

Hydration of Poly(acrylic Acid) Rubidium and Cesium Salts

by

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Drying and water uptake of poly(acrylic acid) rubidium and cesium salts with different degrees of neutralization were studied. Though the equilibrium water uptake increased with increasing neutralization %, the slope of the plot above ca. 45 % neutralization was greater than that below this neutralization %.

INTRODUCTION

The authors have been studying the hydration of poly(acrylic acid) alkali metal salts in solid or very concentrated state. The preceding papers in this series^{1,2,3)} have shown the drying process and equilibrium water uptake of poly(acrylic acid) lithium (PALi), sodium (PANa), and potassium salts (PAK). In the present paper the authors wish to call further attention to the hydration behavior of poly(acrylic acid) rubidium (PARb) and cesium salts (PACs).

EXPERIMENTAL

PAA was prepared by the radical polymerization of acrylic acid in toluene with benzoyl peroxide initiator. The detail of the synthesis is practically the same as that used previously⁴⁾. Molecular weight, which was determined from intrinsic viscosity in dioxane solution at 30°C using the published correlation⁵⁾ $[\eta] = 8.5 \times 10^{-4} M^{1/2}$, was 100,000.

PARb and PACs with degrees of neutralization varying from 0 % to 100 % were prepared by adding the calculated amounts of 1 N aqueous solution of rubidium and cesium hydroxide to the 1 N aqueous solution of PAA.

The drying processes of PARb and PACs at 100°C under atmospheric pressure were 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 PARb and PACs 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

1. Drying process

Drying processes of PARb and PACs are very similar to those of PALi, PANa, and PAK^{1,2,3)}. The previous idea that the drying process of PAA salts is not governed by T_g (diffusion-controlled) but is governed by the release of water molecule from hydrated state (dehydration-controlled) was confirmed by this study.

2. Water uptake

Fig. 1 and 2 show the equilibrium water uptake as a function of the degree of neutralization

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for PARb and PACs, respectively. It is apparent that the equilibrium water uptake does not increase linearly with neutralization %. This is similar to the case of the other PAA salts studied before. The slope of the plots increased distinctly above ca. 45% neutralization. In the case of PALi and PANa, the bending of the plots appeared at 33 % neutralization, whereas PAK had the bending of the plot at 25% neutralization. These surprising phenomena that PAA salts become much more hygroscopic at certain ion content were reasonably

explained by assuming the octet coordination structure of carboxyl oxygen atoms to lithium and sodium ion by chelation, and the bodycentered cubic (b. c. c.) coordination of those to potassium ion by chelation^{1,2,3}). In the case of rubidium and cesium ion, it can be expected that the octet and the b. c. c. coordination by chelation are difficult because the ionic radii of the both metal atoms are considerably greater than those of the internal spheres of the two coordination structure composed of the chelation of carboxyls. Table

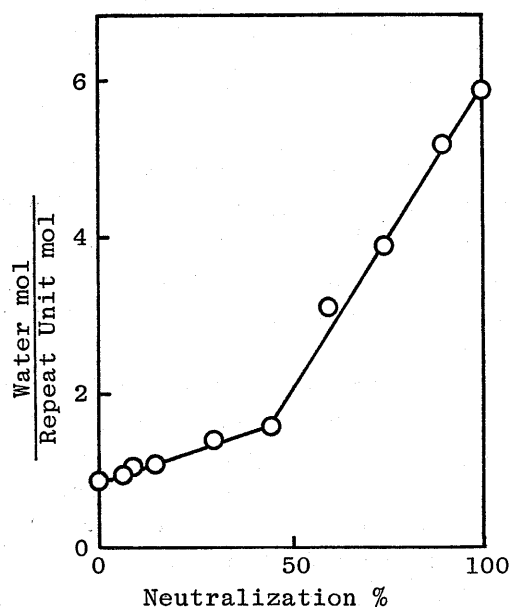


Fig. 1 Equilibrium water uptake at 25°C and 73% relative humidity for poly(acrylic acid) rubidium salts with different degrees of neutralization

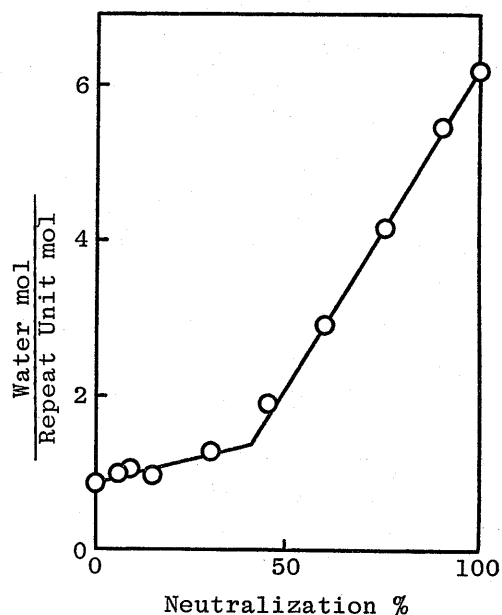


Fig. 2 Equilibrium water uptake at 25°C and 73% relative humidity for poly(acrylic acid) cesium salts with different degrees of neutralization

TABLE 1. Ionic radii and the possibilities of coordination of carboxyls by chelation to the alkali metal ions

Ion	Ionic Radius (Å)		Radius of Internal Sphere		
	H.C.P. ^{a)}	Pauling ^{b)}	Tetrahedral 0.462 Å	Octet 0.923 Å	b.c.c. 1.131 Å
Li ⁺	0.68	0.60	—	fit	fit
Na ⁺	0.97	0.95	—	fit	fit
K ⁺	1.33	1.33	—	—	fit
Rb ⁺	1.47	1.48	—	—	—
Cs ⁺	1.67	1.69	—	—	—

a) Handbook of chemistry and physics, The chemical Rubber Co. (1971), p. F-152.

b) Handbook of chemistry, Edtd. by Lange, McGraw-Hill Book Co. (1967), p. 122.

1 shows the ionic radii and the possibilities of coordination of carboxyls by chelation to the alkali metal ions. It is considered that PARb and PACs can not form even b. c. c. coordination of carboxyl groups to metal atoms. The detailed discussion for the bending at 45 % neutralization will be given in a subsequent paper with other experimental evidences.

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