The state of water in nylon-6 membranes grafted with hydrophilic monomers:
2. Water in acrylic acid, acrylamide and *p*-styrenesulphonic acid grafted nylon-6 membranes

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The state of sorbed water in nylon-6 membranes grafted with acrylic acid (AA), acrylamide (AM) and *p*-styrenesulphonic acid (SS) was investigated by differential scanning calorimetry. There are three kinds of water in AA- and AM-grafted nylon-6 membranes: non-freezing water, intermediate water and free water. The SS-grafted nylon-6 membrane retains both non-freezing water and freezing water. In the latter, the intermediate water and the free water cannot be distinguished. Each kind of grafted membrane with high extent of grafting can retain a good deal of the non-freezing water and the intermediate water. This is due to an increase in the content of hydrophilic repeat units as graft copolymerization progresses. The SS repeat unit can retain a larger amount of water than can AA or AM. It was also found that the amount of non-freezing water per repeat unit increased in the order of AA-, AM- and SS-grafted nylon-6 membranes. The order reflects the nature of the homopolymers.

(Keywords: nylon-6; graft copolymerization; differential scanning calorimetry; non-freezing water; intermediate water; free water)

INTRODUCTION

It is well known that the molecular motion of water that is strongly associated with the hydrophilic groups of a polymer is different from that of pure water. The volume fraction of water in polymer membranes is one of the important factors controlling permeability of water[1,2] and solutes[3–6] through water-swollen membranes. It is important to measure the state of water in polymer membranes in order to understand their permeability.

The states of water in polymers have been investigated by various methods: for example, sorption and desorption isotherms[7], dielectric relaxation spectra[8], differential scanning calorimetry (d.s.c.)[9–20] and nuclear magnetic resonance (n.m.r.) techniques[21–23]. In addition, d.s.c. is a useful method to investigate the phase transition behaviour of the sorbed water.

A number of studies on the states of water in natural and hydrophilic synthetic polymers have been carried out by d.s.c.[9–20]. Many investigators have shown that the properties of sorbed water are markedly different from those of pure water. It has been reported that three kinds of sorbed water exist in cellulosic materials[11] and hydrophilic synthetic polymers[14,24]. One is non-freezing water, which does not show a phase transition in the temperature range 0 to −150°C. The other two are waters that show transition temperatures below 0°C and at 0°C. The freezing sorbed waters are known by different names, and there is a lack of consistency in the nomenclature used. In this paper, the three kinds of water are referred to as follows. (i) Non-freezing water: this is water showing no endothermic peak in the temperature range 0 to −70°C. (ii) Intermediate water: this is the freezing water showing a melting point (T_m) below 0°C (this corresponds to the intermediate water referred to by Sung *et al.*[24] and the freezing bound water used by Hatakeyama *et al.*[11,14]). (iii) Free water: this is another type of freezing water showing T_m at 0°C.

On the other hand, three kinds of sorbed water (two types of bound water with different T_m below 0°C and non-freezing water) have been found in polyelectrolytes and polyelectrolyte complexes[25]. Free water was not observed in these systems. It seems that the state of water in polyelectrolyte materials is different from that in non-electrolyte materials.

There are a few studies[26–28] on water sorbed in grafted polymeric materials. Nishioka *et al.*[26] investigated the state of water in acrylonitrile (AN) grafted cellulose membrane, and found that the amount of intermediate water was reduced by AN grafting onto cellulose. In a previous paper[28], we reported that there are three kinds of water in acrylic acid (AA) grafted nylon-6 membranes, namely non-freezing water, intermediate water and free water. The amount of the sorbed water increased with the extent of grafting.

In the present study, nylon-6 membranes were grafted to various extents with acrylic acid (AA), acrylamide (AM) and *p*-styrenesulphonic acid (SS), and d.s.c. measurements of water sorbed in each kind of membrane were carried out by changing the water content. The

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melting point and the heat of fusion of the sorbed water were also determined. The purpose of this work is to establish the state of water sorbed in each kind of grafted nylon-6 membrane with different extents of grafting, and to investigate how different branch polymers influence the state of sorbed water.

EXPERIMENTAL

Materials

Biaxially stretched nylon-6 (15 μm in thickness, $\bar{M}_v = 2.6 \times 10^4$), supplied by Unitika Co. Ltd, was used as the starting material. The film was washed with 0.1% aqueous non-ionic surfactant solution and rinsed with distilled water several times prior to drying in air.

Acrylic acid (AA) was distilled under reduced pressure, and acrylamide (AM) was purified by recrystallization from hot benzene before use. Potassium *p*-styrenesulphonate (K-SS) was provided by Sankyo Chemical Co. Ltd, and other chemicals were extra-pure grade (Wako Pure Chemical Industries Ltd). They were used without further purification. The water used was doubly distilled and deionized.

Graft copolymerization

The nylon-6 film (ca. 0.5 g) was dried under reduced pressure at 50°C for 20 h. It was irradiated by ^{60}Co γ-rays at a dose rate of 10 kGy h^{-1} for 1 h under a nitrogen atmosphere at room temperature.

Graft copolymerization onto the irradiated nylon-6 film was carried out in reaction systems consisting of AA/water (20/80 wt%), AM/water (5/95 wt%) and K-SS/water (20/80 wt%, with the solution adjusted to pH 6.0 using 1 M acetic acid) under a nitrogen atmosphere at 30°C. The liquor-to-material ratio was 200:1 for each reaction system.

After the reaction time, the samples were added to distilled water (1 litre) to stop the graft copolymerization process. Following this, AA- and AM-grafted nylon-6 (GN) membranes were extracted with hot water to remove homopolymer. The membrane grafted with K-SS was extracted in hot phosphate buffer solution (pH 7.0) to avoid hydrolysis of trunk polymer. Then the membrane was immersed in 0.1% aqueous acetic acid solution to convert it into the acidic form (SS). The extent of grafting was expressed as the percentage increase in weight compared with the original weight of the sample.

Differential scanning calorimetry

The original nylon-6 film and nylon-6 membranes grafted with AA, AM and SS were cut into fine pieces with scissors. The samples were weighed in aluminium pans for volatile samples. The pans had been treated with boiling water for 1 h to eliminate any reaction between the aluminium surface and the water. Water (1 μl) was added to each sample using a micro-syringe and the pans were sealed hermetically. The sample pans were left at room temperature for several days to allow complete diffusion of the water into the grafted membranes.

A Rigaku differential scanning calorimeter DSC 8230 was used to measure the phase transition of sorbed water in the samples. Each sample was cooled to −70°C at 20°C min^{-1} and held for 10 min at that temperature. Then, the d.s.c. curve of the sample was measured up to 30°C at a heating rate of 10°C min^{-1}. The melting point (T_m) of sorbed water was defined as the extrapolated onset temperature of melting, at which the steepest tangent of the left side of the peak intersects the baseline. The temperature scale and the heat of fusion were calibrated using pure water as a standard material.

Water content

After d.s.c. measurements, the d.s.c. sample pans were pricked with a pin to remove water from the samples. The samples were dried completely *in vacuo* at 50°C and were weighed. The water content (*WC*) of the samples was determined as follows:

$$\text{Water content} = \frac{\text{Weight of water in polymer}}{\text{Weight of dry polymer}}$$

RESULTS AND DISCUSSION

Figure 1 shows d.s.c. curves of water in AA-grafted nylon-6 (AA-GN) membrane with 108% grafting. No peak is observed for the AA-GN membrane with low water content (see d.s.c. curve of $WC = 0.05$), but a broad endothermic peak with T_m below 0°C appears on the d.s.c. curves with increasing water content. As the water content increases further, a new endothermic peak appears at higher temperatures, and its intensity increases remarkably with water content. The T_m determined from the sharper peak is 0°C. However, the broad peak changes to a shoulder of the new peak with increasing water content, and the position of the shoulder shifts to the higher-temperature side. Similar results are obtained

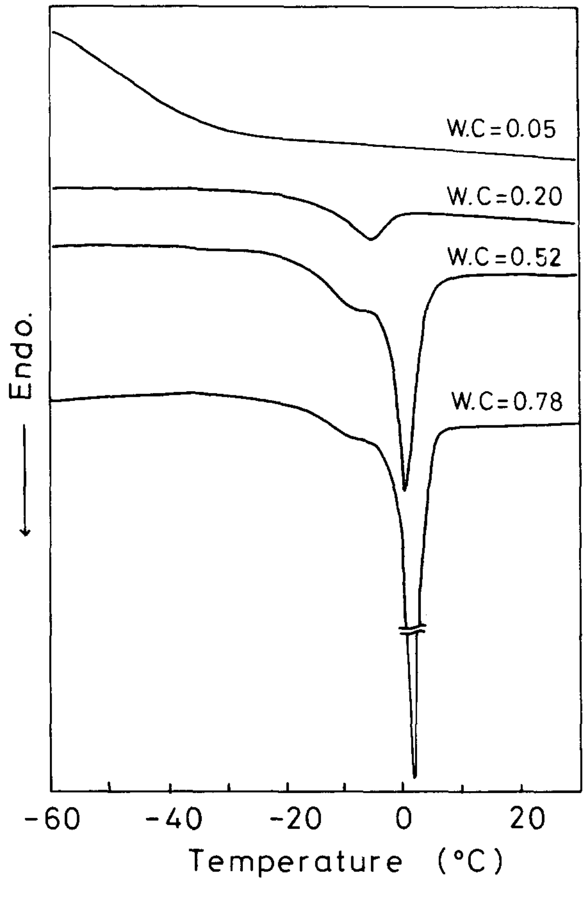

Figure 1 D.s.c. melting endotherms of water in acrylic acid grafted nylon-6 membranes with 108% grafting

for water in AA-GN membranes with 56% and 187% grafting.

It appears, therefore, that there are three kinds of water in water-swollen AA-GN membranes, namely non-freezing water, intermediate water and free water.

Figure 2 shows d.s.c. curves of water in AM-GN membranes with 108% grafting. Although no peak is observed for the membrane with low water content (see the curve of $WC=0.10$), a broad endothermic peak with T_m below 0°C appears as the water content is increased (i.e. $WC=0.39$). The broad peak is due to the intermediate water. As the water content further increases, a new peak showing T_m at 0°C appears. This peak represents the melting of the free water. The area of the new peak increases considerably with increasing water content. Similar results were obtained for water in AM-GN membranes with 57% and 207% grafting. It is concluded that three kinds of water also exist in AM-GN membranes.

The d.s.c. curves of water in SS-GN membrane with 87% grafting are shown in *Figure 3*. In the low water content region, water in the membrane does not show any peak on the d.s.c. curve (i.e. $WC=0.12$). A broad endothermic peak showing T_m below 0°C appears as the water content is increased, and this is similar to that observed with AA- and AM-GN membranes. The broad peak increases with increasing water content and T_m approaches 0°C, but the other peak showing T_m at 0°C is not observed. Water in SS-GN membranes with 48% and 201% grafting shows similar trends. The fact that the d.s.c. curve shows a single peak indicates that the state of freezing water in SS-GN membranes differs from that in AA- and AM-GN membranes. Therefore, there are two kinds of water in SS-GN membrane, non-freezing water and freezing water; in the latter the intermediate water and free water are not distinguishable.

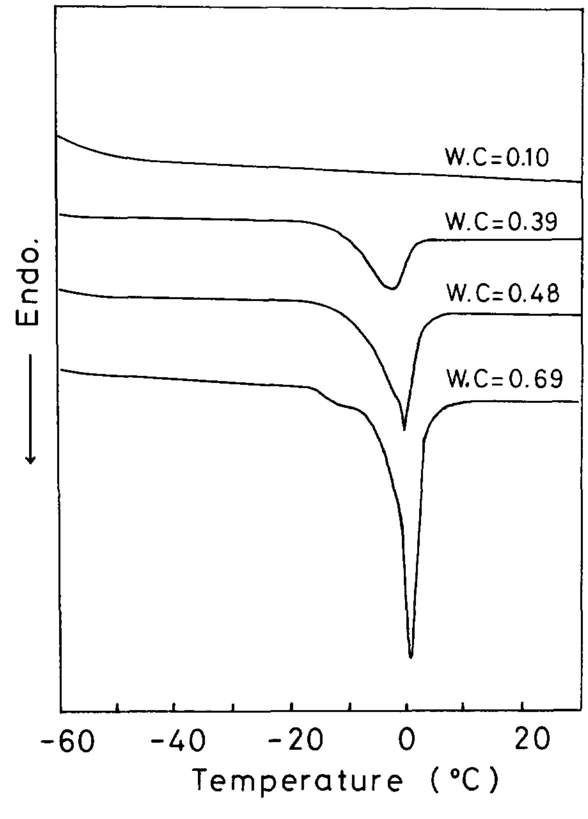

Figure 2 D.s.c. melting endotherms of water in acrylamide grafted nylon-6 membranes with 108% grafting

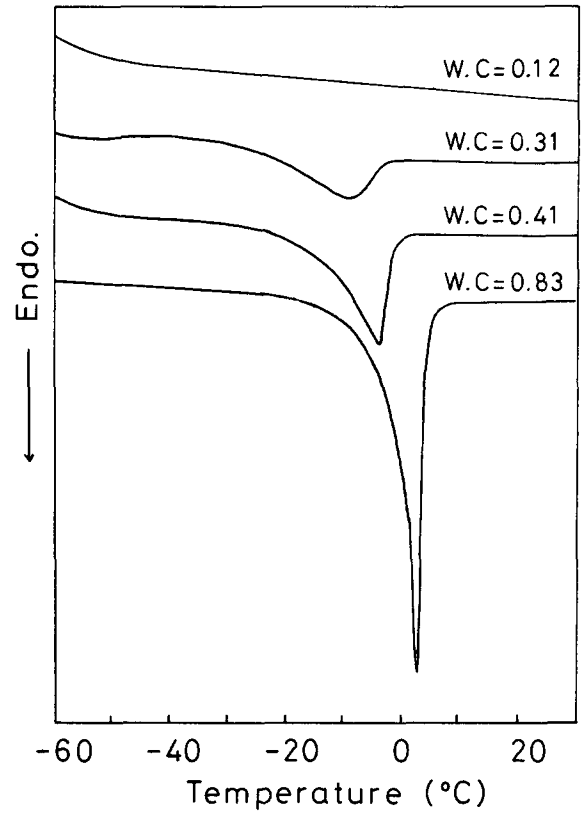

Figure 3 D.s.c. melting endotherms of water in *p*-styrenesulphonic acid grafted nylon-6 membranes with 87% grafting

To investigate the state of water quantitatively, the heat of fusion of sorbed water (d*H*, cal/g sorbed water) in each kind of grafted nylon-6 membrane was determined from the peak area of the d.s.c. curves.

Figure 4 shows the relationships between d*H* and water content of AA-GN membranes with 56, 108 and 187% grafting. The sorbed water in each AA-GN membrane shows small d*H* values in the region of water content less than 0.25. The value of d*H* increases rapidly with increasing water content up to ca. 0.6, and thereafter increases more slowly.

For the GN membranes with different extents of grafting but with similar water contents, the water in the membrane with the highest extent of grafting shows the lowest d*H* value. This means that the AA-GN membranes with high extent of grafting can hold a great deal of water as bound water. The change of d*H* with increasing water content is due to the increase in the fraction of free water in the sorbed water. However, the d*H* value of the membrane with water content of more than 1.0 is smaller than that of bulk water.

Figure 5 shows the dependence of d*H* on water content for AM-GN membranes. The value of d*H* increases with water content initially at a high rate, but this changes after a water content of 0.5. When the three kinds of AM-GN membranes are compared at similar water contents, the 57% GN membrane shows higher d*H* than the other GN membranes. AM-GN membranes with 200% grafting can retain a larger amount of water as intermediate water.

The relationships between d*H* and water content for SS-GN membranes are shown in *Figure 6*. The value of

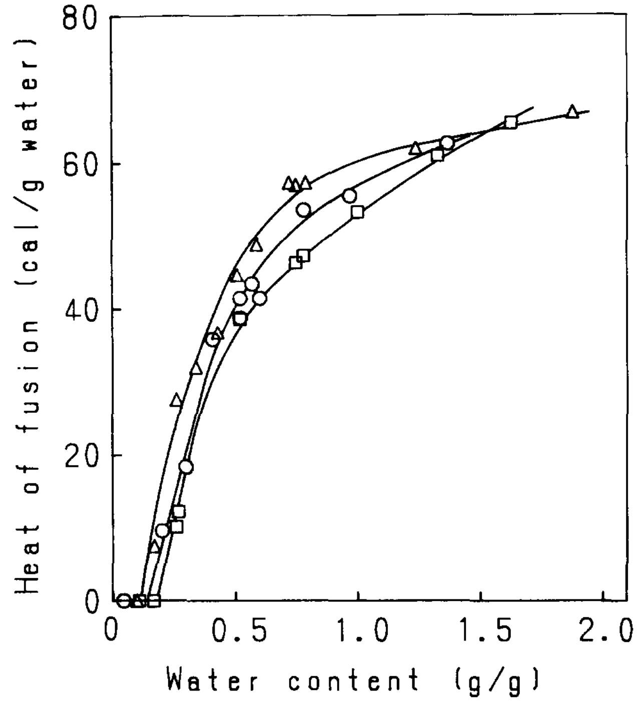

Figure 4 Relationships between water content and heat of fusion of water in acrylic acid grafted nylon-6 membranes: (△) 56% grafting; (○) 108% grafting; (□) 187% grafting

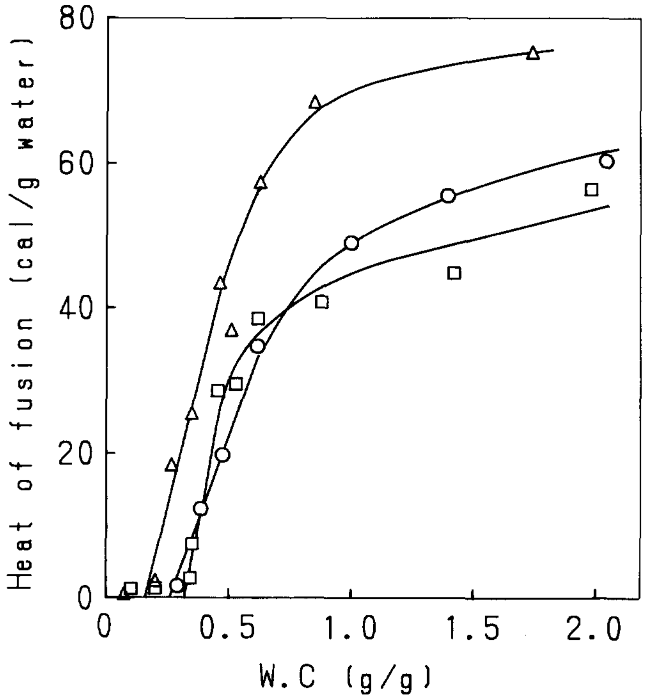

Figure 5 Relationships between water content and heat of fusion of water in acrylamide grafted nylon-6 membranes: (△) 57% grafting; (○) 108% grafting; (□) 207% grafting

d*H* shows a similar pattern to that obtained in *Figures 4* and *5*, with an initial steep increase that levels off at higher water content. When compared to SS-GN membrane with similar water content, the membrane with the highest extent of grafting shows the lowest d*H*. Thus SS-GN membranes with high extent of grafting can retain a great deal of water bound by polymer networks compared with the membranes with low extent of grafting.

The sorbed water in each kind of GN membrane shows small values of d*H* compared with that of bulk water. This is especially noted at low water content. However, since no correction for the weight of the non-freezing water is made in the calculation of d*H*, the d*H* value is underestimated. In order to arrive at a more accurate value, the heat of fusion of sorbed water was calculated based on the weight of freezing water, which was determined by subtraction of the weight of non-freezing water from the total weight of sorbed water. The corrected d*H* values increased with water content up to ca. 0.6. Above 0.6 the increase is not so pronounced for each kind of GN membrane. When the experimental error is considered, the corrected value is smaller than 79.7 cal g^{-1}, except for 57% AM-GN membranes at water content values higher than 0.6.

Accordingly, it is inferred that the heat of fusion of the intermediate water is lower than that of bulk water. It has been reported that water in a hydrogel system based on poly(hydroxyethyl methacrylate)[24] and in water-swollen elastin[29] showed smaller values of heat of fusion than that for bulk water. These workers proposed that the decrease in the heat of fusion is due to volume shrinkage and the structuring of water in the gel network.

Since the water content of nylon-6 film is remarkably increased by graft copolymerization, most of the water in the GN membranes should be sorbed by the hydrophilic branch polymers. If it is assumed that all water in the GN membranes is retained by the branch polymers, the molar ratio of water molecules to monomer repeat units of the branch polymer (N_w) can be determined as follows:

$$N_w = \frac{WC \times (100 + G_{on}) \times MW}{G_{on} \times 18}$$

where *WC* is water content, G_{on} is extent of grafting (%)

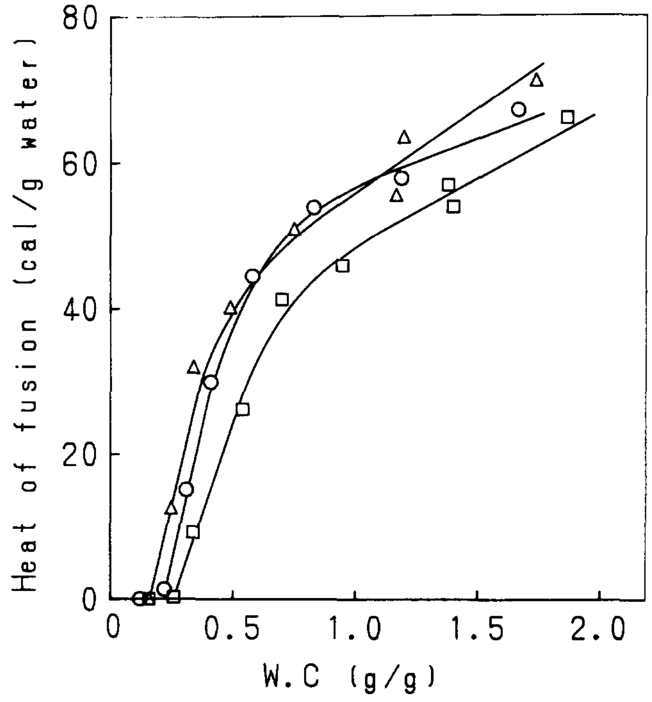

Figure 6 Relationships between water content and heat of fusion of water in *p*-styrenesulphonic acid grafted nylon-6 membranes: (△) 48% grafting; (○) 87% grafting; (□) 201% grafting

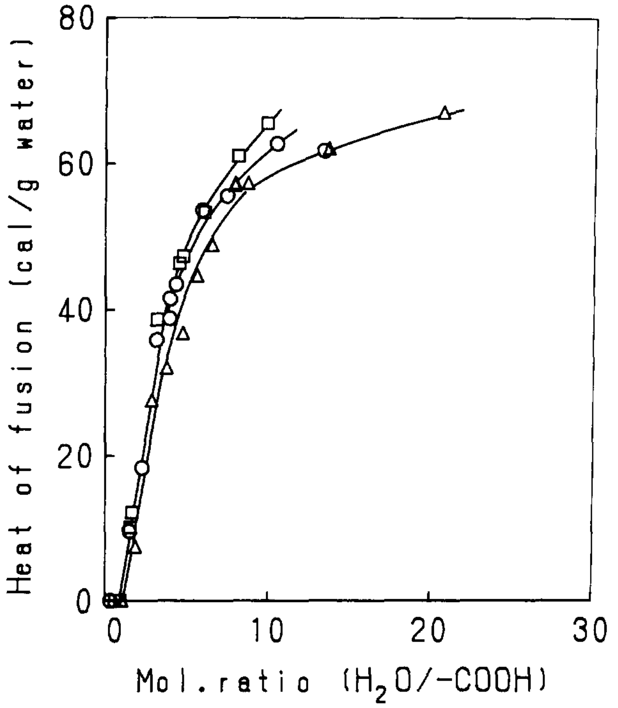

Figure 7 Heat of fusion of water *versus* molar ratio of water molecules to monomer repeat units of the branch poly(acrylic acid): (△) 56% grafted membrane; (○) 108% grafted membrane; (□) 187% grafted membrane

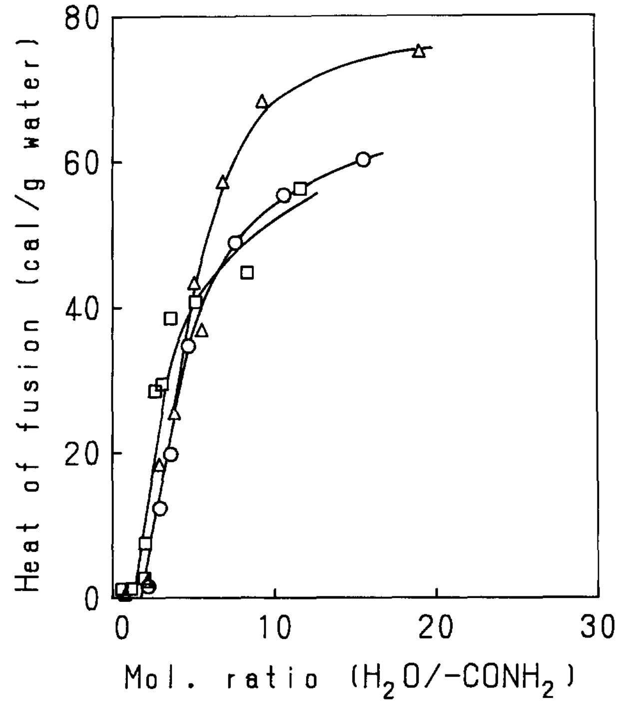

Figure 8 Heat of fusion of water *versus* molar ratio of water molecules to monomer repeat units of the branch poly(acrylamide): (△) 57% grafted membrane; (○) 108% grafted membrane; (□) 207% grafted membrane

and MW is molecular weight of a monomer repeat unit of the branch polymer.

Figure 7 shows the relationship between dH and N_w for AA-GN membranes. The dH of water in 56% AA-GN membrane increases at a high rate initially. The other membranes show a similar trend. The heat of fusion is a measure representing the interaction between polymer and water. Therefore, it is inferred that the strength of retaining water molecules per carboxyl group is almost the same for each AA-GN membrane regardless of the extent of grafting.

Figure 8 shows the relationships between dH and N_w for AM-GN membranes. Again, an initial rapid increase in dH is observed. Although the AM-GN membranes showed similar behaviour at low N_w (i.e. $N_w < 5$), the 57% GN membrane exhibits considerably higher dH value for $N_w > 5$. As mentioned above, water in 57% AM-GN membrane shows higher corrected dH values (about 80 cal g^{-1}) in the high water content region. This may be attributable to the influence of water outside of the membrane (i.e. bulk water).

The relationship between dH and N_w is shown in *Figure 9* for SS-GN membranes. Again, similar to the results obtained with AA- and AM-GN membranes, the value of dH increases rapidly at the lower N_w values. Although the 48% GN membrane exhibits a slightly smaller dH value in the higher N_w region, the other two membranes (87% SS-GN and 201% SS-GN) are similar in their dH values in different N_w ranges. It is proposed that the difference observed for the 48% GN membrane is attributable to a change in the degree of crystallinity of the trunk polymer as a result of the graft copolymerization reaction. The decline of the degree of crystallinity for the 48% GN membrane may be smaller than that for the GN membranes with more than 87% grafting. However, the strength of retaining water molecules per repeat unit is not so dependent on the extent of grafting.

From these results, it is found that, for each kind of GN membrane, the heat of fusion of water, which is affected by the repeat unit of the branch polymer, is similar regardless of extent of grafting. Therefore, the fact that the nylon-6 membranes with higher extent of grafting can hold larger amounts of bound water is primarily due

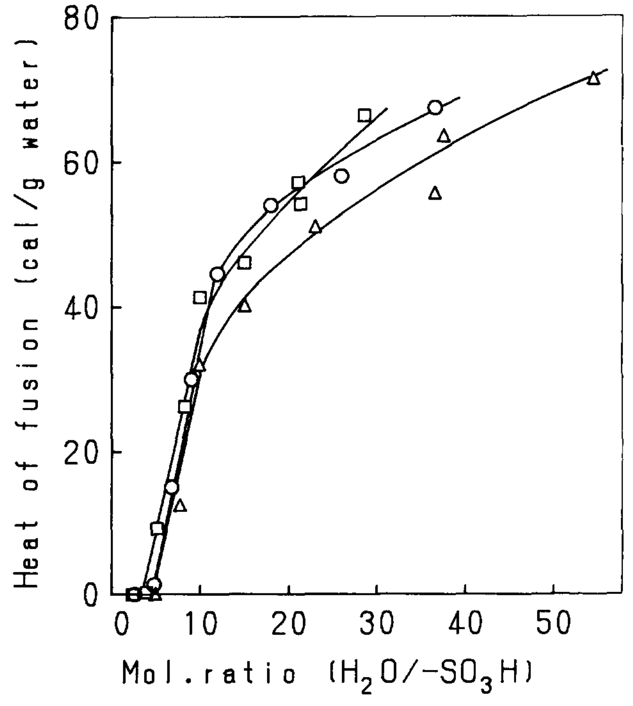

Figure 9 Heat of fusion of water *versus* molar ratio of water molecules to monomer repeat units of the branch poly(p-styrenesulphonic acid): (△) 48% grafted membrane; (○) 87% grafted membrane; (□) 201% grafted membrane

Table 1 Weight of non-freezing water and molar fraction of non-freezing water in various grafted nylon-6 membranes

Sample[a]	Extent of grafting (%)	Weight of non-freezing water (g water/ g polymer)	Molar fraction of non-freezing water (mol water/ mol monomer unit)
AA-GN 56	56	0.14	1.50
AA-GN 108	108	0.19	1.45
AA-GN 187	187	0.22	1.45
AM-GN 57	57	0.20	2.05
AM-GN 108	108	0.27	2.05
AM-GN 207	207	0.34	1.95
SS-GN 48	48	0.22	6.0
SS-GN 87	87	0.24	6.0
SS-GN 201	201	0.27	5.5
Nylon 6	–	0.06	0.38
Poly(AA)	–	0.25	1.00
Poly(AM)	–	0.42	1.66
Poly(SS)	–	0.53	5.42

[a] AA-GN: acrylic acid grafted nylon-6 membrane
AM-GN: acrylamide grafted nylon-6 membrane
SS-GN: *p*-styrenesulphonic acid grafted nylon-6 membrane

to an increasing content of hydrophilic repeat units of the branch polymer in GN membranes.

It is also found that the SS monomer unit can retain larger amounts of intermediate water than can AA or AM. A possible explanation is that the sulphonic groups on the branch polymer would ionize in the presence of water. Branch poly(SS), a strong polyacid, would expand due to the electrostatic repulsive forces between the ionized sulphonic groups. However, since poly(AA) is a weak polyacid and poly(AM) is a non-electrolyte, the branch polymers of AA and AM would not expand in such a way.

If it is assumed that water is preferentially taken up as non-freezing water at an early stage of water sorption and that the sorption of the other kinds of water appears after the non-freezing water has reached a saturated value, the weight of the non-freezing water (W_{nf}, g water/ g dry polymer) and the molar ratio of non-freezing water per repeat unit of the branch polymer (N_{nf}) can be determined by extrapolation of the heat of fusion curves to zero. The values of W_{nf} and N_{nf} thus obtained are listed in *Table 1* for each kind of GN membrane together with the original nylon-6 film, poly(AA), poly(AM) and poly(SS).

The 56% AA-GN membrane exhibits fairly high values of W_{nf} when compared with the original nylon-6 film. The W_{nf} values also increase with the extent of grafting in the samples. Similar results are observed for AM- and SS-GN membranes. It is found that the GN membranes with similar extents of grafting differ in their non-freezing water content (*Table 1*). For example, AA-GN membranes have smaller W_{nf} values compared with AM- and SS-GN membranes. This observation is directly related to the nature of the homopolymer: W_{nf} of homo-poly(AA) is smaller than the values for homo-poly(AM) and homo-poly(SS). However, the values of W_{nf} in each GN membrane are smaller than those for the corresponding homopolymer. This finding is also relevant for the membranes with more than 190% grafting.

On the other hand, all of the GN membranes show considerably higher N_{nf} values than that of the original nylon-6 film. For each kind of GN membrane with different extents of grafting, the value of N_{nf} is almost the same. It is also found that the N_{nf} value depends on the kind of functional groups present in branch polymers. The value of N_{nf} increases in the order of AA-GN, AM-GN and SS-GN membranes. In addition, the SS-GN membranes retain a great deal of non-freezing water compared with the other membranes. This order again is related to the nature of the homopolymer used. The numerical values of N_{nf} for all of the GN membranes are larger by about 0.5 than those for homopolymers. The degree of crystallinity of nylon-6 is decreased by graft copolymerization[30], and this may be due to the influence of water imbibition on the amorphous part of the trunk polymer.

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