

Diffusion of Water in Sulfonated Polystyrene Ionomers

N. R. Manoj* and D. Ratna

Naval Materials Research Laboratory Anand Nagar, Additional Ambernath-421 506, India

R. A. Weiss

Institute of Materials Science University of Connecticut, Storrs, CT 06269-3136, USA

Received Mar. 3, 2003; Revised July 22, 2003

Abstract: Using gravimetry, we have studied the diffusion of water into sulfonated polystyrene ionomers. Diffusion coefficients were calculated from Fick's equation. The water sorption was found to be dependent on the ion content (3.6-11 mol%) and the nature of the cation (H, Na, Li, or Zn). The sorption kinetics indicates a slight deviation from Fickian behavior. We used the analytical solution of Fick's equation to evaluate the concentration profiles, which are in good agreement with the experimental results.

Keywords: diffusion, sorption, barrier polymers, ionic polymers, ionomers, sulfonated polystyrene.

Introduction

All synthetic polymers absorb moisture in a humid atmosphere, or when they are immersed in water, through diffusion. The driving force for diffusion is the change in the chemical potential of the diffusing substance and it involves a reduction in the free energy of the system.¹⁻³ Diffusion of small molecules into polymers occurs nearly in all situations where polymeric materials are involved. The study of molecular transport in polymers has both practical and theoretical importance since polymers are used in many applications where barrier properties are important.

Diffusion of molecules through the polymer depends on a number of polymer properties: glass transition temperature (T_g) or chain stiffness, crosslinking, crystallinity, crystallite size and distribution, and solubility of the diffusing molecule in the polymer. The polarity of the polymer matrix due to the presence of functional groups also has a significant effect on the nature of interaction with diffusing molecules and hence on the diffusion process.^{4,5} A great variety of techniques have been developed to measure diffusion of liquids and gases into polymers viz., gravimetric, vacuum microbalance, volumetric, optical, radiotracer weighing and NMR imaging techniques.^{3,6}

Ionomers are ion-containing polymers, which form an important class of synthetic polymers used for an impressive array of applications.⁷⁻¹⁴ The presences of ionic aggregates as

multiplets and clusters is known to affect the polymer properties such as melt rheology, viscoelasticity, crystallization, dielectric constant and transport properties.^{11,15,16} Ionomers based on styrene methacrylate polymers, polysiloxane dicationomers and perfluoroethylenes are shown to absorb water depending on the type of ions, the nature of polymer chain, the molecular weight, the degree of ionic aggregation and the temperature.¹⁷⁻²¹

Owing to the increasing importance of ionomers in various fields, especially as barrier polymers, there is a need to know, describe and predict the diffusion of small molecules into them. Also, ionomers offer an unusual opportunity to assess the effect of molecular architecture brought about by variation of ion content and cation types. In this work, we studied the diffusion of water into sulfonated polystyrene ionomers gravimetrically and elucidated the diffusion coefficients and sorption kinetics. The analytical solution of Fick's equation was used to calculate the concentration profiles at different times during diffusion.

Experimental

Preparation of Polymers. The starting polystyrene (PS) was a commercial resin, Styron 666 (Dow Chemical Company; $M_n = 103,000$; $M_w = 288,000$). The sulfonation procedure, followed from Makowski *et al.* was as follows^{22,23}: The sulfonating agent, acetyl sulfate, was prepared by slowly adding concentrated sulfuric acid (H_2SO_4) to a solution of acetic anhydride in dichloroethane (DCE) at 0°C. The freshly prepared acetyl sulfate was then added to a

*e-mail: manoj@ncml.ernet.in

1598-5032/02/26-06©2004 Polymer Society of Korea

well-stirred solution of PS in DCE at 50 °C. The reaction was terminated by the addition of 2-propanol after 1 h. The sulfonated PS (SPS) was isolated by steam-stripping, washed with methanol and dried at room temperature for 3 days. Consequently, it was dried under vacuum above T_g for 24 h. The sulfonic acid content was established by titration of SPS in a mixture of toluene and methanol (90/10, v/v) against sodium hydroxide in methanol.

The SPS was converted into sodium (Na), lithium (Li) and zinc (Zn) salts by adding 100% excess of the respective acetates. The polymer was first dissolved in a mixture of toluene and methanol (90/10, v/v) and the base dissolved in a minimal quantity of methanol, was added drop-wise into the stirred solution. The neutralized polymer was recovered, washed and dried as described above.

The polymer samples are denoted as SPS-M-x where x is the degree of sulfonation expressed as mole percent of styrene sulfonate and M denotes the cation (M = H, Na, Li or Zn in the case of free acid, sodium, lithium and zinc salts respectively).

The polymers were compression molded between polyimide sheets in a stainless steel mold (circular cavities of 7.5 mm diameter and 1 mm thickness) at 200 °C. The mold was cooled to room temperature under pressure (100 kg/cm²) and the samples in the shape of discs were taken out. The samples were then placed under vacuum at 90 °C for 24 h to remove any volatiles and to release any residual stress. Upon removal from vacuum, the samples were kept in vacuum desiccator till further use. Typical weights of the samples range from 35 to 45 mg.

Diffusion Studies. The samples were weighed in a Mettler MT5 balance having an accuracy of 0.01 mg. This is taken as the dry weight of the sample. The samples were then submerged in distilled water taken in a glass vial having screw tight cap and kept at test temperature in an air oven at 25 °C. Water uptake was determined by weighing the samples at different time intervals. The sample was taken out from water, pressed lightly between blotting paper and weighed. Care was taken to handle the samples as rapidly as possible while exposed to atmosphere. The whole process of taking out the sample, blotting, weighing and putting back in water used to take approximately 30 s. The amount sorbed was taken as the difference between these measurements and the dry weight. A minimum of three samples was used in each case. There was no observable change in the dimensions of the samples after water sorption.

Results and Discussion

Sorption equilibrium is explained as a balance of opposing forces. The tendency of macromolecular chains to surround themselves with solvent and thus to stretch the matrix (due to the osmotic pressure difference or free energy of mixing with increasing dilution) meets with an increasing resist-

ance by the latter (gain in configurational entropy accompanying the coiling of chains). Equilibrium is attained when the elastic forces of the matrix balance the dissolution tendency.²⁴ The diffusion of a liquid in a polymer matrix is described by Fick's laws.²⁵ This equation is valid only for the systems with a constant diffusion coefficient. However, for cases where there is a deviation, it is still possible to deduce an average diffusion coefficient from the initial gradient of the sorption curve, at short times with negligible error from the exact solution of Fick's law:

$$\frac{M_t}{M_\infty} = \frac{4}{h} \left(\frac{Dt}{\pi} \right)^{1/2}$$

so that the diffusion coefficient D can be calculated from the slope of a plot of M_t/M_∞ versus $t^{1/2}$.^{25,26} Here M_t is the total amount absorbed by the sheet at time t and M_∞ is the equilibrium sorption. h is the thickness of the sheet.

Plots of M_t/M_∞ are shown for all the ionomers and the respective acid derivatives in Figure 1. It is apparent that the sorption curves can be treated as linear from the beginning to 70% weight gain, suggesting that sorption in this region is predominantly diffusion controlled.^{2,25} However, the fact that the linear portion of these plots extends beyond values of $M_t/M_\infty = 0.5$ indicate a departure from Fick's law.^{27,28}

Sorption. Table I gives the diffusion characteristics of all the ionomers. The effect of ion content and counter ions is graphically displayed in Figure 2. On comparing the water sorption of Zn salt and the acid form of SPS, it could be seen that there is a reversion in the total amount of sorbed water between the two forms, depending on the ion/acid content. The Zn salt takes up more water when the ion content is low whereas the acid form takes up more water when the ion content is high. A possible explanation is that as the ion content increases, the ionomer with the metal ion forms stronger ionic aggregates - ionic clusters- compared to the acid form.^{7,15} Such localization of the charges prevents the tendency of ions to form solvation shells and the sorption of water. This is corroborated by the observation that the role reversal takes place just above 5 mol% ion content. It has been shown that for styrene ionomers, the cluster phase becomes dominant over 6 mol% of ions.^{11,17,29-32}

Figure 2 also displays the effect of counter ions in the water sorption by SPS ionomers with 3.6 mol% ion content. It was found that the Na or Li salts of the SPS ionomer could hydrate about 2-3 times more than the Zn salt. The tendency to take up water depends on the number of counterions. In the case of divalent counter ions, the number of ions required to satisfy the charges is half as compared to univalent counterions. Hence, Zn ionomer takes up less water compared to Na or Li ionomers. The volume occupied by the counter ions in its solvated state may explain the higher water uptake of LiSPS as compared to NaSPS. It is well known that the increasing order of volume occupied in its solvated state by alkali metal ions is $\text{Li} > \text{Na} > \text{K} > \text{Rb} >$

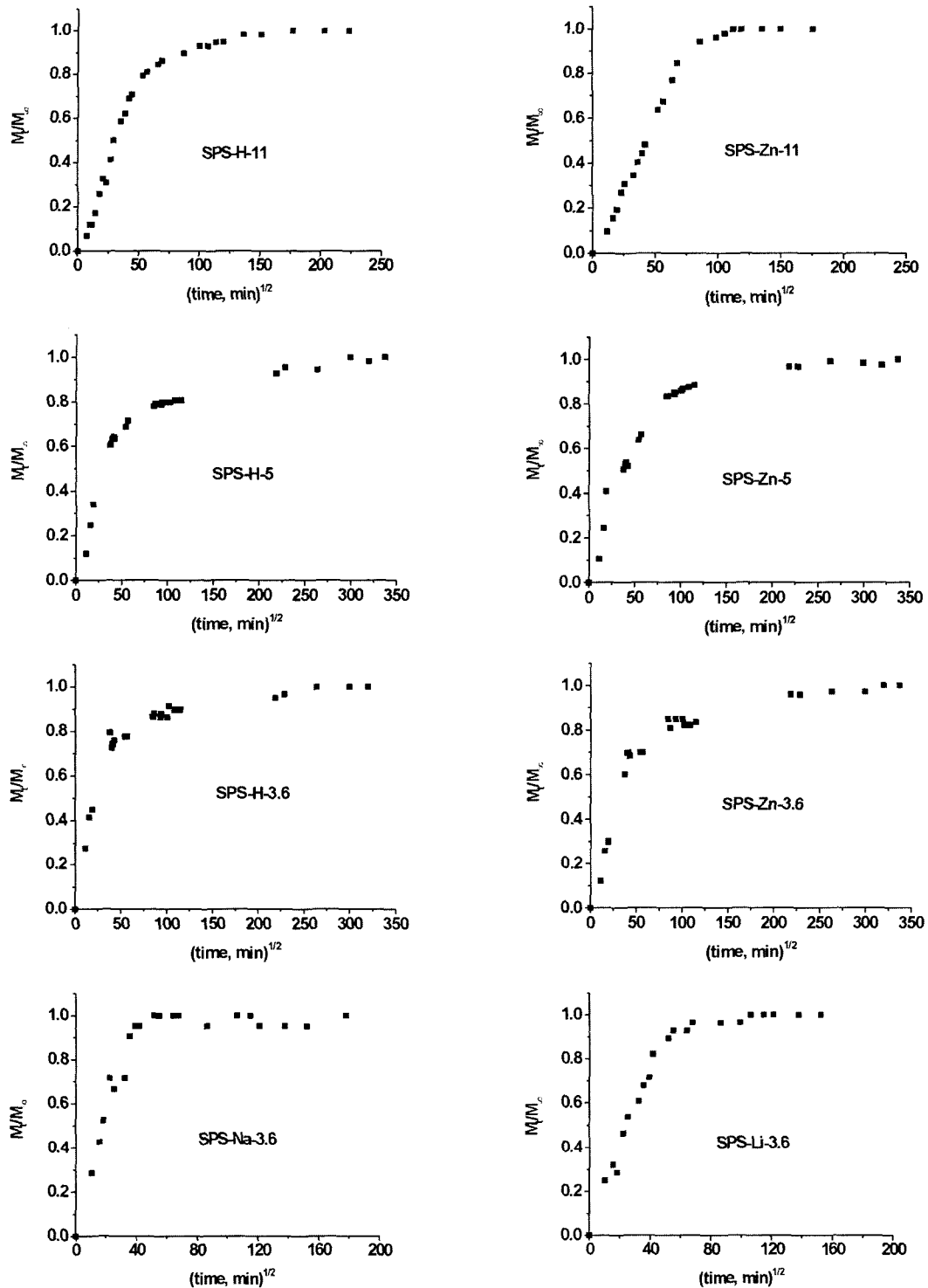


Figure 1. Sorption plots of M_t/M_∞ vs. $(\text{time}, \text{min})^{1/2}$ for all ionomers at 25 °C.

Cs.²⁴ Hence the matrix expands more when the counter ion is Li than Na, and takes up more water molecules. Similar observations of influence of ion content and nature of cation were made in the case of ethylene ionomers also.³³

Sorption Kinetics. A convenient way to represent sorption

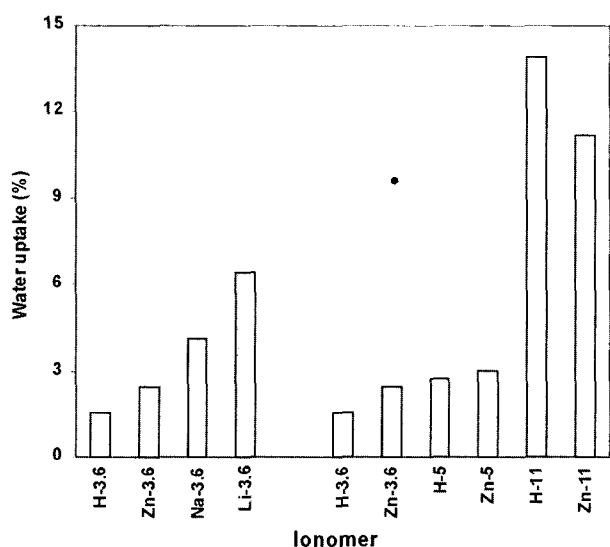
kinetics is by following the empirical equation^{1,25,34}:

$$\frac{M_t}{M_\infty} = kt^n$$

where the value of constant k depends on the nature of

Table I. Diffusion Characteristics of Water Sorption in Sulfonated Polystyrene Ionomers

Ionomer	Amount of Water Sorbed, % (g H ₂ O/100 g Ionomer)	Diffusion Coefficient (cm ² /min)	Value of <i>n</i>	Constant <i>k</i>
SPS-H-3.6	1.57	1.05 × 10 ⁻⁸	0.52	0.029
SPS-Na-3.6	4.13	2.77 × 10 ⁻⁸	0.61	0.021
SPS-Li-3.6	6.43	1.24 × 10 ⁻⁸	0.52	0.023
SPS-H-5	2.77	6.96 × 10 ⁻⁹	0.52	0.198
SPS-H-11	13.92	7.55 × 10 ⁻⁹	0.65	0.052
SPS-Zn-3.6	2.49	4.77 × 10 ⁻⁹	0.54	0.021
SPS-Zn-5	3.03	5.27 × 10 ⁻⁹	0.54	0.025
SPS-Zn-11	11.22	3.69 × 10 ⁻⁹	0.55	0.079

**Figure 2.** Effect of ion content and counter ions on sorption.

polymer-solvent interaction and is usually related to the diffusion coefficient for Fickian behaviour, and to the penetration front velocity for Case II diffusion. In the case of Fickian transport, where the rate of diffusion is much less than the rate of relaxation, $n = 0.5$. For Case II transport, where the diffusion is very rapid compared to the rate of relaxation, $n = 1$. The diffusion is said to be anomalous when n is between 0.5 and 1. Generally Fickian diffusion occurs in polymers where the chain mobility is high, and the mass uptake in the initial sorption period is proportional to the square root of time, even if the D is concentration dependent.^{1,2}

The parameters k and n have been calculated by fitting the values of M_t/M_∞ and t by the method of least squares, at 95% confidence level. The values are shown in Table I. The values of n range from 0.52 to 0.65, indicating a slight deviation from Fickian diffusion.

Diffusion Coefficients. Table I displays the sorption results of various ionomers. When the ion content is low, the amount

of water sorbed is less but D is higher. The ionomers with low ion content may be considered as hydrophobic except for a few ionic sites. So there is not much pressure on the matrix and equilibrium is attained faster. However, when the ion content is high, there are more hydrophilic sites and more water is sorbed. There is a possible clustering of water molecules themselves around ionic sites,³⁵ and there is the resistance of elastic forces of the matrix. So it takes more time to attain equilibrium.

In order to check the validity of D calculated from the linear region of the sorption curve, theoretical sorption curves have been generated by substituting for D using Lavenberg-Maquardt algorithm from the approximate solution equation²⁵:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-D(2n+1)^2 \frac{\pi^2 t}{h^2}\right\}$$

The quality of fitting as shown in Figure 3, by comparing the data points and calculated curves, decides the correctness of the calculated D . Excellent fitting was observed in all cases. This indicates that the D values calculated from the initial slope of the sorption curves can account correctly for the whole sorption kinetics.

The D values can also be calculated from the long times of the sorption curve, using the long time approximation equation, which yields a linear dependence of $\ln M_t/M_\infty$ on time.^{1,25} The D values, so calculated, were found to be slightly higher than those calculated from the linear region. Since it is seen that the D values calculated from the linear region account for the longer times of sorption, we have used these for further calculations.

Concentration Profiles. The sorption of a diffusing molecule in a polymer continues till its concentration is equal throughout the thickness of the specimen. The concentration profile of water diffusion, i.e. the relative concentrations $C_{(t,x)}/C_\infty$ of water in the ionomer sample, has been calculated using equation^{25,26}:

$$\frac{C_{(t,x)}}{C_{\infty}} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{h^2}\right] \sin\left[\frac{(2n+1)^2 \pi x}{h}\right]$$

where h is the thickness of the sample and D is the diffusion coefficient.

Typical plots of $C_{(t,x)}/C_{\infty}$ vs. thickness are shown in Figure

4. It may be seen that SPS-H-11 with a value of D double that of SPS-Zn-1 reaches equilibrium faster. Similarly, SPS-Li-3.6 with a value of D three times that of SPS-Zn-3.6 shows faster sorption, in agreement with the experimental results.

Conclusions

Diffusion of water into SPS ionomer having varying ion

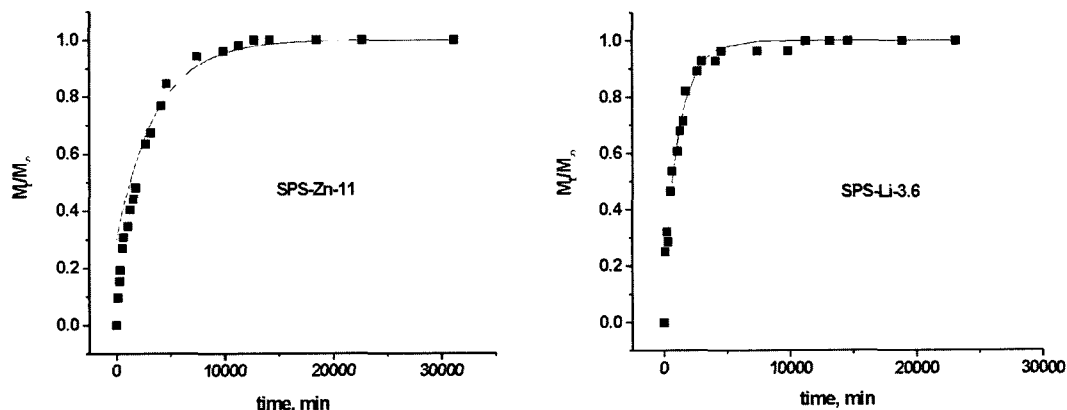


Figure 3. Characteristic sorption plots of M_t/M_{∞} vs. time for two typical ionomers. The solid line shows the theoretical curve from the calculated D .

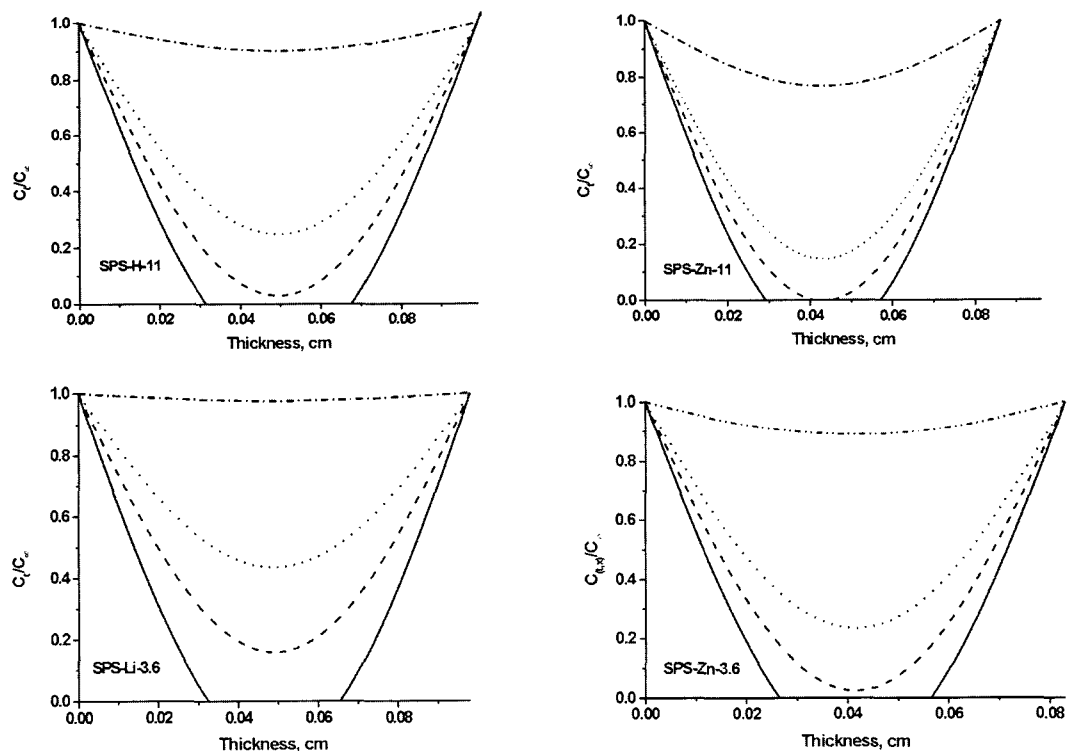


Figure 4. Concentration profiles of some typical ionomers at different times: 100 min (—), 500 min (-----), 1000 min (.....) and 5000 min (-.-.-.-).

content and cations has been studied. The ion content and nature of cation influence the water sorption remarkably. From the knowledge of diffusion coefficients and theoretical analysis, the water transport is found to be exhibiting a small deviation from Fickian behaviour. The water concentration profiles at different times in the specimens were calculated using the analytical solution of Fick's equation. The validity of D calculated for the linear region of the sorption curves over long times of diffusion is also checked.

Acknowledgements. One of the authors (NRM) gratefully acknowledges Department of Science and Technology (DST), New Delhi for a BOYSCAST Fellowship for the above work at University of Connecticut, and Defence Research and Development Organization (DRDO) for the permission to go abroad on the Fellowship.

References

- (1) G. E. Zaikov, A. C. Iordauskii, and U. S. Markin, *Diffusion of Electrolytes in Polymers*, VSP, Netherlands, 1988.
- (2) J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968.
- (3) G. Rossi, *Trends in Polym. Sci.*, **410**, 337 (1996).
- (4) C. E. Rogers, in *Engineering Design for Plastics*, E. Baer, Ed., Reinhold, New York, 1964, Chapter 9.
- (5) F. R. Jones, in *Handbook of Polymer-Fiber Composites*, F. R. Jones, Ed., Longman Scientific, New York, 1994, Chapter 6.
- (6) R. M. Felder and G. S. Huvar, *Methods of Experimental Physics*, Academic Press, London, 1968, Chapter 10.
- (7) A. Eisenberg and M. King, *Ion-containing Polymers*, Academic Press, New York, 1977.
- (8) R. D. Lundberg in M. Pineri and A. Eisenberg, Eds., *Structure and Properties of Ionomers*, NATO ASI Series, Series C: Mathematical and Physical Sciences, 198, D. Reidel Publishing Co., Dordrecht, 1987, p. 279 and 429.
- (9) R. Staz, *J. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **29**, 429 (1988).
- (10) R. D. Lundberg and P. K. Agarwal, *Indian J. Technol.*, **31**, 400 (1993).
- (11) M. R. Tant, K. A. Mauritz, and G. L. Wilkes, Eds., *Ionomers - Synthesis, Structure, Properties and Applications*, Blackie Academic & Professional, New York, 1997.
- (12) S. Mani, R. A. Weiss, C. E. Williams, and S. F. Hahn, *Macromolecules*, **32**, 3663 (1985).
- (13) N. R. Manoj, P. P. De, and S. K. De, *Polymer*, **34**, 2310 (1994).
- (14) J. -S. Kim in J. I. Kroschwitz, Ed., *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, New York, 2002.
- (15) W. J. MacKnight and T. R. Earnest Jr., *J. Polym. Sci. Macromol. Rev.*, **16**, 41 (1981).
- (16) M. A. Del Mobile, G. Mensitieri, L. Nicholas, and R. A. Weiss, *J. Polym. Sci., Polym. Phys.*, **33**, 1269 (1995).
- (17) A. Eisenberg and M. Navratil, *Macromolecules*, **6**, 604 (1973).
- (18) D. Gravier, M. Litt, and E. Baer, *J. Polym. Sci., Polym. Chem.*, **17**, 3589 (1979).
- (19) S. C. Yeo and A. Eisenberg, *J. Appl. Polym. Sci.*, **21**, 875 (1977).
- (20) M. Escoubes, M. Pineri, S. Gauthier, and A. Eisenberg, *J. Appl. Polym. Sci.*, **29**, 1249 (1984).
- (21) N. L. Brockman and A. Eisenberg, *J. Polym. Sci., Polym. Phys.*, **23**, 1145 (1985).
- (22) H. S. Makowski, R. D. Lundberg, and G. E. Singhal, US Patent 3870814 (1975).
- (23) D. Dutta, R. A. Weiss, and J. He, *Polymer*, **37**, 429, 1996.
- (24) F. Helfferich, *Ion Exchange*, McGraw Hill, New York, 1962.
- (25) J. Crank, *Mathematics of Diffusion*, Clarendon Press, Oxford, 1976.
- (26) J. M. Vergnaud, *Liquid Transport Processes in Polymeric Materials - Modelling and Industrial Applications*, Prentice-Hall, New Jersey, 1991.
- (27) J. S. Chiou and D. R. Paul, *Polym. Eng. Sci.*, **26**, 1218 (1986).
- (28) T. M. Aminabhavi and S. F. Harlapur, *J. Appl. Polym. Sci.*, **65**, 635 (1997).
- (29) B. Hird and A. Eisenberg, *J. Polym. Sci., Polym. Phys.*, **28**, 1665 (1990).
- (30) A. Eisenberg, B. Hird, and R. B. Moore, *Macromolecules*, **23**, 4098 (1990).
- (31) J. -S. Kim, R. J. Jackman, and A. Eisenberg, *Macromolecules*, **27**, 2789 (1994).
- (32) J. -S. Kim, Y. H. Nah, and S. -S. Nah, *Polymer*, **42**, 5567 (2001).
- (33) Y. K. Itoh, Y. Tsujita, A. Takizawa, and T. Kinoshito, *J. Appl. Polym. Sci.*, **32**, 3335 (1986).
- (34) N. L. Thomas and A. H. Windle, *Polymer*, **21**, 613 (1980).
- (35) T. D. Gierke, G. E. Munn, and F. E. Wilson, *J. Polym. Sci., Polym. Phys.*, **19**, 1687 (1981).