

# Determination of Diffusion Coefficient of Water in Polymer Films by TGA

TOSHIO OGAWA,\* TOSHIO NAGATA, and YOSHIKAZU HAMADA

Laboratory for Material Design Engineering, Kanazawa Institute of Technology,  
7-1, Ohgigaoka Nonoichi, Ishikawa 921, Japan

## SYNOPSIS

This study is concerned with the determination of the diffusion coefficient of water into polymer films using a thermogravimetric analyzer (TGA). First, the sample film in the sample chamber was dried completely by N<sub>2</sub> gas supplied by a cylinder. Next, the mixture of air and N<sub>2</sub> gas having a given humidity was introduced into the sample chamber of the TGA. The sample weight was recorded as a function of time. The diffusion coefficient was calculated from the initial slope of weight vs. the square root of the time curve. The results were consistent with those obtained using Prager and Long's method. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polymeric materials absorb water at varying rates. Various properties, such as mechanical properties and corrosion, vary with the absorption of water. This is because most organic polymers have an affinity for water. Because of this affinity, it is very important to determine the degree of water absorption and the diffusion coefficient of water in polymeric materials. The measurement of the former quantity is easy, whereas that for the latter one is not. The diffusion coefficient requires an accurate weight measurement of the polymeric material itself. Typically, the sample weight is measured by the extent to which a spring expands when the sample is suspended from it, as in Prager and Long's method.<sup>1</sup> Pressure and vacuum controls are required for such procedures and the instrumentation is complicated and expensive.

A thermogravimetric analyzer (TGA) has been usually applied to detect the weight loss of a sample with the increase of temperature under a given atmosphere. This instrument is excellent for measuring weight under given conditions. It will be possible to apply this instrument for determining the diffu-

sion coefficient without raising the temperature. We tried to use this apparatus for this purpose with some considerations. However, it is not easy to keep a vacuum within the sample chamber in TGA. Instead of that, in this study, the chamber was kept dry by supplying dry N<sub>2</sub> gas or air from a cylinder. After that, the mixture of air and N<sub>2</sub> gas having a given humidity was introduced into it. The sample weight was recorded as a function of time. The diffusion coefficient was calculated from the initial slope of weight vs. the square root of the time curve. In this study, these experiments were performed for nylon 6 and polyimide films.

## EXPERIMENTAL

### Materials

Nylon 6 and aromatic polyimide films were used for the measurement of the diffusion coefficient. These materials were supplied by Ube Industries (Tokyo, Japan), i.e., nylon 6 is 1022B and polyimide films are Upilex R and S, the thickness of which is 25  $\mu\text{m}$ . The chemical structure of the polyimides was shown in another paper.<sup>2</sup> The nylon 6 film was 30  $\mu\text{m}$  in thickness and was cut into strips of 8  $\times$  20 mm. Strips weighing approximately 70 mg were supplied for each measurement. Upilex films were cut into strips of 12  $\times$  20 mm and the strips weighing ap-

\* To whom correspondence should be addressed.

proximately 180 mg were supplied for each measurement. Sample films were dried in advance as completely as possible in a dry desiccator.

### Construction of the Sample Chamber

A TGA called the TAS 100 System (Rigaku Denki Co., Japan) was used for this purpose. The components of the sample holder and of the chamber are shown in Figures 1 and 2, respectively. The top of the glass pipe was covered with aluminum foil to facilitate the quick and complete exchange of atmospheric gas in the sample chamber. Furthermore, a baffle was attached to the entrance of gas for the same purpose as described above. Baffles having various holes were tried and the most suitable baffle was chosen. The sample size and weight should be as large as possible in order to measure with the greatest accuracy, i.e., experimental errors are minimized.

### Response Rate of Hygrometer

The following experiment was carried out to confirm the responsibility of the hygrometer produced by Chino Co. (Japan). First, the sensor was placed in an atmosphere of 0% RH. After showing the correct value, the sensor was moved to the atmosphere having a given humidity. Then, the humidity reading was recorded as a function of time. Thus, time responsibility of the sensor was examined ranging from 20 to 80% RH at 20°C. A typical curve for the time responsibility is shown in Figure 3. The responsibility usually changed slightly depending upon temperature and relative humidity. In any case, the measurement at a given humidity became ready in

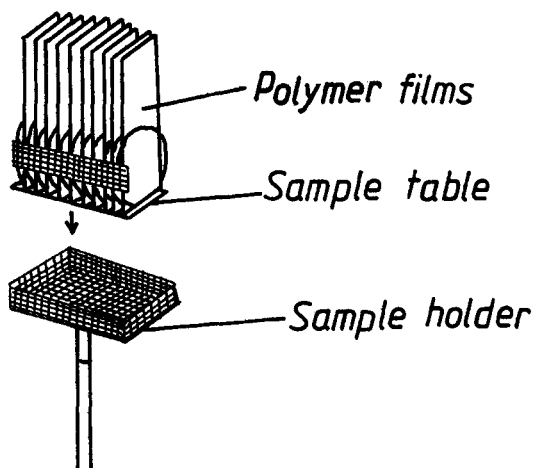


Figure 1 Mounting of polymer films on sample table.

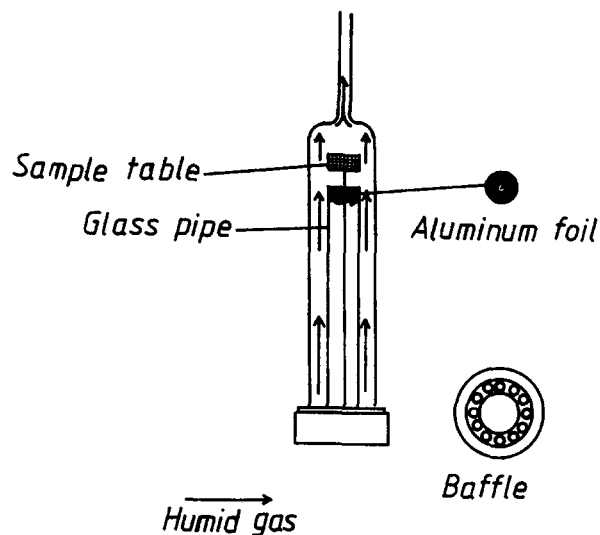


Figure 2 Components of sample holder in TGA.

3 or 4 min after switching the atmosphere. The correction curve for detecting true relative humidity must be prepared in advance based on the responsibility curve, as long as we use a commercial hygrometer.

### Generation of Atmospheric Gas Having a Given Humidity

The scheme for generating the gas is shown in Figure 4. Glass wool and water were put in the No. 1 bottle. High humidity gas was obtained in the No. 1 bottle. However, water droplets often were splashed and attached to the pipe. The No. 2 bottles were used to remove water droplets. These bottles were put into a water bath to keep the temperature constant. A

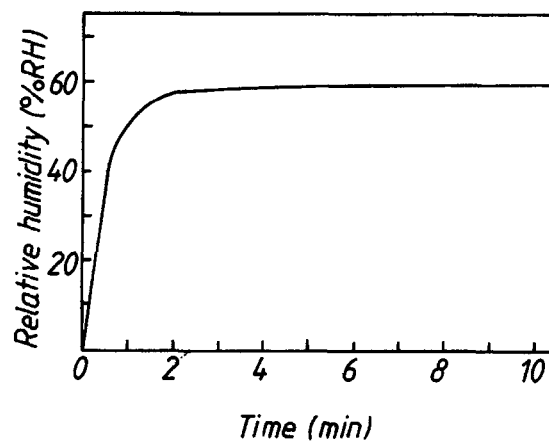
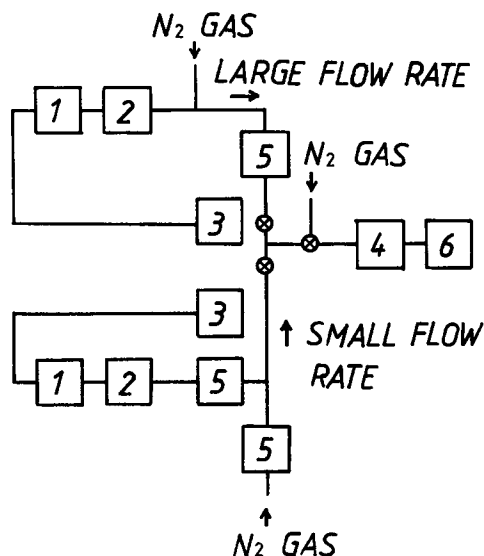


Figure 3 Reading of relative humidity detected by a hygrometer. Temperature: 20°C; relative humidity: 60%.

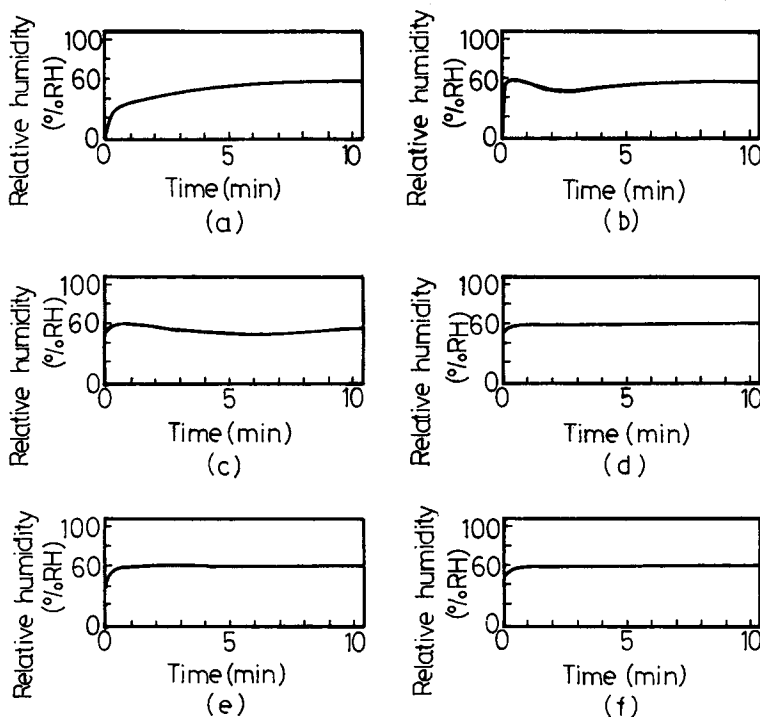


**Figure 4** Preparation of atmospheric gas having a given humidity: ① water and glass wool; ② glass wool; ③ air pump; ④ TGA (balance); ⑤ flowmeter; ⑥ hygrometer.

given humidity was attained by mixing humid gas and N<sub>2</sub> gas from a cylinder, where the humidity of N<sub>2</sub> gas is actually regarded as 0% RH.

### Introduction of Humid Gas into the Sample Chamber

Three different passages were prepared to introduce atmospheric gas into sample chamber, as shown in Figure 4. N<sub>2</sub> gas from a cylinder was supplied from one route, which was actually completely dry. High (1500 mL/min) and low (150 mL/min) flow rate gases were supplied from the remaining two routes, where the low flow rate was set so as to be equal to that of N<sub>2</sub> gas. If we supply humid gas at a low flow rate, it would take a long time to reach the required condition in the sample chamber and we could not measure an accurate diffusion coefficient. On the other hand, if we supplied only high flow rate gas into the chamber, then an accurate diffusion coefficient could not be measured due to the power of flow resistance and slight fluctuation of the balance. Thus, the actual experiment should be performed by the system of switching a high flow rate to a low one. Therefore, we tried to find the optimum flowing time for high flow rate gas. The result is shown in Figure 5. From these curves, the flowing time for the high flow rate gas was set at 3 min and the atmospheric gas was kept at low flow rate in the experiment.



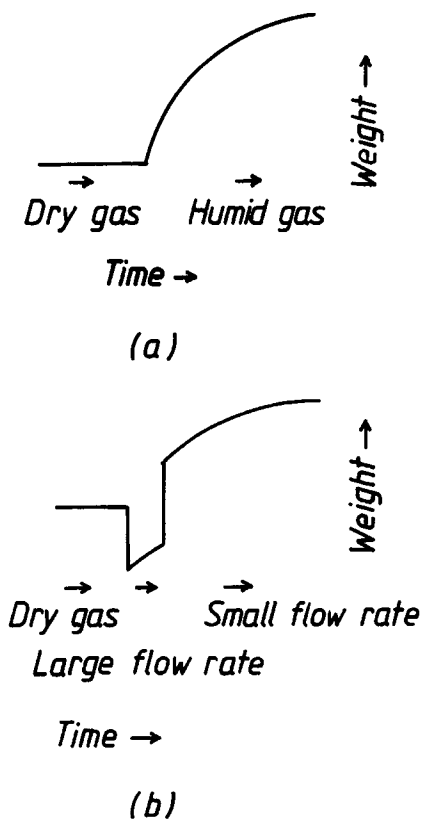
**Figure 5** Relationship between relative humidity and flowing time at high flow rate. After a given period of high flow rate, the rate was switched to the low one. Temperature: 20°C; relative humidity: 60%. (a) Only low flow rate. Time at high flow rate: (b) 1 min; (c) 2 min; (d) 3 min; (e) 4 min; (f) 5 min.

### Correction of Water-absorption Curve

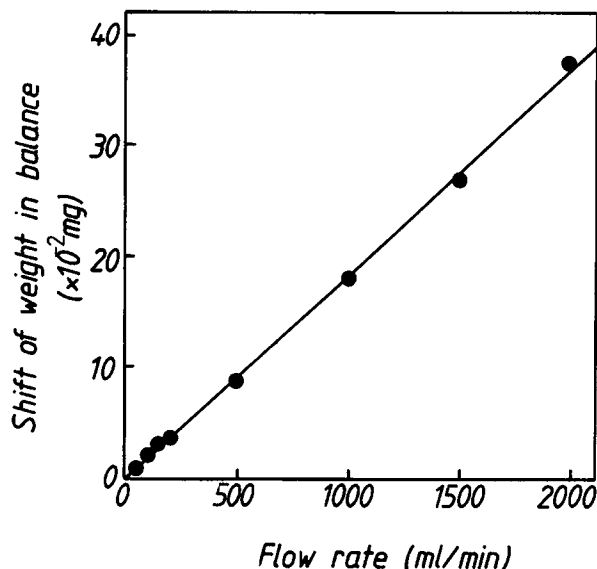
An ideal water-absorption curve of the film should be expressed graphically as in Figure 6(a). However, when the gas flowed in at a high flow rate, the apparent absorption curve was observed as depicted in Figure 6(b) due to the power of the flow resistance. Consequently, we determined in advance the relationship between the apparent weight and the flow rate of gas. The result is shown in Figure 7. This relationship would be variable depending upon the shapes of sample and of the table. However, sample films having very similar shapes are usually mounted through experiment. The relationship may be also influenced by the sample weight. We never significantly altered the weight. Thus, the apparent absorption curve was corrected by applying the above relationship.

### Measurement by Prager and Long's Method

Water-absorption measurements were carried out with an absorption balance using a quartz spring. Details of the apparatus and experimental proce-



**Figure 6** Time dependence of weight change: (a) ideal sorption curve; (b) experimental curve observed in this study.



**Figure 7** Apparent weight change due to power of flow resistance.

dures were described by Inoue and Hoshino.<sup>3</sup> The same apparatus was used in this study.

### DATA TREATMENT

The distribution of water in the film during absorption is expressed in the one-dimensional case of Fick's Second Law as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \quad (1)$$

where  $t$  is time;  $x$ , the coordinate in the direction of the film thickness;  $c$ , the concentration of water; and  $D$ , the diffusion coefficient of water in polymeric film. Equation (1) can be solved if initial and boundary conditions are given. In this study, the initial concentration of water in atmospheric gas is uniform throughout the film surface, i.e.:

$$C = C_0 \quad (-d < x < d, t = 0) \quad (2)$$

where  $d$  is the half-thickness of the film and the origin of the coordinate is fixed at the center of the film. Both surfaces of the film attain equilibrium as soon as the absorption begins. The boundary condition is expressed mathematically as

$$C = C_\infty \quad (x = -d \text{ and } d, t > 0) \quad (3)$$

The solution of eq. (3) is well known for these boundary conditions and constant  $D^4$ :

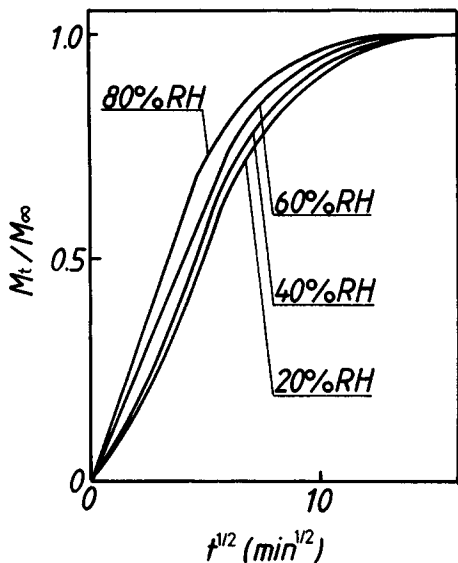


Figure 8 Absorption curves for nylon 6 film under various relative humidities (RH) at 23°C.

$$\frac{c}{c_\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\{-D(2n+1)^2\pi^2t/d^2\} \times \cos \frac{(2n+1)\pi x}{d} \quad (4)$$

If  $M_t$  denotes the total amount of water that is diffused in the film at time  $t$  for a given sample weight,

$$\frac{M_t}{M_\infty} = 4 \left( \frac{Dt^{1/2}}{d^2} \right) \times \left\{ \frac{1}{\pi^{1/2}} + 2 \sum_{n=0}^{\infty} (-1)^n \text{ierfc} \frac{nd}{2(Dt)^{1/2}} \right\} \quad (5)$$

where  $M_\infty$  is the total amount of water in the film at  $t = \infty$ . Usually, the absorption curve is obtained by plotting  $M_t/M_\infty$  against  $\sqrt{t}$ . From this curve, the diffusion coefficient is determined according to eq. (6), where  $I$  is the gradient of the initial slope:

$$D = \frac{\pi}{16} \cdot I^2 \cdot d^2 \quad (6)$$

The initial gradient of the absorption curve is constant, except for low relative humidity. For the latter case, the determination of the coefficient is obtained by the following equation,<sup>5</sup> where  $t_{0.5}$  means the time in  $M_t/M_\infty = 0.5$ :

$$D = 0.04919/(t_{0.5}/d^2) \quad (7)$$

## RESULTS AND DISCUSSION

### Nylon 6

Water-absorption curves for nylon 6 film under various relative humidities at 23°C are shown in Figure 8. The gradient of the absorption curves increases with the relative humidity. The gradient in the region of the initial time for 20 and 40% RH seems to vary slightly with time and Inoue and Hoshino<sup>6</sup> determined it according to eq. (7) for nylon 6. Therefore, we determined the diffusion coefficients of water by eqs. (6) and (7) in order to compare with the results of Inoue and Hoshino,<sup>3</sup> and the results are shown in Table I. There is no significant difference between these values. Therefore, data treatment procedures are not very important. The relationship between the diffusion coefficient and moisture regain is shown in Figure 9 together with the results from Inoue and Hoshino.<sup>3</sup> There is some discrepancy between these results. This is mainly due to the different temperatures used. Even if we adopted iden-

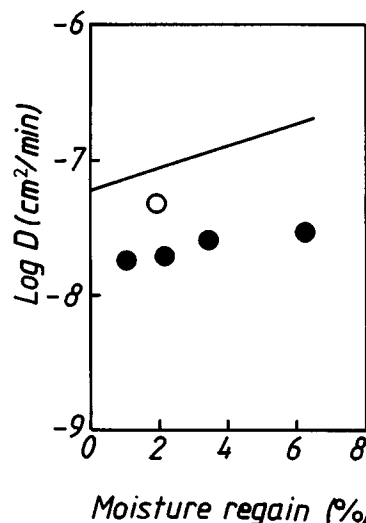
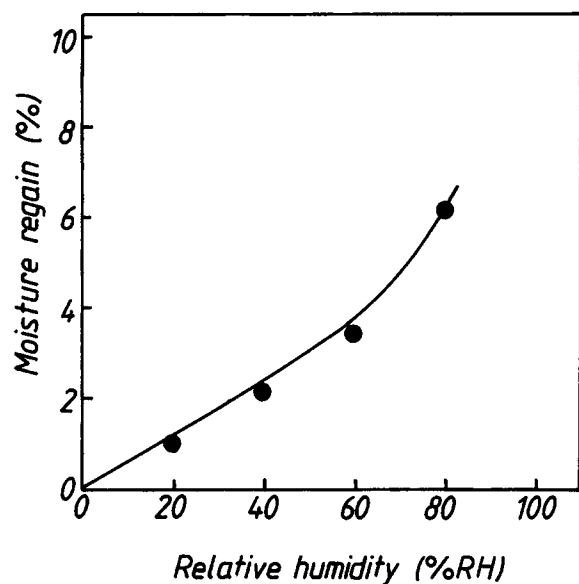


Figure 9 Diffusion coefficient vs. moisture regain: (—) obtained by Inoue and Hoshino<sup>3</sup> at 30°C; (●) obtained by TGA at 23°C; (○) obtained by TGA at 30°C.

Table I Diffusion Coefficients Obtained by Eqs. (6) and (7)

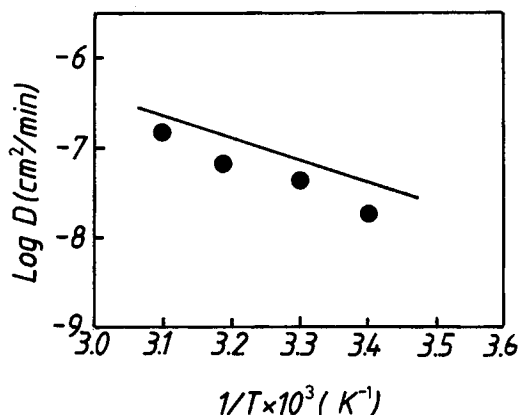
Temperature (°C)	D Obtained by Eq. (6) ( $\times 10^{-8}$ cm <sup>2</sup> /min)	D Obtained by Eq. (7) ( $\times 10^{-8}$ cm <sup>2</sup> /min)
20	2.10	2.05
30	4.75	4.92
40	6.51	6.45
50	13.36	13.38



**Figure 10** Relationship between moisture regain and relative humidity of atmospheric gas: (—) obtained at 30°C by Inoue and Hoshino<sup>3</sup>; (●) obtained at 23°C by TGA.

tical temperatures for this experiment, a slight discrepancy would be observed. Inoue and Hoshino used the nylon 6 film having a 42.1% degree of crystallinity, but we used the film having 43.1%. Therefore, a slightly smaller value in this study is reasonable.

The relationship between relative humidity and moisture regain is shown in Figure 10. The moisture regain increases slowly with relative humidity. The experimental values agree well with those obtained by Inoue and Hoshino<sup>6</sup> who used the same commercial nylon grade. The relationship between the



**Figure 11** Diffusion coefficient vs. reciprocal of absolute temperature for nylon 6: (—) obtained by Asada et al.<sup>7</sup> under 60% RH; (●) obtained by TGA under 40% RH.

**Table II** Activation Energy for Diffusion Coefficient of Water into Nylon 6 Film

	Activation Energy (kJ/mol)
Asada et al. <sup>7</sup>	50.43
TGA method in this study	51.06

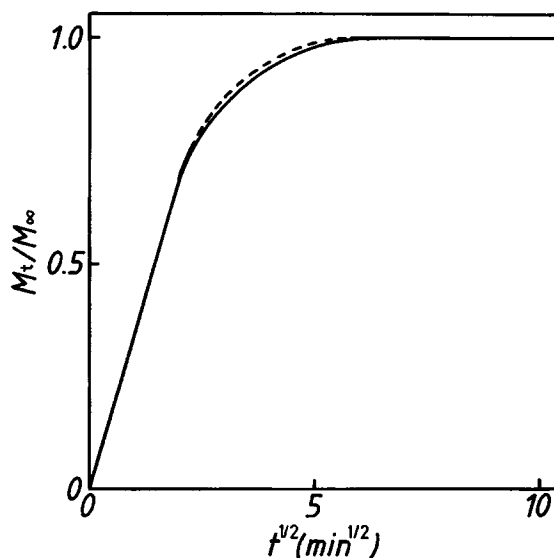
diffusion coefficient and the reciprocal of the absolute temperature was determined, as shown in Figure 11. This relationship can be expressed essentially by a straight line. Activation energy  $E$  for diffusion can be obtained by the Arrhenius equation.

$$D = A \cdot \exp(-E/RT) \quad (8)$$

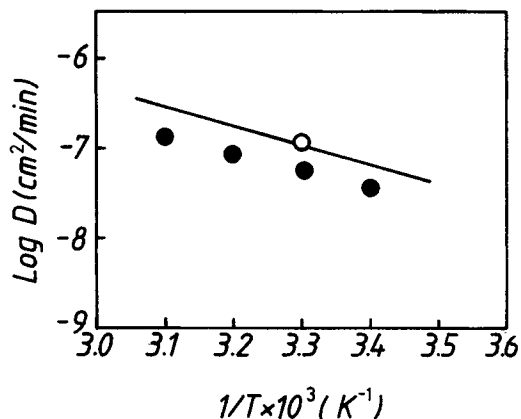
where  $A$  is a constant;  $R$ , the gas constant; and  $T$ , the absolute temperature. The result is shown in Table II together with that obtained by Asada et al.<sup>7</sup> The experimental value agrees well with that obtained by the traditional method.

### Upilex R and S

Aromatic polyimide films have a weak affinity for water as compared with that of nylons. Upilex R and S absorb water only  $\frac{1}{4}$  to  $\frac{1}{5}$  as much as does nylon 6. Therefore, some experimental difficulty might be present. However, the absorption curve obtained by TGA agreed well with those obtained by Prager and



**Figure 12** Absorption curves for Upilex S: (—) obtained by TGA; (----) obtained by Prager and Long's method.



**Figure 13** Diffusion coefficient vs. reciprocal of absolute temperature for Upilex R and S: (a) Upilex R under 60% RH (—); (b) Upilex S under 60% RH; (●) obtained by Prager and Long's method; (○) obtained by TGA.

Long's method, as shown in Figure 12. The relationship between the diffusion coefficient and the reciprocal of the absolute temperature agreed well with those obtained using Prager and Long's method. The result is shown in Figure 13. In other words, the result suggests that the activation energy for diffusion is similar for both. Therefore, the method by TGA is also applicable for low-absorption polymer films.

## CONCLUSION

We tried to determine the diffusion coefficient of water for nylon 6 and aromatic polyimide films by applying TGA apparatus. The results agreed well with those obtained using Prager and Long's method. Therefore, the TGA apparatus is very useful for determining the diffusion coefficient of water into polymer films, even for low-absorption ones.

## REFERENCES

1. S. Prager and F. A. Long, *J. Am. Chem. Soc.*, **73**, 4072 (1951).
2. T. Ogawa and H. Yamane, in *Polyimides: Materials, Chemistry and Characterization*, C. Feger, M. M. Khojasteh, and J. E. McGrath, Eds., Elsevier, Amsterdam, 1989, p. 601.
3. K. Inoue and S. Hoshino, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 1513 (1976).
4. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, London, 1956.
5. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968.
6. K. Inoue and S. Hoshino, *Kobunshi Ronbunshu (Jpn.)*, **36**, 517 (1979).
7. T. Asada, K. Inoue, and S. Onogi, *Polym. J.*, **8**, 21 (1975).

Received May 6, 1992

Accepted March 3, 1993