

# Syntheses of Hydroxypropyl Methylcellulose Phthalate Gels in Organic Solvents by Radiation Crosslinking

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**ABSTRACT:** Cellulose gels were prepared through the crosslinking of hydroxypropyl methylcellulose phthalate (HPMCP) with electron-beam irradiation in concentrated organic solvent solutions. The effects of the solvent species, polymer concentration, and irradiation dose on the formation of the gels were investigated. Some organic solvents, such as alcohols with short alkyl chains, alkyl acetates, and ketones, were found to be suitable as media for the radiation crosslinking of the polymer. The prepared HPMCP gels showed excellent swelling in various organic solvents with medium hydrogen-bonding abilities, such as pyridine,

cresol (meta), acetic acid, dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, 1,4-dioxane, acetone, methyl ethyl ketone, methyl acetate, and chloroform. In an acetone/water mixture, the swelling ratio was significantly dependent on the solvent composition because of the coexistence of both hydrophilic and hydrophobic moieties in HPMCP. These results suggest that HPMCP gels have the potential to be superabsorbents for various kinds of organic solvents. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3002–3007, 2004

**Key words:** gels; irradiation; swelling

## INTRODUCTION

Polymer gels swell in solvents but cannot dissolve in them because of their network structure. For this reason, they are fascinating materials for a wide variety of applications, such as superabsorbents and water reservoirs. Hydrogels have been intensively researched for the past 20 years, and fruitful results have been obtained in this field, such as applications for wound dressings, controlled-release drug-delivery systems, dental materials, and implants. Although using gels as organic solvent absorbents has promising applications because their three-dimensional structure encourages very high absorption capacities, only a few studies have been reported on the syntheses and characterization of gels prepared for such a purpose.

Cellulose derivatives are used in a broad range of applications in diverse industries, such as food, paint, oil recovery, paper, cosmetics, pharmaceuticals, adhesives, printing, agriculture, ceramics, textiles, and building materials.<sup>1</sup> The syntheses of water-soluble cellulosic hydrogels, such as methylcellulose,<sup>2</sup> hy-

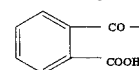
droxypropyl cellulose,<sup>3</sup> and carboxymethylcellulose,<sup>4,5</sup> have been reported. Hydroxypropyl methylcellulose phthalate (HPMCP), a water-insoluble cellulose derivative with good solubility in organic solvents, is widely used in the pharmaceutical industry.<sup>6,7</sup> Generally, HPMCP is processed after its dissolution in a solution of Na<sub>2</sub>CO<sub>3</sub> to dissociate the carboxyl groups on the polymer and to impart a certain hydrophilicity. Our previous article<sup>8</sup> reported the preparation of HPMCP gels by electron-beam radiation in a solution of Na<sub>2</sub>CO<sub>3</sub>. The prepared gels behaved as polyelectrolyte hydrogels, and the hydrophobicity of the polymer was remarkably reduced.

In this study, to preserve the inherent hydrophobicity of HPMCP, we prepared the gels in various organic solvents by the radiation crosslinking method. On the basis of their swelling behavior in various kinds of organic solvents, the gels showed promise as superabsorbents for organic solvents.

## EXPERIMENTAL

### Materials

HPMCP (Shinetsu Chemical Co., Ltd., Tokyo, Japan) was used as received. The chemical structure of the cellulose ether is shown in Scheme 1 [R = —H, —OCH<sub>3</sub>(MeO), —CH<sub>2</sub>CH(OH)CH<sub>3</sub>(HPO), or



MeO, HPO, and CB were 1.9, 0.25, and 0.65, respec-

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tively. The weight-average molecular weight was  $4.5 \times 10^4$ .<sup>9</sup> The solubility parameter was  $19.1 \text{ MPa}^{1/2}$  (as measured by nephelometric titration<sup>10</sup>).

The other chemicals used were analytical-grade.

**Sample preparation and irradiation**

For the preparation of sample solutions of desired concentrations for irradiation, the appropriate amounts of the organic solvents and polymer were mixed with a hybrid mixer for 15 min until the mixture became a homogeneous solution. The samples thus prepared were placed in plastic bags, and the air was removed with a vacuum pump before heat sealing. Samples with high polymer concentrations were pressed (at 200 MPa for 15 min) into sheets 0.5 mm thick with a cold press machine before they were packaged into bags.

Electron-beam irradiation (2 MeV and 1 mA) was performed with an RDI Dynamitron accelerator (Radiation Dynamic, Inc., New York). The dose rate was 1 kGy/pass, and the conveyor moving speed was 17.3 m/min.

**Gel fraction**

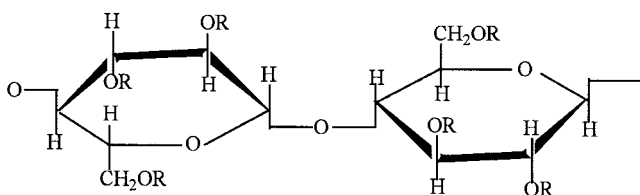
After irradiation, the samples were dried in a vacuum oven for 48 h at 50°C. The gel fraction was estimated gravimetrically through the measurement of the insoluble parts of the samples after extraction in acetone for 48 h. The gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = (G_d/G_i) \times 100 \quad (1)$$

where  $G_i$  is the initial weight of the dried samples and  $G_d$  is the weight of the insoluble parts.

**Swelling ratio**

The hydrogel sheet was cut into a round shape with a diameter of 20 mm and was dried at 50°C in a vacuum oven for 48 h. Then, the dry samples were immersed in the test solvents for 24 h in room temperature. The swollen gels were taken from the solvents via filtration on a stainless net. Extra solvent on the gel surface was gently removed with filter paper, and the weight of the swollen gels was measured immediately. The



Scheme 1

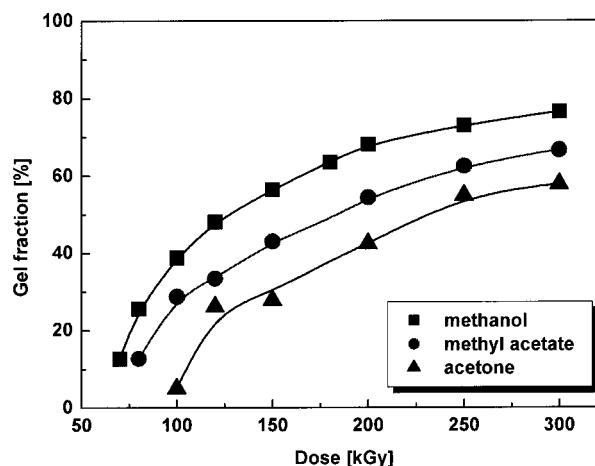


Figure 1 Influence of the solvent species on the radiation crosslinking of HPMCP at 40 wt %.

swollen gels were dried with the aforementioned method. The swelling ratio was calculated with the following equation:

$$\text{Swelling ratio} = (G_s - G_d)/G_d \quad (2)$$

where  $G_s$  is the weight of the gels in the swollen state and  $G_d$  is the dry weight of the gels.

**RESULTS AND DISCUSSION**

**Radiation crosslinking**

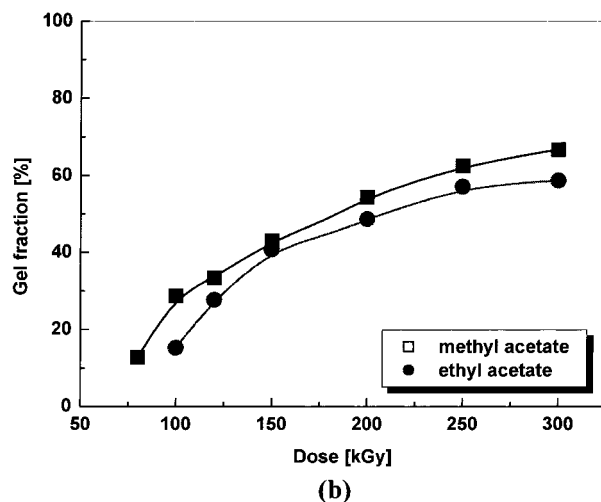
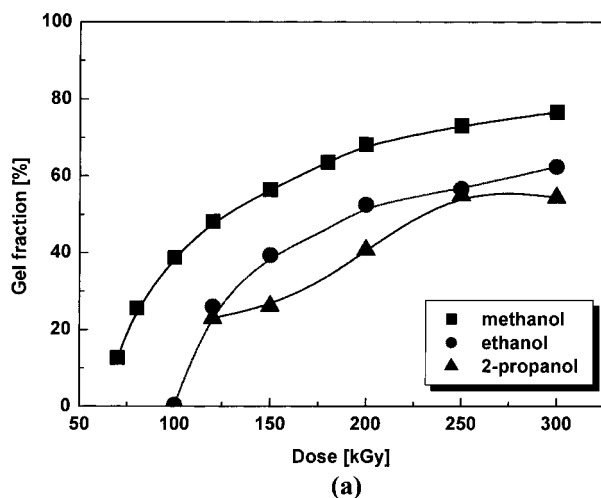
**Effect of the organic solvents**

To the best of our knowledge, the radiation crosslinking of polysaccharides in organic solvents has not been reported to date. Lu et al.<sup>11</sup> reported the radiation-induced grafting of *N*-isopropylacrylamide onto cotton cellulose in organic solvents. Although methanol is thought to be a radical scavenger, methanol/water, ethanol/water, propanol/water, and acetone/water mixtures have been reported to be effective media for the radiation-induced grafting of this system.

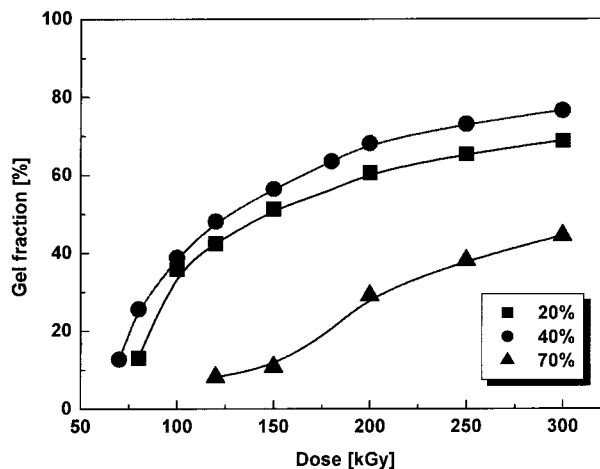
In this study, HPMCP, which was dissolved in various organic solvents in a highly viscous state, was successfully crosslinked with electron-beam irradiation. Figure 1 shows the crosslinking behavior of HPMCP solutions (40 wt %) in methanol, methyl acetate, and acetone. In the case of HPMCP hydrogels, which were prepared from concentrated aqueous solutions,<sup>8</sup> the gel fraction rapidly increased after the irradiation dose reached a gelation dose (ca. 50–60 kGy, depending on the polymer concentration), which was defined as the minimum irradiation dose required to obtain gels, and then leveled off. The relationship between the gel fraction and irradiation dose of these gels crosslinked in organic solvents was qualitatively sim-

ilar to that of the hydrogels, and the gelation doses were 60–100 kGy for methanol, methyl acetate, and acetone. However, the increasing rate of the gel fraction with the irradiation dose was much less significant; the gel fraction still increased gradually as the dose increased, even above 200 kGy. Methanol, a good solvent for HPMCP, may access the active sites in cellulose molecules easily. Moreover, it is a relatively effective chain-transfer agent, which can end the crosslinking reaction and reduce the gel fraction. At the beginning of the reaction, chain transfer takes the main role, so that no gel can be formed in the system. Above the gelation dose, the crosslinking reaction overwhelms chain scission, and a gel network forms.

In the case of water radiolysis, the following free radicals are produced from water:  $H_2$ ,  $H_2O_2$ ,  $e_{aq}^-$ ,  $H\cdot$ ,  $\cdot OH$ , and  $H_3O^+$ . Among these,  $e_{aq}^-$  and  $H\cdot$  are essential in the reduction of the substance in the solution. On the contrary,  $\cdot OH$ ,  $\cdot HO_2$ , and  $H_2O_2$  contribute to



**Figure 2** Influence of the alkyl chain length of (a) alcohol and (b) ester acetate on the radiation crosslinking of HPMCP at 40 wt %.



**Figure 3** Influence of the HPMCP concentration on its radiation crosslinking in methanol.

the oxidation of the substance.  $H\cdot$  and  $\cdot OH$  are very active and very important for the initial crosslinking of polymers.<sup>12</sup> In the case of methanol, the main effect in a radiation field is the loss of the hydrogen atom from the  $\alpha$ -carbon atom ( $H\cdot$  and  $\cdot CH_2OH$  are formed), as well as the loss of the hydrogen atom from the hydroxyl group ( $H\cdot$  and  $\cdot CH_3O$  are formed). The resulting radiolysis products in liquid methanol are hydrogen, ethylene glycol, formaldehyde, methane, and carbon monoxide, the  $G$  values (yield of free radical while 100 eV molecular radiation energy is absorbed) of which are 4.0, 3.0, 1.3, 0.24, and 0.16, respectively, in a  $\gamma$ -radiation field.<sup>13</sup> The generation of the  $H\cdot$  radical and formaldehyde, often used as crosslinkers for cellulose derivatives, may compensate for the chain-transfer effects of methanol. Compared with methanol, the radiolysis free radicals of esters and ketones are less active because the most radiosensitive spots in the molecules are the bonds adjacent to the carbonyl groups.<sup>13</sup> The gel fractions of the gels obtained from methanol, higher than those obtained from other organic solvents such as methyl acetate and acetone, may partly be explained in this way.

HPMCP crosslinking is also influenced by the alkyl chain length of the solvents. As shown in Figure 2, alcohols and alkyl acetates of longer alkyl chains are less effective in gel formation. This might be ascribed to the lower solubility of the polymer in solvents with larger alkyl chains, which leads to more entangled polymer chains and, therefore, a reduced probability of crosslinking.

#### Effect of the polymer concentration

The influence of the polymer concentration on the gel fraction of HPMCP gels obtained from methanol solutions is shown in Figure 3. When the HPMCP solu-

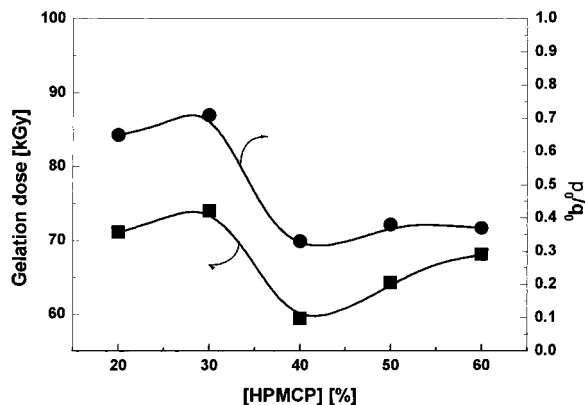


Figure 4 Relationship between the gelation dose,  $p_0/q_0$ , and the HPMCP concentration.

tion is in the fluid state (20–30%), the gel fraction is lower than in the pastelike state (40–60%). In the latter state, the distance between the chains is small and the mobility of the chains is low. Therefore, the probability of radical recombination is higher, and this leads to a higher gel fraction. When the concentration of HPMCP is as high as 70%, the gel fraction significantly decreases compared with that at 60%. It is assumed that, at this concentration, the molecular chain is in an entangled state so that the probability for intramolecular radical recombination is significantly increased and the radiation crosslinking reaction is terminated. As a result, the gel fraction is reduced.

The ratio of degradation to crosslinking ( $p_0/q_0$ ) can be calculated according to the Charlesby–Rosiak equation:<sup>14</sup>

$$s + \sqrt{s} = \frac{p_0}{q_0} + \left(2 - \frac{p_0}{q_0}\right) \frac{D_v + D_g}{D_v + D} \quad (3)$$

where  $s$  is the sol fraction and  $p_0$  and  $q_0$  are the degradation level and crosslinking density, respectively.  $p_0$  represents the yield of scission, and  $q_0$  represents the yield of crosslinking of these polymers.  $D$  is the absorbed dose,  $D_g$  is the gelation dose, and  $D_v$  is the virtual dose. The calculation for each polymer was performed with Gelsol software kindly provided by Rosiak (Technical University of Lodz). This software can also calculate the gelation dose, that is, the critical irradiation dose for gel formation. The results for the gels obtained with different HPMCP concentrations are illustrated in Figure 4. In comparison with other concentrations, at 40% HPMCP,  $p_0/q_0$  and the gelation dose are lowest, and this indicates that the crosslinking probability is highest at this concentration and suggests that 40% is the optimal concentration for the gel synthesized in methanol.

### Swelling of the HPMCP gels

#### Effects of the syntheses conditions

Figure 5 illustrates the differences in the swelling behaviors of the gels prepared in methanol, methyl acetate, and acetone solutions (named methanol gels, methyl acetate gels, and acetone gels). The concentration of the polymer in each of the solutions was 40 wt %. The swelling ratios of all three gels in both acetone and chloroform decreased as the gel fraction increased because of enhanced crosslinking density. At the same gel fraction, the swelling ratio was somewhat dependent on the solvent species used for the gel preparation. In the lower gel fraction region, the swelling ratios of acetone gels in acetone and chloroform were significantly higher than those of methyl acetate and methanol gels. As the gel fraction increased, the difference became less significant. This result suggests that the crosslinking density was lowest for irradiation in acetone solutions, at least under the lower dose conditions.

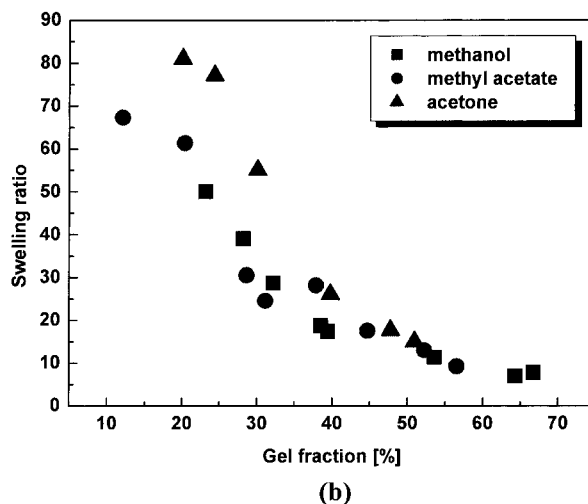
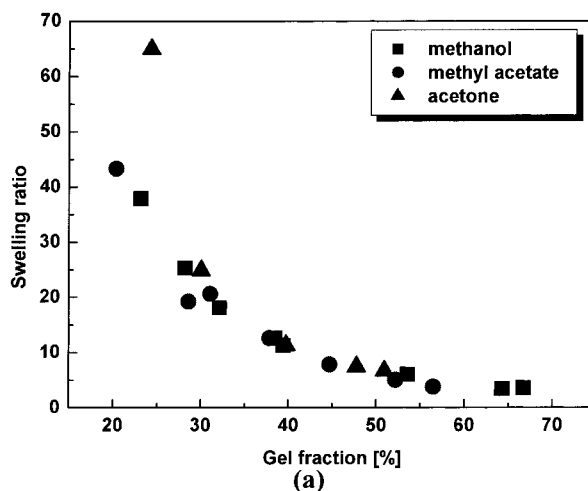
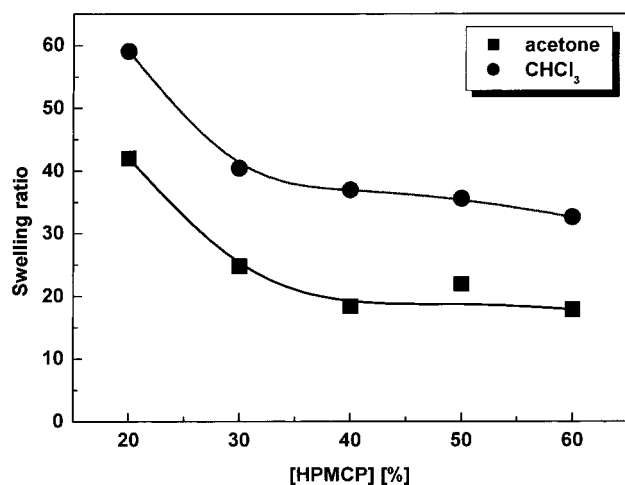


Figure 5 Influence of the gel fraction on the swelling of HPMCP gels in (a) acetone and (b)  $\text{CHCl}_3$ . The gels were prepared from 40 wt % solutions in different solvents.

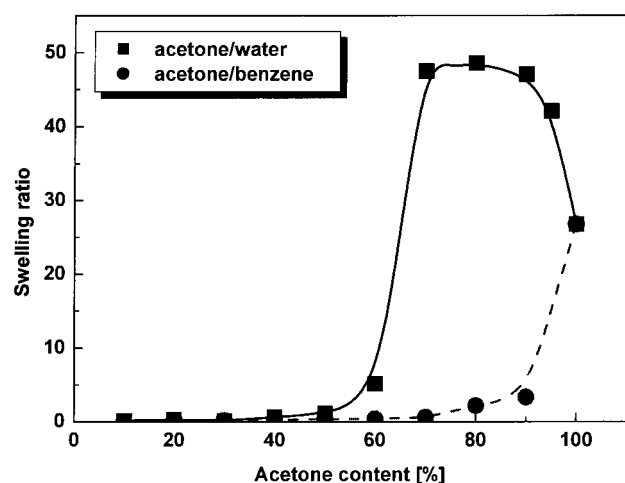


**Figure 6** Swelling ratio as a function of the HPMCP concentration used for the gel preparation. Each gel sample was obtained from a methanol solution with an irradiation dose of 100 kGy.

The influence of the HPMCP concentration on the swelling is demonstrated in Figure 6 (the gels were obtained from 40 wt % methanol solutions with an irradiation dose of 100 kGy). The swelling ratio obviously decreased with an increase in the HPMCP concentration, especially in the fluid state (20–30%). This may be attributed to the larger distance between molecular chains, leading to a lower crosslinking density when the HPMCP concentration was low.

#### Effect of the water content in the swelling media

As water is one of the most widely used solvents, the interaction between water and polymer gels needs to be investigated. Although HPMCP is insoluble in water, the swelling of its gels is significantly influenced by the water content in the immersing solvent. Figure



**Figure 7** Influence of the water content on gel swelling.

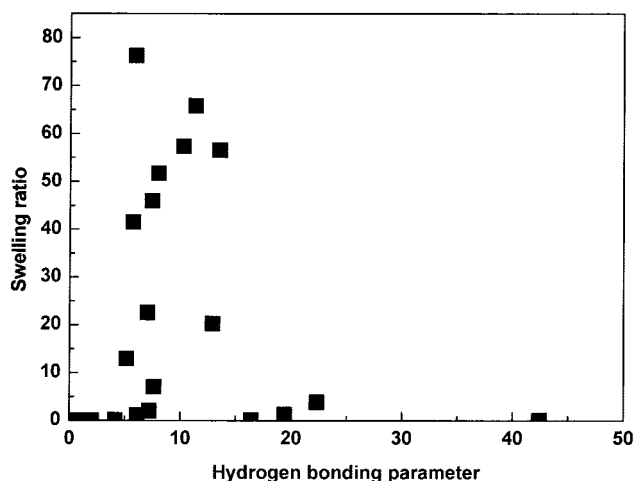
**TABLE I**  
Hydrogen-Bonding Parameters of the Solvents and Corresponding Swelling of the Gels

Solvent	Hydrogen-bonding parameter (MPa <sup>1/2</sup> )	Swell ratio (g of solvent/g of dry gel)
Water	42.4	0.14
Methanol	22.3	3.88
Ethyl alcohol	19.4	1.25
2-Propanol	16.4	0.06
Acetic acid	13.5	56.53
Cresol (meta)	12.9	20.32
Dimethylformamide	11.3	65.83
Dimethyl sulfoxide	10.2	57.38
Tetrahydrofuran	8	51.69
1,4-Dioxane	7.4	45.94
Acetone	7	22.62
Methyl ethyl ketone	5.1	12.94
Methyl acetate	7.6	7.14
Ethyl acetate	7.2	2.04
Pyridine	5.9	76.27
Chloroform	5.7	41.51
Acetonitrile	6.1	1.20
Nitrobenzene	4.1	0.13
Benzene	2	0.02
Chlorobenzene	2	0.04
Carbon tetrachloride	0.6	0.01

7 shows the swelling of HPMCP gels prepared from methanol solutions in acetone/water and acetone/benzene mixed solvents. The interaction between benzene and HPMCP is very poor, and so the swelling with acetone/benzene decreased abruptly with increasing benzene content. The swelling behavior of HPMCP gels in acetone/water mixtures is quite different from that in acetone/benzene mixtures: when the ratio of acetone/water (w/w) is 70/30 to 95/5, the swelling ratio is much higher than that in pure acetone and high water content solutions. Because HPMCP contains both hydrophilic and hydrophobic moieties, the interaction between water and hydrophilic groups as well as the interaction between acetone and hydrophobic groups may be effective at the same time for a certain range of water contents. Thus, in an optimum case, it would cause a strong pressure for the gels to swell. However, when the water content in immersing media is higher than 30%, water molecules might disturb the direct interaction between the acetone and polymer; because of the inherent hydrophobicity of HPMCP, water may serve as a poor solvent for the polymer in the water-rich region.

#### Swelling behavior in different organic solvents

HPMCP gels are assumed to possess excellent swelling ability in various organic solvents because of their hydrophobicity. For this reason, the swelling behavior of HPMCP gels in several kinds of organic solvents



**Figure 8** Correlation between the hydrogen-bonding parameter of the immersing solvents and the swelling ratio of the gels.

was investigated, so that we could determine potential applications of the gels and discuss the interactions between the polymer and solvent.

Mantanis et al.<sup>15</sup> reported on the swelling of compressed cellulose fiber networks in organic solvents. Their results suggested that the hydrogen-bonding capability of the immersing solvent is essential for gel swelling. In our work, organic solvents with a wide variety of structure and solubility parameters<sup>16</sup> were chosen as the immersing media for HPMCP gels. Table I lists the swelling ratios of the gels in different solvents, whereas Figure 8 illustrates the correlation between the swelling ratio of the gels (prepared from 40% HPMCP methanol solutions at an irradiation dose of 100 kGy) and the hydrogen-bonding parameter extracted from the solubility parameter. Unlike HPMCP hydrogels,<sup>11</sup> which showed higher swelling ability in solvents of higher hydrogen-bonding parameters, such as water and methanol, these gels, prepared from organic solutions, could significantly absorb solvents with a medium hydrogen-bonding parameter (5–13.5 MPa<sup>1/2</sup>). However, the swelling ratios in solvents with high hydrogen-bonding parameters, such as water, methanol, ethanol, and 2-propanol, were comparatively low. Furthermore, the gels could not swell in solvents with poor hydrogen-bonding ability, such as CCl<sub>4</sub>, benzene, chlorobenzene, and nitrobenzene.

## CONCLUSIONS

Short alkyl chain alcohols, alkyl acetates, and ketones were found to be effective media for the radiation crosslinking of HPMCP. Among these solvents, the gel fraction of the methanol gels was higher than that of

the other gels. However, the acetone gels showed a higher swelling ability than the other gels. HPMCP was easier to crosslink in a shorter alkyl chain solvent than in a longer alkyl chain solvent. The crosslinking probability was found to be highest for 40% HPMCP.

The effects of the immersing solvent conditions, that is, the water content and hydrogen-bonding parameters of the solvents, on the gel swelling were investigated. The HPMCP gels were proved to have excellent swelling ability in various organic solvents with medium hydrogen-bonding parameters, such as pyridine, cresol (meta), acetic acid, dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, 1,4-dioxane, acetone, methyl ethyl ketone, methyl acetate, and chloroform. Despite the hydrophobicity of HPMCP, water in the immersing media played an interesting role in the swelling of the HPMCP gels. The gels had higher swelling ratios in an acetone/water mixture of a certain ratio than in pure acetone and water because of the coexistence of hydrophilic and hydrophobic moieties in the polymer. These results suggest that the gels have potential as superabsorbents for organic solvents.

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