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PHASE TRANSITION ON THE WATER-SODIUM POLY(STYRENESULFONATE) SYSTEM

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ABSTRACT

Phase transition of the water-sodium poly(styrenesulfonate)(NaPSS) system with various water contents (W_c) ranging from 0 to 2.00 (g/g) was evaluated by differential scanning calorimetry (DSC). In the temperatures from 120 to 320K, four kinds of transitions were observed for the water-NaPSS system quenching from 320K to 120K. They were glass transition, cold-crystallization, melting, and a new transition which was considered to be that from the meso-phase to the isotropic liquid phase. From the DSC data, the phase diagram of the water-NaPSS system was obtained. At the same time, W_c was related to the weight of water calculated from the enthalpy of melting (W_f). By the subtraction of W_f from W_c, the amount of non-freezing water was calculated to be 0.57-0.68 (g/g) depending on molecular weight of NaPSS.

INTRODUCTION

It is known that water associated with hydrophilic groups of polymers exhibits properties different from bulk water. We have already reported that the phase transition of water sorbed on the hydroxyl group of various polymers was observed at temperatures lower than those of bulk water by differential scanning calorimetry (DSC)(refs.1,2). The relaxation times of sorbed water measured by nuclear magnetic resonance spectroscopy (NMR) also showed marked dependence on the water content, suggesting that a certain amount of water interacts with the polymer by strong inter-molecular hydrogen bonding (ref.3).

In the case of polyelectrolyte, water molecules are strongly associated with the ionic group and form the hydration shell (ref.4). Although polyelectrolytes are important not only in industrial application but in biological and medical functionality (refs.5,6), attention has scarcely been paid to the physico-chemical properties of polyelectrolyte, especially in highly concentraed solution (ref.7). In this study, we chose a water-sodium poly(styrenesul-

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fonate)(NaPSS) system with a small amount of water, and thermal properties of the system were investigated. The phase transition temperature of water-NaPSS system was measured as a function of water content. At the same time, the bound water content was determined from the enthalpy of transition.

METHODS

Sample preparation

Powder samples of NaPSS, with molecular weight (M_w) 7.0×10^4, 5.0×10^5 and 6.6×10^6 were obtained from the Scientific Polymer Co. Degree of substitution of the SO_3Na group was ca. 78%. Water content (W_c) of each sample was defined as follows:

$$W_c \text{ (g/g)} = \text{(water)/(dry sample)} \qquad (1)$$

The weight of dry sample was estimated by heating 430K, the evaporation of water being compleated through the observation by thermogravimetry. Wc was varied by placing a sample in a desiccator, the relative humidity of which was controlled from 10 to 90%. W_c higher than W_c=ca. 1.5 was obtained by adding a small amount of water by a micro syringe.

Measurements

A Seiko Denshi differential scanning calorimeter, SSC-560-S and a Perkin-Elmer differential scanning calorimeter, DSC II, both of which were equipped with cooling apparatuses, were used. DSC curves were obtained in the temperature ranging from 120 to 320K, sample weights were 3-5 mg, the scanning rate was varied from 1 to 40K/min. Temperature and enthalpy of crystallization of sorbed water were calibrated using pure water as the standard. The bound water content was calculated by a method reported previously (ref.1).

An isotherm absorption curve for each sample was obtained by weighing at 293K.

RESULTS AND DISCUSSION

Fig. 1 shows schematic DSC curves of the water-NaPSS system (W_c=1.00). Molecular weight of NaPSS was 7.0×10^4. When the sample is cooled from 320K at the rate 10K/min, two exotherms are found at 233K and 224K (Curve I). In the heating curve (II), two endothermic peaks are observed at 270K and 300K. In the curve of the sample quenched from 320K to 120K (III), a gap of base-line at around 200K, an exotherm at around 240K and two endothermic peaks are observed. (When the sample was cooled from 320K at the rate faster than 10K/min, a similar DSC pattern was obtained, although the temperature of transition varied depending on the cooling rate). However, when the sample is cooled at the rate 10K/min from temperatures between two endotherms, for example 280K, a clear

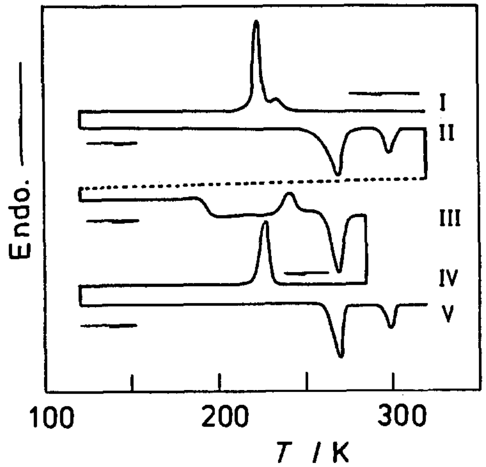

Fig. 1 Schematic DSC curves of water-NaPSS (W_C=1.00)
I;cooling curve, II;heating curve of I, III;heating curve of the sample quenched from 320K to 120K, IV;cooling curve from 285K, V;heating cure of IV. Heating and cooling rate=10K/min.

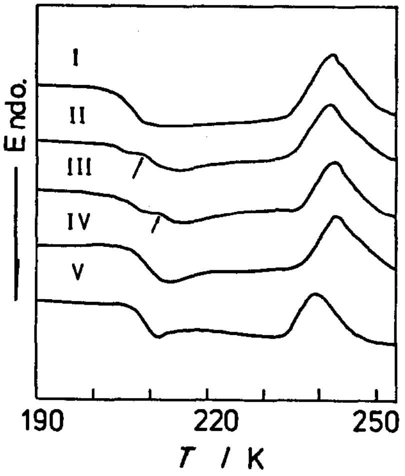

Fig. 2 DSC curves of quenched water-NaPSS(W_C=1.00) at the temperature of glass transition (T_g).
I;the sample quenched from 320K, II; I is heat-treated at 190K for 15 min, III;at 195K for 15 min, IV; at 200K for 15 min, V;200K for 45 min.

exothermic peak is observed (IV). In the heating curve (V), only two endotherms can be observed, similar to the curve II.

By comparing the curve of pure water with those of II, III and V, the endotherm at around 270K was attributed in the melting of water (T_m) of the system. It was obvious that the melting peak of the water-NaPSS system was broad compared with that of bulk water. The temperature of melting shifted to the low temperature side. The melting temperature and peak shape varied not only with water content but with the thermal histroy of each sample. The crystallization peak (T_c) of water at 224K in the system was observed only when the sample was cooled at a rate slower than 10K/min or cooled from the intermediate temperature of two endotherms (IV). The heating curve (V) was similar to the curve II. Above DSC data indicate that the system forms crystalline state by slow cooling and a glassy state by rapid solidification.

In order to confirm the existence of the glass transition of the system, heating rate dependency of the gap of base-line (see Fig. 1 curve III) was measured for the quenched sample. It was found that the temperature linearly increased with increasing heating rate ranging from 1 to 40K/min. The glass transition temperature (T_g) extrapolated to 0 heating rate was 205K for the sample with M_w=7.0x10^4, (W_C=1.0). The quenched sample was heat-treated at around T_g in order to observe the enthalpy relaxation (ref.8). The sample was quenched to temperature of the heat-treatment, kept at those temperatures for a pre-determined time and quenched again to 120K. Fig. 2 shows the DSC curves in temperatures ranging 190K to 250K. Endothermic deviation at around 200K, increases after heat-treatment at 200K for 45 min (V). After heat-teatment at 190K (II) and 195K (III) for 15 min, the sub-peak is observed (see arrow). The above facts indicate that the water-NaPSS system forms a glassy state by quenching.

The glassy state transformed into the crystalline state via cold-crystallization (T_{cc}) (exotherm at 240K in curve III in Fig. 1). The temperature and the shape of the cold-crystallization curve were affected by cooling rate, molecular weight, water content and also the enthalpy of the system at the glassy state. From Fig. 2, it can be seen that the cold-crystallization peak of the sample treated at 200K for 15 min (V) shifts to the low temperature side when compared with the peak temperature of the quenched sample (I).

Concerning the endothermic peak newly observed at around 300K (T*), it was found that T* appeared in the W_c ranging from 0.6-2.0 (NaPSS with M_w=7.0x10^4) and 0.6- 1.5 (M_w=6.6x10^6) and completely vanished at 2.5 (M_w=7.0x10^4) and 2.0 (M_w=6.6x10^6). The enthalpy of the transition was 20cal/g at around W_c=0.7 and linearly decreased with increasing W_c. DSC data showed that only the sample quenched from a temperature higher than T* formed the glassy state at the low temperature region. This suggests that the isotropic liquid state of the system should appear at a temperature higher than this transition. This transition was characterized by the fact that it took a long time to finish rearrangement. When the cooling rate was varied, the temperature of crystallization linearly decreased with increasing cooling rate and the peak changed to a shoulder at the rate 10K/min (I in Fig. 1). By observation using a polarized microscope, the sample showed interference colour under a colour plate (λ=540 mμ) at room temperature. The above data strongly suggest the existence of meso-phase in the water-NaPSS system.

It is notable that this transition can be reconginzed as a peak distinct from the melting, only for sodium salt of polyelectrolytes (ref.9). In other polyelectrolytes, for example, Li, K, Mg, Ba and CaPSS, T* was found, but not clearly separated from T_m. We have observed similar and well-resolved transitions in other water-sodium polyelectrolyte systems, such as sodium cellulose sulfate and sodium lignosulfate. However, it has not been elucidated why a meso-phase appears only in the system of sodium salt.

Fig. 3 shows the phase diagram of the quenched water NaPSS (M_w=7.0x10^4) system. The temperature was evaluated using a DSC curve obtained at the heating rate 10K/min. The T_g increases as W_c increases. The T_g was difficult to observe in samples having W_c lower than 0.6. The temperature of cold-crystallization (T_{cc}) increases with increasing W_c and levells off at about W_c=1.3. The melting

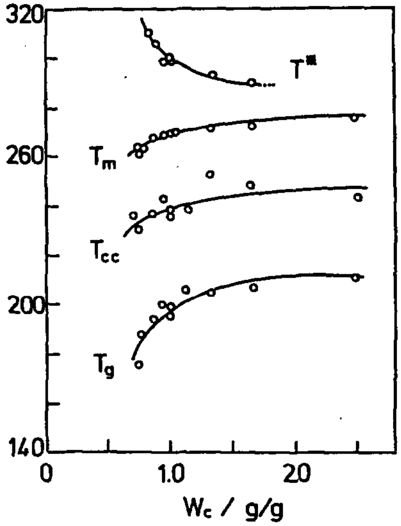

Fig. 3 Relationship between water content (W_c) and phase transition temperatures of quenched water-NaPSS system.

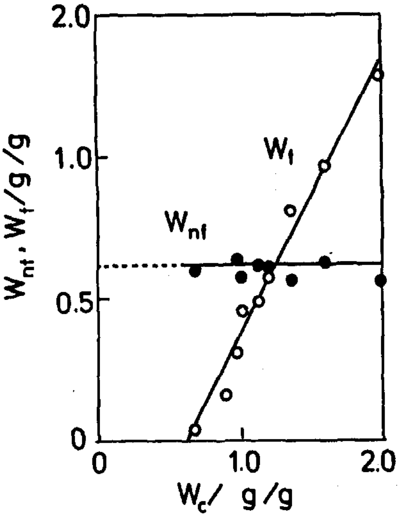

Fig. 4 Relationship between water content (W_c) and freezing water (W_f) and non-freezing water (W_{nf}) of water-NaPSS system.

peak was not observed for samples containing W_c smaller than 0.62. The melting peak started at about 253K and shifted to the higher temperature side with increasing W_c. At the same time, the peak temperature of melting increased with increasing W_c and leveled off at about 1.3. In Fig. 3, the peak temperature was used as the T_m. The endotherm T* decreased with increasing W_c. This transition can be found in the the W_c ranging from 0.6 to 1.7. Fig. 3 increases that the quenched water-NaPSS system consists of glassy-, crystalline-, intermediate- and isotropic liquid states, respectively. The phase diagram of the crystalline water-NaPSS system, obtained by slow cooling, lacks T_g and T_c.

Fig. 4 shows the relationship between W_c and weight of water calculated from the enthalpy of melting (W_f). In the sample having M_n=6.6x10^6, the first order transition was not detected when W_c was smaller than 0.62. By the subtraction of W_f from W_c, the amount of non-freezing water (W_{nf}) was calculated.

$$W_{nf} = W_c - W_f \qquad (2)$$

W_{nf} is also shown in Fig. 4. The slight increase of W_{nf} with increasing W_c suggests that the higher order structure of NaPSS changes as a function of W_c. It is reasonable to consider that the extended W_{nf} line (broken line in Fig. 4) intersects with the longitudinal axis at 0.62, since freezing water begins to appear at 0.62. The W_{nf} value showed slight dependence on the molecular weight.

Water sorbed in NaPSS can be categorized into at least three different types: W_c=0 t0 0.6 non-freezing water; W_c=0.6-1.3 freezing bound water, (which is not distinctly separated from free water as observed in the case of water sorbed in non-electrolyte polymer); and free water. Large amounts of bound water are characteristic of the polyelectrolyte. The fact that the T* of the water-NaPSS system is not observed at the non-freezing water content region (W_c=W_{nf}), suggests that water molecules tightly bound to the SO_3Na group and do not participate in inducing the molecular movement. The system becomes slightly mobile in the W_c ranging 0.6 to 1.3, where W_f is clearly observed and the water-NaPSS system forms a meso-phase. The structure of the molecule associated with the non-freezing water is also considered to be maintained even in glassy state. By contrast the theoretical prediction (ref.10), that the T_g does not decrease with increasing W_c, suggests that a part of the water molecules (W_{nf}) become incorporated with the polymer. However, the remainder moves independently. The glass transition seems to reflect a part of the system where excess free water exsits, the system is consists of two domains: free-water, and polymer with bound water. This may explain the increase in T_g at the high W_c region.

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