Liquid Transport through Mosaic Membranes of Hydrophobic–Hydrophilic Microdomains: Pervaporation of Water and Ethanol through Bisphenol-A Polycarbonate–Polyoxyethylene Multiblock Copolymers

Hideaki TANISUGI and Tadao KOTAKA*

*Department of Macromolecular Science Faculty of Science,
Osaka University, Toyonaka, Osaka 560, Japan*

(Received May 9, 1984)

ABSTRACT: The pervaporation of water and ethanol at 25°C was examined on as-cast and annealed membranes of (AB)_n-type multiblock copolymers of bisphenol-A polycarbonate (PC) and polyoxyethylene (POE) of varying composition and block length. The equilibrium degree of swelling, q_e (in g liquid/100 g dry membrane), for water decreases rapidly with increasing PC content of the samples, while that for ethanol remains nearly constant. The pervaporation rate P of water also decreases with increasing PC content, while that of ethanol is high for samples with 30 and 75 wt% PC content, but low for those with 50 wt% PC content. Swelling and pervaporation of as-cast specimens of these block copolymers appear to be complicated by the incomplete microphase separation between the components. Nevertheless, except for a few cases, annealing the membranes at 60°C appears to cause their microdomain structures to be more like those of equilibrium morphology so that their pervaporation behavior becomes like that expected from simple additivity with respect to the volume fraction of the phases. Our results suggest that the pervaporation of water through these copolymers is governed essentially by solubility, but that of ethanol, by diffusivity.

KEY WORDS Pervaporation / Block Copolymer / Multiblock Copolymer / Bisphenol-A Polycarbonate–Polyoxyethylene Copolymer / Swelling / Pervaporation Rate / Diffusion Coefficient / Microphase Separation / Microdomain Structure /

The permeation of gases and liquids through polymer membranes has been a subject of extensive studies during the past several decades.^{1–3} In recent years, much effort has been devoted to developing new membrane technology in such areas as desalination of sea water⁴ and biomass technology.⁵

To evaluate the quality and performance of such membranes, pervaporation is a convenient technique.^{6,7} In the pervaporation process, the upstream side of the membrane is brought into contact with a liquid at atmospheric pressure. The liquid dissolves into and diffuses through the membrane to its opposite

(downstream) surface, where vaporization of the permeant is achieved by maintaining sufficiently low pressure. This technique is very simple and convenient for evaluating the performance of membranes, and is also useful for separating liquid mixtures, particularly, such as azeotropic and isomeric mixtures which are very difficult to separate by conventional distillation.

During the last decade, many attempts have been made to utilize polymer alloys for special function membranes such as gas barrier and permselective membranes.^{8–16} In the present investigation, an attempt was made to develop special function membranes, particularly permselective membranes for aqueous

* To whom correspondence should be addressed.

ethanol solutions made from multiblock copolymers having the mosaic structures of hydrophilic and hydrophobic microdomains. The membranes studied were the randomly-coupled bisphenol-A polycarbonate (PC) and polyoxyethylene (POE) multiblock copolymers of (AB)_n-type.¹⁷⁻²⁰

These copolymers possess certain microphase separated structures depending on composition and block length. In a previous paper,²⁰ we described the swelling behavior of these copolymers in water, ethanol, and their mixtures, and found their microphase-separated structures to significantly affect their sorption capacity for water and ethanol mixtures. We studied the influence of structure on liquid transport in multiblock copolymers having hydrophobic-hydrophilic microdomains. In particular, we discuss the results of pervaporation of pure water and ethanol in terms of the solubility and diffusivity of the pure liquids in these multiblock copolymer membranes. In the next article, we shall describe the permselectivity of these copolymer membranes for water and ethanol mixtures in detail.

EXPERIMENTAL

Materials

The copolymer samples used were prepared by condensation of bisphenol-A (B) and polyoxyethylene glycol (E) oligomers with phosgene by a method proposed by Goldberg.²¹ The details are described in our previous papers.^{17,18} The product composition was determined by elemental analysis and UV absorption. Their number and weight average molecular weights M_n and M_w , respectively, were estimated on a gel permeation chromatograph (GPC; Toyo Soda Mfg. Co., HLC 801-A) equipped with a refractometer, a UV monitor, and a low-angle laser light scattering photometer (Toyo Soda Mfg. Co., LS-8). The elution solvent was tetrahydrofuran (THF) and narrow distribution polystyrenes (Toyo Soda Mfg. Co., TSK PS's) were used

Table I. Characteristics of multiblock copolymers^a

Sample code (BXEY)	PC Content	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>n</i>
	wt%				
B22E46	73.1	22.9	46	1.1	12
B9E14	77.2	9.6	14	1.1	21
B13E68	51.8	13.9	68	1.1	8
B5E23	52.3	5.5	23	1.2	35
B5E68	30.0	6.1	68	1.2	11
B2E23	30.0	2.8	23	1.6	32

as elution standards.^{17,18}

Table I shows the characteristics of the six copolymer samples¹⁸ used in this study. The copolymers are coded as BXEY with *X* and *Y* as the average degree of polymerization of a polycarbonate (PC) block and polyoxyethylene (POE) precursor, respectively. The average number *Z* of the POE oligomers coupled to form a single POE block and the values of *X* were calculated from the monomer feed-product composition, assuming random coupling of B and EY units.^{17,18,22}

For comparison, a PC homopolymer²⁰ and end-crosslinked POE membranes^{20,23} were also prepared. The PC homopolymer was an impurity free experimental sample provided by Dr. Yoji Murakami, Teijin Co., Ltd. The number-average molecular weight, M_n , and M_w/M_n ratio were estimated by GPC to be 2.98×10^4 and 2.1, respectively.

The copolymer and PC homopolymer samples were cast into membranes 0.020 to 0.10 mm thick from 2 wt% chloroform solutions on a teflon sheet. The solvent was allowed to evaporate slowly at room temperature over a week, and then dried in a vacuum of 10^{-2} torr for two more days. Whenever necessary, the membranes were annealed in a vacuum oven at 60°C for 24 h.

To prepare POE homopolymer membranes, we used a hydroxyl terminated POE with a

nominal molecular weight of 3000 (or $Y=68$) purchased from Nakarai Chemicals Co. The POE was purified and end-crosslinked to make a crosslinked POE membrane (cr-E68) by the method described in our previous paper.²³

Swelling Experiments

Determination of the degree of swelling was carried out by a weighing method using a Mettler semimicrobalance. The degree of swelling, q , was defined as the grams of the liquid absorbed by 100 grams of the dry membrane. Thus,

$$q = 100(W - W^{\text{dry}})/W^{\text{dry}} \quad (1)$$

where W and W^{dry} are the mass (in g) of wet and dry membranes, respectively. To determine the equilibrium degree of swelling, q_e , we soaked thoroughly-dried films in the test liquid, either water or ethanol, and followed the weight change every 4 h until a constant weight was reached. It usually took 4 days for PC rich membranes and a somewhat shorter time for POE rich membranes to reach equilibrium.

Pervaporation

Figures 1 and 2, respectively, show a schematic diagram of the pervaporation apparatus and a vertical sectional view of the pervaporation cell (H) made of glass. A reflux condenser (a) was fitted to the feed reservoir (b). On a sintered glass filter (f) was placed a porous polypropylene filter (e) (Gelman Instrument Co.), on which a test membrane (m) was fitted. Then, a teflon gasket (d) was placed on the membrane, and the lower compartment (g) and the reservoir (b) were held together tightly with clamps. The effective area of the membrane in contact with the liquid was 12.6 cm^2 . The cell (H) was immersed in a bath (I) thermostatted at $25.0 \pm 0.1^\circ\text{C}$. The feed liquid was constantly stirred (c).

Before mounting the membrane (m) onto the cell (H), it was conditioned with the test liquid to swelling equilibrium. After introducing the test liquid into the upstream reservoir

Figure 1. Schematic diagram of the pervaporation apparatus: A, rotary pump; B, E, cold traps; C, diffusion pump; D, ionization gauge; F_1 , F_2 , F_3 , three-way stopcocks; G_1 , G_2 , cold traps for collecting permeates; H, pervaporation cell; I, constant temperature bath.

Figure 2. Schematic diagram of the pervaporation cell: a, reflux condenser; b, feed reservoir; c, stirrer; d, teflon gasket; m, membrane; e, porous polypropylene filter; f, glass filter; g, vacuum compartment.

(b), the downstream compartment (g) was evacuated to 10^{-2} torr by diffusion (C) and rotary (A) pumps with cold traps (B) and (E). The vacuum was monitored with a cold-cathode ionization gauge (D; Tokuda Seisakusho, Model PST-5). The permeates were collected in cold traps, (G_1) or (G_2), chilled with liquid nitrogen, alternately. After a certain amount of the permeate had condensed in a trap, say G_1 , the vacuum line was switched to another trap, G_2 , by operating the three-way stopcocks, (F_1), (F_2) and (F_3). Trap G_1 was removed from the line and the permeate was recovered for weigh-

Table II. Density and reduction factor k at 25°C of multiblock copolymers and homopolymers

Sample code	Density $d_m/\text{g cm}^{-3}$		Reduction factor $10^{-3} k/\text{g cm}^{-3}$			
	As-cast film	Annealed film	As-cast film		Annealed film	
			Water	Ethanol	Water	Ethanol
PC K1300	1.20	—	11.9	11.5		
B22E46	1.13	1.18	11.22	9.52	11.7	9.87
B9E14	1.13	1.22	11.1	9.52	11.9	10.1
B13E68	1.11	1.17	8.12	8.75	8.43	8.17
B5E23	1.12	1.19	7.55	9.34	8.54	8.54
B5E68	1.13	1.18	4.43	6.36	4.52	8.67
B2E23	1.12	1.23	5.27	6.79	5.51	8.84
cr-E68	1.19	—	1.85	9.28		

ing. This procedure was repeated at appropriate intervals to determine the permeation rate.

Membrane Density

The membrane density was determined by picnometry, usually using a 50 cm³ picnometer. The immersion solvent used was *n*-tetradecane, since it is a non-solvent to both PC and POE. The results of the density measurements are listed in Table II.

Method of Data Analysis

The steady-state pervaporation rate of a liquid through a membrane may be described by Fick's first law of diffusion¹¹⁻¹³

$$J = -D \frac{dc}{dx} \quad (2)$$

where J is the flux (g cm⁻² s⁻¹), D , the concentration dependent diffusion coefficient (cm² s⁻¹), dc/dx , the concentration gradient at a distance x from the upstream surface and, c , the local concentration (g cm⁻³) of the permeant.

Assuming steady-state pervaporation and integrating both sides of eq 2 with respect to x across the membrane with thickness l , we have

$$J \int_0^l dx = - \int_{c_u}^{c_d} D dc \quad (3)$$

where c_u and c_d are the permeant concentration at the upstream ($x=0$; the liquid side) and downstream ($x=l$; the vacuum side) surfaces of the membrane.

For permeation of a liquid through a membrane swollen with the liquid itself, the diffusion coefficient D is usually dependent on the local concentration c of the permeant, because it often acts as a plasticizer of the membrane. For such pervaporation processes, the concentration dependence of D was often approximated by an exponential equation,

$$D = D_0 \exp(\gamma c) \quad (4)$$

where D_0 is the D in the limit of zero permeant concentration, and γ , a coefficient characteristic of the membrane/permeant interaction.^{12,24,25} The parameter γ may as well be a function of c , but is assumed independent of c here. Then, substituting eq 4 for D in eq 3 leads to

$$J = \frac{D_0}{\gamma l} (e^{\gamma c_u} - e^{\gamma c_d}) \quad (5)$$

Equation 5 shows that the flux J is inversely proportional to the membrane thickness l .

Aptel *et al.*¹¹⁻¹³ extended the method of data analysis for gas permeation to such a pervaporation process, introducing the average diffusion coefficient, $\bar{D}$, across the mem-

brane defined by

$$\bar{D} = \frac{D_u - D_d}{(c_u - c_d)} = \frac{D_u - D_d}{\ln D_u/D_d} \quad (6)$$

Here, D_u or D_d are obtained by replacing c in eq 4 by c_u or c_d , respectively. They¹² also assumed the relation between c and q at x as

$$c = kq \quad (7)$$

with the factor k defined by

$$k^{-1} = q/d_s + 100/d_m \quad (8)$$

Here, d_s and d_m are the density of the sorbed liquid and the membrane, respectively. They further assumed that $c_u = kq_e$ at the upstream surface where the membrane is in equilibrium with the pure liquid, while $c_d = 0$ at the downstream surface where the liquid is constantly evacuated.¹² Substituting these relations for $\bar{D}$ and c in eq 5, they finally obtained

$$J = \bar{D}(c_u - c_d)/l = \bar{D}kq_e/l \quad (9)$$

If one defines the rate of pervaporation or transport P ($\text{g cm}^{-1} \text{s}^{-1} \text{atm}^{-1}$) of the liquid as the flux J per pressure gradient across the membrane, and assumes the pressure difference to be 1 atm across the membrane for the pervaporation process, then

$$P = Jl = \bar{D}S_e = \bar{D}kq_e \quad (10)$$

That is, the rate of pervaporation P through a unit area of the membrane can be represented by $\bar{D}$ multiplied by the equilibrium solubility $S_e = kq_e$ (g-liquid/cm^3 polymer) of the permeant in the membrane.^{3,12}

RESULTS

Equilibrium Degree of Swelling

Figures 3 and 4 show the equilibrium degree of swelling q_e at 25°C of the copolymer and homopolymer membranes in water and ethanol, respectively. Using the observed values of q_e and d_m and the literature values²⁶ of d_s for pure water and ethanol and assuming

Figure 3. Equilibrium degree of swelling q_e (g permeant/100 g dry membrane) in water at 25°C of as-cast (open marks) and annealed (closed marks) membranes. Long and short are, respectively, the samples with long and short blocks (see Table I).

Figure 4. Equilibrium degree of swelling q_e in ethanol at 25°C of as-cast and annealed membranes. For the symbols, see Figure 3.

additivity in the density, we calculated the values of k by eq 8. The results are given in Table II.

In water, q_e is very large for membranes with low PC content, but becomes virtually zero for those with PC content above 70 wt%. Therefore, for these PC-rich membranes, the values of q_e could not be determined accurately. In ethanol, q_e is rather small compared to that in water. However, even the PC-

rich membranes absorbed a substantial amount of ethanol.

As to the effect of the block length on q_e , we see that q_e for the two samples, B2E23 and B5E68, with the same 30 wt% PC content but different block length, differ with each other in both water and ethanol. Also, by annealing at 60°C for 24 h, the values of q_e , especially for B5E68 having 30 wt% PC content and long blocks, were reduced significantly in both water and ethanol.

Rate of Pervaporation

Dependence on Membrane Thickness. According to Fick's law of diffusion,²⁷ the flux J is inversely proportional to the thickness l of the membrane. Figure 5 shows a typical example of the flux J versus the reciprocal membrane thickness l^{-1} plot for pervaporation of water at 25°C. The ambiguity in the estimation of J was about 10% for thin membranes, but reached about 20% for thick membranes, through which the permeation was rather slow. Nevertheless, plots give approximately a straight line passing through the origin, implying that eq 5 is obeyed by this system. Thus, we represented the pervaporation rate P by J multiplied by l , according to eq 10.

Pervaporation of Water. Figure 6 shows the rate of pervaporation P of water at 25°C through as-cast and annealed membranes plotted against their PC content. The line represents the simple composition average of the homopolymer values. The rate P of water is virtually zero ($\sim 10^{-9}$) for the PC homopolymer membrane.

The crosslinked POE membrane was greatly swollen with water and became too soft to withstand the vacuum of the downstream side of the pervaporation cell. The membrane was disrupted before steady-state pervaporation was reached. Thus, the values of P of water for highly swellable and soft POE-rich membranes could not be determined accurately.

By annealing at 60°C for 24 h, the rate P became higher for those having short blocks,

Figure 5. Effect of membrane thickness on the pervaporation rate of water at 25°C through B22E46 membranes.

Figure 6. Pervaporation rate P ($\text{g cm}^{-1} \text{s}^{-1}$) of water at 25°C through as-cast and annealed membranes. For the symbols, see Figure 3.

but lower for those having long blocks. This tendency was more pronounced for those having 75 wt% PC content. By annealing, the difference in P between B9E14 and B22E46

Figure 7. Pervaporation rate P of ethanol at 25°C through as-cast and annealed membranes. For the symbols, see Figure 3.

Figure 8. Average diffusion coefficient $\bar{D}$ ($\text{cm}^2 \text{s}^{-1}$) for pervaporation of water at 25°C through as-cast and annealed membranes. The error bars indicate ambiguity due to the estimation of q_e . For the symbols, see Figure 3.

became large, while that between two other pairs with 30 and 50 wt% PC content was reduced.

Pervaporation of Ethanol. Figure 7 shows the rate of pervaporation P of ethanol at 25°C for as-cast and annealed membranes. The rate P of ethanol for the crosslinked POE membrane is slightly higher than that for the PC membrane, reflecting better solubility of ethanol to POE than to PC as shown in Figure 4. Again, the line represents the volume composition average of the homopolymer values.

The rate P of ethanol for as-cast membranes of B5E68 and B9E14 was high, while that of B5E23 was very low compared to the composition averages of the homopolymer values. It is of interest that for B5E68, annealing at 60°C caused a significant decrease in P , but for B5E23, an increase in P . On the other hand, for the PC-rich membranes, the rate P of ethanol was not affected by annealing.

Diffusivity

Figures 8 and 9 show plots of the average

Figure 9. Average diffusion coefficient for the pervaporation of ethanol at 25°C through as-cast and annealed membranes. For the symbols, see Figure 3.

diffusion coefficient $\bar{D}$ of water and ethanol at 25°C, respectively, as estimated from q_e and P data by eq 10 for as-cast and annealed mem-

branes. For water, D in the crosslinked POE membrane is roughly larger by a factor of 5 than that in the PC homopolymer membrane. Nevertheless, $\bar{D}$ of water for the as-cast BXEY membranes with high PC content are larger than that for those with low PC content, although the $\bar{D}$ data are somewhat ambiguous because of the ambiguity in determining small values of q_e for the PC-rich systems. The previous data of D_0 for the same systems determined by Suzuki *et al.*¹⁹ were 2 to 5 times smaller than $\bar{D}$, and roughly given by the composition average of the homopolymer values, except for B13E68.

$\bar{D}$ of ethanol in the PC membrane was slightly larger than that in the POE membrane. Also for $\bar{D}$ of ethanol in the as-cast BXEY membranes, $\bar{D}$ in B5E23 was small, but those in B5E68 and B9E14 large compared to the composition averages of the homopolymer values.

Comparing the as-cast and annealed BXEY membranes, it should be noted that the effect of annealing on $\bar{D}$ of water was large only for the PC-rich membranes, though the data involved ambiguity in determining q_e . There was a remarkably large decrease in $\bar{D}$ of ethanol for B5E68, but a significant increase in $\bar{D}$ for B5E23 by annealing. Thus, by annealing, the $\bar{D}$ data except those for the PC-rich membranes approached the composition averages.

Comparison of Pervaporation of Water versus Ethanol. On comparing the behavior of water and ethanol in the BXEY membranes, it becomes evident that in membranes having 30 and 50 wt% PC content, the rate P of water is higher than that of ethanol, while in those with 75 wt% PC content, the rate P of ethanol is higher than that of water. These results may be attributed to the difference in the affinity of water and ethanol toward PC-rich domains.

It is also noteworthy that for water both q_e and P rapidly decrease with increasing PC content of the membranes. This suggests that the permeability of water through the BXEY membranes (except for the PC-rich ones) is

dominated by its solubility.

Figures 7 and 9 show the dependence of P and $\bar{D}$ of ethanol on PC content to be quite similar, obviously because q_e and thus S_e for ethanol are rather insensitive to the change in PC content of the membranes. That is, the pervaporation of ethanol is governed by the diffusivity rather than the solubility of ethanol in the BXEY membranes.

DISCUSSION

The BXEY polymers examined here are typical short-segment multiblock copolymers consisting of crystallizable segments. The melting temperature T_m of POE blocks ranged from 300 to 315 K, and that of PC blocks, from 470 to 510 K, depending on the block length and composition.^{17,18} Pervaporation through these membranes should be influenced not only by permeant-polymer interactions but also by the microdomain structures existing in the membranes.

From our previous studies on the thermal, dynamic mechanical, and dielectric properties of these BXEY copolymers,^{17,18} we may summarize the features and the effects of annealing on their microdomain structures as follows. In such crystallizable short-segment multiblock copolymers, crystallization of low T_m blocks is hampered, while that of the high T_m blocks is facilitated. Crystallization within each component more strongly induces microphase separation rather than the thermodynamic immiscibility between the components.²⁸ Nevertheless, in such short-segment block copolymers, microphase separation is usually incomplete and a substantial amount of intermixing domains may exist not only in the as-cast membranes but even in those annealed, especially those having short blocks. This tendency is obviously greater in membranes having low PC content and shorter blocks than in those with high PC content and longer blocks. Thus, we may regard the BXEY membranes as consisting of the (presumably crystalline) PC

phase, (presumably amorphous) POE phase, and PC/POE intermixing phase. Particularly, in membranes swollen with either water or ethanol, POE crystallites are dissolved and POE segments may exist almost exclusively as amorphous POE and PC/POE intermixing domains.

Thermal treatment of such as-cast membranes made their microdomain structures more like those with equilibrium morphology.^{18,20} However, since an annealing temperature of 60°C is rather low compared to the glass transition temperature T_g of the PC phase, annealing is more effective for membranes having low PC content and longer POE blocks.^{17,18,20} In fact, for B5E68 and B2E23 having 30 wt% PC content, annealing at 60°C promotes further microphase separation, and the increased PC domains act as more effective physical crosslinks for the rubbery POE blocks. Thus, annealed B5E68 and B2E23 specimens showed mechanical properties similar to those of a thermoplastic elastomer.^{18,20} Ethanol conditioning of these samples also produced a pronounced effect on the microdomain structures similar to that of the annealing.²⁰

Based on these features of the BXEY copolymers, we may interpret the complicated pervaporation behavior and effect of annealing on these membranes as follows. The equilibrium degree of swelling q_e should be essentially a function of the volume fraction of the phases. However, since the intermixing phase is often more swellable than the pure phases,¹⁹ the deviation in q_e from the composition average is quite likely due to the intermixing phase. Thus, in all samples, thermal treatment makes the values of q_e approach the composition averages, although still leaving some discrepancies due to the remaining intermixing phase. Obviously, annealing under the present conditions should produce a more pronounced effect on membranes having low PC content, but almost no effect on q_e of PC-rich B9E14 and B22E46.

The microdomain structures and the effect of annealing on them should also influence the pervaporation rate P and diffusivity $\bar{D}$ of permeants in essentially the same way they influence q_e described above. However, additional complications may arise in the transport processes through a multiphase matrix, depending on the nature of the interactions between the permeant and medium. Often, the permeant appears to diffuse more rapidly through the less lyophilic phase rather than through the lyophilic phase.²⁷ This implies that in the present BXEY membranes, water or ethanol may diffuse more rapidly through the intermixing phase rather than through the pure phases. Another complication is the retardation effect known as the tortuosity induced by the presence of microdomains impermeable to the diffusing liquid.^{29,30}

It should be noted that pervaporation of water through the BXEY membranes is governed essentially by the solubility of water into these membranes, and water diffuses mainly through the POE amorphous and POE-rich intermixing phases. Ethanol may also dissolve into PC domains to some extent, and diffuse through both PC and POE phases and presumably even rapidly through the PC-rich intermixing phases. Thus, pervaporation of water through the PC-rich membranes is retarded, since the phase permeable to water may form discrete domains. Thus, a small rearrangement of the microdomains by annealing may influence the pervaporation of water through the PC-rich membranes, whereas such a change may not influence the behavior of ethanol. In fact, the values of P and $\bar{D}$ of ethanol tend to approximate those predicted by the simple additivity of the homopolymer values by annealing. Still, however, these values for the PC-rich B9E14 and B22E46 are large compared to the composition average values. This result may be due to the presence of the intermixing phase, through which the permeants may diffuse rather rapidly.

Acknowledgements. We wish to thank Dr. Toshitake Suzuki and Mr. Shiro Nishi for their valuable advice and help in carrying out the experiments. This work was supported by the Ministry of Education, Science and Culture (Mombusho) under grants 543026 (to TK) and 58350053 (Professor Michio Kurata, Kyoto University, the coordinator), which are gratefully acknowledged.

REFERENCES

1. See, for example, S. Sourirajan, "Reverse Osmosis," Academic Press, New York, N. Y., 1970.
2. S. Sourirajan, Presented at the 26th International Congress of Pure and Applied Chemistry, Tokyo, 1977; *J. Appl. Chem.*, **50**, 593 (1978).
3. S. Hwang and K. Kammermeyer, "Membrane in Separations," Techniques of Chemistry Series, Vol. VII, John Wiley & Sons, New York, N. Y., 1975.
4. U. Merten, Ed., "Desalination by Reverse Osmosis," MIT Press, Cambridge, MA., 1966.
5. F. F. Hartline, *Science*, **206**, 41 (1979).
6. R. C. Binning and F. E. James, *Petr. Refiner*, **39**, 214 (1958).
7. E. G. Heisler, A. S. Hunter, J. Sciliano, and R. M. Treadway, *Science*, **124**, 77 (1956).
8. P. Aptel, N. Challord, J. Cuny, and J. Neel, *J. Membrane Sci.*, **1**, 271 (1976).
9. J. G. Sikonia and F. P. McCandles, *J. Membrane Sci.*, **4**, 229 (1978).
10. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, **18**, 2117 (1974).
11. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.*, **16**, 1061 (1972).
12. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.*, **18**, 351 (1974).
13. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.*, **18**, 365 (1974).
14. S. Yoshimasu, H. Nomura, K. Komiya, J. Terada, T. Okano, and I. Shinohara, *Nihon Kagaku Kaishi*, 1785 (1980).
15. T. Itoh, Y. Ohkawa, K. Ishihara, and I. Shinohara, *Polym. J.*, **15**, 827 (1983).
16. F. P. McCandles, *Ind. Eng. Chem. Process Design Develop.*, **12**, 354 (1973).
17. T. Suzuki and T. Kotaka, *Macromolecules*, **13**, 1495 (1980).
18. T. Suzuki and T. Kotaka, *Polym. J.*, **15**, 15 (1983).
19. T. Suzuki, H. Chihara, and T. Kotaka, *Polym. J.*, **16**, 129 (1984).
20. H. Tanisugi, H. Ohnuma, and T. Kotaka, *Polym. J.*, **16**, 633 (1984).
21. E. P. Goldberg, *J. Polym. Sci., C*, **4**, 707 (1964).
22. H. J. Harwood and W. M. Richey, *Polym. Lett.*, **2**, 601 (1964).
23. H. Adachi, S. Nishi, and T. Kotaka, *Polym. J.*, **14**, 985 (1982).
24. P. E. Rouse, *J. Am. Chem. Soc.*, **69**, 1068 (1957).
25. D. W. McCall, *J. Polym. Sci.*, **26**, 151 (1957).
26. E. W. Washburn, Ed., "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology," Vol. III, McGraw-Hill, New York, N. Y., 1928.
27. J. Crank and G. S. Park, Eds., "Diffusion in Polymers," Academic Press, London and New York, 1968.
28. S. Krause, "Block and Graft Copolymers," J. J. Burke and V. Weiss, Eds., Syracuse Univ. Press, Ithaca, N. Y., 1973, pp 143—155.
29. A. Michaels, W. Vieth, and J. J. Barrie, *J. Appl. Phys.*, **34**, 13 (1963).
30. H. B. Hopfenberg and V. T. Stannett, "The Physics of Glassy Polymers," R. N. Haward, Ed., Appl. Sci. Publishers, London, 1973, Chapter 9.