polyimide Copolymers

The gas permeability and selectivity of the silicone-polyimide copolymers are compared in Table IV with those of their components, namely, BPADA-*m*-PDA (a polyimide) and PDMS [poly(dimethyl siloxane)] (1,2) at  $\Delta p = 100$  psi (6.8 atm). The gas permeability of PDMS is 3-4 orders of magnitude higher than that of the polyimide, but the selectivity of the polyimide is higher than that of PDMS. In some cases the selectivities are reversed, e.g., PDMS is more permeable to  $\text{CH}_4$  than to  $\text{H}_2$ ,  $\text{O}_2$ , or  $\text{N}_2$ , whereas the reverse is true for the polyimide. Table IV shows that the gas permeability of the copolymers is intermediate between that of PDMS and of BPADA-*m*-PDA. Such a behavior is common in copolymers.

The mean permeability coefficient,  $\bar{P}$ , can be shown to be a product of a mean diffusion coefficient,  $\bar{D}$ , and of a solubility coefficient,  $S$ :

$$\bar{P} = \bar{D} \cdot S, \quad (4)$$

where  $\bar{D}$  (a kinetic factor) and  $S$  (a thermodynamic factor) have been defined elsewhere (6-9). Therefore, the ideal separation factor,  $\alpha^*$ , which is an index of the overall selectivity of a polymer, can be expressed in terms of eqn. (3) by the relation:

$$\alpha^* \left( \frac{A}{B} \right) \equiv \frac{\bar{P}(A)}{\bar{P}(B)} = \left[ \frac{\bar{D}(A)}{\bar{D}(B)} \right] \left[ \frac{S(A)}{S(B)} \right]; \quad (4)$$

the ratio  $\bar{D}(A)/\bar{D}(B)$  is known as the "diffusivity selectivity" or "mobility selectivity", and the ratio  $S(A)/S(B)$  is the "solubility selectivity".  $\bar{D}(A)/\bar{D}(B)$  and  $S(A)/S(B)$  represent the contributions to the overall selectivity arising from



differences in the diffusivities and solubilities, respectively, of the penetrant gases A and B. While no gas diffusion and solubility coefficients are available for the polymers of interest here, the relative importance of these factors to the permeability and overall selectivity of the polymers can be inferred from phenomenological considerations.

Referring to Figures 3-5, it is seen that the values of  $\bar{P}$  for four penetrant gases in the three silicone-polyimide copolymers studied decrease, at constant  $\Delta p$ , in the order:

$$\bar{P}(\text{CO}_2) > \bar{P}(\text{CH}_4) > \bar{P}(\text{O}_2) > \bar{P}(\text{N}_2),$$

which is also the order of decreasing critical temperatures,  $T_c$ , of the penetrants. Since  $T_c$  is a "scaling" factor for the solubility (2), this indicates that the overall gas selectivity of the silicone-polyimide copolymers is largely controlled by the solubility selectivity. Such a behavior has also been observed with silicone polymers (1). However, two exceptions have been noted with these three copolymers:

(i)  $\text{H}_2$  has the lowest  $T_c$ , and hence the lowest solubility in the silicone-polyimide copolymers, of all the five penetrant gases studied. However, the permeability of these copolymers to  $\text{H}_2$  is higher than expected from the solubility of this gas alone. Thus, copolymers A, B, and C are more permeable to  $\text{H}_2$  than  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{CH}_4$ . This is probably due to the relatively high diffusivity of  $\text{H}_2$  in the copolymers, as compared with that of  $\text{N}_2$ ,  $\text{O}_2$ , or  $\text{CH}_4$ , because of the small size of the  $\text{H}_2$  molecule.

(ii) Copolymer C, which has the smallest weight-% of Si-O groups, shows a slightly higher selectivity to  $\text{H}_2$  relative to  $\text{CH}_4$  than copolymers A and B.

Reduction in the number of -Si-O- linkages in the amine-terminated poly(dimethyl siloxane) from 15 in copolymers A and B to 9 in copolymer C stiffens the copolymer backbone chains. This should cause a reduction in the diffusivity of all penetrants, but the diffusivity of O<sub>2</sub> probably decreases less than that of CH<sub>4</sub>, which is a larger molecule (1).

Figures 3-5 also show that the permeability of the copolymers to any given gas decreases from copolymer A to copolymer C, i.e., with decreasing weight-% of siloxane (SiO) groups, and thus with increasing weight -% of polyimide. Such a behavior is expected from the much lower permeability of the polyimide component of the copolymers. The selectivity of copolymers A, B, and C to different gas pairs is only slightly higher than that of PDMS, but their permeability is more than an order of magnitude lower. This indicates that most of the gas transport through the copolymers probably occurs through the phase-separated silicone domains (the lowest T<sub>g</sub> domains), whereas the phase-separated polyimide domains (the highest T<sub>g</sub> domains) act mostly as transport barriers.

## 2. Silicon-Modified Polyimides

Figures 6 and 7 show that the permeability coefficients for H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> are either independent of  $\Delta p$  or decrease slightly as  $\Delta p$  is increased.  $\bar{P}(\text{CO}_2)$  for SiDA-4,4'-ODA increases slightly with increasing  $\Delta p$ . The gas permeability and selectivity of the silicon-modified polyimides are compared in Table V with similar data for PDMS (1) and PMDA-4,4'-ODA (5) at  $\Delta p = 100$  psi (6.8 atm). The gas permeability of SiDA-4,4'-ODA is substantially higher than that of PMDA-4,4'-ODA, possibly because the large silicon atoms in the backbone

chains of the silicon-modified polyimides increase the free volume of these polymers. As a result, the selectivity of the former polymer is generally lower than that of the latter. It is interesting to note that SiDA-*p*-PDA also has a significantly higher gas permeability than PMDA-4,4'-ODA, but about the same overall selectivity.

Referring to Figures 6-7, it is seen that the values for  $\bar{P}$  for five penetrant gases in the two silicon-modified polyimides studied decrease at constant  $\Delta p$  in the order:

$$\bar{P}(\text{H}_2) > \bar{P}(\text{CO}_2) > \bar{P}(\text{O}_2) > \bar{P}(\text{N}_2) \gtrsim \bar{P}(\text{CH}_4) ;$$

this is also the order of increasing kinetic molecular diameter and, probably, of decreasing diffusivity ( $D$ ) of these penetrants (13). Hence, the overall gas selectivity of silicon-modified polyimides, in contrast to that of silicone-polyimide copolymers, appears to be largely controlled by the mobility (or diffusivity) selectivity, as is also the case for polyimides (5). Exceptions to this behavior may occur when the molecular sizes of the penetrants are very similar, in which case the solubility selectivity may become the controlling factor in the overall selectivity. It should be noted that the values of  $\bar{P}$  for  $\text{CH}_4$  and  $\text{N}_2$  in SiDA-4,4'-ODA are within the experimental error of one another, cf. Figure 6.

#### 4. Comparison of Silicone-Polyimide Copolymers

Copolymers A and B differ in that the former has 20% more of the flexible amine-terminated siloxane groups and 7% less of the relatively stiff *m*-phenylene diamine. Therefore, the mobility of copolymer A chains should be significantly higher than that of copolymer B chains. As a result, the permeability of copolymer A to the gases studied is higher than that of copolymer B. Since the solubilities of the penetrant gases in the two copolymers are

probably similar, the greater permeability of copolymer A must be attributed to a greater gas diffusivity in this copolymer.

It is interesting to note that, while the permeabilities of the two copolymers differ significantly, their selectivities are similar. This may be attributed to the fact, mentioned earlier, that the selectivity of the silicone-polyimide copolymers to different gases is controlled by the solubility selectivity.

Copolymers B and C have about the same weight-% of siloxane groups. However, they differ in the number of consecutive -Si-O- linkages. Thus, copolymer B has 15 consecutive siloxane linkages whereas copolymer C has only 9. Therefore, the chain mobility of copolymer B is larger than that of copolymer C, which is reflected in the fact that the gas permeability of B is significantly higher than that of C. Hence, the relative position of the flexible linkages in a polymer backbone is a more important factor in determining overall chain mobility than the mere presence of such linkages. Copolymer C has a higher  $H_2/CH_4$  selectivity than copolymer B because of its lower chain mobility. However, the overall selectivity of copolymer C for the other gas pairs, which differ less in molecular sizes than  $H_2$  and  $CH_4$ , is similar to that copolymer B.

##### 5. Comparison of Silicon-Modified Polyimides and PMDA-4,4'-ODA

The permeability of SiDA-*p*-PDA is significantly lower than that of SiDA-4,4'-ODA because of the rigid *p*-PDA linkages in the former polymer. By contrast, the selectivity of SiDA-*p*-PDA is larger for the same reason.

It is also interesting to compare the permeability and selectivity of SiDA-4,4'-ODA and of PMDA-4,4'-ODA. Replacement of the flat, rigid, and easily packed PMDA moiety in PMDA-4,4'-ODA with SiDA probably increases the polymer free volume because the larger Si atoms may act as "spacers" (see below). As a result, the

gas permeability of SiDA-4,4'-ODA is higher than that of PMDA-4,4'-ODA, while the selectivity of the former polymer is lower than that of the latter (provided that the molecular sizes of the penetrants are not too similar), cf. Table V. It should be noted that the two polymers have reverse overall  $N_2/CH_4$  selectivities, SiDA-4,4'-ODA being more permeable to  $CH_4$  than to  $N_2$  [ $\alpha^*(N_2/CH_4) < 1$ ] and PMDA-4,4'-ODA being more permeable to  $N_2$  than to  $CH_4$  [ $\alpha^*(N_2/CH_4) > 1$ ]. The reason for this behavior may be found in the relative magnitudes of the ratios  $S(N_2)/S(CH_4)$  and  $\bar{D}(N_2)/\bar{D}(CH_4)$  of the two polymers, as discussed below.

The solubility of  $CH_4$  is probably higher than that of  $N_2$  in both SiDA-4,4'-ODA and PMDA-4,4'-ODA because  $T_C(CH_4) > T_C(N_2)$ , cf. ref.(2);  $T_C(CH_4) = 190.6^\circ K$ ,  $T_C(N_2) = 126.2^\circ K$ . Hence, the solubility selectivity of both polymers favors  $CH_4$  over  $N_2$ , i.e.,  $S(N_2)/S(CH_4) < 1$ . Moreover, it is likely that the values of the solubility selectivity of the two polymers are not very different. By contrast, the diffusivity of  $CH_4$  is likely to be lower than that of  $N_2$  in both SiDA-4,4'-ODA and PMDA-4,4'-ODA because the kinetic molecular diameter,  $\sigma_k$ , of  $CH_4$  is larger than that of  $N_2$ :  $\sigma_k(CH_4) = 3.8 \text{ \AA}$ ,  $\sigma_k(N_2) = 3.64 \text{ \AA}$  (12). Therefore, the mobility (diffusivity) selectivity of the two polymers favors  $N_2$  over  $CH_4$ , i.e.,  $\bar{D}(N_2)/\bar{D}(CH_4) > 1$ .

However, the mean free volume of PMDA-4,4'-ODA is smaller than that of SiDA-4,4'-ODA, as would appear from their mean intersegmental distances which are  $4.45 \text{ \AA}$  and  $5.2 \text{ \AA}$ , respectively. Hence, the  $N_2/CH_4$  mobility selectivity of PMDA-4,4'-ODA should be larger than that of SiDA-4,4'-ODA, the former polymer being a better "molecular sieve" (assuming that the chain stiffness of the two polymers is similar). As a result, the overall selectivity of PMDA-4,4'-ODA is probably dominated by the mobility selectivity, and therefore this polymer is  $N_2$ -selective, whereas the overall selectivity of SiDA-4,4'-ODA is probably dominated by the solubility selectivity, which makes the latter polymer  $CH_4$ -

selective, cf. eqn. (4). The above arguments require validation by solubility and diffusivity measurements.

### CONCLUSIONS

The selectivity of the three silicone-polyimide copolymers studied is about the same as that of PDMS, whereas their permeability is substantially lower than that of PDMS. Therefore, these copolymers offer no advantages as materials for gas separation membranes.

The silicon-modified polymers are much more promising membrane materials. Thus, the permeability of SiDA-4,4'-ODA to the gases studied is at least 3 times higher than that of PMDA-4,4'-ODA, whereas the selectivity of the former polymer is over 50% of that of the latter polymer. Hence, the substitution of SiDA for the PMDA moiety of a polyimide appears to result in a significant increase in gas permeability, without a correspondingly large decrease in selectivity. SiDA-*p*-PDA also has a higher gas permeability than PMDA-4,4'-ODA and about the same selectivity. Therefore, silicon-modified polyimides deserve further study.

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# REFERENCES

1. S. A. Stern, V. M. Shah, and B. J. Hardy, "Structure/Permeability Relationships in Silicone Polymers", *J. Polym. Sci.: Part B: Polym. Phys.*, 25, 1263 (1987).
2. V. M. Shah, B. J. Hardy, and S. A. Stern, "Solubility of Carbon Dioxide, Methane, and Propane in Silicone Polymers: Effect of Polymer Side Chains", *J. Polym. Sci.: Part B: Polym. Phys.*, 24, 2033 (1986).
3. B. D. Bhide and S. A. Stern, "The Permeability of Silicone Polymers to  $\text{NH}_3$  and  $\text{H}_2\text{S}$ ", Accepted by *J. Appl. Polymer Sci.*
4. B. D. Bhide and S. A. Stern, "The Permeability of Silicone Polymers to  $\text{H}_2$ ", Accepted by *J. Appl. Polym. Sci.*
5. S. A. Stern, Y. Mi, H. Yamamoto, and A. K. St. Clair, "Structure/Permeability Relationships of Polyimide Membranes. Applications to the Separation of Gas Mixtures", Accepted by *J. Polym. Sci.: Part B: Polym. Phys.*
6. J. Crank, "The Mathematics of Diffusion", 2nd Ed., Clarendon Press, Oxford 1975.
7. S. A. Stern and H. L. Frisch, "The Selective Permeation of Gases through Polymers", *Ann. Rev. Mater. Sci.*, 11, 523 (1981).
8. H. L. Frisch and S. A. Stern, "Diffusion of Small Molecules in Polymers", *Critical Rev. Solid State and Mats. Sci.*, 11(2), 123 (1987), CRC Press, Boca Raton, FL.
9. W. J. Koros and R. T. Chern, Chapt. 20 in "Handbook of Separation Process Technology", R. W. Rousseau, Ed., Wiley-Interscience, New York, 1987, pp. 862-953.
10. J. R. Pratt and S. F. Thames, "Organosilicon Compounds XVIII. Silicon-Containing Dianhydrides", *J. Org. Chem.*, 38, 4271 (1973).
11. K. C. O'Brien, W. J. Koros, and G. R. Husk, "Polyimide Materials Based on Pyromellitic Dianhydride for the Separation of Carbon Dioxide and Methane Gas Mixtures", *J. Membrane Sci.*, 35, 217 (1988).
12. S. A. Stern and W. P. Walawender, Jr, "Analysis of Membrane Separation Parameters", *Separation Sci.*, 4, 129 (1969).
13. D. W. Breck, "Zeolite Molecular Sieves", J. Wiley & Sons, New York, 1974, pp. 636.

TABLE I  
Physical Properties of Polymers Studied

Polymer	Density, (a) $\rho$ (g/cm <sup>3</sup> )	Glass-Transition Temperature, (b) T <sub>g</sub> (°C)	Mean Intersegmental Distance, (c) d (Å)
Silicone-Polyimide Copolymer A	1.1612	106, 202	5.5
" " " B	1.1702	94, 170	5.8
" " " C	1.1748	85, 210	5.5
SiDA-4,4'-ODA	1.2866	267	5.2
SiDA- <i>p</i> -PDA	1.3005	314	5.4

(a) Densities were measured at 23°C, except for SiDA-*p*-PDA whose density was determined at 26°C.

(b) Determined by differential scanning calorimetry.

(c) Assumed to be represented by the "d" spacing obtained from maxima of wide-angle X-ray diffraction spectra.



TABLE II  
Parameters in Equation (2) for Silicone-Polyimide Copolymers at 35.0°C

Polymer	H <sub>2</sub>		CO <sub>2</sub>		O <sub>2</sub>		N <sub>2</sub>		CH <sub>4</sub>	
	n	m $\times 10^3$	n	m $\times 10^3$	n	m $\times 10^3$	n	m $\times 10^3$	n	m $\times 10^3$
Copolymer A	1.943	0.0445	2.451	4.39	1.638	-0.158	1.267	0.0469	1.759	-1.30
Copolymer B	1.746	2.22	2.123	3.17	1.475	-4.16	1.177	-13.1	1.522	1.18
Copolymer C	1.544	-1.06	1.763	7.53	1.061	-0.352	0.627	-4.55	1.041	-1.50

$$\text{Log } (\bar{P} \times 10^{10}) = n + m \cdot \Delta p \quad (2)$$

Units:  $\bar{P}$  [cm<sup>3</sup>(STP) · cm / (s · cm<sup>2</sup> · cmHg)];  $\Delta p$  (atm); n (dimensionless); m (atm)<sup>-1</sup>

TABLE III  
Parameters in Equation (2) for Silicon-Modified Polyimides at 35.0°C

Polymer	H <sub>2</sub>		CO <sub>2</sub>		O <sub>2</sub>		N <sub>2</sub>		CH <sub>4</sub>	
	<i>n</i>	<i>m</i> × 10 <sup>3</sup>	<i>n</i>	<i>m</i> × 10 <sup>3</sup>	<i>n</i>	<i>m</i> × 10 <sup>3</sup>	<i>n</i>	<i>m</i> × 10 <sup>3</sup>	<i>n</i>	<i>m</i> × 10 <sup>3</sup>
SiDA-4,4'-ODA	0.991	5.05	0.451	10.0	-0.140	-3.36	-0.803	-4.08	-0.750	-3.52
SiDA- <i>p</i> -PDA	0.827	24.0	0.447	-0.898	-0.264	5.98	-0.912	-10.0	-1.150	-6.57

$$\text{Log } (\bar{P} \times 10^{10}) = n + m \cdot \Delta p$$

Units:  $\bar{P}$  [cm<sup>3</sup>(STP) · cm / (s · cm<sup>2</sup> · cmHg)];  $\Delta p$  (atm); *n* (dimensionless); *m* (atm)<sup>-1</sup>

TABLE IV  
PERMEABILITY AND SELECTIVITY OF SILICONE/POLYIMIDE COPOLYMERS,  
PDMS, AND BPADA-*m*-PDA TO DIFFERENT GASES AT 35.0°C

Polymer	$\bar{P}(\text{CO}_2)$	$\alpha^*(\text{CO}_2/\text{CH}_4)$	$\bar{P}(\text{O}_2)$	$\alpha^*(\text{O}_2/\text{N}_2)$	$\bar{P}(\text{H}_2)$	$\alpha^*(\text{H}_2/\text{CH}_4)$	$\bar{P}(\text{CH}_4)$	$\alpha^*(\text{N}_2/\text{CH}_4)$
PDMS (a)	4330	3.3	933	2.2	900	0.7	1312	0.3
Copolymer A	303	5.4	43.4	2.3	88	1.6	56.4	0.3
Copolymer B	139	4.1	28.2	2.3	58	1.7	33.6	0.4
Copolymer C	66	6.0	11.4	2.9	35	3.2	11.0	0.4
BPADA- <i>m</i> -PDA	1.3	37	0.4	7.5	-	-	0.035	1.5

$\bar{P} \times 10^{10} [\text{cm}^3(\text{STP}) \cdot \text{cm} / (\text{s} \cdot \text{cm}^2 \cdot \text{cmHg})]$   
 $\Delta p = 100 \text{ psi (6.8 atm)}; \alpha^*(\text{A/B}) = \bar{P}(\text{A}) / \bar{P}(\text{B})$

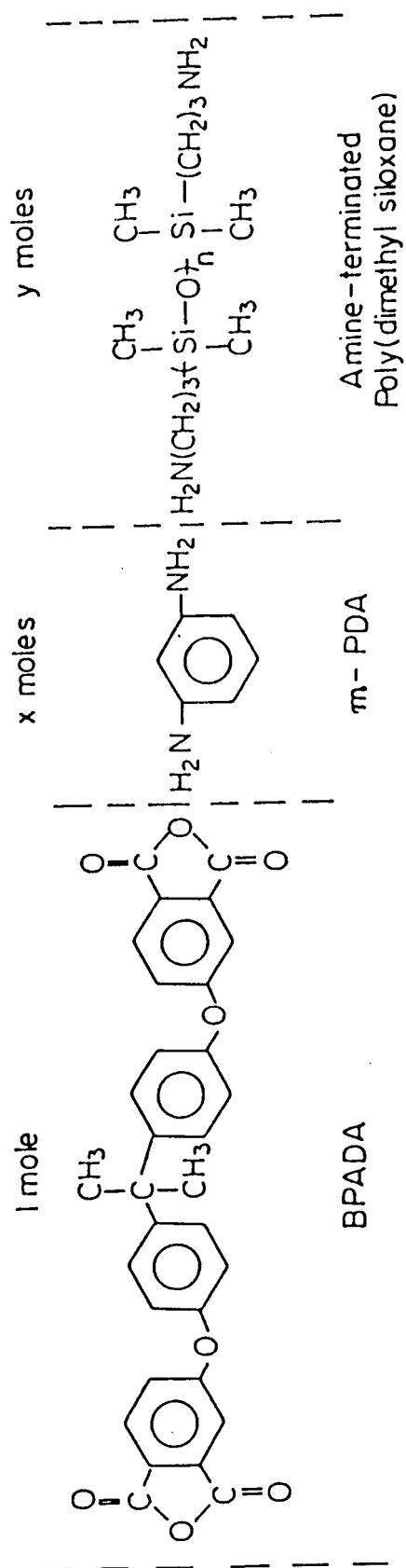
a) Data from ref. (1). The PDMS contained 4.9 vol% of a silica filler.  $\bar{P}$  for PDMS was divided by the amorphous fraction of a polymer.

TABLE V  
PERMEABILITY AND SELECTIVITY OF TWO SILICON - MODIFIED POLYIMIDES,  
PDMS, AND PMDA-4,4'-ODA TO DIFFERENT GASES AT 35.0°C

Polymer	$\bar{P}(\text{CO}_2)$	$\alpha^*(\text{CO}_2/\text{CH}_4)$	$\bar{P}(\text{O}_2)$	$\alpha^*(\text{O}_2/\text{N}_2)$	$\bar{P}(\text{H}_2)$	$\alpha^*(\text{H}_2/\text{CH}_4)$	$\bar{P}(\text{CH}_4)$	$\alpha^*(\text{N}_2/\text{CH}_4)$
PDMS (a)	4330	3.3	933	2.2	900	0.7	1312	0.3
SIDA-4,4'-ODA	3.31	20	0.69	4.6	10.7	63	0.170	0.9
SIDA-p-PDA	2.75	43	0.60	5.7	9.4	147	0.064	1.6
PMDA-4,4'-ODA	1.14	43	0.22	4.5	3.0	116	0.026	1.8

$\bar{P} \times 10^{10}$  [ $\text{cm}^3(\text{STP}) \cdot \text{cm}/(\text{s} \cdot \text{cm}^2 \cdot \text{cmHg})$ ]  
 $\Delta p = 100$  psi (6-8 atm);  $\alpha^*(\text{A/B}) \equiv \bar{P}(\text{A})/\bar{P}(\text{B})$

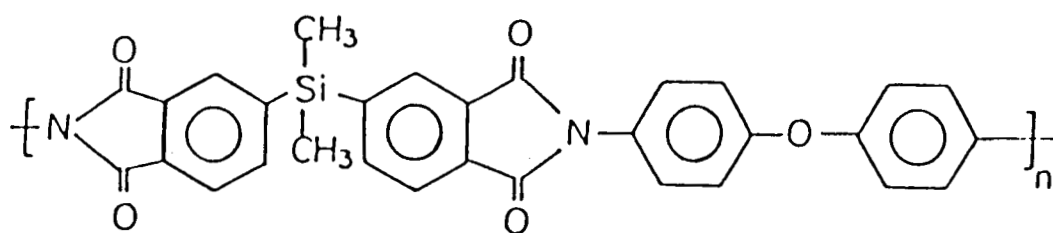
(a) PDMS contained 4.9 vol% of a silica filler.  $\bar{P}$  for PDMS was divided by the amorphous fraction of polymer.



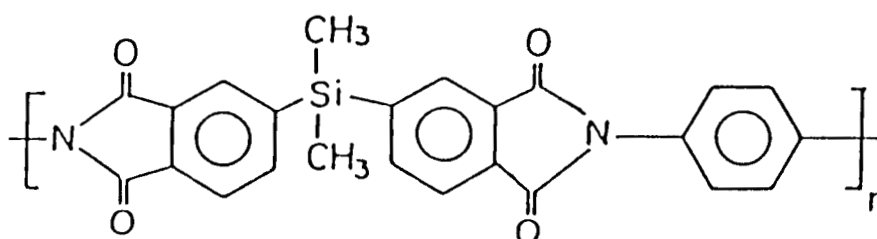
Copolymer (1 mol)	n*	x(moles)	y(moles)	wt % SiO groups
A	15	0.70	0.30	21
B	15	0.75	0.25	19
C	9	0.60	0.4	18

\*  $\text{-(Si-O)}_n$

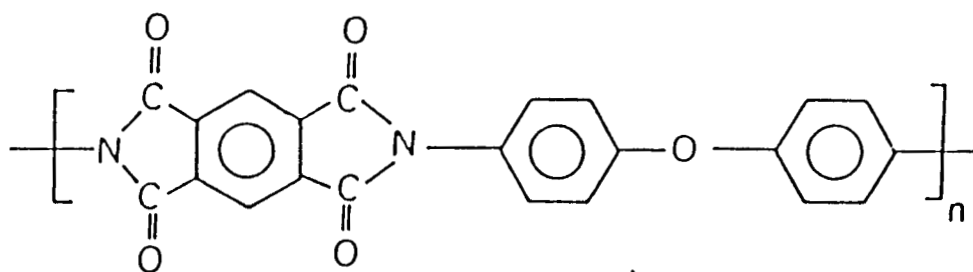
Fig. 1 Composition of Silicone - Polyimide Random Copolymers.



SiDA - 4,4' - ODA



SiDA - p - PDA



PMDA - 4,4' - ODA

Fig. 2 Structures of SiDA-4,4'-ODA, SiDA-p-PDA, and PMDA-4,4'-ODA Polyimide Membranes.

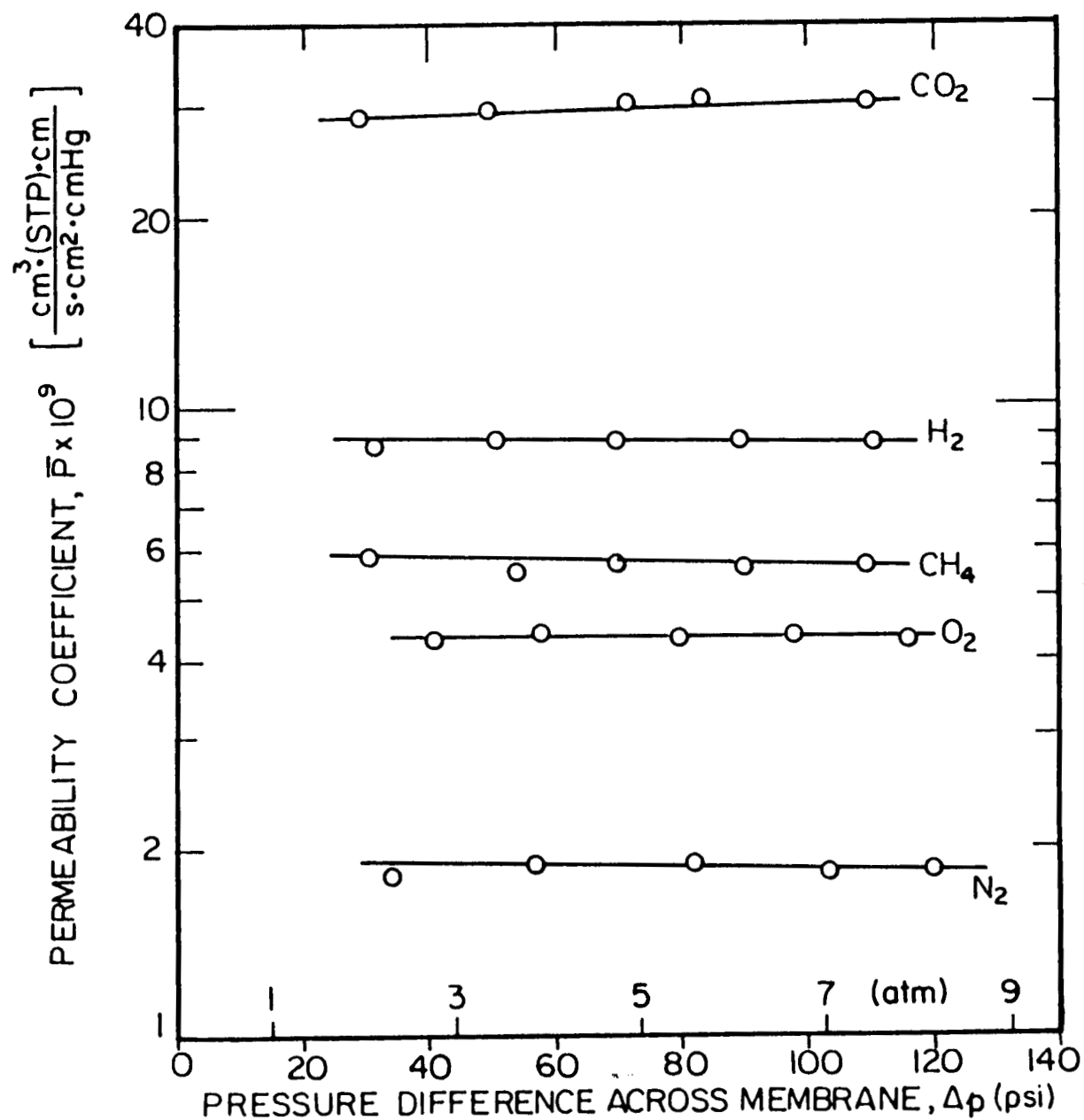


Fig. 3 Mean permeability coefficients as a function of pressure difference across membrane for five gases in Copolymer A at 35.0°C.

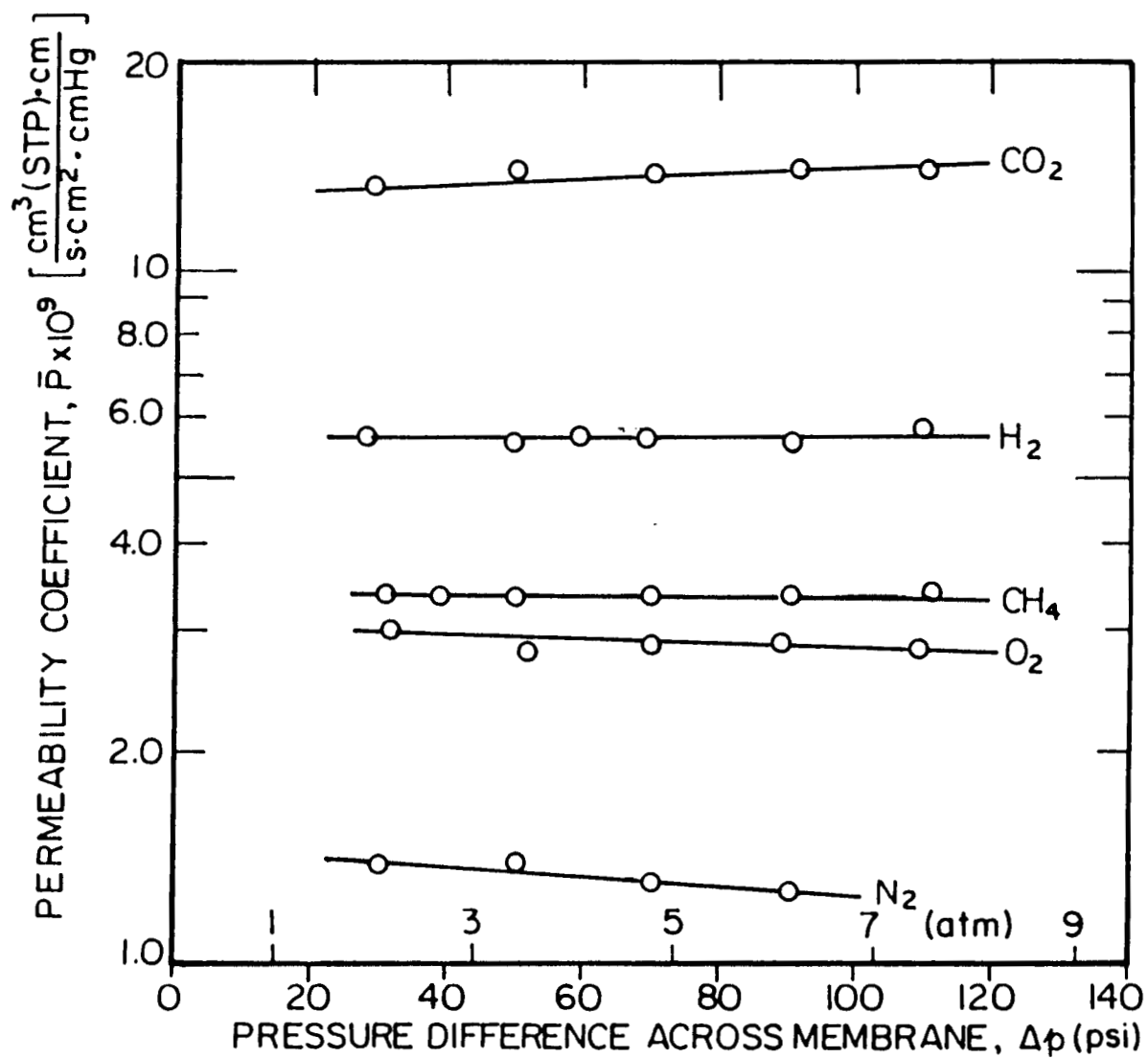


Fig. 4

Mean permeability coefficients as a function of pressure difference across membrane for five gases in Copolymer B at 35.0°C.



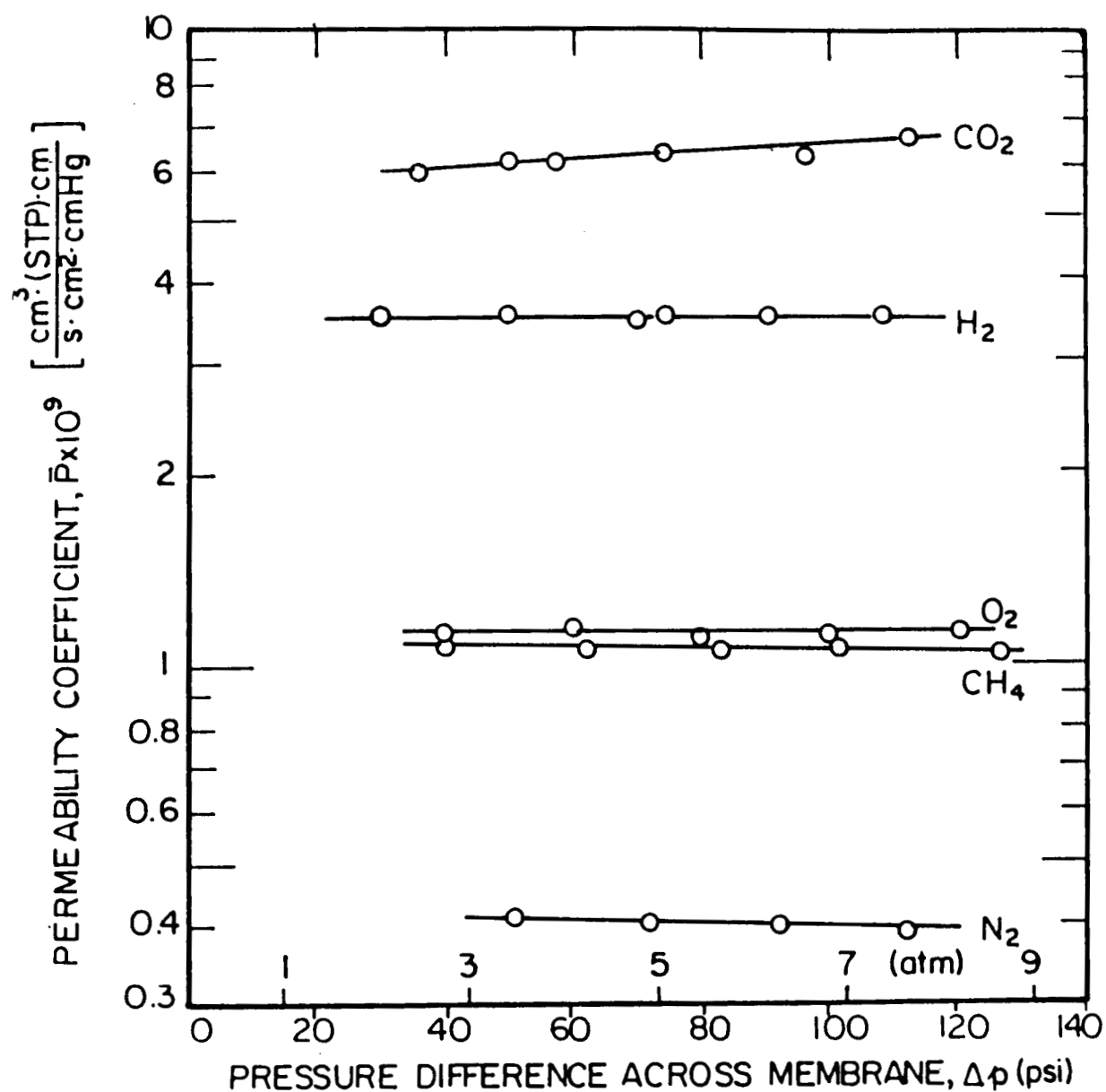


Fig. 5 Mean permeability coefficients as a function of pressure difference across membrane for five gases in Copolymer C at 35.0°C.

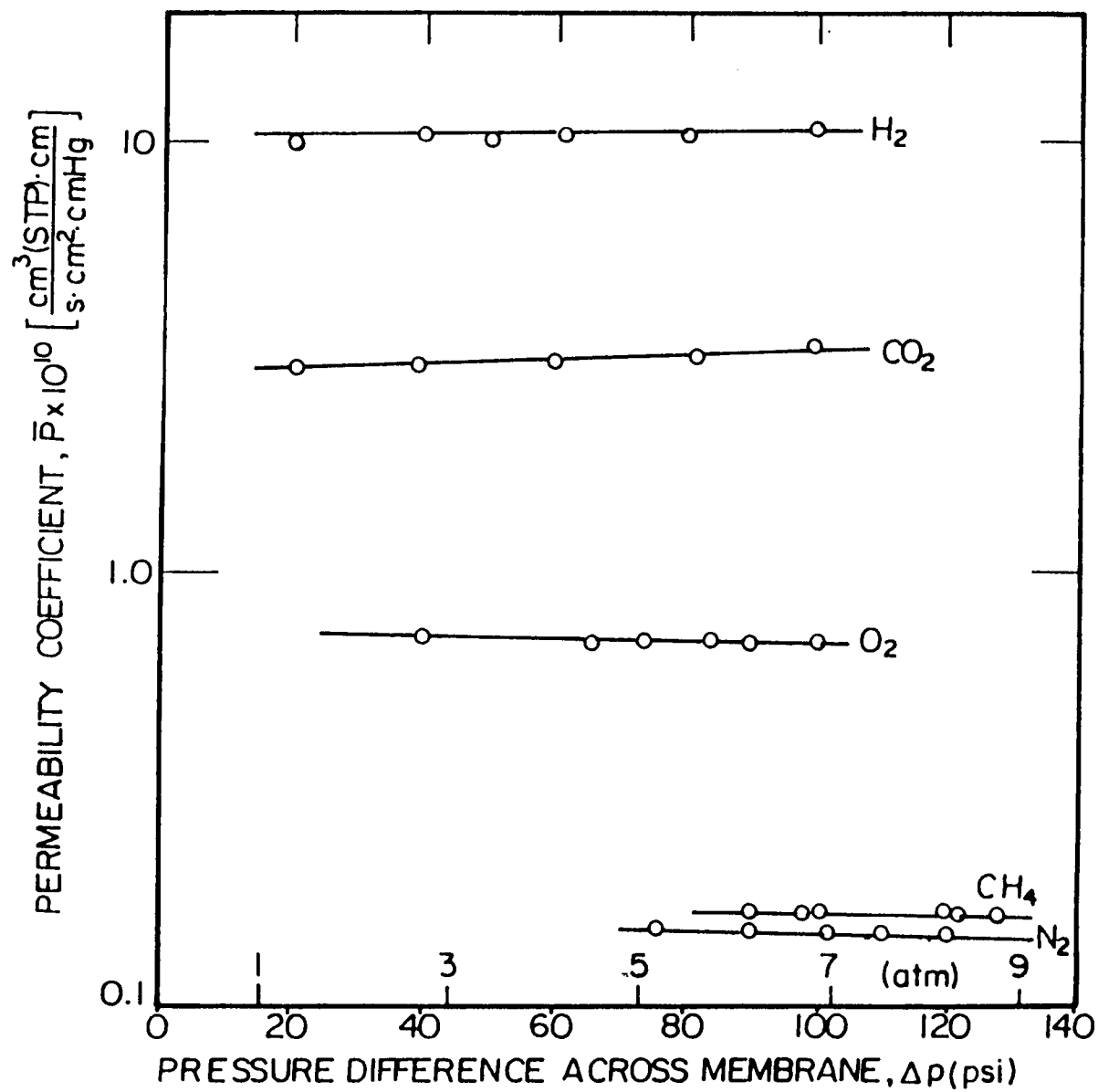


Fig. 6 Mean permeability coefficients as a function of pressure difference across membrane for five gases in SiDA-4,4'-ODA at 35.0°C.

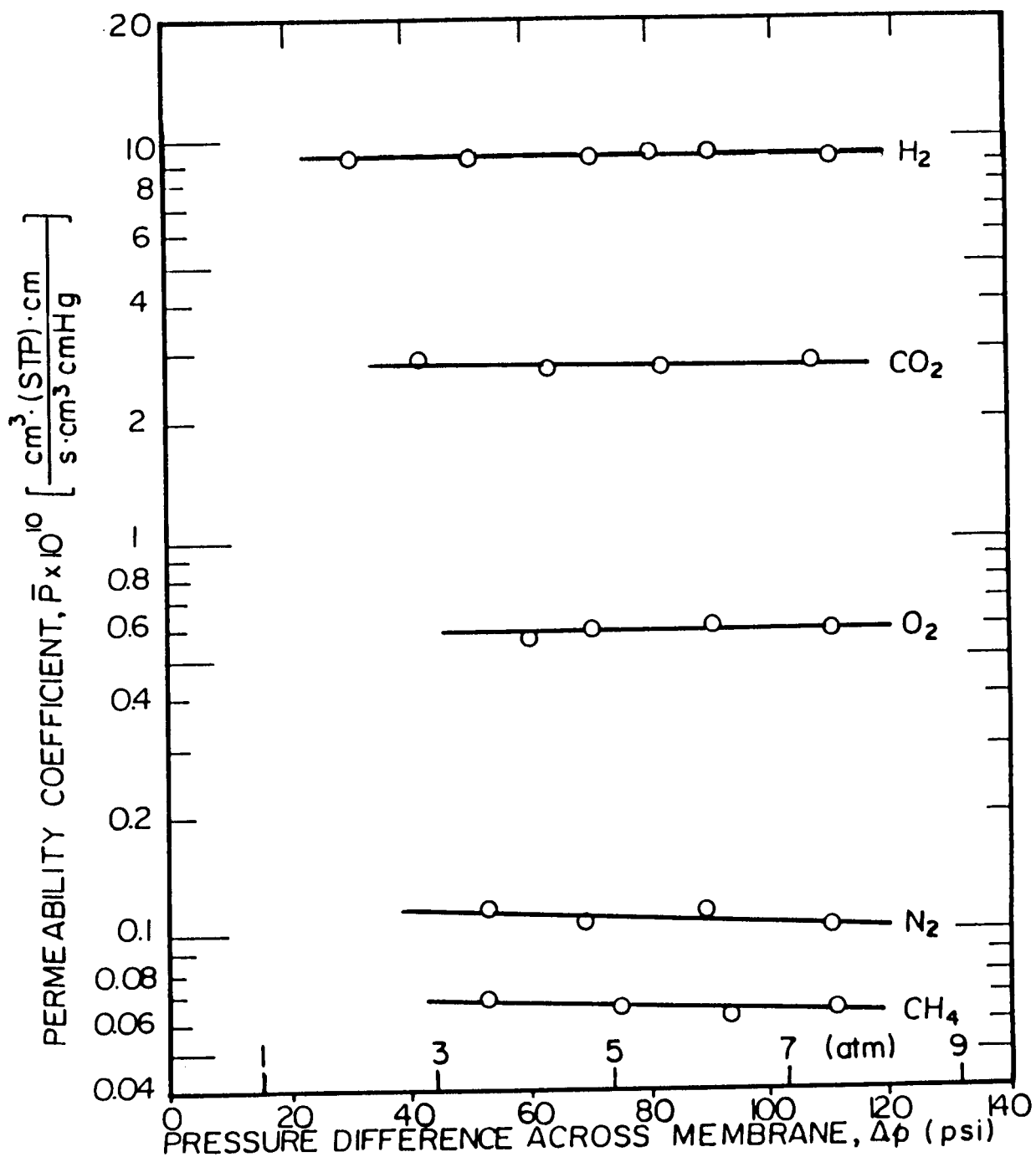


Fig. 7 Mean permeability coefficients as a function of pressure difference across membrane for five gases in SiDA-p-PDA at 35.0°C.



## Report Documentation Page

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16. Abstract <b>The permeability to H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> of (1) three silicone-polyimide random copolymers and (2) two polyimides containing silicon atoms in their backbone chains, was determined at 35.0°C and at pressures up to about 120 psig (~ 8.2 atm). The copolymers contained different amounts of BPADA-m-PDA and amine-terminated poly(dimethyl siloxane) and also had different numbers of siloxane linkages in their silicone component. The polyimides containing silicon atoms ("silicon-modified polyimides") were SiDA-4,4'-ODA and SiDA-p-PDA. The gas permeability and selectivity of the copolymers are more similar to those of their silicone component than of the polyimide component. By contrast, the permeability and selectivity of the silicon-modified polyimides are more similar to those of their parent polyimides, PMDA-4,4'-ODA and SiDA-p-PDA. The substitution of SiDA for the PMDA moiety in a polyimide appears to result in a significant increase in gas permeability, without a correspondingly large decrease in selectivity. The potential usefulness of the above polymers and copolymers as gas separation membranes is discussed.</b>			
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