Novel Poly(aryl ether ketone)s Containing Various Pendant Groups. II. Gas-Transport Properties

ZHONGGANG WANG,[1] TIANLU CHEN,[2] JIPING XU[2]

[1]Department of Chemistry, Peking University, Beijing, 100871, People's Republic of China

[2]Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, People's Republic of China

ABSTRACT: The gas transport of hydrogen, oxygen, nitrogen, carbon dioxide, and methane gases in a series of poly(aryl ether ketone)s was examined. These polymer membranes have a wide range of permeability coefficients and permselectivity coefficients, showing excellent gas-transport properties. The enhanced interchain interaction in the polymers due to intermolecular hydrogen bonds and ionic bonds results in a considerable increase in permselectivity but a decrease in permeability. On the contrary, the polymers with bulky arkyl substituents show significantly increased permeability. The causes of this trend are interpreted in terms of the free volume, interchain distance, and glass transition temperature together with the respective contribution of gas solubility and diffusivity to the overall permeability. Of interest is the observation that the ionomer IMPEK-K$^+$, which simultaneously contains bulky isopropyl substituents and pendant carboxylate groups, exhibits over twice higher CO_2 permeability and 15% higher CO_2/CH_4 permselectivity than those of bisphenol-A polysulfone (PSF). The possibility of using the new synthesized poly(aryl ether ketone)s in gas separation membrane application is also discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1725–1732, 1997

Key words: poly(aryl ether ketone); ionomer; membrane; gas separation

INTRODUCTION

Gas separation by membrane methods is currently used in numerous applications,[1–4] such as hydrogen recovery from reactor purge gas, nitrogen enrichment, and water vapor removal from air and stripping of carbon dioxide from natural gas. Over the past decade, many attempts have been made to find new membrane materials with better separation characteristics, i.e., permeability and permselectivity. In this regard, a complete understanding of the molecular features that control gas-transport properties is required.

Recent studies indicate that the packing density and the segmental motion ability of the polymer chain are two dominant factors that affect gas permeability, and polymers with high T_g's have been shown to have higher permselectivities.[5–8] The strong interchain interaction yields a dense chain packing and restricted segmental motion and subsequently results in a significant increase in gas permselectivity. On the other hand, the introduction of bulky alkyl substituents appears to raise the free volume, and this allows for a high permeability. On the basis of these facts, one can design a new polymer to combine the two favorable factors, and, thus, this new polymer would have both high permeability and high permselectivity.

In previous work,[9] we investigated the synthesis of a series of new poly(aryl ether ketone)s con-

Table I   Chemical Structure of the Four Poly(aryl ether ketones)

Chemical Structure	Abbreviation
	PEK-C
	PEK-H
	PEK-L
	IMPEK-L

taining different functional groups, such as carboxyl, carboxylate, amide, ester, methyl, and isopropyl. The polymers prepared have a high glass transition temperature (above 210°C), excellent thermal stability, and mechanical properties as well as good solubility in a few polar aprotic solvents. These characteristics make them suitable candidates as functional membrane materials.

The present article deals mainly with the gas permeation behavior in a series of poly(aryl ether ketone) membranes. The effects of an intermolecular hydrogen bond, ionic bond, and alkyl substituents on the permeability and permselectivity are examined using a variety of experimental techniques including wide-angle X-ray diffraction, differential scanning calorimetry, and density in addition to the gas permeability and diffusivity measurements.

Table II Gas Permeability and Selectivity Coefficients of the Polymers

Polymer	Permeability					Selectivity		
	H_2	O_2	N_2	CO_2	CH_4	H_2/N_2	O_2/N_2	CO_2/CH_4
PEK-C	11.7	0.951	0.155	2.73	0.0821	75.6	6.22	33.2
PEK-H	9.91	0.663	0.0921	2.36	0.0690	108	7.21	34.2
PEK-L	7.26	0.489	0.0485	1.81	0.0415	150	10.1	43.6
IMPEK-L	49.7	7.20	1.18	22.8	1.35	42.1	6.10	16.9
PSF[15]	13.9	1.4	0.25	5.6	0.025	55.6	5.6	22

Permeability: barrer; 1 barrer = $10^{-10} \times cm^3$ (STP) cm/cm$^2 \cdot$ s $\cdot$ cmHg.

EXPERIMENTAL

Materials

3,3′-Bis(4-hydroxyphenyl)isobenzopyrrolidone, phenolphthalin, 2′,2″-diisopropyl-5′,5″-dimethyl-phenolphthalin, and bis(4-nitrophenyl)ketone were prepared in our laboratory according to Refs. 10 and 11.

All the poly(aryl ether ketone)s studied here were prepared via nucleophilic polycondensation in the DMSO/K_2CO_3 system. By the ionic exchange of H^+ of the carboxyl group with Na^+ and K^+, four ionomers were also obtained. Their chemical structures are listed in Table I.

Preparation of the Dense Films

The dense films, except PEK–Na^+ and PEK–K^+, were cast from a *N,N*-dimethylformamide solution on a glass plate at 60°C. The PEK–Na^+ and PEK–K^+ films were cast from a dimethyl sulfoxide solution. The film samples were dried at 100°C for 10 h, then at 200°C and 10 mmHg in a vacuum oven for additional 48 h before the gas permeability measurement.

Characterization

The polymer densities were determined in a film sample in a density gradient column containing
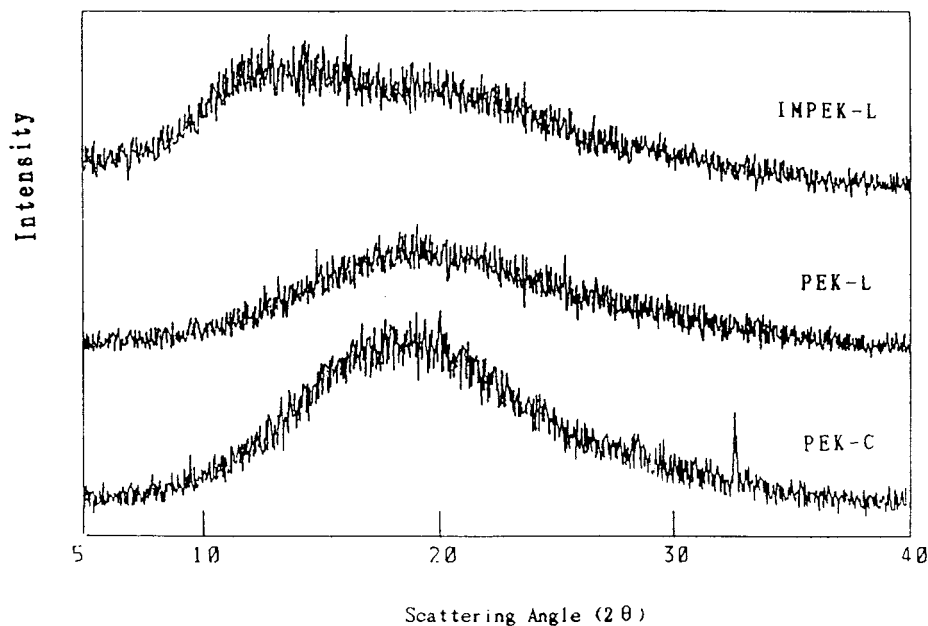
Figure 1 WAXD patterns of the polymer membranes.

Table III   Some Physical Properties of the Polymers

Polymer	T_g	ρ	V_0	$V_{30°C}$	V_F	d-spacing
PEK-C	218	1.249	0.677	0.801	0.124	4.83
PEK-H	263	1.250	0.685	0.800	0.115	4.79
PEK-L	220	1.153	0.697	0.792	0.095	4.73
IMPEK-L	228	1.128	0.737	0.898	0.161	6.69

T_g: °C; ρ: g/cm^3; V_0, $V_{30°C}$, V_F: cm^3/g; d-spacing: Å.

aqueous calcium nitrite at 30°C. The free volume (V_F) of each of the polymers is given by

$$V_F = V_T - V_0 \qquad (1)$$

where V_T is specific volume, which can be calculated from the polymer density value determined, and V_0 is the polymer occupied volume in 0 K and was obtained according to the group contribution method of Sugden.[12]

Wide-angle X-ray diffraction (WAXD) measurements were performed on a D/Max-B X-ray diffractometer with CuKα radiation having a wavelength of 1.54 Å. The intersegmental spacing, or d-spacing, can be calculated with Bragg's equation:

$$\lambda = 2d \sin \theta \qquad (2)$$

where θ refers to the angle of the peak maxima.

Gas Permeability Measurement

The low vacuum apparatus used for the measurement of the gas-transport property has been described in the literature.[13] The permeability coefficient (P) was determined from the slope of pressure–time plots after a steady state had been reached. From the diffusion time lag (θ), the gas

diffusivity coefficient (D) can be calculated by the following equation:

$$D = l^2/6\theta \qquad (3)$$

where l is film thickness.

It is generally accepted that the gas permeation through the polymer membrane obeys the solubility–diffusion mechanism[14]:

$$P = D \times S \qquad (4)$$

By substituting eq. (3) into eq. (4), the gas solubility coefficient (S) can be obtained.

The ideal separation factor ($\alpha_{A/B}$) of gas A through a polymer membrane over another gas B is defined by the relation:

$$\alpha_{A/B} = P_A/P_B = D_A/D_B \times S_A/S_B \qquad (5)$$

where P_A and P_B are the permeability coefficients for gases A and B, D_A and D_B are diffusivity coefficients, S_A and S_B are solubility coefficients, and the ratios D_A/D_B and S_A/S_B are known as the diffusivity selectivity and the solubility selectivity, respectively.

To eliminate the CO_2 plastification effect, CO_2 was determined finally after the other gases. All the gases used here were at least 99.99% in purity.

RESULTS AND DISCUSSION

The presence of the functional groups in the polymers is expected to greatly affect the packing density and chain rigidity and subsequently affect the gas-transport properties of the polymers.

Table IV   Diffusion and Solubility Coefficients of CO_2 and CH_4 Gases

Polymer	Diffusivity		Solubility		D_{CO_2}/D_{CH_4}	S_{CO_2}/S_{CH_4}
	CO_2	CH_4	CO_2	CH_4		
PEK-C	0.746	0.0959	2.78	0.651	7.78	4.27
PEK-H	0.554	0.0665	3.24	0.788	8.33	4.11
PEK-L	0.382	0.0548	3.60	0.575	6.97	6.26
IMPEK-L	4.29	0.794	4.04	1.29	5.40	3.13

Diffusivity: 10^{-8} cm^2/s; solubility: cm^3 (STP)/cm^3 atm.

Table V   Physical Properties of Some Gases[16,17]

| Gas	CO_2	O_2	N_2	CH_4
δ (Å)	3.30	3.46	3.64	3.80
T_c (K)	304.2	154.6	126.2	190.6

Comparison of PEK-C, PEK-H, PEK-L, and IMPEK-L

The permeabilities of H_2, O_2, N_2, CO_2, and CH_4 through the four polymer membranes are summarized in Table II. The lower permeabilities in PEK-H and PEK-L reflect a tight structure due to the strong hydrogen bonds that occur between amide groups in PEK-H and between carboxyl groups in PEK-L. The interchain distance (d-spacing) and free volume (V_F) can be used as a measure of the chain packing density or the "tightness" of the polymer structure. The WAXD patterns for PEK-C, PEK-L, and IMPEK-L are illustrated in Figure 1. It is observed that, relative to PEK-C, the diffraction halo of PEK-L shifts toward a larger diffraction angle (2θ). The values in Table III reveal that the d-spacing of PEK-L is 2.1% smaller than that of PEK-C, and the calculated V_F's of PEK-L and PEK-H are 0.095 and 0.115 cm^3/g, respectively, while it is 0.124 cm^3/g for PEK-C, indicating that the hydrogen-bonded PEK-H and PEK-L have a denser structure than that of PEK-C. Moreover, the formation of intermolecular hydrogen bonds restricts the intersegmental motion ability. As a measure of the rigidity of the polymer chain, the glass transition temperature (T_g) of PEK-H is 45°C higher than that of PEK-C, and the T_g of PEK-L is also slightly higher than that of PEK-C. Both factors allow one to reduce the gas permeability. Especially, the larger gas molecules, such as nitrogen, decrease more rapidly than do the smaller gas molecules; as a result, PEK-H and PEK-L exhibit significantly high gas permselectivity. For example, compared with PEK-C, the selectivities of H_2/N_2 and O_2/N_2 in PEK-L increase by 98 and 62%, respectively.

For IMPEK-L, the bulky isopropyl and methyl substituents are highly effective in reducing the packing density of polymer chain. The V_F and d-spacing of IMPEK-L are 60.5 and 41.4% higher than those of PEK-C, respectively, indicative of a more open structure in IMPEK-L. As expected, the IMPEK-L membrane has the highest gas permeability in this series of poly(aryl ether ketone)s. Compared with the unsubstituted PEK-

L, the permeabilities of hydrogen and oxygen for IMPEK-L increase by a factor of 5–14, and the permeabilities of carbon dioxide, nitrogen, and methane increase by a factor of 21–32. Furthermore, the bulky isopropyls and hydrogen bonds arising from COOH groups severely inhibit the segmental mobility. As shown in Table III, the T_g of IMPEK-L is 10°C higher than that of PEK-C, and this is favorable for its gas permselectivity. Consequently, IMPEK-L has an O_2 permeability of 7.2 barrer, over five times higher than that of commercial bisphenol-A polysulfone (PSF),[15] a popular membrane material. In addition, its O_2/N_2 separation factor is 6.1, also higher than that of PSF. On considering IMPEK-L's simultaneously high O_2 permeability and O_2/N_2 permselectivity as well as its excellent heat-resistant and mechanical properties,[9] it may become a promising candidate to be used as a gas membrane material for a future nitrogen-enrichment application.

An analysis of the effect of the polymer structure on gas permeability requires knowledge of the solubility and diffusivity coefficients in addition to the permeability coefficient. The results of gas diffusion and diffusivity selectivity, with the gas solubility and solubility selectivity, for the four polymers are listed in Tables IV and V, where the diffusion coefficients are obtained according to the time-lag method and the solubility coefficients are calculated by dividing the overall permeabilities by the diffusion coefficients.
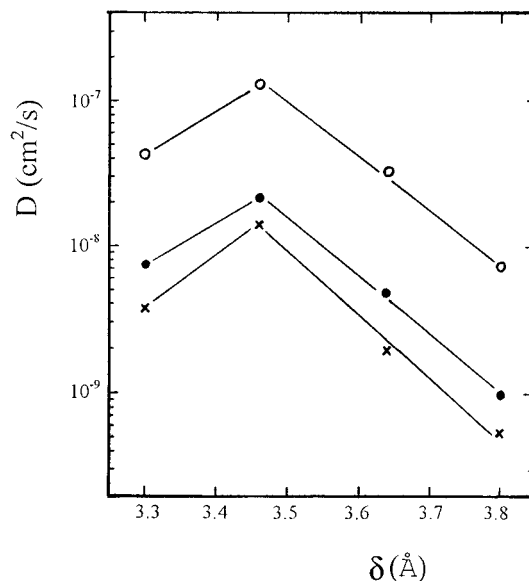
Figure 2 The plots of Log D vs. penetrant size (δ) for these polymers: (X) PEK-L; (●) PEK-C; (○) IMPEK-L.

Table VI   Diffusion and Solubility Coefficients of O_2 and N_2 Gases

Polymer	Diffusivity		Solubility		D_{O_2}/D_{N_2}	S_{O_2}/S_{N_2}
	O_2	N_2	O_2	N_2		
PEK-C	2.15	0.488	0.336	0.238	4.41	1.41
PEK-L	1.40	0.195	0.265	0.189	7.18	1.40
IMPEK-L	12.2	3.26	0.450	0.274	3.72	1.65

Diffusivity: 10^{-8} cm^2/s; solubility: cm^3 (STP)/cm^3 atm.

For the nonpolar O_2/N_2 system, there is no special interaction between gases and the polymer backbone, so the gas permeability behavior in the four polymers is primarily governed by the diffusivity and diffusion selectivity. IMPEK-L has the largest d-spacing and the largest free volume in this series; as a result, its O_2 diffusion coefficient is nearly six times that of PEK-C, with only a slight decrease in diffusion selectivity attributed to its hindrance segment motion. This is why IMPEK-L possess simultaneously higher O_2 permeability and O_2/N_2 permselectivity as compared with bisphenol-A polysulfone.

In general, polymers with a high free volume tend to have high gas solubility coefficients. The solubilities of nonpolar gases (O_2, N_2) in the polymers rank in the order

$$\text{PEK-L} < \text{PEK-C} < \text{IMPEK-L}$$

which obeys this law. However, for CO_2, although PEK-L has a smaller d-spacing, the CO_2 solubility is still higher for PEK-L than for PEK-C. This probably can be attributed to the fact that CO_2 has some energetically favorable interaction with the carboxyl groups in PEK-L. As a consequence, PEK-L exhibits a significantly high CO_2 solubility and solubility selective of CO_2/CH_4. In contrast

to the solubility behavior, as shown in Table V, the CO_2 diffusivity coefficient and diffusion selectivity of CO_2/CH_4 in PEK-L are lower than that of PEK-C.

The relationship between gas diffusion coefficient ($\text{Log } D$) and the gas molecular kinetic diameter (δ) is shown in Figure 2. For O_2, N_2, and CH_4, which have similar critical temperatures (T_c) (see Table V), a straight line is obtained and the gas diffusivities decrease with the increase of penetrant size. However, for CO_2, the high sorption ability in the polymer membrane due to its high critical temperature may appear disadvantageous for its diffusion. As shown in Figure 2, in spite of CO_2's smaller molecule size, its diffusion coefficient is smaller than that of O_2.

The data in Table VI reveal that the gas diffusivities of the four polymers rank in the order

$$\text{PEK-L} < \text{PEK-H} < \text{PEK-C} \ll \text{IMPEK-L}$$

This is also the order of increasing gas permeabilities, so the difference of the gas permeability of this series of polymers is determined mainly by variation in the gas diffusivity, as in the case of most glassy polymer membrane materials.[18-20]

Comparison of PEK-L and Its Ionomers

The gas permeability, diffusivity, and solubility data of PEK-L and its ionomers in a sodium-salt form (PEK-Na$^+$) and potassium-salt form (PEK-K$^+$) are given in Tables VII and VIII. The lower permeabilities for PEK-Na$^+$ and PEK-K$^+$ than that of PEK-L indicate that intermolecular ionic bonds are stronger than are hydrogen bonds. The strengthened interchain interaction seriously inhibits the permeation of gas molecules, especially the gas molecules with larger kinetic diameters. Therefore, the ionomer membranes exhibit extremely high permselectivity. For PEK-K$^+$, the

Table VII   Gas-transport Properties for PEK-L Ionomer Series

Polymer	Permeability			Selectivity	
	H_2	O_2	N_2	H_2/N_2	O_2/N_2
PEK-L	7.26	0.489	0.0485	150	10.1
PEK-Na$^+$	4.67	0.240	0.0231	202	10.4
PEK-K$^+$	3.95	0.155	0.0131	302	11.8

Permeability: barrel; 1 barrer = $10^{-10} \times$ cm^3 (STP) cm/cm$^2 \cdot$ s $\cdot$ cmHg.

Table VIII   Diffusivity and Solubility Coefficients for PEK-L Ionomer Series

Polymer	D_{O_2}	D_{N_2}	D_{O_2}/D_{N_2}	S_{O_2}	S_{N_2}	S_{O_2}/S_{N_2}
PEK-L	1.40	0.195	7.18	0.265	0.162	1.64
PEK-Na$^+$	0.608	0.0771	7.89	0.341	0.258	1.32
PEK-K$^+$	0.343	0.0410	8.37	0.344	0.244	1.41

D: 10^{-8} cm^2/s; S: cm^3 (STP)/cm^3 atm.

permselectivity of H_2/N_2 is twice that of PEK-L and four times that of PEK-C. Its O_2/N_2 and H_2/N_2 ideal separation factors are as high as 11.8. To our knowledge, this is among the highest permselectivity reported previously in the literature. It can be seen in Table VIII that the O_2/N_2 solubility selectivity in PEK-K$^+$ is only 1.41, far smaller than the diffusion selectivity, showing that the high permselectivity for PEK-K$^+$ comes mainly from the contribution of the diffusion selectivity.

Comparison of IMPEK-L and Its Ionomers

As revealed in Table II, the introduction of bulky alkyl substituents causes a considerable increase in IMPEK-L gas permeability. However, the enhanced rigidity, attributed to the steric hindrance of substituents and the hydrogen bonds between carboxyl groups, is insufficient to offset the loss in permselectivity, so that its CO_2/CH_4 gas separation factors are the lowest in the series of polymers studied.

To improve IMPEK-L permselectivity while maintaining its high gas permeability, the present work is undertaken to change the pendant carboxyl groups of IMPEK-L into carboxylate groups by the ion-exchange method so as to strengthen its interchain interaction. As shown in Table IX, for the potassium-salt-form ionomer

Table IX   Gas-transport Properties for IMPEK-L Ionomer Series

Polymer	Permeability			Selectivity	
	H$_2$	CO$_2$	CH$_4$	H$_2$/CH$_4$	CO$_2$/CH$_4$
IMPEK-L	49.7	22.8	1.35	36.8	16.9
IMPEK-Na$^+$	41.9	17.1	0.913	45.9	19.1
IMPEK-K$^+$	36.5	12.8	0.498	54.1	25.7

Permeability: barrer; 1 barrer $= 10^{-10} \times$ cm^3 (STP) cm/cm$^2 \cdot$ s $\cdot$ cmHg.

IMPEK-K$^+$, its CO_2/CH_4 selectivity factor is 52% higher than that of IMPEK-L. In particular, a comparison of IMPEK-K$^+$ and PSF shows that the CO_2 permeability of IMPEK-K$^+$ is over twice higher than that of PSF, whereas its CO_2/CH_4 selectivity is also 15% higher than PSF, exhibiting its excellent gas-transport properties and potential use in the natural gas treatment field.

An important point to note is that, in either the PEK-L or IMPEK-L ionomer series, the possium-salt-form ionomer membrane shows higher permselectivity than does the sodium-salt form one. This is probably because K$^+$ has a stronger chelate ability with COO$^-$ than has Na$^+$.[21,22]

CONCLUSION

The results of the above study clearly demonstrate that the polymer design for the specific application in gas separation membrane can be achieved by the variation of structural factors such as the mobility of polymer chain segments, steric hindrances, and intermolecular interactions. Similar to most glassy polymers, the gas permeability and permselectivity in this series of poly(aryl ether ketone)s are controlled mainly by the gas diffusivity and diffusion selectivity.

The strong intermolecular interaction due to hydrogen bonds or ionic bonds leads to the polymers' dense packing density and restricted segmental motion and thus results in low gas permeability and extremely high permselectivity. For example, the H_2/N_2 and O_2/N_2 ideal selectivity factors of PEK-K$^+$ are over 300 and 11, respectively.

The bulky alkyl substituents are very effective in disrupting polymer chain packing. IMPEK-L, which contains isopropyl and methyl substituents, displays the highest free volume, and this is responsible for its high permeability. The permeability coefficients of IMPEK-L for the five gases

studied here are 7–31 times higher that of unsubstituted PEK-L.

Interestingly, the simultaneous introduction of bulky substituents and strong intermolecular interaction into polymers cause a significant increase in both permeability and permselectivity. The CO_2 permeability of IMPEK-K$^+$ is over twice higher than that of polysulfone (PSF) and its permselectivity of CO_2/CH_4 is also 10% higher than that of PSF. In summary, this series of poly-(aryl ether ketone) materials has excellent gas-transport properties over a wide range of permeability coefficients and permselectivity coefficients, displaying a potential application in the future gas separation membrane.

REFERENCES

1. R. W. Spillman, *Chem. Eng. Prog.,* **85,** 41 (1989).
2. R. J. Gardner, R. A. Crane, and J. F. Hannan, *Chem. Eng. Prog.,* **73,** 76 (1977).
3. W. H. Mazur and M. C. Chan, *Chem. Eng. Prog.,* **78,** 38 (1982).
4. G. Parkinson, *Chem. Eng.,* **91,** 14 (1984).
5. J. S. McHattie, W. J. Koros, and D. R. Paul, *J. Polym. Sci. Part B,* **29,** 731 (1991).
6. F. R. Sheu and R. T. Chern, *J. Polym. Sci. Part B,* **27,** 1121 (1989).
7. S. A. Stern, Y. Mi, and H. Yamamoto, *J. Polym. Sci. Part B,* **27,** 1887 (1989).
8. M. R. Pixton and D. R. Paul, *Macromolecules,* **28,** 8277 (1995).
9. Z. G. Wang, T. L. Chen, and J. P. Xu, to appear.
10. A. Baeyer, *Ann,* **202,** 80 (1980).
11. H. Meyer, *Monatch.,* **20,** 361 (1899).
12. S. Sugden, *J. Chem. Soc.,* 1786 (1927).
13. W. Y. Liu, T. L. Chen, and J. P. Xu, *J. Membr. Sci.,* **53,** 203 (1990).
14. W. J. Koros, G. K. Fleming, and S. M. Jordan, *Prog. Polym. Sci.,* **13,** 339 (1988).
15. C. L. Aitken, W. J. Koros, and D. R. Paul, *Macromolecules,* **25,** 3651 (1992).
16. D. W. Breck, *Zeolite Molecular Sieves,* Wiley, New York, 1994, p. 636.
17. J. Jeans, *An Introduction to the Kinetic Theory of Gases,* Cambridge University Press, London, 1982, p. 183.
18. M. W. Hellums, W. J. Koros, G. R. Husk, and D. R. Paul, *J. Membr. Sci.,* **46,** 93 (1989).
19. C. L. Aitken, W. J. Koros, and D. R. Paul, *Macromolecules,* **25,** 3424 (1992).
20. H. Yamamoto, Y. Mi, and S. A. Stern, *J. Polym. Sci., Part B,* **28,** 2291 (1990).
21. D. Andreare, V. N. Nikitin, and Y. M. Boyartchum, *Macromolecules,* **9,** 238 (1976).
22. L. Holliday, *Ionic Polymers,* Applied Science, London, 1975.