Swelling Behavior of Partially Quaternized Poly(4-vinylpyridine) Gels in Water/Organic Solvent Mixtures

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ABSTRACT: Partially quaternized poly(4-vinylpyridine) (P4VP) gels were prepared by irradiating aqueous solutions with γ-rays. Swelling degrees in water increased with increasing the degree of quaternization (charge density) except for gels of I^- or SCN^- counterions, while those in mixed solvents (water/methanol, ethanol, 2-propanol, dimethyl sulfoxide, acetone, or dioxane) decreased with increasing the charge density and/or with decreasing the dielectric constant of the mixed solvent. This trend was more evident for counterion species having stronger affinity to quaternary ammonium group, e.g., I^- and SCN^-, for which very sharp deswelling, comparable to volume phase transition, was observed even in water. A remarkable finding was that the sharp collapse occurred at almost a constant dielecric constant (D) irrespective of the solvent species; e.g., when the counterion was Cl^-, the collapse was observed at $D = 58 \pm 2$ for 50% quaternized gel and at 71 or 72 for the fully quaternized one. Effects of cross-linking, counterion binding, polymer charge density, and dielectric constant of solvent on the gel collapse are discussed.

Introduction

Conformational changes of polyelectrolytes in both solution and gel phases have attracted much attention from theoretical and experimental points of view.[1−3] The so-called coil−globule transition of weakly charged polyelectrolytes in solution systems has been theoretically predicted to occur with decreasing solvent quality.[1] A corresponding experimental finding has been reported by Klooster et al.;[4] the authors found that reduced viscosity of poly(acrylic acid) (PAA) in methanol sharply decreases with increasing the degree of neutralization ($\alpha \geq 0.1$) with sodium methoxide, while it was much less marked with lithium methoxide. This observation suggests that counterion binding is essentially involved with the conformational change.

In gel systems, similar chain contraction is observed as collapse or volume phase transition. Khokhlov and Kramarenko[5,6] proposed a generalized gel-collapse theory derived by taking into account the ion-pair formation of counterion and polymer charges and predicted the existence of a new gel state, a "supercollapsed" one. Conforming to the theory, Starodoubtsev et al.[7] found that slightly cross-linked poly(diallyldimethylammonium chloride) gels collapse in aqueous NaI solution with increasing the counterion (I^-) concentration and ascribed the phase transition to association of ion pairs of I^- and the quaternary ammonium groups. Further, Philippova et al.[8] demonstrated that there are three regimes for the swelling behavior of poly(methacrylic acid) (PMA) gel when titrated in mixed solvents, i.e., polyelectrolyte, ionomer, and the intermediate, depending on the dielectric constant.

In the above examples for solution and gel systems, it should be noted that the solvent polarity or the dielectric constant, at which collapse occurs, changes depending on the polymer charge density. For example, in the case of Tanaka et al.[2] for partially hydrolyzed poly(acrylamide) gel in aqueous acetone solution and that by Philippova et al.[9] for poly(acrylamide) gel containing small amounts of cationic groups ($\leq$10 mol %) in aqueous ethanol, the collapse point displaced to a less polar medium with increasing the charge density. However, a contrary behavior has been observed for gels of higher charge densities, e.g., in the case of Philippova et al.[8] for PMA gel in aqueous methanol and that by Tong and Liu[10] for PAA gel in aqueous acetone. These behaviors suggest that counterion binding degree must be a key factor determining the polyelectrolyte gel swelling, and in fact, it has been incorporated into Khokhlov's theory.[5,6] Thus, it seems to be interesting and fruitful to investigate a relation between gel collapse and counterion binding degree, which can be estimated as a function of the charge density and the dielectric constant by a counterion condensation theory.[11]

In our previous study,[12] we measured counterion activity and reduced viscosity of partially quaternized poly(4-vinylpyridine) (P4VP) in aqueous alcohols as a function of the solvent composition and found that both of the solution properties decrease with increasing the charge density above a certain critical value, a comparable behavior to PAALi in methanol.[4] We have ascribed the conformational change of quaternized P4VP to an ionomer-like ion-cluster formation. Further, we have found that the conformational change occurs when Manning's charge density parameter,[11] ξ, is ca. 1.0, irrespective of the alcohol species. This strongly suggests that such an ion-cluster formation is triggered by counterion binding.

In the present study, we have investigated swelling behavior of partially quaternized P4VP gels in water/organic solvent mixtures. The correlation between gel collapse and counterion binding is discussed on the basis of the dependence of collapse on the counterion species, solvent species (dielectric constant), and the charge density.

Experimental Section

Quaternization of P4VP. Poly(4-vinylpyridine) (P4VP), purchased from Koei Chemical Co. Ltd., was purified by reprecipitation in diethyl ether. The molecular weight was estimated as 2.3×10^5 by viscometry. P4VP thus prepared was quaternized by ethyl bromide of different amounts (10, 20, 30,

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Table 1. Conditions for Gelation

inner diam of capillary/mm	C_p/ wt %	C_{HCl}/N	γ-ray dose/kGy	equilib gel diam/mm	ratio to capillary diam
0.690	2.0	1.0	100	*a*	
	2.0	1.0	200	*a*	
	2.0	1.0	300	*a*	
	5.0	0	200	*a*	
	5.0	0	300	*a*	
	5.0	1.0	100	*a*	
	5.0	1.0	200	1.006	1.46
	5.0	1.0	300	0.921	1.34
	10.0	0	200	*a*	
	10.0	0	300	0.914	1.33
	10.0	0.1	200	*a*	
	10.0	0.1	300	0.911	1.32
	10.0	1.0	100	*a*	
	10.0	1.0	150	*b*	
	10.0	1.0	200	0.975	1.41
	10.0	1.0	300	0.908	1.32
1.128	2.0	1.0	100	*a*	
	2.0	1.0	200	*a*	
	2.0	1.0	300	*a*	
	3.0	1.0	150	*a*	
	4.0	1.0	150	*a*	
	5.0	1.0	100	*a*	
	5.0	1.0	150	1.702	1.51
	5.0	1.0	200	1.611	1.43
	5.0	1.0	300	1.469	1.30
	10.0	1.0	100	*a*	
	10.0	1.0	150	1.666	1.48

[a] No gelation. [b] Too soft for use.

35, 40, 50, 70, and 150 mol %) in 5 wt % nitromethane solution at 46 °C for 5 days. The degrees of quaternization were estimated by ^{1}H NMR peak area for a proton as 0.095, 0.189, 0.296, 0.347, 0.410, 0.512, 0.709, and 1.0, respectively. We simply use 0.1, 0.2, 0.3, 0.35, 0.4, 0.5, 0.7, and 1 as the respective quaternization degrees or charge densities in the following discussion.

The counterion species of the polymer samples was exchanged to Cl^- by ultrafiltration (Ultrafilter UK-10, Toyo Roshi) in the presence of excess amounts of HCl. Details of the purification procedure are given elsewhere.[12]

Preparation of P4VP Gel. Rodlike gel samples were prepared by irradiating P4VP aqueous solutions in a capillary with γ-rays. To establish an optimum condition for gelation of P4VP, a preliminary experiment was performed by using the 35% quaternized sample. The results are shown in Table 1. First, we tried gelation with a relatively thin capillary (diameter = 0.690 mm) by changing the polymer concentration (C_p), HCl concentration (C_{HCl}), and γ-ray dose. HCl was added to change the polymer charge density, and 1 N HCl was expected to be enough to obtain a fully charged P4VP.[13] To prepare gel samples under a same cross-linking condition irrespective of the degree of quaternization, one must try γ-ray irradiation for fully charged P4VP, namely in 1 N HCl. This condition seemed to be rather severe for gelation to occur because electrostatic repulsion between polymer chains will retard coupling of radicals formed on different polymer chains. However, in fact, gelation was confirmed for 1 N HCl systems-(γ-ray dose ≥ 200 kGy), and higher charge densities seemed to be rather favorable for gelation. (At 200 kGy irradiation, gelation occurred only for 1 N HCl system.) Unfortunately, no reasonable explanation for the unexpected gelation behavior can be given at the present stage.

To obtain less cross-linked gel samples, we tried gelation at a lower C_p and a lower irradiation dose with a capillary of a larger diameter (1.128 mm) (because it is difficult to take out a less cross-linked, "soft", gel from a thin capillary) and found that gelation occurs at 150 kGy when $C_p \geq 5$ wt %. Thus, the following two conditions were employed to prepare respective gel samples of different degrees of quaternization.

1. capillary diameter: 1.128 mm; C_p: 5 wt %; C_{HCl}: 1 N; γ-ray dose: 150 kGy
2. capillary diameter: 0.690 mm; C_p: 10 wt %; C_{HCl}: 1 N; γ-ray dose: 300 kGy

The gel samples prepared under the second condition were used to see effects of cross-linking degree. The degree of gelation was estimated by Soxhlet extraction of free polymer with water. For 150 kGy samples, the degree of gelation was 40−50%, while for 300 kGy samples, 50−60%. We call the gels prepared with the higher γ-ray dose "hard gels" and those with the lower dose "soft gels".

Counterion species of gel samples thus prepared were exchanged to Br^-, I^-, ClO_4^-, NO_3^-, and SCN^- by immersing into the respective sodium salt solutions of 1 N for 3 days and then in water for another 3 days.

Degree of Swelling. The degree of swelling was evaluated by gel diameter (d in millimeters) with a microscope observation at 25 ± 0.1 °C. The weight swelling ratio, W_w/W_p (W_w is the weight of water in a gel and W_p is the weight of the dry polymer), was also determined for gel samples immersed in water.

Immersing solvents were prepared by mixing water (ion-exchanged and distilled one) and one of the following organic solvents (analytical grade from Tokyo Kasei Co. Ltd.): methanol (MeOH), ethanol (EtOH), 2-propanol (2PrOH), dimethyl sulfoxide (DMSO), acetone, 1,4-dioxane. Measurements of gel diameter were performed after 1 day immersion of the respective gel samples (ca. 5−7 mm long) in a solvent (ca. 20 mL), and then the solvent was exchanged to a new one of higher composition by 10 vol %. Around a sharp deswelling, the organic solvent composition was changed by 1 vol %.

Results and Discussion

Swelling Behavior in Water. A ratio of gel diameter, d/d_0 (d_0: diameter of unquaternized P4VP gel), was used to compare the dependence on the charge density (CD) between the two gel samples of different cross-linking degrees (300 and 150 kGy). Figure 1a,b shows the plots for the respective gel systems. When the counterion is Cl^-, Br^-, or ClO_4^-, the swelling ratio (d/d_0) of the hard gel increases almost linearly with CD. For the soft gel, the increase in d/d_0 with CD is quantitatively similar to the hard gel until CD = 0.5, while in the higher CD the swelling tendency becomes less apparent. This is clearly seen in the weight swelling ratio shown in Table 2; for Cl^-/soft gel, W_w/W_p increases by 74 for CD = 0−0.5, while only by 15 for CD = 0.5−1.0. Such a saturating trend may be compared with a viscosity behavior observed in solution. According to our preliminary measurements on the present quaternized P4VP samples, the reduced viscosity in water (counterion: Cl^-) hardly increases with increasing CD above 0.5. Thus, the swelling behavior of the soft gel seems to be closer to the coil expansion of the un-cross-linked polymer in solution, which may be attributed to the lower degree of cross-linking.

When the counterion is I^- or SCN^-, a sharp deswelling above CD = 0.4 is observed for the hard and soft gels. The degree of deswelling is more significant for the soft gel (d/d_0 = ca. 1.17 for I^- at CD = 0.4 and ca. 0.48 at 0.5) than the hard gel (ca. 1.16 at CD = 0.4 and ca. 0.56 at 0.5). This may also be ascribed to the lower degree of cross-linking of the former. This kind of sharp deswelling, or collapse, of polyelectrolyte gels with increasing charge density has also been reported by Starodoubtsev et al.[7] for a polycation (a copolymer of acrylamide and diallyldimethylammonium) gel in water,

Table 2. W_w/W_p Values of the Hard and the Soft Gels

Hard Gel (10 wt %, 300 kGy)

	counterion					
CD	Cl^-	Br^-	I^-	ClO_4^-	SCN^-	NO_3^-
0	31	31	31	31	31	31
0.1	34	34	31	34	31	33
0.2	39	38	35	39	35	37
0.3	39	38	36	39	36	38
0.4	45	44	42	47	42	44
0.5	53	52	4	55	4	49
0.7	68	67	4	71	4	61
1.0	79	78	2	81	2	64

Hard Gel (5 wt %, 150 kGy)

	counterion					
CD	Cl^-	Br^-	I^-	ClO_4^-	SCN^-	NO_3^-
0	120	120	120	120	120	120
0.1	128	124	122	132	119	123
0.2	145	140	137	151	135	140
0.3	159	154	151	165	149	154
0.4	175	170	164	180	154	168
0.5	194	187	11	200	10	185
0.7	200	193	9	201	8	194
1.0	209	203	5	209	5	200

while the collapse was limited to a fully charged sample in aqueous NaI solutions.

The order of d/d_0 according to the counterion species is almost the same for the hard and soft gels as $SCN^- \leq I^- \ll NO_3^- <$ ($\leq$ for the soft gel) $Br^- \leq Cl^- \leq ClO_4^-$, at CD = 1.0. This kind of counterion specificity has often been reported in the literature on physicochemical properties of polycations in solution and gel systems. For example, Burkhardt et al.[14] estimated concentrations of many inorganic salts needed to produce the θ condition for aqueous poly(1,2-dimethyl-5-vinylpyridinium chloride) solutions and found an appreciable anion specificity: $SCN^- < ClO_4^- < I^- < IO_4^- < MnO_4^- < NO_3^- = Br^- < Cl^- < SO_4^{2-} < HCO_3^- < HPO_4^{2-} < F^-$. Kudo et al.[15] measured swelling ratio of a cationic gel from poly(*N*-*n*-butyl-*N*,*N*-dimethyl-4-vinylbenzylammonium bromide) in aqueous solutions of various salts and found that a volume phase transition occurred in the presence of ClO_4^- or I^- and the swelling ratio increased in the order $ClO_4^- < I^- < Br^- < Cl^-$. These two examples suggest that quaternary ammonium groups will form stable ion pairs with larger anions of weaker hydration. In fact, according to Desnoyer's hydration sphere overlapping model,[16] large inorganic ions of weak ionic hydration prefer large counterions, and large hydrophobic ions also apt to be bound by larger counterions rather than smaller ones of stronger ionic hydration. Thus, the anion specificity observed in the present gel systems, except for the position of ClO_4^-, may be attributed to different degrees of polymer charge neutralization or ion-pair formation. Although the unusual behavior of ClO_4^- is not fully understood, an assumption that gel collapse occurs only when stable ion pairs are formed between polymer charges and counterions seems to be very reasonable. In such a collapse, an ionomer-like conformation or an ion cluster must be formed through aggregation of the ion pairs.[8] The above comparison between the swelling behavior of the hard and the soft gels suggests that cross-linking will retard such an ion-cluster formation.

Swelling Behavior in Water/Ethanol Mixed Solvents. To examine the swelling behavior in media of lower dielectric constants, gel diameter was measured as a function of ethanol (EtOH) content in the mixed solvent with water. The results for the soft gels are shown in Figure 2a–d. (Results for Br^- and NO_3^- are omitted because they are almost the same as that of Cl^-.) Typical results for the hard gels are shown in Figure 3a,b.

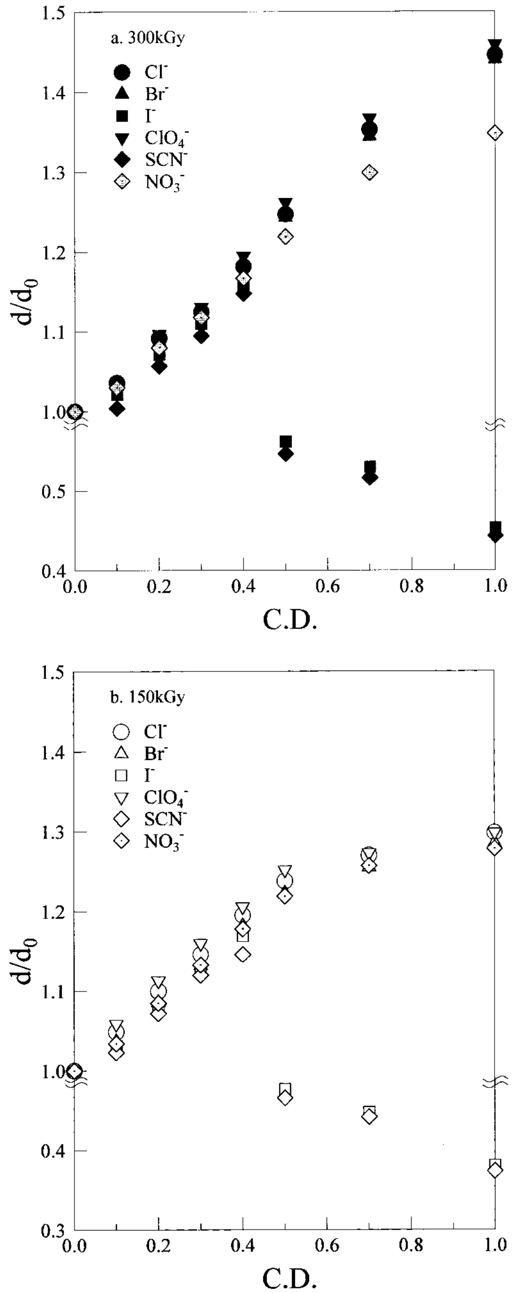

Figure 1. Swelling behavior of the hard gel (a) and the soft gel (b) in water.

In the case of Cl^- counterion (Figure 2a), a sharp deswelling was observed with increasing CD at an EtOH content higher than 20 vol %. (See vertically the data points at the respective EtOH contents.) Further, gels of CD $\geq$ 0.4 significantly deswell with an increase in the EtOH content. These behaviors strongly suggest that ion-pair formation or counterion binding is essentially involved with the collapse-like deswelling since an increase in CD and EtOH content should enhance the degree and stability of ion pairs formed. A similar swelling behavior was also observed for the ClO_4^- system (Figure 2b) though a higher EtOH content ($\geq$40

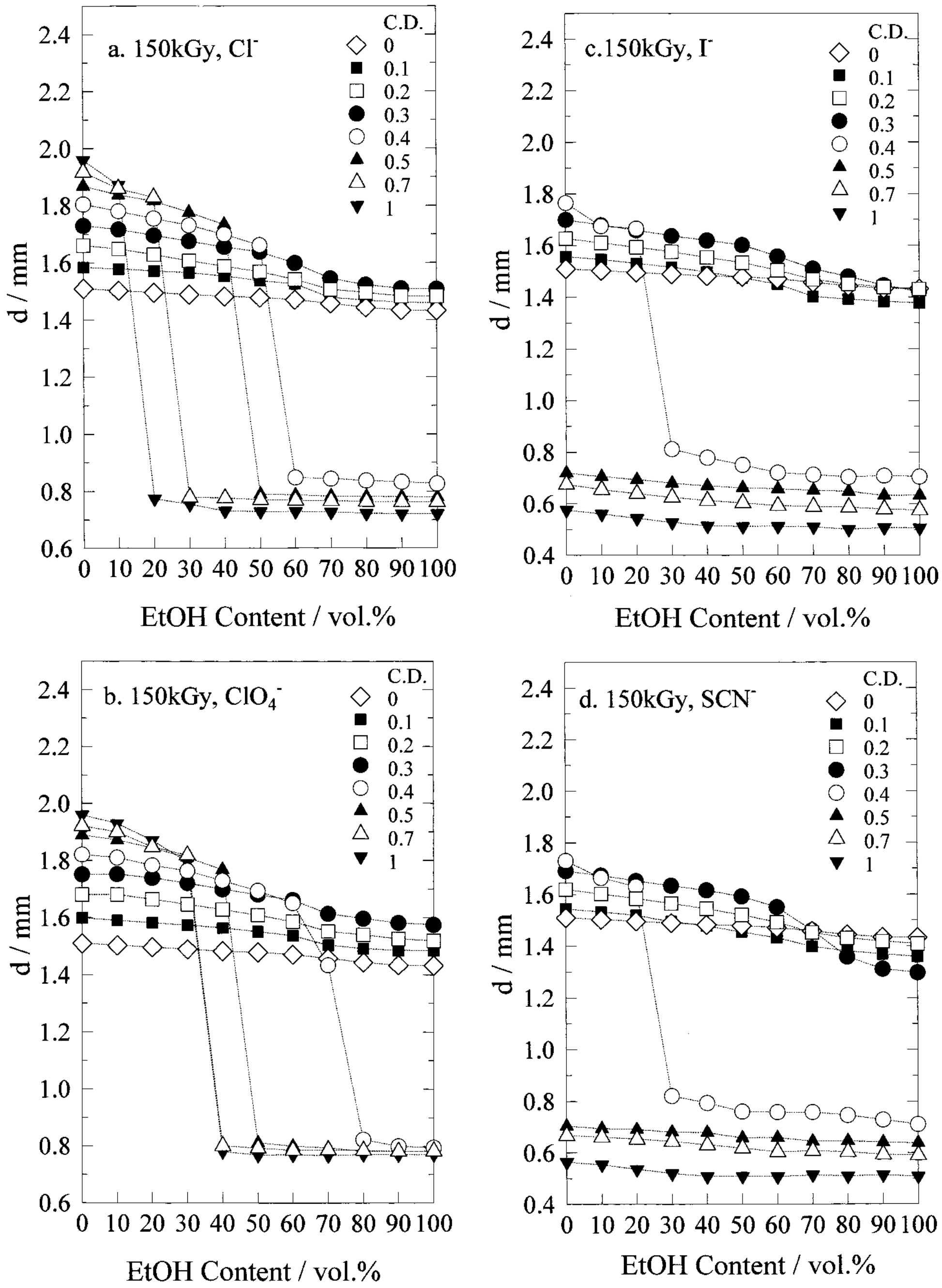

Figure 2. Swelling behavior of the soft gel in aqueous ethanol. The dotted lines are guides to eye. Counterions: Cl^- (a), ClO_4^- (b), I^- (c), SCN^- (d).

vol %) and a higher CD (≥0.5) than those of Cl^- system were necessary for sharp deswelling to occur.

In the case of I^- and SCN^- counterions (Figure 2c,d), a gel collapse with increasing CD was observed in the whole EtOH compositions because it occurred even in water. Collapse with increasing EtOH content was observed only for CD = 0.4, and gels of lower CD's maintained their swollen states even in 100% EtOH.

Qualitatively the same behavior was observed for the hard gels (Figure 3a,b) though the reduction in the gel diameter with CD becomes less remarkable with increasing EtOH content. Further, deswelling of a gel with Cl^- counterion at CD = 0.4 smoothly occurs with EtOH content, while it occurs sharply in the soft gel. These also suggest that the more cross-linking is introduced, the less favorable a sharp collapse becomes.

Dependence on the Dielectric Constant. As seen above, even for the Cl^- counterion which has a relatively low affinity to the quaternary ammonium cation, the present P4VP gel collapses in mixed solvents of lower dielectric constants. Addition of an organic solvent like an alcohol to water reduces the dielectric constant, which in turn enhances the stability or the degree of counterion binding. Then, dipolar attractive force among the ion pairs formed induces the gel collapse. This seems to be a common scenario for charged gels of relatively high charge densities. However, the degree of counterion binding is determined not only by the dielectric constant (D) of the medium but also by the other solvent properties, e.g., Gutmann–Mayer's donor number (DN) and acceptor number (AN),[17] a measure of solvating power of solvent molecules to cations and anions, respectively, and water activity (a_w), a measure of preferential hydration (or solvation) of ions. In fact, it has been found[18] that the activity of Cl^- as a counterion of poly(allylamine) in aqueous alcohols (MeOH, EtOH,

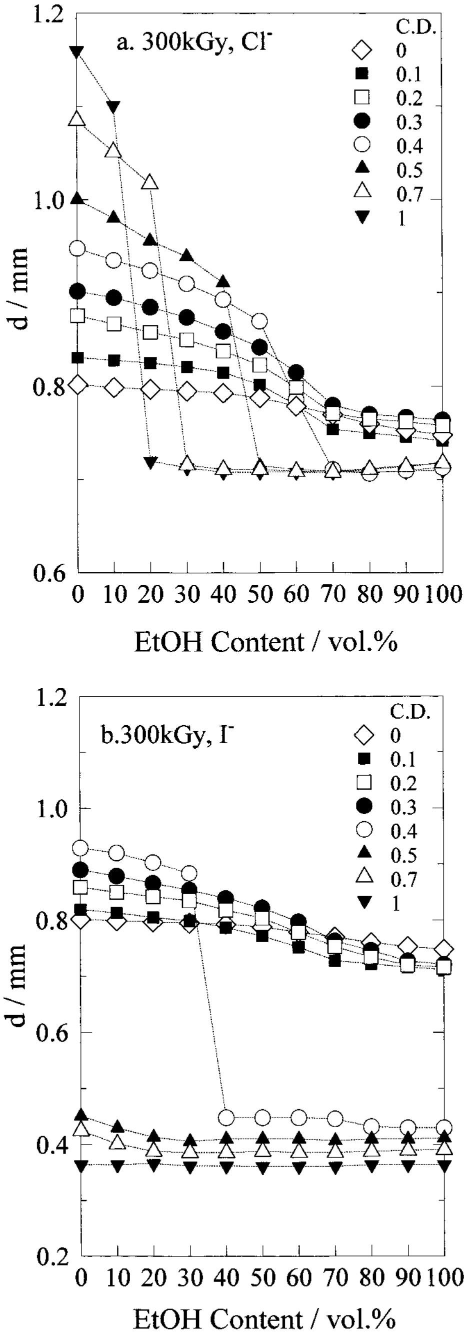

Figure 3. Swelling behavior of the hard gel in aqueous ethanol. The dotted lines are guides to eye. Counterions: Cl^- (a), I^- (b).

2PrOH) depends on the alcohol species, which was ascribed to the preferential hydration of the polyion.[19] Thus, we investigated swelling behavior of the present P4VP gels in a variety of water/organic solvent mixtures, to see how the degree of swelling depends on solvent properties.

Figure 4a shows an example for the supposed solvent specificity in the gel swelling (hard gel, Cl^-, CD = 0.5). Since the plots are made against volume percent of the organic solvents, gel collapse apparently occurs depending on the solvent species. However, in Figure 4b where plotted against *D*, one can see that the gels collapse at almost a constant *D*, irrespective of the solvent species! A similar behavior is observed also for a soft gel (SCN^-, CD = 0.4) as shown in Figure 4c. To see whether the gel collapse shows any hysteresis, the gel diameter was also measured in the course of decreasing the organic solvent content from the pure one. A typical result in aqueous methanol is shown in Figure 5. The gel diameters before and after the collapse are almost the same for MeOH increasing and decreasing courses. Further, the jump of the gel diameter occurs within 1 vol % change in MeOH content, i.e., between 54 and 55 vol %. With this sharpness, the collapse seems to be comparable to the volume phase transition.

Transition points expressed by *D* thus obtained are summarized, together with some solvent properties, in Table 3. The *D* and water activity (a_w) values were estimated on the basis of literature data as a function of solvent composition.[20,21] Almost a constant *D* was obtained as a critical transition point for a given gel system irrespective of the organic solvent species. This means that solvent properties such as DN, AN, and water activity are not essentially involved in the present gel collapse. This unexpected result may be understood as follows:

DN, as a measure for solvation ability to cations, may not be so critical in the present system, since electron-pair donation from organic solvents to the quaternary ammonium cation should not be so effective as to small cations such as alkali metal ones. AN, as a measure for solvation ability to anions, may not be used in the present purpose, since counteranions should be preferentially hydrated as suggested by the high a_w values of the mixed solvents used. Although a_w of MeOH is relatively low, AN of MeOH is relatively high, resulting in a high desolvation energy comparable to the other preferentially hydrated systems. According to the high a_w values of the mixed solvents, P4VP could also be preferentially hydrated. In fact, in the case of poly(allylamine) hydrochloride, an alcohol specificity was observed for counterion activity and was interpreted by the preferential hydration of the polymer and the resultant higher local *D* values. However, it is not the case in the present system as demonstrated by the constant critical *D* values. This may be attributed to the inherent hydrophobicity of P4VP. Further, the introduction of charged group by quaternization with ethyl bromide would not increase, at least significantly, the total hydrophilicity of P4VP, since it is known that hydration of a tetraethylammonium cation is between hydrophilic and hydrophobic ones. Thus, solvent composition around the quaternized P4VP's seems to be comparable to that in bulk phase. The same may be said also for the local *D* values around the polymer. In conclusion, the observed constancy for the critical *D* values seems to be limited to the present polymer system, and it is expected that gel of a more hydrophilic polymer, e.g., poly(allylamine) hydrochloride,[19] would show appreciable solvent specificity in the swelling behavior.

Figure 4d shows a plot of gel diameter against *D* for a gel which collapsed even in water, i.e., soft gel of CD = 0.5 and SCN^- counterion. In this case, too, the swelling degrees seem to be expressed as a function of *D*, irrespective of the solvent species. Here it should be noted that gels in a collapsed state gradually deswelled with decreasing *D*. A similar deswelling is seen in Figure 2c,d and less significant in Figure 2a,b. This means that a kind of "supercollapse" state appears in a gel which has a strongly binding counterion (SCN^-, I^-) with decreasing *D*. This "supercollapse" state may be compared with that found by Starodoubtzev et al.[7]

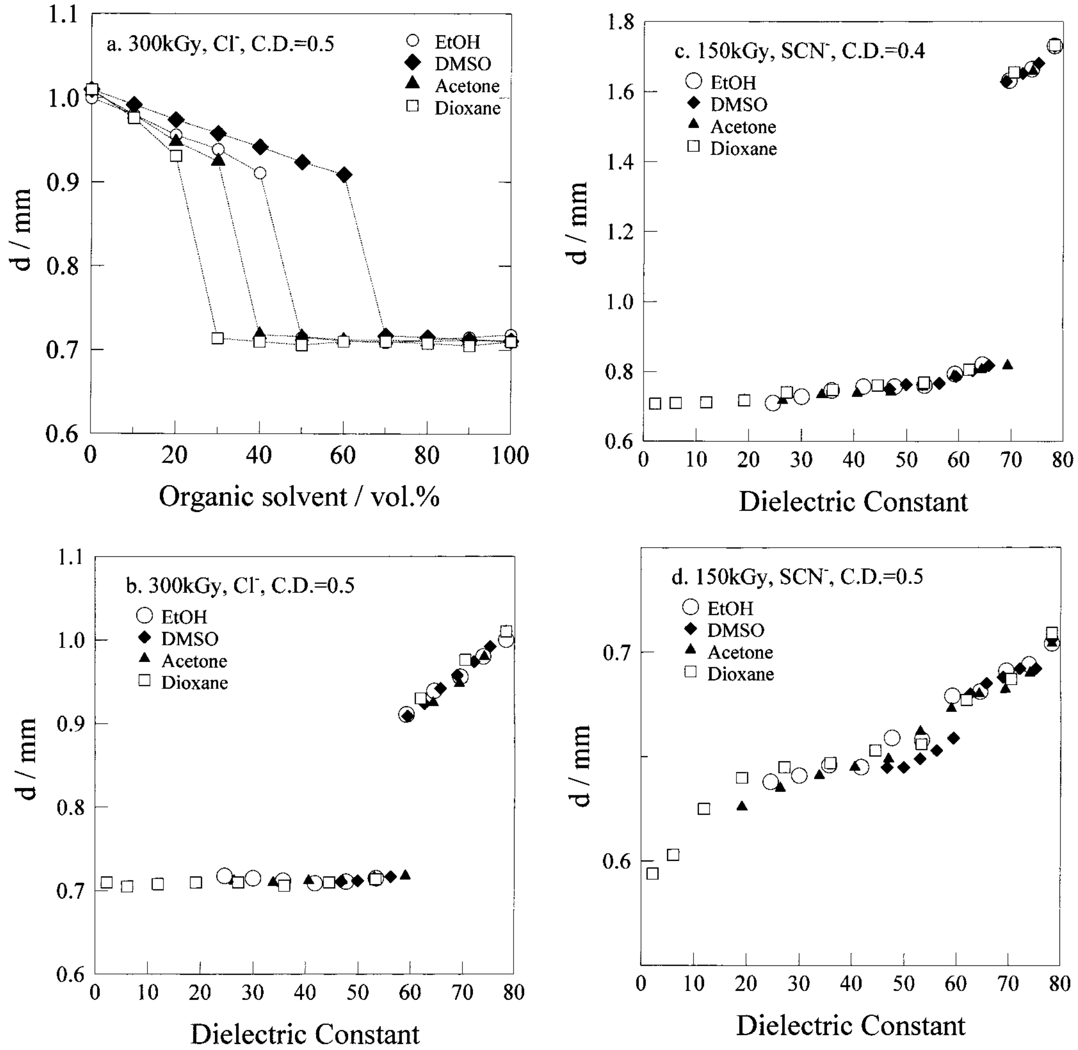

Figure 4. Solvent specificity for the gel collapse: (a) hard gel, CD = 0.4, counterion = Cl$^-$ (the dotted lines are guides to eye); (b) hard gel, CD = 0.4, counterion = Cl$^-$; (c) soft gel, CD = 0.4, counterion = SCN$^-$; (d) soft gel, CD = 0.5, counterion = SCN$^-$.

Table 3. Critical *D* Values and Some Solvent Properties at 25 °C

Critical *D* Values

gel system	water/MeOH	EtOH	2PrOH	DMSO	acetone	dioxane
hard gel, CD = 1.0, Cl$^-$	71	72	72	72	71	72
hard gel, CD = 0.5, Cl$^-$	57	59	60	58	60	57
soft gel, CD = 0.4, SCN$^-$				66	71	69

Solvent Properties

	water	MeOH	EtOH	2PrOH	DMSO	acetone	dioxane
D^a	78	33	25	20	47	21	2
$a_w{}^b$		0.76	0.88	0.95			0.82^c
DN^a	33	19	20		30	17	15
AN^a	55	41	37	34	19	13	11

[a] Values for pure solvents. [b] Values for 50 vol % mixed solvents. [c] Values for 80 vol %.

Gradual decreases in swelling ratio are also observed with increasing CD, as shown in Figure 6. In the figure, a ratio of a gel diameter in 100 vol % EtOH to that for an uncharged gel in water is used in order to see the effect of charge density on deswelling with increasing EtOH. In the case of the hard gels, the swelling ratios significantly depend on the counterion species; those for SCN$^-$ and I$^-$are much lower than the others and gradually decrease with CD, while those for the other counterions are almost constant. On the other hand, for the soft gels the counterion specificity is much less significant, and the decreasing tendency with CD is more apparent than the hard gels. These behaviors suggest that stable ion-pair formation between a counterion and a polymer charged group would enhance the deswelling via ion-cluster formation while cross-linking retards the ion-cluster formation. For example, the much less marked ion specificity in the deswelling behavior for the soft gels may result from a partial compensation of the relatively low ion-pair stability for Cl$^-$, Br$^-$, NO$_3{}^-$, and ClO$_4{}^-$ by the lower cross-linking degree.

Correlation with Manning's Charge Density Parameter. The experimental result that collapse of the

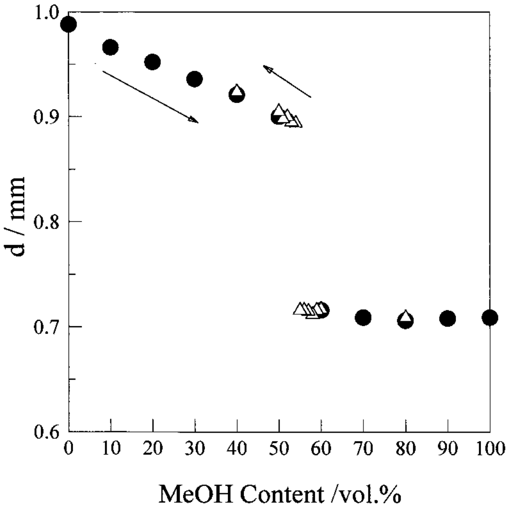

Figure 5. Hysteresis of the gel collapse in aqueous methanol. The gel sample is the same as that for Figure 4a. (●) Measured by increasing MeOH content. (△) Measured by decreasing MeOH content.

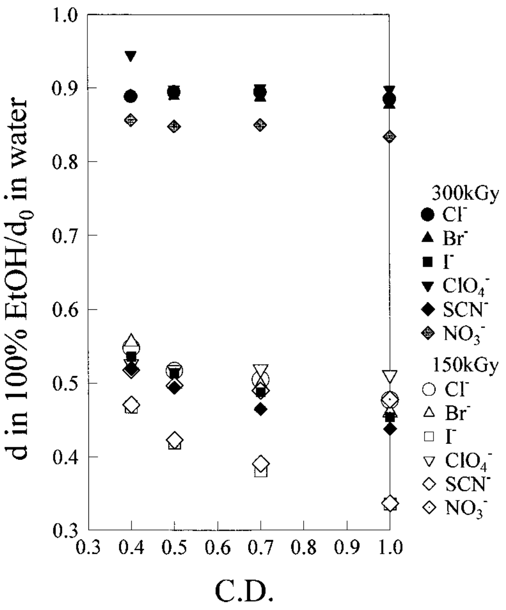

Figure 6. Counterion specificity in the deswelling behavior.

quaternized P4VP gels is controlled by *D* reminds us the similar observation in the solution system; reduced viscosities of the polymer solutions decrease with increasing CD at a critical point that is given by Manning's charge density parameter, ξ, defined by the following equation,[11]

$$\xi = e^2/DkTb \tag{1}$$

where *e* is electronic charge, *D* the dielectric constant, and *b* the axial charge spacing. To see the correlation, if any, between ξ parameter and the collapse points, some examples are compared in Table 4. For Cl$^-$ counterion systems, the critical charge density parameter ξ is larger than 1.4 for the soft gel and 1.6 for the hard gel and not constant. Since the critical values are around unity in the solution system, this comparison also suggests that cross-linking is unfavorable for ion-cluster formation.

On the other hand, the critical ξ values of I$^-$ counterion systems are appreciably lower than those of Cl$^-$ systems in the higher *D* region, i.e., ξ = 1.0−1.3 for 0−50 vol % EtOH. This means that stable ion-pair formation (counterion binding) with I$^-$ partially compensates the retardation of ion-cluster formation by cross-linking. In the lower *D* region (>50 vol % EtOH), however, the ξ values are the same as those of Cl$^-$ systems. Namely, collapse does not occur at the lower CD (≤0.2) even for I$^-$ counterion and even if the solvent *D* is decreased to 25. This is in contrast to the results in the solution system, where a decrease in the reduced viscosity was observed for P4VP with CD = 0.15 at *D* = 36. Thus, the above relation among the gel collapse, CD and *D*, referring to the corresponding relation in the solution system, suggests that a given amount of charged groups with bound counterions is necessary for the ion-cluster formation even at a very low *D* and that the critical amount is increased by cross-linkage. This must be one of the causes for the variable ξ values observed for gel systems.

Table 4. Critical Charge Density, ξ, for Cl$^-$ and I$^-$ Systems

System	Charge density	EtOH (vol.%) 0	10	20	30	40	50	60	70	80	90	100
Cl$^-$ solution	0.1											
	0.15									0.94		
	0.2									↓		
	0.25					0.95		1.2				
	0.3			0.97		↓		↓				
	0.35			↓								
Cl$^-$ 5wt% 150kGy	0.1											
	0.2											
	0.3							1.4	1.6	1.9	2.2	2.7
	0.4						1.7	↓	↓	↓	↓	↓
	0.5				1.7	1.9	↓					
	0.7			2.3	↓	↓						
	1.0		2.0	↓								
			↓									
Cl$^-$ 10wt% 300kGy	0.1											
	0.2											
	0.3							1.9	1.6	1.9	2.2	2.7
	0.4						1.7	↓	↓	↓	↓	↓
	0.5				1.7	1.9	↓					
	0.7			2.3	↓	↓						
	1.0		2.0	↓								
			↓									
I$^-$ 5wt% 150kGy	0.1											
	0.2											
	0.3				1.0	1.1	1.3	1.4	1.6	1.9	2.2	2.7
	0.4	1.1	1.2	1.3	↓	↓	↓	↓	↓	↓	↓	↓
	0.5	↓	↓	↓								
	0.7											
	1.0											

In conclusion, we have found a marked collapse for partially quaternized P4VP gels swollen in aqueous organic solvents, which significantly depended on the counterion species, the charge density, and the dielectric constant. All these dependencies strongly suggest that a scenario for ionomer formation is also valid for gel collapse. Addition of an organic solvent like an alcohol to water reduces the dielectric constant, which in turn enhances the stability or the degree of counterion binding. Then, dipolar attractive force among the ion pairs formed induces the gel collapse. On this mechanism, an increase in the ionic strength should be unfavorable for gel collapse because it reduces the electrostatic attractive force among the ion pairs. However, a finding by Starodoubtsev et al.[7] that a collapse was induced for poly(diallyldimethylammonium iodide) gel in water by increasing I$^-$ concentration seems to be contradictory to our expectation on the salt effect. Investigations for the effect of the ionic strength on ion-cluster formation, together with that on the solvent specificity of gel collapse, are now being undertaken.

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