Relationship between hydrogen bonding and bound water in polyhydroxystyrene derivatives

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Crystallization of water sorbed on polyhydroxystyrene was studied by differential scanning calorimetry (d.s.c.). Two exothermic peaks of crystallization of water sorbed on the polymer were observed. One was a sharp peak (Peak I) observed at about 255 K in a d.s.c. curve; the other was a small broad peak (Peak II) observed at about 235 K. Judging from the amount of water calculated from the enthalpies of crystallization, there seems also to be some non-freezing water which does not crystallize. Therefore, we have categorized water sorbed on the polymer into three different kinds: free water (Peak I), freezable bound water (Peak II) and non-freezing water. The bound water content increases as the amount of hydroxyl groups in the polymer increases. Moreover, the maximum amount of water bound to a monomer unit of the polymer is about 0.7 mol. These facts indicate that there is less than a mole of bound water attached to a hydroxyl group and that part of this bound water does not crystallize. The bound water content estimated above was found to agree well with the critical water content, which was estimated from the decrease in the glass transition temperature of water sorbed polymers. Consequently, the bound water is defined as the water molecules which act to break the intermolecular hydrogen bonding and then are attached closely to hydroxyl groups of polymers. Thus, the bound water content evaluated from d.s.c. correlates with the degree of hydrogen bonding of polymers.

Keywords Polyhydroxystyrene; hydrogen bonding; free water; bound water; non-freezing water; differential scanning calorimetry

INTRODUCTION

Water associated with a polymer having hydrophilic groups exhibits properties different from normal (bulk) water. Generally, water molecules are restricted to the hydrophilic groups of natural polymers such as celluloses and proteins. Such water has been termed 'bound water'. The amount of bound water has been measured using various methods; for example, drying techniques[1], sorption and desorption isotherms[2,3], non-freezing water evaluated by calorimetric methods[4-8], classification of water in polymer gels by dilatometric studies[9,10] and determination of bound water by different relaxation times of n.m.r.[11-14]

Although the above methods have been used to determine the amount of bound water, they have not been used to study the relationship between bound water and molecular motion of polymers.

In a previous paper[15] we reported the relationship between sorbed water and the molecular motion of polyhydroxystyrene derivatives. It was shown that the glass transition temperature (T_g) of polyhydroxystyrene decreases with increasing amount of sorbed water. Moreover, the 'critical water content' which was obtained by calculating the necessary water content in order to decrease the T_g of polyhydroxystyrene to that of polystyrene, could be used to quantify hydrogen bonding in the polymer. It was assumed that water molecules which act as hydrogen bond breakers are distinct from those which act as a plasticizer.

Here, therefore, we have measured the phase transition of water sorbed on polyhydroxystyrene by differential scanning calorimetry (d.s.c.). We defined free water in the following experiments as the unbound water in polymers whose transition temperature, enthalpy and shape of peak in d.s.c. curves are equal to those of pure (bulk) water. 'Bound water' is the water restricted by hydroxyl groups of the polymer, and has a transition temperature which is lower than, and a d.s.c. peak whose shape differs from, that of pure water. We also define 'non-freezing water' as a kind of bound water whose transition is not detected in the first-order transition. Moreover, the study of mutual interactions between hydrogen bonding in the polymer and the bound water content has been undertaken. The results are compared with those obtained from the d.s.c. measurement of the previous work[15].

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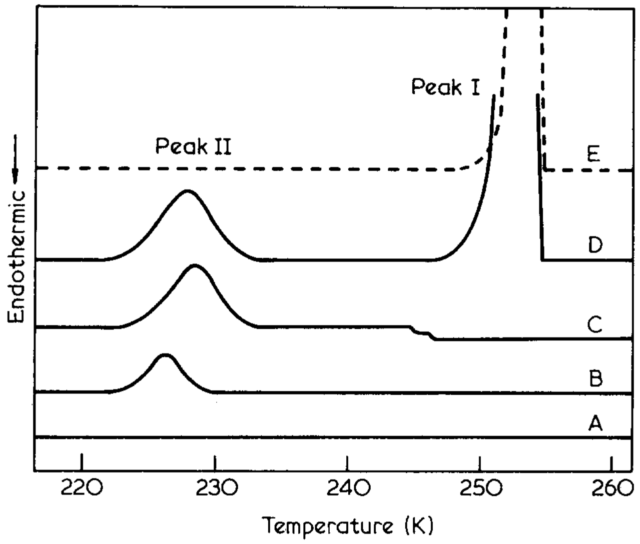

Figure 1 D.s.c. cooling curves of water sorbed on P_pHS: the amount of sorbed water is 7.8% (curve A); 9.2% (curve B); 10.7% (curve C); and 26.3% (curve D); curve E is for pure water

EXPERIMENTAL

Samples

Poly(4-hydroxystyrene) (P_pHS), poly(4-acetoxystyrene) (P_pAS) and partially hydrolysed P_pAS were used in this experiment. These polymers were synthesized by the procedure reported previously[16].

Molecular weight (M_n) *and molecular weight distribution* (M_w/M_n)

M_n and M_w/M_n of the above polymers were measured by a Toyosoda model HLC-801 gel permeation chromatograph. The chromatograph was calibrated by plotting molecular weights of monodisperse polystyrenes (Pressure Chemical Co.) against corresponding elution volume. Values of M_w and M_w/M_n were 1.0×10^5 and 3.1 for P_pAS and 9.2×10^4 and 3.2 for P_pHS, respectively.

Mole fraction of 4-hydroxystyrene (*HS*) *in hydrolysed* P_pAS

P_pHS and partially hydrolysed P_pAS were obtained by hydrolysis of P_pAS. A Perkin–Elmer model 180 grating spectrophotometer was used for infra-red spectrometry. The mole fractions of these polymers were calculated by the procedure reported previously[15].

Thermal analysis of sorbed water

A Perkin–Elmer DSC-II differential scanning calorimeter equipped with cooling cells was used to measure the phase transition of water sorbed on the samples. D.s.c. curves were obtained by cooling at the scanning rate of 10K min^{-1} from room temperature to 200K and then heating to room temperature at the same rate. The temperature of crystallization and melting of water sorbed on the sample were calibrated using the melting and crystallization peaks of pure water. The enthalpy of water sorbed on samples was calculated according to the enthalpy taking into consideration the possible polymorphism of the ice structure. The crystallization enthalpy of water used as the basis for calculation was 334 J g^{-1} regardless of the polymorphism of ice, as the possible error range introduced by this assumption was within 6.6%.[17] The samples of polyhydroxystyrene were dried in a vacuum desiccator for about 1 week, and then each 5 mg sample was weighed in an aluminium pan used for volatile samples. The aluminium pan had previously been heated to 393K in an autoclave with water to eliminate any reaction between the aluminium surface and water. A determined amount of water was added to each sample by a micro-syringe and then the pan was sealed. Weighings were made using a Sartorius model 2405 microbalance. The water content was calculated as follows:

$$\text{water concent}\,(\%) = \frac{\text{weight of added water}}{\text{weight of dry sample}} \times 100 \qquad (1)$$

Each sample pan was heated at 70°C for 1 h and was allowed to stand for a few days in order to have samples with the same thermal history.

A Seiko Co. Ltd SSC/560 differential scanning calorimeter was also used to measure the thermal behaviour of the samples below 300K. Using the apparatus, it was possible to obtain the cooling curves of samples from room temperature to 130K. Heating rate was 5K min^{-1}, and each sample weight was $\sim$5 mg.

RESULTS AND DISCUSSION

Figure 1 shows the d.s.c. cooling curves of water sorbed on P_pHS. In general, when a sample of P_pHS containing sorbed water was cooled from room temperature to 200K, two exothermic peaks of crystallization of water are observed (curve D). One is a sharp peak (Peak I) observed at about 255K in the d.s.c. curve; the other is a broad peak (Peak II) observed at about 235K. However, the first-order transition of water was not observed at first unless the water contents exceeded a certain amount (curve A). This phenomenon was also confirmed by cooling a sample to 130K using a Seiko SSC/560 differential scanning calorimeter. The amount of enthalpy in the first-order transition of water varied according to the chemical structure and/or the higher-order structure of each sample. Before exceeding this water content, a small broad crystallization peak (Peak II) appeared at about 235K (curve B). This peak shifted to a higher temperature range with increasing amount of sorbed water. The enthalpy calculated from the area of Peak II increased with increasing water content until it attained an upper limit (curve C); this value is dependent on the number of hydrophilic groups. A new sharp peak (Peak I) appears when the amount of water in each sample exceeds that needed to show a constant height of Peak II in a d.s.c. curve (curve D). The shape and temperature of Peak I accords well with that for the crystallization of pure water, as shown by the broken curve (curve E) in *Figure 1*, although Peak I is broadened slightly at low temperatures. Generally, with further increase of water the enthalpy of Peak I increases, whereas that of Peak II remains constant. In the case of water sorbed on hydrophobic polymers such as polystyrene (PSt), the crystallization Peak II does not appear but a peak similar to that of pure water is always observed at about 255K.

Figure 2 shows heating curves of water sorbed on P_pHS. The melting curves (curves B, C and D) of sorbed water start from a temperature lower than that of pure water, which is shown by the broken line (curve E). However, the melting of water was not observed when a

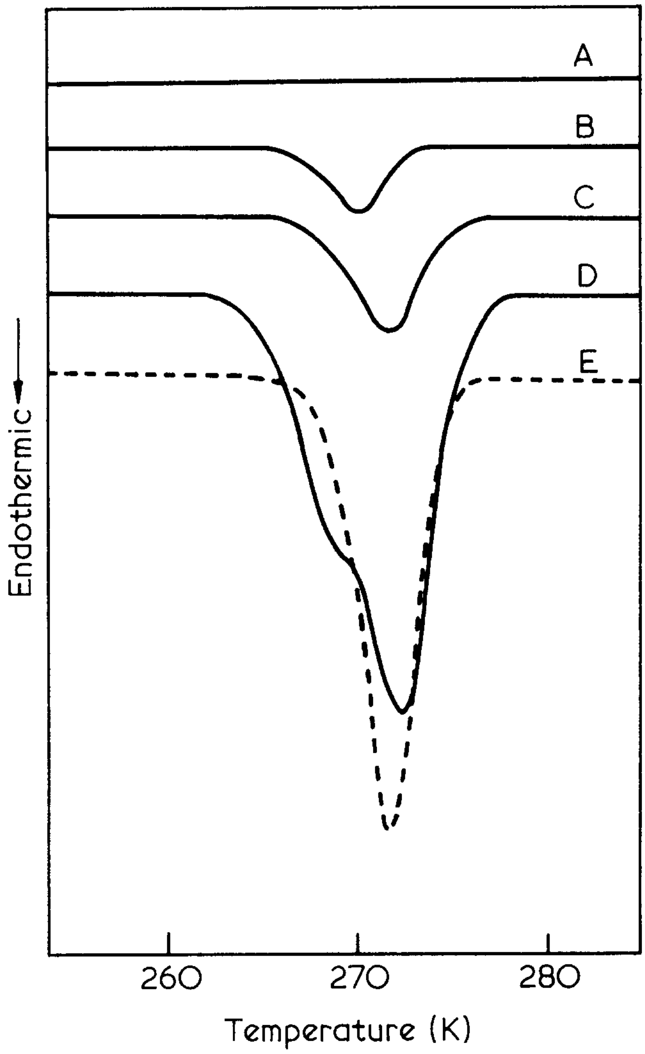

Figure 2 D.s.c. heating curves of water sorbed on P_pHS: the water content is 7.8% (curve A); 9.2% (curve B); 10.7% (curve C); and 26.3% (curve D); curve E is for pure water

very small amount of water was sorbed on P_pHS (curve A). The shape varied according to the water content. In some cases a shoulder was found on the low-temperature side of the melting peak (curve D). The melting of sorbed water produced a characteristic asymmetric pattern. Melting curves of sorbed water corresponding to Peak II showed small broad peaks at about 263K (curves B and C). If water is added to hydrophobic polymers such as PSt, the d.s.c. melting curve of water shows a pattern similar to that of pure water (curve E).

Figure 3 shows the relationship between phase transition temperatures of water sorbed on partially hydrolysed P_pAS samples. The crystallization temperature of Peak I and Peak II was shifted to the low-temperature range with increasing mole fraction of HS. The melting temperature of sorbed water was also depressed with increasing mole fraction of HS. This fact indicates that water molecules are tightly bound to polymers having a high mole fraction of HS.

Figure 4 shows the relationship between the phase transition temperatures and the amounts of water sorbed on P_pHS. The first-order transition of sorbed water was not observed until the water content reached about 8%. The crystallization temperature of Peak II rose as the water content increased up to 10%, after which a constant temperature of 235K was obtained. The crystallization temperature of Peak I shifted to a slightly higher temperature with increasing water content. Melting temperature rose a little at first and then decreased with increasing amount of water sorbed on P_pHS.

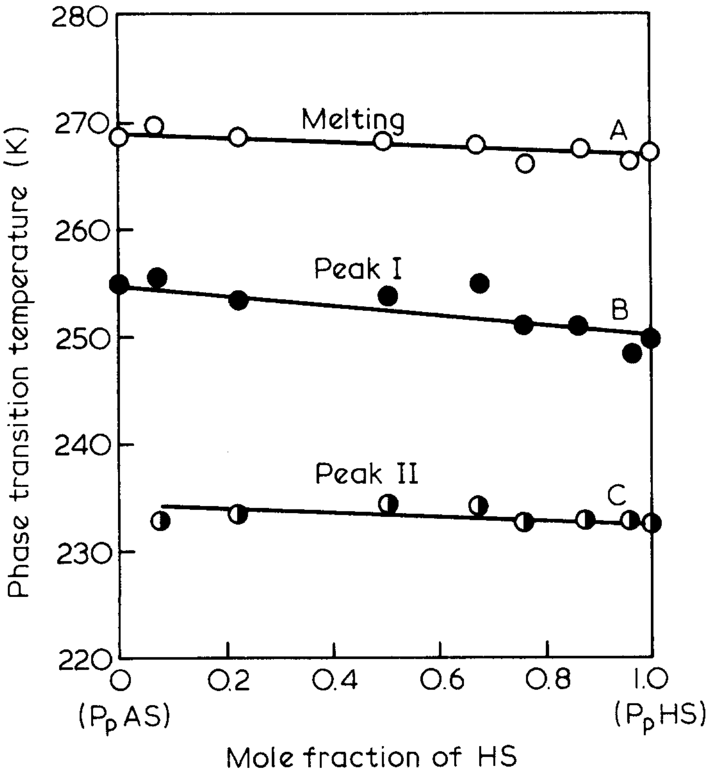

Figure 3 The relationship between phase transition temperatures of water sorbed on the hydrolysed P_pAS and mole fraction of HS: curve A, melting; curve B, crystallization of free water (Peak I); curve C, crystallization of freezable bound water (Peak II)

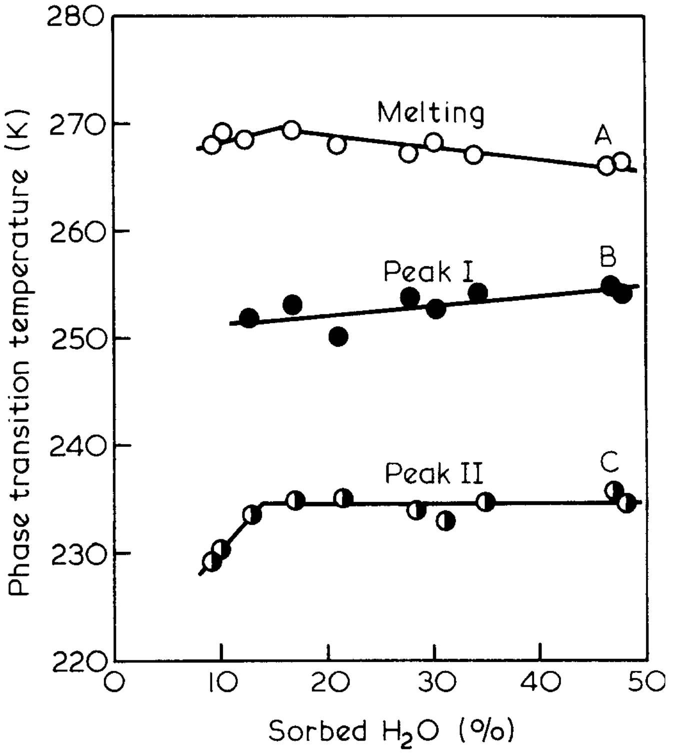

Figure 4 The relationship between phase transition temperatures and the amount of water sorbed on P_pHS: curve A, melting; curve B, Peak I; curve C, Peak II

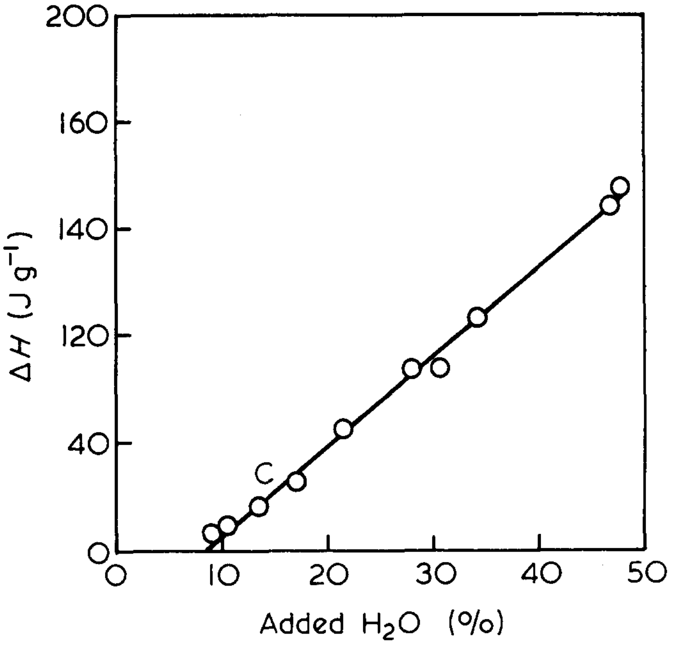

Figure 5 The relationship between amount of added water and the sum of crystallization enthalpies of Peak I and Peak II

Figure 5 shows the relationship between the amounts of water added to P_pHS and the crystallization enthalpies calculated from the areas of Peak I and Peak II in the d.s.c. curve. Crystallization enthalpy (ΔH) increases in proportion to the amount of sorbed water after reaching a certain critical amount, which is obtained by extrapolation of the straight line fitted to the experimental points (point C in *Figure 5*).

In the case of the crystallization of water sorbed on the samples, the sum of the weight of water calculated from enthalpies of Peak I and Peak II is less than the total weight of added water. The water corresponding to the difference between the water added and the amount of water calculated from d.s.c. must be present somewhere. It is very obvious that water cannot escape from a volatile sample pan under our experimental conditions, as no first-order transitions were observed except for crystallization or melting in each of the cooling and heating curves. Accordingly, the only possibility is that this water is bound very tightly to the samples. There seems to be some non-freezing water which does not crystallize.

It is appropriate to consider that there are three kinds of sorbed water, i.e. non-freezing water, Peak I and Peak II, due to the several types of interaction between the polymer and water. Non-freezing water does not seem to have any kind of crystalline structure, as it shows no first-order transition. Peak I corresponds to pure water, i.e. free water. Water represented by Peak II is bound to hydroxyl groups in the polymer and crystallizes at a lower temperature than that of Peak I. Water represented by Peak II seems to have a structure intermediate between free water and non-freezing water. Therefore, we have categorized water sorbed on polyhydroxystyrene into three different kinds: free water corresponding to Peak I, freezable bound water corresponding to Peak II and non-freezing bound water.

As crystallization and melting occur in freezable bound water (Peak II) and free water (Peak I), each must be organized into a certain type of structure, which may be identical to the type of structure found in natural ice, regardless of the particular crystalline morphism. There are nine polymorphic forms of ice, i.e. ice I, Ic, II, III, IV, V, VI, VII and VIII[17]. The structures from ice IV to ice VIII are found only at very high pressures. Therefore, in our experimental conditions the possible structures of ice for freezable bound water can be considered as ice I, Ic, II and III. The maximum value of melting enthalpy of ice (ice I) is estimated as 334 J g^{-1}, and the minimum value of melting enthalpy of ice (ice III) is estimated as 312 J g^{-1}, from the phase diagram of water[17]. In this study, the crystallization enthalpy of Peak II was calculated by using 334 J g^{-1} of pure water, with an error of about 6.6%.

Therefore, the following equation can be applied to water sorbed on the above samples:

$$W_t = W_{p1} + W_{p2} + W_{nf} \qquad (2)$$

where W_t = total weight of water added to a sample, W_{p1} = weight of water calculated from the enthalpy of crystallization Peak I, W_{p2} = weight of water calculated from the enthalpy of crystallization Peak II and W_{nf} = weight of non-freezing water. The weight of bound water can be shown as follows:

$$W_b = W_{p2} + W_{nf} \qquad (3)$$

where W_b = weight of bound water. The percentage bound water content is calculated by the following equation:

$$C_b = (W_b/W_s) \times 100 \qquad (4)$$

where C_b = percentage of bound water and W_s = weight of sample. It will be noted that the amount of bound water (W_b) shown by equation (3) can be obtained directly from the d.s.c. cooling curve (equation (2)), while W_{p2} of crystallization Peak II is difficult to evaluate from a d.s.c. heating curve, because of the difficulty in separating the melting peaks. Therefore, in this study the bound water content (C_b) can be calculated only by using d.s.c. cooling curves. The bound water content and critical water content of polyhydroxystyrene having various HS mole fractions are tabulated in *Table 1*.

Figure 6 shows the relationship between bound water content and the mole fraction of HS of hydrolysed P_pAS. Bound water content (C_b) increases with increasing mole fraction of HS, i.e. C_b increases with increasing hydroxyl groups in the polymer. Freezable bound water corresponding to Peak II increases with increasing mole fraction of HS as shown by curve B. This fact suggests that

Table 1 Bound water content and critical water content of polyhydroxystyrene having various HS mole fractions

HS mole fraction	Molecular weight of monomer ($\bar{M}$)	Bound water content (%)	Moles H_2O per monomer (B_m)	Moles H_2O per OH group	Critical water content (%)
0 (P_pAS)	162	2.9	0.26	–	2.0
0.08	159	3.7	0.33	4.13	2.7
0.22	153	3.5	0.30	1.36	4.0
0.49	141	5.3	0.42	0.86	5.9
0.63	136	5.8	0.44	0.70	6.4
0.76	130	6.8	0.49	0.64	7.2
0.96	122	10.2	0.69	0.72	8.0
1 (P_pHS)	120	10.7	0.71	0.71	7.8

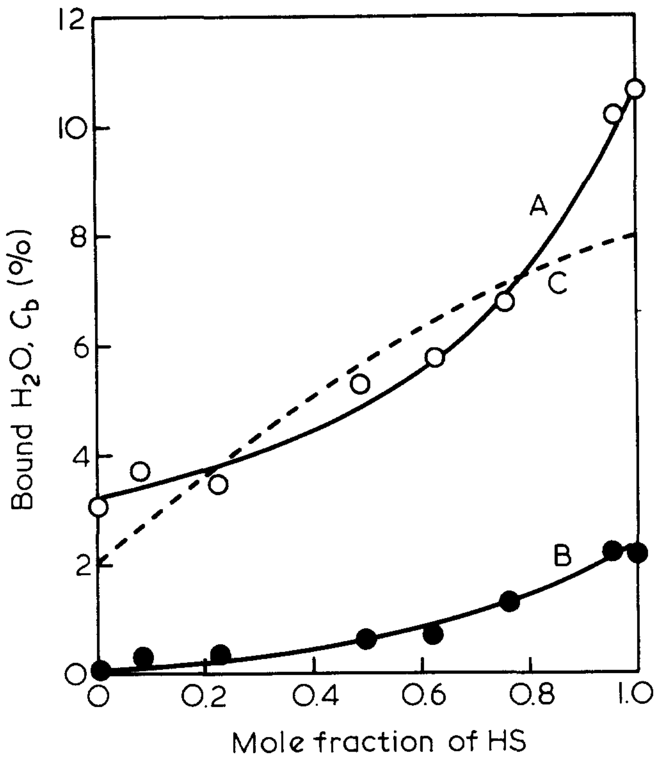

Figure 6 The relationship between bound water content (C_b) and mole fraction of HS of hydrolysed P_pAS: curve A, bound water content; curve B, the amount of freezable bound water (Peak II); curve C, critical water content[15]

water corresponding to Peak II is also affected by hydroxyl groups of the polymer. Water represented in Peak II comprises less than 20% of the total bound water. It is assumed that hydrogen bonds form between the hydroxyl groups in the polymer and that the number of hydrogen bonds increases with increasing numbers of hydroxyl groups. It is necessary to keep in mind that the moisture adsorption depends on the molecular structure of the amorphous part of a polymer[18,19] and that the polyhydroxystyrene derivatives used in this study are amorphous polymers having hydroxyl groups. We reported previously[15] that water molecules act initially to disrupt hydrogen bonds. The critical water content[15], as shown by the broken curve in *Figure 6* and listed in *Table 1*, increases with increasing mole fraction of HS, and correlates closely with bound water content. Moreover, it is demonstrated that the critical water content can be used for the quantification of the degree of hydrogen bonding in the polymer. Therefore, bound water molecules act to disrupt hydrogen bonds and are attached to the hydroxyl groups. The number of hydrogen bonds increases with increasing mole fraction of HS.

Figure 7 shows the relationship between the mole fraction of HS and moles of bound water attached to a monomer unit of the polymer. The molecular weight ($\bar{M}$) of hydrolysed polymer is given by:

$$\bar{M} = M_{oh}H + M_{ac}(1-H) \qquad (5)$$

The calculated values of $\bar{M}$ are listed in *Table 1*, where M_{oh} = molecular weight of monomer unit of completely hydrolysed polymer, M_{ac} = molecular weight of monomer unit of acetate polymer and H = mole fraction of HS. The number of moles of bound water attached to a monomer unit of the polymer can be calculated by:

$$B_m = (\bar{M}C_b)/(18 \times 100) \qquad (6)$$

where B_m = moles of bound water attached to a monomer unit of the polymer and 18 is the molecular weight of water. The number of moles of bound water attached to a monomer unit of the polymer increases with increasing mole fraction of HS and the maximum of B_m is about 0.7 mol of water. This indicates that on the average less than one water molecule is bound to each hydroxyl group and, moreover, that part of the bound water does not crystallize. Moreover, it is ascertained that water molecules are bound only to hydroxyl groups and constitute the monolayer of water adsorbed by the polymer. The increment of B_m in the region of high mole fraction of HS is larger than that in the region of low mole fraction as shown in *Figure 7*. This fact demonstrates that a polymer with a low mole fraction of HS has properties similar to acetate polymer and that diffusion and sorption of water molecules in such a polymer are relatively difficult as the acetate polymer is considered to be hydrophobic. On the other hand, polymer with a high mole fraction of HS has hydrophilic properties. Therefore, diffusion and sorption of water take place very easily. This indicates that hydroxyl groups easily interact with neighbouring hydroxyl groups in the polymer, and, therefore, that the ability of hydrogen bonds to form between hydroxyl groups is relatively high, especially in the high mole fraction of HS.

The bound water content estimated above was found to agree with the critical water content, which was estimated from the decrease in the glass transition temperature of water sorbed polymers. Consequently, bound water is defined as the water molecules which break the intermolecular hydrogen bonding and then become closely attached to each hydroxyl group of the polymers. Thus, the bound water content evaluated from d.s.c. can be related to the amount of hydrogen bonding of polymers.

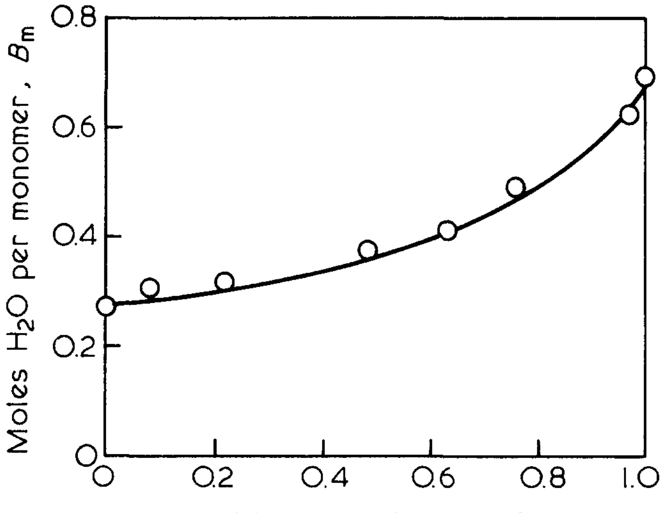

Figure 7 The relationship between mole fraction of HS and moles of bound water attached to a monomer unit of the polymer (B_m)

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