

# Multilayered Polymer Particles. I. Synthesis of Hydrophilic Poly(dimethyl aminoethyl methacrylate) Core Particles

Ratsamee Sangsirimongkolying,<sup>1</sup> Suda Kiatkamjornwong,<sup>2</sup> Somsak Damronglerd,<sup>1</sup> Guang-Hui Ma,<sup>3</sup> Shinzo Omi<sup>3</sup>

<sup>1</sup>Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

<sup>2</sup>Department of Imaging and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

<sup>3</sup>Graduate School of Bio-Application and System Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184, Japan

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**ABSTRACT:** Hydrophilic poly(dimethyl aminoethyl methacrylate) (PDMAEMA) copolymer was obtained by suspension polymerization using 2,2'-azobisisobutyronitrile as an initiator, and by emulsion polymerization using 2,2'-azobis(2-amidinopropane)·2HCl (V-50). The influences of reaction parameters on the particle size and size distribution were investigated. For suspension polymerization, these included the concentrations of ethylene glycol dimethacrylate (EGDMA) crosslinking agent, ethyl acetate (EA), and Na<sub>2</sub>SO<sub>4</sub> electrolyte, the types of comonomer [methyl methacrylate (MMA) or styrene (ST)], solvent (EA or acetone), and stabilizer [poly(oxyethylene nonylphenylether) with 23 units of ethylene oxide (PEO23) or polyvinylpyrrolidone K30 (PVP)], polymerization temperature, and ST content in the comonomer feed. For the emulsion polymerization, the reaction parameters included the concentration of

cetyltrimethyl ammonium chloride and V-50, and types of initiator [V-50 or potassium persulfate] and crosslinking agent [EGDMA or divinylbenzene]. The solubility of hydrophilic comonomers in the aqueous phase was a key factor for the stability and morphology of the PDMAEMA particles. It was found that the stable uncrosslinked PDMAEMA latex could be prepared by charging 20 wt % (based on the monomer) of ST. Moreover, the crosslinking agent significantly affected the coagulum in both the suspension and the emulsion polymerizations. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1057–1070, 2002

**Key words:** dimethyl aminoethyl methacrylate; hydrophilic copolymers; dispersion polymerization; suspension polymerization; emulsion polymerization

## INTRODUCTION

Recently, acrylate latex containing amine groups has been used as a polymeric crosslinking agent of latices with epoxy groups, to reduce the release of harmful components into the environment, and to enhance the properties of water and solvent resistance and the mechanical strength of the films formed from the latices.<sup>1</sup>

However, highly hydrophilic polymers are not easily prepared by conventional polymerization. Dispersion polymerization might give monodisperse microspheres but the polymerization is apt to leave free stabilizers in the medium, which would be a harmful contaminant in their applications.<sup>2,3</sup> The hydrophilic homopolymer may flocculate copolymer particles and coagulate the latex. Consequently, batch and semicontinuous emulsion copolymerizations of methyl

methacrylate–butyl acrylate–dimethyl aminoethyl methacrylate (MMA–BA–DMAEMA) have been carried out using ammonium persulfate (APS) or APS/sodium sulfate as an initiator pair.<sup>1</sup>

The main purpose of this work was to synthesize new kinds of multilayered latex polymers with UV-scattering properties using the hydrophilic PDMAEMA as a core material. This study reports on the synthesis of hydrophilic PDMAEMA seed particles with various polymerization techniques.

## EXPERIMENTAL

### Materials

Dimethyl aminoethyl methacrylate (DMAEMA; Wako Pure Chemicals, Osaka, Japan), methyl methacrylate (MMA), styrene (ST), and ethylene glycol dimethacrylate (EGDMA; Kishida Chemical Industries, Tokyo, Japan) were of commercial grade. They were each distilled under reduced pressure and stored in a refrigerator before use.

2,2'-Azobisisobutyronitrile (AIBN; Wako Pure Chemicals) was used as a hydrophobic initiator for the suspension polymerization and dispersion polymer-

Correspondence to: S. Kiatkamjornwong (ksuda@chula.ac.th).

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ization; whereas 2,2'-azobis(2-amidinopropane)·2HCl (V-50) and potassium persulfate (KPS; Wako Pure Chemicals) were used as hydrophilic initiators for the emulsion polymerization. They were of reagent grade and used as received.

Poly(oxyethylene nonylphenylether), with 23 units of ethylene oxide (PEO23), and polyvinylpyrrolidone K30 (PVP, MW 40,000) were used as stabilizers for the suspension polymerization. Cetyltrimethyl ammonium chloride (CTAC, 30 wt %; Kao Chemicals, Japan) and sodium dodecyl sulfate (SDS; Merck, Darmstadt, Germany) were used as stabilizers for the emulsion polymerization. Methacryloyl-terminated PMMA (AA-6) macromonomers, toluene diisocyanate (MST1), PVP, and poly(vinyl alcohol) (PVA-217; degree of polymerization, 1700; degree of hydrolysis, 88.5%; Kuraray Chemicals, Osaka, Japan) were used as stabilizers for the dispersion polymerization.

Hydrochloric acid (35% HCl; Wako Pure Chemicals) was used for pH adjustment of the aqueous phase for suspension polymerization. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ; Wako Pure Chemicals) was used as an electrolyte. They were of reagent grade and used without further purification.

Ethyl acetate (EA) and acetone (Kishida Chemical Industries) were of commercial grade and distilled before use for suspension polymerization. Toluene, 1-butanol, 2-butanone, acetonitrile, and isobutanol were purchased from Kishida Chemical Industries and distilled before use for dispersion polymerization.

### Polymerization for dispersion polymerization

A four-neck glass separator flask was used as a polymerization reactor. A nitrogen inlet, condenser, and thermometer were equipped at the top of the flask. A magnetic bar and magnetic stirrers were used for agitation at a rate of 200 rpm. The reactor was immersed in a thermostat-controlled bath at 343 K during the polymerization.

### Polymerization for suspension and emulsion polymerizations

A flat-bottom glass separator, 500-cm<sup>3</sup> capacity, was used as a polymerization reactor. A nitrogen inlet, condenser, and feeder for the initiator solution were equipped at the top of the flask. A semicircular flat blade was used as an impeller with the agitation rate kept at 120 rpm. The reactor was immersed in a thermostat-controlled bath at 343 K during the polymerization.

### Preparation of PDMAEMA seed particles by dispersion polymerization

A typical run was prepared as follows. A solution containing 10 g of DMAEMA, 0.5 g of PEO23, 0.2 g of

AIBN, and 90 g of a water/isobutanol solvent mixture (50/50 wt %) was weighed into a 250-cm<sup>3</sup> flask. The mixture was deoxygenated by bubbling nitrogen gas for 1 h and subsequently heated to the reaction temperature at 343 K for 30 min. The polymerization was carried out for 18 h.

### Preparation of PDMAEMA seed particles by suspension polymerization

The detailed preparation conditions are shown in Table I. The mixture of distilled water, PEO23, and 2N HCl was used as the continuous phase. DMAEMA and the comonomer were mixed in the continuous phase in a reactor. During the nitrogen bubbling the agitation was continued at room temperature for 1 h and the flask was subsequently heated to the reaction temperature at 343 K for 30 min. After 5 cm<sup>3</sup> of the initiator solution had been slowly added at a rate of 3 cm<sup>3</sup> min<sup>-1</sup>, the polymerization was carried out for 24 h.

### Preparation of PDMAEMA seed particles by emulsion polymerization

PDMAEMA seed particles were synthesized at 343 K for 12 h based on the recipe in Table II. The synthesis procedure was the same as that for suspension polymerization except that the initiator solution was added immediately (10 cm<sup>3</sup> min<sup>-1</sup>) in the reactor.

### Characterization

After the polymerization, the final monomer conversion was measured gravimetrically. Polymers in a weighed latex sample were precipitated by acetone, centrifuged, washed two times, and dried in a vacuum oven. The size and size distribution of PDMAEMA copolymers were observed by scanning electron microscopy (SEM, SM-35CF II-A; JEOL, Japan) for the suspension polymerization, and by the light-scattering method (Zetasizer 1000HS; Malvern Instruments, UK) for the emulsion polymerization. The mean particle size and its size distribution were determined by a direct measurement of 200 particles per sample on the respective SEM micrographs.

The glass-transition temperature ( $T_g$ ) of PDMAEMA copolymer was investigated using a differential scanning calorimeter (Netzch 200; Germany) with a heating rate of 10°C min<sup>-1</sup> and a cooling rate of 20°C min<sup>-1</sup>. The sample (8–12 mg) was placed in an aluminum pan and was then put on the sample slot at room temperature along with an empty pan as a reference to assist output balance.

TABLE I  
Recipe of PDMAEMA Seed Particles by Suspension Polymerization<sup>a</sup>

Component and property	Run number															
	110	113	115	116	117	119	120	121	126	129	133	134	136	137	144	145
Water (g)	176	176	166	171	176	176	176	176	176	176	176	176	176	176	179	176
PEO23 (g)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	—	4.0
PVP (g)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.5	—
Na <sub>2</sub> SO <sub>4</sub> (g)	—	—	—	—	—	0.26	0.026	—	—	—	—	—	—	—	—	—
2N HCl (g)	1.0	—	1.0	1.0	1.0	1.0	1.0	1.0	—	1.0	1.0	1.0	1.0	1.0	1.0	1.0
0.1N NaOH (g)	—	—	—	—	—	—	—	—	1.8	—	—	—	—	—	—	—
DMAEMA (g)	17.4	17.4	16.0	15.4	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0
ST (g)	2.0	2.0	—	—	—	—	—	—	—	4.0	4.0	4.0	4.0	4.0	4.0	10.0
MMA (g)	—	—	4.0	4.0	4.0	4.0	4.0	4.0	4.0	—	—	—	—	—	—	—
EGDMA (g)	0.6	0.6	—	0.6	—	—	—	—	—	—	—	—	—	—	—	—
AIBN (g)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	—	0.4	0.4	0.4	0.4	0.4	0.4	0.4
EA (g)	—	5.0	5.0	5.0	15.0	10.0	5.0	5.0	—	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Acetone (g)	5.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
KPS (g)	—	—	—	—	—	—	—	—	0.4	—	—	—	—	—	—	—
Agitation rate (rpm)	120	120	120	120	120	120	120	120	120	120	160	160	160	120	160	120
Temperature (K)	343	343	343	343	343	343	343	343	343	343	343	348	338	333	343	343
Conversion	68	88	62	73	68	68	62	65	no latex	64	57	72	72	64	73	87
creased surface	—	coagulum	5.37	coagulum	3.30	22.06	7.63	7.53	—	1.27	8.23	agglomerated	2.26	agglomerated	—	—
d <sub>p</sub> (μm)	—	—	26.7	—	26.1	42.9	38.6	28.7	—	29.7	20.0	—	33.0	—	—	—
% CV	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

<sup>a</sup> Bubbling N<sub>2</sub> for 1 h, adding 5 cm<sup>3</sup> AIBN in 2 min, polymerization time of 24 h.

TABLE II  
Recipe of P(DMAEMA-*co*-ST) Seed Particles by Emulsion Polymerization<sup>a</sup>

Component and property	Run number						
	152	153	154	156	157 <sup>b</sup>	159 <sup>b</sup>	160
DMAEMA (g)	16.0	16.0	16.0	16.0	16.0	16.0	16.0
ST (g)	4.0	4.0	4.0	4.0	2.0	3.0	4.0
DVB (g)	—	—	—	—	2.0	—	—
EGDMA (g)	—	—	—	—	—	1.0	—
Water (g)	180	180	180	180	180	180	180
Na <sub>2</sub> SO <sub>4</sub> (g)	0.25	0.25	0.25	0.25	0.25	0.25	0.25
CTAC (g)	2.50	0.65	1.30	—	1.31	1.31	1.32
SDS (g)	—	—	—	0.65	—	—	—
V-50 (g)	0.40	0.40	0.40	—	0.40	0.40	1.01
KPS (g)	—	—	—	0.40	—	—	—
Water (g)	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Conversion	60	72	76	25	66	67	70
$d_p$ (nm)	64	129	117	— <sup>c</sup>	800/13484	602	47
% CV	25	30	20	—	—	—	18

<sup>a</sup> Agitation rate 120 rpm, bubbling N<sub>2</sub> for 1 h, polymerization temperature 343 K, polymerization time of 12 h.

<sup>b</sup> The lattices were filtered to eliminate the coagulum before observing the particle size.

<sup>c</sup> Spherical and nonspherical morphology.

## RESULTS AND DISCUSSION

### Dispersion polymerization method

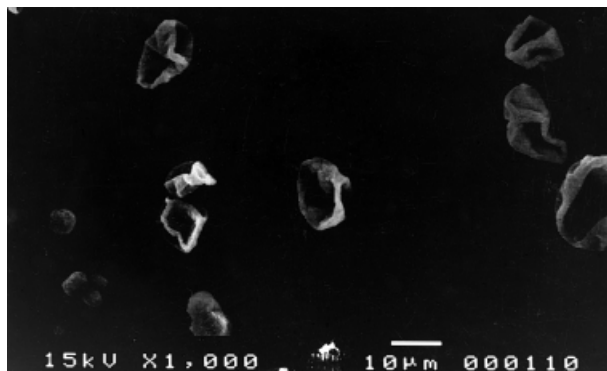
Hydrophilic PDMAEMA particles were prepared by dispersion polymerization using AIBN as an initiator. Various organic solvents were investigated and, among them, an isobutanol/water mixture was most effective. Methacryloyl-terminated PMMA (AA-6), PVP, PVA-217, and MST1 were used as stabilizers. It was found that the reaction did not require any type of stabilizer in a mixed solvent of isobutanol and water (50 : 50 wt %), which produced PDMAEMA particles in the micron range. In the dispersion polymerization, the solvent ratio between good and poor solvents greatly affected the particle size and size distribution. Control of particle size was attempted by varying the ratio between good and poor solvents in the dispersion polymerization of 2-hydroxyethyl methacrylate (HEMA) using poly(styrene-*block*-butadiene) [P(ST-*b*-Bd)] stabilizer. Uniform PHEMA particles in the micron range have been achieved in a mixture of 2-butanone and toluene.<sup>4</sup> We used *n*-butanol, toluene, and isobutanol as good solvents for PDMAEMA. The poor solvents used were 2-butanone, acetonitrile, acetone, and distilled water. The stable PDMAEMA seed latex particles were crosslinked with 3% (by weight) of ethylene glycol dimethacrylate (EGDMA) based on the total weight of the monomer. The crosslinking agent functioned only in a mixture of isobutanol and water. The results demonstrate that PDMAEMA microspheres were obtained in the solvent mixture containing 30–50% water based on the total weight of mixed solvent. Below 30 wt % of water in a mixed solvent, no particles were obtained. These results in-

dicate that a poor solvent of water is essential for the polymer to precipitate from the mixed solution. Because of the hydrophilic nature of the polymer, the swelling of the PDMAEMA particles of course increased as the content of water increased. The polymerization in solvents containing a higher water content yielded smaller PDMAEMA particles because more phase separation in the system controlled the polymer particle size. In this system, the monomer conversion was less than 30%, as determined by the gravimetric method, and the polymer particles were highly viscous. Therefore, it could be concluded that this system was inappropriate for preparing composite lattices with MMA because of the high viscosity, low conversion (<30%), and difficult stripping of isobutanol (bp 381 K) and elimination of unreacted reactants.

### Suspension polymerization method

#### Effect of crosslinking agent

EGDMA was used as a crosslinking agent to prevent the dissolution of DMAEMA from the seed particles, inhibit diffusion of the exterior-layer constituent polymer into the interior of particles, limit swelling in new monomers, and increase the glass-transition temperature and molecular weight of PDMAEMA particles. Crosslinking lattices of PDMAEMA copolymer were easy to apply to substrates.<sup>5</sup> The effect of the crosslinking agent EGDMA on the PDMAEMA copolymer morphology was studied, with AIBN dissolved in acetone and EA, and with different types of comonomers, MMA and ST. Table I shows the results for



**Figure 1** SEM micrograph of the crosslinked P(DMAEMA-*co*-ST) particles using AIBN dissolved in acetone (Run 110).

PDMAEMA copolymers prepared by suspension polymerization.

The effects of EGDMA on the particle size of the copolymers P(DMAEMA-*co*-MMA) and P(DMAEMA-*co*-ST) are given in Table I. In the presence of 3 wt % EGDMA (based on the monomer), the crosslinked P(DMAEMA-*co*-ST) and P(DMAEMA-*co*-MMA) latices gave a large amount of coagulum during the polymerization using AIBN dissolved in EA, as illustrated in Runs 113 and 116, respectively. Additionally, the crosslinked PDMAEMA particle aggregates, which became large enough to be macroscopically visible, differed in density from the surrounding medium and settled quite rapidly, leaving a more or less clear supernatant. As mentioned above, it was concluded that EGDMA exerted a critical influence on the coagulum particles in suspension polymerization using AIBN dissolved in EA. Large amounts of coagulum were formed and precipitated when EGDMA was added. When using acetone as a solvent, crosslinked P(DMAEMA-*co*-ST) particles with increased surfaces were obtained in Run 110, as shown in Figure 1. Figure 1 shows interesting morphology because the walls of the polymer particles almost collapsed. This result confirms the finding of Tawonsree et al.,<sup>6</sup> who found that an increase in EGDMA concentration resulted in coarser, porous spheres. In the absence of EGDMA, the coagulum disappeared and a stable P(DMAEMA-*co*-ST) latex was obtained using 20 wt % of ST in Run 129, whereas a stable P(DMAEMA-*co*-MMA) latex was not obtained using 20 wt % of MMA in Run 115. The cause of these phenomena is considered to be related to the addition of EGDMA. We can conclude that EGDMA produced coagulum and coarser particles, in suspension polymerization using AIBN both in EA and acetone, resulting from phase separation. As mentioned above, uncrosslinked P(DMAEMA-*co*-MMA) stable latex could not be prepared: a large amount of coagulum was generated during the polymerization while the concentration of DMAEMA was high in the aqueous phase, which

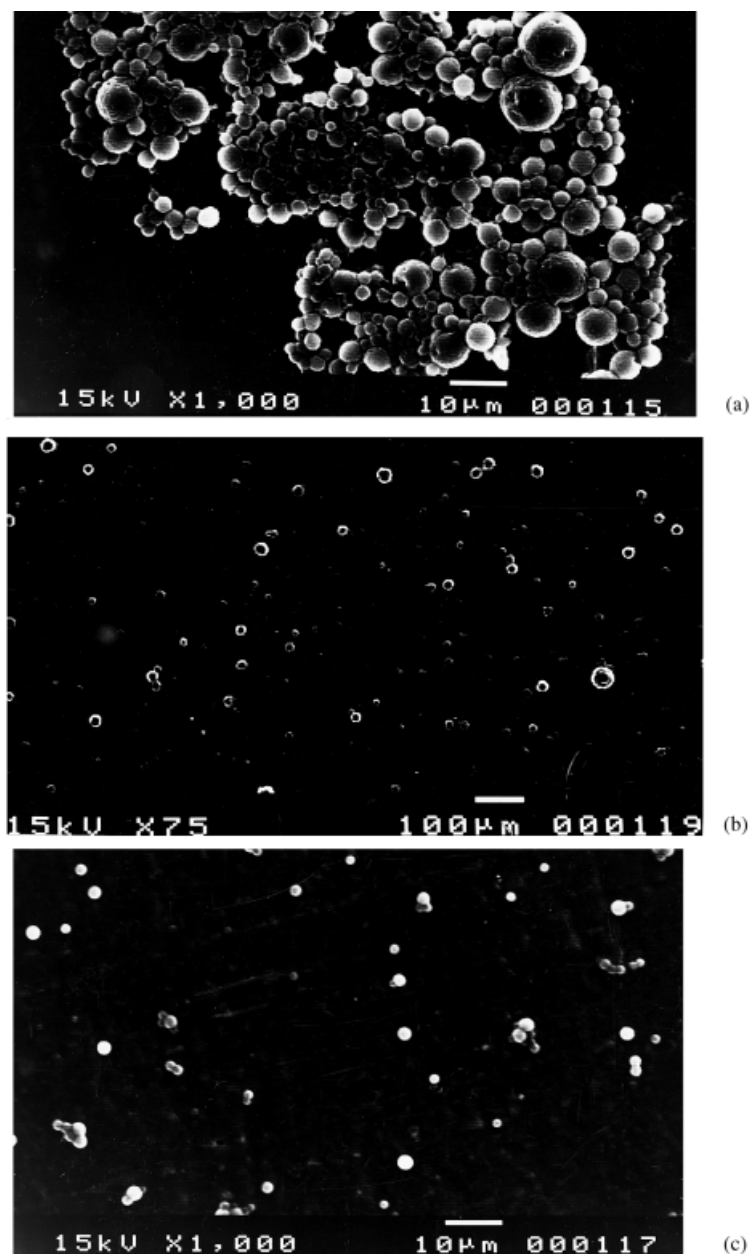
may indicate that unreacted monomers were trapped inside the particles during polymerization. The PDMAEMA is rubbery, composed of mostly soft segments of oligomers or monomers, and sticks together easily.

#### Effect of ethyl acetate concentration

The polymerizations were performed by charging 2.8, 5.8, and 9.0 wt % of EA, respectively, to the reaction. The MMA concentration was 20 wt % based on the total weight of the monomer, as shown for Runs 115, 119, and 117 in Figure 2. However, uncrosslinked, stable P(DMAEMA-*co*-MMA) latex was not obtained from these experiments because of its hydrophilic copolymer chains. Figure 3 shows that the particle size was considerably affected by the addition of EA. The mean particle diameter increased from 5.37 to 22.06  $\mu\text{m}$  when the amount of EA was increased from 2.8 to 5.8 wt %. An exception was found in Run 117 (9.0 wt % of EA), for which the particle diameter did not follow the increasing trend. We consider that this was probably related to the formation of a more homogeneous copolymer composition because of the addition of EA in the continuous phase. The hydrophobicity of copolymer chains increased as the number of MMA units increased. Therefore, the interfacial tension between the continuous phase and the particles increased, and they tended to coagulate to form larger particles so as to decrease the interfacial tension. The second reason was that the electrostatic repulsion force between the particles decreased as the permittivity of the continuous phase decreased, possibly as a result of the increase of particle size and the chain transfer behavior of EA in the particles, as the amount of EA was increased. However, when 9.0 wt % of EA was added into the polymerization system, it was found that the particle diameter decreased. The reason for these drastic changes is considered to be changes in the polarity of the continuous phase resulting from the addition of EA, which decreases the solubility of DMAEMA in the water attributed to the considerable hydrophilicity of PDMAEMA, probably leading to the formation of a hairy layer on the surfaces of microspheres. When the concentration of EA increased in the continuous medium, it forced the hairy layer to collapse.

#### Effect of electrolyte concentration

The electrolyte sodium sulfate was added to stabilize PDMAEMA chains. Sodium sulfate induces charges in the PDMAEMA chains, which are not soluble in water. The effects of the electrolyte on the properties of the resulting latex are also shown in Table I, which indicates that the particle size, particle size distribution, and agglomerated particles were greatly affected



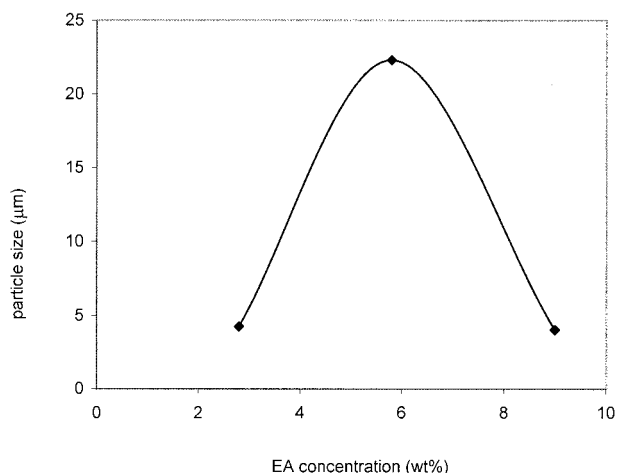
**Figure 2** SEM micrographs of the uncrosslinked P(DMAEMA-*co*-MMA) particles for various concentrations of ethyl acetate: (a) 2.8 wt % (Run 115); (b) 5.8 wt % (Run 119); (c) 9.0 wt % (Run 117).

by the addition of  $\text{Na}_2\text{SO}_4$ . The mean size of the uncrosslinked P(DMAEMA-*co*-MMA) particles prepared by charging  $\text{Na}_2\text{SO}_4$  in Run 121 ( $7.53 \mu\text{m}$ ) was greater than that without  $\text{Na}_2\text{SO}_4$  in Run 115 ( $5.37 \mu\text{m}$ ), but agglomerated particles still occurred in both runs. The mean particle size of the uncrosslinked P(DMAEMA-*co*-MMA) particles increased from  $7.53$  to  $7.63 \mu\text{m}$  when increasing the  $\text{Na}_2\text{SO}_4$  input from  $10^{-3}$  to  $10^{-2} \text{ M}$ , and the coefficient of variation increased, from 28.7% to 38.6% in Runs 121 and 120, respectively, as shown in Figure 4. The hairy layer model is considered to explain why the mean particle sizes of the uncrosslinked P(DMAEMA-*co*-MMA) increased as the

electrolyte concentration increased. This model postulates that the surface of a particle is coated by a layer of flexible polymer chains with terminal ionic groups. These chains can extend into the distant continuous phase, depending on the electrolyte concentration.<sup>7</sup>

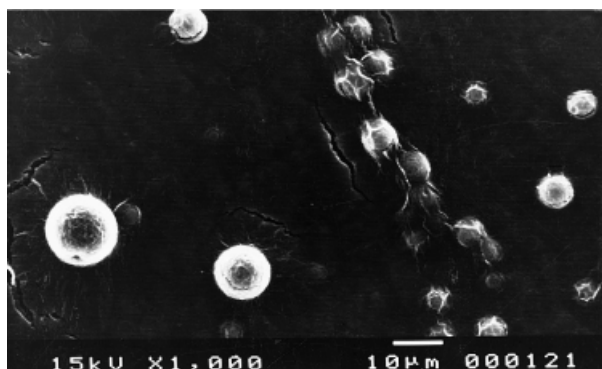
#### Effect of comonomer types

Hydrophilic MMA (dissolved in 15 wt % water) and hydrophobic ST were used as comonomers. Their chemical structures are different, although the glass-transition temperatures of both polymers are very similar ( $T_g$  of PMMA = 378 K,  $T_g$  of PST = 377 K). As

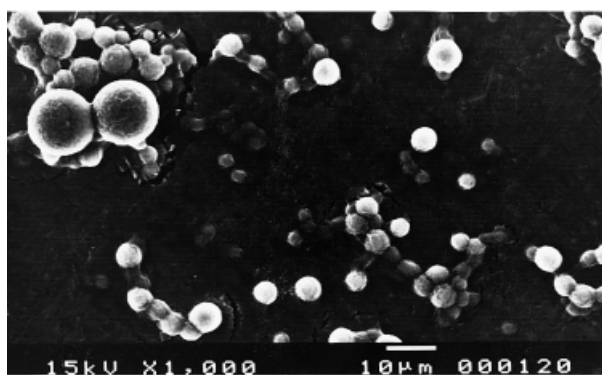


**Figure 3** Dependency of the particle size of P(DMAEMA-*co*-MMA) on the concentration of ethyl acetate in the continuous phase.

shown in Table I, stable P(DMAEMA-*co*-ST) latex was obtained when charging 20 wt % of ST based on the total weight of monomer. However, stable P(DMAEMA-*co*-MMA) latex was not obtained by charging 20 wt % of



(a)



(b)

**Figure 4** SEM micrographs of the uncrosslinked P(DMAEMA-*co*-MMA) particles for various concentrations of Na<sub>2</sub>SO<sub>4</sub> electrolyte: (a) 10<sup>-3</sup> M (Run 121); (b) 10<sup>-2</sup> M (Run 120).

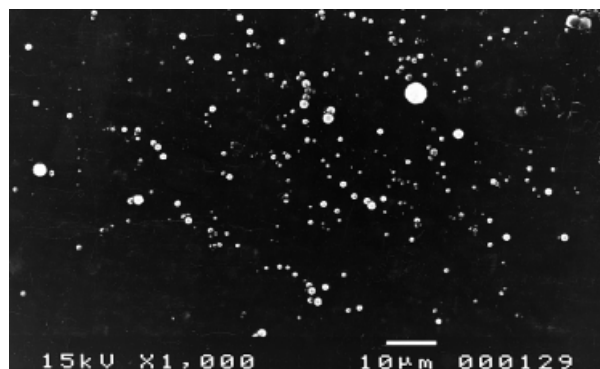
**TABLE III**  
Glass-Transition Temperature of the PDMAEMA Copolymers

Run number	$T_g$ (calc) (K)	$T_{g1}$ (obs) (K)	$T_{g2}$ (obs) (K)
115	303	340.0	428.2
129	304	336.1	436.9
145	327	378.1	430.3

MMA based on the total weight of monomer, and the mean particle size of P(DMAEMA-*co*-MMA) in Run 115 (5.37  $\mu\text{m}$ ) was found to be greater than that of P(DMAEMA-*co*-ST) in Run 129 (1.27  $\mu\text{m}$ ), probably attributable to the rather hydrophilic copolymer of MMA. In the case of the P(DMAEMA-*co*-MMA), the thickness of the hairy layer increased as a result of the increase of PDMAEMA solubility caused by the PMMA moiety. As a consequence of its hydrophilicity, the P(DMAEMA-*co*-MMA) particles were stuck together, forming a necklike or dumbbell-like structure, as shown in Figure 2(a). The observed  $T_g$  values of the uncrosslinked P(DMAEMA-*co*-MMA) and P(DMAEMA-*co*-ST) are shown in Table III. However, both observed  $T_g$  values are close to the  $T_g$  of randomly copolymerized P(DMAEMA-*co*-MMA) and P(DMAEMA-*co*-ST), which should be in the vicinity of 304 K according to Fox's equation for the comonomer DMAEMA-MMA to DMAEMA-ST composition ratio of 8 : 2. Two  $T_g$  values are found in this case, indicating that phase separation occurred in the particles.

#### Effect of solvent types

Suspension polymerization of the uncrosslinked P(DMAEMA-*co*-ST) was carried out by a batch operation to select the solvent. The use of AIBN is noticeable because it is slightly soluble in the aqueous phase. It is possible that coagulation occurred because most AIBN was in the hydrophilic monomer phase. AIBN could enter the interface, where a great number of polar molecules such as water and DMAEMA existed, and the latex was thus obtained as expected. However, the polarity of the interfacial layer would easily decrease because of the presence of a good solvent. The addition of organic solvents was considered to dissolve AIBN and decrease the permittivity of the continuous phase. Based on water, 2.8 wt % of EA and acetone were charged. In this work, acetone and EA were selected so as to lower the polarity of the continuous phase and enhance the stability of PDMAEMA particles. As a result, stable latex was prepared by charging 2.8 wt % of EA and acetone to the initiator system, as shown in Figures 5 and 6, respectively. Solvent types with different solubility parameters, such as acetone ( $\delta = 9.9 \text{ MPa}^{1/2}$ ) and EA ( $\delta = 9.1 \text{ MPa}^{1/2}$ ), influence the particle size of the uncrosslinked P(DMAEMA-*co*-ST). Acetone produced uncrosslinked P(DMAEMA-*co*-ST)



**Figure 5** SEM micrograph of the uncrosslinked P(DMAEMA-*co*-ST) particles using AIBN dissolved in ethyl acetate (Run 129).

having a mean particle size of 8.23  $\mu\text{m}$ , whereas EA produced 1.27  $\mu\text{m}$  mean particle size. Thus the mean particle size of the uncrosslinked P(DMAEMA-*co*-ST) using acetone (in Run 133) was found to be larger than when using EA (in Run 129) because the polarity of acetone was stronger.

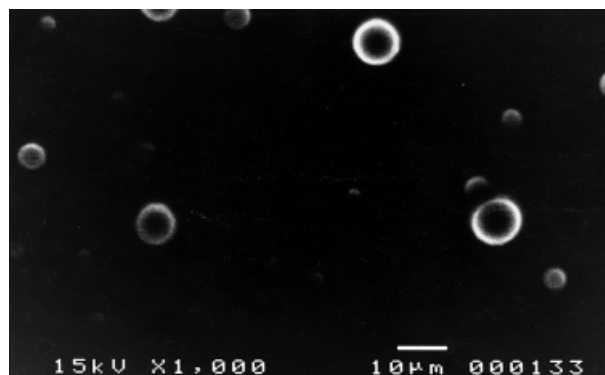
#### Effect of polymerization temperature

The temperature range for copolymerization was from 338 to 343 K, as shown in Table I. Agglomerated particles were produced at both 333 and 348 K reaction temperatures in Runs 137 and 134, respectively. The mean particle size increased from 1.27 to 2.26  $\mu\text{m}$  when decreasing the polymerization temperature from 343 to 338 K in Runs 129 and 136, respectively. The effects of polymerization temperature on the particle size and size distribution are shown in Figure 7 (Runs 137, 136, 129, and 134). Larger particles with a broader distribution (CV = 30%) were obtained when the copolymerization was conducted at a lower temperature. The reasons are probably related to the effects of the reaction temperature on (1) the rate and degree of polymerization and (2) the solubilities of organic compounds. Increasing the reaction temperature usually increases the rate of polymerization and chain transfer of polymer radicals, leading to a decrease in particle size of the uncrosslinked P(DMAEMA-*co*-ST). Increasing the reaction temperature generally promotes dehydration of the polyoxyethylene chains of PEO23, which in turn reduces the monomer solubility.<sup>8</sup> Furthermore, Ni et al.<sup>9</sup> found that the solubilities of 4-vinylpyridine (4VP), EA, and MMA decreased at higher temperatures. The solubility of EA in water is around 8.3 wt % at 298 K, and decreases at higher temperatures (an azeotropic mixture of water 6.1 wt % was formed at 343 K). As mentioned above, this attribute reveals that the particles become smaller as a result of the decreasing solubility of DMAEMA as the polarity of the continuous phase decreases.

In addition, agglomerated particles occurred at 333 and 348 K, resulting from collisions of particles inducing more agglomeration than the transfer of growing radicals through the cluster to each particle. Single radicals also are supposed to be formed from collisions between monomer droplets (particles) saturated with the oil-soluble initiator AIBN. The fraction of such single radicals is proportional to the collisions between droplets (particles). The particles are effectively protected by the stabilizer molecules, and the stability of P(DMAEMA-*co*-ST) depends on the amount of stabilizer.

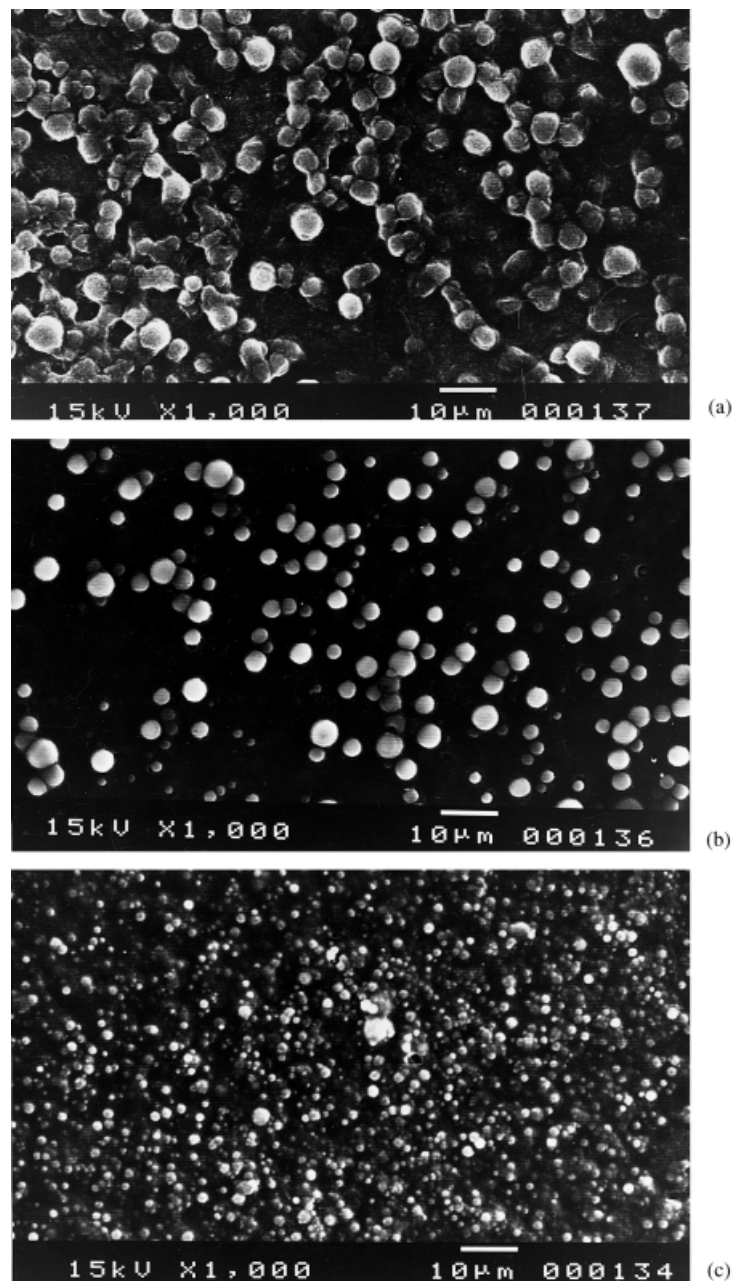
#### Effect of stabilizer types

The stabilizer performs the dual function of providing sites for particle nucleation and providing colloidal stability to the growing particles as a result of their adsorption at the particle–water interface. Nonionic stabilizers are used for controlling latex particle morphology and for enhancing the postpolymerization colloidal stability against mechanical shear, freezing, and added electrolytes. In this work, stabilizers were used to decrease the hydrophilicity of the PDMAEMA surface or increase the charge density of the PDMAEMA surface so as to enhance the repulsive force between microspheres. PVP was used as a stabilizer instead of PEO23, a nonionic stabilizer, because PVP was a good stabilizer for PDMAEMA, given the similarity of functional groups of PVP (–NO) with those of PDMAEMA (–NH<sub>2</sub>). Therefore, PVP can better react with the DMAEMA, providing smaller PDMAEMA particles. The surface-active molecules of PVP with an active amino group of PDMAEMA can chemically bind the stabilizer to the surface of the particles. The diameter of the P(DMAEMA-*co*-ST) particles so obtained using PVP in Run 144 was smaller than that by PEO23 in Run 129 under the same conditions, which seems to be dependent on the type of stabilizer. However, with the



**Figure 6** SEM micrograph of the uncrosslinked P(DMAEMA-*co*-ST) particles using AIBN dissolved in ethyl acetate (Run 133).





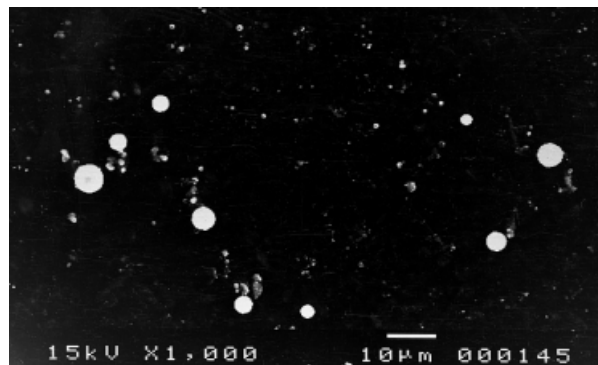
**Figure 7** SEM micrographs of the uncrosslinked P(DMAEMA-*co*-ST) particles prepared at various polymerization temperatures: (a) 333 K (Run 137); (b) 338 K (Run 136); (c) 348 K (Run 134).

addition of the PVP, the particle size of the resultant latex was too small to be observed by SEM.

#### Effect of ST content in monomer

Figure 8 shows an electron micrograph of uncrosslinked P(DMAEMA-*co*-ST) particles with 50% ST content in the monomer. Because of the greater hydrophobicity of ST compared with that of DMAEMA, stable latex was obtained. The particle size distribution of PDMAEMA does not depend on the amount of ST under the investigated conditions of Run 145, as shown in Table I. Moreover, the particle size distribu-

tion of the resultant latex was too broad to be measured on SEM micrographs. This is because the DMAEMA units in the copolymers are concentrated on the surface of the copolymer particles and thus DMAEMA is likely to dissolve in the aqueous phase during the polymerization. However, the glass-transition temperature of the uncrosslinked PDMAEMA copolymer increased when the amount of ST was increased. Increasing the ST content from 20 to 50 wt %, based on the total weight of monomer, leads to the calculated  $T_g$  of the uncrosslinked P(DMAEMA-*co*-ST) from Fox's equation, increasing from 304 K to 328 K. The observed  $T_g$  values of P(DMAEMA-*co*-ST) are



**Figure 8** SEM micrograph of the uncrosslinked P(DMAEMA-*co*-ST) particles with 50% ST content in monomers (Run 145).

shown in Table III. The trends of changing  $T_g$  of the copolymers are in agreement with the values calculated from Fox's equation: the increasing ST content raises the  $T_g$  in the same direction for the observed and calculated values. Two  $T_g$  values are observed in the P(DMAEMA-*co*-ST) latex.

### Emulsion polymerization method

To prepare the cationic P(DMAEMA-*co*-ST) seed particles, 2,2'-azobis(2-amidinopropane)·2HCl (V-50) with a cationic stabilizer was used. Addition of Na<sub>2</sub>SO<sub>4</sub> to the continuous phase produced a positive charge on PDMAEMA chains that restricted the chains' dimension and stabilized them.

### Effect of CTAC concentration

In emulsion polymerization, three particle-formation mechanisms—micellar, homogeneous, and droplet nucleation—may be operating simultaneously. Which mechanism dominates particle formation depends on the stabilizer concentration, the monomer solubility in the aqueous phase, and the level of subdivision of the monomer droplets.<sup>10</sup>

In this study, CTAC was used as a cationic stabilizer in the emulsion copolymerization of DMAEMA and ST. Table II shows the results for the uncrosslinked P(DMAEMA-*co*-ST) particles using CTAC of 0.65, 1.30, and 2.50 wt % (based on the total weight) in Runs 153, 154, and 152, respectively. It reveals that the amount of CTAC influences the particle size. The results indicate that stability of the copolymerization for the DMAEMA-containing system was obtained when CTAC was used. Comparisons of the particle size obtained with different CTAC concentrations are given in Table II. The mean particle size decreased from 129 to 64 nm when the concentration of CTAC was increased from 0.65 to 2.50 wt %. A particle size histogram for the uncrosslinked P(DMAEMA-*co*-ST) from the concentration effect of CTAC is given in

Figure 9. The distribution of the particle diameters was roughly from 16 to 600 nm. For concentrations of CTAC at 0.65, 1.30, and 2.50 wt %, the mean particle diameters were around 129, 117, and 64 nm, respectively. The size distribution imposed by the CTAC at a concentration of 1.30 wt % was rather narrow (CV = 20%) and the peak diameters were 95, 117, and 148 nm. The addition of CTAC caused a low interfacial tension between the monomer phase and the water phase. With increasing concentration, the stabilizer decreased the mean particle size and increased the number of particles or the fraction of interface.

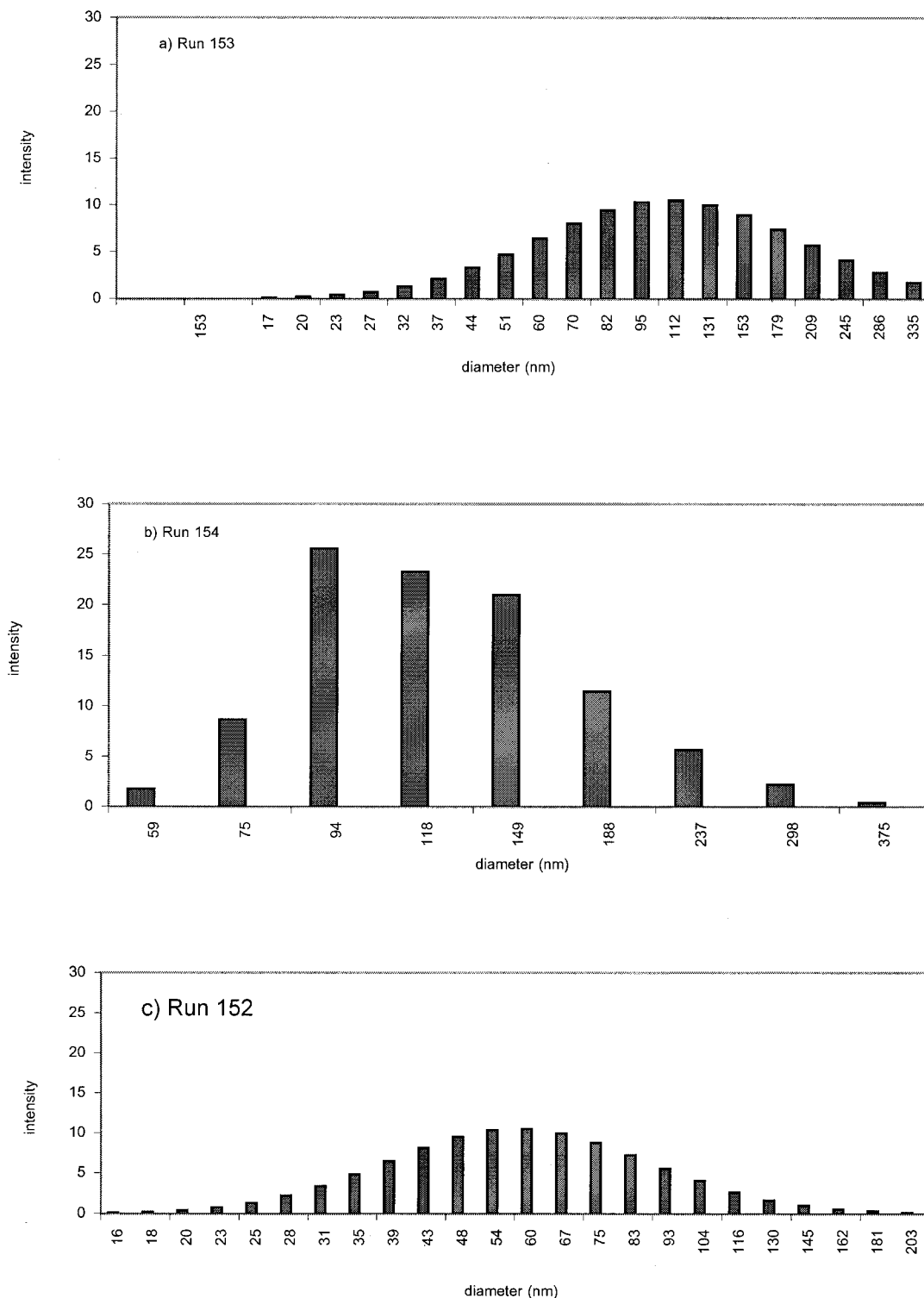
### Effect of initiator types

The monomer phase containing DMAEMA and ST in an 80:20 weight ratio was studied with different types of initiators, V-50 and KPS. Uncrosslinked P(DMAEMA-*co*-ST) particles from emulsion polymerization, using SDS as an anionic stabilizer with KPS as an anionic initiator, could be either spherical or non-spherical and the monomer conversion was lower than 30% in Run 156, as shown in Table II. However, no latex was formed using PEO23 as a nonionic stabilizer with KPS in Run 126, as shown in Table I.

When CTAC was used as a cationic stabilizer with V-50 as an initiator, the uncrosslinked P(DMAEMA-*co*-ST) particles were stable and the monomer conversion was higher than 60% in these experiments. In the case of using KPS, which is a pure inorganic salt, the initiator should be completely dissolved in the aqueous phase where a majority of DMAEMA existed. There should be no initiator in the monomer phase. In this case, latex could not be prepared even by changing the stabilizer. This result indicates that the formation of latex is related to the place where the initiator exists. On the contrary, V-50 is substantially an organic substance, and both the molecule and the radical derived from V-50 can effectively migrate to the interface of the monomer phase, which is an organic phase. These characteristics have proved to be important for the formation of latex. All the results shown above can explain why V-50 more easily enters the interfacial layer than does KPS. The polymerizations are, therefore, faster and conversions are, of course, higher with V-50 than with KPS. This can be explained by one or a combination of the following phenomena: (1) differences in values of the decomposition rate constant of V-50 (343 K;  $k_d = 1.15 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ ) and KPS (343 K;  $k_d = 2.33 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ ); (2) electrostatic interactions between microemulsion droplets and the charged radicals; and (3) chain-transfer reactions to counter-ions.<sup>11</sup>

### Effect of crosslinking agent types

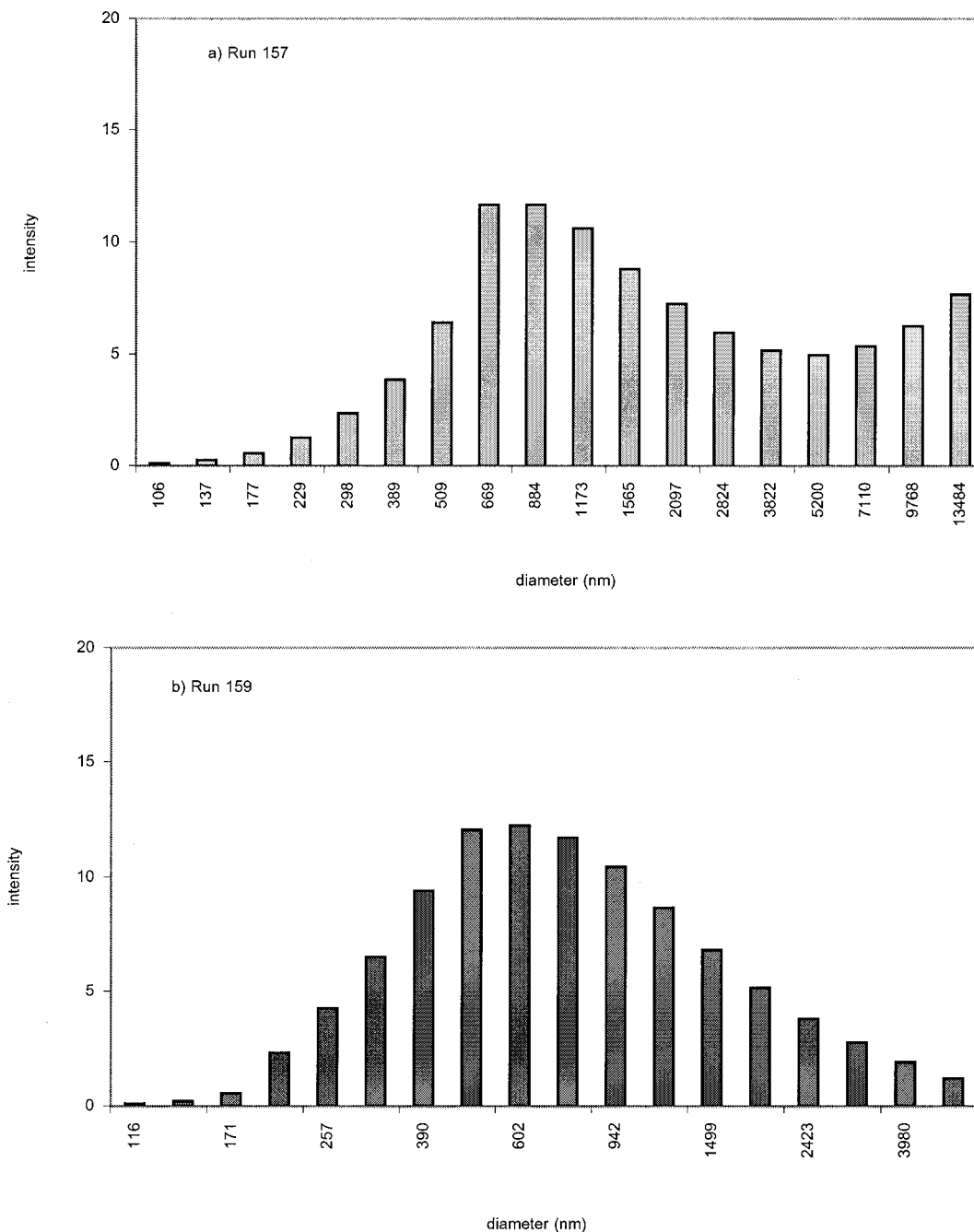
The effect of the crosslinking agent [divinylbenzene (DVB; Kishida Chemical Industries), containing 55%



**Figure 9** Histograms of the size distribution of the uncrosslinked P(DMAEMA-co-ST) particles using different concentrations of CTAC: (a) 0.65 wt % (Run 153); (b) 1.30 wt % (Run 154); (c) 2.50 wt % (run 152).

active isomeric DVB, 40% ethyl vinylbenzene, and 5% saturated hydrocarbons; or EGDMA] on the P(DMAEMA-co-ST) morphology was studied by emulsion polymerization using V-50 as an initiator. The polymerization recipe and experimental results

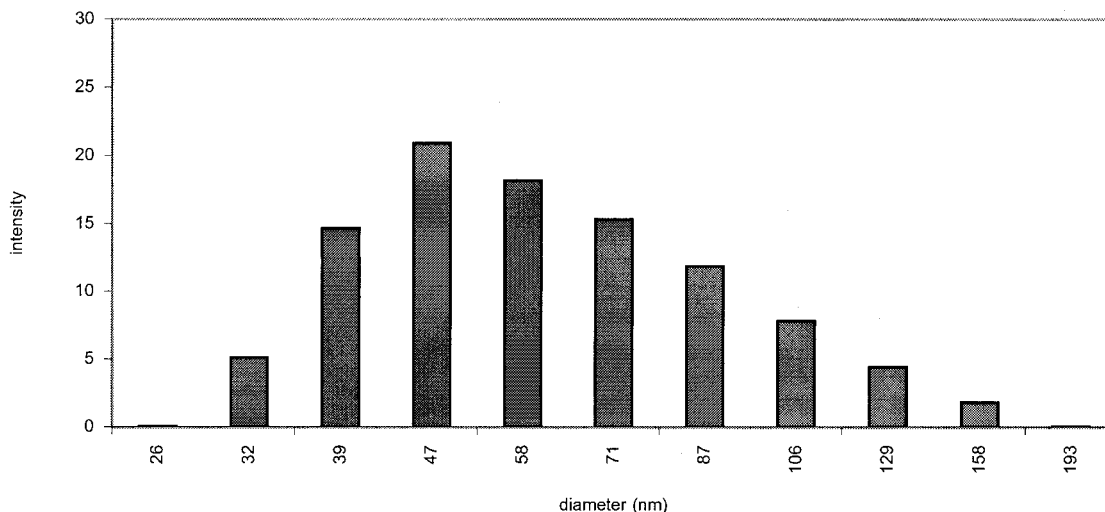
are summarized in Table II. The crosslinking agent DVB at 10 wt % and EGDMA at 5 wt % based on the monomer and crosslinking agent were added to DMAEMA-ST comonomers in Runs 157 and 159, respectively. We found that the addition of the



**Figure 10** Histograms of the size distribution of the crosslinked P(DMAEMA-*co*-ST) particles using different crosslinking agents: (a) DVB (Run 157); (b) EGDMA (Run 159).

crosslinking agent (EGDMA or DVB) caused a phase separation of the highly crosslinked network from the PDMAEMA. EGDMA-rich copolymers containing  $-\text{COOCH}_3$  pendant groups were formed in the early stage of the polymerization because either DVB or EGDMA is more reactive than ST and tends to be consumed earlier. The reaction of EGDMA formed nuclei of the crosslinked copolymer. When the monomer mixture contains a crosslinking agent, the crosslinked copolymer becomes insoluble, both in the monomer and the continuous phase.<sup>12</sup> Phase separa-

tion occurs between the ST and DMAEMA-rich phase, which yields coagulum. As mentioned above, this shows that the addition of a crosslinking agent has a favorable influence on the coagulum, which does not depend on the crosslinking agent type. Therefore, to investigate the effect of crosslinking agent types on the particle size, the latices were filtered to eliminate the coagulum. Then, the particle size of the crosslinked P(DMAEMA-*co*-ST) was observed by light scattering. Particle size histograms for the P(DMAEMA-*co*-ST) from different types of crosslinking agents, given in



**Figure 11** Histogram of the size distribution of the uncrosslinked P(DMAEMA-co-ST) particles using 5.0 wt % of V-50 (Run 160).

Figure 10, show that the particle size increased when the crosslinking agent (DVB or EGDMA) was charged into the polymerization system. Furthermore, it seemed to depend on the type of crosslinking agent. In the presence of 10 wt % DVB, based on the monomer and crosslinking agent, the peak diameters of P(DMAEMA-co-ST) particles, with a bimodal size distribution, were located at 800 and 13,484 nm, as shown in Figure 10(a). In contrast, when adding 5 wt % EGDMA based on the monomer and crosslinking agent, the particle size was also smaller, as shown in Figure 10(b), and the mean particle diameter was around 602 nm. This result implies that the crosslinker affects only one monomer of the particle (i.e., DMAEMA or ST), rather than the whole particle because of the phase separation. This is because the PS phase in the particle is predominantly crosslinked by DVB, and that of PDMAEMA is crosslinked by EGDMA.

#### Effect of V-50 concentration

It is well known that the rate of initiation ( $R_i$ ) is a function of the initiator efficiency ( $f$ ), the initiator decomposition constant ( $k_d$ ), and the initiator concentration ( $[I]$ ), which can be expressed by the following equation:

$$R_i = 2fk_d[I]. \quad (1)$$

The initiation is a two-step process. In the first step, the initiating radicals are formed by the decomposition of the initiator in the aqueous phase. Then, the hydrophilic primary radicals grow by propagation with a dissolved monomer in the aqueous phase to surface-active oligomeric radicals. In the second step, the oligomeric radicals enter the monomer-swollen

emulsifier micelles. The formed oligomer radicals enter the micelles and start the growth events.<sup>11</sup>

For this study, we investigated uncrosslinked P(DMAEMA-co-ST) latex prepared by charging 2.0 and 5.0 wt % of V-50 (based on the monomer) in the emulsion polymerization of DMAEMA-ST comonomers stabilized by CTAC (1.30 wt %) in Runs 154 and 160, respectively. Histograms of size distributions in Figures 9(b) and 11 reveal similar profiles of polymer particles of DMAEMA-ST comonomers. This shows that the mean particle size decreased from 117 to 47 nm as the concentration of V-50 increased from 2.0 to 5.0 wt %. The size distribution imposed by V-50 at a concentration of 5.0 wt % is rather narrow (CV = 18%). Two attributes are responsible for this result. First, the increasing rate of radical formation within the particles increased the number of radicals per particle. Simultaneous generation of single radicals in the particles promotes the narrow size distribution. Second, the increasing polymerization rate with greater initiator concentration is a consequence of the increasing flux of free radicals, which increases the probability of radical capture by droplets or by a monomer in the aqueous phase to induce formation of oligomers to produce active particles.

#### CONCLUSIONS

The polymerization of the hydrophilic monomer DMAEMA is highly sensitive to the type of initiator, such as AIBN, KPS, or V-50. The addition of AIBN to the suspension reaction system containing PEO23, water, and EA at 343 K led to particle diameters in the micron range and a broad size distribution (CV = 30%). On the contrary, emulsion polymerization of

DMAEMA initiated by V-50 at 343 K using CTAC as a stabilizer was found to produce small particle diameters of approximately 117 nm and a narrow size distribution (CV = 20%). Stable P(DMAEMA-*co*-ST) latices were formed as well with final conversion being higher than 60%. However, the MMA comonomer influences the morphology and stability of the PDMAEMA particles so formed. When the PDMAEMA contains 20 wt % of MMA, the P(DMAEMA-*co*-MMA) particles are deformed, stick together, and are unstable. Phase separation caused by addition of the crosslinking agent, either EGDMA or DVB, has a strong influence on the coagulum of PDMAEMA copolymer particles in both suspension polymerization and emulsion polymerization.

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