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Hydration of Poly(Acrylic Acid) Sodium Salts

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Summary

Drying and water uptake of poly(acrylic acid) sodium salts with different degrees of neutralization were studied. The slowing down of drying speed in solid state was not due to Tg but due to the difficulty of the release of water molecule bound to two metal carboxylates or carboxyls. The equilibrium water uptake remained almost constant below 33 % neutralization, whereas it increased linearly with neutralization beyond 33 %. This was explained by the appearance of vacant sites in octet coordination.

Introduction

It appears that the effect of ionic forces on solid properties of ion-containing polymers is not fully elucidated. Evidently, the strong hygroscopic character of ionic polymers makes the results complicated. The discrepancy of the hydrated states of ionic sites will strongly influence the electrostatic interaction between them. Nevertheless, so far as the authors know, the behavior of water molecule in the solid state of ionic polymers have not been well investigated. The present study is an attempt to fill the gap on this respect.

Experimental

Poly(acrylic acid) (PAA) was prepared by the radical polymerization of acrylic acid in benzene with benzoyl peroxide initiator. The detail of the synthesis is practically the same as that used previously (EISENBERG et al. 1969). Molecular weight, which was determined by intrinsic viscosity in dioxane solution at 30°C using the published correlation $[\eta] = 8.5 \times 10^{-4} M^{1/2}$ (NEWMAN et al. 1954), was 100,000.

PAA sodium salts (PANa) with degrees of neutralization varying from 0 % to 100 % were prepared by adding the calculated amounts of 1 N aqueous solution of

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sodium hydroxide to the 1 N aqueous solution of PAA.

The drying process of PANa salts at 100°C under atmospheric pressure was followed by weighing them at appropriate time intervals. Ordinary air oven was used for drying experiments. Equilibrium weights of sample vessels were predetermined before experiments.

Water uptake of PANa salts at 25°C in an atmosphere of 73 % relative humidity was followed by weighing at appropriate time intervals. Glycerine solution (60 %) was used for maintaining constant humidity. A sensitive spring balance made of thin phosphor bronze wire was used for continuous weighing device.

Results and Discussion

Drying process

Drying process of PANa is shown in Fig. 1. In the course of drying the state of samples changes from solution to solid. At the stage of the second curvatures in drying curves, all samples were in solid state

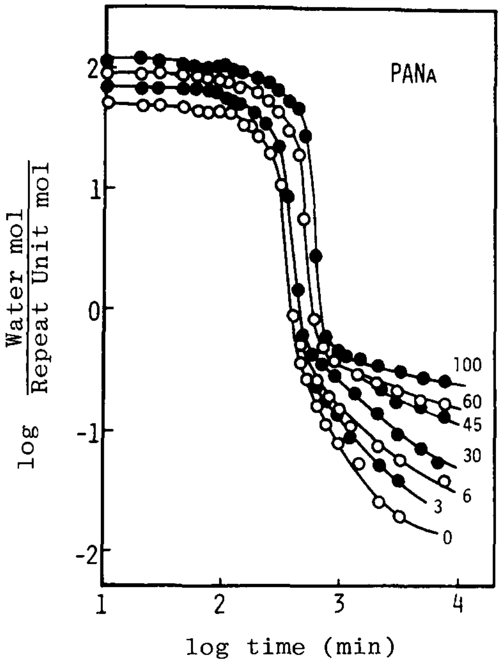


Fig. 1: Drying process curves at 100°C and 1 atm for poly(acrylic acid) sodium salts with degrees of neutralization from 0 to 100 percent, as indicated.

alresdy. The rate of drying in solution state is not affected by the extent of neutralization, indicating that the evaporation of free water is not influenced by the existence of ion. In contrast, the rate of drying in solid state decreased remarkably with increasing neutralization %. It is also noticed that the second curvature becomes indistinct with decreasing neutralization %. The decrease of drying speed at the second curvature may be explained as the result that Tg of the specimen reached the drying temperature. This is usually encountered for ordinary polymer-diluent systems. However, the Tg data obtained in separate experiments seem to disagree with this idea. Fig. 2 illustrates the drying curves of PANa 100 and PANa 15 (The numbers added refers to neutralization %). The arrow on each curve indicates the water content which yields Tg of 100°C. For the other samples the water contents which yield Tg of 100°C line orderly between the two extremes in Fig. 2. Although the slowing down of drying appears to occur when Tg reached drying temperature for high level of neutralization, this relation does not hold for low level of neutralization. Thus it is conceivable that drying process of PANa in solid state is not governed by Tg. It is seen from Fig. 2 that slowing down occurs at the level of nearly 0.5 of H_2O mol/repeat unit mol. The value of 0.5 means that dehydration of water molecule which is bound

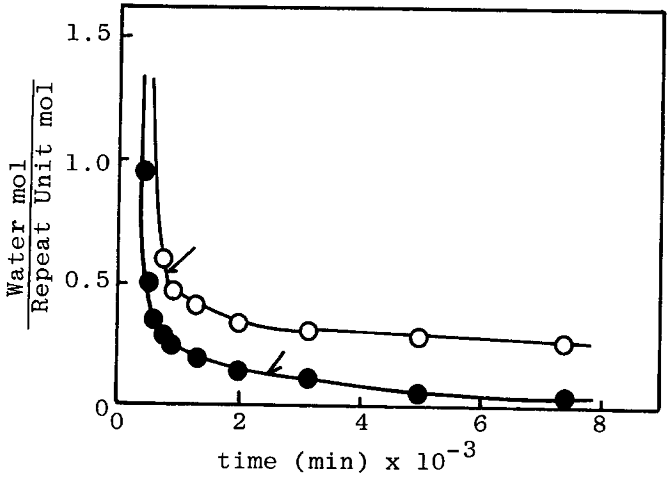
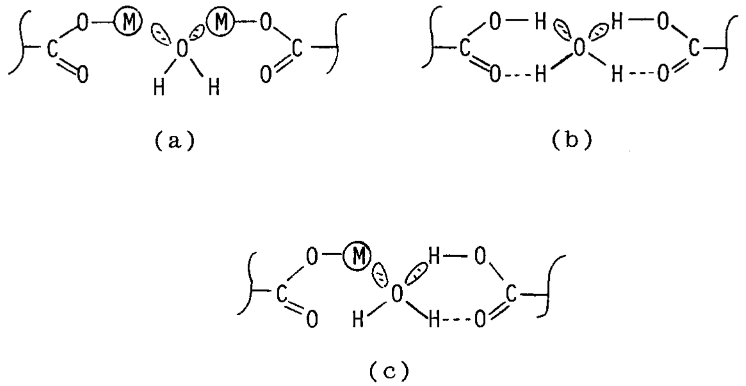


Fig. 2: Drying process curves at 100°C and 1 atm for poly(acrylic acid) sodium salts. 100 % neutralization ○ ; 15 % neutralization ● . The arrows indicate the points where Tg reaches drying temperature.

to two carboxylates or carboxyls is difficult. In the case of carboxylates (Fig. 3a), one water molecule may be strongly bound to two metal ions by means of two electron pairs. For carboxyls (Fig. 3b) one water molecule may be weakly bound to two carboxyl oxygen atoms by means of hydrogen bonding. The intermediate situation may be illustrated by Fig. 3c. In the case of binding to metal atoms it is presumed that the dehydration of the bound water is much more difficult as compared with free water. In the latter two cases dehydration of bound water may not be so difficult. This consideration will explain the observation that the slowing down of drying speed becomes indistinct as the degree of neutralization decreases. Thus, it is considered that the drying process of ionic polymers is not governed by Tg (diffusion-controlled), but is governed by the release from hydrated state (dehydration controlled).

Water uptake

Water uptake proceeds very rapidly in the initial stage, but becomes slow and reaches absorption equilibrium. Fig. 4 shows the equilibrium water uptakes as a function of the degree of neutralization. It is observed that the increase of equilibrium water content is little up to about 30 % neutralization. Then it increases linearly with neutralization. The data for 0 % and 100 % neutralization agree with the reported



(a) (b)

(c)

Fig. 3: Models for the states of water molecule bound by metal carboxylates (a), carboxyls (b), and carboxylate-carboxyl (c).

values (BARRIE and PLATT 1963). The initial rate of water uptake also has minimum at about 30 % neutralization. These rather strange behaviors are reasonably explained if we assume the octet coordination structure of metal ion as illustrated in Fig. 5. If the coordination sites are occupied by carboxyl oxygen atoms, one metal ion for 6 oxygen atoms, that is 3 carboxyl groups, therefore 1/3 neutralization corresponds to equimolar situation. Hence carboxyl oxygen atoms are in excess when the degree of neutralization is less than 33 %. Conversely, when neutralization is higher than 33 %, vacant sites appear which may be available for coordination of oxygen atoms of water molecules. Thus we can understand the linear increase in equilibrium water uptake above 33 % neutralization.

On the other hand, the number of water molecules per repeat unit for PANa 100 is 4 as seen in Fig. 4. At a glance this number seems to agree with the foregoing discussion because the number of vacant sites per metal atom of PANa 100 is 4. However there remains some question. According to the results obtained from X-ray diffraction and neutron scattering study, it has been concluded that in concentrated solution sodium ion has tetrahedral hydration structure with hydration number of 4 (MAEDA and OHTAKI 1975). The change of coordination structure may be possible since the

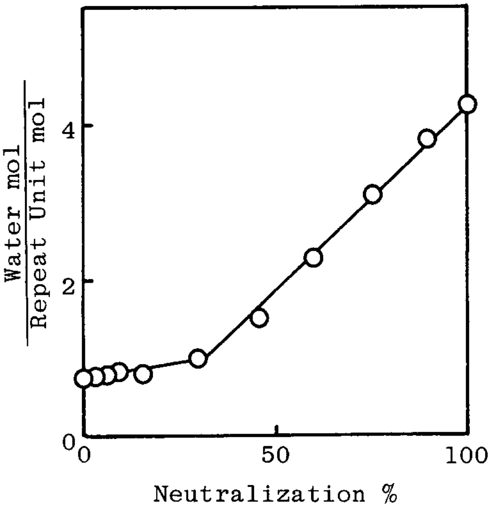


Fig. 4: Equilibrium water uptake at 25°C and 73 % relative humidity for poly(acrylic acid) sodium salts with different degrees of neutralization.

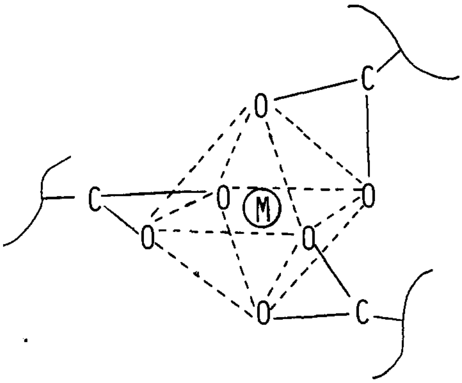


Fig. 5: A model for the octet coordination structure of metal atom. (the state of 1/3 neutralization is illustrated)

samples with relatively high degrees of neutralization is in concentrated solution state at absorption equilibrium. In solid state the ligand exchange may be difficult so that the water molecules may not replace carboxyl oxygen atoms around metal atoms and octet coordination may be preserved. However, once metal ion is hydrated (beyond 33 % neutralization), diffusional motion of ionic segments of polymer will become much easier. Thus the state of the polymer may change from solid to concentrated solution state where carboxyl oxygen atoms are replaced easily by water oxygen atoms, resulting in the change of coordination structure from octet to tetrahedral which is favorable in solution state. To obtain the more detailed informations, the X-ray study of radial distribution function may be promissing.

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