was a known disadvantage of the use of a one residue move per cycle, but the impediment to folding caused by a preformed helix was not anticipated. It is clearly shown that fixing the disulfide bonds does direct the folding process, but a preformed helix has much less effect in directing tertiary structure.

Our primary objective was to compare the folding process and the resulting structures using centrosymmetric and local interaction potentials. Faster folding with the centrosymmetric potential can be anticipated and was observed. We believed that the local interaction potential is a more fundamental quantity, and thus we anticipated that there would be a significant difference in the quality of the structures obtained with the two potentials. This expectation was not borne out by our results. The local interaction potential leads to more NP–NP contacts, as expected, but this is not accompanied by a noticeable improvement in any of the other indices we have used to assess quality. Only in the case of the starting structure containing the native disulfide bonding did the local interaction potential show any advantage, and even in this case the difference was small.

We initially planned that the next step might involve the use of a centrosymmetric potential to achieve a fast collapse of the conformation, followed by a sufficient number of cycles with the local interaction potential to form optimum side chain–side chain contacts. However, in view of these results, it would appear to be more profitable to combine some type of torsional potential with the centrosymmetric potential in an attempt to improve the quality of the present results.

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References and Notes

(1) Burgess, A. W.; Scheraga, H. A. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1221.
(2) Nĕmethy, G.; Scheraga, H. A. *Q. Rev. Biophys.* **1977**, *10*, 239.
(3) Levitt, M.; Warshel, A. *Nature (London)* **1975**, *253*, 694.
(4) Levitt, M. *J. Mol. Biol.* **1976**, *104*, 59.
(5) Kuntz, I. D.; Crippen, G. M.; Kollman, P. A.; Kimelman, D. *J. Mol. Biol.* **1976**, *106*, 983.
(6) Robson, B.; Osguthorpe, D. J. *J. Mol. Biol.* **1979**, *132*, 19.
(7) Hagler, A. T.; Honig, B. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 554.
(8) Taketomi, H.; Ueda, Y.; Gō, N. *Int. J. Pept. Protein Res.* **1975**, *7*, 445.
(9) Gō, N.; Taketomi, H. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 559.
(10) Gō, N.; Taketomi, H. *Int. J. Pept. Protein Res.* **1979**, *13*, 235, 447.
(11) Ueda, Y.; Taketomi, H.; Gō, N. *Biopolymers* **1978**, *17*, 1531.
(12) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
(13) Gō, N.; Abe, H.; Mizuno, H.; Taketomi, H. In "Protein Folding"; Jaenicke, R., Ed.; Elsevier/North-Holland Biomedical Press: Amsterdam, 1980; p 167.
(14) Dashevskii, V. G. *Mol. Biol. (Engl. Transl.)* **1980**, *14*, 105.
(15) King, G. W. "Research in the Physical and Structural Analysis of High Polymers by Punched Card Methods", Final Report, Office of Naval Research.
(16) Verdier, P. H.; Stockmayer, W. H. *J. Chem. Phys.* **1962**, *36*, 227.
(17) Krigbaum, W. R.; Rubin, B. H. *Biochim. Biophys. Acta* **1971**, *229*, 368.
(18) Krigbaum, W. R.; Komoriya, A. *Biochim. Biophys. Acta* **1979**, *576*, 204.
(19) Krigbaum, W. R.; Komoriya, A *Biochim. Biophys. Acta* **1979**, *576*, 226.
(20) Meirovitch, H.; Rackovsky, S.; Scheraga, H. A. *Macromolecules* **1980**, *13*, 1398.
(21) Meirovitch, H.; Scheraga, H. A. *Macromolecules* **1980**, *13*, 1406.
(22) We thank Steven Meador, Gary Hovis, and Jean-Pierre Auffret, who worked on the development of earlier versions of these programs as their undergraduate Independent Study projects.
(23) Huber, R.; Kukla, D.; Ruhlman, A.; Steigemann, W. *Cold Spring Harbor Symp. Quant. Biol.* **1971**, *36*, 141.
(24) Cohen, F. E.; Sternberg, M. J. E. *J. Mol. Biol.* **1980**, *138*, 321.
(25) It should be noted that Levitt and Warshel[2] and Levitt[3] used a different definition of the radius of gyration, so their values for this quantity cannot be compared with ours.
(26) Havel, T. F.; Crippen, G. M.; Kuntz, I. D. *Biopolymers* **1979**, *18*, 73.
(27) Rackovsky, S.; Scheraga, H. A. *Macromolecules* **1978**, *11*, 1168.
(28) Rackovsky, S.; Scheraga, H. A. *Macromolecules* **1980**, *13*, 1440.

Sorption of Water by Epoxide Prepolymers

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ABSTRACT: Water equilibrium in epoxide prepolymers below the glass transition temperature (T_g = 343 K) is described. The heat of mixing and entropy of mixing show that, at low concentrations, the water may be hydrogen bonded, while at moderate or high concentrations, clustering of the water takes place, with an increase in free volume and a decrease in T_g to 323 K.

Introduction

All polymers may contain water in varying amounts according to the polarity of their macromolecular chains. Water content in solid epoxide prepolymers has not yet been described. Information available refers to "cured" epoxy systems, and results are at times contradictory.[1-4] The subject is of significance since the water adsorbed may interfere with the process of curing and, therefore, with the properties of the final products.

Experimental Section

1. Materials. Liquid epoxide prepolymers are usually prepared by reacting epichlorhydrin, bisphenol A, and sodium hydroxide according to the reaction mechanism shown in Scheme I.[5]

Solid epoxide prepolymers are made by two different processes: (i) by direct addition of epichlorohydrin to bisphenol A and (ii) by reaction of the low molecular weight epoxide resin, the main constituent of which is the diglycidyl ether of bisphenol A with bisphenol A. This last reaction is also known as the fusion process.

One solid epoxide prepolymer prepared = the fusion process (Araldite 6097) was supplied by Ciba-Geigy AG (Switzerland).

The glass transition temperature (T_g = 343 K) was measured as the first change in slope of the specific heat vs. temperature curves obtained in a DuPont 900 differential scanning calorimeter, as described elsewhere.[5] During heating of the polymer some volatile material evolved, which was mainly water and possibly

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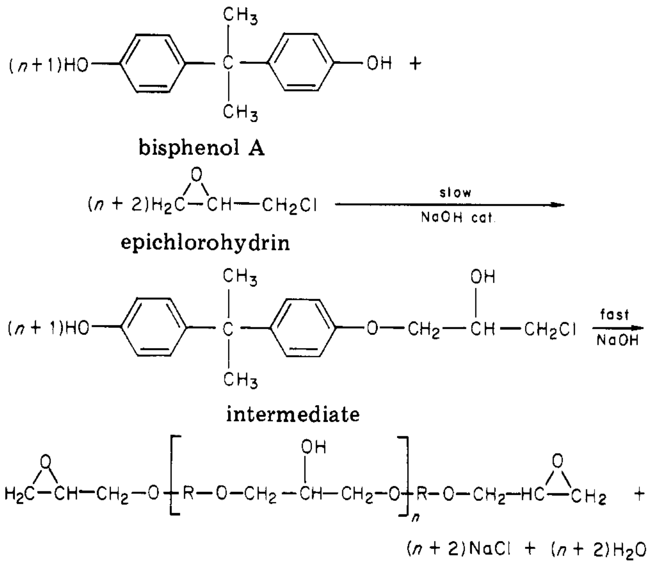
Scheme I



R = $C_6H_4C(CH_3)_2C_6H_4$

Table I
Physical Properties of Epoxide Prepolymers

property	as provided	devolatilized
number-average mol wt ($\bar{M}_n$)	1759	2112
epoxy value ($p = 2000/\bar{M}_n$)	1.14	0.95
weight-average mol wt ($\bar{M}_w$)	3550	4200
polydispersity ($\bar{M}_w/\bar{M}_n$)	2.02	1.99

some toluene from the first steps of the polymerization process. To avoid difficulties with bubbles in the test samples, the polymer was devolatilized in a vacuum oven at 443 K.[6]

The polymer's number-average molecular weight ($\bar{M}_n$) was measured before and after devolatilization in a Model 115 Hitachi Perkin-Elmer vapor pressure osmometer at a temperature of 303 K, with chloroform as the solvent. Results are shown in Table I. With them the epoxide value ($p = 2000/\bar{M}_n$) was computed and was combined with the weight-average molecular weights ($\bar{M}_w$) described elsewhere[7] to provide the weight-average molecular weight of the sample used (see Table I).

2. Procedure. All sorption–desorption experiments were carried out in a Cahn RG electrobalance (sensitivity 10^{-6} g) connected to a conventional vacuum line.

Three samples of ca. 6 × 6 × 0.6 ± 0.06 mm, enough to provide the minimum weight of 0.8 g required by the sensitivity of the balance, were prepared by melting the polymer, powdered and screened to a size of 0.5 mm, on a glass plate in vacuum oven at 443 K and 5 × 10^{-3} torr for 3 h to eliminate the volatile components.

The samples were placed on the balance pan in such a fashion that minimum contact between them was achieved. Then in order to attain volume relaxation, they were conditioned by degassing for 65 h at high vacuum (10^{-6} torr) at the temperature of the experiment.

The level of water concentration required in sorption experiments was provided by allowing different water vapor pressures in the system by means of a mercury differential manometer. In desorption experiments water was eliminated by evacuation and placing a trap immersed in liquid nitrogen near the sorption cell, in order to secure a low residual water pressure in the neighborhood of the sample.

Results and Discussion

Sorption isotherms as a function of temperature and water vapor concentration are shown in Figure 1 for temperatures below T_g (303, 310, 315, 320, 326, and 333 K). Water content w_1 (grams of water per 100 g of dry polymer) decreases with increasing temperature and decreasing water vapor concentration.

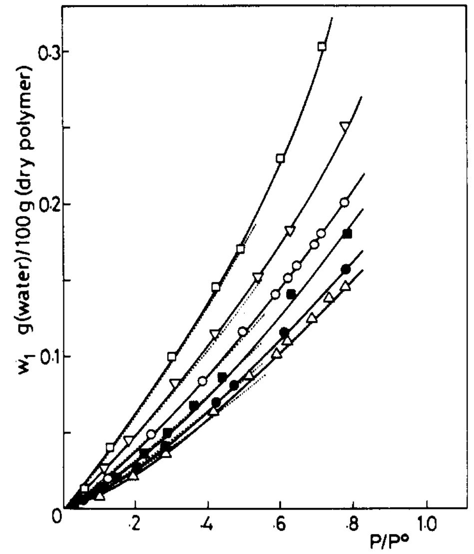


Figure 1. Sorption curves of water in epoxide prepolymers below T_g: (□) 303 K; (▽) 310 K; (○) 315 K; (■) 320 K; (●) 326 K; (△) 333 K; (···) computed for dual mode of sorption.

At 303 K it has the form of a BET type II isotherm:[8]

$$\frac{P/P^0}{w_1(1-P/P^0)} = \frac{1}{cw_{1m}} + \frac{c-1}{cw_{1m}}\frac{P}{P^0} = \alpha + \beta\frac{P}{P^0} \qquad (1)$$

in which c, w_1, w_{1m}, and P/P^0 are the BET constant, weight of water, monolayer weight, and relative vapor pressure, respectively.

A plot of eq 1 provides a straight line from which $\alpha + \beta$ equals 0.7425.

The surface σ occupied by a water molecule is

$$\sigma = 1.091\left(\frac{M}{N_A\rho}\right)^{2/3} = 10.5\ \text{Å}^2 \qquad (2)$$

where M, N_A, ρ, and 1.091 are the water molecular weight, Avogadro's number, water density, and the packing factor, respectively.

The BET model gives for the polymer specific (internal) area accessible to the water molecules

$$S_{BET} = \frac{\sigma}{\alpha+\beta}\left(\frac{w_{1m}}{M}N_A\right) = 2.6 \times 10^4\ \text{cm}^2/\text{g} \qquad (3)$$

The geometrical (external) specific area measured is

$$S_G = \frac{\text{slab area}}{\text{slab weight}} = 17.3\ \text{cm}^2/\text{g} \qquad (4)$$

From eq 3 and 4 the ratio $S_{BET}/S_G = 1500$, being a clear sign of the presence of some porosity or microvoids frozen in the polymer slabs.

The BET model refers to adsorption on solid surfaces and, therefore, may not be fully appropriate for water–polymer systems, mainly at temperatures close to their glass transition temperatures. However, at temperatures (303 K) well below their glass transition temperatures (which for the water–epoxide system is 323 K; see Figure 8), it provides a value of the area factor adequate for explaining the relative effects of Henry's (k_D) and Langmuir's ($C_H'b$) coefficients (eq 12 and Figure 4), as well as deviations from the Freundlich model (eq 7 and Figure 3).

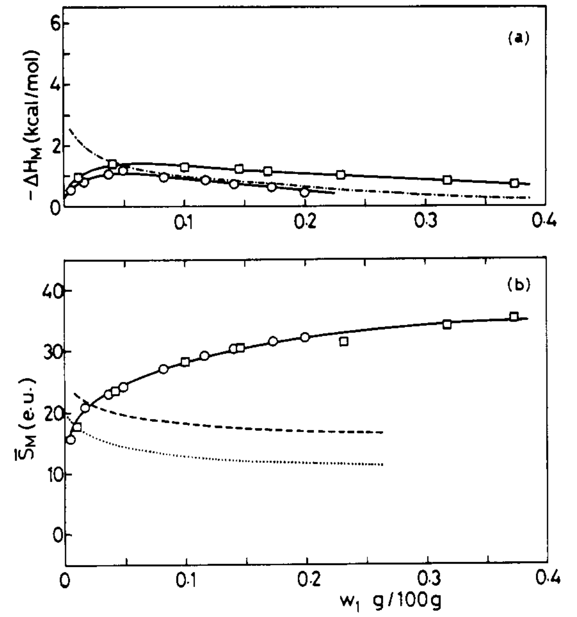


Figure 2. (a) Heat of mixing: (□) 303 K; (○) 315 K; (-·-) theoretical heat of mixing according to Freundlich. (b) Entropy of mixing: (□) 303 K; (○) 315 K; (···) theoretical assuming for the water molecule one rotation; (---) theoretical assuming for the water molecule two rotations.

1. Heat and Entropy of Mixing. Heats of mixing (ΔH_M) were computed with the Flory–Huggins equation:[9]

$$\Delta H_M = kT\chi_1 n_1 \phi_2 \quad (5)$$

where k, T, n_1, and ϕ_2 are the Boltzmann constant, temperature, number of water molecules, and volume fraction of polymer, respectively, and χ_1 is a dimensionless quantity that characterizes the interaction energy per water molecule and may be computed from the activity (a_1) and the number (x) of segments in the polymer molecule (which can be taken as the ratio of the molecular volumes of the polymer and the water):

$$\chi_1 = \frac{\ln a_1 - \ln (1 - \phi_2) - (1 - 1/x)\phi_2}{\phi_2^2} \quad (6)$$

Results are shown in Figure 2.

Attachment of the water molecules to the polymer possibly takes place by hydrogen bonding at the oxygen, as well as at the free OH groups, of the flexible sequence of carbon–carbon single bonds of the glycerin ether groups $OCH_2CH(OH)CH_2O$ in the epoxide prepolymer.

The heat of mixing comprises[10] the energy of attachment of the sorbed molecules to the polymer, the energy of swelling or reorientation caused by penetration of the water molecules into the polymer, and the mutual interaction between sorbate molecules, plus the sorption of water upon water, which occurs as polymer sites are occupied. For epoxide prepolymers the dipole and swelling forces will decrease (ΔH_M will increase since it is negative), while the other forces will increase (decreasing ΔH_M) with increasing sorption.

At low water concentrations (less than 0.04 g/100 g), $-\Delta H_M$ first increases and then levels off, the behavior being explained by a dual mode of sorption (see part 2 later on) composed of an exothermic (increasing ΔH_M) process of trapping water in preexisting holes (which therefore do not require the expenditure of energy to create them), opposed by a dissolution of the water in the polymer and a corresponding reorientation of the segments and creation of new holes, which is an endothermic process and therefore makes ΔH_M decrease.

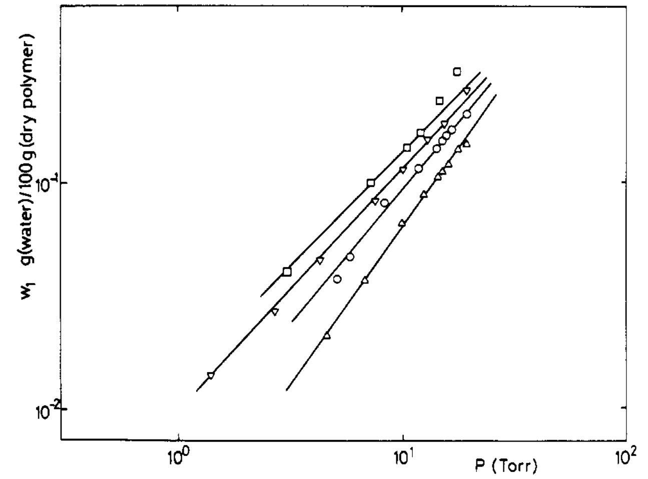


Figure 3. Freundlich isotherms: (□) 303 K; (▽) 310 K; (○) 315 K; (△) 333 K.

Table II
Heats of Sorption Computed according to Freundlich (Eq 7)

$1/n$	T, K	nT, K	nRT, kcal/mol
1.100	310	281.82	0.560
1.259	315	250.20	0.497
1.433	333	232.40	0.462
		av	0.511

At higher water concentrations (greater than 0.04 g/100 g), $-\Delta H_M$ decreases steadily toward 0 kcal/mol, in good agreement (Figure 2) with the theoretical heats of sorption computed from the slopes ($1/n$) of the log–log plot of Freundlich isotherms (Figure 3):

$$w_1 = c'P^{1/n} \quad (7)$$

where c' and n are constants that are functions of temperature.

Sorption isotherms at 303 K and high water vapor pressures do not follow entirely the Freundlich model because of the increased sorption due to the proximity to the sorbate condensation temperature. As already shown, this isotherm is better described by the BET model.

The theoretical heat of sorption according to Freundlich is (Figure 2)

$$H_F = -0.511 \ln (w_1/w_{1m}) \quad (8)$$

−0.511 being the mean heat of sorption[11] as shown in Table II.

Entropies of mixing (ΔS_M) were also computed with the Flory–Huggins equation:[9]

$$\Delta S_M = -k(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad (9)$$

where n_1, n_2, ϕ_1, and ϕ_2 are the number of molecules of water and polymer and the volume fractions of water and polymer, respectively.

With them, the total entropy ($\bar{S}_M$) is

$$\bar{S}_M = S_g^\circ - \Delta S_M \quad (10)$$

S_g° being the standard entropy of the water molecule. Results are shown in Figure 2 as well as the theoretical values computed[12] from statistical thermodynamics, assuming that the sorbed water moves in a plane parallel to the polymer surface with the vibrations of the molecules in the vapor phase and only one or two rotations:

$$\bar{S}_{M(H_2O)} = {}_2\bar{S}_{tr} + \bar{S}_r + \bar{S}_v \quad (11)$$

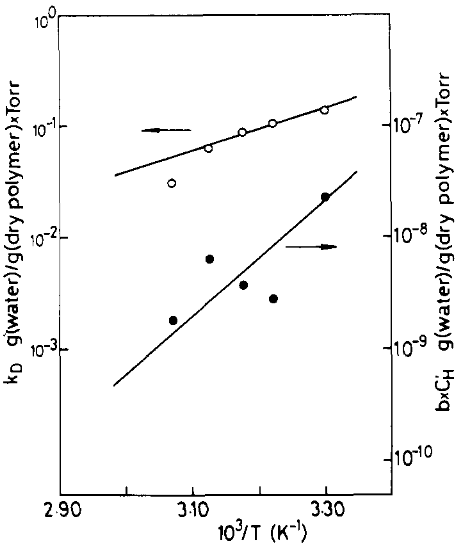


Figure 4. Henry (k_D) and Langmuir (bC_H') constants of the water–epoxide system below T_g.

in which ${}_2\bar{S}_{tr}$, $\bar{S}_r$, and $\bar{S}_v$ are the two-dimensional translational, rotational, and vibrational entropies.

At low concentrations the theoretical and experimental entropies coincide, indicating that the water molecules are adsorbed at the active sites, with a heat of mixing of ca. 1.0 kcal/mol. As the water content increases, other layers are adsorbed. At higher concentrations the entropy values are close to these of the vapor phase, indicating clustering of the water.

The entropy ($\bar{S}_M$) consists of (i) a thermal part, related to the specific heat and thus to ΔH_M, and (ii) a configurational term, the importance of which decreases as sorption increases and which for epoxide prepolymers is important up to higher concentrations because of the numerous sorption sites available to the water. The components of the entropy work in opposition. Thermal entropy falls with ΔH_M and becomes dominant at higher water concentrations. The absolute value of $\bar{S}_M$ indicates that the sorbed water is similar to liquid water.

2. Dual Mode of Sorption and Cluster Formation. Sorption at low water concentrations is consequently a dual mode of sorption provided by sorbed molecules of the Langmuir type and by free molecules of the Henry type, being the equilibrium concentration (C in (g of water)/(g of dry polymer)) of water in the polymer at pressure P:[13]

$$C = k_D P + C_H' bP/(1 + bP) \qquad (12)$$

in which k_D is the Henry's law solubility coefficient ((g of water) (g of dry polymer)$^{-1}$ torr^{-1}), b is the Langmuir affinity constant (torr^{-1}), and C_H' is the Langmuir sorption capacity ((g of water) (g of dry polymer)$^{-1}$).

Their values computed by a nonlinear regression analysis of the data of Figure 1 are shown in Figure 4. Since Henry's coefficient (k_D) is much larger than Langmuir's ($C_H'b$), from the very beginning of the adsorption most of the water is in the liquid state, which is an indication that cluster formation begins to take place at very low water concentrations.

The Zimm–Lumberg clustering parameters,[14] computed as

$$\frac{G_{11}}{v_1} = -\phi_2\left[\frac{\partial(a_1/\phi_1)}{\partial a_1}\right]_{p,T} - 1 \qquad (13)$$

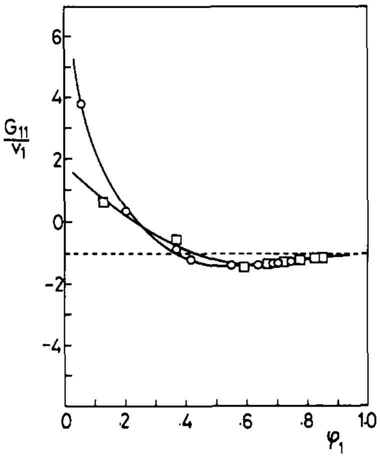


Figure 5. Clustering function of the water–epoxide system: (□) 303 K; (○) 315 K.

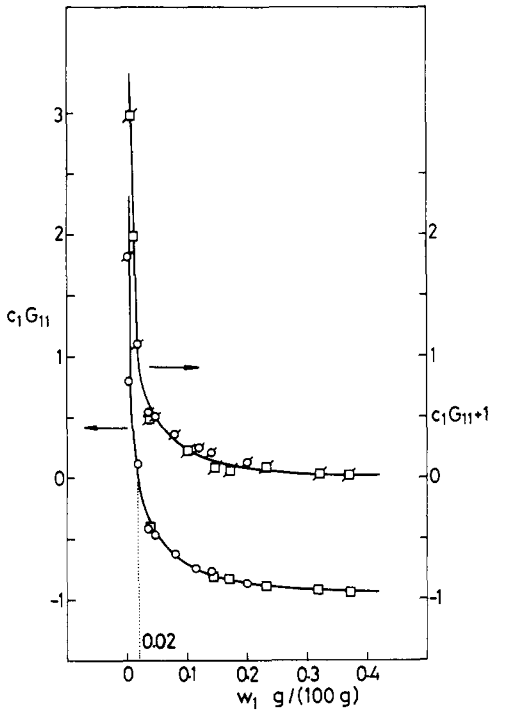


Figure 6. Cluster size: (□) 303 K; (○) 315 K.

where G_{11} is the cluster integral, a_1 is the water activity, v_1 is the partial molar volume of water, and ϕ_1 and ϕ_2 are the volume fractions of water and polymer, are shown in Figure 5. Since $G_{11}/v_1 > -1$ denotes the tendency for the water to cluster, eq 13 confirms that cluster formation takes place at very low water activities. At water volume fractions of 0.40 or higher, the behavior is ideal ($G_{11}/v_1 = -1$).

In order to gain insight into the mechanism of cluster building,[15] one may write eq 13 in terms of the molar concentrations c_1 to give

$$c_1 G_{11} = \phi_2\left[\frac{\partial \ln \phi_1}{\partial \ln a_1}\right]_{p,T} - 1 \qquad (14)$$

which is the mean number of water molecules in the neighborhood of a given water molecule in excess of the mean concentration of water (Figure 6).

The cluster size, i.e., the average number of water molecules in a cluster, is then

$$c_1 G_{11} + 1 = \phi_2\left[\frac{\partial \ln \phi_1}{\partial \ln a_1}\right] \qquad (15)$$

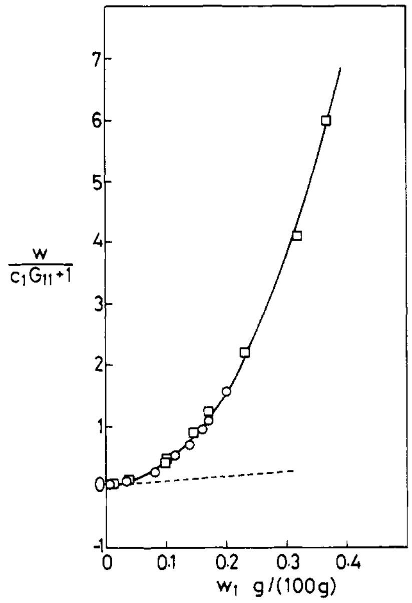


Figure 7. Number of clusters: (□) 303 K; (○) 315 K.

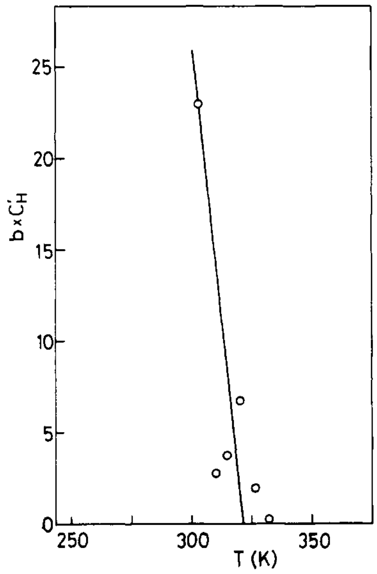


Figure 8. Langmuir's coefficient (bC_H') vs. temperature for the water–epoxide system.

and this quantity is also plotted in Figure 6.

The number of clusters in a given amount of polymer is proportional to

$$w_1/(c_1G_{11} + 1)$$

A plot of this quantity vs. w_1 is shown in Figure 7. Below 0.02 g/100 g, the slope is +1 (dashed line) since $c_1G_{11} = 0$, and, therefore, there is a balance between the water–polymer (active sites) and water–water contacts (the water molecules are accommodated in preexisting holes, the cluster size being greater than two).

As the water interacts with the polymer chains, it may produce some of the following effects in this order: (i) reorientation and chain displacement, i.e., reversible loosening or effective plasticization of the structure; (ii) solvation or reversible rupture of weak interchain bonds; (iii) irreversible disruption of the polymer matrix (microvoids). In the glassy state segmental rotations are restricted, tending to immobilize the holes, and only interchain separation can take place. Above T_g there is free segmental rotation, and the average chain separation of closely packed regions and the number and size of the holes present adjust themselves to yield a true equilibrium state.

As a consequence, the polymer slabs have a large increase in free volume. As the water concentration increases, this increase in free volume causes the water molecules to be further apart from each other and the number of water molecules close to water molecules to decrease. At concentrations of 0.02 g/100 g, the cluster size already becomes equal to 1, and from there on (in spite of the fact that the water–water contacts are still important, as shown by the increase in the number of clusters up to six), their size becomes progressively smaller (0.25 at 0.1 g/100 g and already as low as 0.01 at 0.30 g/100 g).

The effect of temperature on $C_H'b$ is shown in Figure 8. It becomes zero at about 323 K, which is the glass transition temperature of the polymer in the presence of water (the T_g of the pure polymer is 343 K). Because of it the data at 333 K are not shown in Figure 4, since 333 K is slightly over the T_g of the system.

C values computed with eq 12 are shown in Figure 1. They agree well with the experimental ones at relative pressures below 0.40.

References and Notes

(1) Illinger, J. L.; Schneider, N. S. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (2), 671.
(2) Comyn, J.; Brewis, D. M.; Tegg, J. L. *Prepr. IUPAC Macromol. Symp. (Mainz)* **1979**, *2*, 1136.
(3) Appicella, A.; Nicolais, L.; Astarita, G.; Driori, E. *Polym. Eng. Sci.* **1981**, *21* (1), 18.
(4) Moy, P.; Karasz, F. E. *Polym. Eng. Sci.* **1980**, *20* (4), 315.
(5) Aleman, J. V. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2567.
(6) Aleman, J. V. *Polym. Eng. Sci.* **1978**, *18* (15), 1160.
(7) Batzer, H.; Zahir, S. A. *J. Appl. Polym. Sci.* **1975**, *19*, 385.
(8) Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723.
(9) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(10) Day, A. G. *Trans. Faraday Soc.* **1963**, *59*, 1218.
(11) Halsey, G. D. *Adv. Catal.* **1952**, *4*, 259.
(12) Clark, A. "The Theory of Adsorption and Catalysis"; Academic Press: New York, 1970.
(13) Michaels, A. S.; Vieth, W. R.; Barrie, J. A. *J. Appl. Phys.* **1963**, *34*, 1.
(14) Zimm, B. H.; Lumberg, J. L *J. Phys. Chem.* **1956**, *60*, 425.
(15) Starkweather, H. W. *Macromolecules* **1975**, *8* (4), 476.