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ORIGINAL CONTRIBUTION

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Effects of chemical modifications on the swelling behaviors of poly (4-vinyl phenol) gel

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Abstract Poly (4-vinyl phenol) (P4VPh) gels were prepared by crosslinking with a hydrophilic crosslinker [ethyleneglycoldiglycidylether (EGDGE)] and a hydrophobic one [diglycidyl 1,2-cyclohexane dicarboxylate (DGCHDC)], and the former gel was further modified by CH_3I or C_2H_5I to partially convert the hydrogen of phenol OH to the corresponding alkyl groups. Swelling behaviors of P4VPh gels, thus modified, were investigated to see how the hydrophobic groups introduced to the crosslinker and the polymer substrate affect the super salt resistivity to inorganic ions and the high water content (>90%) that have been observed for the original P4VPh gel. Water content and salt resistivity were unexpectedly preserved even for the modified gels. Effects of the chemical modifications on the gel swelling were only observed in the presence of hydrophobic solutes, i.e., tetrabutyl ammonium chloride and ionic surfactants. All these results strongly suggest that hydration around the polymer substrate in the gel phase is specifically stabilized, probably because of the coexistence of the hydrophobic hydration and the π-hydrogen-bonding hydration around the phenol ring.

Keywords Poly (4-vinyl phenol) · Hydrogel · Salt resistivity · π-Hydrogen-bonding hydration · Hydrophobic hydration

Introduction

Ionic effects are ubiquitous in aqueous systems of both synthetic and natural polymer gels, having significant influence on the swelling behavior and playing an important role in industrial applications [1] and in bioscience [2]. Generally, inorganic ions serve as salting-out agents in polymer/water systems and lead to deswelling of hydrogels. The deswelling degree usually follows the Hofmeister series, i.e., $SO_4^{2-} > F^- > Cl^- > Br^- > I^-$ and $Mg^{2+} > Li^+ > Na^+ > K^+$ for anions and cations, respectively [3]. For example, ionic effects on the swelling of gels from poly (vinyl alcohol) [4], poly (vinyl pyrrolidone) [5, 6], poly (*N*-isopropyl acrylamide) (PNIPA) [7] were found to agree with Hofmeister series.

However, as Muta et al. [8] reported, poly (4-vinyl phenol) gel proved to have a quite unique property, "super salt resistivity"; namely, the gel does not deswell even in saturated solutions of various inorganic salts including typical salting-out agents such as KF and Na_2SO_4. The resistivity to strongly hydrated anions (e.g., F^- and SO_4^{2-}) has been ascribed to the stabilization of the hydrogen-bonding hydration of the acidic phenol proton by the anions via ionic hydration because the electron pair donicity (EPD) of water molecules hydrating an anion is enhanced (negative charge on the water oxygen is enriched) [9] as depicted in Fig. 1. On the other hand, the resistivity to strongly hydrated cations like Li^+ and Mg^{2+}, which should be repelled by the polymer's hydrophobic hydration [10], was ascribed to an accessibility of the cations to the hydrophobic phenol ring through a stabilization of the π-hydrogen-bonding hydration to the phenol-π system by the cations via ionic hydration because the electron pair acceptance (EPA) of water molecules hydrating a cation is

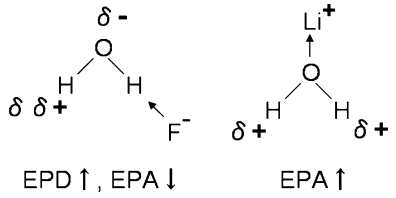

Fig. 1 Perturbation of water EPD and EPA via hydration to an anion and a cation, respectively. Water EPD or negative charge on the oxygen is enhanced upon hydration to anions (*left*). Water EPA or positive charge on the hydrogen is enhanced upon hydration to cations (*right*)

enhanced (positive charge on the water hydrogens is enhanced) as depicted in Fig. 1. These mechanisms have been supported by infrared (IR) spectroscopy and/or ab initio calculations [8, 11].

The salt resistivity, however, failed to work in the presence of hydrophobic cations; poly (4-vinyl phenol) (P4VPh) gel first deswelled and then reswelled with increasing concentration of tetrabutyl ammonium chloride (TBACl) [11] or cationic surfactants [e.g., dodecyl trimethyl ammonium bromide (C_{12}TAB)] [12], while only swelling occurred for anionic surfactant systems [e.g., sodium dodecyl sulfate (SDS)] [12]. A mechanism for this charge-specific swelling behavior was proposed, in which the hydrophobic cations interact with the polymer not only through the common hydrophobic interaction but also via the cation-π interaction of the alkylammonium cation group with the phenol ring of P4VPh [11, 12]. In fact, it was demonstrated [11, 12] that more amounts of cationic surfactants were bound to the P4VPh gel than anionic ones of corresponding alkyl chains.

On the other hand, through the experiment on surfactant binding, especially of SDS, it was revealed that the hydrophobic interaction of P4VPh gel is significantly weaker than that of a typical hydrophobic polymer gel, PNIPA [13]. This suggests that the hydrophobic hydration around the polymer substrate in the former gel phase is more stabilized compared with that of the latter. The same conclusion has also been deduced from the temperature effect on the pertinent gel swelling [11], namely, being different from the remarkable deswelling or the volume phase transition (collapse) of the PNIPA gel, P4VPh gel only shows a slight continuous deswelling with increasing the temperature to ~40°C. This "stable" hydrophobic hydration, in fact, may be responsible for another unique property of P4VPh gel, i.e., the unexpectedly high water content (>90%) for the hydrophobicity of the polymer as judged by the insolubility in water.

As stated above, the hydration around P4VPh in the gel phase consists of several kinds of hydrations: hydrophobic hydration around the main chain and the phenol ring, π-hydrogen-bonding hydration to π-electrons of the phenol ring, and hydrogen-bonding hydrations to the phenol OH. Thus, the coexistence of these hydrations seems to be closely related with the unique properties of the P4VPh gel as described above. It must be interesting to observe how a perturbation on the polymer hydrations would affect the gel properties, especially the swelling behavior.

In the present study, we investigate the effects of chemical modifications of the P4VPh gel on the swelling behaviors in aqueous salt solutions. Two kinds of modifications are introduced: one is by utilizing a more hydrophobic crosslinker than ethyleneglycoldiglycidylether (EGDGE). If the hydrophilicity of EGDGE substantially contributed to the high water content of the gel, with this substitution of the crosslinker to a more hydrophobic one, the water content would be significantly reduced. Furthermore, with this hydrophobidization of the gel, interactions with hydrophobic solutes like TBACl, C_{12}TAB, and SDS may be significantly perturbed. The other modification is a partial *O*-alkylation at the phenol OH. A substitution of the acidic proton with a hydrophobic group would affect the resistivity to inorganic salts as well as the water content. Being contrary to these expectations, however, the super salt resistivity and the high water content were both preserved for the modified P4VPh gels, as shown below.

Experimental

Materials

Poly (4-vinylphenol) (Mw=22,000) was purchased from Polyscience. EGDGE (50% solution) and diglycidyl-1,2-cyclohexane dicarboxylate (DGCHDC), used as crosslinkers for gel preparation, were purchased from Aldrich Chemical. Methyl iodide and ethyl iodide of analytical grade were purchased from Kanto Chemical. Cationic and anionic surfactants used in the present study were decyltrimethyl ammonium bromide (C_{10}TAB) (99%, Acros Organics), C_{12}TAB (99%, Aldrich Chemical), sodium 1-decanesulfonate (SDeSo) (98%, Tokyo Kasei, Japan) and SDS (99.1%, Kanto Chemical, Japan). Inorganic salts (LiCl, KF) and tetramethyl- and tetrabutyl-ammonium chlorides (TMACl and TBACl) were of analytical grade from Acros Organics. Deionized and then distilled water were used for all the experiments.

Preparation of *O*-methylated and *O*-ethylated P4VPh–EGDGE gels

Rod-type P4VPh–EGDGE gel samples were prepared with 6 and 10 mol% of the crosslinker by the same method as reported in our previous papers [8, 11]. Each

gel sample was immersed in ca. 1 ml NaOH solution, which contained OH^- equivalent to the phenol OH group, for 24 h. Water contents of the gel samples before alkylation were 97.2 and 92.7%, respectively, corresponding to the different amounts of the crosslinker. The swollen gel was then put in ca. 1 ml of 70 or 100% EtOH containing equivalent amount of RI (CH_3I or C_2H_5I), respectively. The *O*-alkylation reaction was performed in 25 or 40°C for 24 or 5 h, respectively.

Partial *O*-methylation of P4VPh gel, thus performed, was confirmed by ^{13}C NMR spectroscopy with a JEOL GSX-270NMR spectrometer. The parameters of the apparatus were: carbon frequency 75.45 MHz (proton resonance frequency 300.4 MHz); proton pulse of 90° 4.7 μs; proton rf magnetic field 53 kHz; contact time 3 ms; spin speed 4,200 Hz; scanning times 720; and standard of chemical shift 17.3 ppm for methyl group of hexamethyl benzene relative to tetramethylsilane.

Degrees of the *O*-alkylations were roughly estimated by Fourier transformed infrared (FT-IR) spectroscopy with FT-IR-8200PC (Shimazu, Japan) (resolution 4 cm^{-1}, scanned 40 times) for dried gel samples (120°C, 48 h).

Preparation of P4VPh–DGCHDC gel

P4VPh was dissolved in 1 N NaOH aqueous solution containing 30 wt% EtOH and the polymer concentration was adjusted at 22 wt%. DGCHDC was added into the solution, thus prepared under stirring. The amount of DGCHDC was set at 6, 8.4, or 9.8 mol% of phenol hydroxyl groups of P4VPh. The gel-forming reaction was performed in a glass capillary (Drummond Scientific, 25 μl, $\varphi = 0.690$ mm) at 25±0.1°C for 24 h.

After the completion of the reaction, the gel was taken out from the capillary and immersed in distilled water to remove low molecular wieght substances and unreacted P4VPh. The immersing water was changed every day and the diameter of the gel was measured until the equilibrium was attained. The equilibrium water contents were estimated as 97.6, 94.2, and 92.5% for those prepared with 6, 8.4, and 9.8 mol% of DGCHDC, respectively.

Measurement of swelling degrees

Swelling behaviors of the DGCHDC gels and the *O*-alkylated gels were investigated as a function of salt concentration in the immersing solution. The gel diameter was periodically observed using a microscope (Diaphot 200, Nikon) until each equilibrium swelling was reached, typically after several days. The swelling degree was defined as d/d_0, where d and d_0 are gel diameters swollen in the aqueous salt solutions and water, respectively. All the measurements were performed at room temperature (25°C). The details of the measurement are given elsewhere [8, 11].

Results and discussion

O-alkylation of P4VPh gel

Introduction of methyl group by the *O*-methylation of the phenol OH group was qualitatively confirmed by ^{13}C NMR spectroscopy. A typical spectrum for an *O*-methylated P4VPh gel sample (sample B, see Table 1) prepared at 40°C is shown in Fig. 2. A new peak at 55 ppm is assigned to a methyl carbon of phenol's O–CH_3, while a shoulder at 158 ppm in a large peak at 154 ppm that corresponds to phenol's C–OH carbon may be a phenol's *O*-methylated carbon (C–OCH_3).

To estimate the degrees of *O*-alkylations, we utilized FT-IR spectroscopy. Figure 3 shows the typical spectra for *O*-methylated P4VPh gel samples prepared at 25 and 40°C and a spectrum of the original gel for comparison. A large peak designated as 1 is assigned to the asymmetric vibration of phenol's C–O (C–OH), which is to appear around 1,250 cm^{-1}. A small peak appears at 1,300 cm^{-1} for the methylated samples, which is assigned to the asymmetric vibration peak of the methylated phenol's C–O (C–O–CH_3). Peak 2 is assigned to the asymmetric vibration of the crosslinker's C–O–C and peak 2′ to the asymmetric vibration of the crosslinker's C–O–CH_3. The latter means that *O*-methylation also occurred at the C–OH in the crosslinker. Peaks 3 and 3′ are assigned to the symmetric vibration of the phenol's C–O of the crosslinked residues and that of the methylated phenol's C–O, respectively. We utilized the last two peaks to estimate the degrees of *O*-methylation (*O*-ethylation). In the estimation, we made a peak deconvolution and calculated the alkylation degrees with an assumption that each peak area is proportional to the population and the peak area for the crosslinkage (peak 2) corresponds to 6 or 10 mol%. The results are shown in Table 1 together with the respective reaction conditions and

Table 1 Reaction condition for the *O*-alkylations, water contents of the gel samples before and after the reaction, and degrees of alkylation (mol%) that were estimated on the basis of the relative areas of peaks 3 and 3′ of Fig. 3 [the symmetric vibration of phenol C-O-C (crosslinkage site) and that of methylated phenol C–O–CH_3, respectively]

Sample	Reaction temperature (°C)	Water content (%)		Degree of alkylation (mol%)
		Before	After	
A (methyl)	25	92.7	90.2	4–10
B (methyl)	40	97.2	–	19–25
C (ethyl)	25	97.2	97.9	14–19
D (ethyl)	40	97.2	97.4	23–29

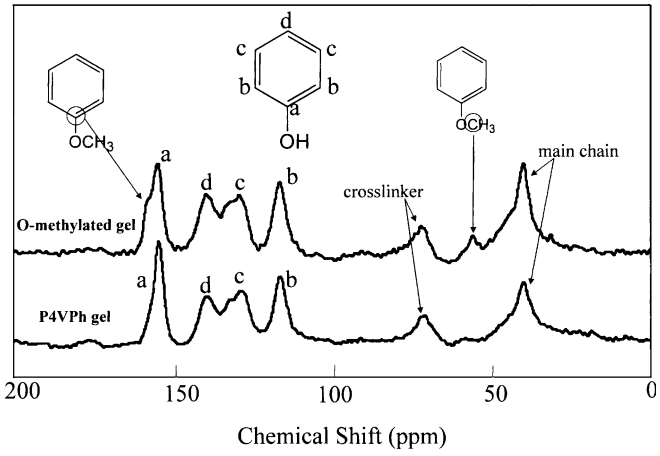

Fig. 2 ^{13}C NMR spectra for *O*-methylated and original P4VPh gel samples. Only the side chain parts are shown for the chemical structure of the polymer

water contents of the gel samples. The alkylation degrees varied from several to a few tens of percent depending on the reaction condition. A higher temperature seems to be favorable for the reaction. The most striking finding is that the high water contents were preserved despite of the hydrophobic modification. A more detailed discussion will be made below.

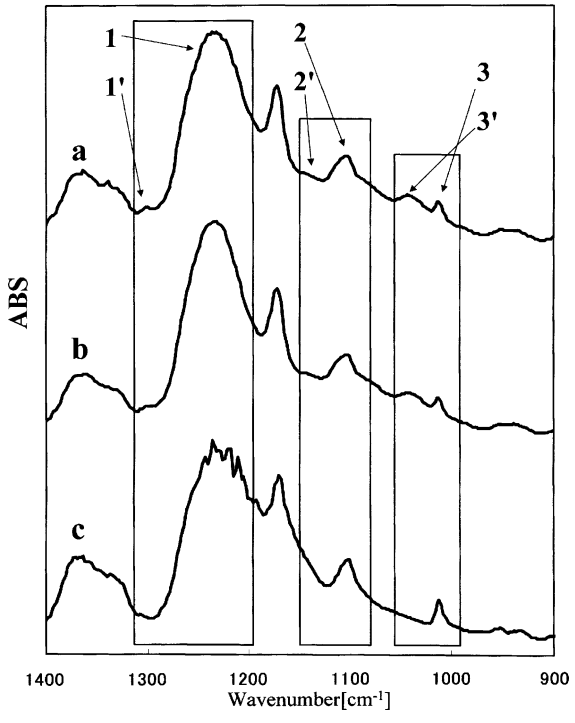

Fig. 3 IR spectra for *O*-methylated and original P4VPh gel samples. **a** *O*-methylated at 40°C, **b** *O*-methylated at 25°C, and **c** original P4VPh gel. *1* asymmetric vibration of phenol C–O, *1′* asymmetric vibration of methylated phenol's C–O (C–O–CH_3), *2* asymmetric vibration of aliphatic C–O (C–O–C in the crosslinker), *2′* asymmetric vibration of methylated crosslinker's C–O (C–O–CH_3), *3* symmetric vibration of phenol C–O–C (crosslinkage site), and *3′* symmetric vibration of methylated phenol C-O-CH_3

Swelling behavior of O-alkylated P4VPh gels

Figure 4 shows swelling degrees (d/d_0) of the *O*-alkylated P4VPh gels as a function of salt concentration. Because the hydrogen-bonding hydration to the phenol acidic proton is to be stabilized by strongly hydrated anions like F^-, it was expected that the *O*-alkylation, even if it is partial, would cause some reduction in the salt resistivity to KF. However, contrary to the expectation, no significant deswelling was observed for the gel samples; even at 10 M, the d/d_0 values were 0.92–0.98. Although these swelling degrees are somewhat lower than the typical value, ca. 1.0, for the intact P4VPh gel, those for common hydrogels, e.g., polyvinyl acetate and PVP, are much smaller as 0.6–0.7 even at 4 M [4–6].

The introduction of methyl or ethyl group instead of the phenol proton should enhance the hydrophobicity of the polymer substrate. However, the swelling degrees for 10 M LiCl systems (0.95–0.99), where Li^+ should act as a salting-out agent to hydrophobic moieties, are only slightly lower than the typical value, ca. 1.0, for the original gel. On the other hand, TMACl systems suggest that the hydrophobic interaction between TMA^+ cation and the alkyl groups contributes to the gel swelling rather than deswelling because the swelling degrees of the *O*-alkylated gels at 6 M TMACl are 0.88–0.99, significantly larger than the typical value, ca. 0.8, of the original gel.

To further investigate the effects of the hydrophobic groups, swelling degrees in TBACl system were measured. The results are shown in Fig. 5, where the swelling degrees of an original P4VPh gel were also shown for comparison. The qualitative swelling behavior for the alkylated gels proved to be similar to the deswelling–reswelling pattern of the original one, while the former's swelling degrees were somewhat larger than those of the latter. The qualitatively the same swelling behavior means that the interaction mode of TBA^+ with the modified polymer substrate is essentially the same as that for the original gel [11]; namely, in the lower concentration region (<1–2 M), one TBA^+ cation is bound in between two phenol rings to physically crosslink the polymer chains, the process of which causes the deswelling. In the higher concentration region (≧2 M), further TBA^+ binding detaches the crosslinking to induce the reswelling. Therefore, the higher swelling degrees of the alkylated gels at the deswelled state (1–2 M), which were measured by the relative swelling ratio d/d_0, suggest that the crosslinking binding of TBA^+ is not so effective as in the original gel. However, if we compare the swelling degrees by the actual water content, instead of the relative swelling degree, the sequence of the deswelling at 1 M TBACl is as follows: *O*-methylated (79%) < original (81%) < *O*-ethylated (84%). Thus, these

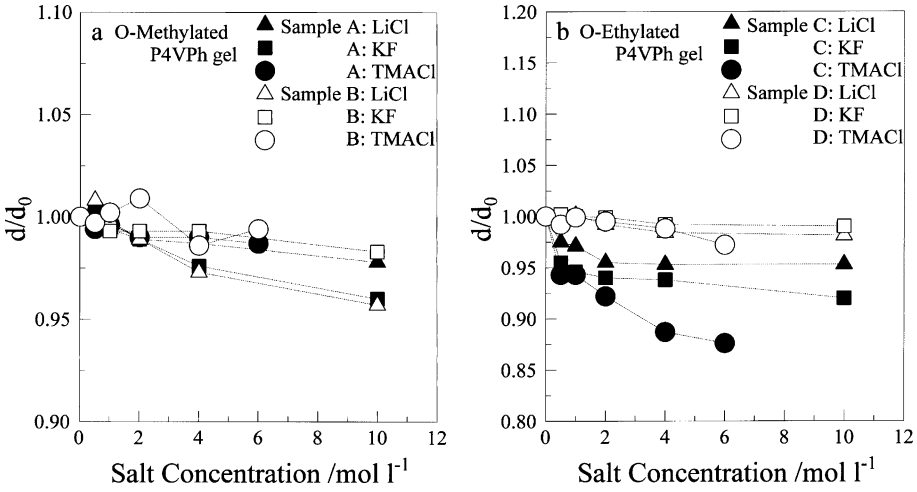

Fig. 4 Swelling behaviors of *O*-alkylated P4VPh gels. **a** *O*-methylated sample A and B. **b** *O*-ethylated sample C and D

differences in the water content may be taken as approximately the same. As a conclusion, the partial *O*-alkylations do not seem to cause any essential changes for the deswelling due to TBA^+ binding.

Finally, we consider about the unexpectedly high water contents (Table 1) observed for the *O*-alkylated P4VPh gels. To propose a possible mechanism which may solve the puzzle, we invoke the common intermolecular hydrogen bond between phenol OH groups [14, 15]. Although this hydrogen bond has been confirmed in the membrane systems, this may also exist in the hydrogel systems. Then, the introduced alkyl groups may reduce the hydrogen bonds between the phenol OH groups, which can be one reason for the high water content of the alkylated gels because the free OH groups would attract more water molecules than the intramolecularly and intermolecularly hydrogen-bonded ones. Furthermore, if the alkylation occurred randomly, the alkyl groups may be far apart from each other to gather via hydrophobic interaction. It should be noted, however, that even though this mechanism thus supposed may contribute, the unexpectedly high water content of the alkylated gels must not be explained without any inherent stability of the hydration structure around the *p*-alkyl phenol residue.

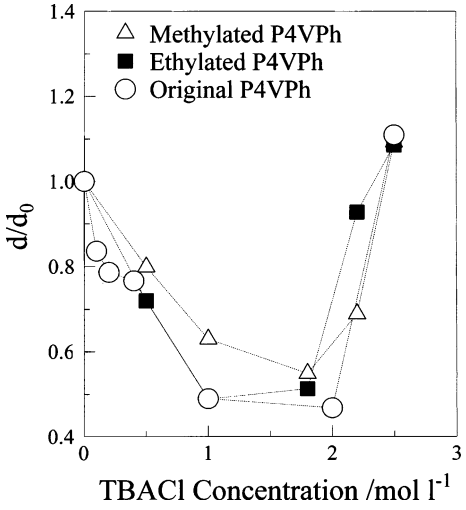

Fig. 5 Comparison of swelling behaviors of the alkylated P4VPh gels (sample A and C) in aqueous TBACl solution with that for the original gel [11]

Swelling behavior of P4VPh–DGCHDC gel

As shown above, the hydrophilicity and the salt resistivity of P4VPh gel crosslinked with EGDGE are both high irrespective of the hydrophobicity of the parent polymer, and the outstanding properties are least damaged by a partial alkylation as a few tens of percent of the phenol OH group. Next, we investigated the effects of replacement of the crosslinker, EGDGE, with a more hydrophobic one, DGCHDC, on the swelling behavior in aqueous solutions of various solutes, inorganic and organic ones. The difference in the two chemical structures is the cyclohexyl dicarbonyl part instead of the two methylene residues at the center of the crosslinkers, which imparts hydrophobicity to DGCHDC to such an extent as being insoluble in water.

As stated in Experimental, the water contents of the P4VPh/DGCHDC gel samples were unexpectedly high, i.e., 97.6, 94.2, 92.5, and 91.7% for 6, 8.4, 9.8, and 15% crosslinkage, which are comparable to 99–89.8% for 3–15% crosslinkage with EGDGE. Thus, the high water content of the original gel cannot be ascribed to the hydrophilicity of EGDGE. The hydration structure or interaction with water of the polymer substrate in the gel phase must be highly stable and favorable. In fact, our previous studies on the temperature effect on P4VPh gel swelling and on the surfactant binding [11] suggested that the hydrophobic hydration of the polymer substrate is stable; hence, the hydrophobic interaction is weaker compared with the typical hydrophobic polymer, PNIPA [13].

In this paper, we must consider how the P4VPh gel, EGDGE, and DGCHDC gels can retain such a high water content. Even if the hydration structure was so stable, the same structure should be formed in the solution system of the polymer. However, the solubility of P4VPh in water is only sparing as stated above. The only answer to this puzzle seems to be a function of crosslinker, i.e., to hamper contact of the polymer segments. Thus, the stable hydration structure was once formed around the polymer, then any occasional approach of the segments far apart may be retarded due to the presence of intervening crosslinkers.

Nevertheless, the crosslinker, DGCHDC, must serve as another hydrophobic site in the pertinent gel and may affect the salt resistivity and interactions with hydrophobic solutes such as TBA^+ and ionic surfactants. Answers to these expectations are given below. First, salt resistivity of a P4VPh/DGCHDC gel (crosslinkage 6%, water content 97.6%) proved to be much the same as the one observed of an EGDGE gel (crosslinkage 3%, water content 97%), as shown in Fig. 6. The super salt resistivity to various inorganic salts remained for the DGCHDC gel, and the deswelling for TMACl system was even less significant. These results strongly suggest, in turn, that the EGDGE crosslinker in the original P4VPh gel made no essential contribution to the super salt resistivity; hence, it may be ascribed to the stabilization of the two kinds of hydrogen-bonding hydrations to the acidic proton of phenol OH and to the π-electron of the phenol ring by ions through their ionic hydration, as previously proposed [8].

For the hydrophobic solute systems, however, the swelling degrees of the DGCHDC gel were significantly different from those for the original gel, which suggested that the hydrophobic crosslinker actually serves as a site for hydrophobic interaction with the pertinent solutes. Figure 7

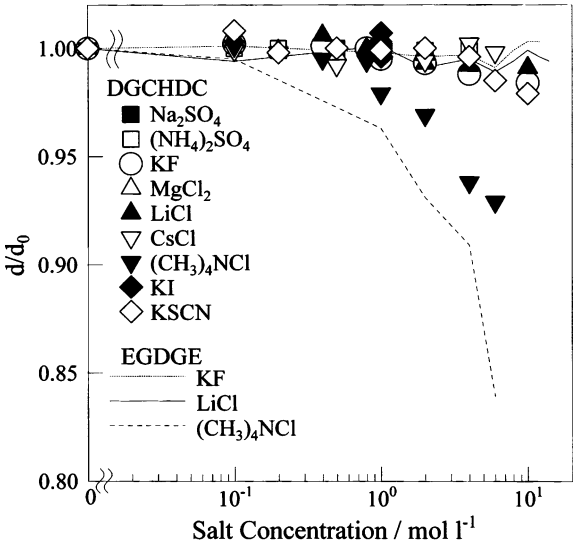

Fig. 6 Swelling behavior of a DGCHDC (6%, W.C. 97.6%) gel in the presence of 10^{-4} N HCl. Comparison is made with those of an EGDGE (3%, W.C. 97%) gel for some typical salt systems

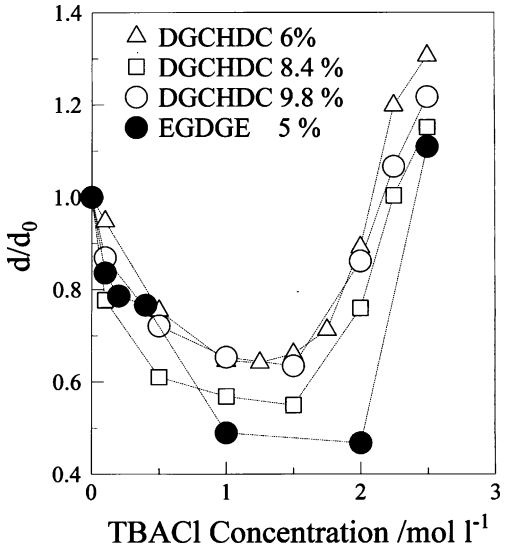

Fig. 7 Swelling behavior of DGCHDC gel samples in aqueous TBACl solution compared with an EGDGE (5%, W.C. 97.3%)

shows the result for TBACl system. Although the deswelling–reswelling behavior was qualitatively similar to that of the original gel, the respective swelling degrees were significantly higher than those of the original gel. According to our model [11], the initial deswelling occurs by crosslinking, binding of one TBA^+, in between two phenol rings through hydrophobic interaction. Thus, any lower deswelling degrees may mean that the crosslinking TBA^+ binding is relatively ineffective for the deswelling of the DGCHDC gel samples. To compare the swelling degrees of the DGCHDC gels with different degrees of crosslinking with those for the original gel, we utilize again the water contents instead of the relative swelling values. The water contents at 1 M TBACl estimated on the basis of the d/d_0 values are ca. 92, 75, and 78%, respectively, for 6, 8.4, and 9.8% DGCHDC gels, which are compared with 81% of the original gel. It should be noted here that the water content of the 6% gel is significantly higher than those of the other two samples as well as the original one. The less marked deswelling of the 6% gel may occur if the crosslinker, e.g., the cyclohexane ring, served as an effective site for hydrophobic interaction, namely, if a TBA^+ cation binds to the newly introduced hydrophobic site besides "the sandwich-type binding" to the phenol rings, then it would contribute to enhance the osmotic pressure and swell the gel. In fact, the reswelling occurred at a lower concentration and the reswelling degree was higher than the original gel.

On the other hand, however, the deswelling degrees of the other two DGCHDC gels were much larger. As one possible explanation for such a complicated behavior, it may be supposed that another type of TBA^+ binding to the crosslinker site can cause a gel deswelling through hydrophobic interaction with other hydrophobic sites such as phenol ring. A possible TBA^+ binding scheme to

the crosslinker site is illustrated in Fig. 8. This supposed mechanism, in fact, seems to be applicable to the swelling behaviors in the ionic surfactant systems as shown below.

As has been reported in our recent study [12], P4VPh/EGDGE gel showed a specific deswelling–reswelling behavior in the presence of cationic surfactants (C_{12}TAB and C_{10}TAB), while it only swelled for anionic surfactant systems (SDS and SDeSo). The deswelling for the cationic surfactant systems that was observed in the lower-concentration region below the respective critical association concentrations (CACs) was ascribed to hydrophobic interaction among the surfactant unimers bound to the polymer substrate via hydrophobic interaction and cation-π interaction. Above the CAC, the cationic surfactant micelles are bound to the polymer to swell the gel substrate because of the enhanced osmotic pressure due to the counterions of the bound micelles. In the micellar binding, the polymer segments are partly incorporated with the micelle core, besides the binding on the micelle surface. In the anionic surfactant systems below the CAC, free unimer molecules of the anionic surfactants are bound to P4VPh via the hydrophobic interaction between the polymer's hydrophobic moieties and the alkyl tail as well as through the nonspecific dipolar interaction with the head group [16]. This unimer binding seemed to be rather weak compared with that of the cationic surfactants, because no appreciable changes in the swelling degree was observed until the surfactant concentrations reached their CAC values just below the respective CMCs. Above the CACs, micelles are formed and bound with the polymer on the micelle surface.

In the case of the present DGCHDC gel, the deswelling–reswelling behavior was observed not only for the cationic surfactant systems but also for the anionic ones, as shown in Fig. 9. The deswelling for the anionic surfactant systems, though only slight, may be ascribed to the hydrophobicity of the crosslinker because a similar deswelling has been observed for hydrophobically modified hydroxyethyl cellulose gel but not for hydroxyethyl cellulose gel [17]. It should be noted here that the reswelling degrees for both of the cationic and anionic surfactant systems are markedly lower than those of the original gel systems. For example, the d/d_0 values at 100 mM for C_{12}TAB and SDS systems are ca. 1.4, which are significantly smaller than 1.8 for the corresponding EGDGE gel systems. Especially for SDeSo system, it is only 0.98 against ca. 1.44. One possible explanation for the small reswelling may be the assumption that the micelle binding to the polymer substrate was weaker than in the original gel. However, this seems quite unlikely because the replacement of the crosslinker to a more hydrophobic one would never hamper the micellar binding.

Another solution to this puzzle is to postulate a stronger crosslinking efficiency for the DGCHDC gel. Reasoning may be given as follows: first, we consider about a mechanism of the initial deswelling observed for the anionic surfactant systems. If the crosslinker served as a binding site for the surfactant unimer, a swelling would be observed. On the other hand, if the unimer surfactant molecules bound to the hydrophobic crosslinker interact with others bound to the polymer substrate, a deswelling may occur. This situation is similar to the TBA^+ binding to the pertinent crosslinker as depicted in Fig. 8. Although the pertinent concentration range for the TBA^+ system is much higher than the cationic surfactants, the difference should be ascribed to the much weaker hydrophobic interaction of the former cation compared with the latter. Thus, if the

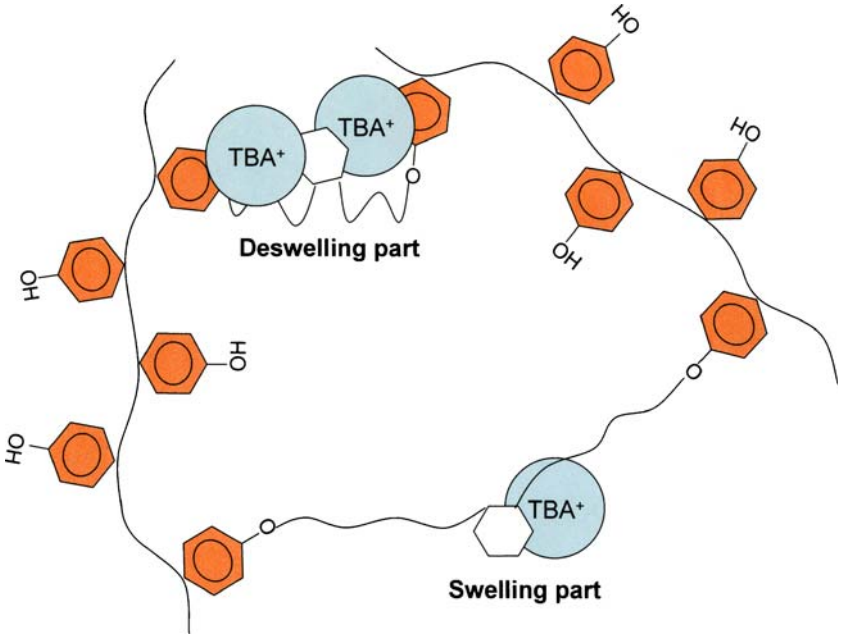

Fig. 8 A scheme for TBA^+ binding to the hydrophobic moiety (cyclohexyl ring) of the crosslinker

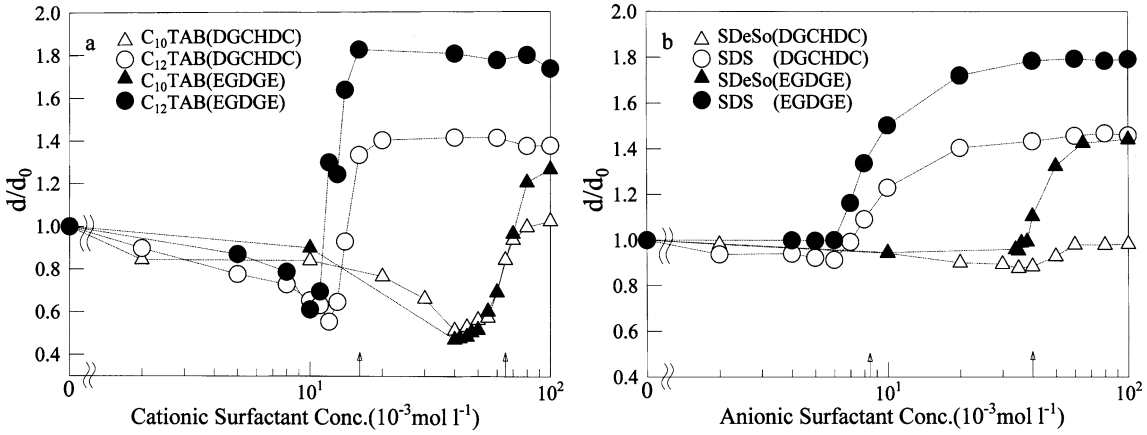

Fig. 9 Dependence of swelling ratio (d/d_0) on the surfactant concentration for P4VPh/DGCHDC gel, compared with those for the original gel systems. *Arrows* show the respective CMC values. **a** Cationic surfactant systems. **b** Anionic surfactant systems

chain aggregation due to the hydrophobic interaction among the bound surfactants predominated over the chain expansion due to the free surfactant binding to the crosslinker, the gel would deswell. The slight deswelling observed for the anionic surfactant systems, therefore, may be only apparent and be a result of a cancellation of local and substantial chain aggregations and expansions. In the case of the cationic surfactant systems, the initial gel deswelling should occur via hydrophobic interaction among the alkyl chains of surfactants which were bound to the phenol rings by the cation-π interaction. Thus, the deswelling due to the hydrophobic interaction among the surfactants where the crosslinker is involved may be masked by the inherent more significant deswelling.

Now we turn back to the consideration on the reswelling. The aggregation that consists of the polymer segments, surfactants, and a crosslinker may serve as a firm crosslinking point. In fact, it has been found that the original P4VPh gel never swelled if once dried [11]. This means that if the hydrophobic residues aggregated directly, namely, without hydrating water, then the collapsed aggregations never dissociate in water of neutral pH. Therefore, if the aggregation involving the crosslinker, phenol rings, and the respective surfactant molecules was formed so tightly that it collapsed, then the suppressed reswelling degrees for the DGCHDC gel may be ascribed to the local collapse of the gel matrix. This speculation is, in fact, consistent with the finding in our preliminary experiment with a DGCHDC gel sample, namely, with increasing SDS concentration, the gel sample significantly deswelled and never reswelled even in 100 mM SDS. The d/d_0 values were constant at ca. 0.6 at SDS concentration ≧1 mM, the gel being nearly collapsed. In this sample, the local gel collapse involving the crosslinker might extend to a macroscopic scale probably due to a heterogeneous physical crosslinking.

Thus, the introduction of a hydrophobic moiety into the crosslinker just enhanced the hydrophobic interaction with the polymer substrate and the hydrophobic solutes although the swelling behaviors were essentially the same as those in the original gel.

Conclusions

In this study, the effects of introduction of hydrophobic groups to the phenol OH or to the crosslinker in the original P4VPh gel on the swelling behavior in solutions of various kinds of solutes and on the water content were investigated to elucidate what causes the unique properties of the original gel, i.e., (1) unexpectedly, high water content irrespective of the insolubility of the parent polymer in water, (2) super salt resistivity to inorganic ions, and (3) deswelling–reswelling behavior in solutions of hydrophobic solutes, such as TBA^+ and cationic surfactants. For the first property, some contributions of the hydrophilic crosslinker (EGDGE) had been postulated [8]. However, the present study clearly denied the possibility; the high water content of P4VPh gel should be ascribed to an inherent property of the polymer substrate, probably due to a stable coexistence of the hydrogen-bonding hydration to the phenol OH, the π-hydrogen-bonding hydration to the phenol ring, and the hydrophobic hydration around the phenol ring and the main chain. For the second one, stabilization of the hydrogen-bonding hydration to the phenol proton and π-hydrogen bonding one to the phenol π-electrons by anions and cations, respectively, has been proposed as a promising mechanism. Thus, it was expected that the alkylation at the phenol proton would substantially damage the super salt resistivity. However, the damage of the resistivity to a typical salting-out anion F^- was rather limited (10% at most). This result also suggests that the hydration around the polymer substrate in the gel phase is highly stabilized and hardly perturbed by partial (up to 10–20%) chemical modifications as in the present study. As for the third one, i.e., specific swelling behavior in hydropho-

bic solute systems, the initial deswelling has been ascribed to crosslinking binding of TBA^+ or crosslinking interaction between the alkyl chains of surfactants bound via cation-π interaction onto the phenol rings. The present hydrophobic modifications that have been exerted to the original gel seemed to affect the cation-π interaction only to a limited extent, and the perturbations in the swelling behavior due to the chemical modifications were explained consistently with the proposed mechanisms on the hydrophobic solute binding to P4VPh.

Throughout the present study, we often encountered a common conclusion, i.e., the (hydrophobic) hydration around P4VPh in the gel phase is highly stable. This has also been suggested by our previous studies [11, 12] on the basis of a weaker temperature effect on gel swelling and of the lower binding amounts of ionic surfactants, respectively, compared with the typical hydrophobic polymer, PNIPA. However, the origin of this stability of the P4VPh hydration has not yet been clarified. An extensive study on the physico-chemical properties of water in the P4VPh gel including the dynamical and structural ones must be performed in future research.

Finally, we must emphasize the significance of the finding in the present study, namely, we first demonstrated that a highly swollen hydrogel can be prepared with "hydrophobic" materials only. This finding must lead to a novel criterion of molecular design for manufacturing "hydrophilic" polymer materials.

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