

Water Sorption in Styrene Crosslinked Polyesters

V. BELLENGER,* B. MORTAIGNE,[†] and J. VERDU,* * *ENSAM, 151 Bd. de l'Hôpital, 75640 Paris Cedex 13, France, and* [†] *ETCA CREA, 16^{bis} Av. Prieur de la Côte d'Or, 94114 Arcueil Cedex, France*

Synopsis

Various polyester samples differing essentially by the diol nature, the proportion of unsaturated diacid, or the prepolymer chain length were studied by gravimetry at 30, 40, or 50°C, 95% RH. The water equilibrium concentration increases with the test temperature and with the polar group concentration: esters, ethers and alcoholic or acidic chain ends. The diffusivity appears as an increasing function of the crosslink density which can be due to the "bonding" effect of chain ends through strong hydrogen bonds and/or to the fact that local motions are as favoured as the chain end concentration decreases.

INTRODUCTION

There is now a great interest for the problem of water absorption and diffusion in tridimensional glassy polymers used as composite matrices, especially polyesters largely used in boat, tank, and tube applications. Concerning water equilibrium concentration, it was shown, in the case of linear polymers, that it is practically a molar additive function, e.g., for a properly chosen "constitutive repeat unit"¹:

$$H = \frac{w \cdot M}{1800} = \sum_i H_i \quad (1)$$

where w is the equilibrium concentration expressed in wt %, M is the molar mass of the CRU, and H_i is the molar contribution of the i th group of the CRU to the water absorption. Typically, $H_i = 1$ or 2 (mole of water per mole of group) for the highly polar groups such as alcohols or acids, is able to play a role of hydrogen donors in hydrogen bonding. $H_i \approx 0$ for hydrocarbon structures of low polarity, and $0 < H_i < 1$ for moderately polar structures such as ethers, esters, ketones etc.¹ Indeed, the presence of microvoids, damage by swelling stresses, etc. can explain some departure from the simple additive law. In the case of glassy networks such as epoxies, it was also shown that eq. (1) can be used if certain intramolecular interactions of hydrophilic groups are taken into account.² Many authors favour interpretations based on the hypothesis that the water equilibrium concentration would be mainly linked to the available free volume.³⁻⁵ Although various experimental studies were reported in the case of crosslinked polyesters,⁶⁻¹³ there is apparently no detailed discussion of the water sorption mechanism in these systems. Concerning the diffusion mecha-

nisms, and the eventual relationships between the water diffusivity and the network structure, there is practically no published data except in the considerably more complicated case of composites.

The aim of the present article is to report some experimental results of classical sorption tests on various polyesters based on the copolymerization of fumaric ester with styrene ($40 \pm 5\%$ by weight), but differing by the diol or saturated diacid nature, by the molar fraction of this latter or by the molecular weight of the starting prepolymer. The experimental conditions (temperature $\leq 50^\circ\text{C}$, time ≤ 52 h) were chosen in order to minimize the eventual effects of an hydrolytic degradation.

EXPERIMENTAL

Materials

The samples under study are described in Table I. Their crosslinking was initiated by a methyl ethyl ketone peroxide (1.5%), cobalt octoate (0.5%) system. The reactive mixture was degassed and casted in a mold of $250 \times 180 \times 0.7$ mm at ambient temperature. After 3 h, the plates were demolded and post-cured 8 h at 80°C plus 2 h at 120°C . This cure schedule allows a practically complete cure of all the samples under study, as established by DSC, IR, and solid state NMR measurements.¹⁴

Sorption Tests

The samples were exposed at 95% RH; 30, 40, or $50 \pm 1^\circ\text{C}$, and periodically weighted with an electronic microbalance whose relative accuracy was 10^{-4} . The acidic I_{ac} and alcoholic I_{al} chain end concentration was determined in the prepolymer-styrene unreacted mixture by chemical titration by KOH, the alcohols being quantitatively transformed into acids by reaction with the acetic anhydride. ($I_{ac} + I_{al}$) is therefore the concentration of the polyester chain ends

TABLE I

Characteristics of the Samples Under Study *Remarks:* (a) Propylene Glycol; (b) Neopentyl Glycol; (c) Diethylene Glycol; (d) Dipropylene Glycol; (e) Isophthalic Acid; (f) Tetrahydrophthalic Acid; (g) Moles of Saturated Diacid/Total Moles of Diacids; (h) Determined by Chemical Titration Before Crosslinking; (i) Shear Modules in Rubbery State (at $T_g + 30$ K); (j) Determined by IR Spectrophotometry

| Sample | Diol | Saturated diacid, molar fraction (g) | $I_{ac} \times 10^6$ mol g^{-1} (h) | $I_{al} \times 10^6$ mol g^{-1} (h) | $G'r$ (MPa) (i) | % Styrene (j) | T_g (K) |
|--------|---------|--|---|---|-----------------------|------------------|--------------|
| A | PG (a) | P/0.54 (e) | 148 | 41 | 13.2 | 44 | 396 |
| B | PG | P/0.54 | 372 | 267 | 11.2 | 42 | 395 |
| C | PG | P/0.54 | 401 | 543 | 8.6 | 40 | 389 |
| D | PG | P/0.30 | 210 | 300 | 29.0 | 45 | 431 |
| E | NPG (b) | P/0.54 | 159 | 249 | 7.1 | 45 | 379 |
| F | DEG (c) | P/0.54 | 175 | 446 | 4.7 | 38 | 353 |
| G | DPG (d) | P/0.54 | 226 | 463 | 4.0 | 42 | 359 |
| H | PG | T/0.54 (f) | 210 | 289 | 14.4 | 43 | 383 |

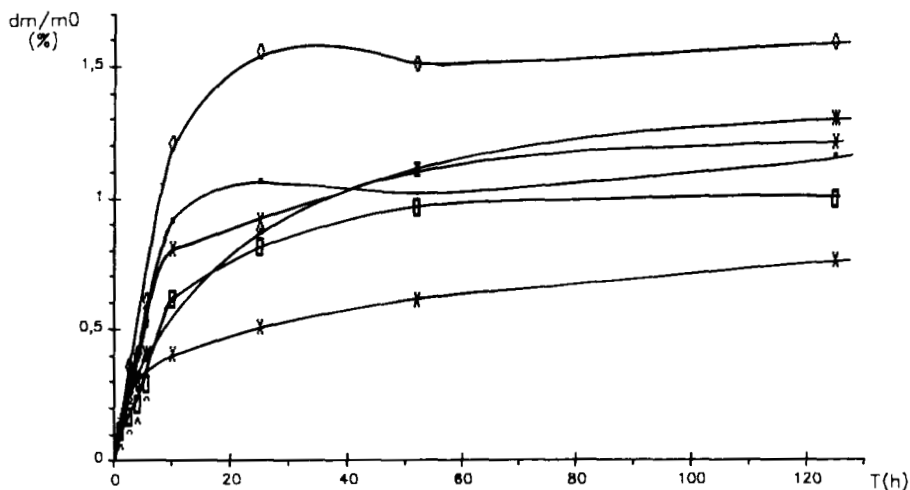


Fig. 1. Sorption curves for sample D (*), E (×), F (◇), G (■), and H (×).

in the final network (neglecting the eventual side reactions). The number average molecular weight \overline{M}_n of the prepolymer is

$$\overline{M}_n = \frac{2(1-s)}{I_{a1} + I_{ac}}$$

where s is the styrene weight fraction.

RESULTS

Some examples of sorption curves showing the structure or temperature effects are presented in, respectively Figures 1 and 2. It is in many cases, difficult

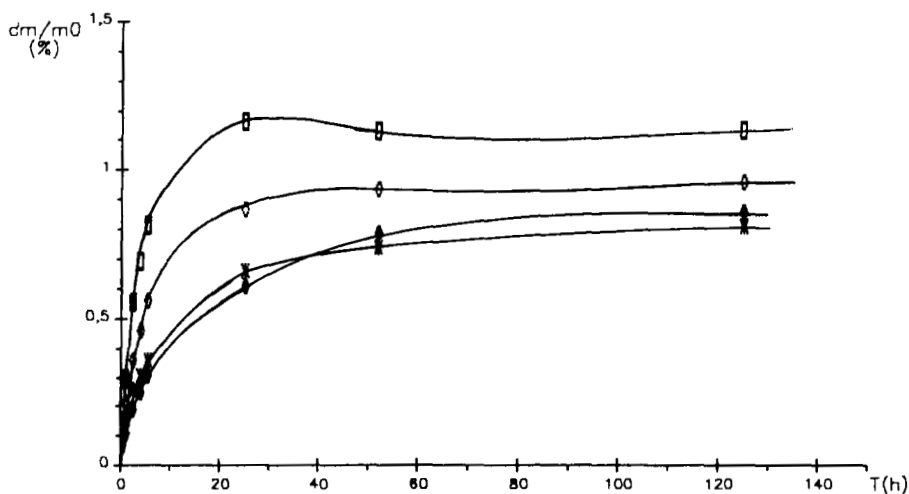


Fig. 2. Sorption curves of sample G at 20 (◇), 30 (*), 40 (◇), and 50°C (□).

to define an equilibrium value of the water concentration, because it increases (essentially at low temperature) or decreases (essentially above 50°C), continuously. It will be arbitrarily considered that a pseudo equilibrium was reached after 52-h exposure. The eventual further variations of the water concentration are characterized by a rate $1/m \cdot \Delta m / \Delta t$ lower than 10^{-5} h^{-1} . Some curves, generally corresponding to the most hydrophilic samples, display a slight overboost. The pseudo equilibrium water concentrations w_e (measured after 52 h), and the corresponding apparent Fickian diffusivities D are listed in Table II. They call for the following comments:

1. w_e is especially high for the diethylene glycol (F) and the high fumarate concentration (D) samples, and especially low for the neopentyl glycol (E) sample.
2. For a given system (propylene glycol), w_e is a decreasing function of the prepolymer molecular weight.
3. w_e increases with the temperature, at least in the temperature range under consideration.
4. D varies in a complex way with the structure and surprisingly appears as an increasing function of the crosslink density in the series based on propylene glycol.
5. The pseudodiffusivity D does not obey to the Arrhenius law as shown by the examples of samples A, B, C, and H in Figure 3.

A detailed analysis of the sorption curves reveals however a noticeable departure from Fick's law (Fig. 4). It appears that in its early period, the time dependance of water concentration w can be represented by a power law: $w = k \cdot t^\alpha$, where α varies with the temperature and chemical structure between 0.5 (Fick's law) and 0.9. The results of a cyclic exposure study on sample H are summarized by Table II. When a second sorption experiment follows the first one, there is a considerable increase of the diffusion rate, and the process becomes practically Fickian ($\alpha = 0.5$). These characteristics are retained after a third cycle. In contrast if the second cycle is carried out after a large delay

TABLE II
Sorption Characteristics at 95% RH of the Samples Under Study

| Sample | 30°C | | 40°C | | 50°C | | tan δ (1 Hz) at T_γ |
|--------|----------------------|---|----------------------|---|----------------------|---|---|
| | w_∞ (wt %) | $D \text{ cm}^2$ ($\text{s}^{-1} \times 10^9$) | w_∞ (wt %) | $D \text{ cm}^2$ ($\text{s}^{-1} \times 10^9$) | w_∞ (wt %) | $D \text{ cm}^2$ ($\text{s}^{-1} \times 10^9$) | |
| A | 0.72 | 6.9 | 0.89 | 12.0 | 0.91 | 14-19 | 0.0207 |
| B | 0.84 | 5.6 | 1.02 | 8.6 | 1.0 | 10 | 0.0190 |
| C | 1.12 | 2.1 | 1.36 | 2.7 | 1.44 | 3-8 | 0.0175 |
| D | 1.13 | 10 | 1.10 | 13 | 1.29 | 22 | 0.0210 |
| E | 0.47 | 10 | 0.56 | 13 | 0.75 | 18 | 0.0167 |
| F | 1.06 | 6.8 | 1.29 | 11 | 1.58 | 21.5 | 0.0245 |
| G | 0.74 | 11.7 | 0.92 | 16.5 | 1.14 | 23 | 0.0200 |
| H | 0.97 | 12.5 | 0.92 | 16 | 1.16 | 24.5 | 0.0211 |

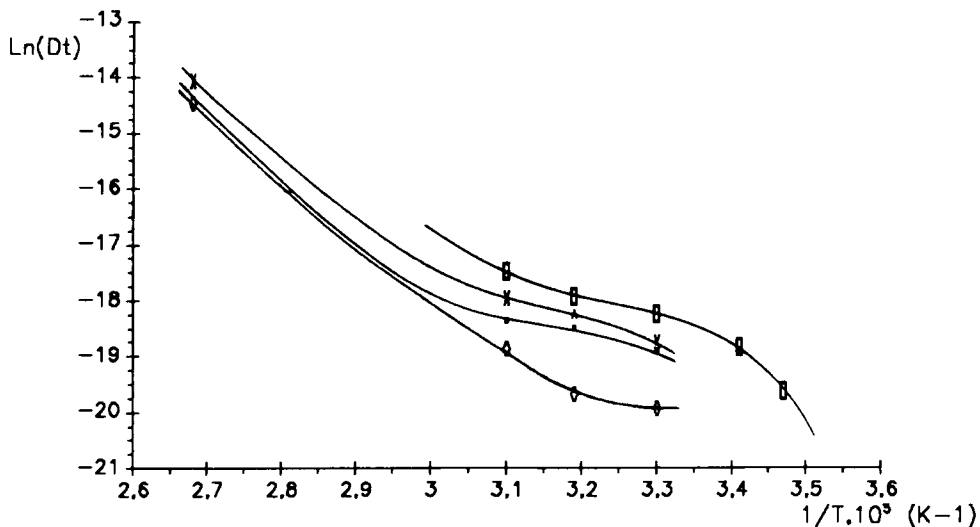


Fig. 3. Arrhenius curves for samples A (\times), B (\blacksquare), C (\diamond), and H (\square).

(4 months in the case under study) there is practically no change in the sorption characteristics.

DISCUSSION

1. Influence of the temperature on the water equilibrium concentration. It is noteworthy that polyesters differ from, for instance, amine-crosslinked epoxies of comparable crosslink density by the fact that w_∞ is an increasing function

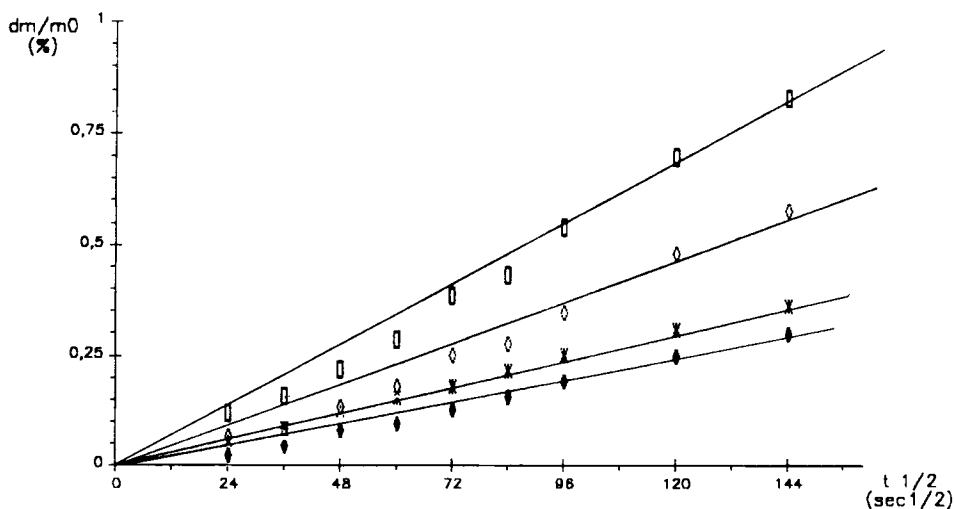


Fig. 4. Water concentration expressed in weight percents vs. \sqrt{t} for sample G; same symbols as in Fig. 2.

of the temperature whereas in epoxies, it is practically constant¹⁵ and seems to depend essentially on the hydrophilic site nature and concentration.² The variations of w_∞ , in the temperature range under study, could be tentatively represented by the following relationship:

$$w_\infty = k(T - T_0) \quad (2)$$

By an appropriate choice of T_0 , k appears reasonably independent of the temperature, as shown in Table III in the case where $T_0 = 223$ K. The corresponding average value of k ranges between 6.5×10^{-5} and $14.5 \times 10^{-5} \text{ K}^{-1}$. Indeed, the temperature coefficient for the volume occupancy by water molecules: $k' = 1/v \cdot dv/dt$ would be in the same order of magnitude, e.g., would be lower, in all the cases under study, than the polymer expansivity, ($\alpha \approx 20 \times 10^{-5} \text{ K}^{-1}$), in glassy state. The chosen T_0 value corresponds approximately to the onset of the transition found in the thermomechanical spectra.¹⁴ It seems reasonable to assume that the water molecules take essentially place in a fraction (depending on the structure) of the volume created by expansion above the γ transition.

2. Influence of the structure on the water equilibrium concentration. The most important structure effects on the water solubility in Polyesters can be observed in Figure 5 where w_∞ (50°C) is plotted versus ester concentration. According to this figure, w_∞ increases almost regularly with the ester concentration, (the same trends would be observed by plotting w_∞ (40°C), w_∞ (30°C), or k (eq. (1)) against [E]), but the presence of an ether in the diol moiety (samples F and G) would involve an increase of about 0.6%. In the propylene glycol series, however, the fact that w_∞ increases in the order A < B < C cannot be simply attributed to the variation of the styrene fraction (Table I), e.g., to the dilution of hydrophilic ester groups by hydrophobic hydrocarbon ones. It seems logical to suppose that the highly polar-hydrogen donors in hydrogen bonding-alcoholic and acidic chain ends contribute noticeably to the water absorption in sample B, and essentially C.

It was intended to apply the hypothesis of the molar additivity of the group contributions to water absorption.¹ It must be first noted that the data reported by these authors would lead to w_∞ values about twice of the observed ones.

TABLE III
Temperature Coefficient: $k = w_\infty/(T - 223)$ for the Water Equilibrium Concentration

| Sample | Ester (mol kg ⁻¹) | δ_p (cm ^{1/2} J ^{-3/2}) | $k \times 10^5 \text{ K}^{-1}$ at 30°C | $k \times 10^5 \text{ K}^{-1}$ at 40°C | $k \times 10^5 \text{ K}^{-1}$ at 50°C | k average value |
|--------|----------------------------------|--|---|---|---|----------------------|
| A | 6.12 | 19.8 | 9.0 | 9.9 | 9.1 | 9.3 |
| B | 6.34 | 20.5 | 10.5 | 11.3 | 10.0 | 10.6 |
| C | 6.56 | 20.6 | 14.0 | 15.1 | 14.4 | 14.5 |
| D | 6.43 | 20.0 | 14.1 | 12.2 | 12.9 | 13.1 |
| E | 5.21 | — | 5.9 | 6.2 | 7.5 | 6.5 |
| F | 5.82 | 20.8 | 13.3 | 14.3 | 15.8 | 14.5 |
| G | 4.81 | 20.7 | 9.3 | 10.2 | 11.4 | 10.3 |
| H | 6.66 | 19.8 | 12.1 | 10.2 | 11.6 | 11.3 |

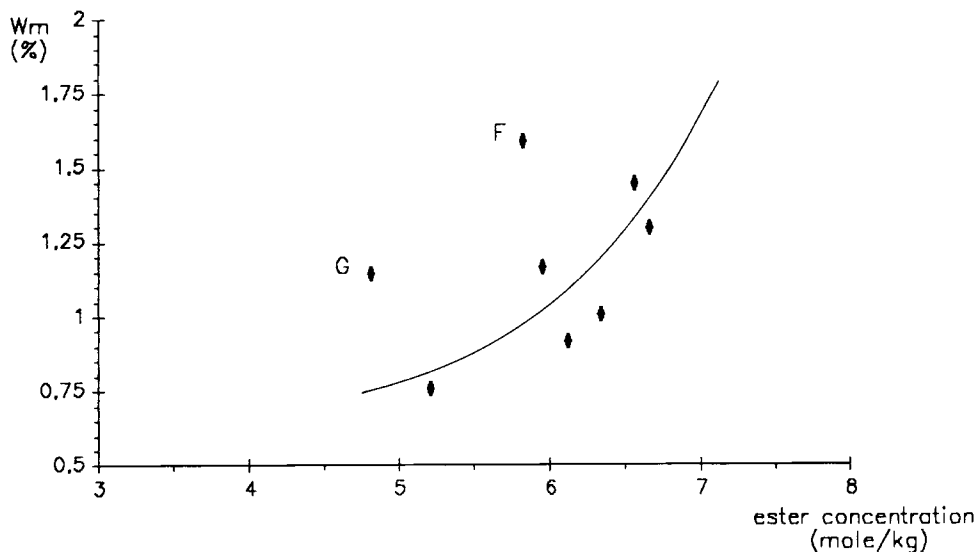


Fig. 5. Water equilibrium concentration at 50°C vs. ester concentration.

Despite of that, we started from the hypothesis that: (i) the contribution of hydrocarbon groups to water absorption is negligible; (ii) the contribution of alcoholic and acidic chain ends is undifferentiated, and we tried to resolve the system of equations:

$$k = k_1[\text{esters}] + k_2[\text{ethers}] + k_3[\text{chain ends}] \quad (3)$$

This system admits the following approximative solution: $k_1 = 1.3 \times 10^{-5} \text{ kg mol}^{-1} \text{ K}^{-1}$; $k_2 = 0.8 \times 10^{-5} \text{ kg mol}^{-1} \text{ K}^{-1}$; $k_3 = 5 \times 10^{-5} \text{ kg mol}^{-1} \text{ K}^{-1}$, w_∞ was calculated for the three temperatures under study using eqns (1) and (2), (with $T_0 = 223 \text{ K}$) and the average error of the prediction was $\approx 12.6\%$ which could be considered acceptable for estimation purposes. The observed order of hydrophilicities, e.g., acids and alcohols \gg esters $>$ ethers corresponds to the previously reported data on linear polymers.¹ Another way to interpret the hydrophilicity variations with structure could be based on solubility parameters considerations. As a matter of fact, the water solubility in the polymer must be a decreasing function of $|\delta_w - \delta_p|$, where δ_w and δ_p are the respective solubility parameters of water and polyester. Since $\delta_w \gg \delta_p$, w_∞ should be an increasing function of δ_p . We can estimate δ_p from the polymer structure using various methods based on the concept of molar additivity.¹⁶ The method used here is the Small's one,¹⁷ applied with the Hoy's component values.¹⁸ w_∞ appears as an almost linear increasing function of δ_p (Fig. 6), which is not very surprising considering the especially high contribution of the hydrophilic groups (esters, ethers, acids, and alcohols), to the solubility parameter or better the cohesive energy density δ_p^2 .

3. Influence of the structure on the apparent water diffusivity. Surprisingly, the apparent diffusivity appears as an increasing function of the crosslink den-

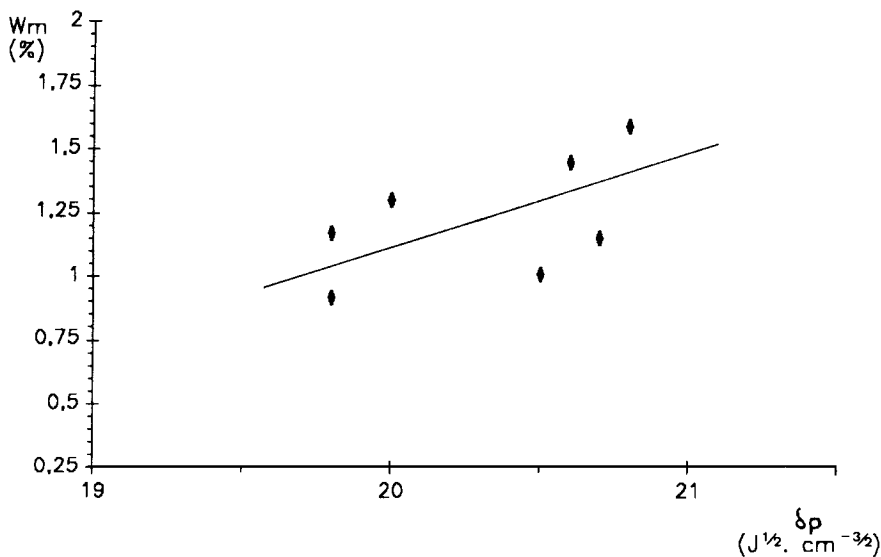


Fig. 6. Equilibrium water concentration against calculated solubility parameter.

sity, (determined theoretically or from rubbery modulus measurements) in the propylene glycol series (A, B, C, D). We can involve two phenomena:

(i) The effect of chain ends, the stronger is the bonding between hydrophilic sites and water molecules, the slower is the diffusion of these latter as found for many moderately hydrophilic polymers,¹ but also in certain epoxy structural series.¹⁹ In the series under consideration, especially strong hydrogen bonds can be established between the water molecules and the alcoholic or acidic chain ends, so that the diffusivity must be a decreasing function of their concentration as experimentally observed.

(ii) The effect of local motions. It is recognized that, in glassy polymers, the local motions can play a crucial role in diffusion,²⁰ (as cooperative motions in rubbery state). The population of segments participating to these motions can be related to the amplitude of the corresponding damping peak in thermomechanical spectrum. For all the samples under study, this latter displays a maximum—corresponding to the γ transition—at 180–186 K. These characteristics will receive a detailed interpretation elsewhere. Here, we shall only report the corresponding maximum values of $\tan \delta$ (Table II). It appears clearly that, at least in the propylene glycol series, the diffusivity is an increasing function of $\tan \delta$ (max), e.g., of the population of segments participating to local motions at the test temperature (the beta transition is located at a temperature generally higher than 50°C).

4. Effect of a sorption-desorption cycle. The fact that the water uptake is better represented by a power law with an exponent higher than 0.5 than by the Fick's law, and the existence of a slight overboost in certain sorption curves could be linked to the existence of a relaxation controlled transport process (case II of diffusion²¹). The occurrence of relaxation phenomena is well attested by the change of the sorption characteristics, which become Fickian in the second cycle where a noticeable increase of diffusion rate is observed. These

effects disappear, however, after a 6-month storage at ambient temperature, which could be linked to the physical aging of the polymer.

CONCLUSIONS

The water equilibrium concentration increases in the range (30–50°C) as a result of expansion which increases the volume fraction accessible to water molecules. The water equilibrium concentration is an increasing function of the ester concentration; the ether group of the dimeric diols increases the hydrophilicity; the contribution of very hydrophilic chain ends cannot be neglected. The water absorption could be estimated from simple empirical relationships involving the concentrations of esters, ethers, chain ends, or the calculated solubility parameter. The diffusivity appears as an increasing function of the crosslink density, which can be explained in terms of "water-chain ends" hydrogen bond strength and/or population of segments participating to local motions.

References

1. D. W. Van Krevelen and P. J. Hoftyzer, *Properties of Polymers, Their Estimation and Correlation with Chemical Structure*, Elsevier, Amsterdam, 1976, p. 422.
2. E. Morel, V. Bellenger, and J. Verdu, *Polymer*, **26**, 1719 (1985).
3. M. J. Adamson, *J. Mater. Sci.*, **15**, 1736 (1980).
4. J. B. Enns and J. K. Gilham, *J. Appl. Polym. Sci.*, **28**, 2831 (1983).
5. P. Johncock and G. T. Tudgey, *Br. Polym. J.*, **18**, 292 (1986).
6. H. P. Abeyinghe, W. Edwards, G. Pritchard, and G. J. Swampillai, *Polymer*, **23**, 1785 (1982).
7. A. Apicella, G. Migliaresi, L. Nicolais, L. Vaccarino, and S. Roccotelli, *Composites*, **14**, 387 (1983).
8. K. H. G. Ashbee, F. C. Frank, and R. C. Wyatt, *Proc. Roy. Soc.*, **A312**, 553 (1969).
9. K. H. G. Ashbee and R. C. Wyatt, *Proc. Roy. Soc.*, **A300**, 415 (1967).
10. J. A. Alekseyeva, G. A. Semerneva, and S. S. Spasskii, *Vysokomol. Soedin.*, **5**, 1297 (1963).
11. B. Alt, *Kunststoffe*, **59**, 986 (1969).
12. E. Nicaise, A. Gandini, and H. Cheradame, *Br. Polym. J.*, **18**, 247 (1986).
13. P. P. Burrell, D. J. Herzog, and R. T. McCabe, *42nd SPI Conference*, Section 15.E.
14. B. Mortaigne, thesis, ENSAM, Paris, 1989.
15. C. A. Loos and G. S. Springer, *J. Compos. Mater.*, **13**, 131 (1979).
16. A. F. M. Barton, *Handbook of Solubility and Other Cohesion Parameters*, CRC Press, Boca Raton, FL, 1985.
17. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
18. K. L. Hoy, *J. Paint Technol.*, **42**, 76 (1970).
19. V. Bellenger, J. Verdu, and E. Morel, *J. Mater. Sci.*, **24**, 63 (1989).
20. J. A. Barrie, in *Diffusion in Polymers*, 4th ed., J. Crank and G. S. Park, Eds., Academic, London, Chap. 8, pp. 282–283.
21. H. P. Hopfenberg and V. Stannet, in *The Physics of Glassy Polymers*, C. E. Roberts and E. F. T. White, Eds., Applied Science, London, 1973, Chap. 9, p. 504.

Received October 31, 1989

Accepted November 6, 1989