

# The Synthesis of Microgels Composed of Polyelectrolytes

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## SYNOPSIS

Microgels composed of dimethylaminopropylacryl amide (MAPA) or sodium salt of vinylbenzenesulfonic acid (VBS) were prepared by the crosslinking of primary polymers poly(MAPA-co-acrylamide) or poly(VBS-co-acrylamide) with glutaraldehyde in aqueous solutions. Almost mono disperse spheric microgels with the diameter of 120 nm were obtained in the very wide concentration range (up to 5 w/v% for the former and 12 w/v% for the latter). In the copolymerization of MAPA and *N*-methylolacrylamide, microgel with the diameter of 120–140 nm was formed during polymerization.

## INTRODUCTION

Microgels and microspheres had been usually synthesized by emulsion copolymerizations or by soap-free copolymerization.<sup>1–20</sup>

It is possible to apply these methods for hydrophilic monomers, but unstable reverse (W/O type) emulsion must be employed. Another method consists of the crosslinking of a primary polymer in a very dilute solution. This method is inefficient but can be applied to all polymer species.

In this study two polyelectrolytes, poly(*N,N*-dimethylaminopropylacryl amide) [poly(MAPA)] and sodium salt of poly(vinyl-benzenesulfonic acid) [poly(VBS)] containing suitable functional groups were crosslinked in aqueous solutions.

The main purposes of this study are the determination of the conditions (the concentrations of the polymers and the crosslinking agents) under which macrogelation is prevented and consequently of the preparation of polyelectrolyte microgels.

10<sup>-5</sup> mmHg. Sodium salt of vinylbenzenesulfonic acid (VBS), acryl amide (AAm), and *N*-methylolacryl amide (MOHAAM, Tokyo Kasei K.K.) were used after crystallization from filtered clear methanol solution. Poly(VBS-co-AAm) was obtained by the copolymerization of VBS with AAm, initiated by 4,4'-azobis(4-cyanopentanoic acid) (V-501, Wako Pure Chemicals K.K.) in vacuum-sealed ampoule. After polymerization, polymer was precipitated in a large volume of methanol, separated by filtration, and dried in vacuum. Accurately weighted polymer (about 100 mg) was dissolved in 100 mL 2*N* NaOH aqueous solution. The refluxing of the solution was continued for 48 h for the hydrolysis of amide or methylolamide groups. Then after cooling this solution was titrated with 0.1*N* HCl solution indicated by pH meter (HM-7E, TOA Ltd.). The AAm content was determined by the volume of aq. HCl between two flexion points in titration graph. Molecular weight was determined by using the following equation for poly(VBS):<sup>21</sup>

$$[\eta] = 17.8 \times 10^{-3} \bar{M}_v^{0.68}$$

## EXPERIMENTAL

### Materials

*N,N*-dimethylaminopropylacryl amide (MAPA, Kozin K.K.) was distilled just before use under 10<sup>-4</sup>–

The detail preparative conditions are summarized in Table I. Poly(MAPA-co-AAm) and poly(MAPA-co-MOHAAM) were prepared by the same manner as poly(VBS-co-AAm), but in this case, 2,2'-azobis(*N,N'*-dimethyleneisobutyramidine) (VA-061, Wako Pure Chemicals K.K.) was used as an initiator. Polymer was purified by the precipitation in a large quantity of acetone. The content of the MAPA

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**Table I Preparative Conditions and Characters of Primary Polymers<sup>a</sup>**

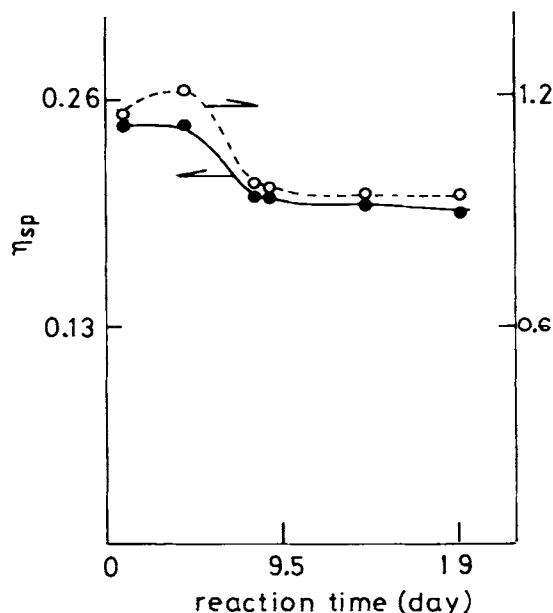
Polymer	Conditions of Polymerization			Results		
	Monomer (g)	AAm (g)	H <sub>2</sub> O (mL)	Yield (g)	AAm (mol %)	$M_w \times 10^{-4}$
P (MAPA-co-AAm)	20	2.5	200	8	30.0	—
P (VPS-co-AAm)	18	2	200	12	11.2	190

<sup>a</sup> At 60°C, in vacuum-sealed ampoules, for 3 days.

unit was determined by acid–base titration indicated by a pH meter. The detail preparative conditions and the composition of the polymers are summarized also in Table I.

### Crosslinking Reaction

The conditions were: crosslinking agent, glutaraldehyde at 70°C; solvent, H<sub>2</sub>O; polymer concentration 0.1–15% (w/v). The crosslinking reaction was traced by the viscometric change of polymer solution (examples are shown in Figures 1 and 3). A part of the reaction solutions was diluted ten times, and the specific viscosity  $\eta_{sp}$  of the diluted solutions was measured at 30°C. When the decrease in  $\eta_{sp}$  stopped,



**Figure 1** Variation of specific viscosity during crosslinking reaction [poly(MAPA-co-AAm)]. (1) Reaction conditions are summarized in Table II (solid and dotted lines correspond to Exp. 1 and 3 in Table II, respectively). (2)  $\eta_{sp}$  was measured for the reaction solutions after 10 times dilution with water.

a small portion of the solution was taken for SEM observation. Then the microfiltration and dissolution of the products into water were repeated several times by using microfilter WPVM047 (Millipore Ltd.; hole size 50 nm, smaller than the diameter of microgels preliminary measured by using the solution before purification). More detail conditions of the crosslinking reaction are shown in Tables II, III, and IV.

### Characterization of the Products

Scanning electron micrographs (SEM) were obtained by HITACHI S-510 apparatus. The diluted sample solutions (about 1 wt/v %) were sprayed on the cover glass, then Pt–Pd was sputtered on by HITACHI E-102. The diameter of the microgels was measured on the microscopic photography.

## RESULTS AND DISCUSSION

### Crosslinking of Poly(MAPA)

The concentration of polymer was increased gradually from very low (0.1 w/v %) to very high range

**Table II Conditions of Crosslinking and Diameter of poly(MAPA-co-AAm) Microgels<sup>a</sup>**

Exp. No.	Crosslinking Reaction		Products
	Polymer Conc. (% w/v)	GA/AAm (mol/mol)	Diameter (nm)
1	1	0.17	120–140
2	1.5	0.12	120–140
3	2	0.087	120–140
4	3	0.058	120–140
5	5	0.035	120–400

<sup>a</sup> Crosslinking reaction: in  $2.2 \times 10^{-2}$  N HCl, at 70°C, for 15 days.

<sup>b</sup> GA: glutaraldehyde.

**Table III** Conditions of Crosslinking and Diameter of Poly(VBS-co-AAm) Microgels<sup>a</sup>

Exp. No.	Crosslinking Reaction		Diameter (mm)
	Polymer Concn. (% w/v)	GA/AAm (mol/mol)	
1	0.4	5.4	120–140
1	2.0	1.1	120–140
3	10	0.22	120–140
4	12.5	0.17	120–160
5	14	0.16	140–400

<sup>a</sup> Crosslinking reaction: in  $2.2 \times 10^{-2}$  N HCl, at 70°C for 15 days.

**Table IV** Conditions of Polymerization and Crosslinking and Diameter of Poly(MAPA-co-MOHAAM) Microgels

Exp. No.	Monomer Concn. (% w/v)	GA/AAm (mol/mol)	Diameter (nm)
1	10	0	140–170
2	10	0.1 <sup>a</sup>	140–170

<sup>a</sup> After polymerization for 30 h GA and HCl was added and crosslinking reaction (in  $2.2 \times 10^{-2}$  N HCl) was continued for 15 days. Temp. 60°C without stirring.

(about 15 w/v %; the solution lost its fluidity). Contrary to our prediction, macrogelation did not take place in all the regions of the concentration. Moreover, the viscosity of the solutions decreased in the course of the reaction (Fig. 1), suggesting the formation of microgels. This suggestion was con-

firmed by SEM observation. The typical electron micrographs are shown in Figures 2(a) and 2(b) along with the conditions of the crosslinking. In this figure the spheric products could be seen clearly. As summarized in Table II, the diameter of the particles is independent of polymer concentrations, and distribution of the size is very narrow. At concentrations higher than 5% (w/v), the size distributions became wide, but macrogelation did not appear. It seems that there appeared a strong repulsive force between particles when the diameter reached about 120 nm, and thereafter no interparticle crosslinking could take place.

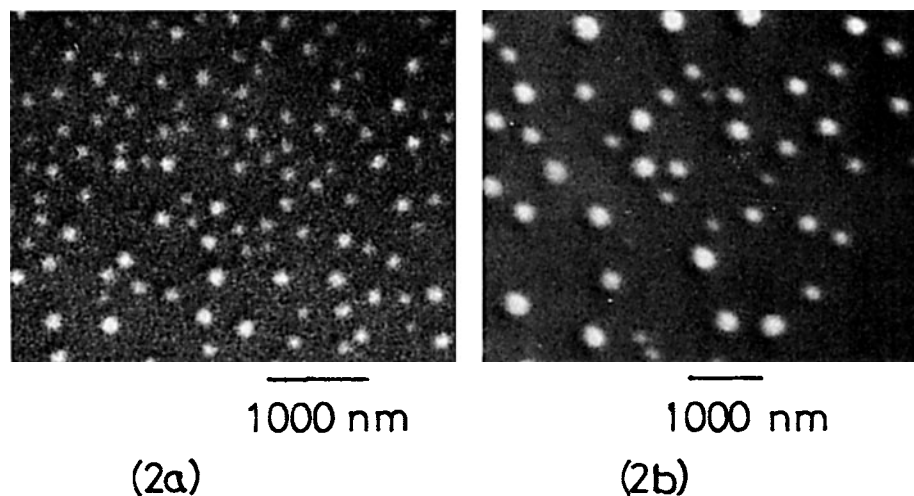
Further consideration will be done after the results with poly(VBS) copolymer are resumed.

### Crosslinking of Poly(VBS) Copolymer

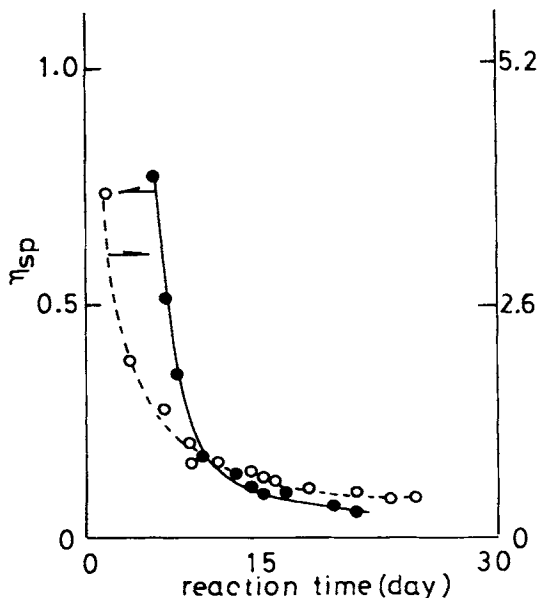
The solutions showed more drastic change in viscosity than poly(MAPA) copolymer solutions (Fig. 3). The electron micrographs and the diameter of the products are also shown in Figure 4 and Table III, respectively. The similar results were obtained as in the case of poly(MAPA) copolymer, except for the critical concentration where the particle size distribution became slightly wide (12%).

### Consideration on the Results

As mentioned previously, gelation was not observed even at very high concentration of the polymer. The molecular weight of the particles  $5.2 \times 10^8$  based on the electron micrographs (weight of a particle  $w_t = 4 \pi d^3 \rho / 3 = 8.6 \times 10^{-16}$ g; where  $d$  is the radius of



**Figure 2** Typical electron micrographs of crosslinked poly(MAPA-co-AAm). (2a and 2b correspond to Exp. 2 and 5 in Table II, respectively.)



**Figure 3** Viscosity of diluted poly (VBS) solution during crosslinking reaction. (1) Reaction conditions are summarized in Table III (solid and dotted lines correspond to Exp. 1 and 5 in Table III, respectively). (2)  $\eta_{sp}$  was measured for the reaction solutions after ten times dilution with water.

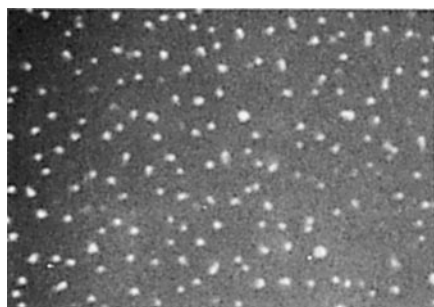
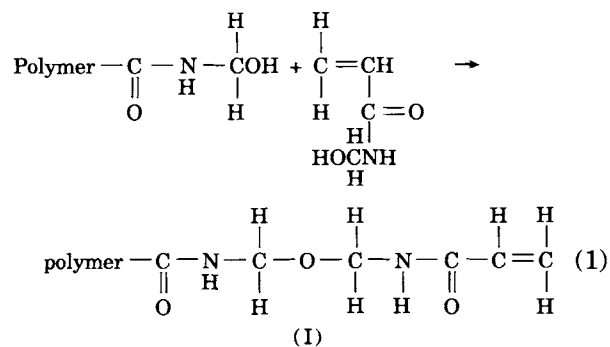
the particle =  $60 \times 10^{-7}$  cm,  $\rho$  is the density of the particle  $\approx 1$ . Molecular weight  $M_w = wt \times 6.23 \times 10^{23}$  is far larger than that of primary polymers ( $10^5$ – $10^6$ ). Moreover, we could not find any spheric particles on the micrographs of the primary polymer before crosslinking. These facts confirm the crosslinking of the primary polymers.

One possible way to explain this extraordinary behavior in the crosslinking reaction is based on two facts: First, these polymers are polyelectrolytes. Second, it is well known that the electric double

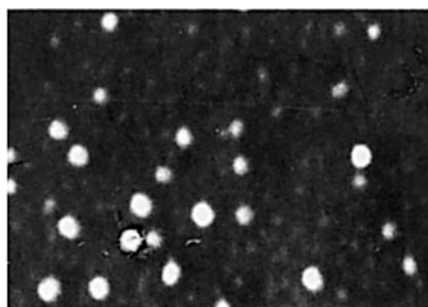
layer is formed around the electrolyte colloids.<sup>22</sup> At the first stage of the crosslinking reaction, small particles are formed. Then, electric double layer is constructed around the particles, and it prevents further coagulation. This double layer expands as charge density increases. With the advances of the intraparticle crosslinking, the segment density (in another words, the density of the electrolytic groups) increases. As a result, the stability of the crosslinked colloid increases.

These considerations are only suppositions, and the reasons the diameter of the particles became constantly 120 nm in the wide range of polymer concentration remain unclear. We think that further quantitative studies have to be carried out.

In the case of the copolymerization of MAPA and MOHAAM, the bluish tint, characteristic turbidity of the colloidal solution, was observed. After 24 h copolymerization, glutaraldehyde and HCl were added to the solution. The conditions and the result of this post-crosslinking are summarized in Table IV. The electron micrograph shows the formation of microgel (Fig. 5). It is supposed that the reaction between the methylor groups had occurred in a basic polymerization medium as follows:

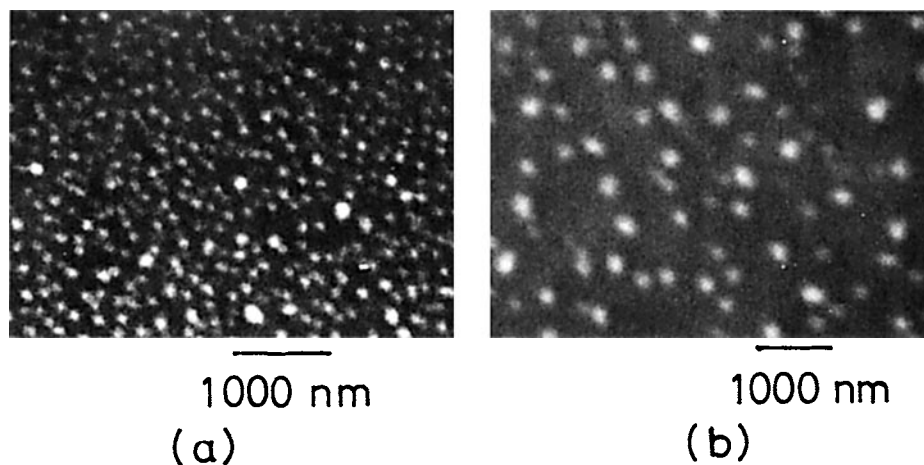


1000 nm  
(4 a)

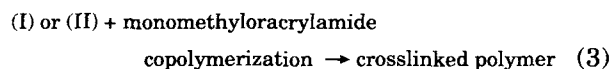
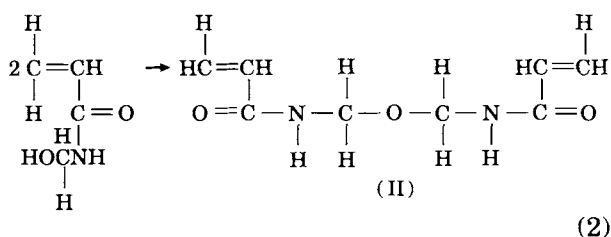


1000 nm  
(4 b)

**Figure 4** Typical electron micrographs of crosslinked poly (VBS-co-AAm). (4a and 4b correspond to Exp. 1 and 5 in Table III, respectively.)



**Figure 5** Electron micrograph of the product (a) obtained by the copolymerization of MAPA and MOHAAM, and of the product (b) obtained by post-crosslinking.



The detail results will be reported in another article.

## REFERENCES

- W. O. Baker, *Ind. Eng. Chem.*, **41**, 511-520 (1949).
- V. E. Shashoua and R. G. Beaman, *J. Polym. Sci.*, **33**, 101-117 (1958).
- M. R. Grancio and D. J. Williams, *J. Polym. Sci., A-1*, **8**, 2617-2629 (1970).
- D. Kuhnle and W. Funke, *Makromol. Chem.*, **139**, 255-267 (1970).
- M. Hoffman, *Makromol. Chem.*, **175**, 613-639 (1974).
- W. Obrecht, U. Seitz, and W. Funke, *Makromol. Chem.*, **175**, 3587-3591 (1974).
- W. Obrecht, U. Seitz, and W. Funke, *Makromol. Chem.*, **176**, 2771-2774 (1975).
- W. Obrecht, U. Seitz, and W. Funke, *Makromol. Chem.*, **177**, 1877-1888 (1976).
- Y. Ch. Yu and W. Funke, *Angew. Makromol. Chem.*, **103**, 187-202 (1982).
- Y. Ch. Yu and W. Funke, *Angew. Makromol. Chem.*, **103**, 203-216 (1982).
- H. Kawaguchi, H. Hoshino, H. Amagasa, and Y. Ohtsuka, *J. Colloid Int. Sci.*, **97**, 465-475 (1984).
- C. Graillat, C. Pichot, A. Guyot, and M. S. ElAasser, *J. Polym. Sci. Chem. Ed.*, **24**, 427-449 (1986).
- M. Alonso, M. Oliveres, L. Puigjaner, and F. Recasens, *Ind. Eng. Chem. Res.*, **26**, 65-72 (1987).
- M. Cmney, J. Hearn, and M. C. Wilkinson, *J. Polym. Sci. Chem. Ed.*, **25**, 505-518 (1987).
- F. Hoshino, T. Fujimoto, H. Kawaguchi, and Y. Ohtsuka, *Polymer J.*, **19**, 241-247 (1987).
- F. Hoshino, M. Sakai, H. Kawaguchi, and Y. Ohtsuka, *Polymer J.*, **19**, 383-389 (1987).
- F. Hoshino, H. Kawaguchi, and Y. Ohtsuka, *Polymer J.*, **19**, 1157-1164 (1987).
- B. W. Brooks, *Colloid Polymer Sci.*, **265**, 58-64 (1987).
- C. S. Cherm and G. W. Pochlein, *J. Polym. Sci. Chem. Ed.*, **25**, 617-635 (1987).
- M. Nomura, *Kobunshi (High Polymers, Jpn.)*, **36**, 680-683 (1987).
- A. Takahashi, T. Kato, and N. Nagasawa, *J. Phys. Chem.*, **71**, 2001 (1967).
- E. J. W. Verway and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.

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