

# Gas Separation Performance of Inorganic Polyphosphazene Membranes

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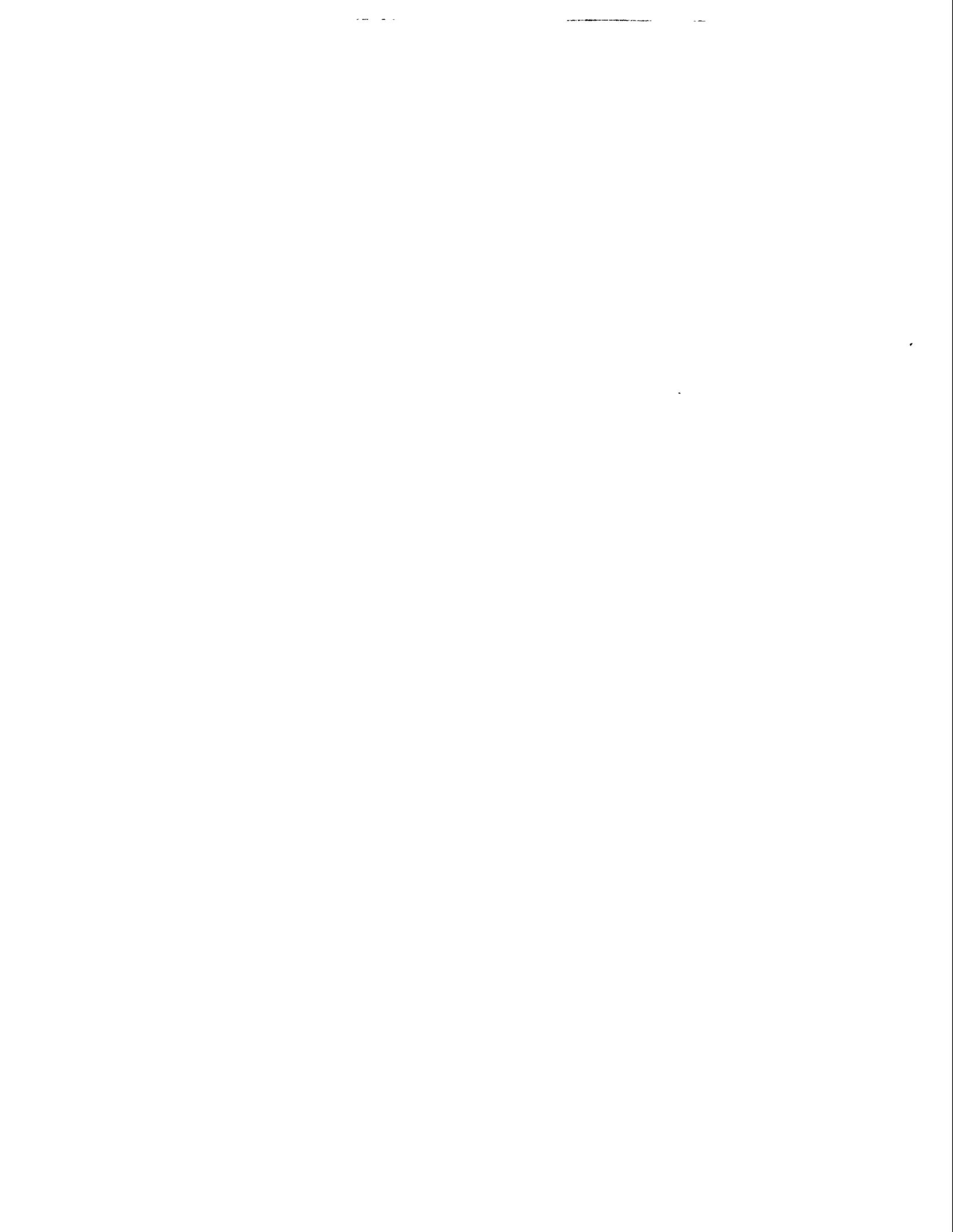
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## ABSTRACT

Phosphazene inorganic polymer membranes have been evaluated for acid gas removal and the separation of helium from methane. Polyphosphazene polymers have proven to be very chemical and temperature resistant. They have survived many hours of exposure to gas mixtures involving 10% SO<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>S/CH<sub>4</sub>, and CO<sub>2</sub>/CH<sub>4</sub> at temperatures of 170°C. The linear polymers are excellent film formers, making it easy to cast dense film membranes. Highly cross linked cyclomatrix membranes were also formed and tested. Experimental results have shown the direct correlation of chemical structure and film morphology with separation performance. Small variations in the functional groups greatly impact the membrane's separation performance.

The poly(bisphenoxy)phosphazene (PPOP) family of polymers efficiently separates SO<sub>2</sub> from nitrogen, as indicated by selectivities of over 350. This high value indicates a window of opportunity for these polymers in SO<sub>2</sub> separations. While not as effective in separating H<sub>2</sub>S or CO<sub>2</sub> from methane, the selectivities of this family of polymers (over 30 and 6, respectively) are very good.

The PPOP polymers also showed the ability to preferentially transport helium over methane. In single pass experiments involving feeds containing 2 and 34% helium, the ratio of helium to methane in the permeate increased from small, in some cases, to almost four in other cases, and in still other cases only helium was observed to cross the membrane. As generally occurs, the flux increased with increasing temperature, accompanied by a decrease in selectivity with increasing temperature. However, in one case where the polymer had been heated and then cooled and retested at ambient conditions, the membrane flux was higher than those of membranes tested which had not previously been heat treated. This observed hysteresis indicates that the polymer morphology may have changed and certainly plays a very important role in separation performance.



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## CONTENTS

ABSTRACT .....	iii
ACKNOWLEDGMENTS .....	v
INTRODUCTION .....	1
EXPERIMENTAL PROCEDURE .....	1
PURE GAS TECHNIQUE .....	3
MIXED GAS TECHNIQUE .....	5
RESULTS AND DISCUSSION .....	5
Pure Gas Test .....	5
Linear Polyphosphazene Membranes .....	5
Cyclomatrix Polyphosphazene Membranes .....	7
Mixed Gas Tests .....	10
HELIUM SEPARATIONS .....	10
SUMMARY AND CONCLUSIONS .....	20
REFERENCES .....	21

## FIGURES

1. Phosphazene polymer backbone structures .....	2
2. Pure gas timelag test schematic and typical results .....	4
3. Gas permeability verses kinetic gas diameter for a knife cast PPOP membrane .....	8
4. Cyclomatrix membrane permeabilities from timelag experiments .....	9
5. Comparison of mixed gas selectivities at 30°C for seven different phosphazene polymers .....	11
6. Comparison of mixed gas selectivities at 80°C for eight different phosphazene polymers .....	12
7. Temperature dependence of the selectivities of eight phosphazene polymers for the 10% SO <sub>2</sub> /N <sub>2</sub> gas mixture .....	13
8. Temperature dependence of the selectivities of eight phosphazene polymers for the 10% H <sub>2</sub> S/CH <sub>4</sub> gas mixture .....	14

9.	Temperature dependence of the selectivities of eight phosphazene polymers for the 10% CO <sub>2</sub> /CH <sub>4</sub> gas mixture .....	15
10.	Helium to methane concentration ratio starting with a feed containing 34% helium and 40% methane .....	17
11.	Helium to methane concentration ratio at 125°C with CH <sub>3</sub> PPOP membrane and feed containing 1.92% helium and 64.58% methane .....	18

## TABLES

1.	Polymer reference chart .....	3
2.	Comparison of permeability data for spin cast and knife cast PPOP membranes .....	6
3.	Comparison of solubility and diffusivity ratios for spin cast and knife cast PPOP membranes .....	6
4.	Polyphosphazene membrane permeabilities from mixed gas research .....	16
5.	Helium separations from natural well gas .....	19

# Gas Separation Performance of Inorganic Polyphosphazene Membranes

## INTRODUCTION

The objective of this research program was to develop, characterize, and evaluate the potential of phosphazene polymers for separations performed in harsh environments. The program was divided into two general areas, gas separations and metal ion separations involving aqueous solutions. Each of these two areas is the subject of a topical report; this report deals with the gas separations.

Throughout the world, there is rapidly growing interest in membrane separation as an energy efficient way to separate components of a process stream or waste stream, such as in desalination of water or clarification of fruit juices. In some cases membranes perform separations that are otherwise very difficult, such as breaking azeotropes. In the early stages of the work reported here, there was interest in separating acid gases from process flue gases and in natural gas sweetening. As a result, research was undertaken to characterize membrane performance. First, a pure gas test apparatus was developed to determine the permeabilities of a number of gases through various membranes at a variety of temperatures. Second, an automated mixed gas test cell was developed in which membranes could be exposed to mixtures of pairs of gases. Each of these approaches has its advantages and each will be discussed separately.

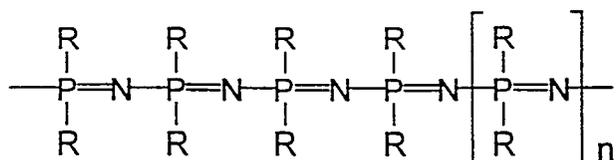
The polyphosphazene polymers are inorganic since their backbones consist of phosphorus and nitrogen instead of carbon as illustrated in Figure 1. The phosphazene monomeric unit is made up of a phosphorus to nitrogen double bond. This entity is singly bonded to similar phosphazene units producing a backbone with alternating phosphorus and nitrogen atoms joined by alternating single and double bonds. In addition, each phosphorus atom is bonded to two side groups. These side groups give the polymers their different chemical functionality. The functionality in turn governs the type of polymerization scheme for the polymer (linear, cycloliner, or cyclomatrix) as well as the chemical characteristics of the polymer itself (hydrophobic, solubility, polymer/permeate interactions, etc.). The polymerization process determines the molecular weight and morphology. With so many possibilities to alter the polymers physical and chemical properties, phosphazene polymers have the potential to be tailored for different applications. The bulk of this work was performed using linear polymers; however, some data will be given for the cyclomatrix membranes. The polymers tested, and their abbreviations, are given in Table 1.

## EXPERIMENTAL PROCEDURE

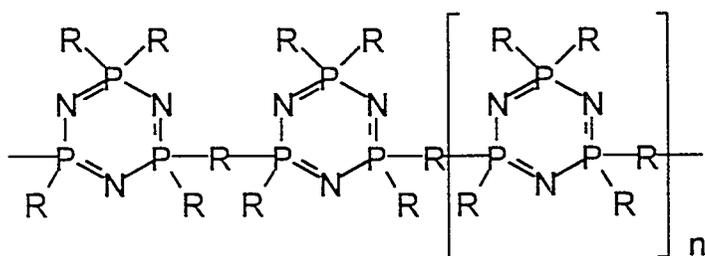
Linear polymer membranes were prepared by solution, spin, and knife casting techniques from prefiltered 2 to 5% polymer solutions in tetrahydrofuran (THF) as reported earlier.<sup>1</sup> Membranes were approximately 0.2 to 50  $\mu\text{m}$  thick.<sup>1</sup>

Cyclomatrix materials were cast onto sodium chloride discs and cured by heating in the oven. The assembly was placed into water which dissolved away the sodium chloride, leaving the cyclomatrix membrane. Membranes which were about one inch in diameter were not difficult to make in this manner. However, making discs as large as 2 inches in diameter proved to be very difficult.

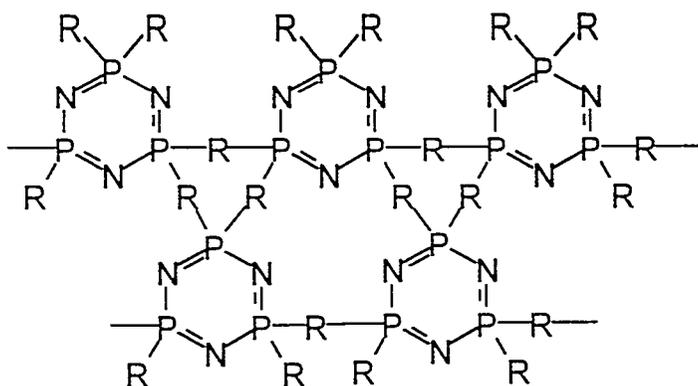
## Backbones Structures



**Linear Backbone**



**Cycloliner Backbone**



**Cyclomatrix Backbone**

**Figure 1.** Phosphazene polymer backbone structures.

**Table 1.** Polymer reference chart.

Abbreviation	Polymer name
PPOP	Poly(bisphenoxy)phosphazene
SO <sub>3</sub> -PPOP	Sulphonated poly(bisphenoxy)-phosphazene
8% Br-PPOP	Poly(bisbromophenoxy)phosphazene (8% substitution)
m-F-PPOP	Poly(bis meta-fluorophenoxy)-phosphazene
8%-COOH-PPOP	Poly(biscarboxyphenoxy)phosphazene (8% substitution)
CH <sub>3</sub> -PPOP	Poly(bis meta-methylphenoxy)phosphazene
PPOP-Ethyl	PPOP made by Ethyl Corp.
PPOP-ATO	PPOP made by Atochem
TFEP	Poly(bistrifluoroethoxy)phosphazene
Cyclomatrix	Hexa-para-hydroxyphenoxycyclotriphosphazene

### Pure Gas Technique

The timelag pure gas permeation technique is considered a static technique. Gas flow across the membrane is measured as a pressure rise with time on the permeate side of the membrane.<sup>1-5</sup> In these experiments, the gas transport parameters determined were permeability (P) and diffusivity (D); solubility (S) can be calculated from P and D based upon the relationship:  
$$P = D \cdot S.$$

A pictorial representation of the timelag technique is shown in Figure 2. After the gas is introduced at the feed side of the membrane, gas flow across the membrane is measured on the permeate side as a pressure rise with time. A typical pressure-time plot is shown in the lower portion of Figure 2. The pressure-time plot usually consists of a linear and a nonlinear region. The linear region occurs when gas flow through the membrane has reached a steady state value. The slope of the linear region is related to the permeability, and the timelag is related to diffusivity.<sup>1,4,5</sup> In actual operation, system lags, measured for all the test gases, ranged from 0.2 to 0.4 s. Membrane timelags were corrected for system lags prior to the calculation of D and S. Since membrane timelags for the fast diffusing gases were of the same order of magnitude as the system timelags, 50 to 100% errors were estimated for the membrane timelag and, consequently, D and S. In the case of CO<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub>, membrane timelags were at least 1 to 2 orders of magnitude greater than system lags. Thus, the timelag error for these gases is expected to be much smaller.

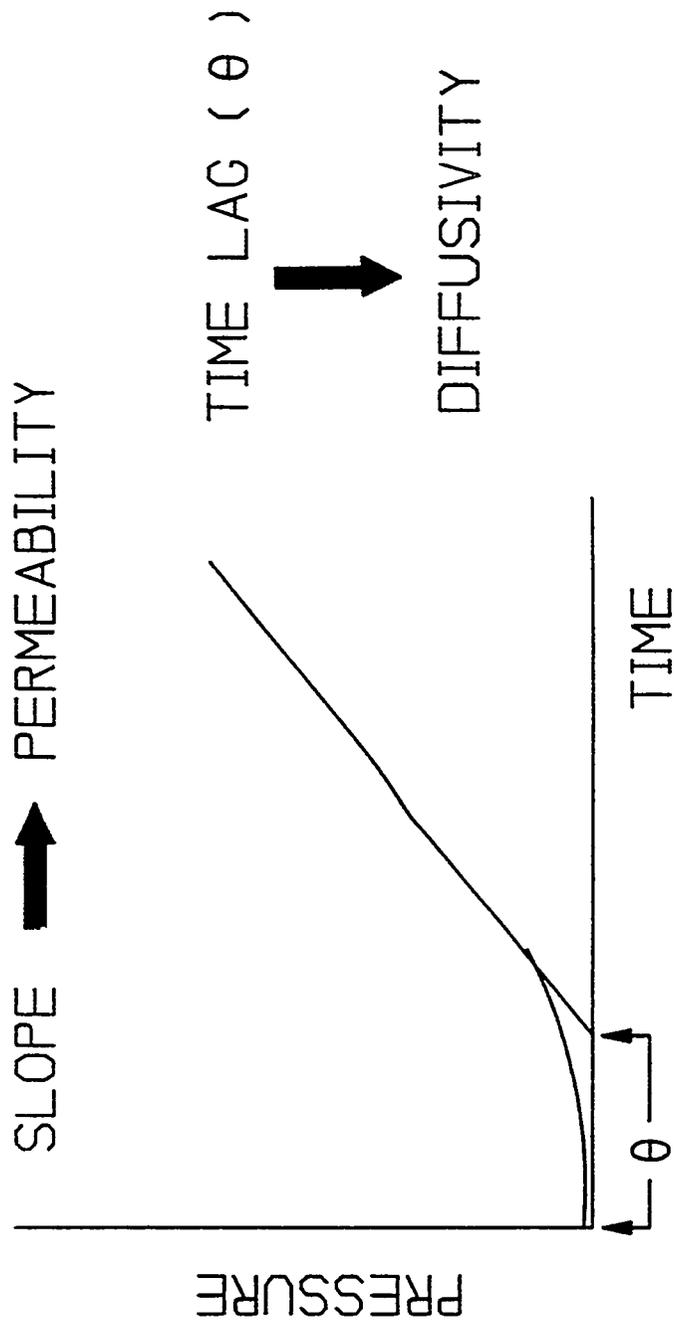
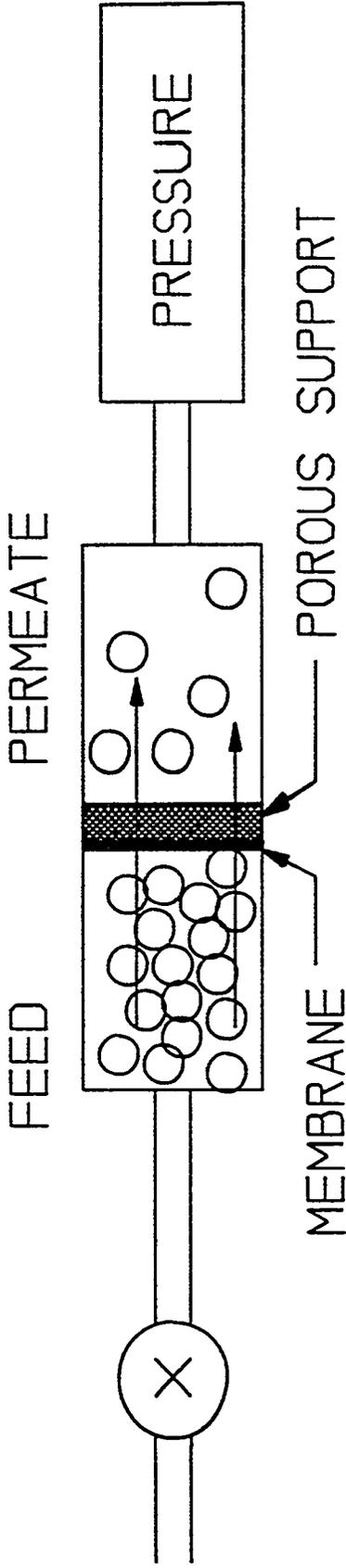


Figure 2. Pure gas timelag test schematic and typical results.

## Mixed Gas Technique

Early experiments suggested that polyphosphazene membranes should be useful for separations in harsh environments such as acid gas removal from process exhaust streams and down hole well gas processes. Consequently, the following gases were selected to represent acid gases and natural gas sweetening separations: 10% SO<sub>2</sub>/N<sub>2</sub>, 10% H<sub>2</sub>S/CH<sub>4</sub>, and 10% CO<sub>2</sub>/CH<sub>4</sub>. To test the separation performance of the membranes for these pairs of gases, a mixed gas test cell was built. During the course of the project the test cell was modified twice. At first, samples of the feed, rejectate (the feed stream after passing over the membrane), and permeate were taken manually by gas syringes and injected into gas chromatographs (GC) for analysis. This method was slow, labor intensive, and was subject to errors in the measurements. The first modification automated the sampling, injection, and analysis. Finally, to further take advantage of the dual analyzers on the GC, a system was developed that simultaneously operates two separate mixed gas cells. The two cells are housed in an oven, which allows the membranes to be tested from room temperature up to 300°C.

The membrane (on its ceramic support) is sealed in the cell on a perforated stainless steel disk that provides mechanical support. The apparatus samples and analyzes the feed gas, the permeate gas, and the rejectate. The data analysis system calculates the concentrations of the component gases in these streams and (using the input values for membrane area and system pressure) calculates the following separation parameters for each timed run:

- Separation factor (enrichment factor), which is the ratio of the concentration of the pair of gases in the permeate divided by the ratio of the concentration of the pair of gases in the rejectate
- Permeability/thickness, which is derived from areas of the component peaks
- Selectivity, which is the ratio of the permeability/thickness values described above for a particular pair of gases.

In the first year all of the mixed gas experiments used membranes of poly(bisphenoxy)phosphazene (PPOP) synthesized in-house.<sup>6</sup> Later, the program included many other linear polymers, either synthesized in-house or contributed by commercial suppliers. Typical operating parameters used were feed gas flow rate, 20 cm<sup>3</sup>/min; helium permeate sweep gas flow rate, 2 cm<sup>3</sup>/min; and system differential pressure, 20 psig. Due to the difficulty in making membranes large enough for the mixed gas test apparatus, no mixed gas experiments were performed with the cyclomatrix materials.

## RESULTS AND DISCUSSION

### Pure Gas Test

#### Linear Polyphosphazene Membranes

One study compared two unfunctionalized PPOP membranes, one produced by spin casting and the other by knife casting. The tests were run at 25°C and 1 atm as a function of test gas. The results of these time-lag experiments are summarized in Tables 2 and 3. As a result of the estimated errors in the membrane time lags, only comparison of the relative magnitudes of S and D for the different gases is valid (small differences in absolute values are insignificant).

**Table 2.** Comparison of permeability data for spin cast and knife cast PPOP membranes.

Gas	Permeability (barrers) <sup>a</sup>		Permeability ratio ( $P_{\text{gas}}/P_{\text{He}}$ )	
	Spin cast	Knife cast	Spin cast	Knife cast
He	6.01	15.08	1.00	1.00
N <sub>2</sub>	2.26	6.04	0.38	0.40
O <sub>2</sub>	2.11	5.90	0.35	0.39
H <sub>2</sub> S	1.96	11.98	0.33	0.80
Ar	2.07	5.18	0.34	0.34
SO <sub>2</sub>	3.86	74.67	0.64	4.95

a. Barrer =  $10^{-10}$  (cc(STP)cm)/(cm<sup>2</sup>·sec·cmHg).

**Table 3.** Comparison of solubility and diffusivity ratios for spin cast and knife cast PPOP membranes.

Gas	Solubility ratio (gas/helium)		Diffusivity ratio (gas/helium)	
	Spin cast	Knife cast	Spin cast	Knife cast
He	1.0	1.0	1.0	1.0
N <sub>2</sub>	0.5	0.6	0.9	0.7
O <sub>2</sub>	2.0	3.0	0.2	0.1
Ar	0.7	6.0	0.5	0.6
H <sub>2</sub> S	3.0	200.0	0.1	0.1
SO <sub>2</sub>	20.0	1000.0	<0.1	<0.1
CO <sub>2</sub>	NR	20.0	NR	<0.1
CO	NR	0.8	NR	1.0
CH <sub>4</sub>	NR	1.0	NR	0.6
C <sub>2</sub> H <sub>6</sub>	NR	0.7	NR	0.8
C <sub>3</sub> H <sub>8</sub>	NR	0.1	NR	6.0
C <sub>4</sub> H <sub>10</sub>	NR	0.1	NR	3.0

NR = Not run. The indicated spin cast experiments were not performed.

Figure 3 shows the permeability results (from Table 2) for the knife cast PPOP polymer plotted as a function of kinetic gas diameters. The general trends are the same for both experiments, i.e., permeability decreases with increasing molecular size. (The knife cast membrane was consistently more permeable to the gases.) The notable exceptions to the size trend are CO<sub>2</sub>, H<sub>2</sub>S, and especially SO<sub>2</sub>.

Gas transport or permeation across a polymer membrane can be thought of as three discrete events: sorption into the membrane, diffusion through the membrane, and desorption out of the membrane. Sorption into and desorption out of the membrane is related to solubility, and transport through the membrane is dependent on diffusion. Factors that affect gaseous diffusion are related primarily to membrane microstructure and gas size. In the case of solubility, the gas/membrane physicochemical properties are important. In the absence of strong solubility effects, overall transport is diffusion controlled and related to molecular size. This type of transport/size trend has been reported as being typical for noble, atmospheric, and nonpolar gases.<sup>2,7,8</sup> The permeability/size correlation of the gases helium, carbon monoxide, nitrogen, oxygen, and argon indicates that gas size was the controlling factor in transport and that solubility factors were negligible. Since sulfur dioxide, and to a lesser extent carbon dioxide and hydrogen sulfide, deviates from the expected diffusion-controlled process, it is apparent that solubility factors are contributing to overall transport. Gas solubility ratios from the timelag experiment for the two membranes are shown in Table 3. Sulfur dioxide solubility is 20 times that of helium in the spin cast membrane and 1000 times that of helium in the knife cast membrane. Tables 2 and 3 give comparisons of the permeabilities, solubilities, and diffusivities for the two membranes.

Examining the data presented in the tables reveals the dependence of the permeability on its component parts, S and D. For example, helium has very little solubility in the polymer and so the high permeability value comes mainly from its diffusivity. SO<sub>2</sub> has much less diffusivity than helium, but because SO<sub>2</sub> is much more soluble in the polymer its overall permeability is substantially greater than that of helium.

Three general observations can be made from this study. First, the polymer molecular structure of the membrane has a direct bearing on the membrane performance. The knife casting technique produced a more open polymer structure and yielded higher overall permeability and solubility values. Second, both diffusion and solution mechanisms contribute to permeability. And third, gases that have a high solubility, generally permeate much more efficiently. This last observation is substantiated by the fact that all of the diffusivity ratios are nearly the same.

### **Cyclomatrix Polyphosphazene Membranes**

A second set of experiments performed in the timelag apparatus involved a highly cross linked cyclomatrix polyphosphazene, hexa-para-hydroxyphenoxycyclotriphosphazene. This material, when heated in the presence of hexamethylenetetramine, forms a highly crosslinked, hard, brittle polymer. Casting a thin film presented many problems. A process was developed in which the polymer was cast onto sodium chloride crystal disks. These disks had a flat surface and could withstand heat during curing. Once the membrane was formed the crystal was dissolved in water. In this way 1 in. diameter membranes were formed for use in the pure gas test cell.

The results for the cyclomatrix membrane are summarized in Figure 4, a plot of the log of the permeabilities of eight gases through cyclomatrix membranes at four temperatures. Helium and hydrogen pass through the membrane very well—these two small gases are about 30 times more permeable than the rest of the gases. The data suggests that cyclomatrix polyphosphazene

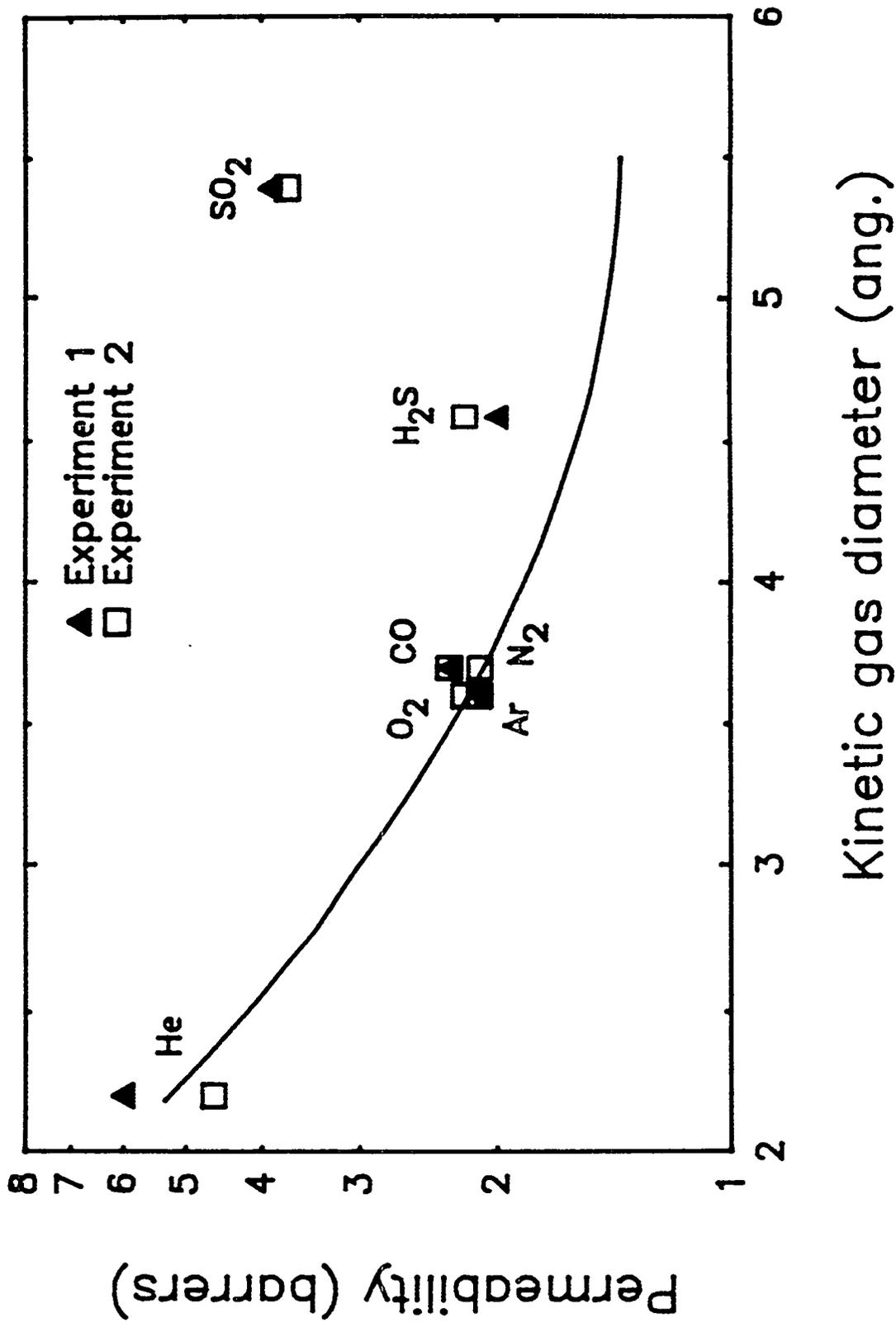


Figure 3. Gas permeability verses kinetic gas diameter for a knife cast PPOP membrane.

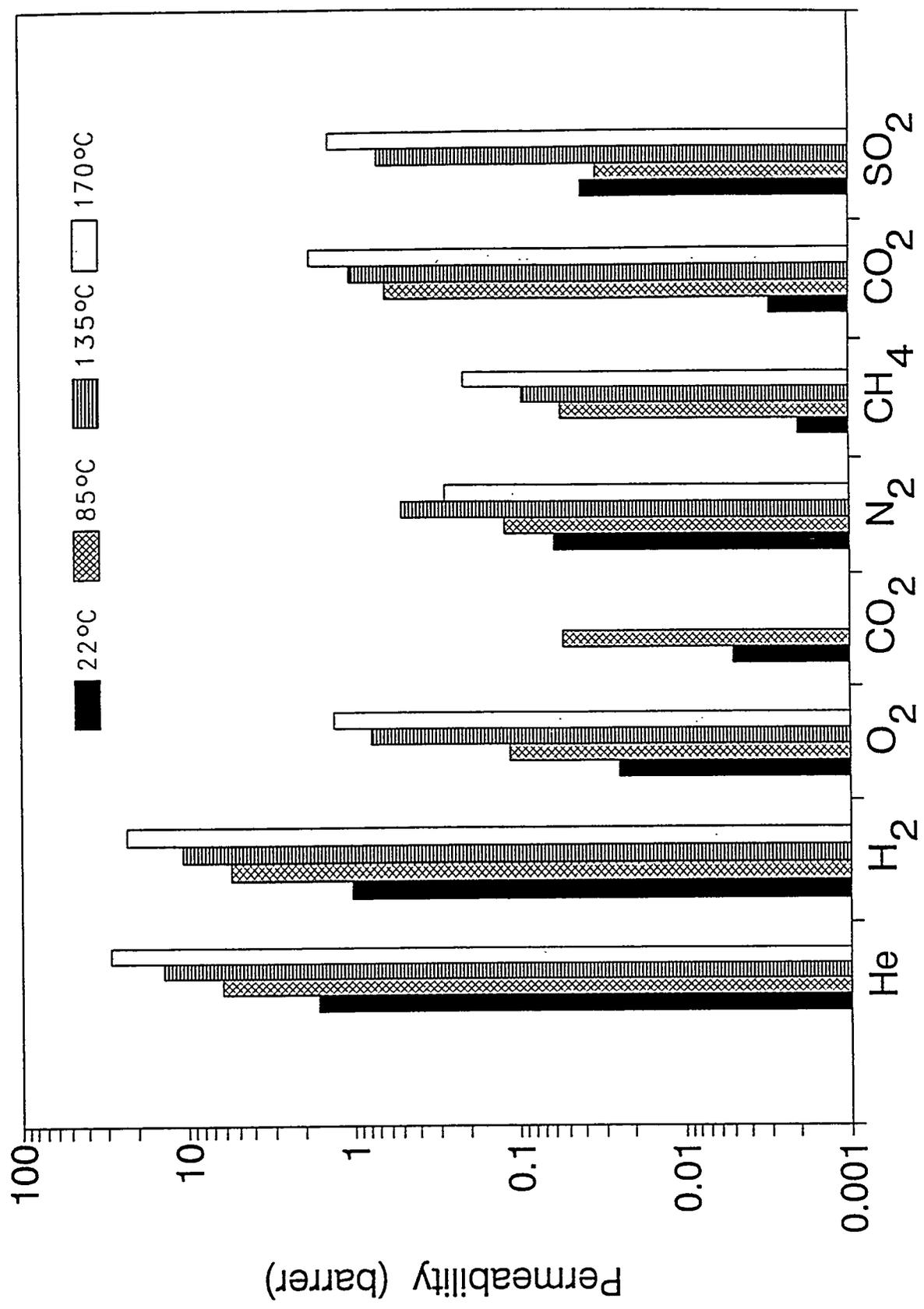


Figure 4. Cyclomatrix membrane permeabilities from timelag experiments.

membranes might separate helium from natural well gas. Casting the larger (2 inch diameter) membranes required for the mixed gas equipment proved very difficult. The cyclomatrix membranes that were fabricated were too thick to use. However, over twenty helium separations were performed with the linear polymers; the results are given in a separate section of this report.

## Mixed Gas Tests

Over 30 runs were performed at a variety of temperatures with PPOP membranes spin cast onto flat Anotec supports. These experiments determined the selectivities of eight different linear polymers (the first eight listed in Table 1) at two temperatures for three pairs of gas mixtures. The mixed gas test results are displayed in Figures 5 through 9.

Selectivities of the membranes at 30°C are shown in Figure 5. The membranes differed in performance with the three gas mixtures. Five membranes were efficient at separating sulfur dioxide from nitrogen, with selectivities over 300; the values are lower for the other two gases. Even so, several of the membranes had selectivities over 20 for H<sub>2</sub>S. Selectivity results at 80°C for the same membranes and gas mixtures are given in Figure 6. Although the general appearance is the same the absolute values are reduced, a trend common to most membrane systems. The temperature dependence of the membranes to the three pairs of gases is shown in Figures 7 through 9. Again, in most cases the selectivity decreases as the temperature increases.

The permeabilities for the membranes at 30 and 80°C are given in Table 4. These results show that generally selectivities decrease and permeabilities increase with increasing temperatures. Two runs were also made at 130°C, giving SO<sub>2</sub> permeabilities of 325 barrer for PPOP and 271 barrer for 8% COOH-PPOP. These tests showed another increase in permeability and further evidence of the integrity of the phosphazene polymers in harsh environments.

The mixed gas separation results illustrate two important points. First, the chemical structure of the polymer plays a significant role in the separation performance. Second, there is a large difference in membrane performance among the three pairs of gases tested; overall, they show excellent selectivities for SO<sub>2</sub>, and very good selectivities for H<sub>2</sub>S and CO<sub>2</sub>.

## HELIUM SEPARATIONS

The pure gas permeability experiments showed that helium was much more permeable than methane. Based on those results, it was hypothesized that it might be possible to separate helium from natural gas well mixtures. The mixed gas test equipment was modified and recalibrated to test this hypothesis. Membranes of several polymers have been tested using preanalyzed gas supplied by the Bureau of Mines. The gases are actual well samples taken from the large underground storage reserve operated by the Bureau in Texas. By sampling at different locations, different mixtures of gases were obtained.

One cyclomatrix polymer membrane and four linear polymer membranes were tested. The cyclomatrix membrane was successfully cast on a support and cured in place. The membrane was leak tight, but it was so thick that no gas permeation over a reasonable time period was observed. Because of the time constraints on the program, it was decided to focus on linear polymers, which are much easier to fabricate.

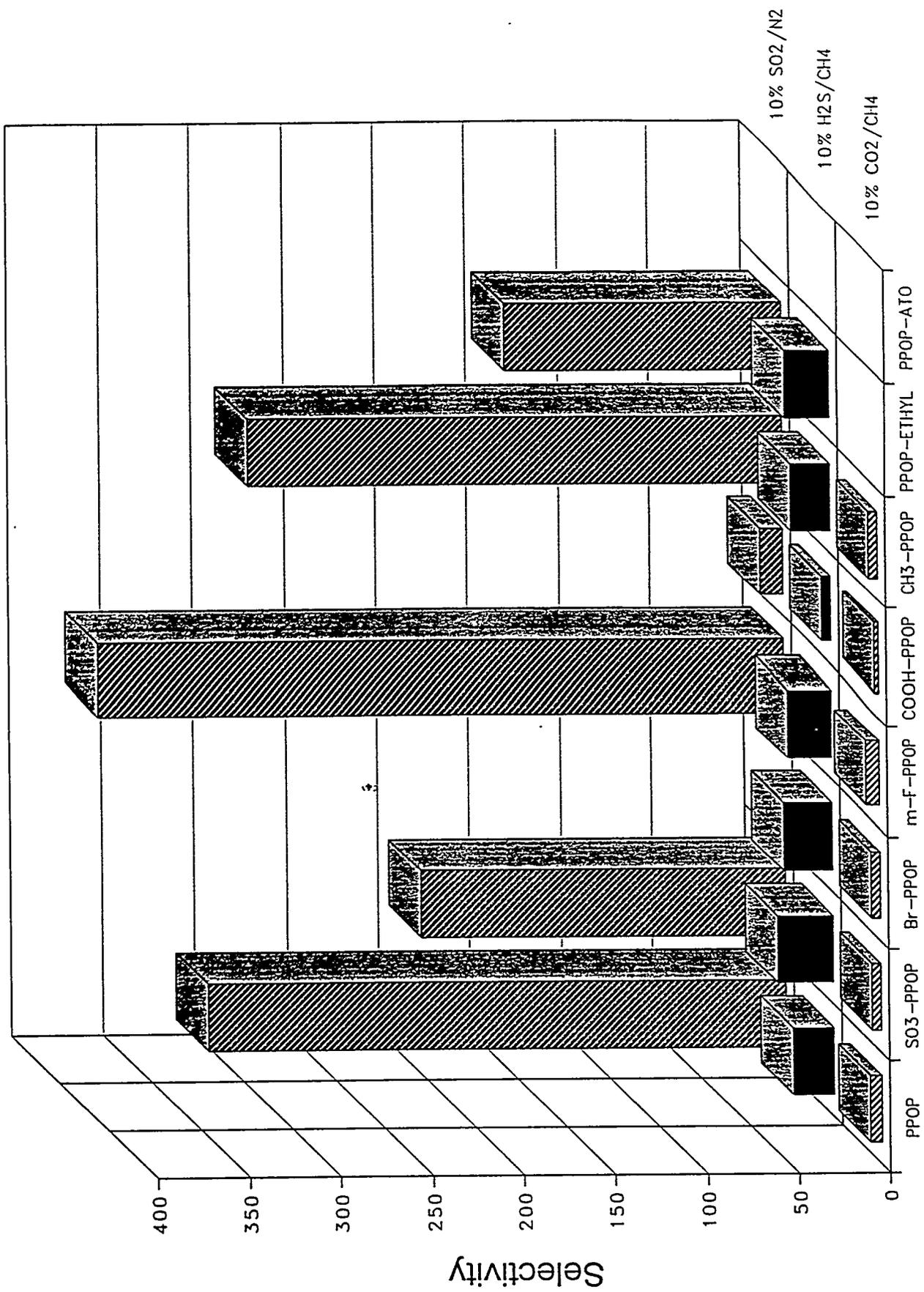


Figure 5. Comparison of mixed gas selectivities at 30°C for seven different phosphazene polymers.

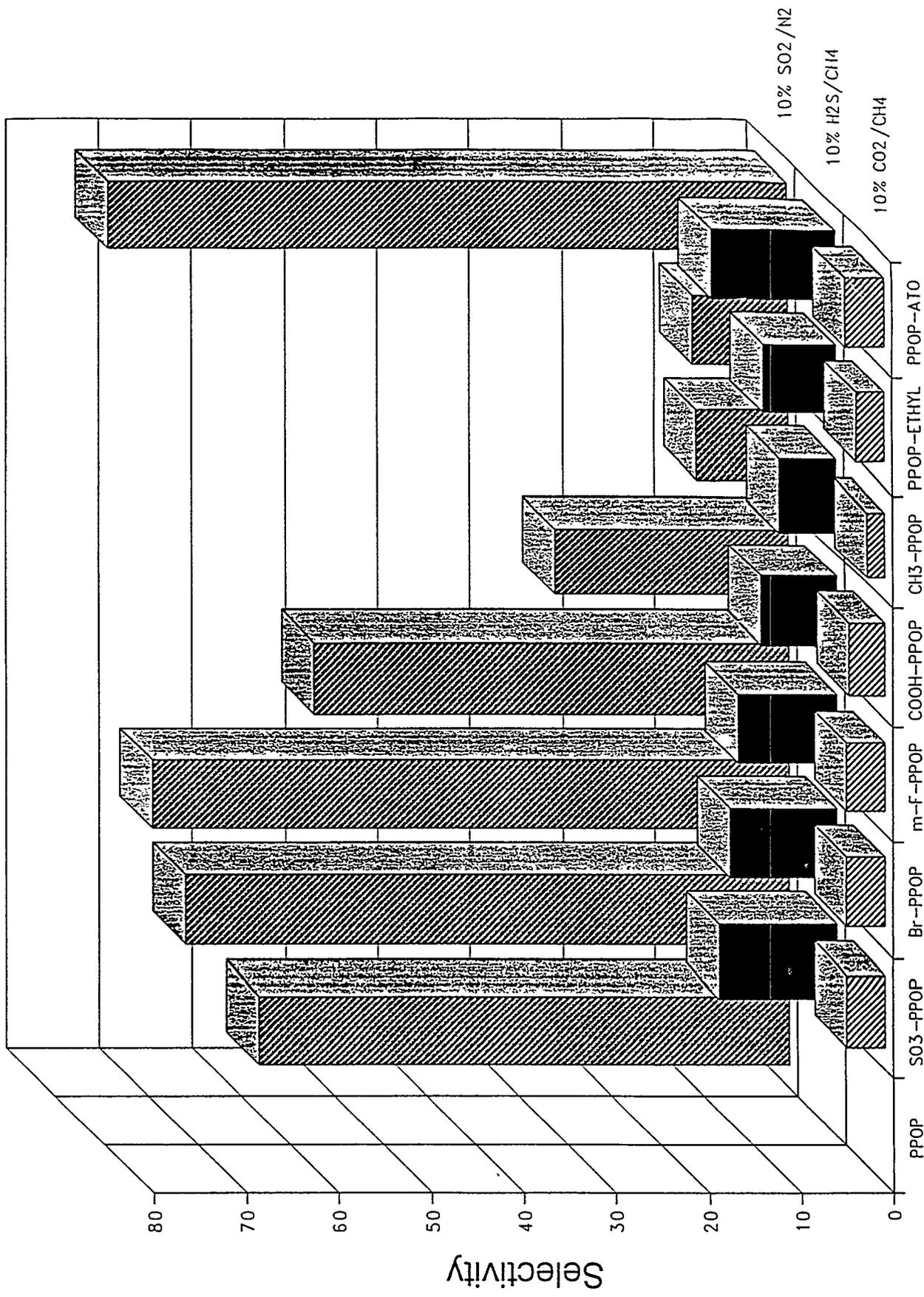


Figure 6. Comparison of mixed gas selectivities at 80°C for eight different phosphazene polymers.

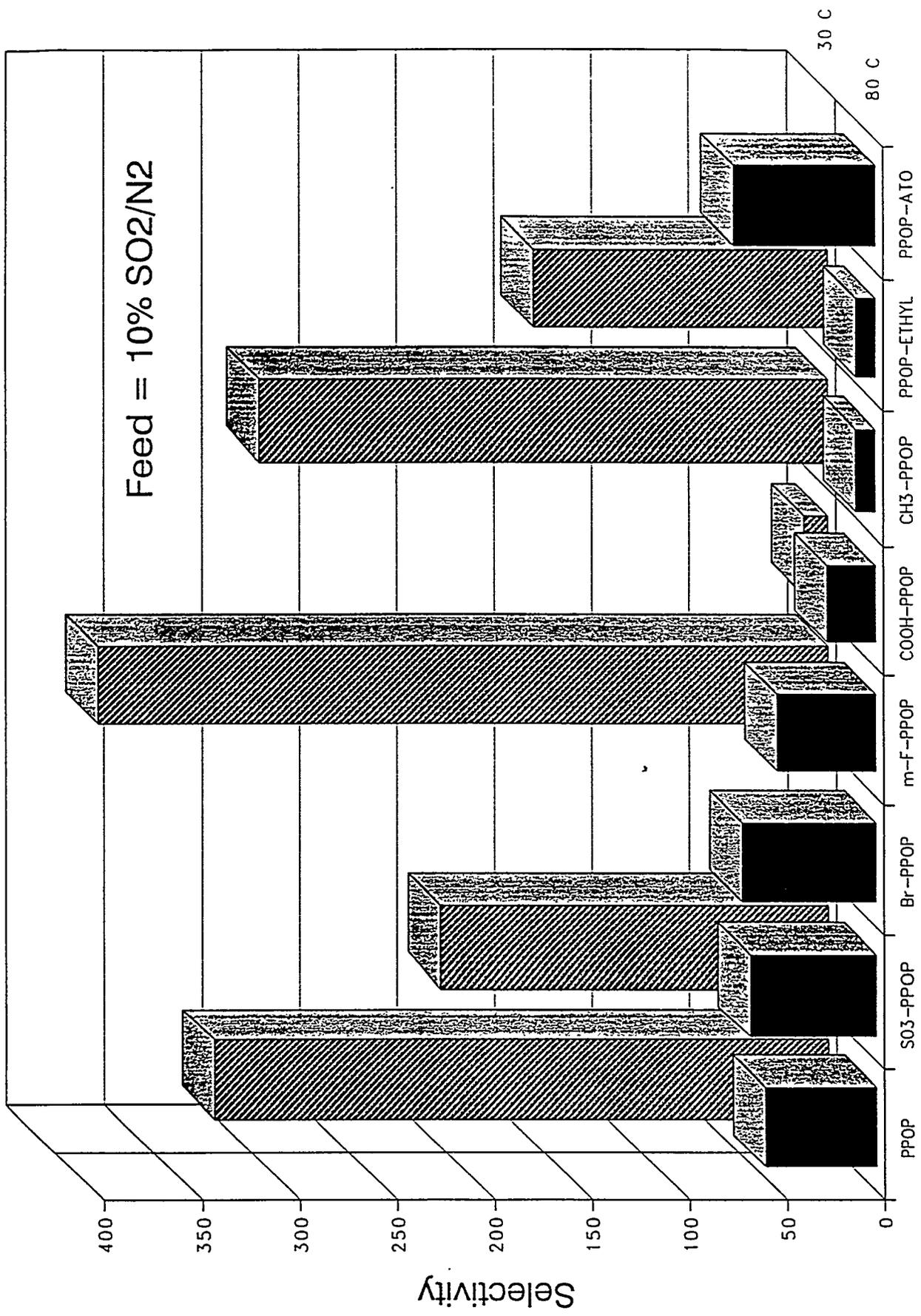
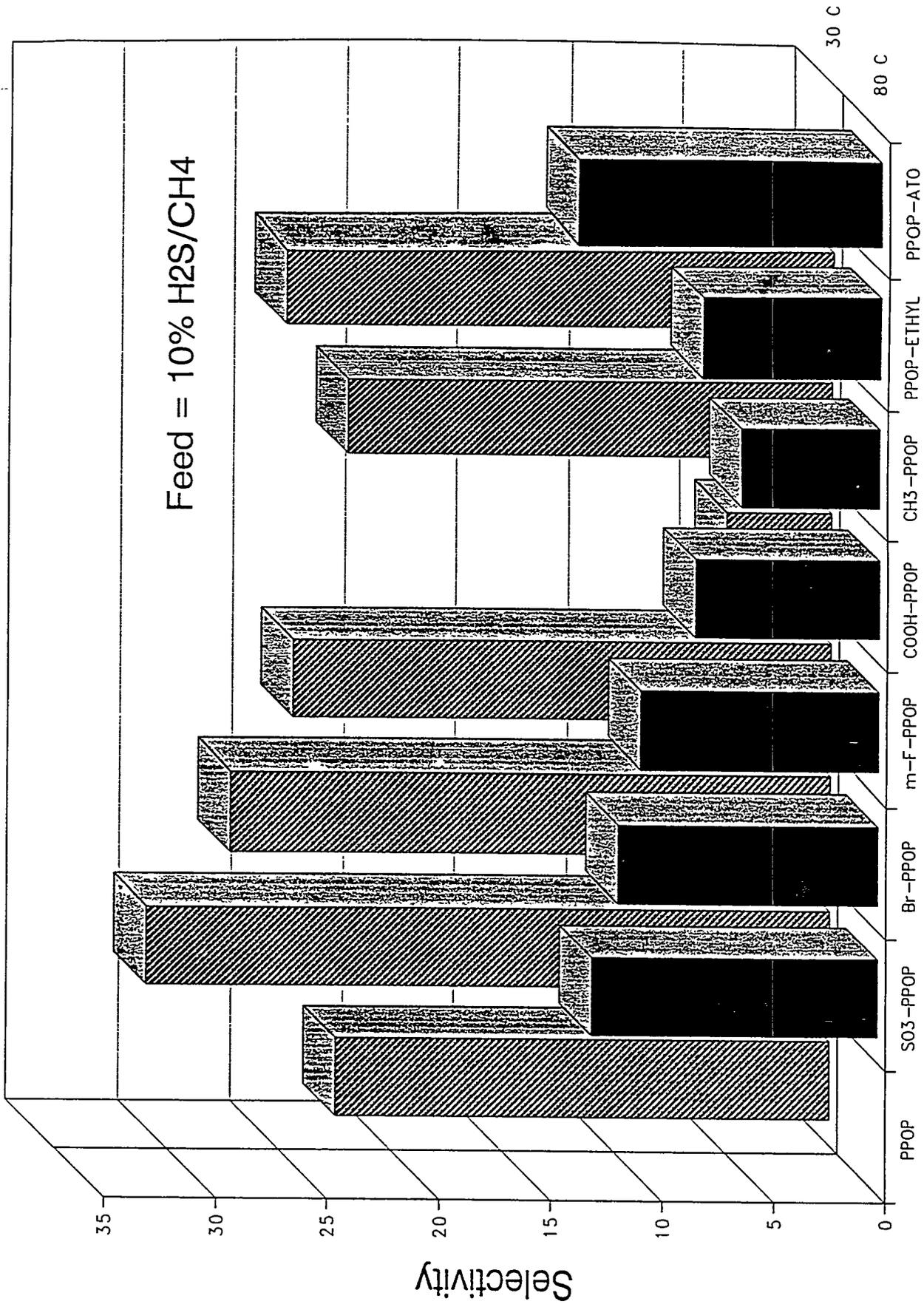


Figure 7. Temperature dependence of the selectivities of eight phosphazene polymers for the 10% SO<sub>2</sub>/N<sub>2</sub> gas mixture.



**Figure 8.** Temperature dependence of the selectivities of eight phosphazene polymers for the 10% H<sub>2</sub>S/CH<sub>4</sub> gas mixture.

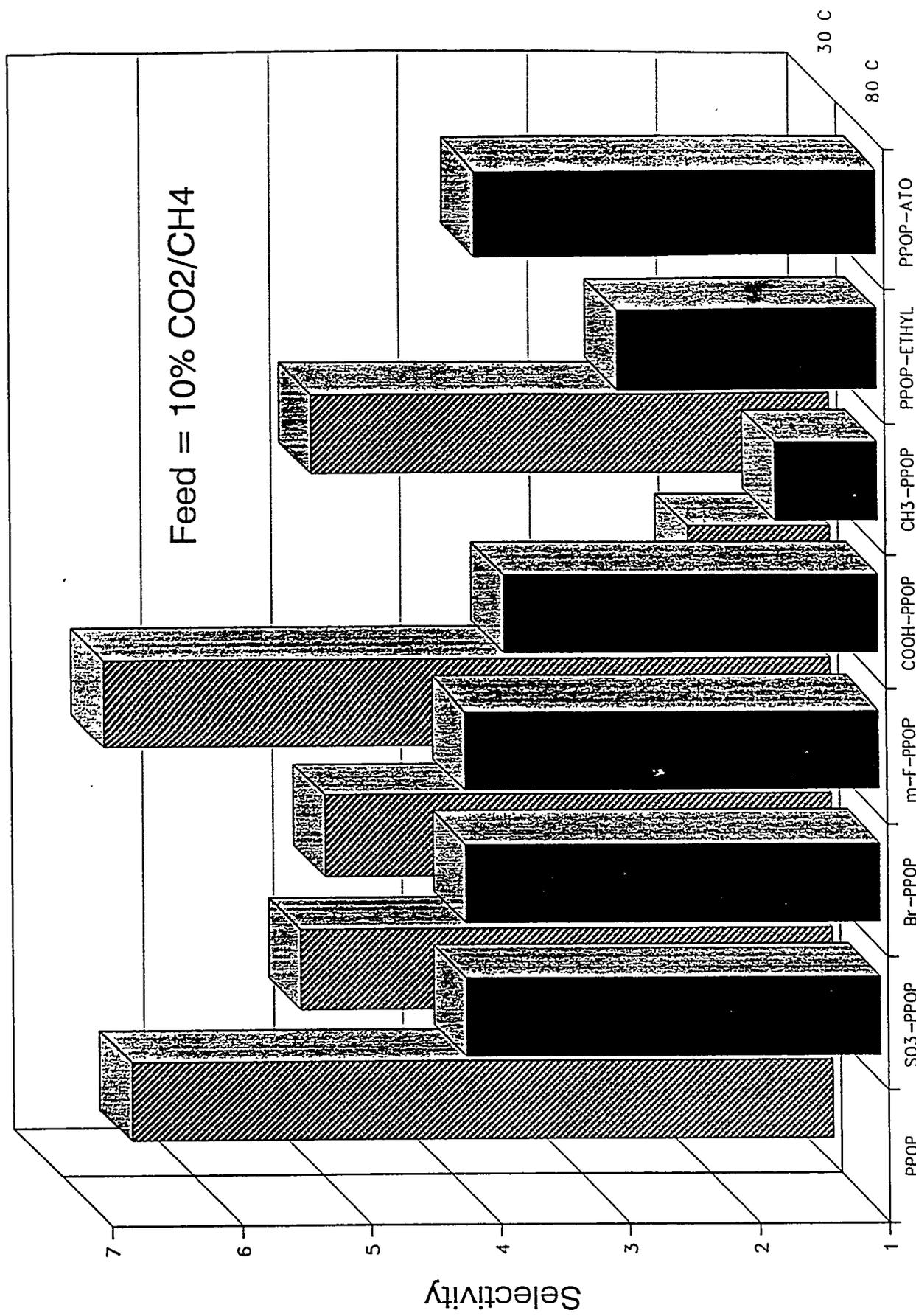


Figure 9. Temperature dependence of the selectivities of eight phosphazene polymers for the 10% CO<sub>2</sub>/CH<sub>4</sub> gas mixture.

**Table 4.** Polyphosphazene membrane permeabilities from mixed gas research (permeability units are barrer  $10^{-10}$  [cc(STP)cm]/[cm<sup>2</sup>·sec·cmHg]).

Polymer	SO <sub>2</sub> in 10% SO <sub>2</sub> /N <sub>2</sub>		H <sub>2</sub> S in 10% H <sub>2</sub> S/CH <sub>4</sub>		CO <sub>2</sub> in 10% CO <sub>2</sub> /CH <sub>4</sub>	
	30°C	80°C	30°C	80°C	30°C	80°C
PPOP	52	177	17	NR	11	NR
SO <sub>3</sub> -PPOP	42	146	13	77	7	30
8% Br-PPOP	48	251	20	120	12	52
m-F-PPOP	104	348	29	176	15	76
8%-COOH-PPOP	48	121	21	109	14	42
CH <sub>3</sub> -PPOP	163	516	51	NR	22	168
PPOP-Ethyl	56	101	20	92	NR	678
PPOP-ATO	NR	413	NR	228	NR	80

NR = Not run. The indicated experimental runs were not performed.

In general terms, all of the membranes showed a preference for helium transport over methane. The data are presented in Figures 10 and 11 and Table 5. There were two mixed gas feed streams. One contained 34% helium and 40% methane, with the remainder being mostly nitrogen, and the other contained ~2% helium and 65% methane, with the remainder nitrogen. The feed stream passed over the membrane at 18 to 20 psig and 2 to 20 cm<sup>3</sup>/min. The permeate was swept away by a nitrogen purge stream of from 2 to 15 cm<sup>3</sup>/min. Aliquots of the feed, rejectate (the feed stream after it has passed over the membrane), and permeate were automatically sampled and analyzed by gas chromatography.

The performance of the membrane can be described by the change in the concentration of helium relative to the concentration of methane in the feed and permeate streams. In some cases the flow of methane was too small to measure, so relative calculations could not be made since it would require dividing by zero. It is significant to note that in some of the situations in which no methane flow was detected, a measurable helium flux was present. This would mean that the permeate would contain essentially no methane. The data for those runs in which methane permeation was measured are presented in Figures 10 and 11.

The feed with the higher helium concentration had a helium to methane concentration ratio of 0.85. The extent that the helium concentration is enhanced relative to methane ranges from 0.99 to 3.2 (Figure 10). Since these numbers are larger than the feed ratio of 0.85, helium is permeating preferentially. Another way to express this is with the separation factor, which is the

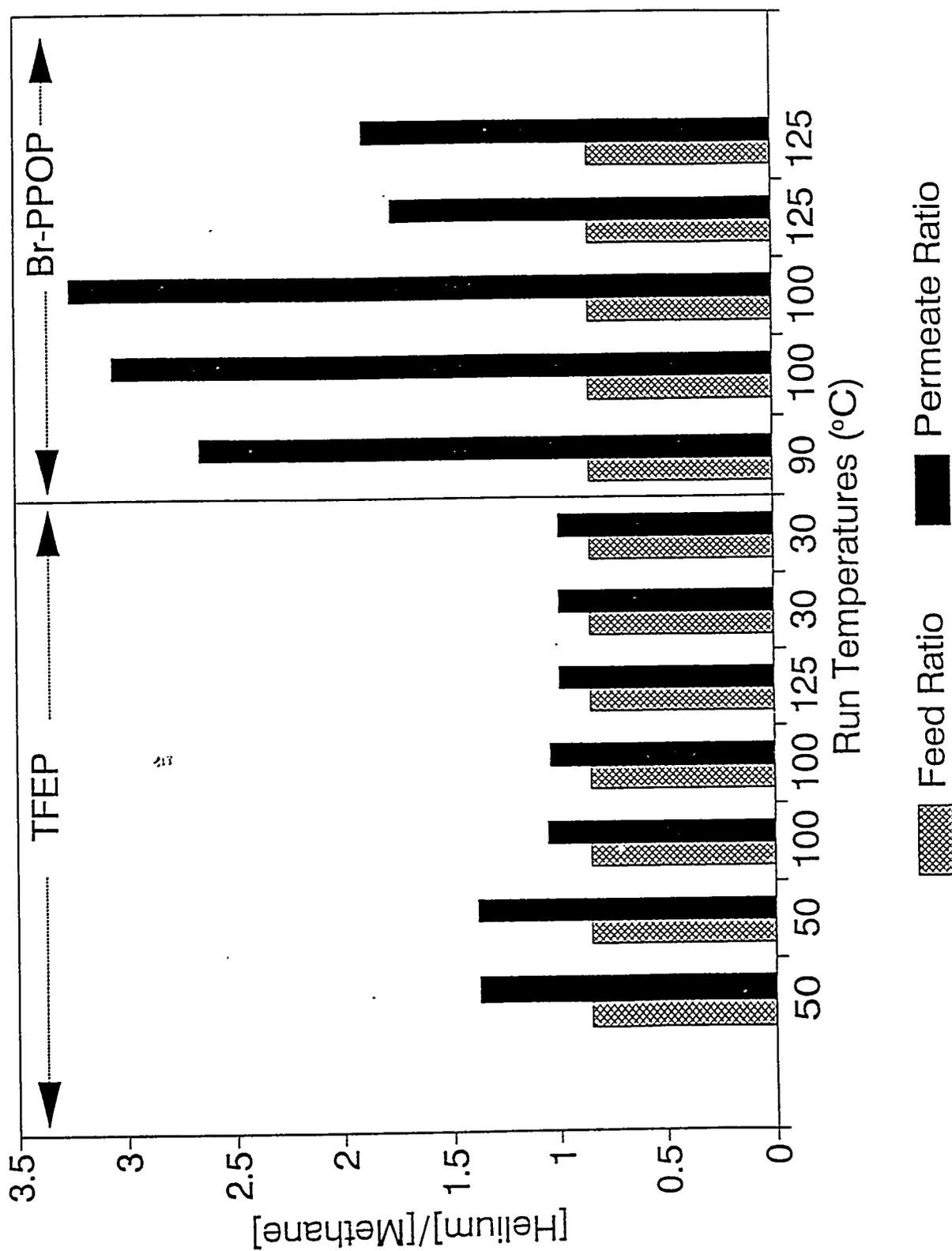


Figure 10. Helium to methane concentration ratio starting with a feed containing 34% helium and 40% methane (remainder is mostly nitrogen).

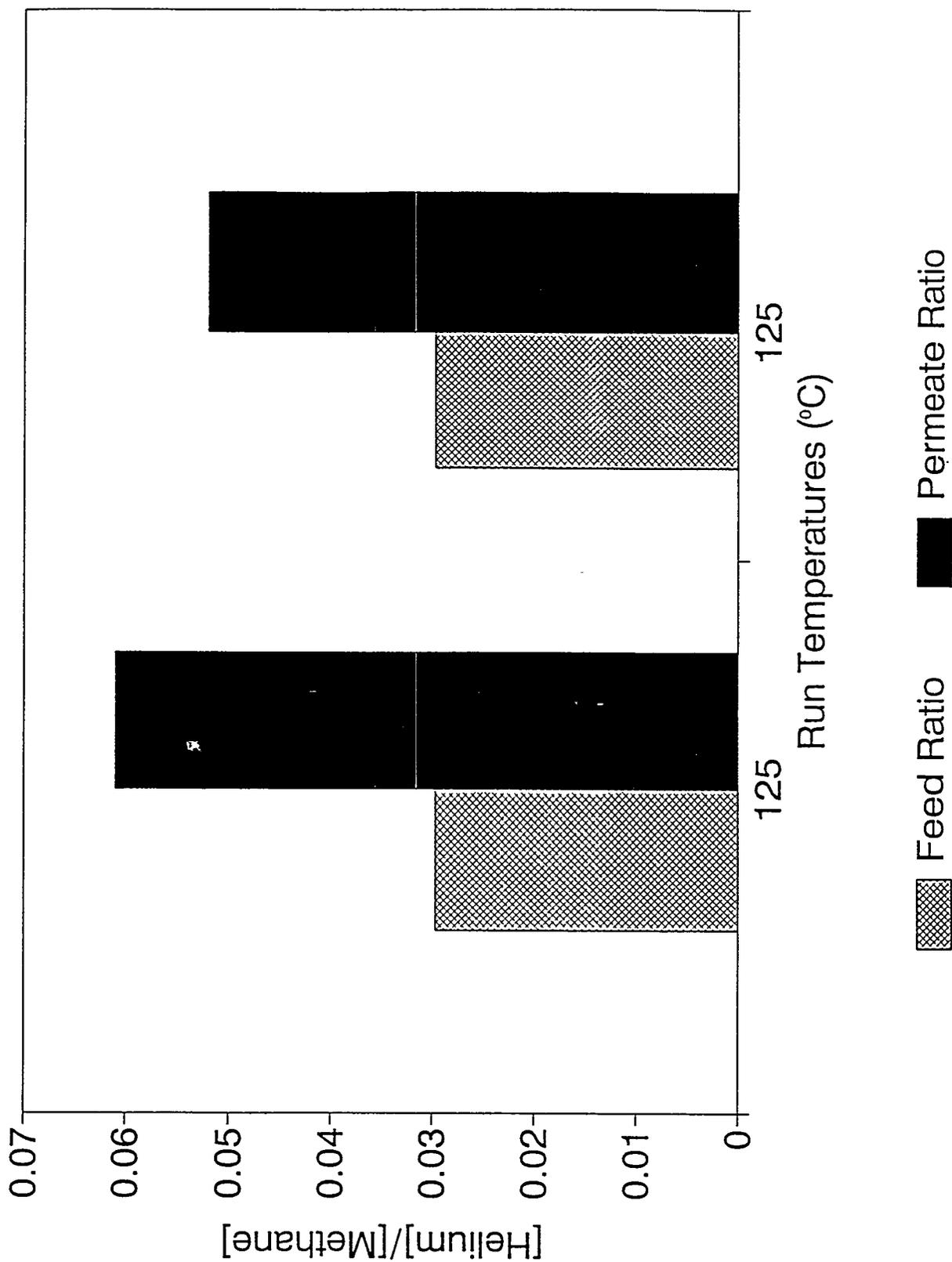


Figure 11. Helium to methane concentration ratio at 125 $^{\circ}\text{C}$  with  $\text{CH}_3$  PPOP membrane and feed containing 1.92% helium and 64.58% methane (remainder is mostly nitrogen). (Duplicate tests.)

**Table 5.** Helium separations from natural well gas.

Membrane	Separation factor <sup>a</sup>	Helium flux (l/m <sup>2</sup> ·h)	Temperature (°C)
<u>Helium feed concentration = 34% (see Figure 8)</u>			
TFEP	1.6	46.9	50
	1.6	49.4	50
	1.2	61.6	100
	1.2	118.4	100
	1.2	122.1	125
	1.2	113.0	30
	1.2	113.0	30
8% Br-PPOP	NC	1.7	50
	NC	1.6	50
	3.1	4.6	90
	3.6	4.3	100
	3.8	4.3	100
	2.1	6.8	125
	2.2	7.8	125
<u>Helium feed concentration = 2% (see Figure 9)</u>			
Meth-PPOP	2.0	2.1	125
	1.7	6.0	125
8% Br-PPOP	NC	8.1	90
	NC	1.7	90
Meth-PPOP	NC	1.5	50

a. Separation factor =  $\{[\text{He}]_p/[\text{CH}_4]_p\}/\{[\text{He}]_f/[\text{CH}_4]_f\}$ ; p = permeate, f = feed.

NC = Not calculated. In cases where the methane was too low to measure (essentially zero) separation factors could not be calculated. In these cases virtually only helium came through the membranes.

ratio of the permeate and feed ratios. The separation factors for these membranes, given in Table 5, range from 1.2 to 3.8. The helium concentration with respect to the methane in the permeate is almost 4 times what it was in the feed. Thus the permeate is enriched when compared with the feed.

The enrichment in helium for the runs using the feed with the lower helium concentration is shown in Figure 11. Even with a very dilute feed stream, an enhancement of over 2 was observed.

The separation results for 19 runs are listed in Table 5. When separation factors could be calculated, the separation factor and the figure in which the separation data are plotted are given.

The helium fluxes through the membranes and the temperatures are also given in the table. In some cases, increasing the temperature increased the flux as expected. In other cases that did not occur. The reason for this discrepancy is not clear. The separation factors and helium flux data seem to indicate that the TFEP membrane gives better fluxes and less separation, while the 8% Br-PPOP provides better separation, but at a lower flux level. The main structural difference between the two polymers is that the 8% Br-PPOP has functionalized phenyl substituents, whereas the TFEP has short, linear, functionalized ethyl types of side groups. Perhaps this difference accounts for the difference in performance. The side groups influence the morphology of the polymer membrane. However, these are preliminary data and factors such as membrane thickness have not been fully taken into account. In all cases the helium preferentially permeated the membrane yielding a permeate richer in helium, in relation to the methane, than the feed. Thus, these early results indicate that the membranes could be used to separate, or at least enrich, the helium in a natural well gas.

## SUMMARY AND CONCLUSIONS

The most successful separation test result was the removal of SO<sub>2</sub> from nitrogen in an acid gas model mixture consisting of 10% SO<sub>2</sub> in N<sub>2</sub>. The permeability of the SO<sub>2</sub> was higher than that of the smaller molecules as a result of higher solubility of the SO<sub>2</sub>, indicating an interaction between the polymer and the SO<sub>2</sub>. The experimental results suggested that the high permeability was due to the fact that the SO<sub>2</sub> was very soluble in the polymer, more soluble than some smaller gas species such as helium, which resulted in higher permeabilities for SO<sub>2</sub> than for most other gases measured. This means that PPOP membranes are good candidates for SO<sub>2</sub> separation.

Another important feature of the test results is that the membranes survived repeated exposure to 10% SO<sub>2</sub>, H<sub>2</sub>S, and CO<sub>2</sub> gas mixtures at temperatures ranging from 30 to 200°C. Some commercial membranes are limited to exposures of less than 5% and temperatures of less than 100°C. This information substantiates that the PPOP polymers are suitable for use in harsh environments.

The PPOP polymers preferentially transported helium over methane. In experiments involving feeds containing 2 or 34% helium, the permeate ratio of helium to methane was higher than the feed ratio by as much as a factor of four. In some cases no methane, only helium, was observed to cross the membrane. In these cases, the resulting separation factors extremely high. The observed fluxes generally increased with increasing temperature, accompanied by a decrease in selectivity with increasing temperature. However, in one case where the polymer had been heated and then cooled, the flux was higher than those of membranes tested at the cooler temperature that had not been heated first. This indicates that the polymer morphology played a very important role in the separation performance. If the separation could be maintained in each stage of a multistage separation process, helium could be recovered and purified from natural gas wells.

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