

Desorption of Water Vapor in Hydrogen-Bonded Polymer Blends

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ABSTRACT: Successive desorption experiments of water vapor in poly(methyl methacrylate) (PMMA) were performed at temperatures from 31.0 to 45.0°C. The solubility of water in PMMA was found to be independent of temperature in agreement with literature findings. But the results for diffusion showed stronger dependence on water concentration than those in literature. The diffusion coefficients of water in PMMA became almost independent of temperature at high water concentrations. However, at lower water concentrations, the temperature effect on diffusion was more pronounced. The observed weak temperature dependence of diffusivity at high concentrations is likely due to a high degree of clustering of water molecules found in the PMMA we prepared. Two modified polystyrenes containing 5 and 15 mol %, respectively, 4-hydroxystyrene as comonomer units were blended with PMMA to form hydrogen-bonded polymer blends. Successive desorption experiments of water vapor in the hydrogen-bonded polymer blends were carried out at 31.0°C. The solubility of water in both blends was found to increase with increasing composition of PMMA. The diffusion coefficients for PMMA and its blends increased with increasing concentration of water first, reached a maximum, then decreased with water concentration. When the desorption results were plotted with the previous study of absorption, hysteresis phenomenon of sorption existed in all blend compositions for our experimental time span. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 39–45, 1998

Key words: desorption; hydrogen bond; polymer blend

INTRODUCTION

For most water–polymer systems, hysteresis is observed in the sorption isotherm. It is most striking with the natural fibers and proteins¹ for which reproducible time-independent hysteresis loops have been obtained over the entire or a limited range of relative pressures. For ethylcellulose and similar plastics,¹ the hysteresis is often time-dependent and associated with slow relax-

ation processes in the swelling or deswelling of the polymer matrix. For polymer blends, there are few reports about hysteresis in water sorption. Therefore, successive absorption and desorption experiments of water in polymer blends were conducted to study the effect of hysteresis.

In an earlier study,² successive absorption of water vapor in hydrogen-bonded polymer blends was reported. Modified polystyrenes containing 5 and 15 mol % of 4-hydroxystyrene as comonomer units were blended with poly(methyl methacrylate) (PMMA) to be cast into films. The polymer blends were miscible, based on the criteria of the transparency of the films and a single glass tran-

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sition temperature for each composition of the blends. The diffusion of water was found to decrease with the increasing concentration of the diffusant. Clustering of water molecules in the polymer rendered a fraction of the sorbed water comparatively immobile. A partial immobilization model was used to estimate the diffusion coefficient of the clusters. Interpolymer hydrogen bonding acted as physical crosslinks, which decreased the diffusivity of clusters. However, the positive excess volume of mixing for one blend composition seemed to have nullified the restrictive effect of hydrogen bonding on cluster diffusivity.

The study has now been extended to successive desorption in the same blends because the diffusion coefficients based on desorption are often different from those from absorption.³ Therefore, the study on desorption can offer additional information, and hysteresis can also be investigated. In this article, solubility and diffusivity measurements of water vapor in the hydrogen-bonded polymer blends were reported, and the effect of clustered water, interpolymer hydrogen bonding, and other factors on diffusivity are presented.

EXPERIMENTAL

Materials

The two poly(styrene-co-p-hydroxystyrene) (PHS) copolymers containing 5 and 15 mol % of hydroxystyrene were designated as PHS-5 and PHS-15, and their syntheses were described previously.⁴

The M_n and M_w/M_n values for PHS-5 and PHS-15 are $8.49 \cdot 10^4$ and 1.70, and $8.56 \cdot 10^4$ and 1.47, respectively. For PMMA, the M_n and M_w/M_n values are $4.64 \cdot 10^4$ and 2.01.

Thin films of individual polymers and their blends [PMMA/PHS-5 (80/20, 50/50); PMMA/PHS-15 (75/25, 50/50)] were prepared by solution casting, and the details of film preparation are described in Hsu et al.²

Vapor Desorption and Diffusion

The amount of water vapor in a polymer was measured by a Cahn 2000 microbalance. The sensitivity of the measurement was $\pm 1 \mu\text{g}$. The temperature of the sorption chamber was controlled to within $\pm 0.2^\circ\text{C}$. The successive desorption method was applied to study solubility and diffusivity.

RESULTS AND DISCUSSION

The desorption of water in the studied polymers was found to be Fickian, and the diffusion coefficients (D_d) were calculated from the initial slopes of the successive desorption curves.⁵ The diffusion coefficients obtained previously² from absorption were defined as D_a . The weight gain is defined as grams sorbed solvent per 100 g of dry polymer, and the relative pressure is the operating pressure divided by the saturated vapor pressure. The diffusion coefficients plotted versus the average concentration of water were used in the following

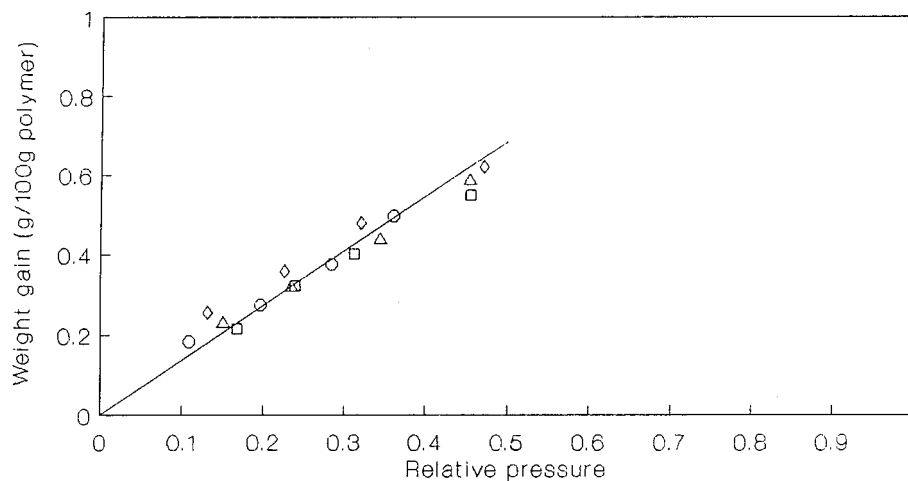


Figure 1 Desorption isotherm of water in PMMA at 4 temperatures: (Δ) 31.0°C; (◇) 35.0°C; (□) 41.0°C; (○) 45.0°C; (—) regression line.

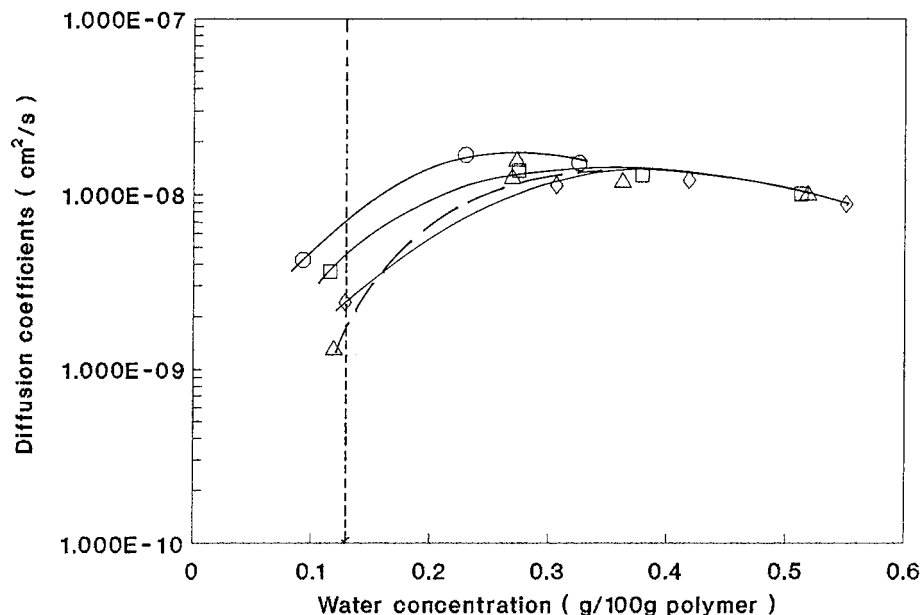


Figure 2 Diffusion coefficients of water in PMMA: (Δ) 31.0°C; (\diamond) 35.0°C; (\square) 41.0°C; (\circ) 45.0°C.

discussion. All the curves (except the regression line) in the figures were drawn for viewing the data only.

Desorption of Water Vapor in PMMA

Successive desorption experiments of water vapor in PMMA were carried out at 31.0, 35.0, 41.0, and 45.0°C. The solubility results are shown in Figure 1. Basically, the desorption isotherm is independent of temperature. At 0.5 relative pressure, 100 g of PMMA absorbs 0.7 g of water, in good agreement with literature values.⁶⁻⁸ Brauer and Sweeny⁹ also found that desorption of water in PMMA is nearly independent of temperature from 0 to 60°C.

The diffusion coefficients of water in PMMA are shown in Figure 2. The dependence of diffusivity on concentration is similar at 4 different temperatures. The diffusion coefficients increase with increasing concentration of water first, reach a maximum, then decrease with water concentration. For the same system, Bueche⁶ found that desorption data gave a constant diffusivity. The difference between our results and Bueche's may be due to different sample preparation procedures. Due to the strong water concentration dependence of diffusion, the temperature effect on diffusion is not obvious. At high concentrations of water (above $C = 0.35$), the diffusion coefficients

become almost independent of temperature (that is, the temperature dependence of the diffusion coefficients at high solvent concentrations is weak). The temperature effect on the diffusivity is more pronounced at lower water concentrations. According to the previous study,² absorbed water forms more clusters at higher water concentrations in PMMA. The weak temperature dependence of the diffusion coefficients at high water concentrations maybe due to comparatively immobilized water clusters desorption.

For accurate estimation of activation energy of diffusion, the diffusion coefficients at zero solvent concentration should be needed. Our data were insufficient for extrapolation to zero solvent concentration, so we tentatively used the diffusivity at C equal to 0.125 as a reference point. The diffusion coefficients at the reference concentration are listed in Table I. The activation energy of

Table I The Diffusion Coefficients of Water in PMMA at C Equal to 0.125

T (°C)	D (10^{-9} cm ² /s)
45.0	6.92
41.0	4.07
35.0	2.40
31.0	1.45

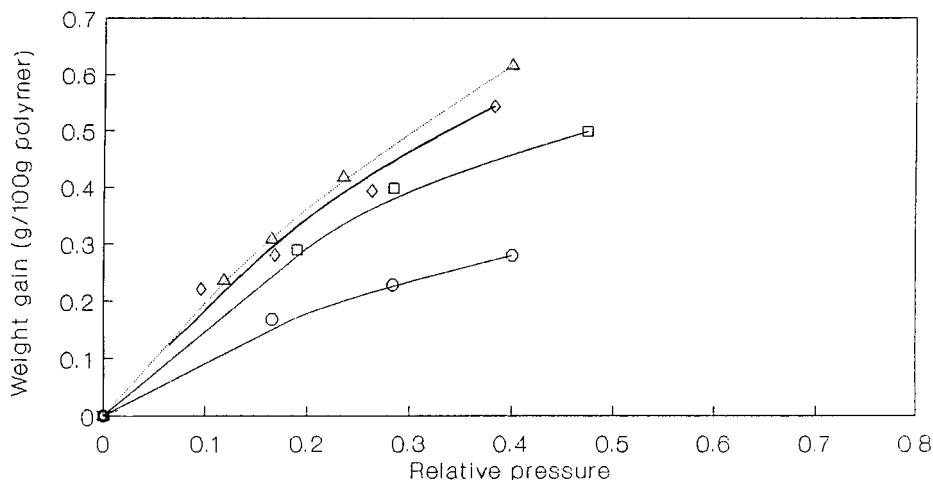


Figure 3 Desorption isotherm of water in PMMA-PHS-5 blends at 31.0°C: (Δ) PMMA; (\diamond) PMMA-PHS-5 (80/20); (\square) PMMA-PHS-5 (50/50); (\circ) PHS-5.

diffusion of water in PMMA is estimated to be about 19.7 Kcal/mol, which is much higher than literature value of 10.0 Kcal/mol.^{6,10}

Desorption of Water Vapor in the PMMA-PHS-5 Blends

The desorption isotherm is shown in Figure 3. PMMA absorbs more water than PHS-5, and water solubility in their blends increases with increasing composition of PMMA. All the solubility

curves are concave downward, except the solubility curve of PMMA, which is almost linear.

The diffusion coefficients versus solvent concentration are plotted in Figure 4. In most polymer compositions, the diffusivity first increases with increasing concentration, goes through a maximum, then decreases. Although there are only 2 data points of diffusivity for PHS-5, it is likely that the diffusion coefficients of PHS-5 are going to decrease at high solvent concentrations. It is interesting to notice that the diffusion coef-

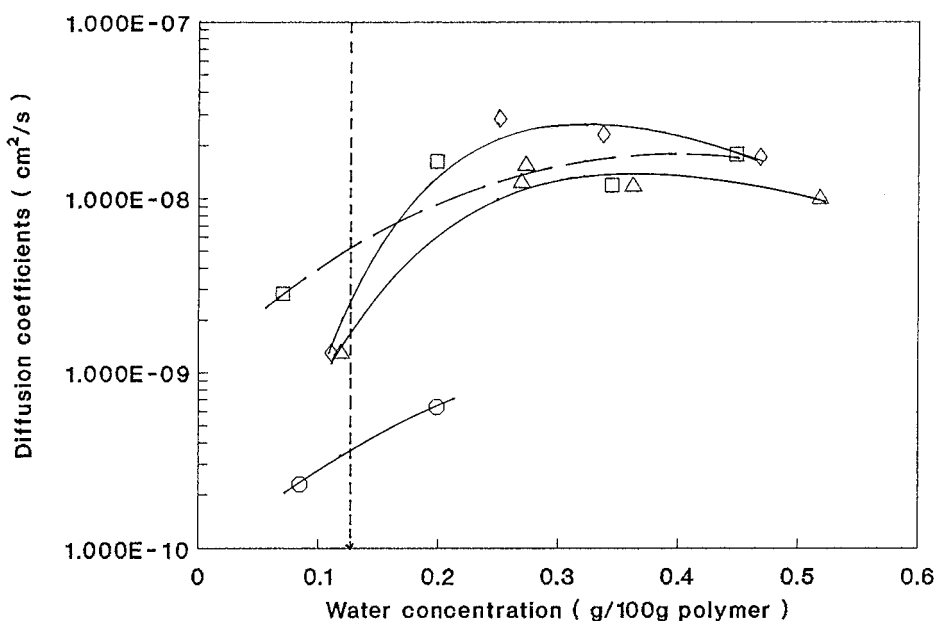


Figure 4 Diffusion coefficients of water in PMMA-PHS-5 blends at 31.0°C (symbols as in Fig. 3).

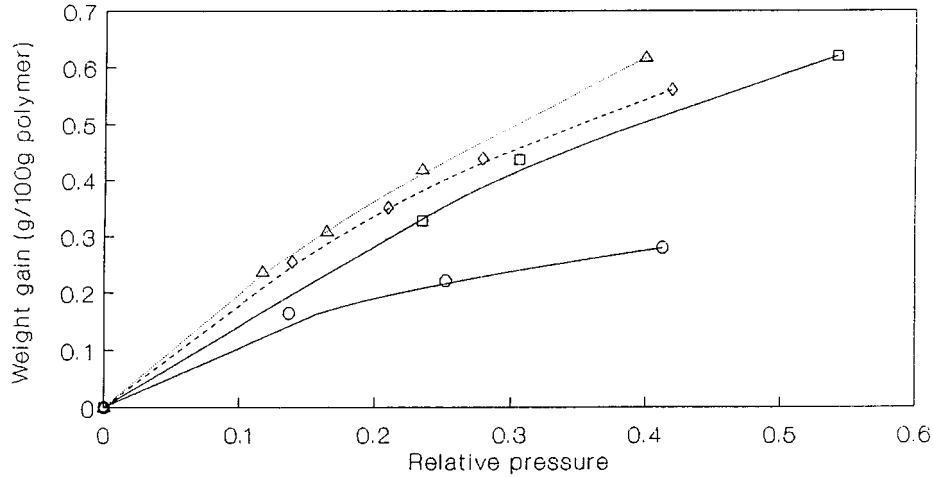


Figure 5 Desorption isotherm of water in PMMA-PHS-15 blends at 31.0°C: (Δ) PMMA; (◇) PMMA-PHS-15 (75/25); (□) PMMA-PHS-15 (50/50); (○) PHS-15.

ficients of PMMA/PHS-5 (80/20 and 50/50) are slightly higher than those of PMMA, even though the diffusion coefficients of PHS-5 are lower than PMMA. However, we do not have a simple, convincing explanation for this observation.

Desorption of Water Vapor in the PMMA-PHS-15 Blends

The desorption isotherms of the PMMA-PHS-15 blends are shown in Figure 5. Obviously, PHS-15

absorbs more water than PHS-5 because of a higher number of hydroxyl groups. The solubility of water in polymers can be arranged in the following order: PMMA > PMMA-PHS-15 (75/25) > PMMA-PHS-15 (50/50) > PHS-15. The desorption isotherm is again concave downward. The diffusion coefficients of water are shown in Figure 6. The concentration dependence of the diffusivity is similar to that of the PMMA/PHS-5 blends. Although the diffusion coefficients of PHS-15 are much larger than those of PMMA, the diffusion

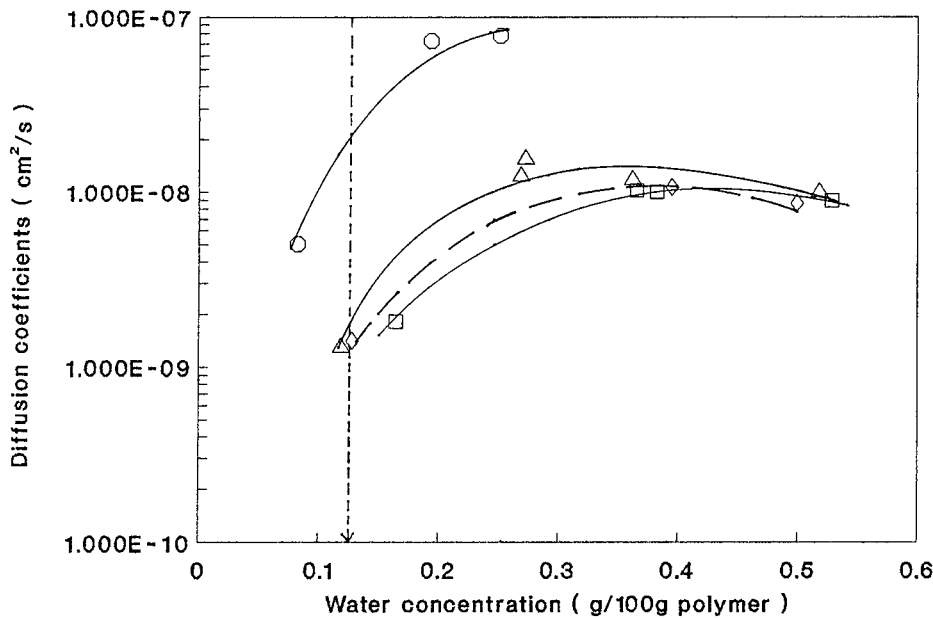


Figure 6 Diffusion coefficients of water in PMMA-PHS-15 blends at 31.0°C (symbols as in Fig. 5).

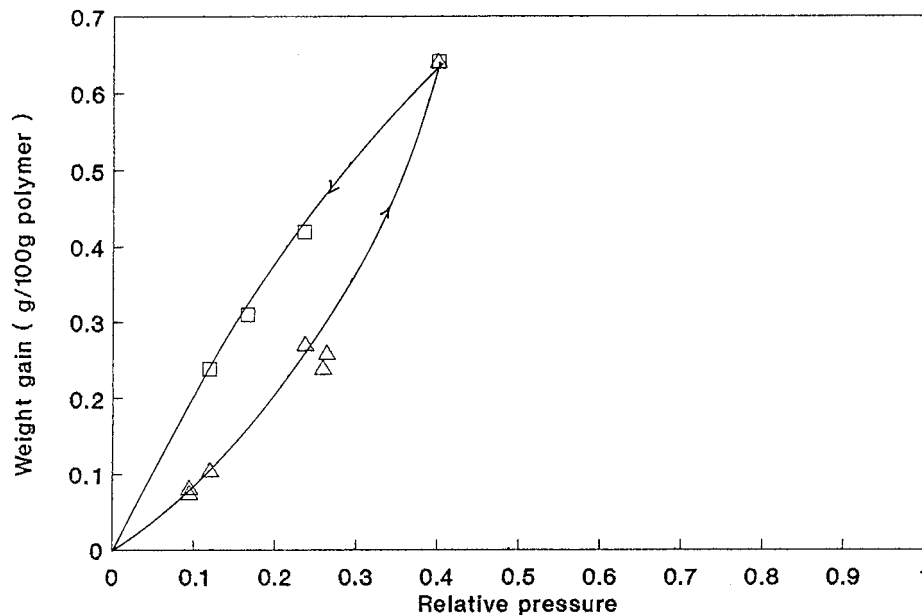


Figure 7 Hysteresis phenomenon of water sorption in PMMA: (Δ) absorption; (□) desorption.

coefficients of PMMA-PHS-15 (75/25 and 50/50) are slightly smaller than those of PMMA. The low diffusion coefficients of PMMA-PHS-15 (75/25 and 50/50) may be due to a large number of hydrogen bonds formed between PMMA and PHS-15.

Hysteresis Phenomenon

When the desorption isotherms of this study are compared with the absorption isotherms in Hsu et al.,² it is found that hysteresis phenomenon exists in all polymer compositions for the experi-

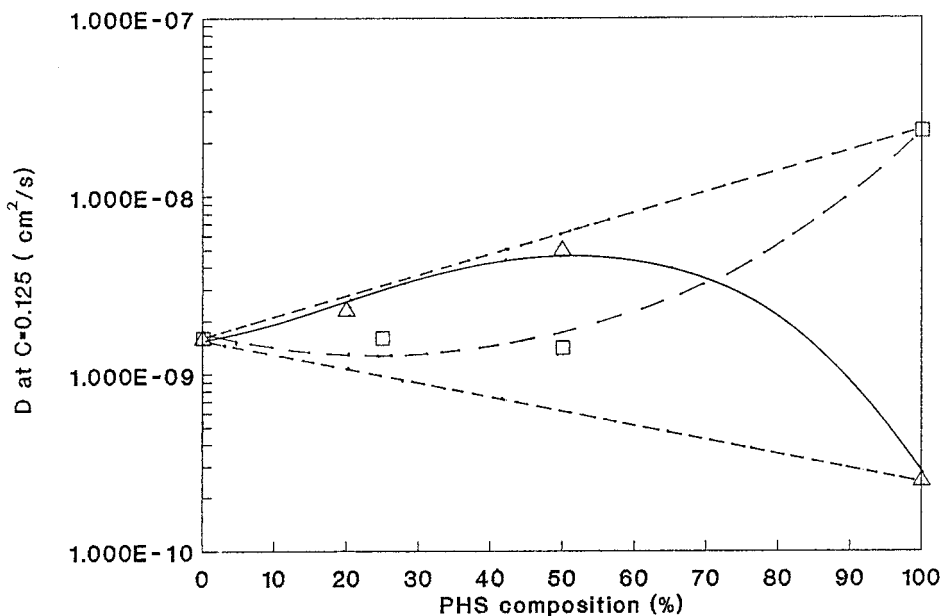


Figure 8 Diffusion coefficients of PMMA-PHS-5 and PMMA-PHS-15 blends at C equals 0.125: (Δ) PMMA-PHS-5; (□) PMMA-PHS-15.

mental time period. Because of the limited amount of data, we are not sure that hysteresis in our systems is time-independent or not. Representative desorption and absorption isotherms of PMMA are shown in Figure 7. Barrie and Platt⁷ also found that hysteresis existed in their study of water vapor in PMMA, although the difference between sorption and desorption in their results is smaller than ours. For the same system, Brauer and Sweeny⁹ reported a similar type of hysteresis. The larger difference between sorption and desorption in our results is possible owing to a higher degree of clustering of water molecules found in the studied PMMA. Recently Schult and Paul¹¹ found hysteresis in water sorption in blends of poly(vinyl pyrrolidone) and polysulfone. Berens¹² proposed that the true equilibrium isotherm lies approximately midway between that for sorption and desorption and would be reached after very long sorption or desorption times. Time long enough to test this proposal was not used in the sorption–desorption experiments presented here.

Composition Dependence of Diffusivity at C Equal to 0.125

Because extrapolation of diffusivity to zero water concentration is not feasible in our study, diffusivity at the reference concentration ($C = 0.125$) is tentatively used. The diffusivity at C equal to 0.125 of these 2 blends taken from Figures 4 and 6 are plotted versus PHS composition and shown in Figure 8. For the PMMA–PHS-5 blends, the diffusivities are above those predicted by the additivity rule, similar to previous findings by absorption.² For the PMMA–PHS-15 blends, the diffusivities are lower than those predicted by the additivity rule, which is different from previous finding that D_a values follow the additivity rule quite well.² It is possible that the diffusivities of PMMA–PHS-15 (75/25 and 50/50) when extrapolated to zero water concentration are larger than that of PMMA. Then the results will be closer to the additivity rule. The free volume theory was used previously in explaining the deviation of zero water absorption diffusivities in the PMMA–PHS-5 and PMMA–PHS-15 blends qualitatively.² Owing to strong concentration dependence of diffusivity obtained from desorption, the extrapolation to zero water concentration is much more inaccurate in desorption than in absorption.

Therefore, no attempt was made on fitting desorption diffusivity with any theory.

CONCLUSIONS

The desorption of water in PMMA is independent of temperature from 31.0 to 45.0°C. For PMMA, the diffusion coefficients of water have a stronger dependence on temperature at lower water concentrations. However, at high water concentrations, the temperature effect on diffusion is weak. The weak temperature dependence of diffusivity is likely due to the immobilization effect caused by a large number of water clusters formed at high concentrations. The solubility of water in the PMMA–PHS-5 and PMMA–PHS-15 blends increases with increasing composition of PMMA in the blends. The concentration dependence of the diffusion coefficients from desorption in these 2 blends are more complex than that from absorption. The diffusion coefficients for PMMA and its blends first increase with increasing diffusant concentration, reach a maximum, then decrease with concentration. Hysteresis exists in all blend compositions for the experimental time period.

REFERENCES

1. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968, Chap. 8 and references therein.
2. W. P. Hsu, R. J. Li, A. S. Myerson, and T. K. Kwei, *Polymer*, **34**, 597 (1993).
3. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968, Chap. 3.
4. K. J. Zhu, S. F. Chen, Tai Ho, E. M. Pearce, and T. K. Kwei, *Macromolecules*, **23**, 150 (1990).
5. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968, Chap. 1.
6. F. Bueche, *J. Polym. Sci.*, **14**, 414 (1954).
7. J. A. Barrie and B. J. Platt, *J. Polym. Sci.*, **4**, 303 (1963).
8. P. P. Roussis, *J. Membr. Sci.*, **15**, 141 (1983).
9. G. M. Brauer and W. T. Sweeny, *Mod. Plast.*, **32**, 138 (1955).
10. T. C. Gsell, E. M. Pearce, and T. K. Kwei, *Polymer*, **32**, 1663 (1991).
11. K. A. Schult and D. R. Paul, *J. Polym. Sci., Part B: Polym. Phys.*, **35**, 655 (1997).
12. A. R. Berens, *J. Macromol. Sci., Phys. Ed.*, **14**, 483 (1977).