

Permeation of Solutes in Water-Swollen Poly(vinyl Alcohol-Co-Itaconic Acid) Membranes

AKON HIGUCHI and TOSHIRO IJIMA,* *Department of Polymer Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan*

Synopsis

Partition and permeability coefficients of urea, NaCl, and saccharose in water-swollen poly(vinyl alcohol-co-itaconic acid) membranes with various water contents ($0.25 \leq H \leq 0.86$) were measured. Partition coefficients and permeability ratios in freezing and nonfreezing water were estimated based on a parallel permeation model. It was suggested that at 25°C the permeation of saccharose in the nonfreezing water was nearly zero due to its negligible partition coefficient, while NaCl and urea were found to be able to permeate even the nonfreezing water. The activation energies of diffusion for three solutes were found to increase with the decrease of water content of the membranes. Since the fraction of nonfreezing water increased with the decrease of water content of the membranes, it is assumed that the increased activation energy of diffusion is due to the fact that the diffusion in nonfreezing water needs higher activation energy than in the pure bulk water.

INTRODUCTION

Permeation of solutes in water-swollen membranes has been paid attention to due to the clinical and industrial importance such as hemodialysis and other separation processes. Several investigators¹⁻¹⁷ studied the characterization of the membranes and solutes (i.e., water content, pore radius, and solute radius) to predict the solute permeability. Pore theory originally developed by Ferry,⁴ Faxen,⁵ and Renkin,⁶ free volume theory,¹¹ and the stochastic approach developed by Mackie and Meares¹² and Ogston¹³ are those of pertinent examples. Peppas and Reinhart^{15,16} developed a theoretical model describing the spherical and quasispherical solute diffusion through highly swollen nonporous polymeric networks.

Permeation models of solutes considering the states of water in the membranes were discussed by several investigators.¹⁸⁻²⁴ Ratner and Miller¹⁸ studied the transport of urea, NaCl, glycine, and glucose through poly(2-hydroxyethyl methacrylate) hydrogel membranes. The higher permeability of urea compared to NaCl and other solutes in the gels was observed. This was attributed to the high affinity of urea for the gels. Activation energies of diffusion for urea and NaCl in the gel were, however, found to be approximately the same to those in bulk water. It was concluded that urea and NaCl diffuse through the gels in an environment similar to the pure solution.

* To whom correspondence should be addressed.

Kim et al.¹⁹ studied the permeabilities of water-soluble nonelectrolytes and hydrophobic solutes in poly(hydroxyethyl methacrylate) membranes. They suggested that the permeation of hydrophilic solutes occurs mainly through free water regions of the membranes. The hydrophobic solutes permeation was considered to occur by a partition mechanism in the highly crosslinked membranes.

Scheuplein²⁰ presented an analysis of the permeability of water in the parallel diffusion pathways. It was suggested that diffusion of water molecules occurred through two pathways consisting of free water and bound water regions in the membranes.

In the present investigation, partition and permeability coefficients of urea, NaCl, and saccharose in water-swollen poly(vinyl alcohol-co-itaconic acid) membranes having various water contents ($0.25 \leq H \leq 0.86$) were measured. The aim of the present study is to elucidate the transport phenomena in freezing and nonfreezing water phases^{25,26} based on a parallel permeation model.^{20,22} The estimation of the partition coefficients and permeability ratios in the two water phases was performed.

EXPERIMENTAL

Materials

Poly(vinyl alcohol-co-itaconic acid) (PVA-IA) used in this investigation were kindly provided by Kuraray Co., Ltd. which has 1.3 mol % of itaconic acid, its saponification value is 97.7 mol %, and its degree of polymerization is 1750, respectively. Distilled deionized water was used throughout experiment. Membrane preparation and the method of crosslinking by acetalization of the membranes with glutaraldehyde were described in previous papers.^{22,27} The water content of the membranes was controlled by the degree of the crosslinking.

Apparatus

The permeation and partition experiments of NaCl performed in this study is similar to that described elsewhere.²⁸⁻³⁰ The cell volume of upstream and downstream side is 245 and 68 mL, respectively. The effective membrane area is 7.28 cm². The downstream concentration C_2 was monitored with electronic conductometer to determine the permeability coefficients of NaCl in the membranes. Permeability and partition coefficients of NaCl were determined for VI-83, 73, 67, 47, 34, and 25 (water content of the membranes are 0.83, 0.73, 0.67, 0.47, 0.34, and 0.25 water (g)/swollen membrane (g), respectively). A glass diffusion cell consisting of two compartments of equal volume (245 mL) was used in the permeation of urea and saccharose. The effective membrane area is 7.28 cm². The solutions of each sides were stirred effectively during the measurements to minimize the stagnant boundary layers on the surface of the membrane. The initial upstream concentration C_1 was 0.2 mol/L for all experiments. The downstream concentration C_2 was monitored with a differential refractometer

to determine the permeability coefficient P . The permeation measurements were carried out within the limit of the concentration range of C_2 less than 1/100 of upstream side. The upstream concentration was, therefore, regarded as constant during the experiments.

The partition coefficient K determined by desorption³⁰ is the ratio of the solute concentration in the membrane to the solution at equilibrium. Permeability and partition coefficients were measured for urea in VI-85, 72, 63, 51, and 44, and for saccharose in VI-86, 70, 66, 59, and 26 membranes. Since the permeability of saccharose decreases more significantly than that of NaCl or urea with the decreasing water content and the detective sensitivity of the solute concentration by the refractometer is more than 10 times worse than that by the conductometer, the permeability of saccharose was measured in the membranes of $H \geq 0.59$ from the point of experimental accuracy. Standard deviations of the permeability and partition coefficients were found to be 5% of P and 2.5% of K , respectively.

NaCl were purchased from Kanto Chemicals, Ltd. as a 1.0M standard aqueous solution. Urea and saccharose were obtained as extra pure reagent from Nakarai Chemicals Ltd. Measurements were performed at 25, 30, 35, 40, and 45 $\pm 0.05^\circ\text{C}$ in a thermostated water bath.

RESULTS AND DISCUSSION

Figure 1 shows $\log D$ against $1/H-1$ for NaCl, urea, and saccharose at 25°C, where D is the diffusion coefficient calculated by P/K . It is known that Yasuda's free volume theory¹¹ predicts linear dependence of $\log D$ on $1/H-1$. The values of $\log D$ at $H = 1$ in the figure are those in pure bulk water taken from the literature.³¹⁻³³ The diffusion coefficients of NaCl, urea, and saccharose in the bulk water are 1.61×10^{-5} , 1.39×10^{-5} , and $5.24 \times 10^{-6} \text{ cm}^2/\text{s}$ at 25°C, respectively. The diffusion coefficients of NaCl, urea, and saccharose were found to decrease with decreasing water content of the membranes. Urea, which has a larger molecular size and a smaller diffusion coefficient than NaCl in the bulk water,¹⁸ was found to have a larger diffusion coefficient than NaCl in the membranes at $0.51 \leq H \leq 0.85$. This suggests that the hydration radii of NaCl and urea in the membranes are different from those in the bulk water and/or that the diffusion

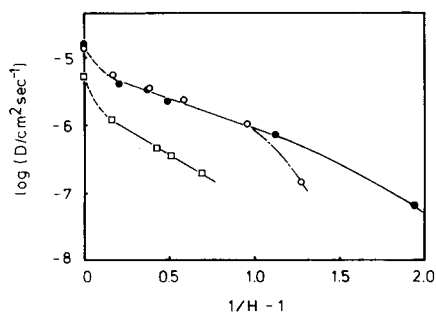


Fig. 1. $\log D$ against $1/H$ at 25°C: (●) NaCl; (○) urea; (□) saccharose.

coefficient of urea is higher than that of NaCl in the nonfreezing water. The diffusion coefficient of urea in VI-44 is, however, found to be lower than that of NaCl at $H = 0.44$. This may be due to the sieving effect,⁴⁻⁶ as the mesh size of the membranes will be reduced with decreasing water content^{15,16} and urea has a larger molecular size than NaCl. It is found that the diffusion coefficients of saccharose decrease more noticeably than those of urea and NaCl at $H \geq 0.59$.

The fact that no linear correlation between $\log D$ and $1/H-1$ was observed (Fig. 1) is explained with considering the states of water in the membranes. As was discussed in several investigations,¹⁸⁻²⁷ the water in membrane is frequently in multistates while the free volume theory assumes that the state of water is only one.¹¹

The partition coefficient K of NaCl, urea, and saccharose as a function of water content of the membranes at 25°C is shown in Figure 2. In the case of saccharose, K decreases monotonously with the decrease of water content of the membranes. In the membranes of $H < 0.26$, K is found to be practically zero. This indicates that saccharose does not dissolve in the nonfreezing water phase, since the state of water in the membranes at $H < 0.375$ is solely nonfreezing in nature.²² The partition coefficients of NaCl also decrease with the decrease of water content of the membranes. In the case of the membrane of $H = 0.25$, K was observed to be 0.42 where all of the water is in the nonfreezing state. In our previous DSC investigation,²² partition coefficients of NaCl and urea in the freezing water of PVA-IA were estimated as being equal to unity from melting point depression of the water. The above consideration, therefore, suggests that NaCl can dissolve in the nonfreezing water but less than in the freezing water. The partition coefficient of urea shows different behavior as a function of water content from those of NaCl and saccharose. The partition coefficient of urea is estimated to be approximately 1.1 and to be almost independent of water content. Kim et al.¹⁹ reported partition coefficients of thiourea and Na methotrexate greater than unity. This phenomenon was explained by specific interactions of the solutes with the macromolecular chains. Further possibility of specific interactions between the solutes and the nonfreezing water is proposed.

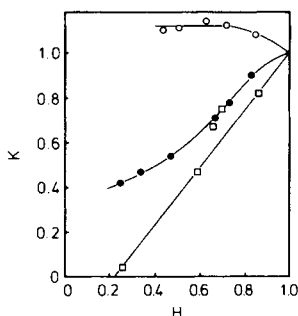


Fig. 2. Dependence of partition coefficients on water content at 25°C: (●) NaCl; (○) urea; (□) saccharose.

The partition coefficients of solutes in freezing water and nonfreezing water phases in the membranes, K_1 and K_2 , can be estimated, assuming that the solutes dissolve in two distinct phases in the membranes^{21,22}:

$$\begin{aligned} K &= K_1 + K_2 \\ &= v_1 K_1^0 + v_2 K_2^0 \end{aligned} \quad (1)$$

where v_1 and v_2 are the volume fraction of freezing and nonfreezing water and $v_1 = 1 - v_2$. K_1^0 and K_2^0 are the partition coefficients in purely freezing and nonfreezing water. K_1^0 was estimated to be unity from the previous study.²² As the weight ratio of nonfreezing water to dry polymer for PVA-IA membranes is approximately 0.6,²² v_1 could be calculated from $1.6 - 0.6/H$ at $H \geq 0.375$, and v_1 was zero at $H < 0.375$ with the assumption that the density of nonfreezing water was the same to that of freezing water.

K_2^0 was estimated by eq. (1) and plotted as a function of water content in Figure 3. K_2^0 of urea is found to be more than unity at $0.44 \leq H \leq 0.85$. This is due to the contribution of the solute's interactions with the macromolecules¹⁸ and nonfreezing water. It is also observed that K_2^0 of urea decreases with the decrease of water content of the membranes. The contact area of a polymer chain with solutes will decrease with decreasing water content, as the polymer chains are much exposed to the water in high water content and some part of the polymer chains is probably embedded in the polymer matrix in low water content. The decreasing tendency of K_2^0 of urea may be, therefore, explained by the less contact area of the polymer chains surrounded by the nonfreezing water with the decrease of water content.

K_2^0 of NaCl and saccharose was found to be less than unity, as was already discussed qualitatively. It is known that ions and sugars are excluded from "polarized" or bound water (nonfreezing water).^{24,34} K_2^0 of saccharose is found to be approximately zero, while K_2^0 of NaCl is found to be 0.42 for VI-25. Taniguchi and Horigome³⁵ investigated the states of water in cellulose acetate membranes and suggested that there are two kinds of nonfreezing water (bound water in Ref. 35), one of which can dissolve salts and the other of which does not. Their argument is consistent with the results in the present work.

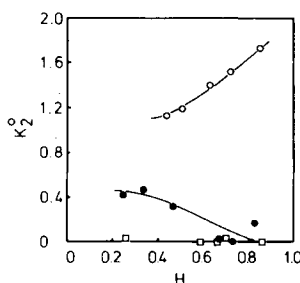


Fig. 3. Dependence of K_2^0 on water content at 25°C: (●) NaCl; (○) urea; (□) saccharose.

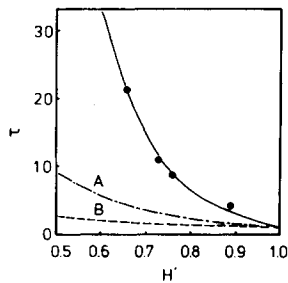


Fig. 4. τ against water content: (●) estimated from eq. (3) for saccharose; (A) Mackie and Meares equation; (B) Fricke's equation.

The permeability coefficients in freezing and nonfreezing water, P_1^0 and P_2^0 , can be expressed as follows by the parallel permeation model^{21,22}:

$$\begin{aligned} P &= H'(P_1^0 v_1 + P_2^0 v_2)/\tau \\ &= H'(D_1^0 K_1^0 v_1 + D_2^0 K_2^0 v_2)/\tau \end{aligned} \quad (2)$$

where τ is the tortuosity factor and D_1^0 and D_2^0 are the diffusion coefficients in freezing and nonfreezing water phase, respectively. τ is assumed to be the same as both in the nonfreezing and the freezing water.^{21,22} D_1^0 is assumed to be equal to the diffusion coefficient in the bulk water. As is suggested from Figure 3 that saccharose does not dissolve in nonfreezing water at 25°C, permeation of saccharose mainly occurs in the freezing water. τ is, therefore, estimated from eq. (3) using P values for saccharose:

$$\tau = H'D_1^0 v_1/P \quad (3)$$

Dependence of τ on H' thus obtained is shown in Figure 4. H' is the volume fraction of water in the swollen membrane and is estimated from $H' = Hd$, where d is the density of the swollen membrane. τ which is calculated by Mackie and Meares equation,¹² $[(1 + \phi)/(1 - \phi)]^2$, and by Fricke's equation,³⁶ $(1 + \phi/2)/(1 - \phi)$, is also shown in the same figure. ϕ is the volume fraction of polymer in the swollen membrane and is estimated from $1 - H'$. The values of τ estimated from eq. (3) are found to be higher than those obtained from the two theoretical calculations. This suggests that significant amounts of dead void which cannot contribute to the permeation of solutes exist in the PVA-IA membranes.

TABLE I
 P_2^0/P_1^0 of Urea and NaCl in Water-Swollen PVA-IA Membranes

Membranes	Urea	NaCl
VI-85	9.4	
VI-83		2.1
VI-72	17	
VI-67		6.6
VI-63	19	

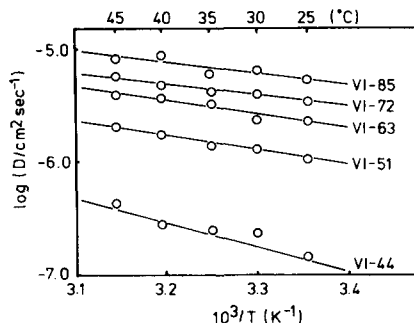


Fig. 5. Arrhenius plot of $\log D$ against $1/T$ for urea.

P_1^0 and P_2^0 of urea and NaCl in the membranes of $H \geq 0.59$ were calculated using τ estimated from eq. (3). The ratios, P_2^0/P_1^0 , of urea and NaCl are summarized in Table I. It is found that P_2^0/P_1^0 is much larger than unity for both NaCl and urea. Toprak et al.³⁷ studied the state of water in cellulose acetate membranes by infrared spectroscopy and concluded that water sorbed in the membranes has weaker bonds between water and cellulose acetate than the hydrogen bonds in the bulk water. It was suggested that the weak hydrogen bonds in the membranes lead to high molecular mobility. The high ratios of P_2^0/P_1^0 of NaCl and urea in PVA-IA membranes are probably due to the high molecular mobilities of the solutes in the non-freezing water.

Permeability coefficients of NaCl in the membranes at low water content are significantly lower than the value in the bulk water, although P_2^0 of NaCl is higher than P_1^0 . For example, the permeability coefficient of NaCl in VI-25 is 4.02×10^{-9} cm²/s, which is about 4000 times lower than that in the bulk water. This is caused by the increase of the tortuosity factor with the decrease of water content. Reverse osmosis membranes such as cellulose acetate membranes developed by Loeb and Sourirajan³⁸ are known to possess high salt rejection ratio. The high salt rejection is usually explained by poor partition of the salts in nonfreezing water.³⁹ However, NaCl can dissolve in nonfreezing water as found in Figure 3. Table I suggests that permeability of NaCl in the nonfreezing water is higher than that in the freezing water in PVA-IA membranes. It may be possible to consider that the high salt rejection in the reverse osmosis membranes is due to the

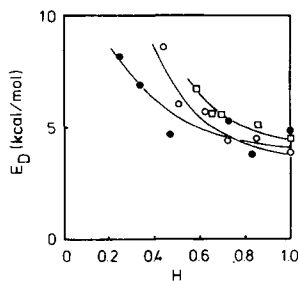


Fig. 6. Dependence of the apparent activation energies of diffusion on water content: (●) NaCl; (○) urea; (□) saccharose.

TABLE II
Water Content of PVA-IA Membranes at 25-45 °C

Membranes	25°C	30°C	35°C	40°C	45°C
VI-86	0.86	0.86	0.86	0.86	0.84
VI-70	0.71	0.71	0.70	0.71	0.70
VI-66	0.67	0.67	0.67	0.66	0.66
VI-59	0.59	0.60	0.60	0.59	0.59
VI-26	0.26	0.26	0.26	0.26	0.26

high mobility of water in the nonfreezing phase; a high molecular mobility is expected in the nonfreezing water as Toprak et al.³⁷ suggested. There is another possibility that the water in the nonfreezing phase may diffuse by a proton jump process, which may extremely reduce the tortuosity in the membranes for water compared with other solutes such as NaCl.

Apparent activation energies of diffusion for NaCl, urea and saccharose in the membranes are calculated by¹⁷

$$D = D^0 \exp(-E_D/RT) \quad (4)$$

where E_D is the activation energy of diffusion, D^0 is preexponential term, and R and T have conventional meanings. An example of the Arrhenius plots for urea are shown in Figure 5. It is found that the slope becomes steeper with the decrease of water content of the membranes. The dependence of the activation energies of diffusion on water content of the membranes is shown in Figure 6. E_D at $H = 1.0$ are the values in the bulk water taken from the literature³¹⁻³³ and are 4.9, 3.9, and 4.5 kcal/mol for NaCl, urea, and saccharose, respectively. The activation energies of diffusion for three solutes are found to increase with the decrease of water content of the membranes. Care must be taken to discuss the activation energies of diffusion as there is a possibility that water content and/or membrane thickness changes with elevated temperature. This may contribute to the high activation energy of diffusion in the membrane of low water content. Water content and thickness of VI-86, 70, 66, 59, and 26 at 25-45°C are summarized in Tables II and III. In these tables it is found that there is no dependence of the water content or the thickness on temperature in the range from 25 to 45°C. Ebra-Lima and Paul⁴⁰ studied hydraulic permeation of water swollen poly(vinyl alcohol) membranes. They found that activation energy of diffusion for water was 6.5 kcal/mol and this was higher than the value of 4.3 kcal/mol for viscous flow of water. They argued that polymer-liquid interaction influenced the activation en-

TABLE III
Membrane Thickness (μm) at 25-45°C

Membranes	25°C	30°C	35°C	40°C	45°C
VI-86	101	104	105	101	97
VI-70	73	70	72	70	71
VI-66	100	99	100	100	97
VI-59	79	76	75	76	73
VI-26	82	80	81	80	80

ergy of the diffusion process in those systems. It is, therefore, concluded from the above arguments that the high activation energies observed in Figure 6 are due to the fact that diffusion in nonfreezing water needs a higher activation energy than in the bulk water, as the fraction of nonfreezing water increases with decreasing water content of the membranes.

References

1. C. N. Satterfield, C. K. Colton, and W. H. Pitcher, *AIChE J.*, **19**, 628 (1973).
2. J. L. Anderson and J. A. Quinn, *Biophys. J.*, **14**, 130 (1974).
3. C. K. Colton, C. N. Satterfield, and C. J. Lai, *AIChE J.*, **21**, 289 (1978).
4. J. D. Ferry, *J. Gen. Physiol.*, **20**, 95 (1936).
5. H. Faxén, *Arkiv. Mat. Astron. Fys.*, **17**, 27 (1923).
6. E. M. Renkin, *J. Gen. Physiol.*, **38**, 225 (1954).
7. H. Brenner and L. J. Gaydos, *J. Colloid Interface Sci.*, **58**, 312 (1977).
8. D. M. Malon and J. L. Anderson, *Chem. Eng. Sci.*, **33**, 1429 (1978).
9. W. M. Deen, M. P. Bohrer and N. B. Estein, *AIChE J.*, **27**, 952 (1981).
10. E. D. Glands, *J. Membr. Sci.*, **8**, 331 (1981).
11. H. Yasuda and L. E. Lamaze, *J. Macromol. Sci. Phys.*, **B5**, 111 (1971).
12. J. S. Mackie and P. Meares, *Proc. Roy. Soc. London*, **A232**, 498 (1955).
13. A. G. Ogston, *Trans. Faraday Soc.*, **54**, 1754 (1958).
14. Y. Kojima, K. Furufata, and K. Miyasaka, *J. Appl. Polym. Sci.*, **29**, 533 (1984).
15. N. A. Peppas and C. T. Reinhart, *J. Membr. Sci.*, **15**, 275 (1983).
16. C. T. Reinhart and N. A. Peppas, *J. Membr. Sci.*, **18**, 227 (1984).
17. C. K. Colton, K. A. Smith, E. W. Merrill, and P. C. Farrell, *J. Biomed. Mater. Res.*, **5**, 459 (1971).
18. B. D. Ratner and I. F. Miller, *J. Biomed. Mater. Res.*, **7**, 353 (1973).
19. S. W. Kim, J. R. Cardinal, S. Wisniewski, and G. M. Zentner, *Water in Polymer*, S. P. Rowland Ed., ACS Symposium Series 127, American Chemical Society, Washington, DC, 1980, p. 347.
20. R. J. Scheuplein, *Biophys. J.*, **6**, 1 (1966).
21. A. Higuchi, M. Abe, J. Komiyama, and T. Iijima, *J. Membr. Sci.*, **21**, 113 (1984).
22. A. Higuchi, H. Fushimi, and T. Iijima, *J. Membr. Sci.*, **25**, 171 (1985).
23. S. C. Yoon and M. S. Jhon, *J. Appl. Polym. Sci.*, **27**, 3133 (1982).
24. S. Wisniewski and S. W. Kim, *J. Membr. Sci.*, **6**, 229 (1980).
25. M. A. Frommer, M. Shporer, and R. M. Messalem, *J. Appl. Polym. Sci.*, **17**, 2263 (1973).
26. A. Higuchi, J. Komiyama, and T. Iijima, *Polym. Bull.*, **11**, 203 (1984).
27. A. Higuchi and T. Iijima, *Polymer*, **26**, 1833 (1985).
28. H. Vink, *Acta Chem. Scand.*, **A33**, 547 (1979).
29. Y. Ando, T. Iwamoto, Y. Atsumi, N. Sakai, J. Komiyama, and T. Iijima, *Nippon Kagaku Kaishi*, 1376 (1979).
30. Y. Kimura, H.-J. Lim, and T. Iijima, *J. Membr. Sci.*, **18**, 285 (1984).
31. J. Tourancheau and M. Mange, *J. Chem. Phys.*, **64**, 1466 (1967).
32. P. N. Henrion, *Trans. Faraday Soc.*, **60**, 72 (1964).
33. *International Critical Tables*, National Research Council, McGraw-Hill, New York, 1933, Vol. 5.
34. G. N. Ling, *Water and Aqueous Solutions*, R. A. Horne, Ed., Wiley-Interscience, New York, 1972, p. 688.
35. Y. Taniguchi and S. Horigome, *J. Appl. Polym. Sci.*, **19**, 2743 (1975).
36. H. Fricke, *Phys. Rev.*, **24**, 575 (1924).
37. C. Toprak, J. N. Agar, and M. Falk, *J. Chem. Soc., Faraday Trans. I*, **75**, 803 (1979).
38. S. Loeb and S. Sourirajan, *Adv. Chem. Ser.*, **38**, 177 (1962).
39. S. Sourirajan, *Ind. Eng. Chem. Fundam.*, **2**, 51 (1963).
40. O. M. Ebra-Lima and D. R. Paul, *J. Appl. Polym. Sci.*, **19**, 11381 (1975).

Received July 26, 1985

Accepted January 11, 1986