

Swelling of Crosslinked Polyelectrolytes Composed of Vinyl alcohol and Acrylic acid Units

By

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(Received October 30, 1961)

Crosslinked copolymers of different polymer composition and density of crosslinking points were prepared by copolymerization of methylacrylate and vinylacetate in the presence of divinylbenzene as a crosslinking agent, the copolymers then being converted by saponification into polyelectrolytes containing carboxyl groups along the chains. The degree of swelling of the sodium salts of these polyelectrolytes was measured in pure water. The osmotic coefficients in water were estimated from the degree of swelling in water, taking into consideration the effect of large deformation of the unit chains on the contractile pressure of the gel. The calculated values of the osmotic coefficient were very small and comparable to those previously found for the linear polyelectrolyte composed of the same components. The characteristic features of the results were discussed by considering the factors which may influence the activity of the counter-ions, such as the hydrolysis of the polyelectrolytes, the counter-ion fixation and the excluded volume effect of the macro-ions.

Introduction

In a previous paper¹⁾ the osmotic pressure of a linear polyelectrolyte composed of the sodium salt of acrylic acid and vinyl alcohol units, in which the content of ionizable groups was 7.8 mole percent, was measured in water in a polymer concentration range of 0.2-1.2 g/l. It was found that the osmotic coefficients are small and increase with increasing polymer concentration in this range. These results were explained by considering the Donnan-type equilibria in connection with the effect of hydrolysis and counter-ion fixation together with the effect which originates in the excluded volume of the macro-ion.

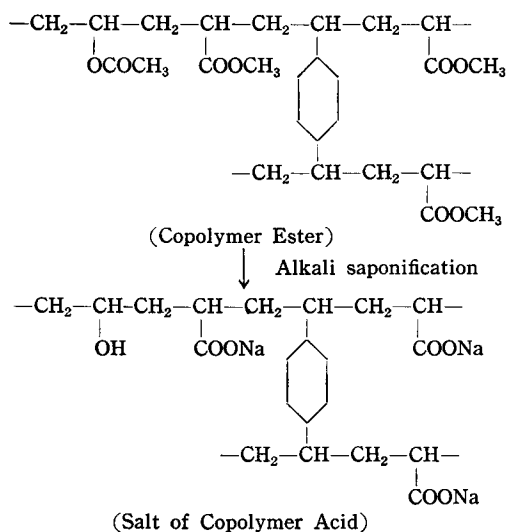
In this paper we will deal with crosslinked polyelectrolytes composed of the same components and discuss their thermodynamic properties as compared with those obtained for the linear molecule.

The preparation and characterization of the crosslinked polyelectrolytes will also be described in the early part of this paper.

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Preparation of Crosslinked Polyelectrolytes Composed of Acrylic Acid and Vinyl Alcohol Units

The copolymerization of methyl acrylate and vinyl acetate has been fully investigated by Sakurada². If methyl acrylate may be expected to copolymerize with divinylbenzene by analogy with its readiness to copolymerize with styrene, we can prepare crosslinked copolymer esters by copolymerization of methyl acrylate and vinyl acetate in the presence of a small amount of divinylbenzene. The copolymer esters thus obtained are converted by saponification into cross-linked copolymer acids composed of acrylic acid and vinyl alcohol units.



The copolymerization was carried out in benzene (66.7 g per 100 g of monomer mixture), in a sealed tube filled with nitrogen in the presence of benzoylperoxide (0.166 g per 100 g monomer mixture), at 80°C. The polymerization products thus obtained were perfectly extracted and the soluble part (linear polymers) was removed at the boiling point of acetone in a soxhlet through several renewals of the solvent. The conditions of copolymerization, the degree of conversion, and the weight fractions of the crosslinked copolymers in the polymerization products are listed in Table 1.

The composition of the copolymer esters was analysed by the conductometric titration³; the copolymer esters were saponified with alkali, then neutralized with a definite amount of excess hydrochloric acid and titrated with sodium hydroxide solution⁴. The analysis was carried out for both linear and crosslinked polymers. In the latter case the measurements were performed with pulverized samples. The results on the samples of M_5V_5 series are shown in Table 2. The

Table 1. Copolymerization of Methyl acrylate (MA) and Vinyl acetate (VAc) in the Presence of Divinylbenzene (DVB), at 80°C.

Sample Designation	Monomer Ratio (Mole %)		DVB (Wt. %)*	Polym. Time (Hrs)	Conversion (Wt.)	Crosslinked Polymer (Wt. %)**	MA Content (Mole %)
	MA	VAc					
$M_{10}V_0-0$	100	0	0	1	73.7	0	100
$M_{10}V_0-1$	100	0	0.05	1	74.5	57.44	100
$M_{10}V_0-2$	100	0	0.10	1	76.0	66.49	100
$M_{10}V_0-3$	100	0	0.20	1	74.2	68.33	100
$M_{10}V_0-4$	100	0	0.40	1	74.4	69.89	100
M_7V_3-0	70	30	0	8	94.0	0	74
M_7V_3-1	70	30	0.06	8	95.6	48.43	73
M_7V_3-2	70	30	0.12	8	96.7	59.25	72
M_7V_3-3	70	30	0.28	8	98.8	65.78	71
M_7V_3-4	70	30	0.47	8	97.0	73.81	72
M_5V_5-0	50	50	0	1	69.2	0	68
M_5V_5-1	50	50	0.05	1	68.4	0	69
M_5V_5-2	50	50	0.10	1	66.3	74.40	69
M_5V_5-3	50	50	0.20	1	62.8	69.48	71
M_5V_5-4	50	50	0.40	1	47.9	88.98	76
M_3V_7-0	32	68	0	55	96.4	0	31
M_3V_7-1	32	68	0.06	55	96.0	64.89	31
M_3V_7-2	32	68	0.12	55	90.5	61.66	33
M_3V_7-3	32	68	0.23	55	91.0	64.06	33
M_6V_7-4	32	68	0.46	55	91.2	68.09	33
M_1V_9-0	10	90	0	58	92.7	0	11
M_1V_9-1	10	90	0.06	58	93.7	5.01	11
M_1V_9-2	10	90	0.12	58	93.9	40.26	11
M_1V_9-3	10	90	0.24	58	—	—	—
M_1V_9-4	10	90	0.48	58	80.5	54.65	11

* Weight percent to the weight of monomer mixture.

** Weight percent to the weight of polymerization product.

Table 2. Comparison of Theoretical and Observed Methyl acrylate Contents in Copolymer Esters.

Sample Designation	MA Mole % (obs.)		MA Mole % (calc.)
	Linear Polymer	Crosslinked Polymer	
M_5V_5-0	65.1	—	67.35
M_5V_5-1	64.1	—	67.62
M_5V_5-2	68.9	72.7	69.33
M_5V_5-3	67.3	77.7	71.17
M_5V_5-4	74.2	77.5	76.08

experimental values were compared with the theoretical ones calculated from the monomer ratio of methyl acrylate to vinyl acetate and from the conversion, using the monomer reactivity ratios, $r_{VAc}=0.2$ and $r_{MA}=5.0$, which were obtained by Sakurada and Yoshida²⁾.

From Table 2 it may be permissible to regard that the composition of the linear copolymer is approximately equal to that of the corresponding crosslinked copolymer, though the former is slightly lower than the latter. The observed value agrees with the theoretical one. The contents of methyl acrylate listed in Table 1 are those obtained by calculation.

The crosslinked copolymer esters were then converted to crosslinked polyelectrolytes by alkali saponification. In each case about 1g of the copolymer esters was saponified in a mixture of methanol and water (9:1) at 60°C for about 40 hours. After completion of saponification the excess of sodium hydroxide and other impurities were extracted by methanol in a soxhlet. After extraction for about 80 hours with occasional changes of methanol, no extracted solution became colored upon addition of phenolphthalein. Then the samples were dried in a vacuum desiccator at room temperature. The samples thus prepared were believed to be the perfect sodium salts (the degree of neutralization=1) and did not include any free sodium hydroxide.

Dimension of Crosslinked Copolymers

The crosslinked copolymers are composed of unit chains crosslinked with divinylbenzene units. The length of the unit chain in a crosslinked copolymer acid, i.e., the molecular weight per unit chain M_c or the degree of polymerization per unit chain P_c , was estimated from that of crosslinked copolymer ester.

If the polymerization of vinyl acetate and methyl acrylate is carried out under such conditions as yield a large number of branches, which may be removed from the backbone chain by saponification, changes in the molecular dimensions due to the saponification process should be taken into consideration. However, our polymerization conditions were so chosen as to minimize the number of branches. The branching units to which these branches attach are tri-functional in nature, and we may assume that the removal of the branches will not affect the length of the unit chains connected by divinylbenzene units. Further we may assume that the composition of the crosslinked copolymers will not be changed essentially by removal of the branches because copolymerization in this case occurs randomly for both monomers. Thus the length of the unit chains in the copolymer esters was assumed unchanged by saponification.

M_c or P_c was evaluated from measurements of the swelling ratio of cross-

linked copolymer esters in benzene at 30°C. The amount of divinylbenzene in the copolymerization systems was relatively small; and even in the polymerization products of nearly 100% conversion, the contents of crosslinked copolymer were far less than 100% (see Table 1.). This may suggest some imperfect network structures in our present samples.

With such imperfect networks the molecular weight per unit chain, M_c , is calculated by the following equation⁵⁾.

$$-\left[\ln(1-v_2) + v_2 + \chi v_2^2\right] = \frac{V_1 \rho_2}{M_c} \left(v_2^{1/3} - \frac{v_2}{2} \right) \left(1 - \frac{2M_c}{M} \right). \quad \dots\dots\dots (1)$$

Where v_2 is the reciprocal of the degree of swelling in volume ratio Q_v , ρ_2 the density of the polymer, V_1 the molar volume of the solvent, χ the interaction parameter between polymer and solvent, and M the molecular weight of the primary molecule. Here the molecular weight of the samples polymerized without divinylbenzene—samples denoted by -0—was assumed to be that of the primary molecules.

The degree of polymerization of the primary molecules, P , (here P is adopted instead of M) was estimated from the intrinsic viscosities in benzene at 30°C by the following equation;

$$\begin{aligned} [\eta] &= KP^n \quad \dots\dots\dots (2) \\ K &= [3.08x + 8.91(1-x)] \cdot 10^{-3}, \\ n &= 0.71x + 0.62(1-x), \end{aligned}$$

where x denotes the mole fraction of methyl acrylate in the polymer chain. This equation was formulated by assuming K and n as linear functions of x , using the numerical values obtained for polyvinyl acetate⁶⁾ ($K=8.91 \cdot 10^{-3}$, $n=0.62$), and polymethyl acrylate⁷⁾ ($K=3.08 \cdot 10^{-3}$, $n=0.71$). The results are given in Table 3.

Table 3. Degree of Polymerization, P , of Primary Molecules.

	$M_{10}V_0-0$	M_7V_3-0	M_5V_5-0	M_3V_7-0	M_1V_9-0
$[\eta]$ (dl/g)	1.394	1.724	1.451	1.648	1.400
P	5210	5300	4090	4410	3660

The crosslinked copolymer esters reached their equilibrium swelling in three days in benzene at 30°C. The measured weight swelling ratios, Q_w , were reduced to the volume ratios, Q_v , and then M_c were calculated from Eq. (1) in which $\rho_2=1.17$ and $\chi=0.44$ were used for all polymers, taking into consideration the experimental results, i.e., $\rho_2=1.17$ for copolymer ester⁸⁾ containing about 40 mole%

of methyl acrylate, $\rho_2=1.173$ for polyvinyl acetate⁹⁾, $\chi=0.44$ for polymethyl acrylate⁷⁾ and $\chi=0.44$ for polyvinyl acetate¹⁰⁾, and that the change in ρ_2 does not greatly affect the calculated M_c value. The length, in P_c , of the unit chain thus obtained is shown in Table 4.

Table 4. Length of Unit Chain, P_c , in Crosslinked Copolymers.

Sample Designation	Swelling Ratio by Weight	P_c	Sample Designation	Swelling Ratio by Weight	P_c
$M_{10}V_0-1$	38.27	2150	M_5V_5-4	13.81	950
$M_{10}V_0-2$	23.86	1730	M_3V_7-1	70.88	2080
$M_{10}V_0-3$	18.21	1430	M_3V_7-2	51.20	1990
$M_{10}V_0-4$	15.69	1220	M_3V_7-3	32.79	1780
M_7V_3-1	54.82	2370	M_3V_7-4	23.77	1540
M_7V_3-2	28.73	1940	M_1V_9-1	81.97	1760
M_7V_3-3	21.95	1640	M_1V_9-2	85.75	1770
M_7V_3-4	12.14	900	M_1V_9-3	78.21	1760
M_5V_5-2	35.29	1710	M_1V_9-4	45.07	1650
M_5V_5-3	25.07	1500			

The degrees of swelling in weight ratio were plotted against P_c in Fig. 1, from which it may be pointed out that the swelling ratio is increased with decreasing methyl acrylate content.

This result reflects the fact that the molecular weight of the primary molecule decreases with decreasing methyl acrylate content, i.e., the imperfection in network structure increases with decreasing methyl acrylate content. Sample M_1V_9 is to be most influenced by such an effect and was eliminated for this reason from the succeeding experiment on crosslinked polyelectrolyte.

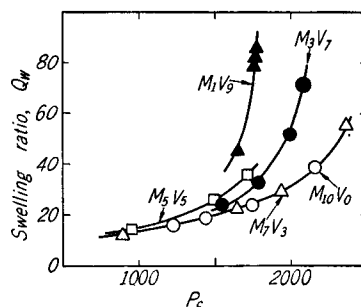


Fig. 1. The degree of swelling in weight ratio, Q_w , in benzene at 30°C plotted against the number of monomers between two adjacent crosslinks, P_c , for the crosslinked copolymers composed of methyl acrylate and vinyl acetate.

Swelling of Crosslinked Polyelectrolyte Copolymers

The equilibrium swelling ratios in pure water at 30°C of the crosslinked polyelectrolyte copolymers prepared by the method mentioned above were measured. The observed swelling ratios in water are listed in Table 5.

The behavior of a crosslinked polyelectrolyte in solvent may be associated with three factors, i.e., the osmotic pressure due to the mixing of polymer and

solvent, π_{mix} , the osmotic pressure arising from the mobile counter-ions, π_{ion} , and the contractile pressure of the network, P_{e1} .

The excess pressure, P_{ex} , which is exerted in the crosslinked polymer gel during the swelling process, may be given by the equation:

$$P_{\text{ex}} = \pi_{\text{mix}} + \pi_{\text{ion}} - P_{e1}. \quad \dots\dots\dots(3)$$

With equilibrium swelling, the excess pressure should be zero and π_{mix} is equal to the left hand member of Eq. (1). $-P_{e1}$, which is equal to the right hand member of Eq. (1) in the case of small deformation, is in the present experiment of large deformation corrected by a factor λ according to Katchalsky^{11,12}). Thus at swelling equilibrium, Eq. (3) may be written in the following form:

$$0 = -\frac{RT}{V_1} [\ln(1-v_2) + v_2 + \chi v_2^2] + \pi_{\text{ion}} - \frac{RT\rho_2\lambda}{M_c} \left(v_2^{1/3} - \frac{v_2}{2} \right) \left(1 - \frac{2M_c}{M} \right) \quad \dots\dots(4)$$

in which λ is a correction factor for highly swollen gels derived from the use of the inverse Langevin function¹²):

$$\lambda = 1 + \frac{0.6sv_2^{-2/3}}{P_c - sv_2^{-2/3}} \quad \dots\dots\dots(5)$$

where s is the number of monomers per statistical element in Kuhn's theory¹³. v_2 , the reciprocal of the degree of swelling in volume ratio Q_v , is so small under the present experimental conditions that the first term on the right-hand side of Eq. (4) may be neglected in comparison with the other two terms. To a similar approximation $v_2/2$ may also be neglected compared with $v_2^{1/3}$. In this manner we obtain

$$\pi_{\text{ion}} = \frac{RT\rho_2\lambda}{M_c} Q_v^{-1/3} \left(1 - \frac{2M_c}{M} \right). \quad \dots\dots\dots(6)$$

The osmotic coefficient g is given by the ratio of the observed value of π_{ion} to the ideal osmotic pressure produced by the polymer when it perfectly dissociates. Denoting the mole fraction of acrylic acid in the copolymer by x and the degree of neutralization of acrylic acid by α (in the present experiment $\alpha=1$), g is given by the following equation;

$$g = \frac{\lambda Q_v^{2/3}}{\alpha x P_c} \left(1 - \frac{2M_c}{M} \right). \quad \dots\dots\dots(7)$$

In Table 5, the osmotic coefficients of the crosslinked polyelectrolytes in water at 30°C, calculated from Eq. (7), are summarized. In this calculation, s in Eq. (5) was assumed to be 10 according to the results obtained for the equilibrium swelling in water of gels of crosslinked polymethacrylic acid^{12,14}), and for P_c the values listed in Table 4 were used. In the fourth column of Table 4 the

Table 5. Swelling Ratio in Water of Crosslinked Polyelectrolytes Composed of Vinylalcohol and Sodium Acrylate, and Osmotic Coefficient Calculated by Eq. (7).

Sample Designation	Mole Fraction of Sodium Acrylate x	Swelling Ratio by Weight	Polymer Conc. $c(g/l)$	λ	g
$M_{10}V_0-1$	1.00	574	1.74	1.332	0.008
$M_{10}V_0-2$	1.00	441	2.27	1.355	0.017
$M_{10}V_0-3$	1.00	223	4.48	1.239	0.016
$M_{10}V_0-4$	1.00	143	6.99	1.194	0.016
M_7V_3-1	0.73	1004	0.92	1.520	0.010
M_7V_3-2	0.72	486	2.06	1.328	0.018
M_7V_3-3	0.71	410	2.44	1.290	0.026
M_7V_3-4	0.72	114	8.77	1.245	0.034
M_3V_7-1	0.31	1990	0.50	4.252	0.066
M_3V_7-2	0.33	1281	0.78	2.146	0.041
M_3V_7-3	0.33	796	1.28	1.693	0.059
M_3V_7-4	0.33	374	2.89	1.401	0.059

polymer concentration in gels was given by $c(g/l)$ as calculated from the swelling ratio by $c = \rho_2 1000/Q_v$.

The osmotic coefficient g in water is plotted against the polymer concentration in Fig. 2, in which g of M_3V_7 first decreases in the very low concentration range, passes through a minimum and increases with increasing polymer concentration and then levels off. On the other hand g of M_7V_3 or $M_{10}V_0$ increases in the low polymer concentration range and then levels off. The latter behavior is similar to that obtained for a linear polyelectrolyte¹⁾ composed of sodium acrylate (7.8 mole%) and vinylalcohol (92.8 mole%) in the same concentration range. The magnitude of g is also nearly the same as that of the linear polymer ($g=0.014\sim 0.055$ in the concentration range $c=0.2\sim 1.2$). Such a tendency of g to increase with c was also found with the kalium salt of glyoxylic acid-partial acetal of polyvinyl alcohol linear polymer in water¹⁵⁾. Thus the behavior of g vs. c obtained from the swelling ratio of crosslinked polyelectrolyte is said to be comparable to that from the osmotic pressure of linear polyelectrolyte. In other words, the crosslinked polyelectrolyte in a highly swollen gel may be considered to be the microscopic analog of a linear polyelectrolyte in dilute solution. Thus

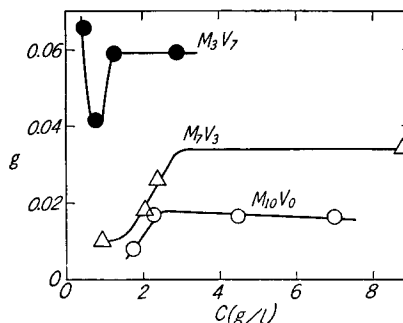


Fig. 2. The osmotic coefficient, g , plotted against the polymer concentration in gels, c , for the crosslinked polyelectrolytes composed of sodium acrylate and vinyl alcohol, in water at 30°C.

the osmotic coefficient based on the swelling measurement of crosslinked polyelectrolyte may provide a useful means to discuss the osmotic pressure of linear polyelectrolyte in dilute solution range.

The behavior of g as shown in Fig. 2 can not be explained by such theoretical considerations as Osawa's¹⁶⁾, according to which g decreases with polymer concentration because of the increase in counter-ion fixation. On the contrary, the theory proposed by Sakurada, Hosono and Ise¹⁷⁾ is different from the former in that it takes into consideration the distribution and volume effects of macro-ions with the aid of Wick-Eigen's theory. According to the latter theory the osmotic coefficient decreases and then increases through a minimum with increasing polymer concentration, if both the number of the effective charges and the expansion of the macro-ion are constant. At a constant number of the effective charges, the larger the expansion of the macro-ion, the lower will be the concentration of the minimum point. In the concentration range in which g increases with concentration, a larger g is expected for a larger expansion of the macro-ion.

Such theoretical considerations contribute to a discussion of the results with crosslinked polyelectrolytes as shown in Fig. 2. If the effect of the excluded volume of macro-ions to increase g , i.e., the interaction between unit chains (macro-ion), is larger than the effect to reduce g such as the increase of the counter-ion fixation, then we may expect a region in which g increases with polymer concentration. Such behavior was realized in Fig. 2.

The second feature of the results shown in Fig. 2 is that the numerical values of g are very small in the experimental range. This may come¹⁾ from the decrease in the effective charges due to the hydrolysis of sodium acrylate and the counter-ion fixation. The experimental results show that the decrease in the effective charges is larger for samples of larger acrylic acid content. This conclusion accords with the theoretical result¹⁶⁾ that the counter-ion fixation decreases with increasing content of ionizable groups, and also with the experimental results obtained on carboxymethyl celluloses¹⁸⁾ of various degree of etherification.

Acknowledgment—The authors are indebted to Professor Ichiro Sakurada and Dr. Yasuyoshi Sakaguchi for their comments and suggestions.

References

- 1) I. Sakurada, A. Nakajima and H. Sotobayashi; *Chem. High Polymers, Japan*, **16**, 363 (1959).
- 2) I. Sakurada and M. Yoshida; *Chem. High Polymers, Japan*, **7** 334 (1950).
- 3) I. Sakurada and T. Matsumoto; *Chem. High Polymers, Japan*, **7**, 142 (1950), **8**, 412 (1951).
- 4) I. Sakurada and K. Kawashima; *Chem. High Polymers, Japan*, **8**, 142 (1951).
- 5) P. J. Flory; *J. Chem. Phys.*, **18**, 108 (1950).

- 6) A. Nakajima; Chem. High Polymers, Japan, **6**, 451 (1949), **11**, 142 (1954).
- 7) S. Basu and H. Roy; J. Sci., Ind. Res., **11B**, 90 (1952), C. A., **46**, 7847 (1952).
- 8) M. Yoshida; private communication.
- 9) A. Nakajima, H. Sotobayashi and I. Sakurada; Chem. High Polymers, Japan, **14**, 566 (1957).
- 10) I. Sakurada, A. Nakajima and H. Aoki; J. Polymer Sci., **35**, 507 (1959).
- 11) A. Katchalsky, O. Künzle and W. Kuhn; J. Polymer Sci., **5**, 283 (1950).
- 12) A. Katchalsky, S. Lifson and H. Eisenberg; J. Polymer Sci., **7**, 571 (1951).
- 13) W. Kuhn; Koll-Z., **68**, 2 (1934). W. Kuhn and F. Grün, J. Polymer Sci., **1**, 183 (1946).
- 14) W. Kuhn, B. Hargitay, A. Katchalsky and H. Eisenberg; Nature, **165**, 514 (1950).
- 15) I. Sakurada, H. Sotobayashi and A. Nakajima; Chem. High Polymers, Japan, to be published.
- 16) F. Osawa, N. Imai and I. Kagawa; J. Polymer Sci., **13**, 93 (1954).
- 17) I. Sakurada, M. Hosono and N. Ise; THIS MEMOIRS, **19**, 402 (1957).
- 18) I. Kagawa, H. Yamada and I. Imai; J. Chem. Soc., Japan (Ind. Chem. Section), **53**, 120 (1950).