Hydration and Dehydration of Poly (Acrylic Acid) Lithium Salts

by

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Drying and water uptake of poly(acrylic acid)lithium 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. Though the equilibrium water uptake increased with increasing neutralization %, the slope of the plot above ca.33% neutralization was greater than that below this neutralization %. The enhanced water uptake was explained by the appearance of vacant sites in octet coordination of lithium ion.

INTRODUCTION

As a part of the investigation of the properties of ion-containing polymers, it became desirable to know the hydration of ionic sites which will strongly influence the electrostatic interaction between them. The preceding papers in this series[1,2] have shown the drying process and equilibrium water uptake for poly(acrylic acid) sodium salts(PANa) and potassium salts (PAK). In the present paper we wish to call further attention to the hydration behavior of poly(acrylic acid) lithium salts(PALi).

EXPERIMENTAL

PALi with degrees of neutralization varying from 0% to 100% were prepared from poly(acrylic acid) (PAA, MW=100,000) according to the procedure described before[1] .

The drying process of PALi at 100℃ under atmospheric pressure was followed by weighing them at appropriate time intervals.

Water uptake of PALi at 25℃ in an atmosphere of 73% relative humidity was followed by weighing them at appropriate time intervals. A sensitive spring balance made of thin phosphor bronze wire was used. The method and the apparatus used here were virtually identical with those described for PANa[1] .

RESULTS AND DISCUSSION

1.Drying process

Drying process of PALi is shown in Fig.1. At the beginning of drying experiment, samples were aqueous solution. At the stage of the second curvatures in drying curves, all samples were in solid state already. The rate of drying in solution state was 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 %. These behaviors are quite similar with those of PANa and PAK. However, residual water levels are different among ion species and do not depend simply upon ionic radius. By consulting the data presented before[1,2] it is noticed that the residual water level was the highest in PALi, followed by PAK and PANa, in order of decreasing level. Fig.2 illustrates the drying curves of PALi 60 and 15 (the numbers added refer to neutralization %). The arrow on each curve indicates the water content which yields Tg of 100℃ (drying temperature). Although the slowing down of drying appeared to occur when Tg reached drying temperature for high level of neutralization in the case of PANa and PAK, this relation does not hold for PALi. As seen from Fig.2, the
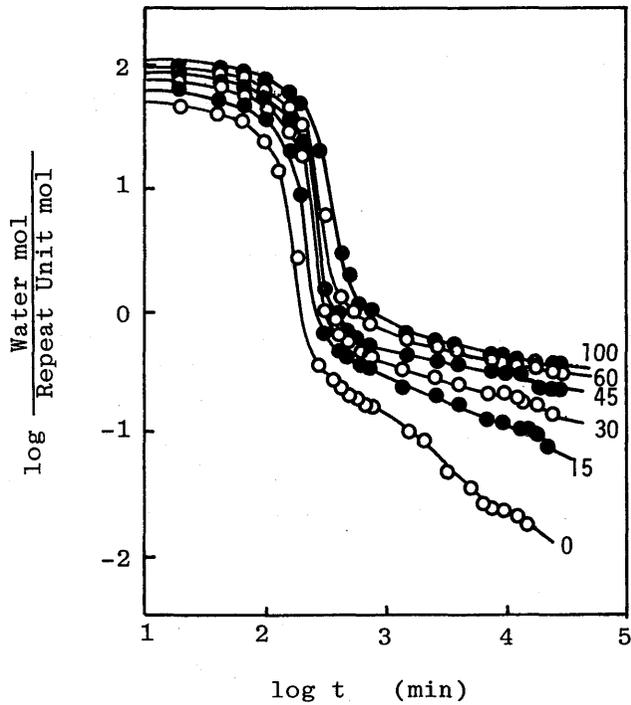
Fig. 1. Drying process curves at 100℃ and 1 atm for poly(acrylic acid) lithium salts with degrees of neutralization from 0 to 100 percent, as indicated.
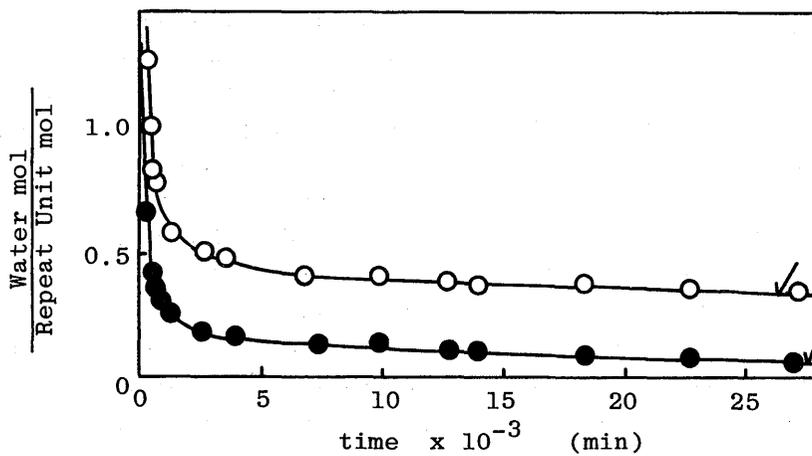
Fig. 2. Drying process curves at 100℃ and 1 atm for poly(acrylic acid) lithium salts. 60%neutralization ○ ; 15%neutralization ● The arrows indicate the points where Tg reaches drying temperture.

slowing down of drying speed occured before the samples reached glassy state. This observation confirms the idea that drying process of PAA salts in solid state is not governed by Tg. The level of water content where slowing down occurs is around 0.5 of H_2O mol/repeat unit mol as in the case of PANa and PAK. The value of 0.5 means that dehydration of water molecule which is bound to two carboxylates or carboxyls by means of two electron pairs is difficult. The situation of water molecules and the possible structure have been discussed already[1] . Also, the trend that the slowing down of drying speed becomes indistinct with decreasing neutralization % can be explained as in the case of PANa. Thus, it is concluded that the drying process of PALi is not governed by Tg (diffusion-controlled), but is governed by the release of water molecule from hydrated state (dehydration-controlled).
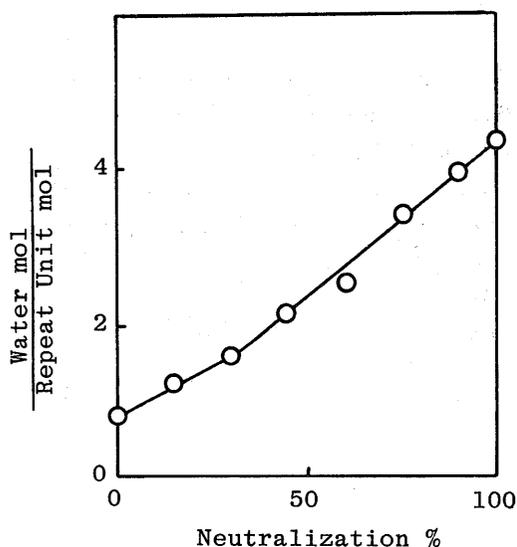
Fig. 3. Equilibrium water uptake at 25°C and 73% relative humidity for poly(acrylic acid) lithium salts with different de- grees of neutralization.

2.Water uptake

Water uptake proceeds very rapidly in the initial stage, but becomes slow and reaches absorption equilibrium. Fig.3 shows the equilibrium water uptake as a function of the degree of neutraliztion.

Though the equilibrium water content increases with increasing neutralization %, the slope of the plot above ca. 33% neutralization is greater than that below ca. 33% neutralization. This neutralization % where hydration is enhanced is identical with that encountered for PANa and is reasonably explained by assuming the octet coordination structure (Fig.4) as in the case of PANa[1] .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 oxgen atoms are in excess when the degree of neutralization is less then 33%. Conversely, when neutralization is higher than 33%, vacant sites appear which may be available for coordination of
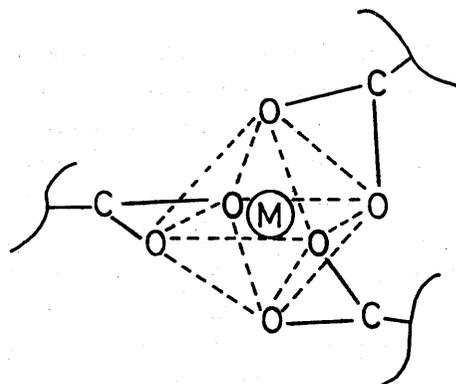
Fig. 4. A model for the octet coordination structure of metal atom. (the state of 1/3 neutralization is illustrated).

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 PALi 100 is 4 as seen in Fig.3. At a glace this number seems to agree with the foregoing discussion because the number of vacant sites per metal atom of PALi 100 is 4. However there remains some question. The reported values of the hydration numbers of alkaline metal ions are given table 1. According to the results obtained from X-ray diffraction, it has been concluded that lithium ion in a concentrated aqueous solution has tetrahedral hydra-

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Table 1 Hydration numbers of alkaline metal ions in dilute and concentrated aqueous solutions.

Ions	Dilute					Concentrated	
	Compressibility[3,4]	Entropy[3]	Mobility[3,4]		ApparentMolar[3] Volume(density)	NMR[3]	X-ray[5]
Li^+	4.5, 5—6	5	3.5,	3.5—7	2.5	4	4
Na^+	4.5, 6—7	4	2.0,	2.4	4.8	3.1	4
K^+	3.8, 6—7	3	——		1.0	2.1	4
Rb^+	3.0	3	——		—	1.6	6
Cs^+	2.5	—	——		—	1.0	6

tion structure with hydration number of 4[5] . To obtain the more detailed informations, the X-ray study of radial distribution function and/or pulsed NMR study may be promising.

The slope of the plot of equilibrium water uptake in the low neutralization range acquires additional interest. For PAK the slope in problem was negative, whereas it was positive for PANa. The slope for PALi is positive and much greater than that for PANa. This is in line with the consideration that the equilibrium water uptake in the low neutralization percent is determined by the competing effects of the increasing dielectric constant and the decreasing amount of free carboxyls. The detail of the discussion on this slope has been described in the preceding paper[2] .

ACKNOWLEDGMENT

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