

## CHAPTER 11

# ANALYSIS OF CROSSLINKED PVAL

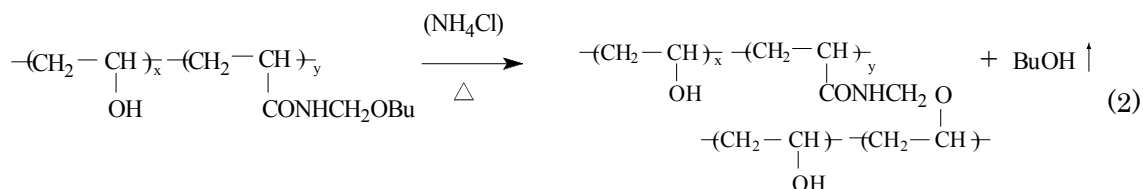
Well-defined gel has been synthesized, analyzed and compared with the theories on gel network formation and swelling. The starting polymer is modified poly(vinyl alcohol) containing 0.025 to 5 mol% of functional units capable of making crosslinking with hydroxyl group. They have been synthesized by copolymerization of vinyl acetate and N-(n-butoxymethyl)-acrylamide followed by alcoholysis. Film of the polymer has been crosslinked in the solid state by heat-treatment. Experimentally determined molecular parameters are sol fraction, gel point, average degree of polymerization for sol molecules, the mole fraction of crosslink units in gel and volumetric swelling degree for gel. Good agreement has been found between experiment and the classical gel network formation theory concerning gel point, sol fraction and degree of polymerization of sol molecules. The polymer-solvent interaction parameter,  $\chi$ , has been determined for poly(vinyl alcohol) solely from swelling experiment in water at 20°C as 0.47 ( $v_2 = 0$ ) where  $v_2$  is volume fraction of polymer. In Appendix, the equations derived from the classical gel network formation theory are summarized and typical calculation results are illustrated in figures.

### 11.1 INTRODUCTION

Crosslinking or gel formation is a significant technology for polymer industry in many fields such as rubber, plastic, adhesive, coating, printing, fluid absorber and membrane. In PVAL, a typical water-soluble polymer, crosslinking has been extensively applied for increasing water resistance<sup>1</sup> and for preparing hydrogels.<sup>2-18</sup> A new crosslinking system of modified PVAL containing crosslinkable units or poly(vinyl alcohol-co-N-(n-butoxymethyl)-acrylamide) has been demonstrated in Chapter 10.<sup>19</sup>



This has been synthesized by copolymerization of vinyl acetate (VAc) and N-(n-butoxymethyl)-acrylamide (BMAM) followed by alcoholysis. In the crosslinking system using the modified PVAL, timing of crosslinking is so controllable that no crosslinks are included in the powder and in the aqueous solution, and crosslinked materials having high water-resistance can be produced in the solid state with the aid of ammonium chloride. The following crosslinking reaction can be assumed:



In the present chapter, well-defined gel has been synthesized from the modified PVAL containing 0.025 to 5 mol% of BMAM units as starting polymer. Film of the polymer has been crosslinked in the solid state by heat-treatment based on the method shown in the preceding chapter. The gel has been analyzed and compared with the theories on gel network formation and swelling. Experimentally determined molecular parameters are sol fraction, gel point, average degree of polymerization for sol molecules, the mole fraction of crosslink units in gel and its volumetric swelling degree.

Crosslinking has been a significant scientific subject specific to macromolecules and sometimes reviewed in literature.<sup>20-31</sup> From the theoretical aspects, many reports on gel network formation process have been presented since the pioneering work of Flory<sup>20,32</sup> and Stockmayer.<sup>33</sup> The classical theory has been developed by Charlesby,<sup>34</sup> Scott<sup>35</sup> and others.<sup>36-38</sup> There have been presented more precise statistics considering extinction probability,<sup>39,40</sup> conditional probability,<sup>41,42</sup> vinyl-divinyl copolymerization<sup>43-46</sup> and theory based on percolation.<sup>25,47</sup> The theories make it possible to predict the relationship among molecular parameters characterizing gel such

Table 25 Experimental works on gels in relation to network formation theory and swelling in literature

Authors	Year	Subject		Polymer	Solvent at Crosslinking		Crosslinking Method	$X$ used	Observed Parameters
		Network <sup>†1</sup>	Swelling		Crosslinking	Method			
Scott <sup>18</sup>	1962	Y	—	Rubber	None	Peroxide	—	—	$S$ (Molecular scission)
Mukherjee; Prins <sup>34</sup>	1964	—	Y	CA <sup>†2</sup>	Dioxane	Diisocyanate	Osmometry	—	$q_v$
Langley; Ferry <sup>35</sup>	1968	Y	Y	PDS <sup>†3</sup>	None	EB Radiation <sup>†6</sup>	Theoretical	—	$S, q_v, \text{Elasticity}$ (Molecular scission)
Bray; Merrill <sup>36</sup>	1973	—	Y	PVAL <sup>†4</sup>	Water	EB Radiation <sup>†6</sup>	Osmometry	—	$q_v$
Peppas; Merrill <sup>37</sup>	1976	—	Y	PVAL <sup>†4</sup>	Water	EB Radiation <sup>†6</sup>	Osmometry	—	$q_v$
Mark; Sullivan <sup>38</sup>	1977	Y	Y	PDS <sup>†3</sup>	None	Orthosilicate	—	—	$q_v, \text{Elasticity}$
Gottlieb et al. <sup>39,40</sup>	1981	Y	—	PDS <sup>†3</sup>	None	DMHS <sup>†7</sup>	—	—	$\rho, S, \text{Elasticity}$
Hoffmann <sup>41</sup>	1982	Y	—	PI, PB <sup>†5</sup>	None	Peroxide	—	—	$S, \bar{P}'$ (Molecular scission)
Hoffmann <sup>42</sup>	1982	—	Y	PI, PB <sup>†5</sup>	None	Peroxide	—	—	$q_v, \text{Elasticity}$ (Molecular scission)
Matsumoto et al. <sup>43</sup>	1995	Y	—	PMMA	Dioxane	EDMA <sup>†8</sup>	—	—	(Gel point)

<sup>†1</sup> Molecular parameters on gel network

<sup>†2</sup> Cellulose acetate

<sup>†3</sup> Poly(dimethyl siloxane)

<sup>†4</sup> Poly(vinyl alcohol)

<sup>†5</sup> PI: Polyisoprene, PB: Polybutadiene

<sup>†6</sup> Electron beam radiation

<sup>†7</sup> Diphenyl di(dimethylhydroxy)silane

<sup>†8</sup> Ethylene dimethacrylate

<sup>†9</sup>  $S$ : Sol fraction

$q_v$ : Swelling degree

$\rho$ : Crosslinking density

$P'$ : Degree of polymerization of polymer

in sol fraction

(Vinyl-divinyl copolymerization)

as crosslinking density, gel point, sol fraction, and degree of polymerization and molecular weight distribution (MWD) of sol molecules. In addition to the network formation theory, theories on swelling and elasticity have been progressed.<sup>20,22,48-50</sup>

In contrast to the bewildering advance in theory on gel, actual gels have been sometimes too complicated to be treated quantitatively. Table 25 shows the ten reports<sup>35,51-60</sup> concerning experimental works on gels in relation to network formation theory or swelling. The following difficulties have been found in actual gels: 1) Molecular scission is accompanied by crosslinking in cases of using peroxide, electron beam or gamma radiation.<sup>35,52-54,57,59</sup> 2) Solvent used in crosslinking causes loop or intra-molecular crosslinking as dilution effects.<sup>51,53,54,60</sup> Swelling of crosslinked PVAL has been investigated by Bray, Peppas and Merrill<sup>53,54</sup> at various temperatures. In their studies, however, the  $\chi$  parameter from osmometry has been used as a calibration standard. Similar calibration method has usually been adopted in swelling experiment of gel for other polymers,<sup>50</sup> although the determination is possible in principle by using well-defined gels.

In the present work, the crosslinking system made from modified PVAL with BMAM units has been analyzed and compared with the theories on gel network formation and swelling.

## 11.2 EXPERIMENTAL

### 11.2.1 *Synthesis of Modified PVAL*

The modified PVAL samples containing 0.025 to 5 mol% of BMAM units in polymer chain were synthesized from copolymerization of VAc and BMAM, followed by alcoholysis of the copolymers.

**Copolymerization** Copolymerization was carried out in homogeneous system using methanol and benzoyl peroxide (BPO) as solvent and initiator, respectively, at boiling temperatures of the system, 60° to 62°C. As an initiator in copolymerization, BPO was used instead of 2,2'-azobisisobutyronitrile which had been used in the preceding works. This is because BPO does not contain nitrogen and therefore does not affect the analysis of crosslink units in crosslinked films by elementary analysis of nitrogen. For the purpose of obtaining homogeneous composition in copolymerization at any degree of conversion, the

conversion, the “feeding-comonomer method”<sup>61, 62</sup> was adopted. As a control, a sample of PVAC homopolymer was also synthesized.

**Alcoholysis** The methanol solution of the modified PVAC was mixed with the methanol solution of sodium hydroxide as a catalyst. Gelatinous blocks comprising modified PVAL and solvent was obtained. It was ground, heated in the mixture of methanol, methyl acetate and small amount of water in order to convert residual sodium hydroxide to sodium acetate, and thereafter soaked in a large quantity of methanol with stirring for 24 hours in order to removing sodium acetate as a byproduct. After drying at 90°C, the final product was obtained as powder.

**Characterization** The mole fraction of BMAM units,  $\Delta(\text{PVAL})$ , in the modified PVAL was determined by elementary analysis of nitrogen using NC-80 from Shimadzu Corp., Kyoto. The degree of hydrolysis, DH, and the viscosity of 4 % aqueous solution at 20°C,  $\eta_{4\%}$ , were measured by the usual method.<sup>63</sup> The limiting viscosity numbers,  $[\eta]$ , in water were determined using a capillary viscometer at 30°C. The weight-average degree of polymerization,  $\overline{P}_w$  was obtained by using  $[\eta]$  observed and the following equations presented for PVAL homopolymer.<sup>64-66</sup>

$$\overline{P}_v = \left( \frac{[\eta]}{0.833} \right)^{1/a}, \quad \overline{P}_w = 2 \left[ (a+1) \Gamma(a+1) \right]^{-1/a} \overline{P}_v = 1.097 \overline{P}_v, \quad a=0.62 \quad (3)$$

### 11.2.2 Preparation and Analysis of Crosslinked Film

**Primary Crosslinked Film and Insoluble Film** Crosslinked film (50  $\mu$  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 2.4 g/100g-PVAL, casted on a rotating drum at 75°C. The film thus obtained was heat-treated or cured for crosslinking at 150°C for 20 min inside an electric oven equipped with a safeguard against explosion.

The samples of crosslinked film, called as “primary crosslinked film” below, were soaked in water at 90°C for one hour. Soluble part was extracted in this procedure. The “insoluble film” or gel part was filtered off and filtrate including sol part was collected. The four items of analysis were determined for sol and gel in the following manner:

**a) Sol Fraction, S :** The samples of the primary crosslinked film (0.1 to 1 g) were weighed precisely and soaked in water at 90°C for one hour and the insoluble film was filtered off. The weight of polymer

dissolving in water ( $W_s$ ) was obtained from the concentration of polymer observed and the weight of the water. The concentration was determined by an iodine method.<sup>19,67</sup> The solid weight of the primary crosslinked film ( $W_0$ ) was determined by considering the correction of the volatile content measured separately.<sup>63</sup> The sol fraction,  $S$ , can be obtained as  $S = W_s/W_0$ .

**b) Weight-Average Degree of Polymerization for Sol Molecule,  $\overline{P'_w}$** : After the insoluble film was filtered off, the filtrate was evaporated under reduced pressure to more concentrated aqueous solution. The solution was poured into large amount of acetone. The precipitate was ground, washed with methanol by a Soxhlet extractor and dried. The weight-average degree of polymerization was obtained from the measurement of  $[\eta]$  by the same method described before. The prime mark in  $\overline{P'_w}$  denotes value on sol part.<sup>20</sup>

**c) Volumetric Swelling Degree,  $q_v$** : The insoluble film filtered off above was soaked in distilled water at 20°C for 5 days and weighed after removing liquid water on the surface. Volumetric swelling degree,  $q_v$  was obtained using the observed data on  $W_0$  = weight of primary crosslinked film including sol and  $W_w$  = weight of swollen film.

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

$$= \left[ W_w - W_0(1-s) + W_0(1-s)/d_w \right] / \left[ W_0(1-s)/d_0 \right] \quad (4)$$

$$W''_0 = W_0(1-s) \quad (5)$$

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,  $d_{H_2O}$  = density of water ( $\cong 1$ ). The values,  $d_0 = 1.29$  ( $\phi_x = 29\%$ ) and  $d_w = 1.269$  ( $\phi_x = 0\%$ ) were used from the values in literature,<sup>66,68,69</sup> where  $\phi_x$  is the volume fraction of crystallinity. In the above equation, additivity on volume in mixing is assumed. The volume fraction of polymer in swollen film,  $v_2$ , is the reciprocal of  $q_v$  from the definition.

$$v_2 = q_v^{-1} \quad (6)$$

**d) The Mole Fraction of Amido Units for Gel Part,  $\Delta''$** : The amount of nitrogen was analyzed for dried samples of the insoluble film using elementary analysis. The mole fraction of amido units,  $\Delta''$ , has been determined from the observed data. The double-prime mark denotes value on gel part.<sup>20</sup>

## 11.3 THEORETICAL CALCULATION

### 11.3.1 Gel Network Formation Theory

Theoretical calculations for crosslinked polymers were made for obtaining various molecular parameters, such as sol fraction,  $s$ , crosslinking densities,  $\rho'$  and  $\rho''$ , the degrees of polymerization,  $\overline{P}'_w$  and  $\left[\overline{P}''_w\right]$ , for sol and gel parts, respectively. The equations for calculating them as functions of one starting parameter,  $\rho$ , the crosslinking density for entire crosslinked system, are summarized in Table 30 in *Appendix*. These equations are essentially almost the same ones already presented in literature, but rearranged and partly corrected by the present author as shown in the table. The main assumptions included in the equations are: 1) Random distribution of crosslinking, 2) Lower crosslinking density, 3) Neglecting loop or intra-molecular crosslinking, and 4) Schultz-Zimm molecular weight distribution (MWD) for starting polymer.

The core of the calculation is regarded as obtaining sol fraction,  $s$ , by solving the following equation:

$$s = \left(\lambda \cdot (\lambda + \rho \cdot g)^{-1}\right)^{\sigma+1} \quad (7)$$

where  $g$  is gel fraction ( $g = 1 - s$ ), and the parameters,  $\lambda$  and  $\sigma$ , are parameters related to  $\overline{P}'_w$  and a parameter  $\xi$  determining MWD or the ratio of weight-average degree of polymerization to number-average degree of polymerization for the polymer before crosslinking,  $\xi \equiv \overline{P}'_w / \overline{P}'_n$ . Therefore, for the crosslinking system using a polymer characterized by the known  $\overline{P}'_w$  and  $\xi$ , *Equation (7)* determines the relation between  $\rho$  and  $s$ . This equation is an implicit function concerning  $s$ , and therefore the value,  $s$ , has been computed by using Newton's method based on BASIC program.

Using  $s$  computed from *Equation (7)* and using the parameters,  $\sigma$ ,  $\lambda$ ,  $\gamma$  and  $\delta$

directly determined by  $\xi$ ,  $\overline{P}_w$  and  $\rho$ , other significant molecular parameters,  $g$ ,  $v$ ,  $r$ ,

$\rho'$ ,  $\rho''$ ,  $\gamma'$ ,  $\gamma''$ ,  $\delta'$ ,  $\delta''$ ,  $\overline{P}'_n$ ,  $\overline{P}'_w$ ,  $[\overline{P}'_n]$ ,  $[\overline{P}''_n]$ ,  $[\overline{P}'_w]$  and  $[\overline{P}''_w]$  have been determined

successively by the equations in Table 30. The parameters,  $v$  and  $r$  are intermediate parameters for computing. The definitions of molecular parameters are as follows:<sup>20,34</sup>

$\rho$ ,  $\rho'$ ,  $\rho''$ : Crosslinking densities for entire system, sol and gel, respectively

(The mole fraction of crosslinked units in polymer)

$\gamma$ ,  $\gamma'$ ,  $\gamma''$ : Crosslinking indices for entire system, sol and gel, respectively

(The average number of crosslinks per a “number-average” molecule)

$\delta$ ,  $\delta'$ ,  $\delta''$ : Crosslinking coefficients for entire system, sol and gel, respectively

(The average number of crosslinks per a “weight-average” molecule)

$\overline{P}'_n$ : Number-average degree of polymerization for sol

$\overline{P}'_w$ : Weight-average degree of polymerization for sol

$[\overline{P}'_n]$ ,  $[\overline{P}''_n]$ : Number-average degree of polymerization for original chains constructing sol and gel, respectively, in the case of removing crosslinks

$[\overline{P}'_w]$ ,  $[\overline{P}''_w]$ : Weight-average degree of polymerization for original chains constructing sol and gel, respectively, in the case of removing crosslinks

The calculation results based on the gel network formation theory are shown in Figure 59, where experimental results are also shown. Examples of calculations are also illustrated in Figures 61 to 65 in *Appendix*.

### 11.3.2 Theory of Swelling Degree

The following equation on swelling has been presented<sup>20,49</sup> based on the assumptions, 1)Random distribution of crosslinking, 2)Lower crosslinking density, 3)Neglecting intra-molecular crosslinking and entanglements, and 4)Gaussian distribution of end-to-end chain length:

$$\ell n(1 - v_2) + v_2 + \chi v_2^2 + \frac{V_1 d}{M_c} \left(1 - \frac{2Mc}{M}\right) (v_2^{1/3} - v_2/2) = 0 \quad (8)$$



where  $v_2$ : Volume fraction of polymer in swollen gel ( $v_2 = q_v^{-1}$ )

$\chi$ : Polymer-solvent interaction parameter

$V_1$ : Mole volume of solvent (18.1 ml<sup>3</sup> in case of water)

$d$ : Density of polymer (1.269 g/cm<sup>3</sup> in case of PVAL at no crystallization degree)<sup>66</sup>

$M$ : Number-average molecular weight of chain molecules in the case of removing crosslinks.

$M_c$ : Molecular weight per a crosslinked unit

Using a parameter described above in the gel network formation theory,  $M$  should be written using  $[\bar{P}_n^{\prime\prime}]$  defined above as

$$M = M_0 \cdot [\bar{P}_n^{\prime\prime}] \quad (9)$$

where  $M_0$  is molecular weight of a monomer unit (44.1 for PVAL).  $M_c$  has a relation with crosslinking density of gel,  $\rho''$

$$\rho'' = M_0 / M_c \quad (10)$$

Using *Equations (8) to (10)*, the original *Equation (8)* can be rewritten as

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + \frac{v_1 d}{M_0} \left( \rho'' - \frac{2}{[\bar{P}_n^{\prime\prime}]} \right) (v_2^{1/3} - v_2 / 2) = 0 \quad (11)$$

The polymer-solvent interaction parameter,  $\chi$ , can be explicitly obtained by the following equation:

$$\chi = \left[ V_1 d \cdot M_0^{-1} \cdot \left( 2 \cdot [\bar{P}_n^{\prime\prime}]^{-1} - \rho'' \right) (v_2^{1/3} - 0.5 \cdot v_2) - \ln(1 - v_2) - v_2 \right] v_2^{-2} \quad (12)$$

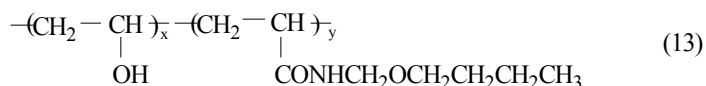
It must be significant to emphasize now that “number-average molecular weight”,  $M$ , in *Equation (8)*, the original form by Flory, is not that of starting polymer before crosslinking but that of polymer constructing gel and not including sol fraction. This is the reason why  $[\bar{P}_n^{\prime\prime}]$  is used explicitly in *Equations (11) and (12)*. As shown later,  $[\bar{P}_n^{\prime\prime}]$  can have double value of  $\bar{P}_n$  in the case of gel having small amount of crosslinks and the

distinction between them can be critical in the analysis.

## 11.4 RESULTS AND DISCUSSION

### 11.4.1 Modified PVAL

Table 26 summarizes the results of the synthesis for one sample of non-modified PVAL (No. 1) and eight samples of modified PVAL with BMAM from 0.025 to 5 mol% (Nos. 2 to 9). The table shows the theoretical mole fractions of BMAM units, the amounts of reagents fed in copolymerization (described as weight part), reaction time and the degree of conversion of VAc. Analytical results of the modified PVAL samples are also shown for the mole fraction of BMAM units in modified PVAL,  $\Delta_{(PVAL)}$ , degree of hydrolysis, DH, the viscosity of 4 wt% aqueous solution,  $\eta_{4\%}$ , limiting viscosity number,  $[\eta]$ , and weight-average degree of polymerization,  $\overline{P}_w$ . The mole fraction of BMAM units in modified PVAL,  $\Delta_{(PVAL)}$ , has been determined using elementary analysis of nitrogen. The BMAM unit is kept stable in all the process of synthesis, copolymerization and alcoholysis, as already shown in the preceding chapter. The modified PVAL has essentially the following structure:



All the samples were highly hydrolyzed and their degrees of hydrolysis are higher than 98.5 mol%. The degree of polymerization is in the range of 1881 to 2378 and 2026 on the average. No crosslinking is regarded to be included because degree of polymerization observed is almost the same among the samples and independent of the amount of BMAM units.

### 11.4.2 Molecular Parameters for Crosslinked Film

The film was prepared by casting the aqueous solution of modified PVAL and ammonium chloride as a catalyst. The film was heat-treated for crosslinking. The film thus obtained, "primary crosslinked film", was soaked in water at 90°C and filtered off after cooling. The insoluble film or gel part and the extract or sol part were analyzed and the observed results are summarized in Table 27.

**11.4.2.1 Sol Fraction** Sol fraction is the weight ratio of sol part to primary crosslinked film. It decreases with increasing the mole fraction of crosslinkable BMAM units in starting polymer: 0.84 and 0.054 wt% of sol fraction for starting PVALs including 0.89 (No. 7) and 5.44 mol% (No. 9) of BMAM units, respectively.

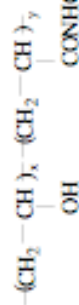
**11.4.2.2 Degree of Polymerization for Sol Molecules,  $\overline{P_w}$**  Limiting viscosity number,  $[\eta]$ , of the modified PVAL extracted in water as sol part was measured, and weight-average degree of polymerization,  $\overline{P_w}$ , was determined by using  $[\eta]$  and the by the mechanism that polymer molecules of higher degree of polymerization are preferably entrapped into gel in crosslinking process.

**11.4.2.3 Amido Crosslink Units in Insoluble Film** The weight fraction of nitrogen has been analyzed for insoluble film. As has been shown in the preceding chapter, the BMAM units in the modified PVAL can be converted to the following two structures in the crosslinking reaction by the heat-treatment in the presence of ammonium chloride:

Table 26 Syntheses and analysis of modified poly(vinyl alcohol)s (PVALs)<sup>\*1</sup> with N-(n-butoxymethyl)-acrylamide (BMAM), by copolymerization and alcoholysis

Sample No.	$\Delta\text{calc}^{*2}$	Feed in copolymerization (part)			Reaction time min	Conversion of VAc %	Modified PVAL (Not crosslinked)		$\bar{P}_v^{*8}$		
		VAc mol%	BMAM Initial/Additional	Methanol Initial/Additional			$\Delta(\text{PVAL})^{*4}$	DH <sup>*5</sup>		$\eta_{\text{sp}}^{*6}$	$[\eta]^{*7}$
1	0	1000	0/0	299/16	240	52.6	0.0	99.0	35.7	90.5	2109
2	0.025	1000	0.052/0.24	299/16	135	52.2	0.025	98.7	29.2	94.6	2265
3	0.05	1000	0.10/0.44	299/16	150	54.4	0.05	99.0	27.2	97.5	2378
4	0.1	1000	0.20/0.88	299/15	200	51.8	0.13	98.7	32.5	88.5	2034
5	0.2	1000	0.36/1.76	299/14	150	37.3	0.19	98.6	30.9	84.3	1881
6	0.5	1000	0.8/4.4	299/12	155	53.9	0.49	97.9	27.1	81.7	1788
7	1	1000	1.8/8.6	299/7.4	155	53.3	0.89	97.8	28.0	86.5	1961
8	3	1000	5.6/25.6	300/0	180	50.0	3.10	98.8	28.8	82.9	1831
9	5	1000	9.2/42.4	302/0	180	48.7	5.44	98.7	27.6	87.2	1986

\*1



\*2 Theoretical mole fraction of BMAM units in copolymer.

\*3 Benzoyl peroxide.

\*4 Observed mole fraction of BMAM units in modified PVA

\*5 Degree of hydrolysis of VAc units

\*6 Viscosity of 4% aqueous solution at 20°C.

\*7 Limiting viscosity number in water at 30°C

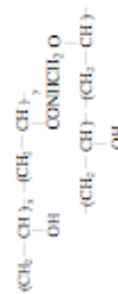
\*8 Weight-average degree of polymerization calculated from the equations:

$$\bar{P}_v = \left[ \frac{[\eta]}{0.833} \right]^{1/a} \cdot \bar{P}_n = 2[(a+1)\Gamma(a+1)]^{1/a} \bar{P}_v \cdot a=0.62$$

Table 27. Molecular parameters for the crosslinked film<sup>1</sup> made from poly(vinyl alcohol) modified with N-(n-butoxymethyl)-acrylamide.

Sample No.	Starting Polymer		Sol Part		Gel Part (Insoluble film)			Primary crosslinked film		Polymer-Solvent	
	$\Delta(\rho_{VAL})^{*2}$	$S^{-1}$	$[\eta]^{*4}$	$P_w^{1/3}$	$\Delta^{*4}$	Crosslinking density <sup>7</sup>	Swelling degree <sup>8</sup>	Fraction of Polymer in Gel	Crosslinking density ( $\times 10^{19}$ ) <sup>9</sup>	$\Delta^{*11}$	Interaction Parameter
	mol%	%	cc/g		mol%	$\rho'' (\times 10^9) [\bar{P}_w]$	$q_s$	$v_2 = q_s^{-1}$	$\rho = \rho''(1+s)^{-1}$	mol%	$\chi^{*12}$
1	0.0	100	90.5	21.09	0.0	NA	NA	NA	0	0	NA
2	0.025	84	94.4	22.58	0.05	NA	NA	NA	0.060	0.030	NA
3	0.05	62	97.2	23.67	0.07	1609	33	0.0303	0.086	0.043	0.484
4	0.13	21.1	60.2	10.93	0.13	1268	12.8	0.0781	0.21	0.11	0.494
5	0.19	9.9	41.3	5.95	0.19	1137	6.5	0.154	0.35	0.18	0.537
6	0.49	2.9	31.9	3.92	0.29	1046	4.5	0.222	0.56	0.28	0.569
7	0.89	0.84	16.2	1.32	0.65	1050	3.1	0.323	1.3	0.65	0.614
8	3.10	0.26	14.9	1.15	2.20	936	2.3	0.435	4.4	2.2	0.656
9	5.44	0.054	12.6	0.88	3.75	1006	2.1	0.476	7.5	3.75	0.661

\*1 Structure of crosslinked polymer



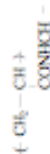
\*2 Observed mole fraction of N-(n-butoxymethyl)-acrylamide units in copolymer.

\*3 Sol fraction of the crosslinked (primary) film after soaking in water at 90°C for 60 min.

\*4 Limiting viscosity number for PVAL of the sol fraction, in water at 30°C.

\*5 Weight-average degree of polymerization, calculated from the equations:  
 $\bar{P}_w = \left[ \frac{[\eta D / 0.833]}{P_w} \right]^{1/2}$ ,  $P_w = 2[(e + D)(e + 1)]^{1/2}$ ,  $P_w = 1.097 P_w$ ,  $a = 0.62$

\*6 Observed mole fraction of the amido crosslink units shown below in insoluble film



determined by elementary analysis of nitrogen.

\*7 Crosslinking density for insoluble film (gel),  $\rho'' = 2 \cdot \Delta^{*4}$ .

\*8 Number-average degree of polymerization for original chains which form gel in the case of removing crosslinks. See Table 5.

\*9 Volumetric swelling degree of insoluble film (gel fraction) in water at 20°C.

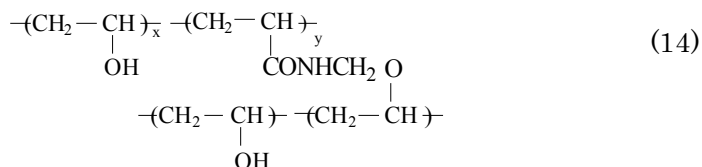
\*10 Crosslinking density in primary film, calculated from  $\rho = \rho'' / (1+s)$ .

\*11 The mole fraction of the amido crosslink units for primary crosslinked film, calculated from  $\Delta_s = \rho / 2$

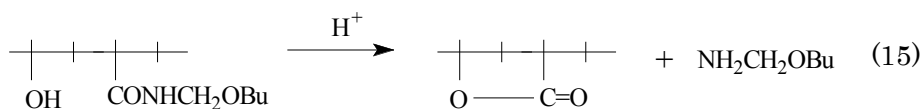
\*12 Calculated using the equation below and observed data for  $\rho''$ ,  $v_2$  and  $[\bar{P}_w]$   
 $\chi = \left[ \frac{V_1 d \cdot M_0^{-1} \cdot \left( 2 \cdot [\bar{P}_w]^{-1} - \rho'' \right) \left( v_2^{-0.5} - v_2 \right) - \ln(1 - v_2) - v_2}{v_2^{-2}} \right]$

$$(V_1 = 18.1, d = 1.269, M_0 = 44.1)$$

1) Crosslinks with hydroxyl group with the form shown below.



2) Lactone formed with neighboring hydroxyl group by the decomposition of amido linkage as follows.



Other structures can be assumed: unchanged BMAM group itself and carboxylic acid,  $\text{---COOH}$ . It has been concluded analytically, however, that both the structures are not included. The potential carboxylic acid necessarily converts to lactone in an acidic environment.

The side reaction shown by *Equation* (15) makes a part of crosslinkable BMAM units useless or not crosslinkable structure, lactone, which does not contain nitrogen. The byproduct generated by the reaction is regarded removed from the film to hot water. Therefore, the following discussions are possible:

- (1) BMAM units in the modified PVAL can convert in the crosslinking process to link units,  $\text{---CONHCH}_2\text{O---}$ , and lactone. Butoxymethyl and carboxyl groups are essentially not included in the insoluble film.
- (2) The mole fraction of amido units,  $\Delta$ , obtained from the elementary analysis of insoluble film is equal to the mole fraction of the link between amido and hydroxyl group,  $\text{---CONHCH}_2\text{O---}$ .
- (3) The mole fraction of the link observed is regarded to be equal to the mole fraction of "crosslinks" on the assumption that all the links are formed as intermolecular crosslinking or any intramolecular linking is negligible.

The third discussion can be supported by the fact that crosslinking reaction occurred in the solid state and there are any dilution effects. The validity of neglecting intramolecular crosslinking, however, should be investigated by the comparison between the experiment and the network formation theory. In contrast to the case in insoluble film, the direct analysis of the crosslink units has not been applied for primary crosslinked film because

crosslinked film because nitrogen analysis is affected by ammonium chloride used in crosslinking and by the byproduct from the side reaction. The amido units for sol molecules,  $\Delta'$ , was not analyzed in this work although it is regarded possible to determine the mole fraction analytically either by elementary analysis or by  $^1\text{H-NMR}$ .

**11.4.2.4 Crosslinking Densities** Experimental determination of crosslinking densities is essentially important for network studies.<sup>70</sup> As discussed above, the mole fraction of amido units,  $\Delta''$ , obtained from the elementary analysis of insoluble film can be equal to the mole fraction of the crosslink units with hydroxyl group,  $-\text{CONHCH}_2\text{O}-$  if it can be assumed that any intramolecular linking is negligible. On this assumption, crosslinking density in insoluble film,  $\rho''$ , can be determined from  $\Delta''$ ,

$$\rho'' = 2 \Delta'' \quad (\text{On the assumption of negligible intramolecular linking}) \quad (16)$$

The above simple assumption is one of main subjects which will be discussed in the comparison between experiment and theory later.

Crosslinking density in entire crosslinking system,  $\rho$ , is the parameter of basic significance, but the mole fraction of amido units in primary crosslinked film,  $\Delta$ , has not been determined by analytical method unfortunately, as stated before. Instead, it has been obtained from semi-empirical method by the aid of the following equation derived from gel network formation theory.

$$\rho = \rho''(1 + s)^{-1} \quad (17)$$

On the same assumption stated before,  $\Delta$  can be obtained.

$$\Delta = \rho/2 \quad (\text{On the assumption of negligible intramolecular linking}) \quad (18)$$

The  $\rho$  and  $\Delta$  calculated using observed values of  $s$  and  $\rho''$  are shown in Table 27.

**11.4.2.5 MWD** MWD for the starting polymers has not been determined but assumed approximately as the most probable distribution, namely  $\xi = \overline{P}_w / \overline{P}_n = 2$ . This must be essentially the case because polymerization terminates mainly by chain transfer to

methanol. Such mechanism of polymerization termination has been known to generate the most probable MWD.<sup>20</sup>

**11.4.2.6 Average Degree of Polymerization** Four kinds of weight-average degree of polymerization are illustrated in Table 30:  $\bar{P}_w$ ,  $\bar{P}'_w$ ,  $\left[\bar{P}'_w\right]$ , and  $\left[\bar{P}''_w\right]$ . The former two, the degree of polymerization for starting polymer and sol molecules, have been determined and already discussed before. The values of  $\left[\bar{P}'_w\right]$  and  $\left[\bar{P}''_w\right]$ , the degree of polymerization for original chains constructing sol and gel, respectively, in the case of removing crosslinks, have not been obtained experimentally now, although it is regarded as possible to determine them analytically based on the method removing all the crosslinks by hydrolyzing amido linkage.

For the analysis of swelling experiment,  $\left[\bar{P}''_n\right]$  is necessary to be determined. In this work, it has also been obtained from semi-empirical method by the aid of the following equations derived from gel network formation theory and on the assumption of  $\xi = 2$ .

$$\left[\bar{P}''_n\right] = \bar{P}_n \cdot (1-s) \cdot (1-r)^{-1} \quad (19)$$

where 
$$\bar{P}_n = \bar{P}_w / 2 \quad (20)$$

$$r = 2\bar{P}_w^{-1} \left[ 2\bar{P}_w^{-1} + \rho(1-s) \right]^{-1} \quad (21)$$

The value of  $\left[\bar{P}''_n\right]$  derived from observed values of  $s$ ,  $\bar{P}_w$  and  $\rho$  from Equation (17) is shown in Table 27.

**11.4.2.7 Swelling Degree and Volume Fraction of Polymer in Swollen Gel,  $q_v$  and  $v_2$**  Volumetric swelling degree,  $q_v$ , of insoluble film in water at 20°C has been determined from gravimetric observation and densities and shown in Table 27: 3.1 and 2.1 of  $q_v$  for No. 7 and No. 9, respectively. From the definition,  $v_2$  is determined as the reciprocal of swelling degree,  $v_2 = 1/q_v$ .



**11.4.2.8 Molecular Parameters Determined and Assumption Used** The molecular parameters determined experimentally are summarized in Table 28 together with the assumptions used. It must be significant that direct analytical determination has been done for the mole fraction of amido units of gel part,  $\Delta$ ”, and crosslinking density of gel,  $\rho$ ”, can be obtained as  $\rho''=2 \cdot \Delta$ ” on the assumption of neglecting intramolecular linking. The observed values,  $s$  and  $\overline{P}'_w$ , are used for the investigation of consistency between theory and experiment on network formation while  $q_v$  and  $\left[\overline{P}''_n\right]$  are used for the derivation of  $\chi$  parameter below.

**Table 28 Molecular parameters determined and assumptions used**

	Directly Determined	Determined under Assumptions		
		I	I + II	II + III
Starting Polymer	$\Delta(\text{PVAL}), \overline{P}'_w$ *1	—	—	—
Primary Crosslinked Film	—	—	$\Delta, \rho$	—
Sol (Extract)	$s, \overline{P}'_w$ *1	—	—	—
Gel (Insoluble Film)	$g, \Delta'', q_v$ *2, $v_2$ *2	$\rho''$	—	$\left[\overline{P}''_n\right]$

Assumptions \*1 Application of the equation concerning the relation of  $[\eta]$  and  $\overline{P}_w$  for PVAL homopolymer

\*2 Additivity on volume in mixing

I : Neglecting intramolecular linking

II : Network formation theory (Table 30)

III :  $\xi=2$  (The most probable molecular weight distribution) for the starting polymer.

### 11.4.3 Comparison of Experiment with Gel Network Formation Theory

In order to investigate the consistency between the present experiment and the network formation theory, sol fraction,  $s$ , of primary crosslinked films as well as on the

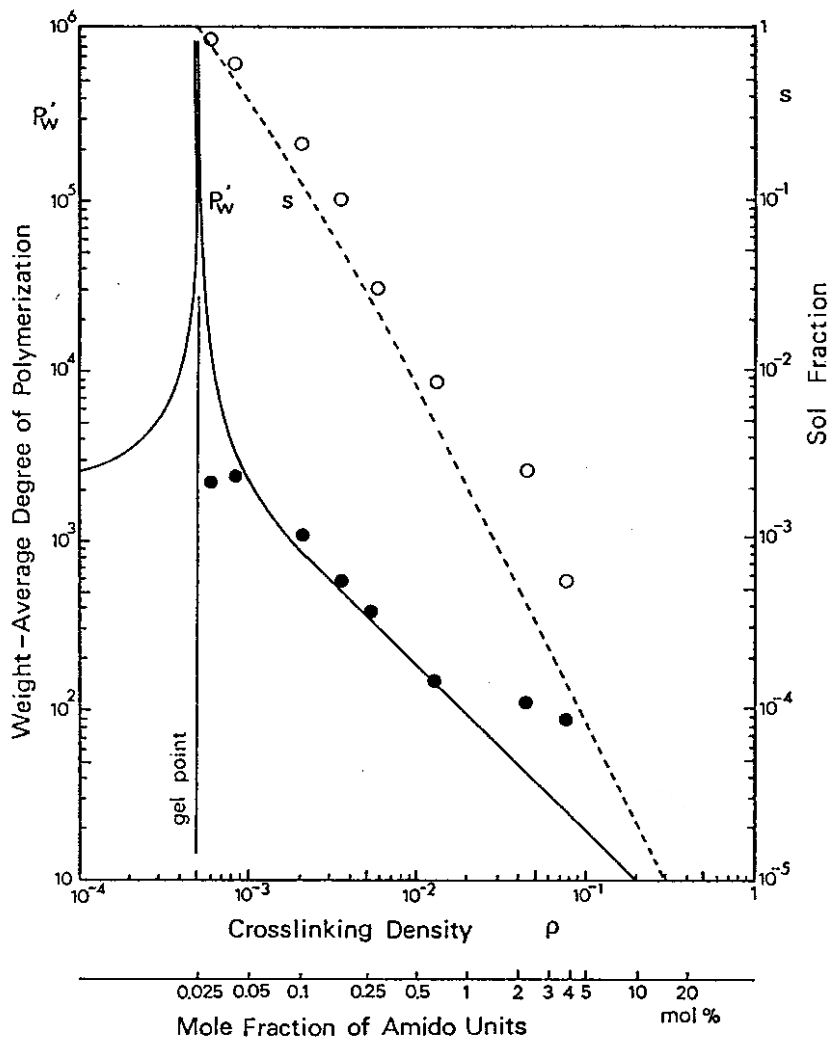
weight-average polymerization degree of sol molecules,  $\bar{P}'_w$  are quantitatively compared in Figure 59, where both observed and theoretical results are illustrated as functions of crosslinking density,  $\rho$ . The theoretical calculation is based on the parameters,  $\bar{P}_w=2000$  and  $\xi = 2$ . The mole fraction of amido units corresponding to *Equation (18)* are also illustrated for a measure of modification degree of BMAM units in modified PVAL.. An excellent agreement between theory and experiment is shown for gel point, sol fraction,  $s$ , and degree of polymerization of sol molecules,  $\bar{P}'_w$ , although deviation from theory is observed for the two samples having higher crosslinking densities and for the  $\bar{P}'_w$  value of the samples of the lowest crosslinking density. From the excellent agreement for the crosslinking system having  $\rho$  in the range of  $10^{-3}$  to  $10^{-2}$ , it can be concluded that the classical gel network formation theory and the assumptions included it can be applied to the present system.

The deviation from theory for the samples having higher crosslinking densities,  $\rho_\Delta$  0.044 and 0.075, can presumably be explained by an assumption of neglecting loop or intra-molecular crosslinking. If this is the case, the crosslinking densities  $\rho_{eff}$  obtained from observed data on sol fraction are obtained as 0.0019 and 0.0042, from the following equation:

$$\rho = 2 \cdot (s^{-1/2} - 1)(1 - s)^{-1} P_w^{-1} \quad (22)$$

The double values of the difference,  $\rho_\Delta - \rho_{eff}$ , are calculated as 0.50 and 0.66 mol%, which can be interpreted as “non-effective” amido units which do not contribute crosslinking effectively.

The reason for the deviation of degree of polymerization of sol molecules for the sample of lowest  $\rho$  is not clear enough now. The sample is in the state close to gel point and the sole molecules are believed to have quite high degree of polymerization due to crosslinking, about 20000, according to the theory. More careful investigation must be necessary for understanding sol molecules in the region close to gel point.



**Figure 60**—Sol fraction,  $s$ , and weight-average degree of polymerization of the sol molecules,  $P'_w$ , for crosslinked polymer as functions of crosslinking density,  $\rho$ . The solid and dashed lines are calculation results of the case of the polymer having  $P'_w = 2000$  and most probable molecular weight distribution ( $\xi = P'_w / P_n = 2$ ). Closed and open circles are the observed data on the crosslinked film made from poly(vinyl alcohol) modified with N-(n-butoxymethyl)-acrylamide (BMAM). The mole fraction of amido units corresponding to  $\rho$  is also shown.

#### 11.4.4 Swelling and $\chi$ Parameter

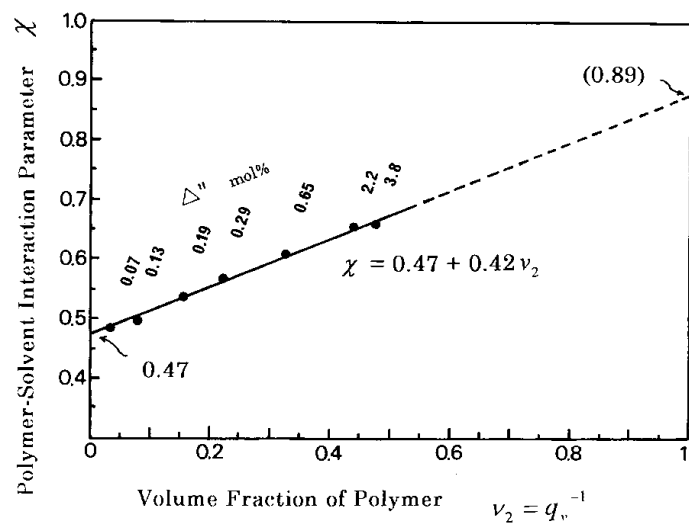
Volumetric swelling degree,  $q_v$ , of insoluble film in water has been observed at 20°C. It decreases from 33 to 2.1 wt/wt with increasing crosslinks, as shown in Table 27. The polymer-solvent interaction parameter,  $\chi$ , has been obtained using Equation (12) and using observed data on  $v_2 = q_v^{-1}$ ,  $\rho''$  and  $[\bar{P}''_n]$ . Results are also shown in Table 27 and Figure 61. The parameter  $\chi$  has been determined in the range of  $v_2$  of 0.0303 to 0.476. It varies linearly in this range, and the best fit relation using the least square method has provided the following relation:

$$\chi = 0.47 + 0.42 v_2 \quad (23)$$

The usage of  $[\bar{P}''_n]$  has been found significant in this analysis. If  $\bar{P}_n$  of the starting polymer is used as an approximate instead of  $[\bar{P}''_n]$ ,  $\chi$  shows a singular value at lower range of  $v_2$ .

Table 29 shows the  $\chi$  parameter for the modified PVAL as a function of  $v_2$  obtained in this work. In this table,  $\chi$  parameters reported so far in literature are also shown. For the higher range of  $v_2$ , 0.5 to 1.0, Yano,<sup>71</sup> Sakurada, Nakajima and Fujiwara,<sup>72</sup> and others<sup>73</sup> have reported  $\chi$  values using the experiment of vapor sorption, as 0.75 ( $v_2=0.5$ ) and 0.85 - 1.0 ( $v_2=0.8$ ). The value of  $\chi$  at  $v_2 = 0$  has also been reported using osmotic pressure by Nakajima and Furutachi,<sup>74</sup> as 0.494 and by Matsuo,<sup>75</sup> as 0.49 and also reported using intrinsic viscosity by Koopal,<sup>76</sup> as 0.478. Swelling experiment has already been carried out by Peppas and Merrill<sup>54</sup> in the broad range of temperature, 5° to 90°C, although the value  $\chi = 0.494$  determined by Nakajima and Furutachi<sup>74</sup> has been used for a calibration standard. Kawai<sup>77</sup> has reported freezing-point depression of solvent in relation to  $\chi$  parameter but the value obtained seems unusual possibly due to lower temperature in experiment.

The temperature of present experiment, 20°C, is different from the previous works, 30°C, and the PVAL in this work contains small amount of amido units for crosslinking, 0.043 to 3.75 mol%, but the  $\chi$  at  $v_2 = 0$  obtained in this work, 0.47, is regarded as  $\chi$  for PVAL homopolymer as the extrapolation of no modification of the polymer. It has been solely by swelling experiment without any aid of "calibration" from some other measurement.



**Figure 61** The relationship between polymer-solvent interaction parameter,  $\chi$  and the volume fraction of crosslinked modified poly(vinyl alcohol),  $v_2$ , in water at 20°C. This is obtained from swelling experiment of the insoluble film made from poly(vinyl alcohol)s modified with 0.05 to 5.4 mol% of N-(n-butoxymethyl)-acrylamide (BMAM) units.  $\Delta$  denotes mole fraction of crosslinkage observed. Closed circles are the observed data and the line and the equation shows the best-fit relation by using the least square method.

Table 29. Polymer-solvent interaction parameter,  $\chi$ , for poly(vinyl alcohol) modified with N-(n-butoxymethyl)-acrylamide, and for poly(vinyl alcohol) reported in the literature.

Authors	t, °C	Polymer-Solvent Interaction Parameter $\chi$							Method	Year
		$v_2=0$	$v_2=0.2$	$v_2=0.4$	$v_2=0.5$	$v_2=0.6$	$v_2=0.8$	$v_2=1$		
<b>This work</b>	20	0.47 <sub>0</sub>	0.55 <sub>4</sub>	0.63 <sub>8</sub>	—	—	—	—	Swelling	1998
( $\Delta$ ) <sup>*1</sup>		(0)	(0.25)	(1.5)						
Nakajima; Furutachi <sup>73</sup>	30	0.494	—	—	—	—	—	—	Osmotic pressure	1949
Matsuo <sup>74</sup>	30	0.49	—	—	—	—	—	—	Osmotic pressure	1953
Yano <sup>75</sup>	30	—	(0.6) <sup>*2</sup>	—	0.75	0.8	1.05	0.7	Vapor sorption	1955
Kawai <sup>76</sup>	-2.4	—	0.05	—	—	—	—	—	Freezing-point depression of solvent	1958
Sakurada; Nakajima; Fujiwara <sup>71</sup>	30	—	—	—	0.62-0.7	0.85	1.15	1.15	Vapor sorption	1959
Peppas; Merrill <sup>35</sup>	20	0.457 <sup>*3</sup>	—	—	—	—	—	—	Swelling <sup>*4</sup>	1976
	30	0.494 <sup>*3</sup>	—	—	—	—	—	—		
Koopal <sup>75</sup>	30	0.478	—	—	—	—	—	—	Intrinsic viscosity	1981

<sup>\*1</sup> The mole fraction of N-(n-butoxymethyl)-acrylamide units in poly(vinyl alcohol) modified with N-(n-butoxymethyl)-acrylamide

<sup>\*2</sup> Measurement by swelling method for film (Details are not reported).

<sup>\*3</sup> The value of  $\chi$  obtained by Nakajima and Furutachi (0.494) is used for a calibration standard.

<sup>\*4</sup> Temperature range in experiment: 5 ~ 90°C

## ***APPENDIX : Theoretical Expressions of Gel Network Formation Theory and Examples of Calculation***

**11.A.1 Theoretical Expressions.** Table 30 summarizes the theoretical expressions for calculating various molecular parameters for crosslinked polymers based on the gel network formation theory presented by Flory,<sup>20,32</sup> Stockmayer,<sup>33</sup> Charlesby,<sup>34</sup> Scott<sup>35</sup> and others.

**11.A.2 Two Types of Crosslinking and Their Effects to Sol Fraction.** Figure 62 shows the two types of crosslinking and their effects to sol fraction, illustrated by the theoretical relationship among crosslinking density,  $\rho$ , sol fraction,  $s$ , and weight average degree of polymerization,  $\overline{P}_w$ . The most probable molecular weight distribution or  $\xi = \overline{P}_w / \overline{P}_n = 2$  is assumed. The dashed lines indicate the relations in the case (A) where all crosslinkable units can make crosslinking with any units in polymer. The solid lines in the case (B) where crosslinkable units can make crosslinking only each other. The following conclusions are obtained from the comparison of (A) and (B):

Gel point,  $\rho_0$ , the minimum value of  $\rho$  giving gel, can theoretically obtained as  $\rho_0 = 1/\overline{P}_w$  for (A) and  $\rho_0 = 1/\sqrt{\overline{P}_w}$  for (B). For example, in the case of  $\overline{P}_w = 2000$ ,  $\rho_0 = 0.0005$  (0.025 mol% of crosslinkable units) in the case (A) while  $\rho_0 = 0.024$  (2.4 mol% of crosslinkable units) in (B). Crosslinking density,  $\rho_0$ , giving gel point in (A) is lower than that in (B) at the amount of two orders. Similar discussion is possible on the required crosslinking density giving a target of sol fraction. When the target of sol fraction is 1 % for a polymer of  $\overline{P}_w = 2000$ , required crosslinkable units are 0.45 mol% ( $\rho = 0.009$ ) in (A) and 9.5 mol% ( $\rho = 0.095$ ) in (B). Much lower amount of crosslinkable units in (A), about one-twentieth of that in (B), can give the target of sol fraction.

**11.A.3 Molecular Weight Distribution and Molecular Parameters.** Figures 63 to 66 show calculation results of molecular parameters for crosslinked polymer as functions of crosslinking density,  $\rho$ , using the equations shown in Table 30:

The molecular parameters illustrated are:  $s$ : sol fraction,  $g$ : gel fraction,  $\rho'$ ,  $\rho''$ :

crosslinking densities for sol and gel,  $\bar{P}'_n, \bar{P}'_w$  : number- and weight-average degree of polymerization for sol,  $[\bar{P}'_n], [\bar{P}'_w]$  : number-average degree of polymerization for original chains constructing sol and gel, respectively, in the case of removing crosslinks,  $[\bar{P}''_n], [\bar{P}''_w]$  : weight-average degree of polymerization for original chains constructing sol and gel, respectively, in the case of removing crosslinks.

Figures 63 to 65 are results for the polymer of  $\bar{P}_w = 2000$ . The results for most probable distribution ( $\xi = 2$ ) is illustrated in Figure 63, mono-dispersed distribution ( $\xi = 1$ ) in Figure 64, and broader distribution ( $\xi = 5$ ) in Figure 65. Figure 66 is the results for the polymer of  $\bar{P}_w = 500$  and most probable distribution.



**. Calculation of molecular parameters for crosslinked system based on gel network formation theory. (\*1)**

	Prior to gel point		Gel point		After gel point	
			Sol		Gel	
swelling density	$\rho$	$\rho$	Total	$\rho_0 = \bar{P}_v^{-1}$		
			Sol part	$\rho' = \rho_0$	$\rho' = \rho \cdot s$	$\rho'' = \rho \cdot (1+s)$
			Gel part	$\rho'' = 2 \cdot \rho_0$		
swelling index	$\gamma$	$\gamma = \rho \cdot \bar{P}_v$	$\gamma_0 = \xi^{-1}$	$\gamma' = \gamma \cdot s^2 \cdot r^{-1}$	$\gamma'' = \gamma \cdot (1-s^2) \cdot (1-r)^{-1}$	
linking coefficient	$\delta$	$\delta = \rho \cdot \bar{P}_v$	$\delta = 1$	$\delta' = \delta \cdot v \cdot s^{-1}$	$\delta'' = \delta \cdot (1-v)(1+s) \cdot g^{-1}$	
Sol fraction	$s$	$s = 1$	$s = 1$	$s = (\lambda \cdot (\lambda + \rho \cdot g)^{-1})^{v+1}$ (*2)	—	
Gel fraction	$g$	$g = 0$	$g = 0$	—	$g = 1-s$	
number-average degree of polymerization	$\bar{P}_n$	$\bar{P}_n = \bar{P}_v \cdot (1-2^{-1} \cdot \gamma)$	$\bar{P}_n = \bar{P}_v \cdot (1-2^{-1} \cdot \xi^{-1})^{-1}$	$\bar{P}_n = \bar{P}_v \cdot s \cdot (r - \gamma \cdot 2^{-1} \cdot s^2)^{-1}$ (*3)	$\left[ \frac{\bar{P}_n}{\bar{P}_v} \right] = \bar{P}_v \cdot g \cdot (1-r)^{-1}$ (*4)	
Weight-average degree of polymerization	$\bar{P}_w$	$\bar{P}_w = \bar{P}_v \cdot (1-\delta)^{-1}$	$\infty$	$\bar{P}_w = \bar{P}_v \cdot v \cdot s^{-1} \cdot (1-\delta \cdot v)$	$\left[ \frac{\bar{P}_w}{\bar{P}_v} \right] = \bar{P}_v \cdot (1-v) \cdot g^{-1}$ (*4)	
Parameters related to molecular weight distribution (*5)		$\xi = \bar{P}_v \cdot \bar{P}_w^{-1}$	$\sigma = (\xi - 1)^{-1}$	Intermediate parameters: $r = (\lambda \cdot (\lambda + \rho \cdot g)^{-1})^v$	$v = (\lambda \cdot (\lambda + \rho \cdot g)^{-1})^{v+2}$	
		$\varepsilon = 1 - \xi^{-1}$	$\lambda = (\sigma + 1) \cdot P_w^{-1}$			

equations can be applied to polymers having Schulz-Zimm molecular weight distribution.

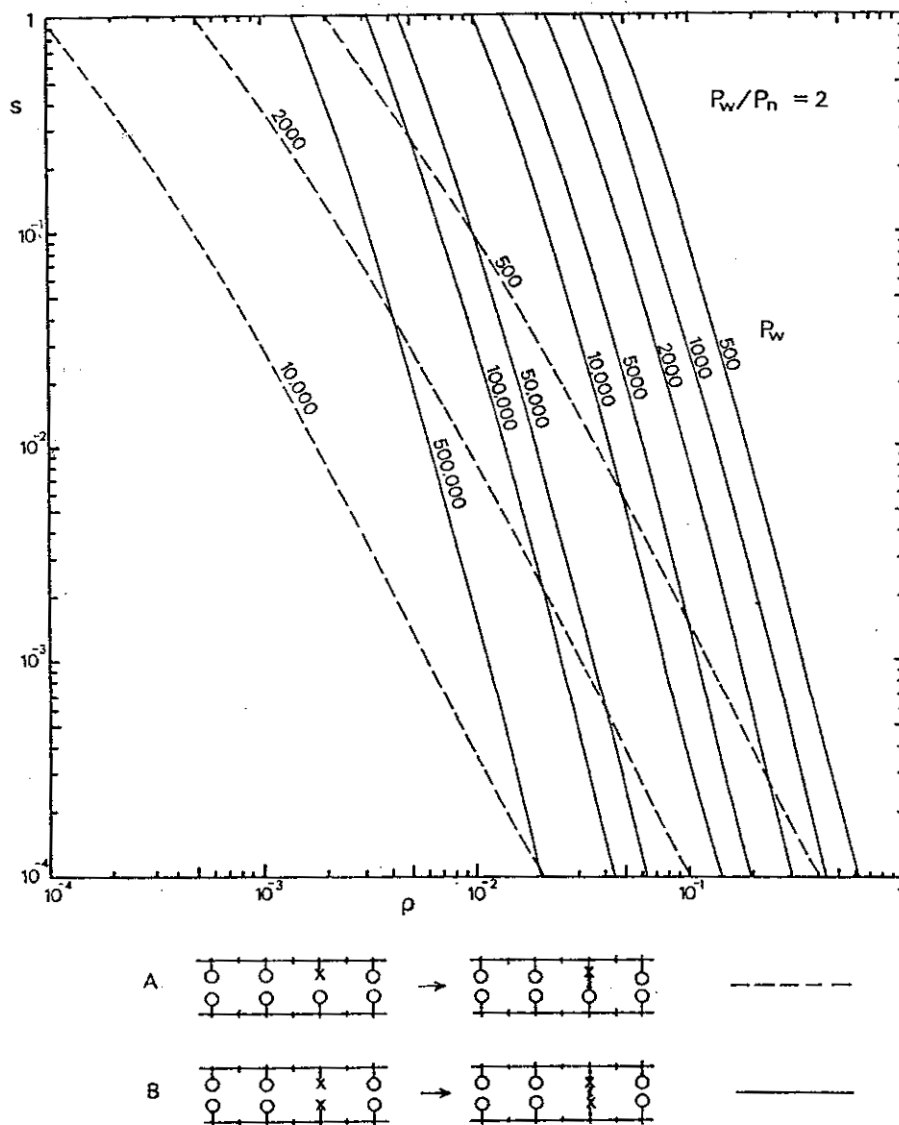
Parameters with prime mark denotes values on sol part, and double prime mark those on gel part.  $\rho$  with no mark is used for entire system.

\*1: most probable molecular weight distribution ( $\xi = 2$ ), the equation is simplified as follows:  $\rho = 2 \cdot (s^{-0.7} - 1) \cdot (1-s)^{-1} \cdot \bar{P}_v^{-1}$

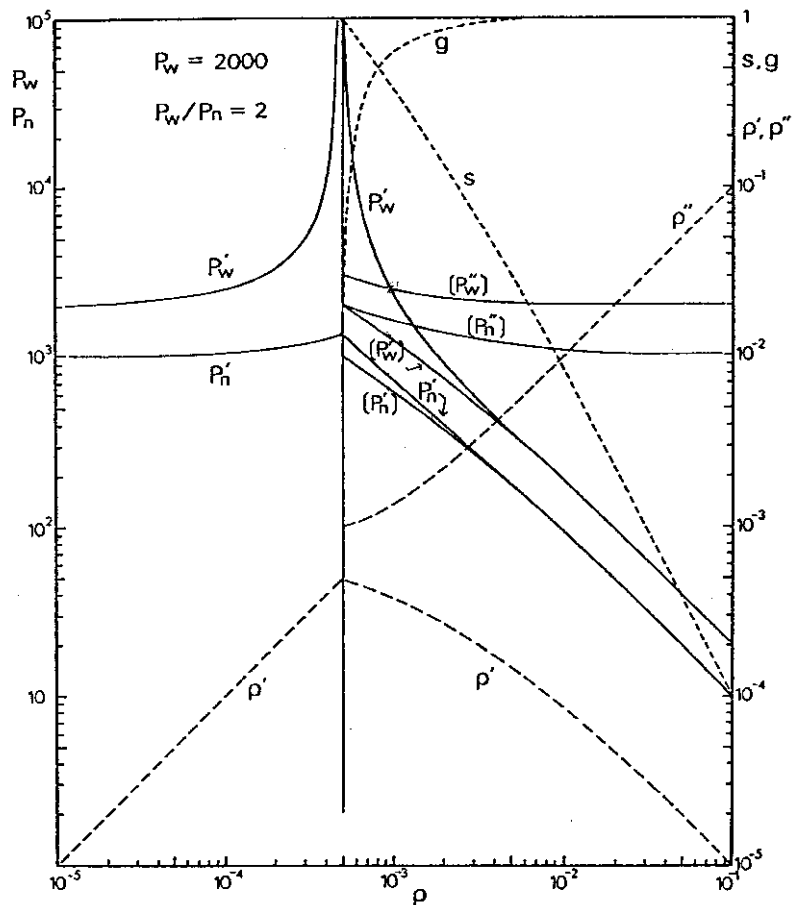
\*2: corresponding expression by Charlesby,<sup>15</sup>  $\bar{P}_v = \bar{P}_v \cdot s \cdot (r - \gamma \cdot 2^{-1} \cdot s^2)^{-1}$ , is regarded as incorrect or a misprint and is corrected here.

\*3:  $r$  or weight-average degree of polymerization of original chain molecules constructing sol or gel in the case of removing crosslinks

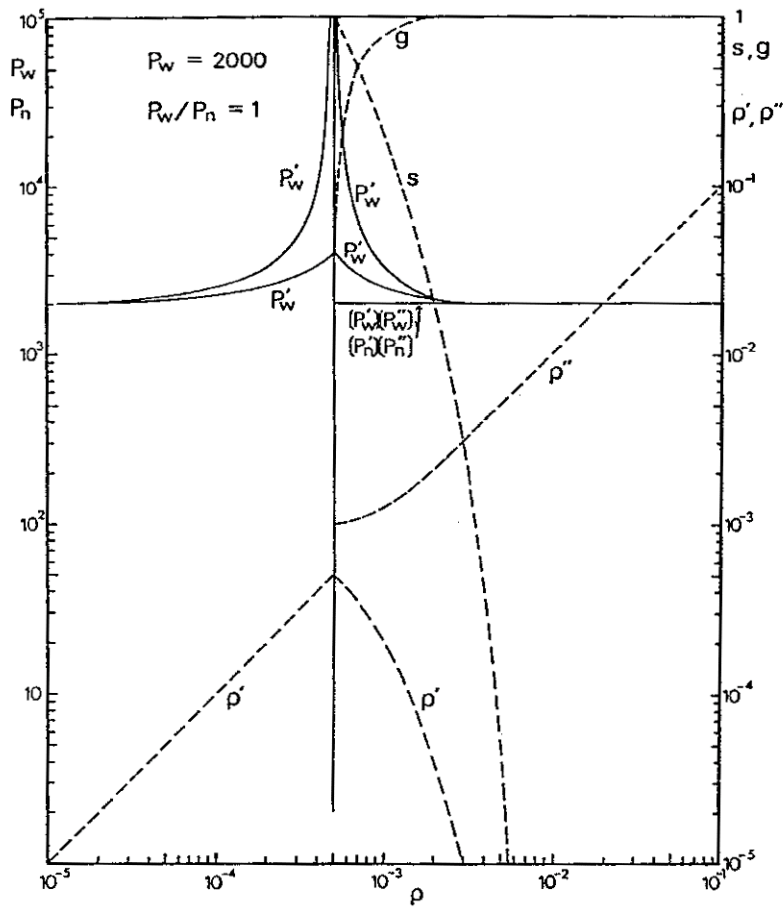
\*4:  $\bar{P}_w$  distribution:  $\xi = 1$ ; Most probable distribution:  $\xi = 2$ ; Broader distribution:  $\xi >$



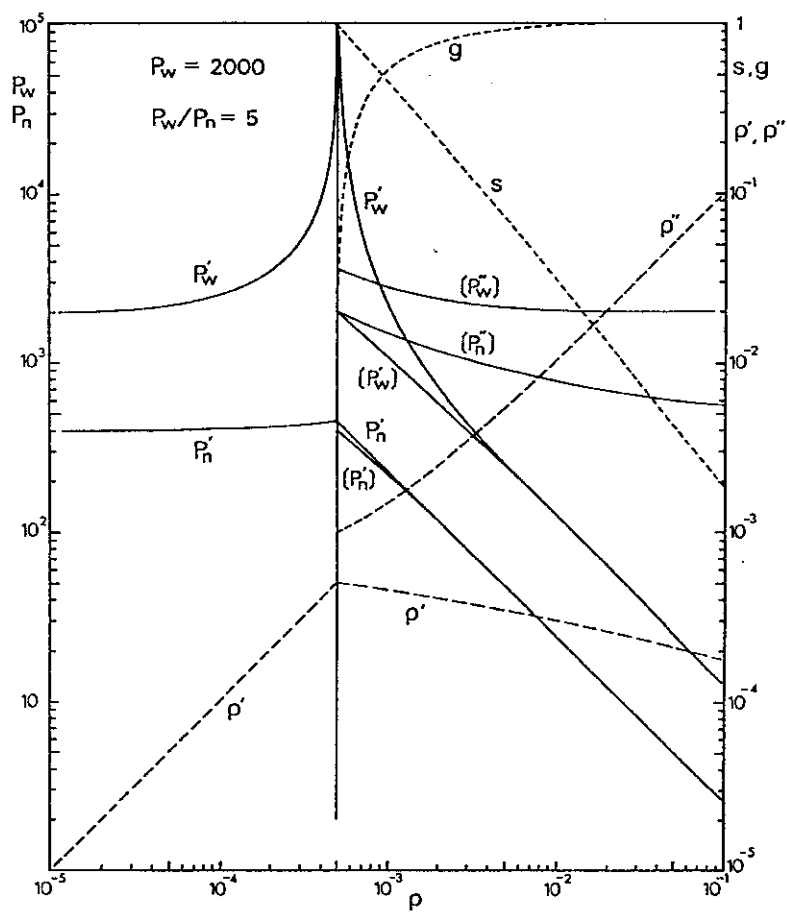
**Figure 62** Two types of crosslinking and their effects to insolubilization of polymer. Theoretical relationships are illustrated among crosslinking density,  $\rho$ , sol fraction,  $S$ , and weight average degree of polymerization,  $\bar{P}_w$ , where the most probable molecular weight distribution or  $\xi = \bar{P}_w / \bar{P}_n = 2$  is assumed. The dashed lines indicate the relations in the case (A) where all crosslinkable units can make crosslinking with any units in polymer. The solid lines indicate the relations in the case (B) where crosslinkable units can make crosslinking only each other.



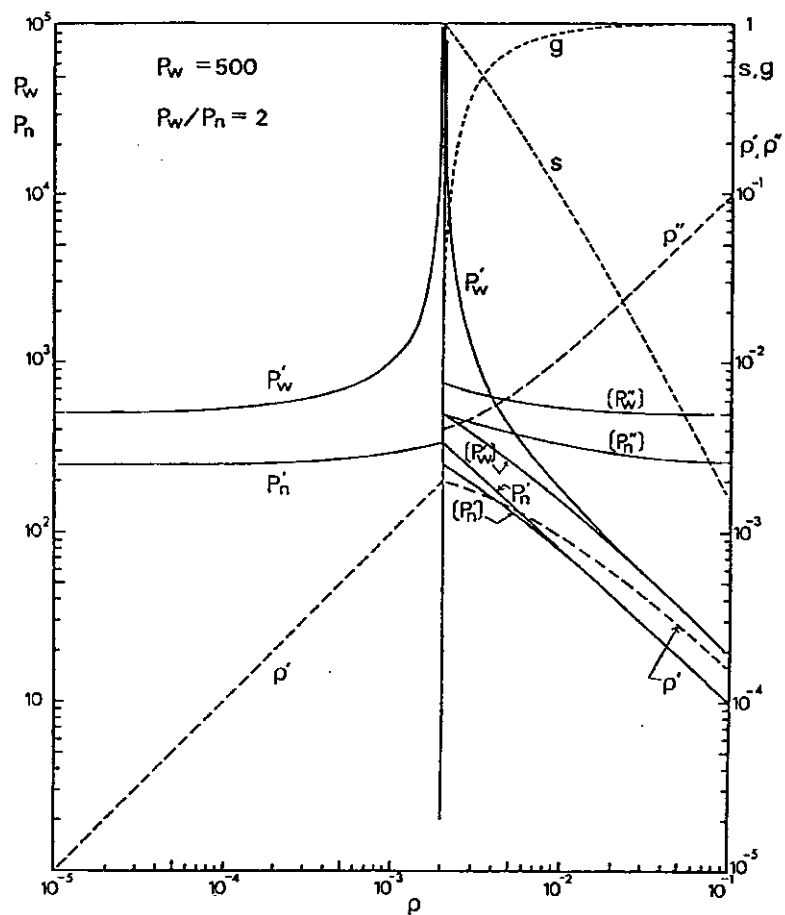
**Figure 63** Molecular parameters for crosslinked polymer as functions of crosslinking density,  $\rho$ , using starting polymer having  $\overline{P}_w = 2000$  and most probable molecular weight distribution ( $\xi = \overline{P}_w / \overline{P}_n = 2$ ).  $S$ : sol fraction,  $g$ : gel fraction,  $\rho'$ ,  $\rho''$ : Crosslinking densities for sol and gel,  $\overline{P}'_n$ ,  $\overline{P}'_w$ : Number- and weight-average degree of polymerization for sol,  $[\overline{P}'_n]$ ,  $[\overline{P}''_n]$ : Number-average degree of polymerization for original chains constructing sol and gel, respectively, in the case of removing crosslinks,  $[\overline{P}'_w]$ ,  $[\overline{P}''_w]$ : Weight-average degree of polymerization for original chains constructing sol and gel, respectively, in the case of removing crosslinks.



**Figure 64** Molecular parameters for crosslinked polymer as functions of crosslinking density,  $\rho$ , using starting polymer having  $\bar{P}_w = 2000$  and mono dispersed molecular weight distribution ( $\xi = \bar{P}_w / \bar{P}_n = 1$ ).



**Figure 65** Molecular parameters for crosslinked polymer as functions of crosslinking density,  $\rho$ , using starting polymer having  $\overline{P}_w = 2000$  and broader molecular weight distribution ( $\xi = \overline{P}_w / \overline{P}_n = 5$ ).



**Figure 66** Molecular parameters for crosslinked polymer as functions of crosslinking density,  $\rho$ , using starting polymer having  $\overline{P}_w = 500$  and most probable molecular weight distribution ( $\xi = \overline{P}_w / \overline{P}_n = 2$ ).

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