The Diffusion of Nonionic Penetrants in Polyamide

TAKAO SHIBUSAWA, *College of Technology, University of Gumma, Kiryu, Gumma Prefecture, Japan,* and TOSHIRO IIJIMA, *Polymer Chemistry Department, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan*

Synopsis

The diffusion behavior of nonionic penetrants in aqueous solution into nylon 6 was examined in the temperature range 5°–95°C. The Arrhenius plot of the diffusion coefficients is linear and its slope changes at 30°–40°C higher than the glass transition temperature in water, as determined by dilatometry and viscoelastic measurements. The results are discussed in relation to the molecular size of the penetrant and the segmental motion of polymer chains.

INTRODUCTION

It is known that the diffusion behavior of a penetrant in a polymer is influenced by transitions in the polymer substrate.[1-7] Thus, the dyeing process, that is, the diffusion of dye molecules in fibers in the presence of water, is affected by transition phenomena. A number of workers have studied the relationship between diffusion coefficients of dyes and transition in the substrate. Thus, Rosenbaum,[8,9] Hossain et al., [10,11] and Morita et al.[12] have examined polyacrylonitrile, Sprague,[13] cellulose acetate and Iwabori et al.,[14] cellulose triacetate.

In these studies it was recognized that an Arrhenius plot of diffusion coefficients changes in slope in the vicinity of the transition temperature of the substrate and that the activation energy of diffusion increases above that temperature. Such behavior is similar to that of gas molecules in polymers in the absence of water.[1,2] In the presence of water the transition temperature decreases, especially in the case of hydrophilic polymers.[15]

From measurements of viscoelastic properties of polyamide, Woodward et al.,[16] Becker et al.,[17] and Illers[18] found that the glass transition temperature (T_g) is 60°–80° C lower in the wet state than in the dry state. This was also confirmed by Bryant et al.[15] by resilience measurement of nylon 6,6. From these observations it follows that the T_g of nylons 6 and 6,6 in water should be in the region between 0°C and −10°C.

Bell[19] observed that in the relation between mechanical properties of nylon 6,6 and the diffusion behavior of an acid dye, an Arrhenius plot of diffusion coefficients fell on a curve similar to that of cationic penetrants in polyacrylonitrile above the T_g. These results agree with Fujita's equation,

which was derived in a manner similar to that of the WLF equation. Furthermore, he concluded that the rate of diffusion is related to time-dependent mechanical properties such as creep and stress relaxation which are governed by the segmental mobility of the polymer chains. When diffusion is strongly concentration-dependent, as in the case of acid dyes, great care must be exercised in the interpretation of apparent diffusion coefficients.[20]

In a study of diffusion of disperse dyes in nylon 6, Nishio[21] found that an Arrhenius plot of diffusion coefficients of p-aminoazobenzene gave a straight line which changed in slope at 30°C, a result which is incompatible with that found in the case of acid dye diffusion described above. In the present work, nonionic penetrants were used to elucidate the temperature dependence of diffusion of dyes in water-swollen polyamide.

EXPERIMENTAL

Materials

The nylon 6 film was prepared by Unitika Ltd. by extrusion and biaxial drawing and had the following properties: thickness, $27 \pm 0.3 \mu$; crystallinity, 46% (by density measurements); $\bar{M}_v$, 1.41×10^4.

The film was rinsed with a solution of a nonionic surfactant and soaked in water at 95°C for 25 hr prior to the experiment.

Penetrants

The penetrants used were analytical-grade p-nitroaniline (PNA) and p-aminoazobenzene (PAAB) and C. I. Disperse Yellow 1 (DY), which was purified by repeated crystallization from ethanol. The purity was then tested by paper chromatography and by elemental analysis which gave 15.2% N(calc. 15.3% N). The stability of the penetrants in water in the temperature range required was checked by preliminary experiments.

The concentration profile of penetrants in nylon 6 was obtained by the cylindrical film roll method[22] by rolling a strip 3×50 cm on a glass rod 1 cm in diameter in water at 40°C and securing the end of the film strip with a small glass rod by means of cotton yarn. After keeping the film roll in the dyebath for a certain time at a given temperature, the film was unrolled and dried. The concentration of penetrant in each layer was determined colorimetrically by means of a Shimadzu SV-50A recording spectrophotometer. Beer's law was found to hold on the film for the penetrants used. The diffusion coefficients and surface concentrations of the penetrants were calculated from the concentration profile by means of Sekido and Matsui's method.[22]

Dilatometry

Dilatometry of the dried specimen was carried out by the usual method. In the case of the wet specimen, a modified dilatometer was used (Fig. 1).
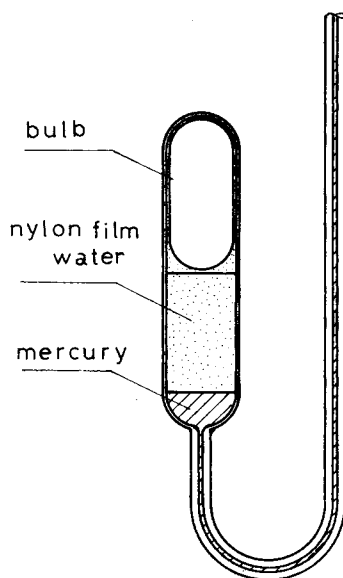
Fig. 1. Dilatometer.

The wetted specimen was enclosed in the bulb which was then cooled to 0° C and evacuated. After evacuation, cold water and mercury were introduced. The rates of temperature increase were 0.5°C/min for the dry specimen and 0.2°C/min for the wetted specimen.

Dynamic Loss Measurement

The loss factor, tan δ, and the dynamic modulus, $|E|$, were determined by means of a Vibron DDV-1 (Toyo Measuring Instrument Co. Ltd.). During the measurement in the dry state, care was taken to avoid moisture adsorption by placing silica gel in the specimen chamber. Wet cotton gauze was used in the case of the wet specimen. Measurements were carried out at 11, 35, and 110 cps at 1% initial strain. The temperature was increased at the same rate as in the case of dilatometry.

RESULTS

The diffusion profiles are shown in Figure 2 and indicate that the diffusion coefficients are independent of the concentration of penetrants in the polymer. The surface concentration during diffusion seemed to keep fairly constant. However, DY showed marked surface adsorption, the cause of which is not clear. In this particular case, the diffusion coefficient was calculated neglecting the first layer of the roll.

The diffusion coefficient of the dyes in polyamide is increased by hot water treatment as a result of change in the fine structure.[23] Therefore, it was necessary to ascertain the stability of the fine structure during the experiment. Figure 3 shows diffusion coefficients of PNA in polyamide
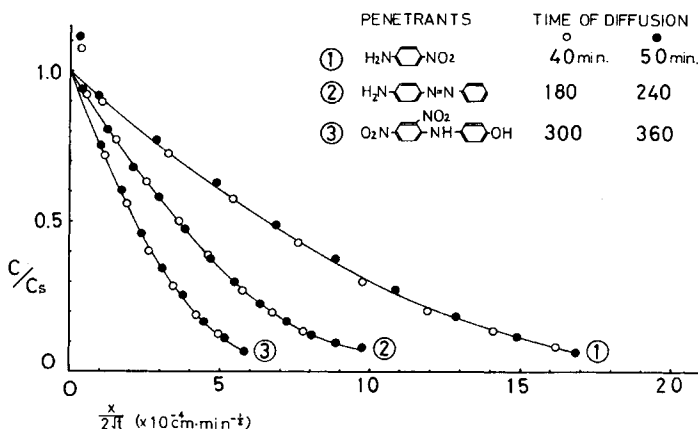
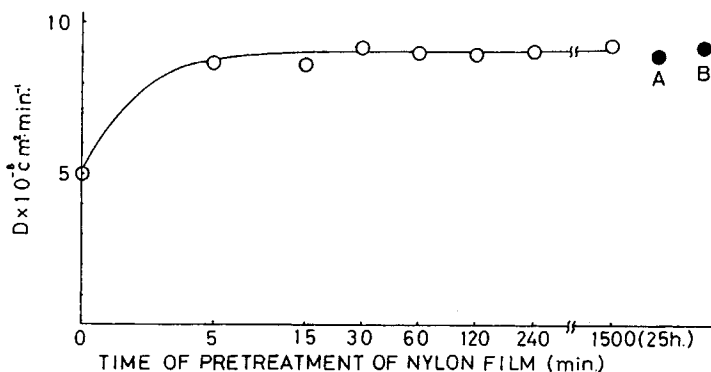Fig. 2. Concentration profile of nonionic penetrants in nylon 6 (80°C).

Fig. 3. Diffusion coefficient of p-nitroaniline in nylon 6 (40°C).
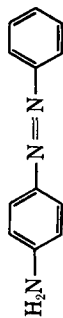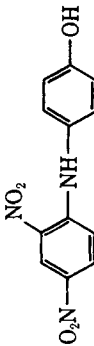A: Treated in water 95°C, 25 hr, 15°C, 105 days.
B: Treated in water 95°C, 25 hr, in vacuo 95°C, 45 hr.

which has been treated in various ways. As a result of these experiments, it was concluded that the fine structure of the film treated for 25 hr at 95°C was unaltered during the diffusion experiments.

An Arrhenius plot of the results, shown in Figure 4, indicates that the points fall on a straight line with a change in slope at 32°C for PNA, 35°C for PAAB, and 40°C for DY. The results are summarized in Table I. During the diffusion experiment, the concentration of a penetrant at the outer surface of the film roll, $[P]_F$, was maintained constant and this corresponds to the equilibrium concentration of adsorption against the concentration in the solution, $[P]_S$. $[P]_S$ and $[P]_F$ are known and hence the partition coefficient K and the apparent standard affinity $\Delta\mu°$ can be calculated as follows:

$$-\Delta\mu° = -RT \ln K = -RT \ln \frac{[P]_F}{[P]_S}$$

TABLE I
Diffusion Profiles of Penetrants PNA, PAAB, and DY

	PNA	PAAB	DY
	$O_2N-\!\!\!\bigcirc\!\!\!-NH_2$	$H_2N-\!\!\!\bigcirc\!\!\!-N=N-\!\!\!\bigcirc$	$O_2N-\!\!\!\bigcirc\!\!\!-NH-\!\!\!\bigcirc\!\!\!-OH$ (with NO_2)
Molecular weight	183.12	197.24	275.23
Molecular volume,[a] Å³	118.	204	410
Critical temperature,[b] °C	32	35	40
Ed above crit. temp, kcal/mole	17.0	17.9	19.5
Ed below crit. temp, kcal/mole	20.3	23.8	22.1

[a] Volume of rectangular prism enclosing the molecule.
[b] The temperature at which Ed changes.
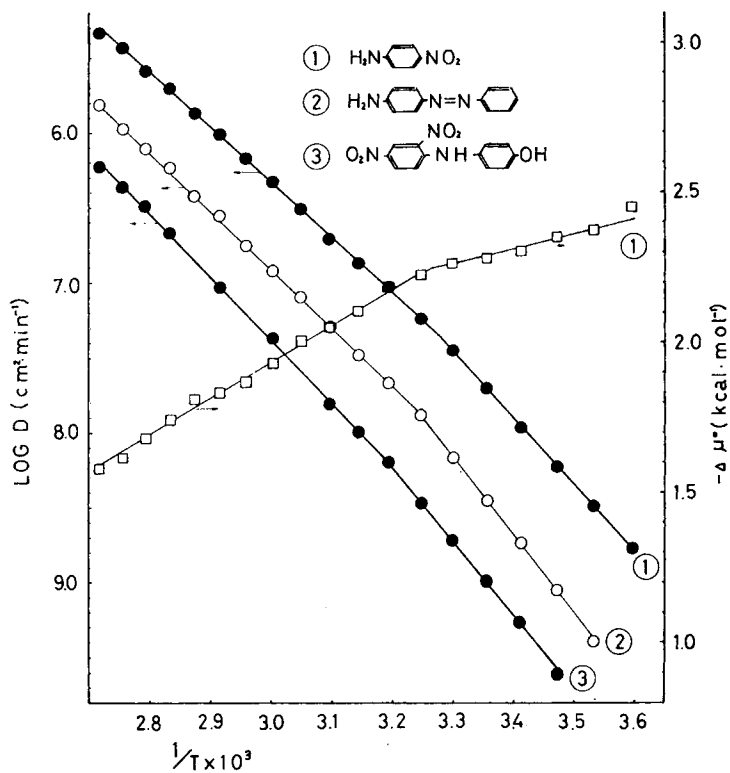
Fig. 4. Log D and $-\Delta\mu°$ vs. reciprocal temperature.

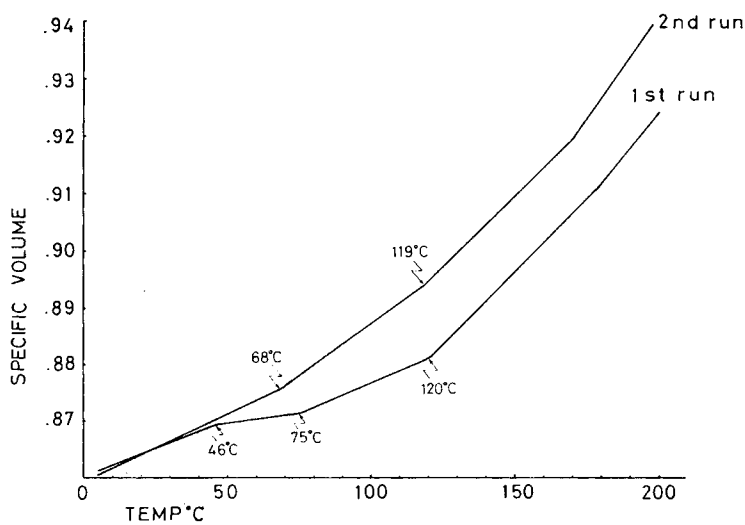Fig. 5. Dilatometry of dried specimen.

A plot of $\Delta\mu°$ for PNA against reciprocal temperature is shown in Figure 2 and gives a straight line, with a change in slope at about 30°C. In view of the above results, it seemed reasonable to deduce that some kind of transition takes place in the wet state at or near this critical temperature.

The relation between the specific volume of the dry specimen and temperature is shown in Figure 5. Remarkable discontinuities in the slopes can be observed at 46°, 75°, and 110°C. The first may be due to relaxation of the highly oriented state of the specimen, since it disappeared in the second run of the measurements. Furthermore, the same kind of discontinuity at the same temperature was not observed for a nylon chip. The change in slope at 75°C is the glass transition temperature of the film. This is in accord with data reported earlier[5,16,17,24] and also with dynamic mechanical
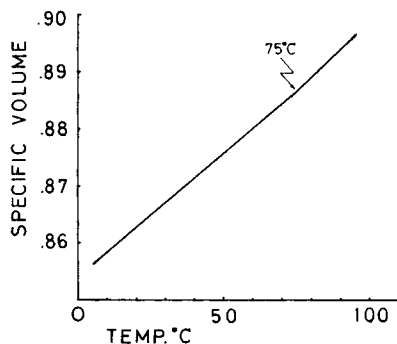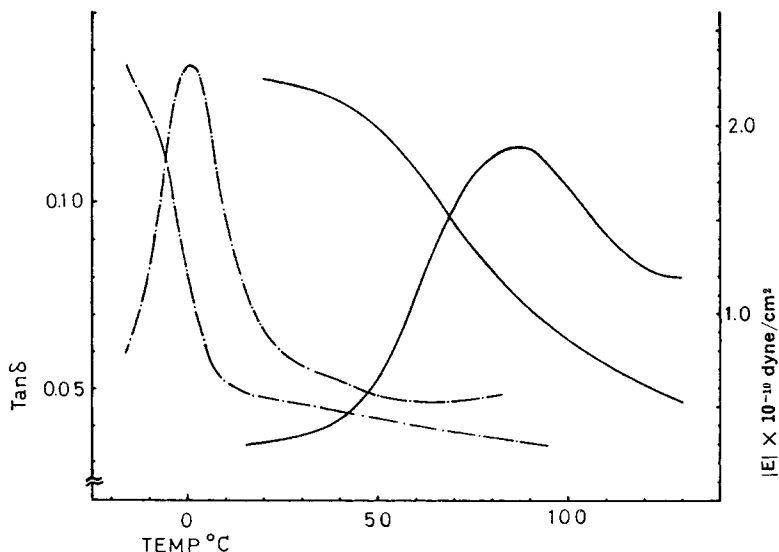

Fig. 6. Dilatometry in water.

Fig. 7. Change of viscoelastic properties in presence of water: (—) dry specimen; (−·−·−) wet specimen.

properties of the film. The change at near 110°C was attributed[24] to a transition from the β to the α crystal form.

The results of dilatometry on the wet specimen are shown in Figure 6. No change in the slope was observed in the temperature range 30°–40°C, at which a change of activation energy of diffusion was observed (Fig. 4). Figure 7 shows the temperature characteristics of the loss factor, tanδ, and the dynamic modulus, $|E|$, for wet and dry specimens at 11 cps. The loss peak temperatures at 1 cps obtained by extrapolation were 75°C for the dry specimen and 0°C for the wet specimen.

The above data suggest that the glass transition temperatures in water of the nylon 6 used is ca. 0°C.

DISCUSSION

The activation energy of diffusion, Ed, was 3.3–5.9 kcal/mol less above the critical point than below (Table I). A similar pattern in diffusion behavior was found for nonionic penetrants in drawn polyethylene terephthalate.[25,26] In the case of disperse dyes in undrawn secondary acetate filaments[13] and triacetate film,[14] the increase in activation energy above the point was 19–23 kcal/mol. A similar pattern was observed in the diffusion of gas molecules in the polymer[1,2,6,7] and of sulfuric acid in undrawn nylon 6 film.[28] By stretching the undrawn secondary acetate fibers 200%, the activation energy of diffusion below the T_g was increased from 11 kcal/mol to 21.8 kcal/mol[13] and consequently the difference between the activation energies (Ed) above and below the T_g was diminished. The results lead us to the conclusion that the large increases in Ed below the T_g point is due to the diffusion of large penetrant molecules in the highly oriented po'ymer. We can see (Table I) that the temperature at which the slope changes decreases with decrease in the molecular size of the penetrant and should approach the T_g in water with further decrease in penetrant size. A similar tendency was found by Hossain et al.[11] in the diffusion of cationic penetrants in polyacrylonitrile. The observed phenomena could be interpreted by suggesting that a rather large segmental movement is required by relaxation to permit the diffusion of penetrants of a certain volume. An abrupt increase in the free volume occurring at T_g is detected as a discontinuity in the volume-versus-temperature relation and reflects viscoelastic behavior. On the other hand, the diffusion of penetrant of a certain volume requires the existence of a certain space for the admission of a penetrant molecule in its neighboring position. At the T_g such a space may be made available with adequate frequency for a small penetrant molecule as well as for a gas molecule. A small increase in temperature will result in the formation of a space large enough to admit larger penetrant molecules.

CONCLUSION

The diffusion coefficient of nonionic penetrants in polyamide from aqueous solutions is independent of concentration in the temperature range of 5°

to 95°C. The Arrhenius plot of the diffusion coefficient gives a straight line, with a change in slope at a higher temperature than the T_g of this polymer in water. The shift of the point depends on the size of penetrant. The activation energy of diffusion decreases above the point at which the slope changes. These results can be explained by considering the segmental motion of the polymer.

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