

Characterization of Sorbed Water in Saponified Start-g-Polyacrylonitrile with Differential Scanning Calorimetry*

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Synopsis

A saponified starch-polyacrylonitrile graft copolymer containing water was studied using differential scanning calorimetry. The samples had a moisture content in the range of 0–1.05 g water per gram of dry polymer. Molar heat capacity measurements at temperatures higher than 273 K gave partial molar values between those of ice and bulk liquid water. No crystallizable water was detected in samples with water contents lower than 0.44 g/g dry polymer. In samples containing larger amounts of water, both the amount of "bound" uncrystallizable water and the amount of "free" crystallizable water increased linearly. Two melting endotherms were detected, suggesting that the free water could be divided into two components with different melting points (268 K and 274 K, respectively).

INTRODUCTION

The recent developments of a highly water-absorbing polymer at this laboratory^{1,2} gave reason to study the water structure in hydrophilic polymers. Many investigators have tried to interpret the structure of water in aqueous solutions of polymers as well as adsorbed water or water in swollen polymeric substances.^{3–9} Most of the work regarding water structure has been carried out using broad-line nuclear magnetic resonance spectroscopy (NMR)³ and differential scanning calorimetry (DSC).^{3–9} Broad-line proton-NMR experiments investigate the mobility of protons in various energy states. Using DSC measurements, the heat capacity, the heat of fusion, the melting temperature, and the amount of water that can crystallize can be estimated.

Although there are many different hypotheses on the structure of water in polymers, it is generally accepted that water molecules in a polymer matrix behave differently from those in bulk water because of interaction between water and polymer. Schematically there are two opinions; first, that water in hydrophilic polymers can be divided into bound water and free liquid water,^{3–6} and second, all sorbed water is liquidlike.^{7–9}

Yasuda et al.³ studied the hydrogel of a polymer of glycerol monomethacrylate (poly-GMA) with NMR and DSC. They suggested that a constant amount of water is strongly associated with the macromolecules and does not crystallize when the temperature is lowered well below the freezing

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temperature of water. The residual water crystallizes and melts with the normal heat of fusion of bulk water. Lee et al.⁴ proposed a model containing three different types of water (bulk, bound, and interfacial) in poly(2-hydroxyethyl methacrylate) (PHEMA) based on dilatometric, conductivity, and heat of transition measurements. Ikada et al.⁵ and Taniguchi et al.⁶ presented DSC data for mucopolysaccharides and cellulose acetate membranes, respectively, which contained multiple endothermic peaks. They suggested different states of water in the vicinity of the polymer segments.

On the other hand, on the basis of heat capacity measurements on water-swollen poly[2-(2-hydroxyethoxy)ethyl methacrylate] (PHEOEMA), Pouchly et al.⁷ claimed that the structure of water sorbed by the polymer is similar to liquid water and rather labile. After investigations of heat capacities of the water-collagen system, Hoeve^{8,9} suggested a liquidlike, one-phase model consisting of chains of hydrogen-bonded water molecules that diffuse through the interstices preserving their mutual hydrogen bonding to each other.

This work has been carried out using DSC on water-containing hydrolyzed starch-polyacrylonitrile graft copolymers to clarify the water structure in this highly water-absorbing polymer.

EXPERIMENTAL

Sample Preparation

Starch-graft-polyacrylonitrile was prepared as described previously using the Mn^{3+} initiator¹ with initially equal amounts of gelatinized starch and acrylonitrile. The grafting ratio of the graft copolymer was 82%. Saponification was carried out for approximately 2 h at 363 K in a 1% sodium hydroxide water solution, followed by precipitation in methanol and washing to neutrality. Samples for DSC measurement from the same batch were dried in vacuum at 343 K for approximately 24 h. The samples were equilibrated in desiccators at different relative humidities to give different moisture contents.

DSC Measurements

The differential scanning calorimeter used was a Perkin-Elmer DSC-2 instrument. Sample pans used in this study were weighed "large-volume DSC capsules," sealed with a rubber O-ring to prevent water evaporation during the experiments. The powdered samples (3–9 mg) were equilibrated in the sample pans for several days. They were cooled to 245 K at a rate of 5 K/min and allowed to come to equilibrium at that temperature before heating to 320 K at a rate of 10 K/min was initiated. All samples were measured several times in different experiments to check reproducibility. After the DSC measurement, the pan was weighed in order to check that it had been properly sealed and that no water had evaporated. Heat capacity measurements and measurements of the amount of crystallizable water were made in separate experiments.

Calculations

The water content of the samples, in grams of H₂O per gram of dry polymer, was calculated after the experiment by puncturing the seal and heating the sample pans at 398 K for 24 h to evaporate sorbed water.

Heat capacities were calculated at three temperatures (305, 295, and 285 K), using distilled water as a reference. Corrections were made for the differences in capsule weight.¹⁰

The heat of fusion of distilled water was evaluated by integration of the melting endotherm, and calibration was carried out using highly pure indium and tin as reference materials. The amount of water able to crystallize was calculated after integration of the melting endotherm.

Temperature calibration was carried out using the same reference materials, and the transition temperature was taken as the peak value.

RESULTS AND DISCUSSION

The heat capacity of water can be used to investigate the mobility of water molecules. The partial molar heat capacity, \bar{C}_p , of liquid water is 18.2 cal/K-mol and is approximately twice the value of ice (9.1 cal/K-mol.)¹¹ If water molecules are immobilized, their \bar{C}_p contribution is expected to be close to that of ice. The heat capacity of a polymer/water sample as a function of water content is, therefore, a quantitative measure of the mobility of water molecules, which makes it possible to classify the water in bound and free water.

In this work, the heat capacity of hydrolyzed starch-graft-polyacrylonitrile with water contents between 0 and 1.05 g/g dry polymer was estimated at 285, 295, and 305 K. Any free water in the polymer should be liquidlike at these temperatures and have a \bar{C}_p of 18.2 cal/K-mol.

As an example, the heat capacity in calories per Kelvin-gram of dry sample is plotted as a function of water content at 305 K (Fig. 1). The samples are heterogeneous, and this causes the scatter in the \bar{C}_p values. Each individual sample gives reproducible results on which the data in Figure 1 are based. The partial molar heat capacity, \bar{C}_p , of water is obtained from the slope of the straight line in Figure 1. \bar{C}_p values at the three different temperatures and the heat capacity of the dry sample obtained from the intercept are given in Table I. At these temperatures, above 273 K, the partial molar heat capacity is concentration independent—in our measurements—in the range of water content from 0 to 1.05 g. At still higher water content, a concentration dependence is expected. The \bar{C}_p value is between that of ice and bulk liquid water, indicating that most of the water in this system does not form stable icelike structures near the polymer segments and is not sorbed in the form of bulk water. The lower \bar{C}_p value at 285 K is expected because of decreasing mobility with decreasing temperature.

The DSC traces show two endothermic peaks, one broad (I) around 268 K, and one narrow (II) at 274 K when the water content exceeds 0.44 g/g dry polymer (Fig. 2). The crystallizable water melting with the narrow peak at 274 K is interpreted as bulk water that has not been absorbed and bonded

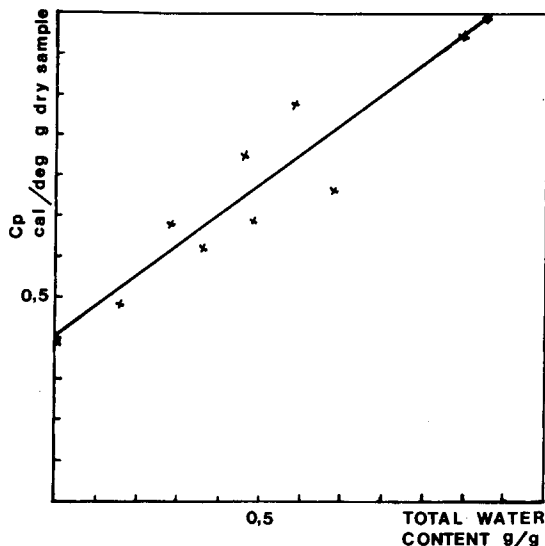


Fig. 1. The heat capacity at 305 K for hydrolyzed starch-graft-polyacrylonitrile in calories per Kelvin-gram of dry sample as a function of water content in the sample.

into the polymer matrix. Assuming that the water melting at 274 K has the same heat of fusion as distilled water, the heat of fusion of the water melting at 268 K can be calculated from eq. (1):¹²

$$\Delta H_F = \Delta H_0 + \Delta \bar{C}_p(T_F - T_0) \quad (1)$$

where ΔH_F = heat of fusion at T_F (268 K), ΔH_0 = heat of fusion at T_0 (274 K), and $\Delta \bar{C}_p$ = difference in the molar heat capacities of liquid water and ice.

The heat of fusion (ΔH_0) of distilled water was calculated by integration of the melting endotherm to be 77.7 cal/g water. The melting temperature was 274 K.

Using eq. (1), a calculated ΔH_F value of 74.7 cal/g H_2O was obtained for the water melting with the broad peak at 268 K. This crystallizable water is probably bulk water that interacts weakly with water-soluble hydrophilic groups such as sodium carboxylate and carboxamides in the interstices of the polymer.

Using the calculated ΔH_F value of 74.7 cal/g for water melting at 268 K, and 77.7 cal/g for water melting at 274 K, the amount of free water, w_f ,

TABLE I
Heat Capacity (\bar{C}_p) for Dry Hydrolyzed Starch-Graft Polyacrylonitrile and Partial Molar Heat Capacity (C_p) for Water in the Saponified Starch-Polyacrylonitrile/Water System at Three Temperatures Above 273 K

Temperature (K)	\bar{C}_p for dry sample (cal/K-g sample)	C_p for water (cal/K-mol H_2O)
305	0.41	13.0
295	0.40	13.5
285	0.29	10.0

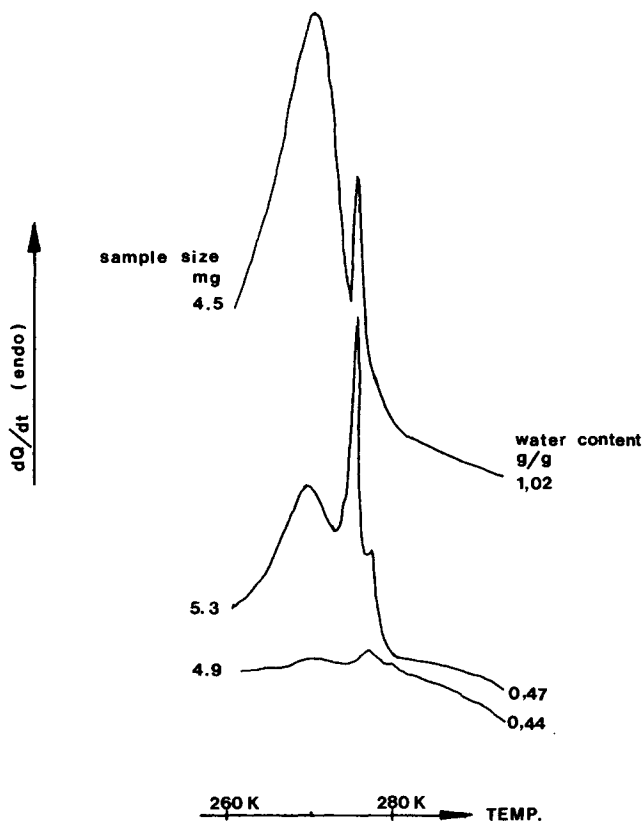


Fig. 2. DSC thermograms of moistured hydrolyzed starch-graft-polyacrylonitrile during heating at a rate of 10 K/min.

can be separated into w_f (268 K) and w_{fl} (274 K). In Figure 3, w_f and w_{fl} are plotted as a function of water content: w_f increases with the water content, whereas w_{fl} remains relatively constant.

The amount of bound but not crystallizable water (w_b) can thus be calculated from the relation:

$$w_b = w_{tot} - w_f \quad (2)$$

where w_{tot} = total amount of water in the sample, w_b = amount of bound water, and w_f = amount of free water ($= w_f + w_{fl}$)

In Figure 4, the total amount of water and the amount of free and bound water are plotted as a function of water content. There is no detectable free water below 0.44 g H₂O/g dry polymer. The amounts of both bound and free water increase linearly above that water content, and the quantity of bound water is approximately 0.4 g/g dry polymer higher than the quantity of free water. The fact that the amount of bound water does not reach a plateau value within the range of these moisture contents supports the idea that there are still available sites left for water bonding, even if part of the water is sorbed as free water.

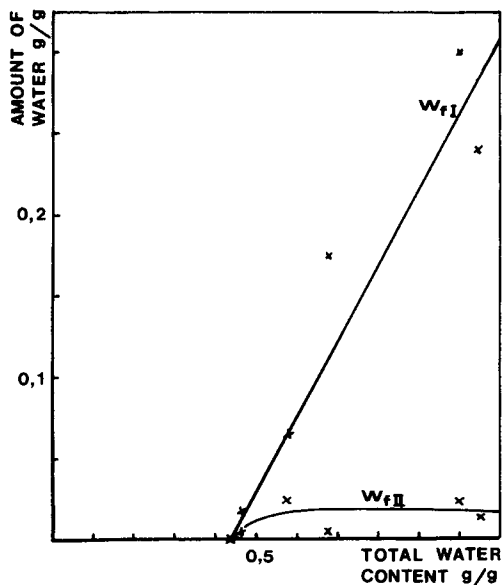


Fig. 3. The amount of water melting at 268 K and at 274 K per g dry hydrolyzed starch-graft-polyacrylonitrile (w_{fI} and w_{fII} , respectively) as a function of water content.

CONCLUSIONS

In the water/saponified starch-polyacrylonitrile system with water contents between 0 and 1.0 g/g dry polymer, most of the sorbed water is bound to the hydrophilic groups of the polymer. Heat capacity measurements above 273 K show that the partial molar heat capacity, \bar{C}_p , is concentration independent within the range of these moisture contents. The \bar{C}_p values (10–13 cal/K mol) between ice (9.1 cal/K mol) and liquid water (18.2 cal/K mol) indicate that most of the water is bound to the polymer but is not attached in the form of stable icelike structures. Free crystallizable water

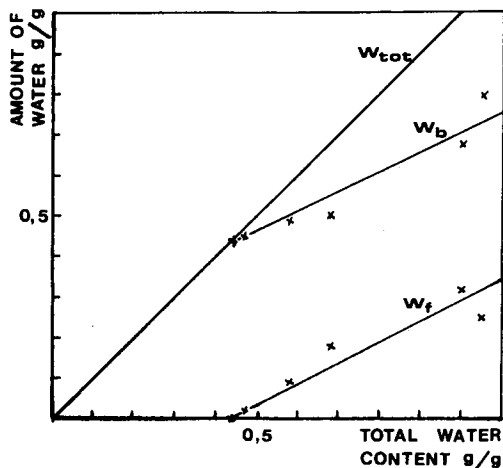


Fig. 4. The total (w_{tot}), free (w_f), and bound (w_b) amount of water per gram of dry hydrolyzed starch-graft-polyacrylonitrile as a function of the water content in the polymer.

is detectable when the water content exceeds 0.44 g/g dry polymer. Both free and bound water increase linearly above that water content. This supports the hypothesis that the water-bonding capacity has not reached a maximum. Two peaks in the melting endotherms, one broad around 268 K and the other small but sharp at 274 K, indicate that the crystallizable water can be divided into two types. If the assumption is made that the narrow peak is ordinary bulk water with the same heat of fusion as distilled water (calculated to 77.7 cal/g H₂O), the heat of fusion of the other type of crystallizable water can be calculated from the depression of the melting temperature to 74.2 cal/g H₂O. The water melting at 268 K is probably bulk liquid water which very weakly interacts with hydrophilic groups in the interstices of the polymer. The other melting endotherm is probably due to the melting of ordinary bulk water which has not been absorbed into the polymer matrix.

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