

Effect of composition of polyacrylamide gels on exclusion limits

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ABSTRACT

An aqueous ethanol solution of acrylamide, N,N'-methylenebisacrylamide as cross-linked agent, and a third monomer was dispersed in an *n*-alkane and the three monomers were copolymerized to spherical porous gels. The effect of the composition of the third monomer in the feed on the exclusion limits of the gels was investigated. As the third monomers, acrylonitrile, methacrylamide, N,N-dimethylacrylamide, N,N-dimethylaminopropylacrylamide hydrochloride and N,N-dimethylaminopropylmethacrylamide hydrochloride were used. The logarithm of the exclusion limits of the polyacrylamide terpolymer gels bears a linear relationship to the difference between the values of the solubility parameter of the solvent and gels.

INTRODUCTION

Among the packing materials used for the separation and purification of various compounds by size exclusion, the advantage of polyacrylamide (PAAm) gels is the lower content of ionic groups and the lower adsorption capacity for samples other than gels. For the Bio-Gel P type (Bio-Rad Labs., Richmond, CA, U.S.A.), used for this purpose, an increase in exclusion limits is accompanied by a narrowing of the fractionation ranges and an increase in gel softness.

Dawkins and co-workers [1,2] carried out more rapid separations (flow-rate 1 ml/min) of water-soluble materials with spherical PAAm gels; these were prepared by inverse suspension polymerization. This gel has an exclusion limit of *ca.* $1 \cdot 10^5$ and a wider fractionation range than the Bio-Gel P types. The gel particles are porous, rigid and of the macroreticular (MR) type, and have a swelling coefficient of *ca.* 1.15. With a view to obtaining gels that have macropores and a wide fractionation range, we studied the preparation of terpolymer gels, composed acrylamide of (AAm), N,N'-methylenebisacrylamide (MBAA) and a third monomer by inverse suspension polymerization and characterized the MR type for these terpolymer gels by testing them as packing materials [3,4].

When using acrylonitrile (AN) or methacrylamide (MAAm) as the third monomer, having a lower solubility parameter (δ) than AAm, the exclusion limits of the gel (AN-AAm-MBAA or MAAm-AAm-MBAA) increased as the molar ratio of AN or

MAAm to AAm increased [5]. When using N,N-dimethylacrylamide (DMAAm), having about the same δ value as AAm, the exclusion limits of the gel (DMAAm-AAm-MBAA) have the same value, independent of an increase in the molar ratio of DMAAm to AAm.

When using N,N-dimethylaminopropylacrylamide hydrochloride (DMPAA · HCl) or N,N-dimethylaminopropylmethacrylamide hydrochloride (DMPMA · HCl) as the third monomer, having higher δ values than AAm, the exclusion limits of the gel (DMPAA · HCl-AAm-MBAA or DMPMA · HCl-AAm-MBAA) decreased as the molar ratio of DMPAA · HCl or DMPMA · HCl to AAm increased [6].

EXPERIMENTAL

The terpolymer gels used have been reported previously, together with their characteristics when used as packing materials [3,4]. Macroporus gel particles were produced in an inverse suspension process by polymerizing AAm, MBAA and the third monomer. The inverse suspension polymerizations of terpolymers were carried out under nitrogen in a 1-l cylindrical flask, fitted with a turbine-type stirrer and gas inlet and outlet tubes. The reaction was performed by dispersing an aqueous ethanol solution (11.4 vol.%) of three monomers in an *n*-alkane (Solvent M; Nichibeikoyu, Tokyo, Japan) ($d_4^{20} = 0.749$; b.p. = 220–245°C), containing a nonionic surfactant (sorbitan monostearate), with stirring. Ammonium peroxydisulphate as an initiator was introduced as an aqueous ethanol solution after mixing the two phases, and the reaction flask was kept at $55 \pm 2^\circ\text{C}$ for 2 h.

The particles were filtered, washed with toluene, extracted with acetone to remove water and dried in a stream of warm air at $50 \pm 2^\circ\text{C}$. Monomers were purified in the usual way, and other materials were used without further purification. The gel particles were swollen in water and were sieved to obtain a 100–200-mesh (74–148 μm) sieve fraction. The sieved gel particles were packed into a glass column (500 \times 8 mm I.D.) at atmospheric pressure.

The chromatographic apparatus consisted of a Model 396-31 pump (Milton Roy, Boca Raton, FL, U.S.A.), and a Shodex RI SE-11 differential refractometer (Showa Denko, Tokyo, Japan). Degassed, deionized water and 0.001 mol/l sodium chloride solution were used as eluents. The chromatographic behaviour was studied by elution of the water-soluble compounds, oligo (ethylene oxide)s and poly(ethylene oxide)s, at a pressure of 0–2 kg/cm² and flow-rate 82 cm/h (0.69 ml/min) as shown in Table I.

Tables II and III show the compositions and properties of the terpolymer gels used.

The solubility parameter (δ) of the gels was determined by a swelling method [7]. Dry gel particles were placed in a graduated cylinder and their weight (g/ml) was measured. They were then swollen at $25 \pm 1^\circ\text{C}$ in various liquids [8] and their volumes on swelling equilibrium were measured. Other swelling agents used were mixtures of two liquids. The value of δ for liquid mixtures may be calculated as follows [9]:

$$\delta_{\text{mix}} = (x_1 v_1 \delta_1 + x_2 v_2 \delta_2) / (x_1 v_1 + x_2 v_2)$$

TABLE I
SAMPLE MATERIALS

Sample	MW	Concentration of aqueous solution (% , w/w)
Polystyrene latex ^a		0.2
BD ^b	$2.00 \cdot 10^6$	0.2
PEO-SE 150 ^c	$1.20 \cdot 10^6$	0.5
PEO-SE 70 ^c	$6.61 \cdot 10^5$	0.5
PEO-SE 30 ^c	$2.78 \cdot 10^5$	0.5
PEO-SE 15 ^c	$1.48 \cdot 10^5$	0.5
PEO-SE 8 ^c	$7.3 \cdot 10^4$	0.5
PEO-SE 5 ^c	$4.0 \cdot 10^4$	0.5
PEO-SE 2 ^c	$2.5 \cdot 10^4$	0.5
PEG 6000 ^d	7900	1.0
PEG 4000 ^d	3300	1.0
PEG 2000 ^d	2100	1.0
PEG 600 ^d	650	1.0
PEG 200 ^d	230	1.0
Ethylene glycol	62	1.0
Acetone	58	5.0
Methanol	32	1.0

^a Dow Chemical (Midland, MI, U.S.A.) (particle diameter 0.109 μm).

^b Pharmacia (Uppsala Sweden)

^c Poly(ethylene oxide) standard sample (Toyo Soda, Tokyo, Japan).

^d Poly(ethylene glycol) (Wako, Osaka, Japan).

where x is the molar fraction and v is the molar volume of components 1 and 2 at 25°C. The degree of swelling (Q) was defined as the ratio of the wet bed volume (ml) in a liquid per unit weight (g) of the gel. The values of Q for various liquids were plotted against the δ values of the liquids used.

The values of δ for the gel were obtained as the maximum value obtained on the curve. Further, the values obtained for the gels were confirmed according to the method of Mangaraj [10] and Mangaray *et al.* [11].

TABLE II
COMPOSITION AND EXCLUSION LIMITS OF GELS

Gel No.	AAm (g)	MBAA (g)	Third monomer		MBAA in monomer feed (mol %)	Molar ratio of third monomer to AAm	Exclusion limits (molecular weight)
			Compound	Amount (g)			
1	30	10.0	None		13.3	0	$1.6 \cdot 10^4$
2	27.5	10.0	NA	2.5	13.0	0.120	$2.5 \cdot 10^4$
3	25.0	10.0	AN	5.0	12.7	0.270	$6.9 \cdot 10^4$
4	20.0	10.0	AN	10.0	12.2	0.670	$2.6 \cdot 10^5$
5	15.5	10.0	AN	15.0	11.6	1.34	$1.4 \cdot 10^6$
6	27.5	10.0	MAAm	2.5	13.5	0.075	$4.5 \cdot 10^4$
7	25.0	10.0	MAAm	5.0	13.6	0.168	$7.2 \cdot 10^4$
8	20.0	10.0	MAAm	10.0	14.0	0.416	$2.0 \cdot 10^5$
9	15.0	10.0	MAAm	15.0	14.4	0.834	$4.4 \cdot 10^5$

TABLE III
COMPOSITION AND EXCLUSION LIMITS OF GELS

Gel No.	AAm (g)	MBAA (g)	Third monomer		MBAA in monomer feed (mol %)	Molar ratio of third monomer to AAm	Exclusion limits (molecular weight)
			Compound	Amount (g)			
10	29.7	10.0	DMAAm	0.42	13.3	0.010	$1.3 \cdot 10^4$
11	29.1	10.0	DMAAm	1.29	13.3	0.032	$1.1 \cdot 10^4$
12	28.5	10.0	DMAAm	2.09	13.3	0.052	$1.1 \cdot 10^4$
13	27.1	10.0	DMAAm	4.16	13.3	0.110	$1.0 \cdot 10^4$
14	24.0	10.0	DMAAm	8.37	13.3	0.249	$1.1 \cdot 10^4$
15	29.7	10.0	DMAPMA · HCl	0.72	13.3	0.10	$5.5 \cdot 10^4$
16	29.1	10.0	DMAPMA · HCl	2.21	13.3	0.032	$1.6 \cdot 10^4$
17	28.5	10.0	DMAPMA · HCl	3.59	13.3	0.052	$7.9 \cdot 10^3$
18	27.1	10.0	DMAPMA · HCl	7.15	13.3	0.110	$7.9 \cdot 10^3$
19	24.0	10.0	DMAPMA · HCl	14.37	13.3	0.249	$4.7 \cdot 10^3$
20	29.7	10.0	DMAPAA · HCl	0.66	13.3	0.010	$1.4 \cdot 10^4$
21	29.1	10.0	DMAPAA · HCl	2.03	13.3	0.32	$3.9 \cdot 10^3$
22	28.5	10.0	DMAPAA · HCl	3.30	13.3	0.52	$3.8 \cdot 10^3$
23	27.1	10.0	DMAPAA · HCl	6.56	13.3	0.110	$8.7 \cdot 10^2$

RESULTS AND DISCUSSION

Table II shows the compositions and properties of the terpolymer gels prepared. The results have been reported previously [3,4]. As shown in Table II, when AN was used as the third monomer, at a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of the resulting gels (AN–AAm–MBAA) increased from $1.6 \cdot 10^4$ to $1.4 \cdot 10^6$ with an increase in the molar ratio of AN to AAm from 0 to 1.34. Similarly, when MAAm was used as the third monomer at a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of the gels obtained (MAAm–AAm–MBAA) increased from $1.6 \cdot 10^4$ to $4.4 \cdot 10^5$ with an increase in the molar ratio of MAAm to AAm from 0 to 0.834.

In general, aggregation and growth of microgels occur in the process of gel formation. Therefore, the increase in the exclusion limit on addition of AN and MAAm is assumed to occur as follows. Addition of the third monomer decreases the solubility of the polymers that constitute the microgels as shown in Fig. 1. Consequently, it promotes aggregation of the microgels rather than growth of polymerization; in other words, phase separation is accelerated. As shown in Fig. 2, the δ values for AN–AAm–MBAA gels decreased from 17.60 to 17.24 with an increase in the molar ratio of AN to AAm from 0 to 1.34. Also, the δ values for MAAm–AAm–MBAA gels decreased from 17.60 to 17.35 with increasing molar ratio of MAAm to AAm.

As shown in Table III, when DMAAm was used as the third monomer with a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of the gels obtained (DMAAm–AAm–MBAA) were in the range $1.0 \cdot 10^4 - 1.6 \cdot 10^4$, unlike the results for the other terpolymer gels whose exclusion limits were influenced by the molar ratio of the third monomer to AAm.

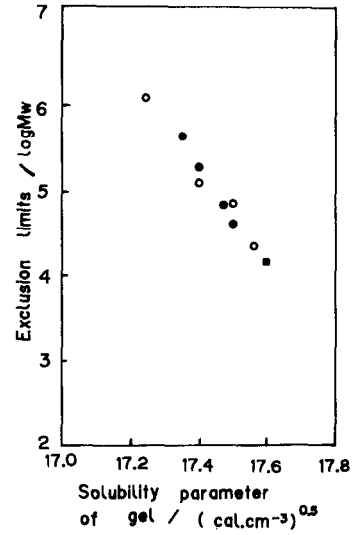
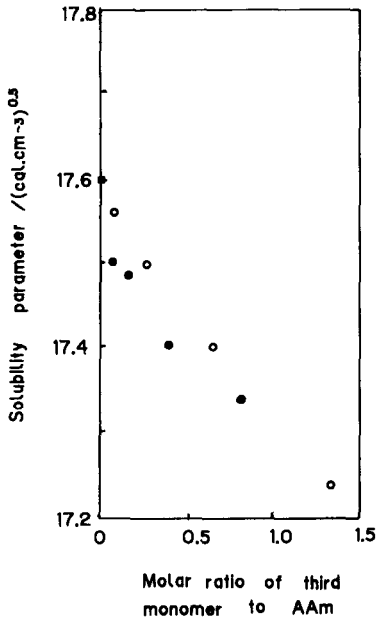


Fig. 1. Correlation of solubility parameters of the gels with molar ratio of the third monomer to AAm. ■ = AAm-MBAA gel; ○ = AN-AAm-MBAA gel; ● = MAAm-AAm-MBAA gel.

Fig. 2. Correlation of exclusion limits with the solubility parameters of the gels. ■ = AAm-MBAA gel; ○ = AN-AAm-MBAA gel; ● = MAAm-AAm-MBAA gel. Mw = Molecular weight

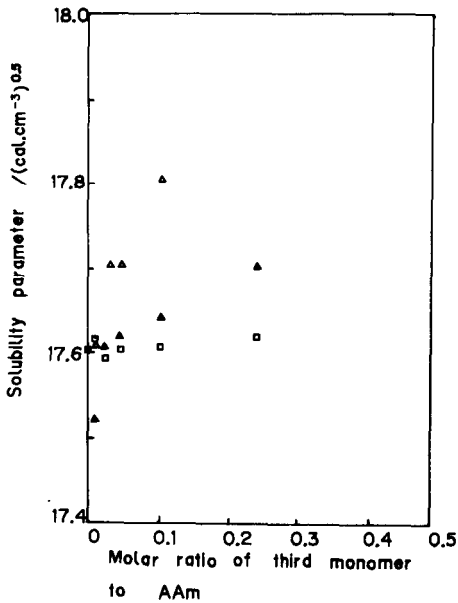


Fig. 3. Correlation of solubility parameters of the gels with molar ratio of third monomer to AAm. ■ = AAm-MBAA gel; ▲ = DMAPMA · HCl-AAm-MBAA gel; △ = DMAPAA · HCl-AAm-MBAA gel; □ = DMAAm-AAm-MBAA gel.

When DMAPAA · HCl was used as the third monomer with a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of the gels obtained (DMAPAA · HCl-AAm-MBAA) decreased from $1.6 \cdot 10^4$ to $8.7 \cdot 10^2$ as the molar ratio of DMAPAA · HCl to AAm increased from 0 to 0.110.

When DMAPMA · HCl was used as the third monomer with a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of the gels obtained (DMAPMA · HCl-AAm-MBAA) decreased from $5.5 \cdot 10^4$ to $4.7 \cdot 10^3$ as the molar ratio of DMAPMA · HCl to AAm increased from 0.01 to 0.249, but increased from $1.6 \cdot 10^4$ to $5.5 \cdot 10^4$ as the molar ratio of DMAPMA · HCl to AAm increased from 0 to 0.010.

Fig. 3 shows that the δ values for DMAAm-AAm-MBAA gels ranged from 17.58 to 17.65 and were independent of increase in the molar ratio of DMAAm to AAm. The δ values for DMAPAA · HCl-AAm-MBAA gels increased from 17.60 to 17.80 as the molar ratio of DMAPAA · HCl to AAm increased from 0 to 0.110. The δ values of DMAPMA · HCl-AAm-MBAA gels increased from 17.60 to 17.70 as the molar ratio of DMAPMA · HCl to AAm increased from 0.01 to 0.249, but decreased from 17.60 to 17.50 as the molar ratio of DMAPMA · HCl to AAm increased from 0 to 0.010.

These results with respect to DMAPMA · HCl-AAm-MBAA gels were contrary to the assumption that as the molar ratio increases, the exclusion limits and the δ values of the gels increase, as was found to be true with DMAPAA · HCl-AAm-MBAA gels. We consider that this difference results from the presence of the α -methyl group in DMAPMA. This was supported by the finding of acceleration of phase separation by the α -methyl group in the MAAm-AAm-MBAA gels. Based on the relationship between exclusion limits and molar ratio for DMAPMA · HCl-AAm-MBAA gels, we hypothesize that there are factors which depress phase separation,

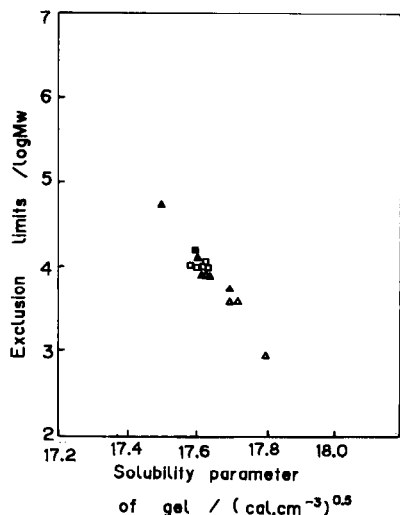


Fig. 4. Correlation of exclusion limits with the solubility parameters of the gels. ■ = AAm-MBAA gel; ▲ = DMAPMA · HCl-AAm-MBAA gel; △ = DMAPAA · HCl-AAm-MBAA gel; □ = DMAAm-MBAA gel.

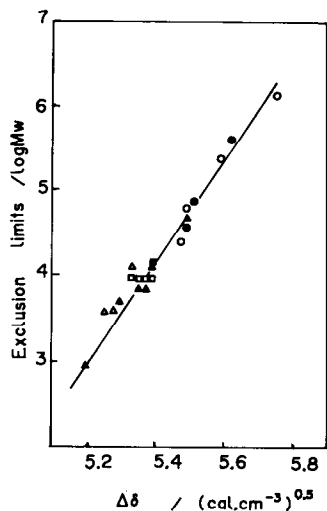


Fig. 5. Correlation of exclusion limits with the difference in the solubility parameters between the polymerization solvent and the gels, $\Delta\delta$. ■ = AAM-MBAA gel; ○ = AN-AAm-MBAA gel; ● = MAAm-AAm-MBAA gel; □ = DMAA-AAm-MBAA gel; ▲ = DMAPMA · HCl-AAm-MBAA gel; △ = DMAPAA · HCl-AAm-MBAA gel.

e.g., electrostatic repulsion between the dimethylaminopropyl groups and the hydrophilic nature of the pedant group, and factors that accelerate phase separation, *e.g.*, hydrophobic interaction between α -methyl groups. With a molar ratio of 0–0.010, the factors accelerating phase separation are stronger than the opposing factors.

Fig. 4 shows the correlation between the values for the terpolymer gels and exclusion limits. The exclusion limits of DMAPAA · HCl-AAm-MBAA and DMAPMA · HCl-AAm-MBAA gels correlated with the δ values of the gels.

Fig. 5 also clearly shows that an approximately linear relationship exists between the logarithm of the exclusion limits of the gels and the difference in the solubility parameters between the polymerization solvent and gels ($\Delta\delta$). This relationship applied in the three instances in which the third monomer component of the terpolymer gels has a lower δ value than AAm, a δ value about the same as that of AAm and a higher δ value than AAm. The straight line obeyed the equation.

$$\log (\text{mol.wt.})_{\text{lim}} = 5.58\Delta\delta - 25.94 \quad (r=0.990)$$

CONCLUSION

The logarithm of the exclusion limits of the polyacrylamide terpolymer gels bears a linear relationship to the difference between the value of the solubility parameter of the polymerization solvent and the gels, and the magnitude of δ for the polymer chains of the PAAm terpolymer gels governs the aggregation and growth of microgels in the process of gel formation.

ACKNOWLEDGEMENTS

We thank Professor Yasuji Ohtsuka and Haruma Kawaguchi of Keio University for helpful discussions.

REFERENCES

- 1 J. V. Dawkins and N. P. Gabbott, *Polymer*, (1981) 291.
- 2 J. V. Dawkins, N. P. Gabbott and M. C. J. Montenegro, *J. Chromatogr.*, 371 (1986) 283.
- 3 K. Suzuki, K. Nakazato and T. Takasaki, *Nippon Kagaku Kaishi*, (1979) 1327.
- 4 K. Nakazato and K. Suzuki, *Nippon Kagaku Kaishi*, (1984) 1919.
- 5 K. Nakazato and K. Suzuki, *Macromolecules*, 22 (1989) 1497.
- 6 K. Nakazato and K. Suzuki, *Macromolecules*, 23 (1990) 1800.
- 7 T. A. Orobino, H. B. Hopfenberg and V. Sanett, *J. Macromol. Sci. Phys.*, B3 (1963) 717, 777.
- 8 C. M. Hansen, *J. Paint Technol.*, (1967) 39, 104.
- 9 H. Burrell, *Encyclopedia of Polymer Science and Technology*, Vol. 12, Interscience, New York, 1971, p. 618.
- 10 D. Mangaraj, *Makromol. Chem.*, 65 (1963) 29.
- 11 D. Mangaraj, S. Patra and S. Rashid, *Markomol. Chem.*, 65 (1963) 39.