# The Swelling and Mechanical Properties of Hydrogels of Tactic Poly (2-Hydroxyethyl Methacrylate)

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The swelling and stress-elongation experiments have been performed for two kinds of gels of tactic poly (2-hydroxyethyl methacrylate) (P-HEMA) with varying crosslinker concentrations. The gels of isotactic and syndiotactic P-HEMA were swollen in aqueous salt solutions upon varying molal concentrations. The solute used were NaCl, $MgCl_2$, $Na_2SO_4$, $MgSO_4$ and urea. The water content at equilibrium swelling and the salt partition coefficient were determined, and stress-elongation curves of the gels were obtained. From these results, the effective number of chain ($\nu_e$) and the Flory-Huggins interaction parameter ($\chi_1$) were also obtained. The swelling experiment was also performed under varying solvents, and the degree of swelling was determined. The solubility parameter of P-HEMA was obtained as 13.4 $(cal/mole)^{1/2}$ using the correlation between the degree of swelling and the solubility parameter ($\delta_1$) of solvents. The mechanical properties of syndiotactic P-HEMA is stronger than that of isotactic P-HEMA, and the water content of both gels become smaller when the crosslinking increases. Isotactic P-HEMA contains more water content than syndiotactic P-HEMA does.

## Introduction

The present and potential biomedical applications of synthetic hydrogels were reviewed by Ratner and Hoffman.[1]

It has been proposed that the relatively large fraction of water within certain gels results in a low gel-solution interfacial tension, which may be responsible for the tissue compatibility of gel biomaterials.[2]

For this important role of hydrogels, the mechanical and swelling properties have been studied for many years.[3-9] The lattice theory of Flory and Huggins[5] has been widely used in interpreting the thermodynamic properties of polymer-liquid mixtures.

Dusek *et al.*[8] suggested that a number of salts possess the salting-in and salting-out effects on the equilibrium swelling, and these effects are explained in terms of the change in the water structures (hydrophobic interactions), and by specific interactions between the polymer and the ions. This specific interactions have been reported by Refojo[7] between P-HEMA to urea and its methyl derivatives. He marked a hydrophobic mechanism that these solutes probably occur to the breaking of hydrophobic bonds in the hydrogel.

It has been suggested that water molecules absorbed in polymeric media exist in two or more different states.[12,13] Some water molecules are bound to polymer molecules through hydrogen bonding and are immobilized, while others are relatively free to move.

Lee *et. al.*[14] and Jhon *et. al.*[15] have proposed that water in hydrogels is classified into three groups according to their experimental results for atactic and tactic poly (2-hydroxyethyl metacrylate) (P-HEMA), respectively.

The increasing number of biomedical applications[10] of P-HEMA gels require efficient control of their structures and properties. The introduction of tacticity into P-HEMA structure makes it possible to modify considerably the physical properties of the gels. Gregonis *et al.*[11] have made the stereoregular P-HEMA hydrogels. This stereoregular P-HEMA gels have been also made in our laboratory to study their swelling and mechanical properties.

In this paper, we study the swelling and mechanical properties of P-HEMA with the change of polymer conformation and give theoretical considerations. To do this, the water content and salt partition coefficient are measured by direct weighing method with NaCl, $MgCl_2$, $Na_2SO_4$, $MgSO_4$, and urea solutions, and the stress-elongation experiments are carried out at room temperature. And the degree of swelling on various solvent systems is measured by the direct weighing method.

The theoretical considerations are carried out with extended Flory-Huggins equation of swelling which may be applicable to salting-out solutions, and further considerations are suggested.

## Theoretical Considerations

*Flory-Huggins Equation.* According to Flory,[5,16,17] the free energy change $\Delta G$ involved in the mixing of solvent with the polymer network can be considered to consist of two parts; the free energy of mixing $\Delta G_m$, and the elastic free energy $\Delta G_{el}$.

$$\Delta G = \Delta G_m + \Delta G_{el} \tag{1}$$

A suitable expression for $\Delta G_m$ may be written as follows

$$\Delta G_m = kT(n_1 \ln v_1 + \chi_1 n_1 v_2) \tag{2}$$

where $v_1$ and $v_2$ are the volume fractions of solvent and solute, respectively.

The chemical potential of the solvent in the swollen gel is given by

$$\mu_1 - \mu^0{}_1 = N(\partial \Delta G_m/\partial n_1)_{T,P} + N(\partial \partial \Delta G_{el}/\partial n_1)_{T,P} = (\mu_1 - \mu^0{}_1)_m + \mu_{1el} \tag{3}$$

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By differentiating Eq. (2), and substituting in Eq. (3)

$$\mu_1-\mu^0{}_1=RT[\ln(1-v_{2m})+v_{2m}+\chi_1 v_{2m}{}^2]+\mu_{1el} \quad (4)$$

And $v_{2m}$ is defined as the volume fraction of network polymer at which the activity of the solvent is unity. At equilibrium swelling $\mu_1-\mu_1{}^0=0$, one can obtain the following equation.

$$\chi_1=-\{[\ln(1-v_{2m})+v_{2m}]+\mu_{1el}/RT\}/v_{2m}{}^2 \quad (5)$$

If the informations of $v_{2m}$ and $\mu_{1el}$ are obtained, the Flory-Huggins interaction parameter $\chi_1$ may be estimated. Then $v_{2m}$ can be determined from the water content of hydrogel in a pure solvent and $\mu_{1el}$ is determined from the following

$$\mu_{1el}=\left(\frac{\partial \Delta G_{el}}{\partial \lambda}\right)_{T,P}\left(\frac{\partial \lambda}{\partial n_1}\right)_{T,P} \quad (6)$$

where the extension ratio $\lambda$ in an isotropically swollen elastomer is related to the polymer volume fraction $v_2$ by

$$\lambda^3=1/v_2=(V_0+n_1\bar{V}_1)/V_0 \quad (7)$$

where $n_1$ is the number of moles of solvent, and $V_0$ and $V_1$ are the volume of the unswollen elastomer and molar volume of the solvent, respectively. The phenomenological theory developed by Mooney[18] and Rivlin[19] has been widely used in a closer agreement with experimental results. This theory yields

$$\mu_{1el}=2\frac{\bar{V}_1}{V_0}\left(\frac{C_1}{\lambda}-\frac{C_2}{\lambda^5}\right)=A\left(\frac{1}{\lambda}-\frac{C_2}{C_1\lambda^5}\right)$$
$$A=\nu_e RT\bar{V}_1/V_0 \quad (8)$$

where $C_1$ and $C_2$ are the two empirical elastic constants, and $\nu_e$ is the effective number of chains in the network, the second equality is obtained by identifying $2C_1$ with $\nu_e$RT in the statistical theory.

To obtain stress-elongation equation, the following relationship is used.

$$\left(\frac{\partial \Delta G_{el}}{\partial l}\right)_{T,P}=f, \qquad \lambda=l/l_0$$

thus,

$$\sigma=f/l_0{}^2=\left(\frac{\partial G_{el}}{\partial l}\right)_{T,P}/l_0{}^2=\left(\frac{\partial \Delta G_{el}}{\partial \lambda}\right)_{T,P}/l_0{}^3 \quad (9)$$

where, $\sigma$ and $f$ are the stress and the retractive force exerted by stretched network, $l$ and $l_0$ are the length of stretched sample and unstretched swollen sample, respectively.

Therefore, the equation of relation between stress and elongation can be derived from Eq. (7), (8) and (9).

$$\sigma V_0=\left(\frac{\partial \Delta F_{el}}{\partial \lambda}\right)_{T,P}=3\nu_e RT\left(\lambda-\frac{c_2}{c_1}\lambda^{-3}\right) \quad (10)$$

*Extended Flory-Huggins Equation.* The equilibrium condition for isotropic swelling classically requires that, by Eqs. (4), (7) and (8).

$$\mu_1-\mu_1{}^0=RT[\ln(1-v_2)+v_2+\chi_1 v_2{}^2]$$
$$+\nu_e\frac{\bar{V}_1}{V_0}\left(v_2{}^{1/3}-\frac{c_2}{c_1}v_2{}^{5/3}\right)=0 \quad (11)$$

This equation of swelling equilibrium can be applied to a simple solvent system only.

When the swelling occurs in a suitable liquid solution of solute, for example an aqueous salt solution, the salting-in and salting-out effects are included.[8] Perchlorates, thiocyanates and iodides are typical salting-in anions, while sulphates, fluorides and most chlorides are typical salting-out anions. Generally, both the salting-in and the salting-out effects become smaller with increasing salt concentrations. The salting-in effect is explained not only by the change in the water structures (hydrophobic interaction), but also by specific interactions between the polymer and the ions. In this paper, the only salting-out effect will be discussed because of its simplification of treatment.

Let us designate the composition of the membrane phase by the number of moles, $n_1$, $n_2$ and $n_3$ moles of water, salt and polymer, respectively, which contained in a certain volume of the swollen membrane. Its mixing free energy change $\Delta G\{(n_1, n_2), n_3\}$, when $n_3$ mole of polymer is mixed with the aqueous salt solution, can be then written as

$$\Delta G_m\{(n_1, n_2), n_3\}=\Delta G_m(n_1, n_2, n_3)-\Delta G_m(n_1, n_2) \quad (12)$$

where $\Delta G_m(n_1, n_2, n_3)$ and $\Delta G_m(n_1, n_2)$ are the free energy change when $n_1$, $n_2$ and $n_3$ moles of each pure component is mixed.

In calculating $\Delta F\{(n_1, n_2), n_3\}$, Eaton *et al.*[20] marked the following simplifying assumption; (1) the entropy increase on mixing arises solely from the large accessible volume in the mixture and can be estimated approximately by the Flory-Huggins entropy of mixing, and (2) the salt ions are hydrated and thus are prevented from making direct contact with the polymer molecules.

It the salt was dissociated perfectly in aqueous solutions, for example NaCl, the changes of free energy of mixing may be expressed as following equations.

$$\Delta G_n(n_1, n_2, n_3)/RT$$
$$=n_1\chi_1 v_3+n_1\ln v_1+n_2\ln v_2{}^+ +n_2\ln v_2{}^- \quad (13)$$
$$\Delta G_m(n_1 n_2)/RT$$
$$=n_1\ln\frac{v_1}{v_1+v_2{}^+ +v_2{}^-}+n_2\ln\frac{v_2{}^+}{v_1+v_2{}^+ +v_2{}^-}$$
$$+n_2\ln\frac{v_2{}^-}{v_1+v_2{}^+ +v_2{}^-} \quad (14)$$

where $v_1$, $v_2{}^+$, $v_2{}^-$ and $v_3$ are the volume fraction of each component, respectively. Substituting above expressions into Eq. (12), the result is given by

$$\Delta G_m\{n_1, n_2), n_3\}/RT$$
$$=n_1\chi_1 v_3+(n_1+2n_2)\ln(v_1+v^+{}_2+v_2{}^-) \quad (15)$$

And the volume fractions are given as follows

$$v_1=n_1/V_{123}, \qquad v_3=V_3/V_{123}$$
$$v_2{}^+=n_2x_{21}{}^+/V_{123}, \qquad v_2{}^-=n_2x_{21}{}^-/V_{123} \quad (16)$$
$$V_{123}=n_1+n_2(x_{21}{}^+ +x_{21}{}^-)+V_3$$

where $x_{21}{}^+$ and $x_{21}{}^-$ are the molar volume ratios of cation and anion to water, respectively, and $V_3$ is the corresponding volume of polymer to water which is equal to $V_0/\bar{V}_1$. Now, the expressions of the total molar volume ratio ($x_{21}=x_{21}{}^+ +$

$x_{21}^-$) and the total volume fraction of salt ($v_2 = v_2^+ + v_2^-$) may be employed. These equations are rewritten as

$$\Delta G_m\{(n_1, n_2), n_3\}/RT = n_1\chi_1 v_3 + (n_1 + 2n_2)\ln(v_1 + v_2) \quad (17)$$

At equilibrium swelling, the free energy change should be considered not only about the swollen network, but also about the solution outside the membrane.

Differentiating of $\Delta G_m\{(n_1, n_2), n_3\}$ with respect to $n_1$ and substituting in Eq. (3) give the chemical potential of water in the membrane phase, and by equating it with the chemical potential of water in the solution outside the membrane, we obtain,

$$(\mu_{10} - \mu_1^0)/RT = \ln(1 - v_3) + (1 + 2n_2/n_1)v_1 v_3/(1 - v_3) + \chi_1 v_3^2 + \nu_e \frac{\bar{V}_1}{V_0}\left(v_3^{1/3} - \frac{c_2}{c_1} v_3^{5/3}\right) \quad (18)$$

where $\mu_{10}$ and $\mu_1^0$ are the chemical potentials of water in the solution outside the membrane at equilibrium state and that of the salt solution contaning $n_1$ moles of water and $n_2$ moles of salt, respectively. There are three physical constants in this equation, of these $\chi_1$ which depend on the chemical nature of the polymer network, can be determined from the degree of swelling in pure water, while $x_{21}$ is a parameter which depends on the molar volume of the salt ions[21], and $\nu_e$ which depends on the elastic property of the polymer network, obtained by the stress–elongation experiment.

The information of the chemical potential in the aqueous salt solution give the estimate of the volume fraction of polymer network at equilibrium swelling with various salt concentration.

## Materials and Experimental Methods

The gels of isotactic and syndiotactic P–HEMA were synthesized from commercial 2–hydroxyethyl methacrylate by using U.V. photopolymerization at −40°C and by anionic polymerization, respectively.[15,22] The anionic polymerization requires the blocking of the benzoxyl group on the free hydroxyl of HEMA. Each tactic P–HEMA both have more than 80 % tacticity which was taken from $^{13}C$ n.m.r. spectra.[22,30] These P–HEMA were crosslinked with the desired molar amount of hexamethylene diisocyanate (HMDIC) and the catalyst[23] (dibutyltin dilavrate: $6.6 \times 10^{-5}$ mole/$l$).

In this way, 2.5, 5, 7.5 and 10 mole % crosslinked dense P–HEMA with different tactic precursors were obtained, and were equilibrated in the distilled water for at least one month.

*Water Content of P–HEMA.* The water content of P–HEMA was measured by the direct weighing method. The syndiotactic and isotactic P–HEMA crosslinked with various concentration of HMDIC were dipped into distilled water, until the solvent was perfectly removed. The hydrogel membrane were soaked in various concentrations of each salt solutions and distilled water, and these were placed in a thermostat where the temperature was fixed at 25 ± 0.1 °C for 5 days–the water content of P–HEMA had been almost consistent after 70 hrs [24] The hydrogel was wiped up with bibulous paper carefully, and then immediately put into a weighing bottle which was preweighed its own weight. The weighing bottle was weighed again, then the weight of swollen hydrogel ($W_s$) was obtained.

After then, the hydrogel was placed in a vacuum oven for 3 days, which may be sufficient for the dehydration of the hydrogel, and then the weight of hydrogel ($W_1$) which possessed certain amount of salt was obtained. This hydrogel was dipped into distilled water for 5 days. then the salt was excluded from the hydrogel. This was dehydrated again under vacuum, and the weight of hydrogel ($W_2$) was measured. In this way, the water content of P–HEMA and the molar salt partition coefficient $K_{Dm}$ were determined,

$$\text{Water Content } (\%) = \frac{W_s - W_1}{W_s} \times 100(\%) \quad (19)$$

$$K_{Dm} = \frac{\dfrac{W_1 - W_2}{W_0 - W_1} \times \dfrac{1000}{18}}{C_m^0} \quad (20)$$

where $C_m^0$ is the molar concentration of salt in the solution.

*Stress–Elongation Experiment.* The sample for a stress–elongation experiment was prepared with a proper shape which composed with an elongate section (1.0 cm width and 3.0 cm length) and two gripping sections. The thickness of this sample was measured with a micrometer (Model 549, Testing Machines Inc.) of which the minute sensitivity was 1/1000 inch.

The sample was placed in a thermostat with settled temperature at 25°C after 5 days, the stress–elongation measurement was carried out with an Instron (Model 1127, Instron Inc.).

For this measurement, we used a road cell which maximum sensitivity range was 2KgG, and full range of the chart was 0.2KgG. The crosshead speed and the chart speed were 5mm/min and 50mm/min, respectively. Next, the values of retractive force ($f$) and elongation ($\Delta l$) were converted into stress ($\sigma$) and elongation ratio ($\lambda$), thus we obtained a stress–elongation curve.

$$\sigma = \frac{f}{s} = f/d_1 d_2$$
$$\lambda = l/l_0 = (l + \Delta l)/l_0 \quad (21)$$

where $d_1$, $d_2$ and $s$ are the thickness, width and cross sectional area of the sample, respectively.

*Degree of Swelling on Various Solvent Systems.* For isotactic and syndiotactic P–HEMA, the degree of swelling on various solvent systems was measured by an analogous treatment of the sample such as the measurement of water content. The sample had been perfectly dehydrated under vacuum, and its dry weight had been determined before it was soaked in the solvent. The weight of swollen P–HEMA was determined after 5 days at 25°C, using the same method of measurement for water content.

## Results and Discussion

*Water Content.* The water contents of the gel with various salt concentrations were obtained from the direct weighing methods by Eq. (19). The results are shown in Figures 1 to 4 for the salt effect and Figures 5 to 6 for the crosslinking effect.

The water contents of the crosslinked isotactic and syndio-

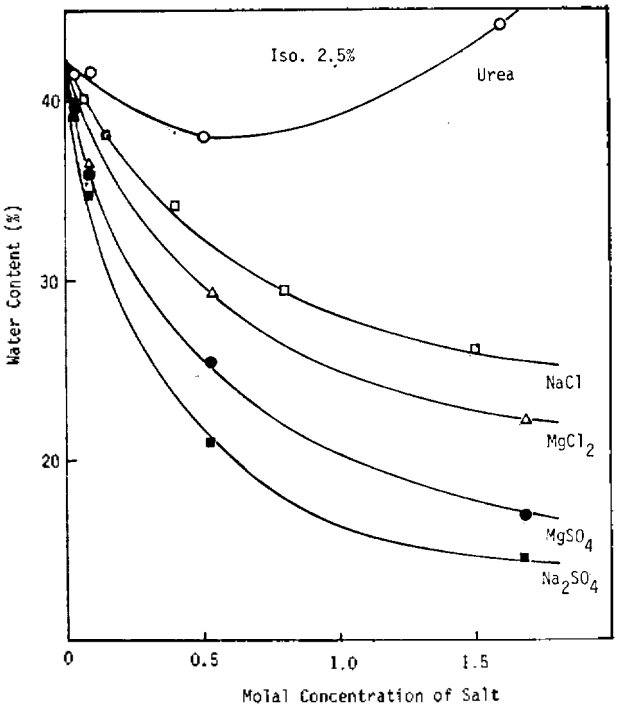


**Figure 1.** The water content of 2.5 % crosslinked isotactic P-HEMA with various salt concentration.

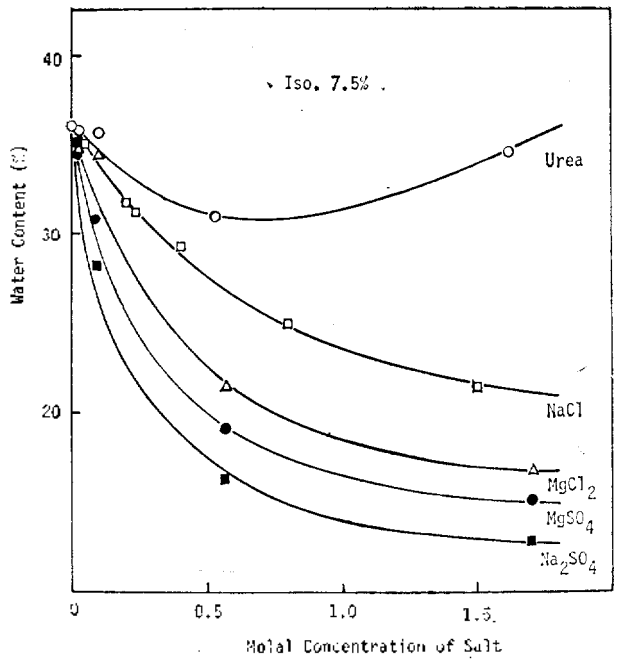


**Figure 2.** The water content of 7.5 % crosslinked isotactic P-HEMA with various salt concentration.

tactic P-HEMA in distilled water are shown in Table 1. These results show that the syndiotactic P-HEMA swells less than the isotactic P-HEMA does, and that as the crosslinking increases, the water content is reduced with a linear correlation to the crosslinker concentrations.

Figure 1 shows the salt effect of 2.5 % crosslinked isotactic P-HEMA. Urea has specific interactions between the gels and the solute molecules. These interactions contribute to the hydrophobic mechanism.[9] In other words, urea is a salting-in

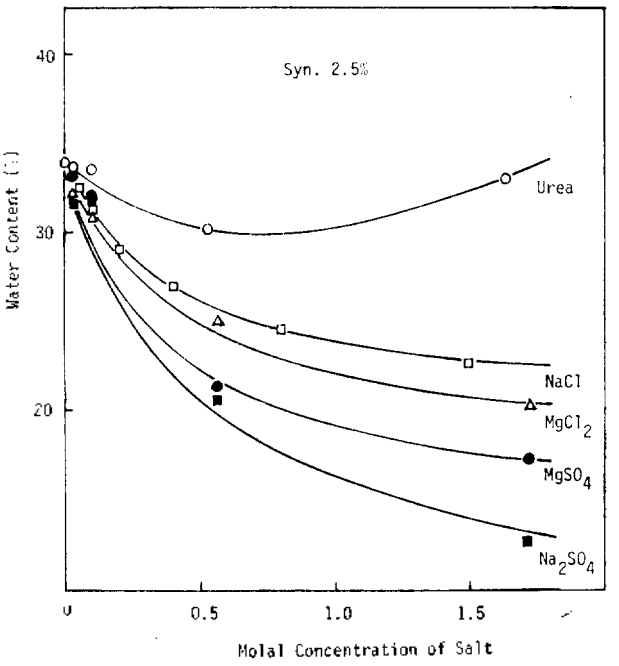


**Figure 3.** The water content of 2.5% crosslinked syndiotactic P-HEMA with various salt concentration.

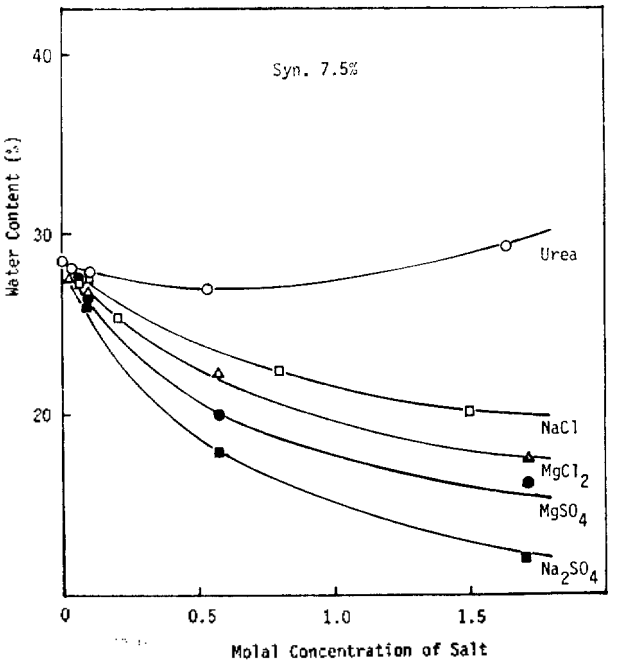


**Figure 4.** The water content of 7.5% crosslinked syndiotactic P-HEMA with various salt concentration.

**TABLE 1: The Water Content of Tactic P-HEMA in Distilled Water with Various Concentration of Crosslinker**

| mole % HMDIC | water content (%) Isotactic | Syndiotactic |
|---|---|---|
| 2.5 | 41.8 | 33.8 |
| 5.0 | 38.9 | 31.1 |
| 7.5 | 36.0 | 28.5 |
| 10.0 | 33.1 | 26.0 |

solute. Other salts except urea, indicate the general salting-out effects (Figure 1 to 6). And salting-out effect becomes greater in the order of NaCl, $MgCl_2$, $MgSO_4$ and $Na_2SO_4$, respectively. It is noted that these are of the same order of increasing molar volume and hydration energy of ions from empirical data.[21]

When the crosslinking increases up to 7.5 % (Figure 2), the whole water contents decrease simultaneously, but other comparisons are shown almost the same tendency with 2.5 % crosslinked gel.

For the syndiotactic P-HEMA (Figure 7 and 8) the same results are obtained when the crosslinking increases.

Figure 5 and 6 show the crosslinking effect on the swelling of tactic P-HEMA. In these cases, the water contents are converted into g water/(g swollen gel-g crosslinker weight) ratio.

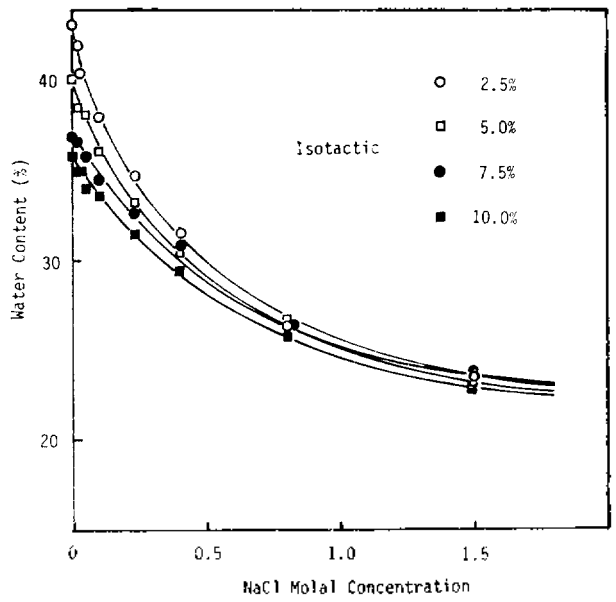


**Figure 5.** The water content of isotactic P-HEMA in NaCl aqueous solution with various concentration of crosslinker.

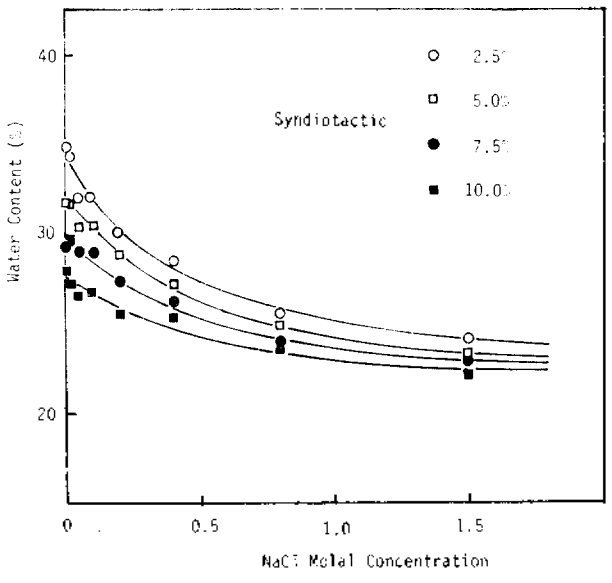


**Figure 6.** The water content of syndiotactic P-HEMA in NaCl aqueous solution with various concentration of crosslinker.

In relatively inert salt solution such as NaCl, the water contents decrease slowly with increasing salt concentration. And the curves are placed at a range of water content more than 20 %. This amount of water content is similar to the experimental data of bound water-like (namely Z water) observed from the dilatometric measurement by Kim *et al.*[15] Their experimental results indicate that the amount of bound water-like were 21 % g weight for isotactic P-HEMA and 19 % g weight for syndiotactic P-HEMA.

Assuming various water structures in the hydrogel, it is noted that the salting-out effect may be strongly contributed from the free water-like more than the bound water-like,

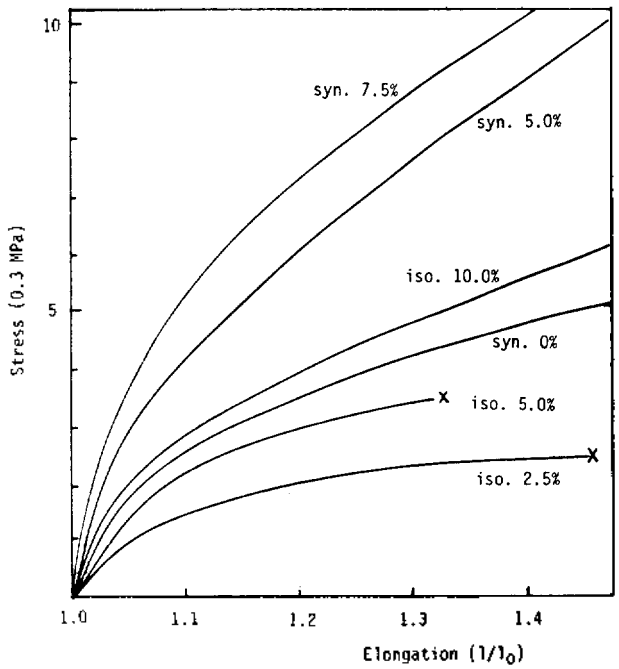


**Figure 7.** The stress-elongation curve of tactic P-HEMA.

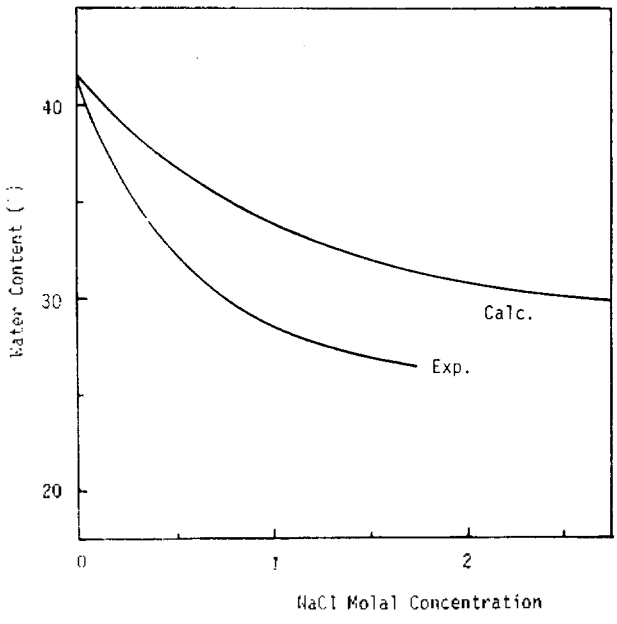


**Figure 8.** Experimental curve and theoretical curve of the water content for 2.5 % crosslinked isotactic P-HEMA.

**TABLE 2: The Molal Salt Partition Coefficient ($K_{Dm}$) of *P*-HEMA**

| Salt | $K_{Dm}$ |
|---|---|
| NaCl | 0.79 |
| KCl | 0.82 |
| $MgCl_2$ | 0.85 |
| $MgSO_4$ | 0.44 |
| $Na_2SO_4$ | 0.40 |
| Urea | 1.54 |

because the bound water-like strongly interacts to the hydrogel network and weakly interacts to the salt ions. Thus, the salting-out effect may depend on the fraction of free water-like. The water content decreases with the increase in the salt concentration. So the fraction of free water-like also decreases, and the salting-out effect becomes smaller.

As shown in Figure 5, the crosslinking effect of isotactic P-HEMA is considered. The difference in water contents with various crosslinker concentrations (2.5 % mole to 10 % mole) is about 7 % in distilled water, but this difference becomes smaller with the increase in the salt concentration. At 1.5 molal concentration of NaCl the difference is about 1.5 % within error limit. From these results, it is considered that the bound water-like fraction of P-HEMA with various crosslinker concentrations may be almost constant. The same result is obtained by Yoon *et. al.* with DSC measurement.[22] For the syndiotactic P-HEMA, the similar crosslinking effect is also obtained (Figure 6).

To obtain the information of salt in the swollen hydrogel, the molal salt partition coefficient is determined by Eq. (20). The results are shown in Table 2. The molar salt partition coefficient of chlorides are roughly 0.8 and those of sulfates are roughly 0.4. Urea is a salting-in solute, therefore this value is more than 1.

*Stress-Elongation Curve.* The stress-elongation curve of tactic P-HEMA is obtained by converting the retractive force into the stress. As shown from the stress-elongation curves of the gels in Figure 7, the mechanical property of these gels increases with the increase of crosslinker concentration. And the syndiotactic P-HEMA has more strong stress than that of the isotactic P-HEMA at the equivalent elongation. This indicates that the syndiotactic P-HEMA has a more physical crosslinked structure than the isotactic P-HEMA does. The conformational difference in stereoregular P-HEMA was already proposed by Kim *et. al.*.[15] For understanding the molecular structures, they had referred to the Russell *et al.*'s CPK® spacefilling molecular models.[25]

From these models, the isotactic and syndiotactic P-HEMA molecules have the following difference. The polar groups in the isotactic chain are all displaced outward from the helical backbone, giving rise to a helix which has a hydrophobic inner surface and hydrophilic outer surface. This hydrophilic outer surface more strongly interact with water and more weakly interact with other chains, therefore the physical crosslinking is reduced. For the case for syndiotactic P-HEMA this effect is not appear where polar and apolar groups are interspersed along the helix.

To evaluate the effective number of chain ($\nu_e$), Eq. (10) was

**TABLE 3: Calculated Values of the Effective Number of Chain ($\nu_e$) per Unit Volume and the Flory-Huggins Interaction Parameter ($\chi_1$) of Tactic P-HEMA**

| Sample | | $\nu_e/v_0(10^{-5}$mole/cm$^3)$ | Volume Swelling (%) | $\chi_1$ |
|---|---|---|---|---|
| iso | 2.5 % | 5.64 | 50.25 | 0.77 |
| | 5.0 % | 8.48 | 46.81 | 0.80 |
| | 10.0 % | 11.02 | 39.39 | 0.88 |
| syn | 5.0 % | 17.24 | 31.51 | 1.00 |
| | 7.5 % | 19.60 | 28.57 | 1.05 |

rewritten as

$$\sigma V_0=\nu_e RT\left\{\lambda_x+\lambda_y+\lambda_z-\frac{C_1}{C_2}\left(\frac{1}{\lambda_x^3}+\frac{1}{\lambda_y^3}+\frac{1}{\lambda_z^3}\right)\right\} \quad (22)$$

where $\lambda_x$, $\lambda_y$ and $\lambda_z$ are the extension ratios of $x$, $y$ and $z$-axis, respectively.

In the stress-elongation experiment, the gel elongates with $x$-axis only, thus $\Delta\sigma$ can be expressed as

$$\begin{aligned}\Delta\sigma V_0&=\sigma V_0-\sigma_0 V_0\\&=\nu_e RT\left\{(\lambda_x-\lambda_x^0)-\frac{C}{C_2}\left(\frac{1}{\lambda_x^3}-\frac{1}{\lambda_x^{0\,3}}\right)\right\}\end{aligned} \quad (23)$$

where $\Delta\sigma$ is the observed stress, $\sigma_0$ is the hypothetical stress which originates from swollen network, and $\lambda_0$ is the extension ratio of swollen network which may be expressed as $\lambda_0^3=1/v_{2m}$, and $C_1/C_2=5/7$ is adjustable in the case of hydrogel.[26] The density of this swollen gel is obtained as 1.2g/cm$^3\pm$0.01 and is constant in all the gels. Therefore we can determine $v_{2m}$, and $\lambda_0$ from the values of water content in distilled water (Table 1). Table 3 shows the calculated results of the effective number of chain from Eq. (23).

The Flory-Huggins interaction parameter ($\chi_1$) can be calculated from Eqs. (5) and (11), the result is shown in Table 3 . According to the result, the Flory-Huggins interaction parameters of isotactic P-HEMA are smaller than those of syndiotactic P-HEMA because of its hydrophilic nature:

*Extended Flory-Huggins Equation.* The evaluated Flory-Huggins interaction parameter ($\chi_1$), the effective number of chain and the molar salt partition coefficient are utilized in the following argument. Eq. (18) is solved to get water content in P-HEMA gel versus NaCl molal concentration using the literature data of water activity in NaCl solution.[27] The result shows the trend of salting-out effect in Figure 8.

*Degree of Swelling on Various Solvent Systems.* The degree of swelling is determined using Eq. (19) with various solubility parameters of solvent,[28] using 5 % mole crosslinked tactic P-HEMA. As shown in Table 4, relatively nonpolar solvents have lower degree of swelling in both cases of isotactic and syndiotactic P-HEMA, and polar solvents have higher degree of swelling on the gels. The most effective solvents of isotactic P-HEMA are ethylene diamine and N, N-dimethyl formamide, and that of syndiotactic P-HEMA is N, N-dimethyl acetamide.

The solubility parameter of polymer may be estimated by using the group contributions of cohesive energy ($E_i$) and molar volume ($V_i$) thus,

**TABLE 4: The Degree of Swelling on 5 % Mole Crosslinked Tactic P-HEMA with Various Solubility Parameters ($\delta_1$) of Solvents**

| Solvent | $\delta_1$(cal/cm$^3$)$^{1/2}$ | Isotactic | Syndiotactic |
|---|---|---|---|
| n-hexane | 7.3 | 1.10 | 1.10 |
| cyclohexane | 8.2 | 1.06 | 1.09 |
| toluene | 8.9 | 1.22 | 1.16 |
| chloroform | 9.3 | 1.53 | 1.36 |
| methylene chloride | 9.7 | 1.39 | 1.34 |
| acetone | 9.9 | 1.42 | 1.39 |
| 1, 4-dioxane | 10.0 | 2.01 | 1.97 |
| tert-butyl alcohol | 10.6 | 3.86 | 3.32 |
| N, N-dimethyl acetamide | 10.8 | 5.43 | 6.28 |
| EGMME* | 11.4 | 5.14 | 4.64 |
| acrylic acid | 12.0 | 5.27 | 4.26 |
| N, N-dimethyl formamide | 12.1 | 5.90 | 5.11 |
| ethylene diamine | 12.3 | 6.32 | 5.33 |
| formamide | 19.2 | 4.93 | 5.31 |
| water | 23.4 | 1.63 | 1.45 |
| THF | 9.1 | 3.84 | 3.38 |
| furfural | 11.2 | 1.97 | 1.71 |
| acetonitrile | 11.9 | 1.27 | 1.30 |

*ethylene glycol monomethyl ether

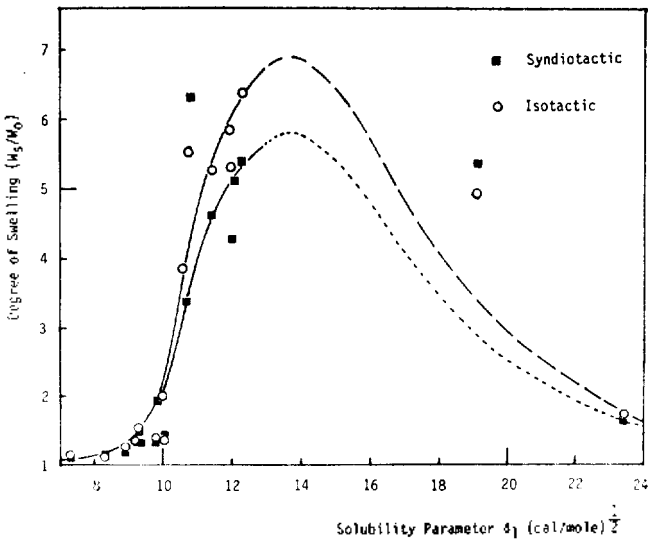


**Figure 9.** The degree of swelling on 5 % mole crosslinked tactic P-HEMA as a function of the solubility parameters of solvent.

$$\delta = \left(\frac{\sum E_i}{\sum V_i}\right) \tag{24}$$

For P-HEMA, $\sum E_i$=68,340 $J$ and $\sum V_i$=90.6 cm$^3$.[29] The solubility parameter of P-HEMA is determined as 13.43 (cal/mole)$^{1/2}$ This result is in good agreement with experimental result of swelling (Figure 9).

The concept of solubility parameter is adequate only in the case of non polar systems. However, P-HEMA is considerably a polar material, and therefore the concept is not applicable to the upper range over the maximum swelling as shown in Figure 9.

The difference in solubility parameters between isotactic and syndiotactic P-HEMA is not found in this swelling experiment.

## Conclusions

The swelling and the mechanical properties of hydrogels of tactic P-HEMA have been dealt on the basis of experimental results of water content, stress-elongation curve, and degrees of swelling.

From the water content in these gels and the stress-elongation curve, we have verified the consideration of the structure of tactic P-HEMA that the isotactic P-HEMA is more hydrophilic than syndiotactic P-HEMA because of their conformational effect.

The major purpose of the present work is to study the swelling phenomena of the gels in salt solutions. To explain these phenomena, the followings are obtained; the Flory-Huggins interaction parameter, the effective number of chain for the information of polymer network and water in the hydrogel, and the molal partition coefficient for the information of salt.

The Flory-Huggins equation of swelling is extended in inert salt solutions, however, this is not sufficient for experimental data.

It is also found that the water content decreases with increasing crosslinker concentration and that the mechanical properties increase accordingly.

In addition, to see the solvent effect of swelling, the degree of swelling is measured with varying solubility parameters.

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# Homogeneous Catalysis (IV). Hydrogenation of Acrylonitrile with *trans*-Chlorocarbonylbis(triphenylphosphine)rhodium(I)

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It has been found that the acrylonitrile solution of *trans*-$RhCl(CO)(Ph_3P)_2$ produces propionitrile catalytically at 90°C under $P_{H_2}=3$ atm. This catalytic hydrogenation proceeds only for a certain period of time producing *ca.* 50 moles of propionitrile per mole of the rhodium complex. The hydrogenation with *trans*-$RhCl(CO)(Ph_3P)_2$ in the presence of formaldehyde is much faster than in the absence of formaldehyde, and continues without a decrease in the rate for a prolonged period of time. It is suggested that the hydrogenation with *trans*-$RhCl(CO)(Ph_3P)_2$ proceeds through the unsaturated route initiated by the dissociation of CO from *trans*- $RhCl(CO)(Ph_3P)_2$ to give coordinatively unsaturated $RhCl(Ph_3P)_2$.

We recently reported the catalytic hydrogenation of acrylonitrile to propionitrile by a four coordinated iridium complex, *trans*-$IrCl(CO)(Ph_3P)_2$ ($Ph_3P$ = triphenylphosphine) at 80°C under hydrogen ($P_{H_2}=3$ atm.).[1] We have subsequently become interested in the catalytic hydrogenation by the rhodium analog, *trans*-$RhCl(CO)(Ph_3P)_2$(**1**)[2]. In general, rhodium complexes are more active for the catalytic hydrogenation of olefins than the corresponding iridium complexes.[3] It is well established that the hydrogenation of an olefin with Wilkinson's catalyst, $RhCl(Ph_3P)_3$ (**1**) proceeds *via* two different routes, so-called the hydride route (eq. 1) and the unsaturated route (eq. 2), both of which involve the formation of the six coordinated dihydridoolefinrhodium(III) complex, $RhClH_2(olefin)(Ph_3P)_2$.[4-8] The intermediate ($RhClH_2(olefin)(Ph_3P)_2$) undergoes the intramolecular olefin insertion reaction into Rh-H bond to give the five coordinated RhClH (alkyl) $(Ph_3P)_2$ which finally produces alkane and the three coordinated intermediate $RhCl(Ph_3P)_2$(**3**) back into the catalytic cycle.[4-8] No investigation has been reported for the

$$RhCl(Ph_3P)_3 \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} RhClH_2(Ph_3P)_3 \underset{Ph_3P}{\overset{-Ph_3P}{\rightleftharpoons}}$$

**2**

$$RhClH_2(Ph_3P)_2 \underset{-olefin}{\overset{olefin}{\rightleftharpoons}} RhClH_2(olefin)(Ph_3P)_2 \qquad (1)$$

$$RhCl(Ph_3P)_3 \underset{Ph_3P}{\overset{-Ph_3P}{\rightleftharpoons}} RhCl(Ph_3P)_2 \underset{-olefin}{\overset{olefin}{\rightleftharpoons}}$$

2 **3**

$$RhCl(olefin)(Ph_3P)_2 \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} RhClH_2(olefin)(Ph_3P)_2 \qquad (2)$$

catalytic hydrogenation of olefins with **1** where a CO is coordinated in the place of a triphenylphosphine in **2**. It would be interesting to compare the catalytic activity of **1** with that of **2** with respect to the rate of hydrogenation as well as the reaction pathways.

In this article, we wish to describe the catalytic hydrogenation of acrylonitrile with **1** and suggest a reaction route. It has been found that the acrylonitrile solution of **1** under hy-