

Swelling behavior of poly(α -hydroxy acrylic acid) gel in water/organic solvent mixtures

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Summary

Swelling behavior of poly(α -hydroxy acrylic acid) (PHA) gel was investigated in water/organic solvent mixtures (acetone, dioxane, dimethyl sulfoxide: DMSO) in comparison with poly(acrylic acid) (PAA) gel. The swelling degrees of PHA and PAA gels significantly decreased with increasing acetone or dioxane content in the mixed solvents, while the deswelling in aqueous DMSO was less apparent. The deswelling region was dependent on the dissociation state of the carboxyl group; when the carboxyl group in the gels was dissociated ($-\text{COO}^-$), significant deswelling occurred in 30–60 vol.% of acetone or dioxane for PHA gel and in 40–80 vol.% for PAA gel. When the carboxyl group was in an acid form ($-\text{COOH}$) or only slightly dissociated, the deswelling region was 0–30 vol.% for PHA and 80–100 vol.% for PAA. The unique swelling behavior of PHA gel was ascribed to intermolecular hydrogen bonding. Effects of dielectric constant on the swelling are also discussed.

Introduction

We have investigated solution and gel properties of poly(α -hydroxy acrylic acid) (PHA) to find many unique properties, e.g., time dependence of pKa value upon titration due to slow lactone formation (1), significant $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding selectivity (2,3), gel formation with γ -rays irradiation for a polymer having no α -proton (4), and irreversible Ca^{2+} binding in the gel (5), etc. All these rather "strange" properties come from the α -OH group and formation of intramolecular lactone ring in the presence of H^+ . In fact, poly(acrylic acid) (PAA) shows no such strangeness.

Recently, collapse of charged polymer gels has been extensively studied in less polar medium from theoretical and experimental points of view (6,7). According to them, gel collapse is induced by decreasing the dielectric constant (addition of less polar solvents), which enhances counterion binding, and is driven by electrostatic attraction between ion-pairs of polymer charges and counterions to form an ionomer-like conformation or an ion cluster (8). Thus, factors that will influence electrostatic interactions and ion-pair formation, such as dielectric constant, ionic strength and solvation energy for charged groups, must be essential in the collapse phenomena. In fact, many experimental studies have supported the above scenario for the collapse of charged polymer gels (8,9). However, studies on the other factors that may affect the solvent-induced collapse (e.g., hydrophobic interaction (10), solvation to

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moieties other than charged groups (11) and inter-, intra-molecular hydrogen bonding (12,13) are much less available.

In the present paper, we report swelling behavior of poly(α -hydroxy acrylic acid) (PHA) gel in aqueous organic solvent mixtures. We expected that the existence of α -OH groups and lactone rings, i.e., a donor and acceptors for hydrogen bond, in the polyelectrolyte may cause a unique response of the gel to changes in solvent quality. The present study can provide fundamental data for a total elucidation in future of solvent effect on physico-chemical properties of polymer gels.

Experimental

Materials and gel preparation

PHA (M.W. = 8.7×10^4) was kindly supplied as an aqueous solution of the Na salt by Nippon Peroxide Co. Ltd. PAA (M.W. = 9.0×10^4) was purchased from Polysciences Inc. Gels were prepared by irradiating the respective 15.0 wt.% aqueous solutions, the pH of which was adjusted to 2.0 with HCl and NaOH, in a capillary (inner diameter = 0.44 mm) with γ -rays. The γ -ray dose was 350 kGy and 50 kGy for PHA and PAA, respectively. Gels thus prepared were immersed in distilled water for a week to establish the equilibrium with water.

Measurements of swelling degree

Swelling degree was estimated as d/d_0 , where d is the gel diameter and d_0 is that of the above gel swollen in distilled water. The diameters were measured with a microscope (Olympus SF20).

Dimethyl sulfoxide (DMSO), acetone or dioxane (Tokyo Kasei Co., analytical grade), was mixed with distilled water to prepare immersing solvents of various compositions; 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 vol.%. Here two series of immersing solvents were used to observe swelling behavior of gels having different charge densities; pH of one series was not adjusted and pH (apparent value) of the other one was set to 9.0 by adding small amounts of 1 N NaOH (ca. $1 \mu\text{L}/100 \text{ mL}$ solvent). Thus, it is expected that carboxyl groups in gels immersed in the former solvents are only slightly dissociated since the gels were prepared in acidic solution (pH = 2.0). On the other hand, the gels immersed in the latter solvents must be almost fully charged (14).

Gel samples that were pre-equilibrated with distilled water were first immersed into either 10 vol.% solvent, pH of which was not adjusted, or 0 vol.% solvent (water), pH of which was adjusted to 9.0, for one day. Then, each sample was transferred into a next concentrated solvent and immersed for another one day. All the gel samples were kept at $25.0 \pm 0.5 \text{ }^\circ\text{C}$ when immersed in the solvents and the measurement of gel diameter was carried out at room temperature (ca. 25°C).

Results and discussion

Comparison of PHA and PAA gels

In Figs.1-3, the swelling ratios (d/d_0) are plotted against vol.% of the organic solvents to compare the (de)swelling behavior of PHA gel with that of PAA gel. Typical results

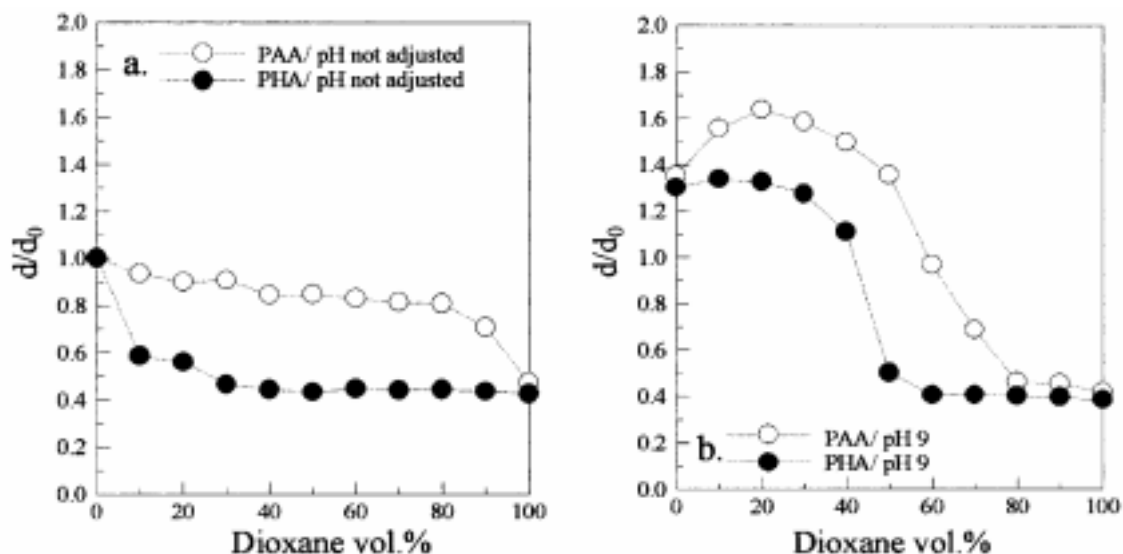


Figure 1. Swelling behavior of PAA and PHA gels in aqueous dioxane.

are seen for dioxane system in Fig.1; when the gels were immersed in solvents, pH of which were not adjusted (Fig.1-a), d/d_0 for PAA gel decreases only slightly with increasing dioxane content, and finally shows a definite fall at 80 - 100 vol.%. On the other hand, a comparable deswelling is seen at 0 - 10 vol.% for PHA gel. When the gels were immersed in alkali solvents (pH = 9, Fig.1-b), the deswelling behaviors of the two gels are qualitatively comparable. (Although one may note that the initial swelling in a region of 0 to 10 vol.% is significant for PAA gel and also for the other solvent systems (Figs.2 and 3), we confine the discussion to the deswelling behavior with increasing solvent composition. Swelling of charged gels accompanying a decrease in the solvent polarity is not reasonably explained at the present stage.)

The behaviors shown by PAA gel, namely, "deswelling with decreasing solvent polarity (dielectric constant)" and "shift of the deswelling composition to more polar

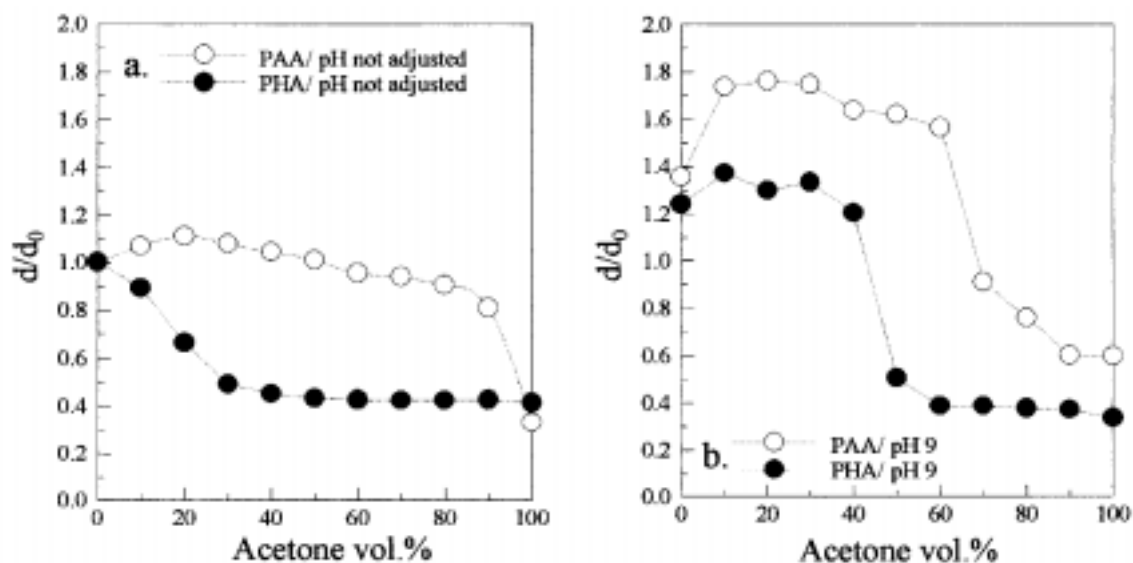


Figure 2. Swelling behavior of PHA and PAA gels in aqueous acetone.

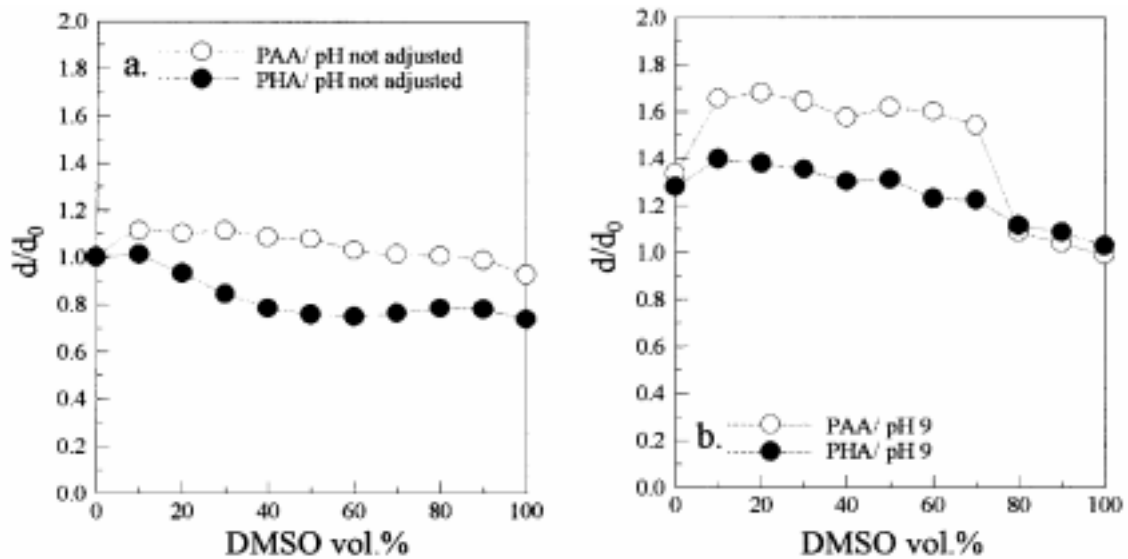


Figure 3. Swelling behavior of PHA and PAA gels in aqueous DMSO.

one with increasing the charge density", has also been observed for other charged gels in mixed solvents (8,9). As stated in Introduction, this kind of gel deswelling or collapse has been ascribed to formation of an ion-cluster, and the dependence on the solvent polarity and the polymer charge density has been theoretically predicted (6). Thus, the deswelling behavior of PHA gel, i.e., "shift of the deswelling composition to less polar one with increasing the charge density" may not be ascribed to an ionomer-like ion-cluster formation only. (Deswelling can occur at a less polar solvent with increasing the polymer charge density if the charge density is lower than ca. 10 % (7).)

Among possible causes for the initial deswelling of PHA gel shown in Fig.1-a, intermolecular hydrogen bonding seems to be most likely. In fact, a previous IR study (14) suggested that hydrogen bonding, though intramolecular one, among C=O of lactone, -COOH, -COO⁻ and OH groups is strengthened with decreasing pH of PHA aq. solution. Since PHA gels were prepared at pH = 2, hydrogen bonding must be potentially available also in the gel phase. Addition of organic solvents, or decrease in

Table 1. Solvent composition and D in the deswelling region of PHA and PAA gels.

	PHA		PAA	
	vol. %	D	vol. %	D
pH not adjusted				
dioxane	0 - 30	78 - 53	80 - 100	12 - 2
acetone	0 - 30	78 - 64	80 - 100	34 - 19
DMSO	0 - 50	78 - 62	-	-
pH = 9				
dioxane	40 - 60	45 - 27	50 - 80	36 - 12
acetone	60 - 90	59 - 47	60 - 90	47 - 26
DMSO	-	-	70 - 100	56 - 49

the dielectric constant, would enhance the hydrogen bonding among the donor and acceptor groups to induce the gel deswelling. This point is further discussed below.

Effect of organic solvents

Solvent compositions and dielectric constants (D) where the appreciable deswelling occurs depend on the solvent species. Table 1 summarizes the deswelling region and the corresponding dielectric constant.

For PAA gel, the dielectric constant, D, for the deswelling region is no constant, but decreases in the order, DMSO > acetone > dioxane. This is a contrast to the deswelling behavior observed for quaternized poly(4-vinyl pyridine) (P4VP) gels in water/organic solvent mixtures (9); the gel collapse occurred almost at a constant D (ca. 70 for fully charged P4VP with Cl⁻ counterion). This was ascribed to the hydrophobicity of the polymer, which allowed, to some extent, free access of organic solvents to the polymer to make the local solvent composition and hence the local D value to be the same as the bulk ones. Thus, D, a measure of the degree of counterion binding, played an essential role for the gel collapse with ion-cluster formation. In the present system, however, PAANa is much more hydrophilic than quaternized P4VP. Therefore, the local solvent composition and D may be much different from those in bulk. For example, dioxane has the lowest D (ca. 2) among the three organic solvents used here, and may be repelled from PAANa. Thus, PAA may be selectively hydrated in the mixed solvent and the local D would be higher than the bulk value. This speculation explains the order of D for the deswelling region as shown in Table 1. On the other hand, the lack in an appreciable deswelling region for PAA in aq. DMSO may be ascribed to the high D value (ca. 49) of pure DMSO, namely, too high for ion-cluster to be stabilized.

In the case of PHA gel at unadjusted pH or of slightly charged PHA gel, effect of D may be through intermolecular hydrogen bonding. With decreasing D, hydrogen bonding will be strengthened. In fact, deswelling starts with addition of only small amounts of solvents to water and the D values at the deswelling region are not so different among the solvents. This suggests that the intermolecular hydrogen bonding is potentially available even in water and triggered by the addition of small amounts of less polar solvents.

For PHANa gel (pH = 9), the order of D can be explained as in the case of PAANa. The D values at the deswelling regions for dioxane and acetone systems are somewhat higher than those of PAANa gel. This should be explained by other factors such as degree of cross-linking and chain flexibility.

In conclusion, we have found that D values at the deswelling region of PHA gel in water/organic solvent mixtures decrease with increasing the polymer charge density and ascribed it to intermolecular hydrogen bonding which is effective for slightly charged PHA. We will further investigate the hydrogen bonding supposed for PHA with spectroscopies like IR and NMR, and with ab initio calculations.

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