CHAPTER 12

HIGH-SWELLING MODIFIED PVAL FILMS

Crosslinked films showing highly swelling property in water have been prepared from modified PVALs containing crosslinkable and ionic groups. The modified PVALs were synthesized by the alcoholysis of ternary copolymers made from vinyl acetate, N-(n-butoxymethyl) acrylamide as a crosslinkable monomer and ionic monomers like maleic anhydride, acrylic acid, sodium 2-acrylamide-2-methyl propane sulfonate and trimethyl-(3-methacrylamidopropyl)ammonium chloride. Using the aqueous solution of the modified poly(vinyl alcohol)s and small amount of ammonium chloride as a curing initiator, film has been made and heat-treated for forming crosslinkage. The crosslinked film shows highly swelling degrees, about 400 in distilled water and about 60 in 0.1M sodium chloride aqueous solution depending on the combination of the contents of linkage and ionic group. Theoretical calculation has also been carried out for obtaining volumetric swelling degree of polyelectrolyte gels. Most of the observed data have been regarded as almost consistent with theoretical calculation results, and thus the theoretical calculation can be used as a tool for designing the high-swelling materials.

12.1 INTRODUCTION

In Part B of this thesis, functional modification of PVAL with ionic groups like sodium carboxylate,[1] sodium sulfonate[2] and cationic groups[3] by copolymerization method has been reported. Self-crosslinkable PVAL [4,5] has also been reported by copolymerization of N-(n-butoxymethyl) acrylamide (BMAM) as a crosslinkable monomer. The experimental results on crosslinked films made thereof have been compared with the theories of gel formation and swelling. In the present chapter, modified PVALs containing both the functional groups, ionic and self-crosslinkable, have been synthesized for the purpose of

obtaining novel PVALs which can be convert to film and fiber showing highly swelling ability.

Now several polymer materials are known to show showing highly swelling property. Typical ones are crosslinked poly(sodium acrylate) and graft-type copolymer of starch and poly(sodium acrylate) They have extensively been developed as water absorbent used for applications like diaper, sealing and planting in these two decades. Most products are produced as powder although highly swelling materials as fiber have been known like alkali hydrolysis products of acrylonitrile fiber and carboxymethylated products of cellulose fiber. There have been little known film type products as high- swelling materials, which are shown in this chapter. High- swelling materials based on PVAL are also known, such as graft type copolymers of PVAL with poly(sodium acrylate), and poly(vinyl alcohol-co-sodium maleate) crosslinked. Both the products can be supplied only as powder because they can not be convert to film or fiber.

In this work, experimental observation has been reported for the swelling behavior of crosslinked film. Next, theoretical calculation has also been carried out regarding swelling. This calculation is based on the theories presented by Flory,[6] Katchalsky and Michaeli,[7] Hasa, Ilavsk and Dusek,[8] and Ilavský.[9] Similar comparisons of experiment with theory for polyelectrolyte gels have already been reported before in the literature concerning poly(methacrylic acid),[7,10-12] poly(acrylic acid)[13] or acrylamide[14-18] crosslinked with divinyl monomers: these hydrogels reported so far were prepared from the polymer crosslinked in copolymerization process. In contrast, crosslinking is formed under solid state in the present case of modified PVALs.

12.2 EXPERIMENTAL

12.2.1 Modified PVAL

The modified PVALs containing 0.05 to 0.5 mol% of BMAM units and 3 to 20 mol% of ionic monomer units were synthesized. As ionic comonomers, maleic anhydride(MAn), acrylic acid(AA), sodium 2-acrylamide-2-methyl propane sulfonate (SAMPS) and trimethyl-(3-methacrylamidopropyl)ammonium chloride (QAPM) were used. In order to obtain copolymers having homogeneous composition in the ternary copolymerization of semi-batch process, more reactive monomers in copolymerization, BMAM and ionic monomer, were supplied continuously during copolymerization and the supply speed was regulated

according to the solid content analyzed occasionally.[19] ^{1}H NMR spectra were obtained by Varian EN-390 and used for the determination of the degree of hydrolysis (DH) from residual acetyl units in the modified PVAL. Viscosity of 4 wt% aqueous solution was measured using a Brookfield viscometer at 20℃. Data of copolymerization and analytical data of the modified PVAL obtained are summarized in Table 31.

12.2.2 Crosslinked film

Crosslinked film (50 μ thick) was prepared from the modified PVAL in the following manner. The aqueous solution of the modified PVAL (about 10 wt%) was mixed with the aqueous solution of ammonium chloride at the amount of 2.0 g/100g-polymer, casted on a rotating drum at 75℃. The film thus obtained was heat-treated or cured for crosslinking at 150℃ for 15 min inside an electric oven equipped with a safeguard against explosion.

12.2.3 Swelling degree and sol fraction

The crosslinked film of 0.1 to 1 g weighted precisely was immersed in distilled water or in 0.1 M sodium chloride aqueous solution at 27℃ for one hour and took out.. It had been observed that hydrogels were swollen to equilibrium within ten minutes. The insoluble film filtered off and weighed. Volumetric swelling degree, q_v was obtained using the observed data on W_0 = weight of primary crosslinked film including sol, W_w = weight of swollen film and s = sol fraction.

$$q_v \equiv V''_w / V''_0 = \left[W''_0 / d_0 + \left(W_w - W''_0 \right) / d_{H_2O} \right] / W''_0 / d_0$$
$$= \left[W_w - W_0(1-s) + W_0(1-s) / d_w \right] / \left[W_0(1-s) / d_0 \right] \tag{1}$$
$$W''_0 = W_0 (1 - s) \tag{2}$$

where V''_w = volume of swollen gel (not including sol), V''_0 = volume of primary crosslinked film not including sol, W''_0 = weight of primary crosslinked film not including sol, d_0 = density of primary crosslinked film, d_w = density of polymer in swollen state, d_{H2O} = density of water (≒ 1). The values, $d_0 = 1.29$ (ϕ_x= 29%) and $d_w = 1.269$ (ϕ_x= 0%) were approximately assumed from the values for PVAL homopolymer in the literature, [20-22] where ϕ_x is the volume fraction of crystallinity. In the above equation, additivity on volume in mixing is assumed.

The sol fraction was measured by the difference of weight between original sample and dry gel after immersion in water. The observed data are summarized in Table 31.

12.3 THEORETICAL CALCULATION OF SWELLING DEGREE FOR
POLYELECTROLYTE GEL

The computer program was made for calculating volumetric swelling degree, q_v, of a polyelectrolyte gel from the input data of crosslinking density (ρ")[23] of the gel, the mole fraction of ionic group of the polyelectrolyte (α) and the concentration of salt in the solution (C_s^*). Swelling properties of polyelectrolyte gel are theoretically determined by the six types of swelling pressures classified as ϕ_{MIX} to ϕ_{E_S}, and the sum of them should be zero at equillibrium.[6-9]

Swelling pressure: $P = \phi_{MIX} + \phi_{OSM} + \phi_{C\_G} + \phi_{C\_NG} + \phi_{E\_PN} + \phi_{E\_SP}$ (3)

   $P = 0$ at equilibrium   (4)

The swelling pressures can be formulated using the mole fraction of the polymer in swollen gel, v_2, which is equal to the reciprocal of swelling degree.

$$v_2 = q_v^{-1} \tag{5}$$

12.3.1 Mixing ϕ_{MIX}: The pressure due to the mixing of polymer with solvent can be express as Flory-Huggins equation.[6] ϕ_{MIX} favors swelling of the gels.

$$\phi_{MIX} = -\frac{RT}{V_1}\left\{\ell n(1-v_2) + v_2 + \chi \cdot v_2^2\right\} \tag{6}$$

where R is the gas constant, T is temperature, V_1 is the molar volume of the solvent and χ is the polymer-solvent interaction parameter. Concentration dependence of χ is empirically be assumed as a linear function of v_2.[24-26]

$$\chi = \chi_0(1-v_2) + v_2 \cdot \chi_1 \tag{7}$$

where χ_0: χ at $v_2 = 0$, χ_1: χ at $v_2 = 1$

12.3.2 Osmotic Pressure ϕ_{OSM}: Osmotic pressure due to the difference of the concentration of ion between gel and solution. ϕ_{OSM} favors swelling.

a) Osmotic pressure can be expressed as

$$\phi_{OSM} = RT\left[i \cdot d \cdot v_2 / M_0 + 2f^*(C_s - K \cdot C_s^*)\right] \tag{8}$$

where $i = \phi\,\alpha$ (9)

ϕ　：Degree of dissociation

α　：The mole fraction of ionic group in polyelectrolyte

d　：Density of polymer　　(1.269 in case of PVAL at no crystallinity)

M_0：Molecular weight of monomer unit　(44.1 for PVAL)

C_s　：Concentration of salt inside gel

C_s^*　：Concentration of salt outside gel, or in solution

$K = f / f^*$

f　：Activity coefficient of salt inside gel

f^*　：Activity coefficient of salt outside gel, or in solution

b) Donnan's equilibrium equation showing the electric neutrality in the system is described below and gives the relationship between C_s and C_s^*.

$$C_s = \left[(i \cdot d \cdot v_2 / 2M_0)^2 + \left(K \cdot C_s^* \right)^2 \right]^{1/2} - i \cdot d \cdot v_2 / 2M_0 \tag{10}$$

c) Ion binding effects

It has been known that there is an effects that the degree of dissociation, ϕ in *Equation* (9) decreases with increasing ionic group in gels even for ionic group of strong electrolytes. The effects have been explained by condensation theory,[27] and theoretical equations have been presented.[28,29] In the present calculation, the following empirical equations proposed by Oosawa[30] are adopted due to its simplified expression:

$\phi = 1 - \lambda / 2$　　　　when $0 \leqq \lambda \leqq 1$　　　　　　　　　　(11)

$\phi = 1 / 2\lambda$　　　　　when $1 < \lambda$　　　　　　　　　　　　(12)

where

$\lambda = \alpha \ \varepsilon^2 / D\, b_0\, k\, T$　　　　　　　　　　　　　　　　(13)

　　　D　　　：Dielectric constant

　　　b$_0$　　：The length of a monometric unit

　　　ε　　：Elementary charge

12.3.3　Configurational Elasticity ϕ_C：Configurational elasticity effects has been divided into Gaussian, ϕ_{C_G}, and non-Gaussian contributions, ϕ_{C_NG}.[8,9, 31] ϕ_C favors deswelling.

$\phi_C = \phi_{C\_G} + \phi_{C\_NG}$　　　　　　　　　　　　　　　　(14)

$$\phi_{C\_G} = -v_d RT \left\{ v_2^{1/3} <\alpha_0^2> -v_2 / 2 \right\} \tag{15}$$

$$\phi_{C\_NG} = -v_d RT \left\{ \frac{3}{5} < \alpha_0^2 > v_2^{-1/3} n^{-1} + \frac{99}{175} < \alpha_0^2 >^3 v_2^{-1} n^{-2} + \frac{513}{875} < \alpha_0^2 >^4 v_2^{-3/5} n^{-3} \right\}$$

(16)

12.3.4 Electrostatic Interaction ϕ_E : Electrostatic interaction term has been divided into polyelectrolyte network term, ϕ_{E_PN} , and small ion-polyelectrolyte term, ϕ_{E_SP} : the latter is from the electrostatic interaction between the small ions and the polyelectrolytes and favors deswelling while the former is from the repulsive forces among the fixed charges on polyelectrolyte network and favors swelling.[7]

$$\phi_E = \phi_{E\_PN} + \phi_{E\_SP}$$

(17)

$$\phi_{E\_PN} = -\frac{v_d NZi^2 \varepsilon^2 v_2^{4/3}}{3D(h_0^2 < \alpha_0^2 >)^{1/2}} \left\{ \frac{\overline{A}}{1+\overline{A}} - \ell n(1 + \overline{A}) \right\}$$

(18)

$$\phi_{E\_SP} = -\frac{v_d NZi^2 \varepsilon^2 v_2^{4/3}}{2D(h_0^2 < \alpha_0^2 >)^{1/2}} \left\{ \frac{\overline{A}}{1+\overline{A}} \right\}$$

(19)

$$\overline{A} = \frac{6 < \alpha_0^2 >^{1/2}}{h_0} v^{-1/3} \kappa^{-1}$$

(20)

$$\kappa^{-1} = \left[\frac{DkT}{8\pi\varepsilon^2 N(\frac{id}{2M_0} v_2 + fC_s)} \right]^{1/2}$$

(21)

$$Z = 1 / \rho''$$

(22)

$$\overline{h_0^2} = Z\sigma b_0^2$$

(23)

where

σ : The number of monomers per statistical segment in the chain

N: Avogadro Number

It is assumed that σ is built linearly from the contributions of unionized and ionized

groups.[32]

$$\sigma = (1 - i) \cdot \sigma_0 + i \cdot \sigma_i \tag{24}$$

where σ_0 and σ_i are empirical constants characteristics of the unionized and ionized groups.
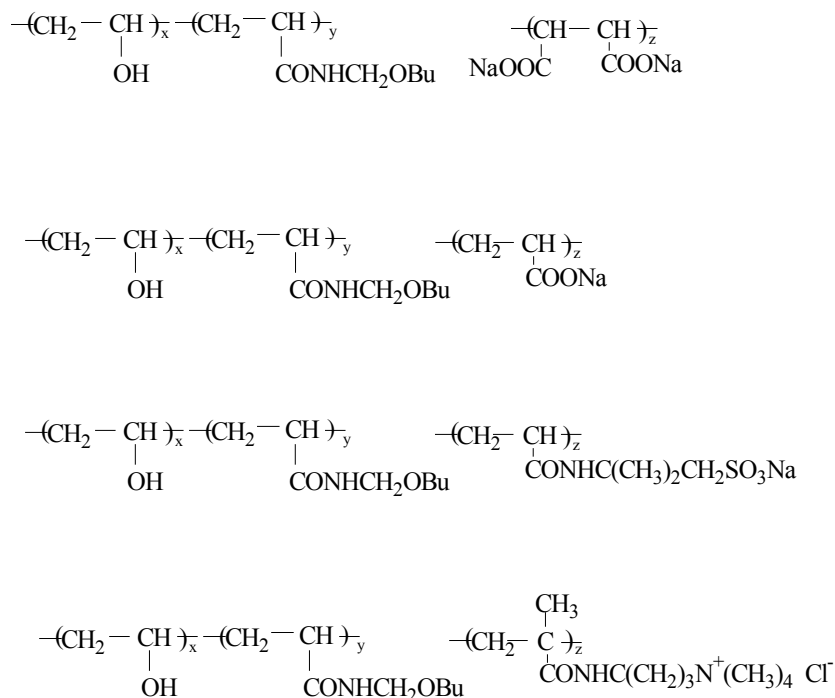
12.3.5 Numerical Calculation

The above equations were solved using BASIC program. The scheme of calculation is shown below.

1) Input data:

ρ'' :	Crosslinking density of gel
α :	The mole fraction of ionic group in gel
C^* :	Concentration of salt in solution
$\overline{P_w}$:	Weight-average degree of polymerization

2) Constants used

T = 300.15 (27℃); v_1 =18.1, D =80, M_0 = 44.1, d = 1.293

$f = 1$, K = 1 , $<\alpha_0^2> = 1$, $b_0 = 2.55$ (Å) , $\sigma_0 = 3$,

$\sigma_1 = 10$, $\chi_0 = 0.494$, $\chi_1 = 0.9$,

3) Output data q_v :   Volumetric swelling degree of gel

12.4 RESULTS AND DISCUSSION

12.4.1 Modified PVAL

In order to obtain copolymers having homogeneous composition of monomer ratio at higher conversions, terpolymerization of VAc, BMAM and ionic monomers has been carried out using "the feeding-comonomer method", where more reactive BMAM and ionic monomers were continuously added to the reaction system. The balance amount of comonomers was determined from the monomer reactivity ratios and from the solid content analyzed occasionally. Under the usual conditions of alcoholysis procedures, modified PVALs have been obtained as dried powder. They show good solubility in water. The results of synthesis are shown in Table 31: comonomers used for modification, feed amount in copolymerization, reaction time, conversion, DH and viscosity of aqueous solution. Consequently the modified PVALs having the following chemical formula are obtained as new water-soluble polymers.

$$\text{+(CH}_2-\underset{\underset{OH}{|}}{CH})_x\text{+(CH}_2-\underset{\underset{CONHCH_2OBu}{|}}{CH})_y \qquad \text{+(CH}-CH)_z\text{+} \atop \underset{NaOOC \quad COONa}{}$$

$$\text{+(CH}_2-\underset{\underset{OH}{|}}{CH})_x\text{+(CH}_2-\underset{\underset{CONHCH_2OBu}{|}}{CH})_y \qquad \text{+(CH}_2-\underset{\underset{COONa}{|}}{CH})_z\text{+}$$

$$\text{+(CH}_2-\underset{\underset{OH}{|}}{CH})_x\text{+(CH}_2-\underset{\underset{CONHCH_2OBu}{|}}{CH})_y \qquad \text{+(CH}_2-\underset{\underset{CONHC(CH_3)_2CH_2SO_3Na}{|}}{CH})_z\text{+}$$

$$\text{+(CH}_2-\underset{\underset{OH}{|}}{CH})_x\text{+(CH}_2-\underset{\underset{CONHCH_2OBu}{|}}{CH})_y \qquad \text{+(CH}_2-\underset{\underset{CONHC(CH_2)_3N^+(CH_3)_4}{\overset{\overset{CH_3}{|}}{|}}}{C})_z\text{+ Cl}^-$$

12.4.2 High-Swelling Films

Observed data for the sol fraction, s, and the volumetric swelling degree for crosslinked film from the modified PVALs are shown in Table 31. Sol fraction shows 8 to 56%. It increases with the decrease of crosslinks. Quantitative discussion has already been in the preceding chapter. The network formation theory shown there predicts that the polymer with $\overline{P_w}$ of 2000 and including crosslinks of 0.1 mol% or crosslinking density, ρ, of 0.002 gives sol fraction of 12.1 wt%. In the present experiment for the six samples of modified PVAL containing BMAM of 0.1 mol%, the figures of sol fraction are distributed from 18 to 40 wt%. The difference from the theoretical value and the distribution of experimental values must mainly be from experimental error because it is comparatively difficult to collect all the gel due to its weakness.

The volumetric swelling degree, q_v, shows 36 to 418 in distilled water and 13 to 38 in 0.1M sodium chloride aqueous solution. The crosslinking density, ρ, in total system is assumed here as the double of the mole fraction of BMAM units in the modified PVAL,

although it has been known that some part of BMAM units does not contribute crosslinking due to decomposition to lactone.[4] In Table 31, the figures of crosslinking density, ρ ", of gel part are shown using the following equation:[5,33]

$$\rho '' = (1 + s) \cdot 2 \ \rho = (1 + s) \cdot 2 \triangle / 100$$

where $\triangle$ stands for the mole % of BMAM for the original samples of the modified PVAL.

12.4.3 Theoretical Calculation on Swelling

Based on the theory described above, calculation has been carried out concerning swelling degree of gels. Figure 66-(a) shows the relationship between volumetric swelling degree of gel, q_v, and the mole fraction of ionic group in gels, α, using crosslinking density of gels, ρ", as a parameter when the gels are immersed in distilled water. Figure 66-(b) shows similar relationship for gel immersed in 0.1M sodium chloride aqueous solution. In the former figure, highly swelling degrees, about 100 to 3000, are predicted for the gels of α =0.1 and ρ " = 0.004 to 0.001. It has been also predicted that the swelling degree almost saturates above α =0.2. The decrease of swelling degree of gel when it is immersed in aqueous solution of salt is shown in the latter figure. In this case, swelling degrees, 20 to 150, are predicted for the gels of α =0.1 and ρ " = 0.004 to 0.001.

Observed data are plotted for comparison in the two figures, and most of them are regarded as almost consistent with theoretical values. Thus the theoretical calculation can be used as a tool for designing the present high-swelling materials. A comparatively clear difference between observed and theoretical values is observed for the case of the PVAL modified with acrylic acid, Sample No. 5, in 0.1M sodium chloride aqueous solution: the observed value show much lower than the theoretical one. At present the reason has not yet been explained.

Figure 67 shows the same calculation results as Figure 66-(a) by different expression: the relationship between volumetric swelling degree of gel, q_v, and crosslinking density of gel, ρ", in distilled water using the mole fraction of ionic group in gel, α, as a parameter. Observed data are also plotted.

Figure 68 shows the calculation results showing the effects of the concentration of salt on swelling degree for the gel having the crosslinking density of 0.001. It can be predicted that higher salt concentration like 1M cramps the activity of ionic group on swelling phenomenon. Figure 69 shows the calculation results showing the effects of the

concentration of salt on swelling degree for the gel having the mole fraction of ionic group of 0.2 or 20 mol%.

The effects of weight-average polymerization degree of the polymer before crosslinking on swelling degree are shown in Figure 70. The polymer of the lower polymerization degree results in the higher swelling degree. On the other hand, it is necessary to consider that the starting polymer of the lower polymerization degree shows the higher sol fraction from the point of practical point of view for applications.

Figure 71 shows the contribution of six types of swelling pressures, ϕ, at various concentrations of salt. It is understood that osmotic pressure, ϕ_{OSM}, and non-Gaussian elasticity, $-\phi_{C\_NG}$, are main factors determining swelling in distilled water. With increasing the concentration of salt, the contribution of mechanical factor, ϕ_{E_PN}, Gaussian elasticity, $-\phi_{C\_G}$, and electrostatic factor, $-\phi_{E\_SP}$, increases.

Table 31 Syntheses of highly swelling poly(vinyl alcohol)s containing crosslinkage and ionic group: copolymerization of vinyl acetate (VAc), N-(n-butoxymethyl) acrylamide (BMAM) and ionic comonomers, modified PVAL by the hydrolysis of the copolymer, and crosslinked PVAL.

Sample No.	Comonomer[1]	Mole fraction of Comonomers in PVAL	VAc	Comonomer[2] Initial/Additional	Methanol Initial/Additional	AIBN[3]	Reaction time min	Conversion of VAc mol%	DH[4] mol%	η[5] (4 wt%) cP	Sol fraction[6] wt%	Swelling degree q_v in distilled water	Swelling degree q_v in 0.1M NaCl	Crosslinking density of gel ρ[7]
1	BMAM / MAn	0.5 / 6	1000	1.0/5.2 / 5.6/39.6	178/45	3.0	180	57.1	91.7	37.0	8	86	13	0.013
2	BMAM / MAn	0.2 / 6	1000	0.4/2.0 / 5.6/39.6	178/42	3.0	165	60.4	92.6	52.0	28	149	82	0.0067
3	BMAM / MAn	0.1 / 3	1000	0.2/1.0 / 2.8/19.2	178/20	3.0	160	62.7	95.8	43.4	18	94	18	0.0024
4	BMAM / MAn	0.1 / 6	1000	0.2/1.0 / 5.6/39.2	178/40	10.0	110	69.7	93.3	27.1	36	146	59	0.0027
5	BMAM / AA	0.1 / 20	1000	0.2/1.0 / 4/75	112/8	0.6	195	35.9	96.0	48.0	27	418	17	0.0025
6	BMAM / SAMPS	0.1 / 3	1000	0.2/1.0 / 4.4/38.3	177/0	3.0	55	55.9	98.8	38.0	33	143	58	0.0027
7	BMAM / SAMPS	0.1 / 6	1000	0.2/1.0 / 8.8/87.6	252/238	1.4	120	57.3	98.2	26.0	40	200	22	0.0028
8	BMAM / SAMPS	0.05 / 3	1000	0.092/0.4 / 4.2/38.3	177/104	1.4	80	52.9	98.0	48.0	56	389	57	0.0015
9	BMAM / QAPM	0.1 / 5	1000	0.2/0.8 / 12/60	252/25	4.8	230	57.4	98.1	25.7	22	96	23	0.0024

[1] MAn: Maleic anhydride; AA: Acrylic acid; SAMPS: Sodium 2-acrylamide-2-methylpropane sulfonate; QAPM: Trimethyl-(3-methacrylamidopropyl)ammonium chloride
[2] Upper: BMAM; Lower: Ionic monomer [3] Azobisisobutylonitrile [4] Degree of hydrolysis of VAc units [5] Viscosity of 4 wt% aqueous solution at 20°C. [6] $100 \cdot s$.
[7] Calculated from ρ[7] $= (1+s) \cdot 2A_{...}/100$.

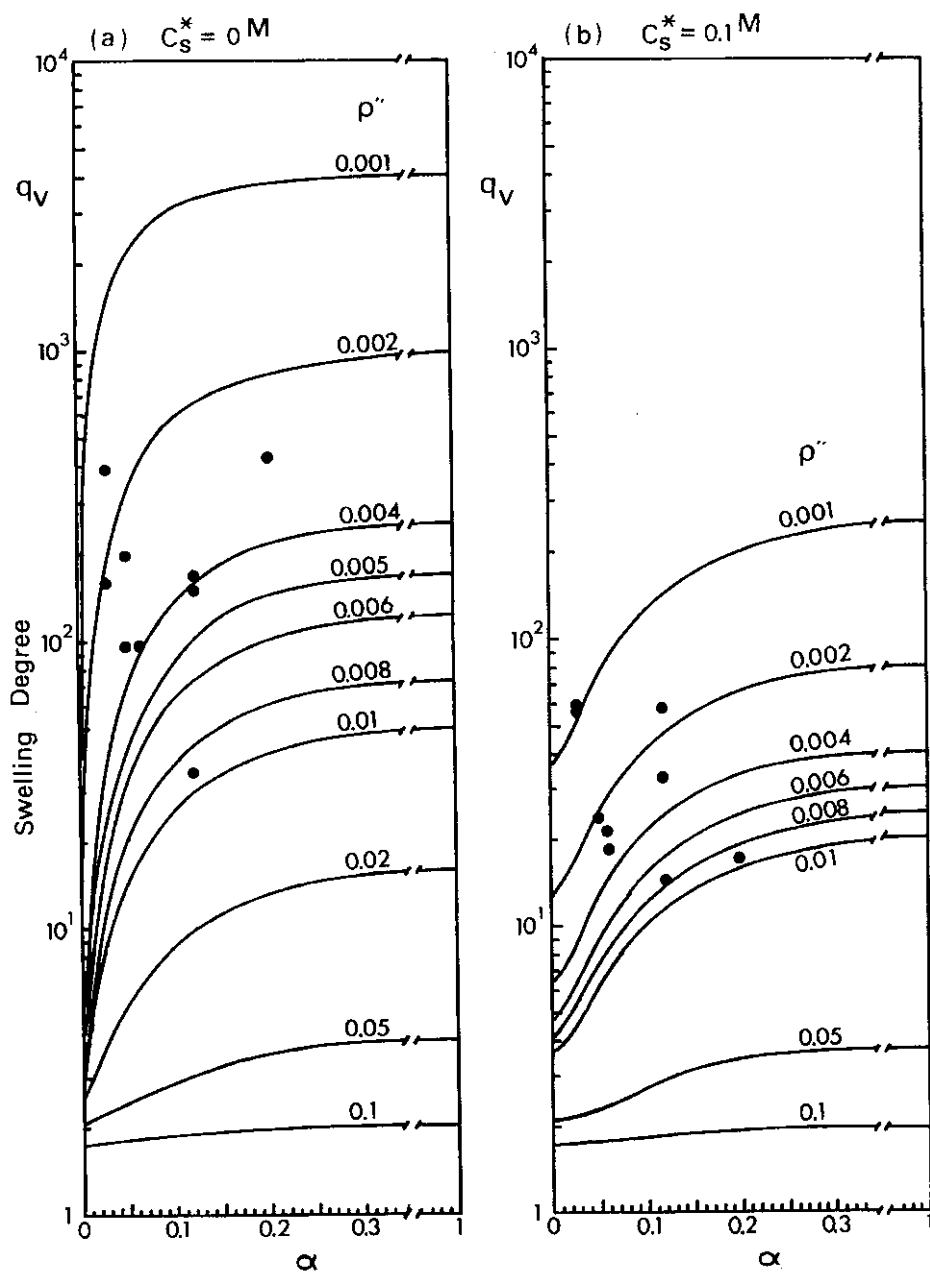**Figure 67** The relationship between volumetric swelling degree of polyelectrolyte gel, q_v, and the mole fraction of ionic group in gel, α, using crosslinking density of gel, ρ ", as a parameter. (a) in distilled water. (b) in 0.1M sodium chloride aqueous solution. Plotted are the observed data for the modified poly(vinyl alcohol).
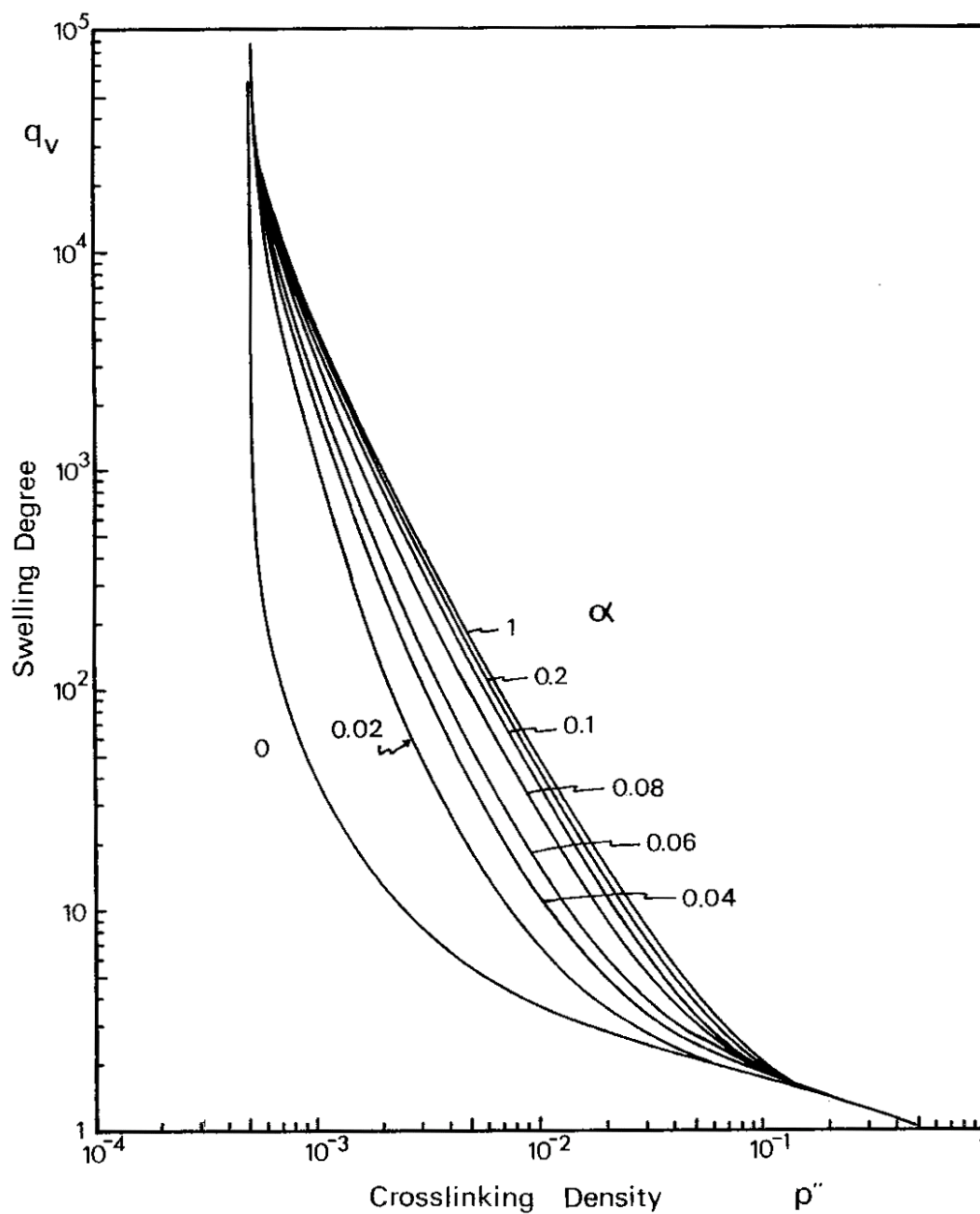
Figure 68 The relationship between volumetric swelling degree of polyelectrolyte gel in distilled water, q_v, and crosslinking density of gel, ρ'' using the mole fraction of ionic group in gel, α, as a parameter.
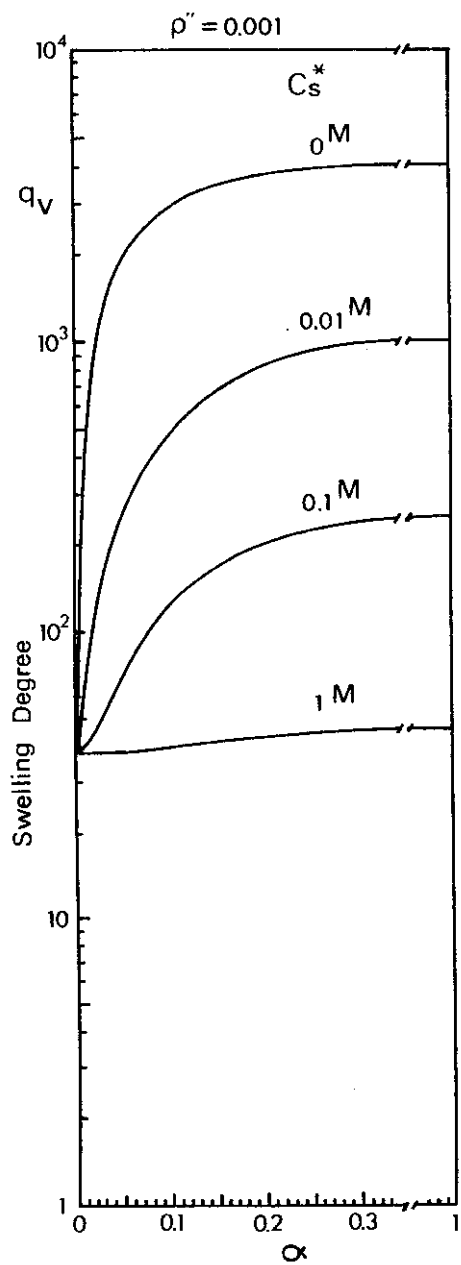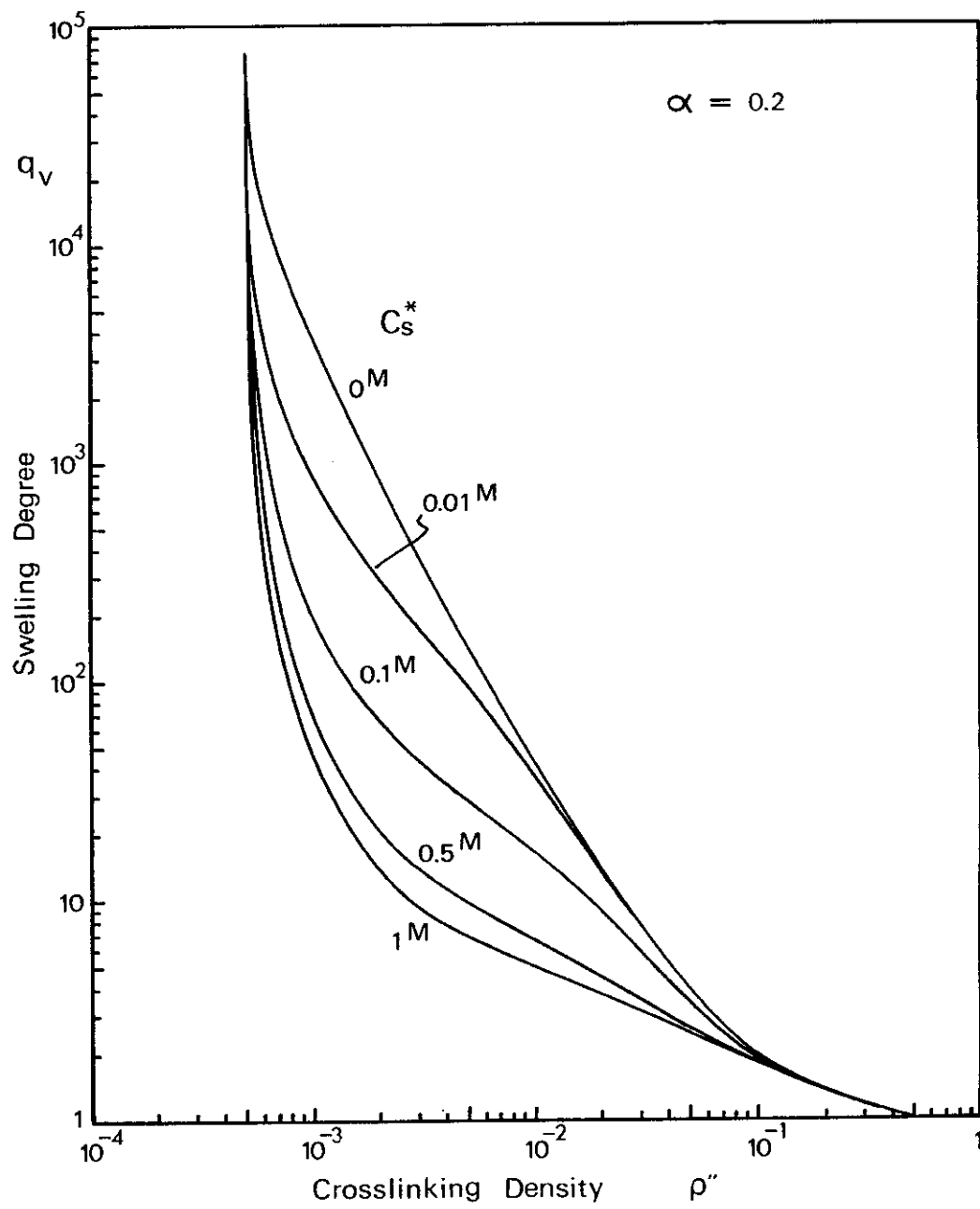
Figure 69 The effects of the concentration of salt in solution on the relationship between volumetric swelling degree of polyelectrolyte gel, q_v, and the mole fraction of ionic group in gel, α, at a crosslinking density ρ " = 0.001.

Figure 70   The effects of the concentration of salt in solution on the relationship between volumetric swelling degree of polyelectrolyte gel, q_v, and crosslinking density of gel, ρ ", at the mole fraction of ionic group in gel α = 0.2.
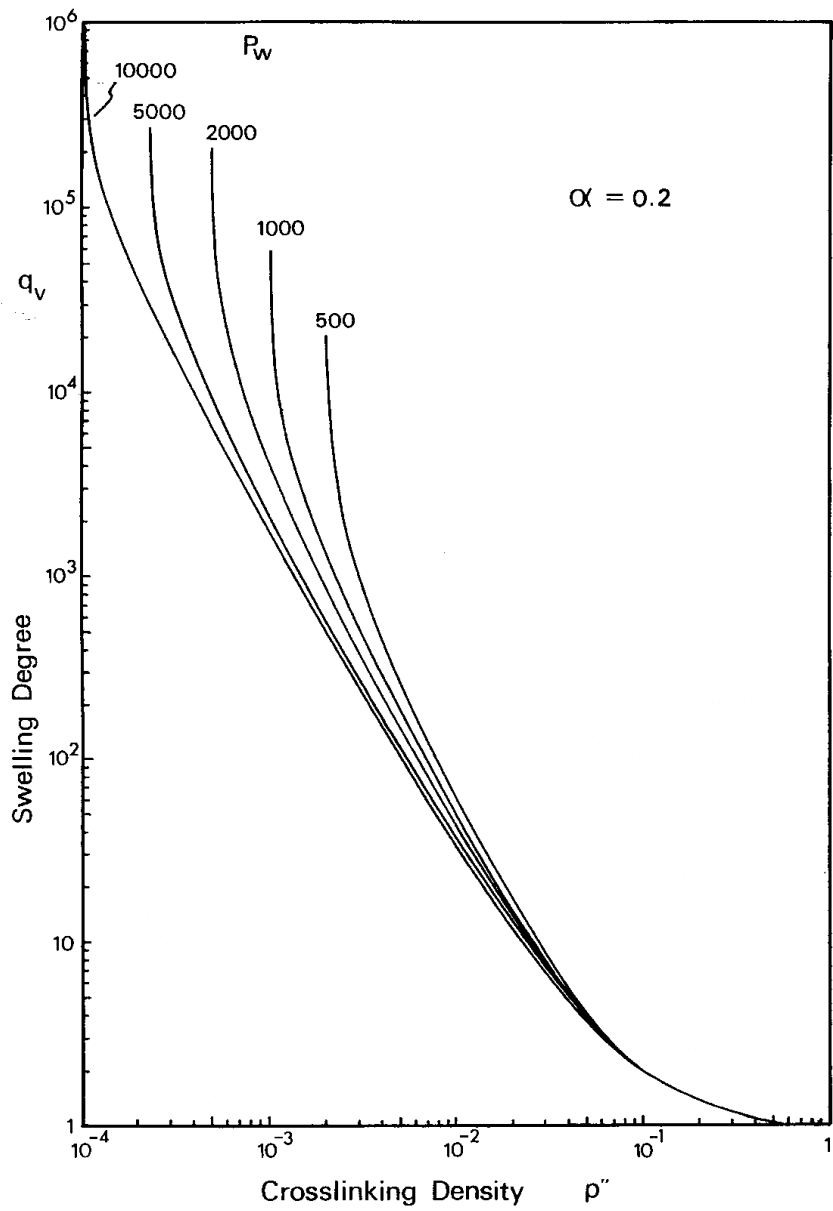
Figure 71   The effects of the weight-average polymerization degree of constituent polymer of gel on the relationship between volumetric swelling degree of polyelectrolyte gel in distilled water, q_v, and crosslinking density of gel, ρ ", at the mole fraction of ionic group in gel α = 0.2.
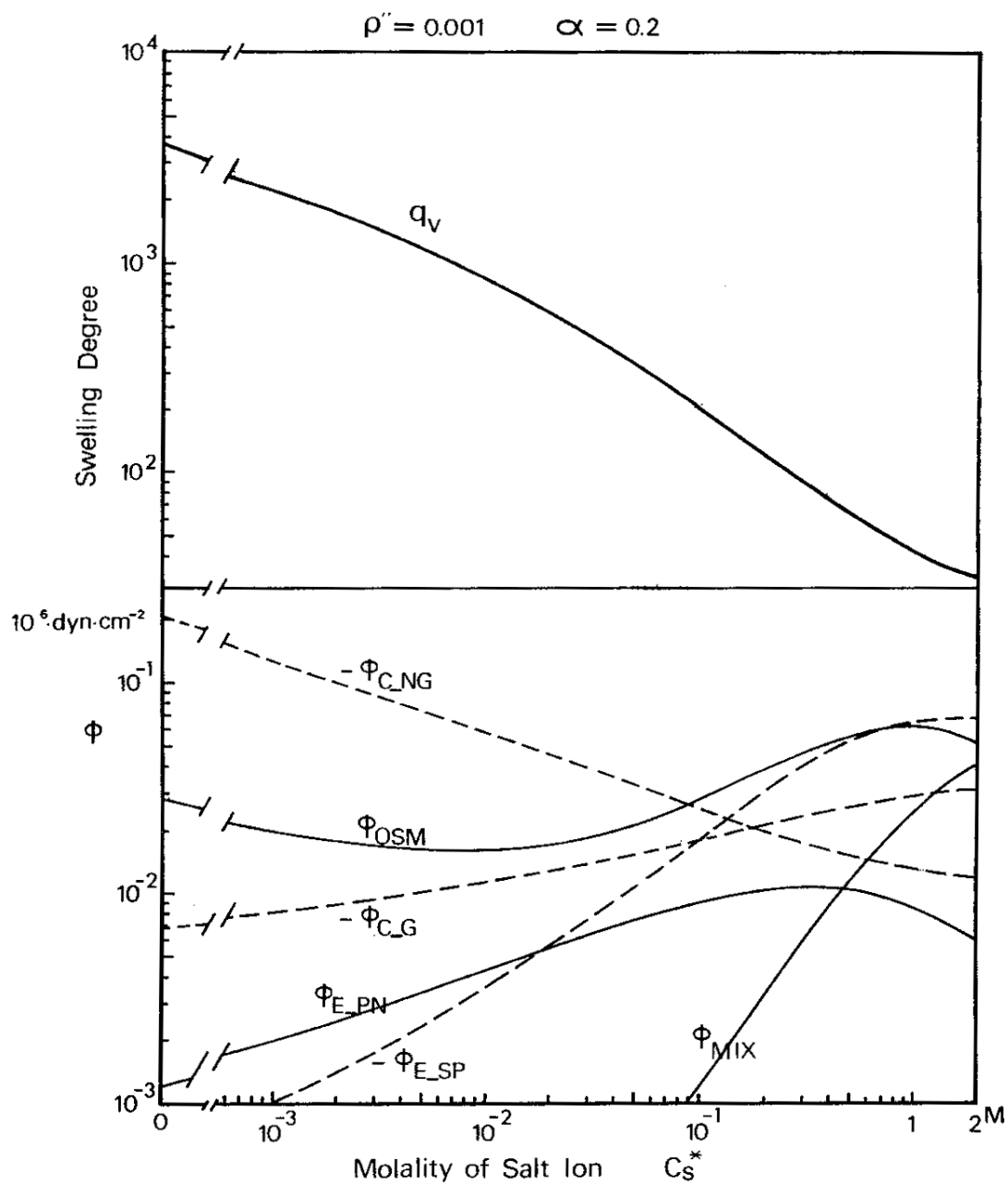
Figure 72   The effects of the concentration of salt on the volumetric swelling degree of polyelectrolyte gel, q_v, and the contribution of six types of swelling pressures, ϕ, determining the swelling degree, at a crosslinking density of gel, $\rho'' = 0.001$ and the mole fraction of ionic group in gel $\alpha = 0.2$.

REFERENCES

1   Chapter 7 in this thesis; Moritani, T. and Kajitani, K., *Polymer.*, 1997, **38**, 2933.

2   Chapter 8 in this thesis; Moritani, T. and Yamauchi, J., *Polymer*, 1998, **39**, 553..

3   Chapter 9 in this thesis; Moritani, T. and Yamauchi, J., *Polymer*, 1998, **39**, 559.

4   Chapter 10 in this thesis; Moritani, T. and Okaya, T., *Polymer*, 1998, **39**, 924.

5   Chapter 11 in this thesis; Moritani, T., *Macromolecules*, 1998, to be published.

6   Flory, P. J., *Principles of Polymer Chemistry*, Chap. ⅩⅢ-3c, *Swelling of Ionic Networks* ,Cornell Univ. Press, Ithaca, New York (1953).

7   Katchalsky, A. and Michaeli, I., *J. Polym. Sci.*, 1955, **15**, 69.

8   Hasa, J., Ilavsky, M. and Dusek, K., *J. Polym. Sci. Polym. Phys. Ed.*, 1975, **13**, 253.

9   Ilavsky, M., *Polymer*, 1981, **22**, 1687.

10   Katchalsky, A., Lifson, S. and Eisenberg, H., *J. Polym. Sci.*, 1951, **2**, 571.

11   Hasa, J. and Ilavský, M., *J. Polym. Sci.*, 1975, **13**, 263

12   Ilavský, M., Dusek, K., Vacík, J. and Kopecek, J., *J. Appl. Polym. Sci.*, 1979, **23**, 2073.

13   Skouri, R., Schosseler, F., Munch, J. P. and Candau, S. J., *Macromolecules*, 1995, **28**, 197.

14   Tanaka, T., *Polymer*, 1979, **20**, 1404.

15   Ilavsky, M., *Macromolecules*, 1982, **15**, 782.

16   Nicoli, D., Young, C., Tanaka, T., Pollak, A. and Whitesides, G., *Macromolecules*, 1983, **16**, 887.

17   Baker, J. P., Hong, L. H., Blanch, H. W. and Prausnitz, J. M., *Macromolecules*, 1994, **27**, 1446.

18   Baker, J. P., Blanch, H. W. and Prausnitz, J. M., *Polymer*, 1995, **36**, 1061.

19   Hanna, R. J., *Ind. Eng. Chem.*, 1957, **49**(2), 208.

20   Sakurada, I., *Polyvinyl Alcohol Fibers*; Marcel Dekker, Inc.: New York, 1985.

21   Sakurada, I. Nukushina, Y. and Sone, Y., *Kobunshi Kagaku*, **1955**, *12*, 506.

22   Pritchard, J. G., *Poly(vinyl alcohol). Basic properties and uses*; Gordon & Breach Sci. Pub.: London, 1970, chap 3.

23   The symbol, ρ ", with double prime is used because they stand for parameters of gel fraction and should be distinguished from those of total system, ρ . See Chapter 11.

24   Holly, E. D., *J. Polym. Sci. Part B*, 1964, **2**, 541.

25   Koningsveld, R. and Staverson, A. J., *J. Polym. Sci. Part A*, 1968, **6**, 305.

26   Carpenter, D. K., *Encyclopedia of Polymer Science and Technology*, Vol. 12, 649, 1970.

27   Manning, G. S., *J. Chem. Phys.*, 1969, **51**, 924.

28   Lifson, S. and Kachalsky, A., *J. Polym. Sci.*, 1954, **13**, 43.

29   Russel, W. B., *J. Polym. Sci. Polym. Phys. Ed.,* 1982, **20**, 1233.

30   Oosawa, F., *Polyelectrolytes*, pp 38 - 39, Marcel Dekker, New York, 1971.

31   Treloar, L. R., *The Physics of Rubber Elasticity*, Second ed., Oxford University Press, London, 1958.

32   Katchalsky, A. and Lifson, S., *J. Polym. Sci.*, 1953, **11**, 409.

33   Charlesby, A., *Proc. Roy. Soc. Lond.*, 1954, **A222**, 542.