Polymer 50 (2009) 3680–3685

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Novel PVA-based polymers showing an anti-Hofmeister Series property

Jianquan Wang [a,b,*], Mitsuru Satoh [b]

[a] School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China
[b] Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo 152-8550, Japan

ARTICLE INFO

Article history:
Received 21 January 2009
Received in revised form
19 May 2009
Accepted 27 May 2009
Available online 3 June 2009

Keywords:
Hofmeister Series
Salt-resistivity
Hydrogel

ABSTRACT

A series of poly(vinyl alcohol)-trimellitate (PVA-T) polymers with different esterification degrees (ED: 82, 61, and 32 mol%) were prepared through the esterification of PVA and trimellitic anhydride (TA). Solubilities of these polymers and the swelling properties of PVA-T hydrogels, which were prepared by crosslinking with ethylene glycol diglycidyl ether (EGDGE), were investigated in various salt solutions comprising of SO_4^{2-}, Cl^-, SCN^- and Li^+, Na^+, K^+, Cs^+. The PVA-T polymers proved to have larger solubilities in salt solutions (1 M) than in pure water, and the ionic "salting-in" effect was significant in order of $SO_4^{2-} > SCN^- > Cl^-$ for anions, and $Li^+ > Na^+ > K^+ > Cs^+$ for cations, regardless of their ED values. The PVA-T hydrogels also showed corresponding swelling properties; they significantly swelled in sulfate solutions of medium concentration (0.1–1 M), while in other salt solutions no appreciable swelling occurred. The marked salting-in effects exerted by sulfate anion, which is otherwise a typical "salting-out" agent, means that PVA-T polymers have an "anti-Hofmeister Series" (anti-HS) property. This is naturally ascribed to the trimellitic acid group because the degree of swelling in sulfate solutions was more significant for PVA-T with higher ED values; the combination of π-electron system and acidic protons seems to be essential to endow polymers with the anti-HS property.

1. Introduction

It is well known that the solubility of hydrophilic polymers in aqueous systems is influenced by ions. This phenomenon is ubiquitous for both synthetic and natural polymers, and the ion effect usually follows Hofmeister Series (HS), which was first introduced in 1888 to describe the ability of salts to precipitate certain proteins from aqueous solution. In fact, HS has been observed in many physico-chemical phenomena such as polymer cloud points, chromatographic selectivity, critical micelle concentration, surface tension, gel–coagel transitions, molecular forces, and colloid stability [1]. A representative HS can be given for anions as follows [2,3],

$$SO_4^{2-} > F^- > BrO_3^- > Cl^- > ClO_3^- > Br^- > NO_3^- > ClO_4^- > I^- > SCN^-$$

Ions on the left side are referred to as kosmotropes or water structure makers, while ions on the right are called chaotropes or water structure breakers. For anions, the positions of various ions may only slightly alter in different systems, while the order of cations is not so regular as that of anions and even inverted depending on systems. For example, Li^+ can be a kosmotrope or a chaotrope depending on the polymers; hydrophilic polymer gels prepared from PVA and poly(vinyl pyrrolidone) slightly swell in a concentrated solution of LiCl, while those from less hydrophillic polymers such as poly(*N*-isopropyl acryl amide) and uncharged poly(acrylic acid) significantly deswell [4–6].

The HS was originally explained in terms of the ability of various ions to "make" or "break" bulk water structure. However, recent researches [7–14], both experimental and theoretical, have clearly showed the contradiction to this water structure maker/breaker concept. Alternatively, the Hofmeister effect should be treated as interfacial phenomenon, and the water structure at the interface of macromolecule plays a key role in the thermodynamic and kinetic properties of polymers dissolved in aqueous solution [15]. On the basis of the direct interactions of the anions with the macromolecule and its first hydration shell, Zhang et al. successfully elucidated the effect of anions on water solubility of typical thermo-sensitive poly(*N*-isopropylacrylamide) (PNIPAM) [16,17]. In our previous studies on some polymer hydrogels such as poly(vinyl alcohol) (PVA), poly(allylamine) (PAlAm) and poly(vinylpyrrolidone) (PVP) [4,18], the ion specificities proved to be explained in terms of (de)stabilization of hydrogen-bonding hydration (HBH) to polar groups on polymer by ions, as well as the common ionic effects on the hydrophobic hydration (i.e., salting-in by the binding of large anions and salting-out by cations and small anions). And it was

---

[*] Corresponding author. Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo 152-8550, Japan. Tel.: +81 3 5734 2133; fax: +81 3 5734 2888.

E-mail address: wang.j.ah@m.titech.ac.jp (J. Wang).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.05.050

proposed that changes in the electron pair donicity (EPD) and acceptability (EPA) of water molecule via ionic hydration are responsible for the (de)stabilization of HBH to polymers. Namely, water's EPD is enhanced and EPA is reduced upon hydration to an anion because the partial negative charge on water oxygen increases and the positive charge on the protons decreases. On the contrary, water's EPA is enhanced with hydration to a cation as the proton charge increases [19]. Thus, strongly hydrated anions (cations) destabilize (stabilize) HBH to negative atoms of polar groups (e.g., O of OH, C=O, –O–, etc.).

In a series of works on the ionic effects on polymer gel swelling, we discovered that poly(4-vinyl phenol) (P4VPh) gel shows unexpected and extraordinary super salt-resistivity in many kinds of salt solutions [20]. This unique property is ascribed to specific stabilization of HBH to benzene ring (π electrons) and phenol OH acidic proton by cations and anions, respectively, and supported by ab initio calculations. As an extension, we further studied poly(4-vinyl benzoic acid) (P4VBA) [21], which also contains acidic proton and π electron system, and found super salt-resistivity was available too. This experimental fact is quite contrastive to the swelling behavior of poly(acrylic acid) (PAA) gel that remarkably deswells in concentrated solutions of strongly hydrated anions and/or cations (e.g., SO_4^{2-} and Li^+), and swells in the presence of weakly hydrated anions (e.g., SCN^-). Thus, the coexistence of acidic proton(s) and π electron system seemed to be essential for the polymer to show a salt-resistivity.

On the basis of the above reasoning, introduction of such a structure, i.e., benzene ring with acidic proton(s), to a conventional water-soluble polymer that has no salt-resistivity, may endow the polymer with salt-resistivity. In our preceding study, we have actually tested the above expectation by introducing trimellitic anhydride (TA) to PVA (PVA-T) with 73 mol% of esterification degree (ED) [22]. Beyond the expectation, the polymer showed an anti-HS property; i.e., SO_4^{2-}, a typical salting-out agent, behaved as a marked salting-in agent and SCN^-, a typical salting-in agent, made no notable effect. This phenomenon is quite specific and contrary to the common sense of traditional HS. Thus, an anti-HS property was observed for PVA-T with 73% ED value, and how about the polymers with higher or lower ED values? In the present work, PVA-T polymers with different esterification degrees were prepared and examined for the salt-resistivity and ion-specificity to clarify effects of introduction of acidic protons and a π electron system to PVA, a common polymer.

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) (PVA) (Degree of hydrolysis: 99–100 mol%, M_W: 86 000) was obtained from Acros Organic. Trimellitic anhydride (TA) was purchased from Tokyo Chemical Industry Co., Ltd. 4-(*N*,*N*-dimethylamino)pyridine (DMAP), triethylamine (TEA), dimethyl sulfoxide (DMSO), hydrochloric acid (HCl), sodium hydroxide (NaOH), and all the inorganic salts used were products of Kanto Chemical Co. Inc. Ethylene glycol diglycidyl ether (EGDGE) was obtained from Aldrich. All the chemicals were used as received.

2.2. Preparation of PVA-T polymers

PVA-trimellitate (PVA-T) polymers were prepared by modifying the preparation procedure described previously [22]. PVA (0.66 g, 15 mmol OH) was dissolved in DMSO (15 mL) by stirring overnight. Under N_2 atmosphere, catalytic amounts of TEA and DMAP and required amount of TA (5.77 g, 30 mmol, two times of PVA OH) were added to the PVA solution. The reaction was continued under stirring for 24 h at 30 °C. The esterificated polymer was obtained as precipitates by pouring the polymer solution into 2 L of 0.1 M HCl, and then was collected through filtration. The residue was dissolved in 1 M NaOH, and the solution was repeatedly ultrafiltrated through an ultrafilter Q2000 (Advantec, fractionation $M_W = 2 \times 10^5$). The polymer in the filtrate solution was again precipitated in 0.1 M HCl, and then filtered and dried *in vacuo* to obtain purified polymer (PVA-T1). Using the same procedure, we synthesized PVA-T2 and PVA-T3 by changing the feed ratio (TA/OH, mol/mol) to 1/1 and 0.5/1, respectively.

2.3. Characterization of PVA-T polymers

The esterification degree (ED) was determined through conductometric titration. FT-IR spectra were recorded on SHIMADZU FTIR 8200PC using KBr method. ^1H NMR spectra were obtained using JEOL AL-400 with DMSO-d_6 as solvent.

2.4. Solubility measurement of PVA-T polymers

Firstly, PVA-T polymers were dispersed in pure water by sonication for at least 1 h using VC-1 ultrasonic cleaner (AS ONE), to get stock dispersions. Certain amount of concentrated salt solution was added into 2 mL polymer dispersions to adjust the salt concentration in system at 1 M. If the liquid mixture became transparent, it was judged that polymer was solubilized in the 1 M salt solution. Then further solubilization of more amounts of polymer dispersion was tested. If the mixture was still turbid, 1 M salt solution was added little by little until the polymer was dissolved. The solubility was calculated on the basis of the mass of polymer and the volume of mixture in the relevant system.

2.5. Preparation of PVA-T hydrogels

PVA-T polymers were dissolved in 0.3 M NaOH solution to prepare 12 wt% of polymer solution. Then 5 mol% of EGDGE with respect to the amount of side groups of PVA-T was added to the solution, which was mechanically stirred to ensure uniform mixing. Glass capillaries ($\varphi = 0.69$ mm) were set into the solution to obtain rod-type gel samples. After 24 h reaction at 30 °C, the gel samples were taken out of the capillaries. The gels were then immersed in pure water for one week in order to remove unreacted linear polymers and crosslinkers. Then swelling medium was changed to 1 mM HCl solution, which was daily exchanged with fresh HCl solution (1 mM). The neutralization was completed after several days, judged from the unchanged diameter values of rod-type gels.

2.6. Swelling properties of PVA-T hydrogels

Rod-type PVA-T hydrogels were swollen in different salt solutions (3 mL) including 1 mM HCl in order to prevent the dissociation of COOH groups on the macromolecule. First, equilibrium diameter of rod-type gel sample in 1 mM aqueous HCl (denoted as d_0) was determined. Then respective swelling medium was changed to one containing a salt (0.01 M). After equilibrium, the diameter of sample was determined (d). This procedure was repeated by changing the swelling medium to one of a higher salt concentration. The swelling degree was defined as d/d_0. In this paper, the diameters of hydrogels were determined using Nikon Diaphot 200 microscope. Due to the limited solubilities, the concentration of Na_2SO_4 and Li_2SO_4 were changed up to 1.5 M and 2.0 M, respectively. The highest concentrations used were 3.0 M for NaCl, KCl, and CsCl, and 5.0 M for LiCl, LiSCN, NaSCN, and KSCN.

Table 1
Characterization of PVA-T polymers.

	PVA-T1	PVA-T2	PVA-T3
Feed ratio (OH/TA)/(mol/mol)	1:2	1:1	1:0.5
Esterification degree/%	82.4[a]/81.3[b]	60.6[a]/62.4[b]	31.8[a]/35.4[b]
Yield/%	72.3	80.8	88.3

[a] Obtained from titration.
[b] Calculated from ^1H NMR spectra.

3. Results and discussion

3.1. Preparation of PVA-T polymers

PVA was successfully esterified with trimellitic anhydride (TA) in DMSO in the presence of DMAP and TEA. By changing the feed ratio of PVA to TA, three PVA-T polymers with different esterification degrees (ED) were synthesized, and their structure was confirmed by FT-IR and ^1H NMR. Some characteristics of them were summarized in Table 1. The ED value increased with increasing the feed ratio of TA, while the yield became lower, probably due to the steric hindrance.

3.2. Solubilities of PVA-T polymers in different salt solutions

As a physical parameter directly reflecting salting-out or -in effect of ions, the solubilities of PVA-T polymers in various salt solutions and in pure water were measured. Nine kinds of inorganic salts comprising of SO_4^{2-}, Cl^-, SCN^- and Li^+, Na^+, K^+, Cs^+ were employed, which are located in different positions in the HS. The salt concentration was fixed at 1 M, where salt or ion effects on the solubility should become significant. As shown in Fig. 1, solubilities of PVA-T polymers in salt solutions were higher than those in water; in other words, "salting-in" effect was found in all the salt solutions used in the present study. And the salt- or ion-specificity was also significant. In the present study, one can see anion- and cation-specificities by comparing the solubilities among sodium salts (or lithium salts) and those of chlorides, respectively. Thus, the solubility increases as $SO_4^{2-} \gg SCN^- > Cl^-$ for anions, and $Li^+ > Na^+ > K^+ > Cs^+$ for cations.

The salting-in effect found for ions compared to pure water must result from an improvement of polymer hydration, which is composed of the hydration of substituted trimellitic part and unesterified PVA part. Thus, either or both of these hydrations should be enhanced by ions to some extent. As discussed in the previous paper [22], the highest salting-in effect found for the sulfates cannot be ascribed to any reason except for the introduction of the trimellitic residue to PVA, because the parent polymer is largely subject to the salting-out effect by this anion. So it may be safely concluded that the stabilization of the hydrogen-bonding hydration (HBH) to the acidic proton of substituted group by SO_4^{2-} played an important role. And this specific stabilization effect is expected only for anions with strong hydration ability such as SO_4^{2-} and not for SCN^- that is a typical structure breaker. Actually, SCN^- showed no salting-in or even slight salting-out effects for P4VPh and P4VBA gels [20,21]. On the other hand, it has been well known that the weakly hydrated anions or structure breakers such as I^- and SCN^- serve as salting-in agents since they are specifically bound on the hydrophobic interface of common polymers (e.g., PVA) [23–25]. For PVA-T polymers, SCN^- is unfavorable for the HBH to the acidic proton of substituted group, while it may serve as a significant salting-in agent for the remained unesterified PVA part. The experimental results, after all, indicate that the latter salting-in effect is less effective than that of SO_4^{2-} via HBH to the acidic proton. For Cl^-, however, neither it can intensely strengthen HBH to acidic proton like SO_4^{2-} nor can it access hydrophobic interface like SCN^-. So chlorides behaved as a weaker salting-in agent than thiocyanates, and this appeared salting-in effect mainly came from the counterions of Cl^-.

Next we focus on effects of the ED values in sulfate and thiocyanate systems. As mentioned above, SO_4^{2-} stabilizes HBH to the acidic proton of trimellitic residue, while SCN^- is bound to the unesterified PVA part. Therefore, it may be expected that the solubilities increase for SO_4^{2-} systems and decrease for SCN^- with increasing the ED values, respectively. In fact, the latter proved to be the case. As seen from Fig. 1, the solubility order for thiocyanates systems was PVA-T1 < T2 < T3, irrespective of the counterion species. For SO_4^{2-}, however, an unexpected result was observed; the solubility showed no systematic dependence on the ED value of PVA-T polymers. This strongly suggests that the salting-in effect by sulfate anion via stabilization of HBH onto the acidic protons may be counterbalanced by intermolecular hydrogen bonds among the introduced carboxyl groups that should be enhanced with increasing ED. In addition, the crowd of benzene

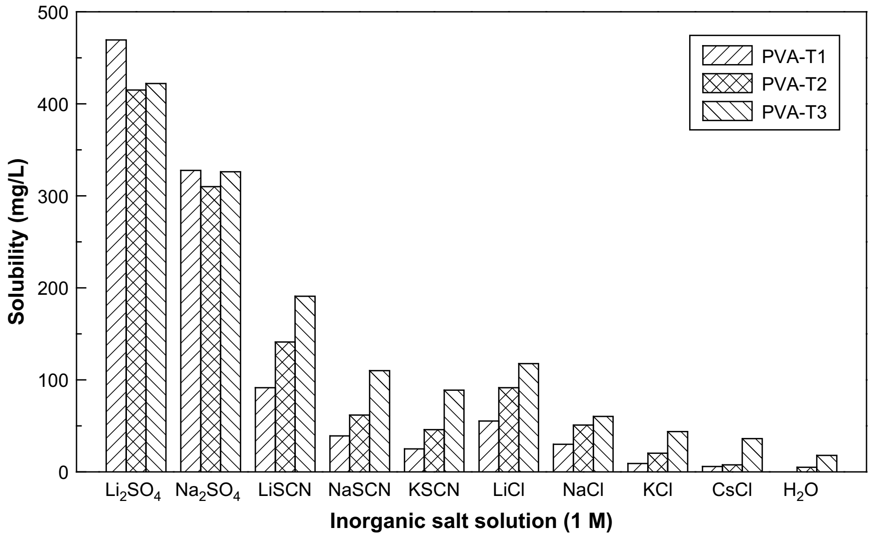

Fig. 1. Solubilities of PVA-T polymers in different salt solutions (1 M) and water. (Solubility of PVA-T1 in water is not shown because it was so low as to be negligible.)

rings around PVA, which is enhanced for PVA-T with higher ED values, may cause some decrease in the solubility due to the inherent hydrophobicity.

For cation specificity, which was not explicitly reported in the previous study, the present results clearly show that smaller ions are more effective for salting-in, as $Li^+ > Na^+ > K^+ > Cs^+$, irrespective of the anion species and of the ED values. This means that PVA and the trimellitic part both interact favorably with strongly hydrated cations. For PVA, it has been known that the OH group is responsible for the favorable interaction with the small cations [4]. For the trimellitic group, two types of HBHs, one is for the oxygen of the carboxyl groups and the other for the π electron system, are to be stabilized by cations, and the stabilization should be enhanced for the smaller cations of strong ionic hydration. Thus the observed cation specificity for the solubility may be straightforwardly understood. It is worth noting that the observed chaotropic behaviors by Li^+ and SCN^-, the latter of which is a typical chaotrope, are much surpassed by that of SO_4^{2-}, a typical kosmotrope for common polymers.

3.3. Swelling properties of PVA-T hydrogels in different salt solutions

Swelling degrees of PVA-T hydrogels in various salt solutions were investigated as a function of their concentrations, as shown in Fig. 2. Only in sulfate systems, significant gel swelling was observed, and the other systems showed only slight swelling or slight deswelling. In other words, significant salting-in effect for the PVA-T polymers in gel system are exerted only by sulfates. The swelling property of PVA-T gels is different from those of super salt-resistive P4VPh and P4VBA gel systems, which hardly change the swelling degree in many kinds of salt solutions including those used here even at their saturated concentrations [20,21]. The obvious difference may come from the much higher water contents of P4VPh and P4VBA gels compared with the present ones. For PVA-T1, T2 and T3 hydrogels, water contents were 29 wt%, 43 wt% and 47 wt%, respectively, while typical ones for P4VPh and P4VBA were well above 90%. This means that the side chains of the latter polymers in gel were predominantly surrounded by water molecules, while it is not the case for the former. In the case of PVA-T, two carboxyl groups are linked to one benzene ring. Thus, the followings may be involved as typical interactions in the gel phase; HB between –COOH groups, –OH groups, –COOH/–OH, –COOH(–OH)/π electrons and π–π stacking of the benzene rings. Besides chemical crosslinkage in gels, these attractive interactions should act as effective physical crosslinkages, resulting in such low water contents. In the case of P4VPh and P4VBA, such intermolecular interactions may be effectively "screened" by the stable hydration. This may partly lead to the almost constant swelling degree of the "super salt-resistive" gels. On the contrary, however, the stabilization of HBHs to –COOH, –OH and π electrons (benzene ring) of PVA-T polymers by anions and cations would cause gels to swell because the intermolecular HBs among the groups as physical crosslinkage may be broken.

As for anion-specificities, a similar order was found for the gel system as that obtained from the solubility, i.e., $Cl^- < SCN^- < SO_4^{2-}$ on the basis of Na salts, while no systematic differences were observed among the cations except for sulfate systems and PVA-T3 hydrogels in thiocyanate systems. The significant swelling in sulfate systems seems to depend on the ED values. In fact, the maximum swelling degrees of PVA-T1, PVA-T2 and PVA-T3 at 0.5 M are 2.46, 2.35 and 1.86 for Li_2SO_4, and 2.05, 2.03, and 1.64 for Na_2SO_4, respectively. Only PVA-T3 gel showed less marked swelling. One may consider this is inconsistent with the results of the solubility where no essential difference was observed among the polymers with different ED values. However, we must remember here that the water content of PVA-T hydrogels in water increases from 29 wt% to 47 wt%, with decreasing ED. Therefore, the respective water (or solution) contents for PVA-T1, T2 and T3 gels at 1 M sulfate solutions that were roughly estimated on the basis of the swelling degree (gel volume) are 94%, 94% and 82% for Li_2SO_4 and 87%, 89% and 80% for Na_2SO_4, respectively. Although the water contents of PVA-T3 gel are still lower than the others, the difference as much as ca. 10% may not be of essential and seems to be comparable with the scatter in the solubility data. Thus, judged on the basis of the water content instead of the gel diameter, these three PVA-T polymers have similar affinities to aqueous solutions of 1 M Li_2SO_4 or Na_2SO_4, respectively.

The significant swelling observed for the sulfate systems may be also ascribed to the stabilization of HBH to the acidic proton of the carboxyl groups by SO_4^{2-} and the subsequent scission of intermolecular hydrogen bond involving –COOH. The deswelling observed in the higher concentration region may be safely ascribed to a common salting-out effect by the divalent anion for the vinyl main chain and/or phenyl group. Since the swelling peak was observed at the same concentration (0.5 M) irrespective of the ED values, the salting-out for the main chain seems to be the primarily responsible for the later deswelling.

One question remained is the different ED dependencies observed for Li_2SO_4 and Na_2SO_4 systems; namely, significant gel swelling in the former salt system starts around at 0.01 M, 0.05 M and 0.05 M for PVA-T1, T2 and T3, respectively, while in the latter it appears around at 0.2 M, 0.1 M and 0.05 M, respectively. Namely the start point for the swelling moves to the lower concentration in aqueous Na_2SO_4 solution and the difference with Li_2SO_4 becomes closer with decreasing ED. In order to explain this tendency, we consider three contributions made by cations to the gel swelling: stabilization of HBHs to (1) carboxyl group and (2) π-electron (π HBH) of the substituted trimellitic acid, and (3) hydroxyl group on the parent PVA. Qualitatively, all these three should contribute to the gel swelling, and the former two increases and the latter one decreases with increasing ED, respectively. On the other hand, HBHs including the above three types are more stabilized by Li^+ than Na^+ since the hydration water of the former cation has a larger EPA than the latter [19]. Thus, if the relative stabilization degree of HBH on the trimellitic acid residue (HBH to the carboxyl group and the π-HBH) by Li^+ compared with that by Na^+ was the same as that to PVA OH group, no ED dependence would be observed for the cation specific swelling behavior. The experimental results then suggest the much stronger interaction of Li^+ with the trimellitic acid group than that of Na^+. Furthermore, PVA-T3 gel starts to swell at almost the same concentration for Li_2SO_4 and Na_2SO_4 solutions. This may be attributed to the higher water content of the gel. As previously stated, the higher water content should come from the weaker intermolecular HB between the carboxyl groups, which may be easily broken without additional contribution from cations, only with the stabilization of HBH to the acidic proton by SO_4^{2-}.

As for the chloride and thiocyanate systems, the swelling was limited to large extent. As shown in Fig. 2(b), PVA-T1 hydrogel with lowest water content (29 wt%) showed slight swelling (5% in the gel diameter at most), while PVA-T2 and T3 showed subtle swelling and deswelling. The insensitivity to the salt concentration may be ascribed to the weak stabilization effect by Cl^- on the hydration of PVA-T polymers. Also in thiocyanate systems (Fig. 2(c)), PVA-T1 and PVA-T2 showed qualitatively similar slight swelling behavior as those for chlorides. For PVA-T3 with ED as low as 32%, however, a continuous swelling trend was observed with increasing the salt concentration. This is comparable with behaviors usually observed for common hydrogels. Thus, the unesterified PVA part must be responsible for the appreciable swelling in thiocyanate systems.

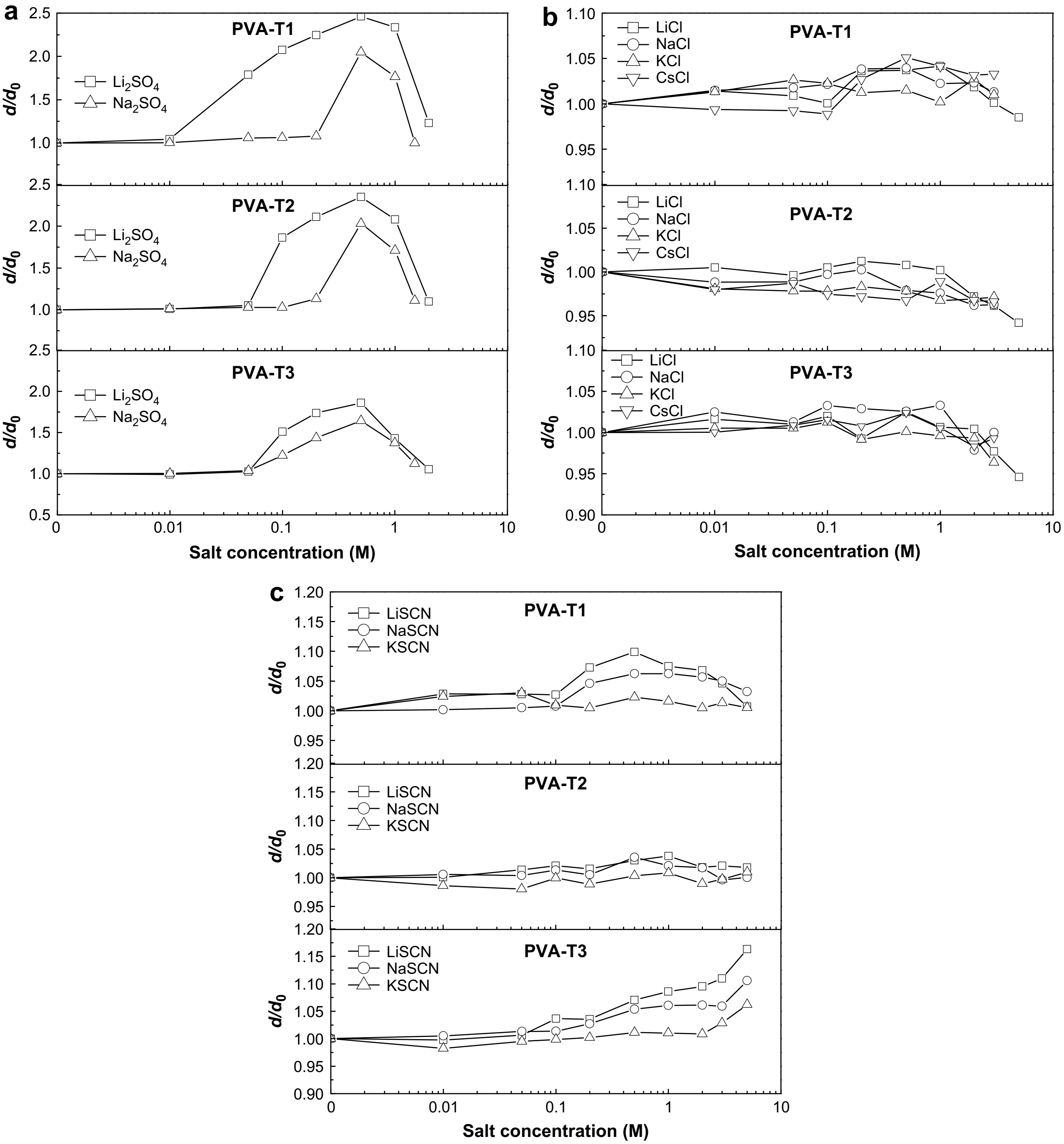

Fig. 2. Swelling behaviors of PVA-T gels as a function of different salt concentrations (a) sulfate solutions, (b) chloride solutions, (c) thiocyanate solutions.

Finally, we consider the apparent difference between the ion specificities observed in the solubility measurement and the gel swelling. Namely, why is the former ion-specificity so distinct compared with the latter? The answer may be found in the difference of the experimental condition. In the solubility measurements, PVA-T polymers exist in two phases at equilibrium, as a solute in solution and a component in solid (or in aggregation), and polymer chains must exchange between the two phases at a short time scale. Thus, strongly hydrated polymers, even few, must exist in the solution. Therefore, when the hydrations were stabilized, even if only slightly, by any ions added, the equilibrium should be displaced to the solution, leading to an enhanced solubility. On the contrary, however, in the gel system, every polymer chain exists in only one phase. As previously discussed, the present PVA-T polymer gels are in rather collapsed states in water, and many intermolecular HBs act as physical crosslinking. Of course some polymer segments may be exposed to inner water phase to be hydrated, and some of them may be partly exchanged with those in the crosslinking moiety. Therefore any stabilization of the hydration due to interactions with ions added would lessen the polymer segments that are involved in the physical crosslinking. However, in order that the local scission of the physical crosslinking may lead to macroscopic gel swelling, all of the intermolecular HBs involved in a physical crosslinking region must be disrupted at the same time. As a matter of fact, it would be rather difficult, as inferred from the present experimental result. For example, in the case of SCN^-

systems, the specific absorption of the anion onto hydrophobic moieties of PVA-T polymers should explicitly contribute to the moderately high solubility observed in the pertinent systems. However, such a local and partial scission of HBs may not lead to substantial gel swelling.

4. Conclusion

On the basis of the consideration that the super salt-resistivity of P4VPh and P4VBA is ascribed to the coexistence of benzene ring (π-electron system) and acid proton, the present study demonstrated that PVA, a common hydrophilic polymer, is conveniently modified into a salt-resistive polymer through introducing the trimellitic acid group, and the salt-resistivity may be modulated depending on ED values. Regardless of the ED values, however, "salting-in" effect was observed and the ion-specificity followed as $SO_4^{2-} \gg SCN^- > Cl^-$ for anions, and $Li^+ > Na^+ > K^+ > Cs^+$ for cations. In other words, this means that even such a relatively low level of substitution (ED = 32% for PVA-T3) is able to essentially alter the response of the parent polymer (PVA) to ions, especially to anions. Thus, the present study, as well as our previous one, opened a way to a facile preparation of salt-resistive polymers.

In our previous papers, we found that P4VPh and P4VBA hydrogels which are composed of a monomer residue containing an acidic proton and a benzene ring show neither swelling nor deswelling in sulfate solutions [20,21]. In the present study, a contrastive swelling behavior was observed for PVA-T polymers that also contain acidic protons and a benzene ring. This may be safely ascribed to the increase in the acidic proton; two protons per one benzene ring (or π electron system) for the latter instead of the one acidic proton for the formers. The existence of more than one acidic proton, however, causes another unfavorable effect: significant decrement in the water content of pertinent hydrogels. In fact, highly swollen hydrogels can be prepared from P4VPh and P4VBA, while only collapsed gels were obtained by introducing at least 30 mol% of trimellitic acid group to PVA, which can otherwise afford to provide a highly swollen hydrogel. This unfavorable collapsed state for hydrogels comes from the enhanced intermolecular HB. Thus, the present study clearly showed that an optimum balance between the intermolecular HB and the HBH onto the acidic protons must be taken into account to design polymers for hydrogels with high water content and anti-HS property. Some experimental studies are now being undertaken from such points of view.

Acknowledgement

This study was supported by Grant-in-Aid for JSPS fellows (19.07798).

References

[1] Kunz W, Lo Nostro P, Ninham BW. Curr Opin Colloid Interface Sci 2004;9:1–18.
[2] Mcbain JW. In: Colloid science. Boston: Heath; 1950. p. 131.
[3] Schleich T, Von Hippel PH. Biopolymers 1969;7:861–77.
[4] Muta H, Miwa M, Satoh M. Polymer 2001;42:6313–6.
[5] Suzuki A. Adv Polym Sci 1993;110:199–240.
[6] Muta H, Kawauchi S, Satoh M. Colloid Polym Sci 2003;282:149–55.
[7] Omta AW, Kropman MF, Woutersen S. Science 2003;301:347–9.
[8] Batchelor JD, Olteanu A, Tripathy A, Pielak GJ. J Am Chem Soc 2004;126:1958–61.
[9] Gurau MC, Lim SM, Castellana ET, Albertorio F, Kataoka S, Cremer PS. J Am Chem Soc 2004;126:10522–3.
[10] Bostrom M, Williams DRM, Ninham BW. Phys Rev Lett 2001;87:168103.
[11] Bostrom M, Williams DRM, Ninham BW. Biophys J 2003;85:686–94.
[12] Bostrom V, Kunz W, Ninham BW. Langmuir 2005;21:2619–23.
[13] Smith JD, Saykally RJ, Geissler PL. J Am Chem Soc 2007;129:13847–56.
[14] Mancinelli R, Botti A, Bruni F, Ricci MA, Soper AK. J Phys Chem B 2007;111:13570–7.
[15] Chen X, Yang T, Kataoka S, Cremer PS. J Am Chem Soc 2007;129:12272–9.
[16] Zhang Y, Furyk S, Bergbreiter DE, Cremer PS. J Am Chem Soc 2005;127:14505–10.
[17] Zhang Y, Furyk S, Sagle LB, Cho YC, Bergbreiter DE, Cremer PS. J Phys Chem C 2007;111:8916–24.
[18] Takano M, Ogata K, Kawauchi S, Satoh M, Komiyama J. Polym Gels Networks 1998;6:217–32.
[19] Muta H, Kawauchi S, Satoh M. J Mol Str (Theochem) 2002;620:65–76.
[20] Muta H, Taniguchi T, Watando H, Yamanaka A, Takeda S, Ishida K, et al. Langmuir 2002;18:9629–31.
[21] Xu L, Iwata K, Kobayashi S, Ishizone T, Satoh M. Colloid Polym Sci 2007;285:485–9.
[22] Mori M, Wang J, Satoh M. Colloid Polym Sci 2009;287:123–7.
[23] Oh SH, Ryoo R, Jhon MS. Macromolecules 1990;23:1671–5.
[24] Masuda Y, Tanaka T, Nakanishi T. Colloid Polym Sci 2001;279:1241–4.
[25] Jungwirth P, Tobias DJ. J Phys Chem B 2002;106:6361–73.