

Emulsifier-Free Emulsion Copolymerization Of Styrene With Quaternary Ammonium Cationic Monomers

ZUIFANG LIU, HUINING XIAO, NICHOLAS WISEMAN

Department of Paper Science, UMIST, Manchester, M60 1QD, UK

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ABSTRACT: Emulsifier-free emulsion binary copolymerizations of styrene with four types of quaternary ammonium cationic monomers, diallyldimethylammonium chloride (DADMAC), (3-(methacryloylamino) propyl) trimethyl ammonium chloride (MAPTAC), (2-methacryloyloxy ethyl) trimethyl ammonium chloride (MATMAC), and vinylbenzyl trimethyl ammonium chloride (VBTMAC), were conducted at 70°C. 2, 2'-azobis (2-methylpropionamide) dihydrochloride (V50) and potassium persulphate (KPS) were used as cationic and anionic initiator, respectively. Ternary copolymerizations were also carried out in the presence of acrylamide as a second comonomer. Monomer conversions were followed by ultraviolet spectroscopy and the polymer microparticles were characterized using photon correlation spectroscopy, electrophoresis, colloid titration, and scanning electron microscopy. The results indicated that VBTMAC and MATMAC were highly reactive in the copolymerization with styrene whereas the incorporation of DADMAC was slow. MAPTAC had an intermediate reactivity. Binary copolymerization with VBTMAC, MATMAC, and MAPTAC produced particles smaller in size, but higher in surface-charge density, than styrene homopolymer particles. However, significant agglomerates were detected in the VBTMAC and MATMAC-containing latexes. In contrast, DADMAC-containing polymer particles were almost identical to styrene particles. Continuous nucleation took place in the binary copolymerizations with VBTMAC and with MATMAC when using V50 initiator. In the case of using KPS, VBTMAC-containing particles grew continuously to a mean size much larger than the corresponding particles initiated by V50. The presence of acrylamide reduced DADMAC-containing particle size and diminished the agglomeration in the VBTMAC- and MATMAC-containing latexes. The results were interpreted via particle formation mechanism. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1129–1140, 2000

Key words: emulsifier-free emulsion polymerization; styrene; quaternary ammonium monomer; ionic initiator; cationic polymer microparticle

INTRODUCTION

In the past decade, much attention has been paid to the synthesis and characterization of functional polymer particles for their application in a wide variety of fields. A number of techniques

have been developed for preparing polymer microparticles bearing surface charge.¹ Conventional emulsion polymerization requires the use of emulsifiers whose removal could lead to a loss of latex stability. Emulsifier-free emulsion polymerization is especially suitable for the generation of particles free of added contaminating surface-active agents. The surface ionic groups can be easily introduced by using ionic initiators, as pioneered by Goodwin et al.² For tailored synthesis

Correspondence to: H. Xiao

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Table I Polymerisation Recipes

Materials	Amount		
	Homopolymerisation	Binary Copolymerisation	Ternary Copolymerisation
styrene	9.4 g	9.4 g	9.4 g
QACM	—	St : QACM = 9 : 1 (molar)	St : QACM = 9 : 1 (molar)
AAM	—	—	St : AAM = 9 : 1 (molar)
V50/KPS	10.0 g (0.1M solution)	10.0 g (0.1M solution)	10.0 g (0.1M solution)
water	100.0 g	100.0 g	100.0 g

of ionic polymer microparticles, however, emulsifier-free emulsion copolymerization of a sparingly water-soluble basic monomer (e.g., styrene) with an ionic comonomer is more versatile. The copolymerization can be conducted by using a batch process. In addition to suitable control of experimental conditions (including ionic strength,^{3–5} pH,⁶ temperature,^{7,8} and agitation speed⁹), the particle size and size distribution can be adjustable in a certain range by varying monomer feed ratio.^{4,7,10,11} Moreover, the incorporation of ionic monomer repeat-unit usually leads to the formation of particles with higher surface-charge density.^{4,5,11} Alternatively, surface-charged polymer microparticles can be obtained by a two-stage shot-growth process using a part of the ionic comonomer in the batch period. This method is rather efficient for the incorporation of ionic comonomer at particle surface.¹²

Over recent years, the development of novel functional microparticle flocculation systems has attracted increasing interest because of their potential applications in papermaking and water treatment.¹³ The research has so far mainly focused on the anionic inorganic microparticles in conjunction with a high molecular-weight cationic polymer.¹⁴ It is anticipated that cationic microparticles could be more effective than the others in flocculating negatively charged fiber fines and waste solids. However, studies are surprisingly limited in this area. Our current research concerns the preparation of cationic polymer microparticles and their application as retention aids in papermaking. This article focuses on the synthesis of a series of cationic polymer microparticles by emulsifier-free emulsion copolymerization of styrene with different quaternary ammonium cationic monomers (QACMs). Their flocculation performance will be presented elsewhere.

EXPERIMENTAL

Materials

Double-distilled water was used throughout. Styrene (St) (Fisher Scientific, UK) was distilled under reduced pressure prior to polymerization. 2, 2'-azobis (2-methylpropionamide) dihydrochloride (V50) and potassium persulphate (KPS) were both purchased from Sigma-Aldrich Co. Ltd. The former was recrystallized in water-acetone mixture (50/50 wt %) whereas the latter was used as received (99.99% pure). All comonomers were used without further purification. The following four types of QACMs were used: diallyldimethylammonium chloride (DADMAC); (3-(methacryloylamino) propyl) trimethyl ammonium chloride (MAPTAC); (2-methacryloyloxy) ethyl trimethyl ammonium chloride (MATMAC); and vinylbenzyl trimethyl ammonium chloride (VBTMAC). DADMAC (65 wt % aqueous solution), MAPTAC (50 wt % aqueous solution), and MATMAC (75 wt % aqueous solution) were all purchased from Sigma-Aldrich Co. Ltd., UK and VBTMAC (60 : 40 para : meta mixture) was purchased from Fisher Scientific. Acrylamide (AAM) (Sigma-Aldrich Co. Ltd., UK) was used as a second comonomer in ternary copolymerizations.

Synthesis of Polymer Microparticles

All emulsifier-free emulsion polymerizations were conducted under identical experimental conditions. The recipes are listed in Table I. For each run of polymerization, all materials of designated amount, except the initiator, were first added to a 250-mL round-bottomed flask that was fitted with a mechanical stirrer, water-cooled reflux condenser, and nitrogen inlet and outlet. The flask was then immersed in a thermostatically con-

trolled water bath with a temperature fluctuation of $\pm 0.1^\circ\text{C}$. The reaction mixture was purged with nitrogen at 25°C for about 1 h under an agitation of 400 rpm. After this, the water bath was heated to 70°C and this temperature was thereafter kept constant throughout the course of polymerization. Finally, the initiator in aqueous solution was injected to start polymerization and the time was recorded afterward.

Measurement of Monomer Conversion

Monomer conversions were only measured for the styrene homopolymerization and the binary copolymerizations. Samples withdrawn from the reaction mixture at various time intervals were diluted with cold water immediately and put in an ice bath. Each of the cooled diluted samples was then mixed with heptane (high-performance liquid chromatography [HPLC] grade, Fisher Scientific) and vigorously shaken. The sample mixtures were finally left to stand overnight to separate the two phases. The separated aqueous phase and "oil" phase were used to measure the residual QACM and styrene, respectively, by ultraviolet (UV) spectroscopy (Lambda 18 UV/VIS spectrometer, Perkin Elmer, Germany). The polymer particles in the aqueous phase were filtered using syringe filters ($0.02\ \mu\text{m}$, Whatman, UK) before the measurements. The UV measurements were performed at wavelengths of 204, 209, and 248 nm for MAPTAC, MATMAC, and VBTMAC, respectively, and at a wavelength of 248 nm for styrene. The residual monomer levels were calculated using standard calibration curves. However, the measurement of residual DADMAC by this method was unsuccessful because its absorption at low wavelength (maximum absorption at around 191 nm) was interfered by the absorption of impurities.

Characterization of Particles

The latexes were cleaned by dialysis against deionized distilled water until the conductivity of the surrounding water reached a constant level (close to the conductivity of deionized water). A Zetasizer 3000 (Malvern, UK) was used to measure the hydrodynamic diameter, electrophoretic mobility, and zeta potential of the polymer particles. The measurements were conducted in 1.0 mM NaCl aqueous solution at 25°C .

The apparent surface-charge density of the particles and the charge in the water-soluble

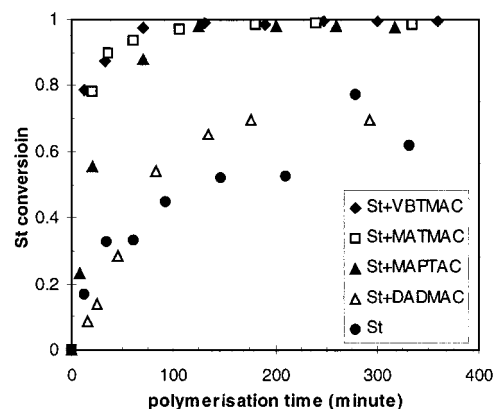


Figure 1 Styrene conversion curves for homopolymerization and binary copolymerizations using V50 initiator.

polyelectrolytes were both determined by colloid titration.¹⁵ Prior to titration, the latexes were further purified by repetitive centrifugation (4 h under 14 000 rpm, using an Eppendorf Centrifuge 5415C), decantation, and re-dispersion in water to remove the water-soluble polyelectrolytes that were collected in serums for further characterization. The purified particles and the water-soluble polyelectrolytes were titrated with 0.1 and 1.0 mN potassium polyvinyl sulfate (PVSK), respectively. Toluidine blue-O was used as color indicator.¹⁶ The surface-charge density of the particles is expressed as equivalent mole of charge groups per gram of particles, whereas the charge in the water-soluble polyelectrolytes is presented as equivalent mole of charge groups per gram of polymer (particles + polyelectrolytes).

The morphology of the particles was examined by using a scanning electron microscope (SEM) (SM-300, Topcon, Japan).

RESULTS

Kinetics of Binary Copolymerizations

It has been reported in the literature that, for the copolymerization of styrene with MAPTAC, particle size decreased and surface-charge density increased with increased MAPTAC fraction in monomer feed up to about 10% (mol).¹¹ For comparison, binary copolymerizations of styrene with the four types of QACMs were initially conducted at the same monomer feed ratio of St : QACM = 9 : 1 (mol). V50 was used as a cationic initiator. Figure 1 shows the conversion curves of styrene

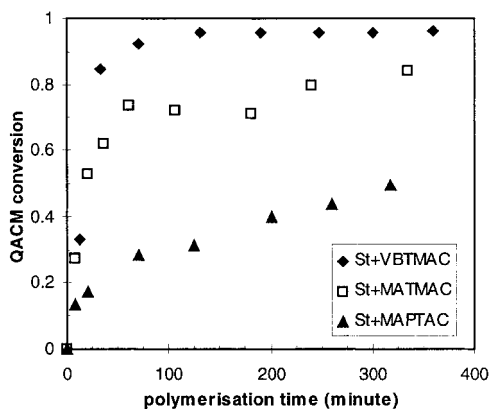


Figure 2 conversion curves of QACMs for binary copolymerizations using V50 initiator.

for the four copolymerizations. The conversion curve for styrene homopolymerization is also presented for comparison. It is evident that the presence of VBTMAC, MATMAC, and MAPTAC significantly enhanced the consumption rate of styrene. This is in accord with the reported phenomena for the emulsifier-free emulsion copolymerizations of styrene with cationic monomers.^{6,17} However, the effect of DADMAC was not significant. The individual monomer conversion curves of VBTMAC, MATMAC, and MAPTAC are shown in Figure 2. It is seen that VBTMAC and MATMAC had higher polymerization rates than MAPTAC. Figures 1 and 2 also indicate that the QACMs were consumed at relatively lower rates than styrene. This implies a favorable polymerization of styrene in the binary copolymerizations.

Particle Characteristics

The hydrodynamic diameter, surface-charge density, electrophoretic mobility, and zeta potential

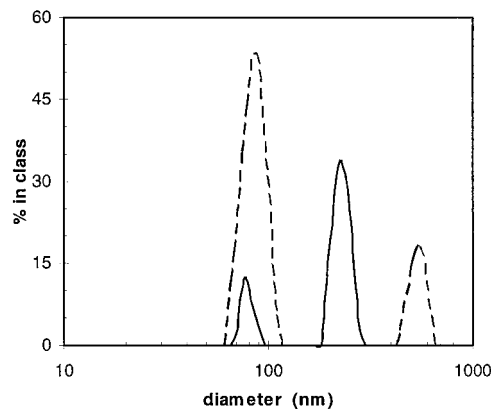


Figure 3 PCS profiles of VBTMAC and MATMAC-containing bipolymer latexes. Solid line: St/VBTMAC system; broken line: St/MATMAC system.

values of the different types of particles are presented in Table II. Both the homopolymer particles and the copolymer particles are positively charged. The three copolymerizations with VBTMAC, MATMAC, and MAPTAC led to the formation of particles with smaller sizes, but higher surface-charge densities, than the particles of styrene homopolymer. However, only slight changes in particle characteristics were induced by the copolymerization with DADMAC. These agree well with the polymerization kinetic results and further confirm the differences in copolymerization behavior with styrene between the QACMs.

Photon correlation spectroscopy (PCS) indicated bimodal size distributions for the VBTMAC-containing and MATMAC-containing particles (Fig. 3). This suggests that there were two populations of particles in these two types of latexes. The SEM images of these two types of copolymer particles are shown in Figures 4b and 4c, respectively. It is clear that a population of agglomer-

Table II Characteristics of Polymer Particles Initiated by V50

QACM	St : QACM (mol)	Hydrodynamic Diameter (nm)	Electrophoretic Mobility ($\mu\text{mcm/Vs}$)	Zeta Potential (mV)	Particle Surface Charge Density ($\mu\text{eq/g}$)
—	9 : 0	520	1.42	17.9	14.2
DADMAC	9 : 1	426	2.06	25.9	24.4
MAPTAC	9 : 1	149	3.56	45.0	95.4
MATMAC	9 : 1	252 (92)*	3.25	41.0	97.7
VBTMAC	9 : 1	196 (87)*	3.42	43.1	106.2

* Bimodal distribution was observed and the mean diameter of non-aggregated particles is presented in bracket.

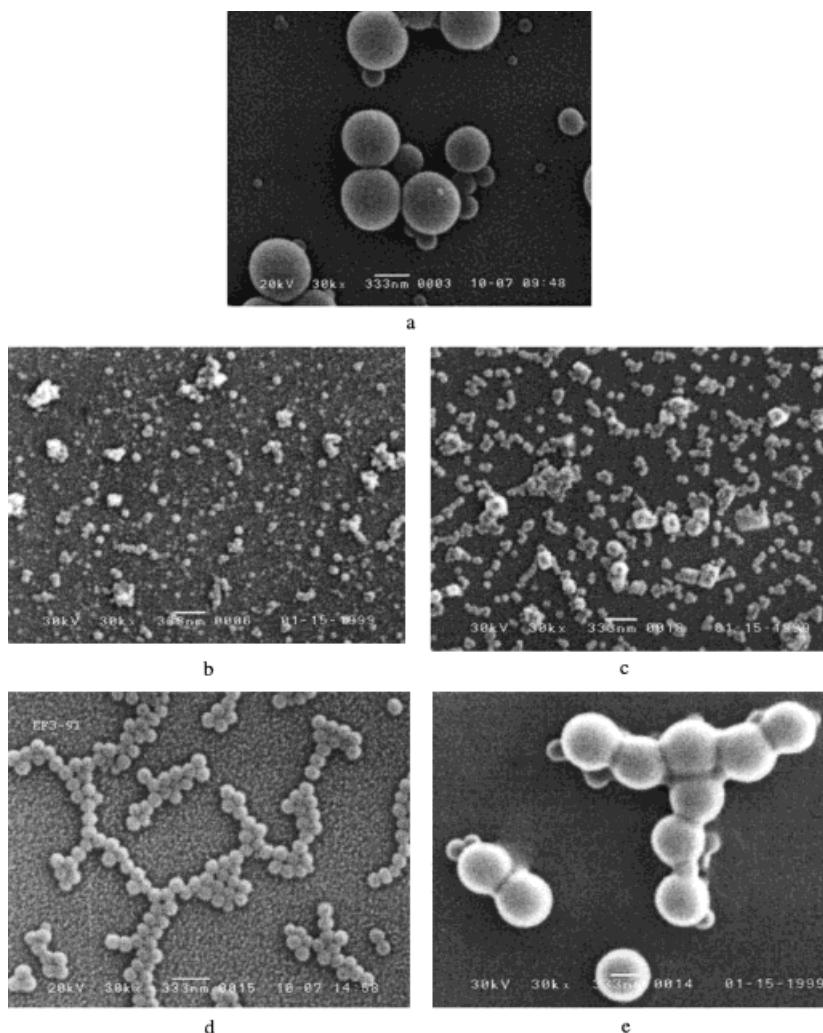


Figure 4 SEM images of polymer particles using V50 initiator. (a) styrene homopolymer particles; (b), (c), (d), and (e) VBTMAC, MATMAC, MAPTAC, and DADMAC-containing bipolymer particles, respectively.

ates for the both latexes accompanies individual spherical particles. The size of individual particles was much smaller than that of the agglomerates. Obviously, the bimodal size distributions of the PCS results were attributed to the presence of the agglomerates rather than the large individual particles. However, the SEM image of MAPTAC-containing particles (Fig. 4d) shows individual spherical particles, with rather uniform size but no significant agglomeration.

Figure 4 also shows the SEM images of the styrene homopolymer particles and of the DADMAC-containing particles. As can be seen, these two types of particles were very similar, reflected in both size and morphology. Again, this implies that the influence of DADMAC on the particle formation was of little importance.

Effect of Monomer Feed Ratio

In order to investigate the influence of QACM concentration on final particle characteristics, a series of copolymerizations of styrene with MATMAC were conducted at varied monomer feed ratios. SEM imaging revealed that uniform spherical particles were obtained up to monomer feed ratio of St : MATMAC = 9 : 2.5 (mol). However, significant agglomeration occurred at St : MAPTAC = 9 : 5 (mol). The variations of hydrodynamic diameter with the monomer feed ratio are presented in Table III. It is interesting that the final particle size initially decreased and then increased with increased MATMAC concentration. This implies complicated effects of MATMAC on particle formation. Agglomeration

Table III Effect of MATMAC Initial Concentration on Particle Characteristics

St : QACM (mol)	Hydrodynamic Diameter (nm)	Particle Surface Charge Density ($\mu\text{eq/g}$)	Charge in Polyelectrolytes ($\mu\text{eq/g}$)
9 : 0.5	114	65.36	1.58
9 : 1.0	98	96.92	10.40
9 : 2.5	121	109.51	85.53
9 : 5.0	298*	—	297.53

* Significant agglomerates were observed.

at high ionic monomer concentration has been reported in the literature and was attributed to the formation of large amount of polyelectrolytes.¹⁸

The amount of MATMAC repeat-unit incorporated in the water-soluble polyelectrolytes was determined by titration of polyelectrolytes in serum (see Table III). The higher the MATMAC fraction in monomer feed, the more MATMAC molecules incorporated in the water-soluble polyelectrolyte chains. This also implies that the amount of water-soluble polyelectrolytes increased with increased QACM initial concentration. Similar phenomenon was observed for the binary copolymerization of styrene with VBTMAC.

Binary Copolymerizations Using Anionic Initiator

Styrene homopolymerization and copolymerizations of styrene with VBTMAC and with MATMAC were conducted using KPS as an anionic initiator. The concentrations of all reactants and the experimental conditions were the same as that using V50 initiator. Table IV shows the particle characteristics. As expected, the styrene homopolymer particles were negatively charged. However, the VBTMAC-containing and the MATMAC-containing particles possessed positively charged surfaces. This implies the presence

of a large amount of the QACM repeat-units at the particle surfaces. Although the hydrodynamic diameters of the particles were rather close to the corresponding ones using V50 initiator, the PCS results revealed mono-modal size distributions for these two latexes. SEM imaging revealed two types of fairly uniform spherical particles with little agglomerate (Fig. 5). The sizes of the individual particles for both latexes are larger than the corresponding ones obtained by using V50 initiator.

Evolution of Particles

The variations of hydrodynamic particle diameter with monomer conversions for the binary copolymerizations with VBTMAC and with DADMAC using V50 initiator are shown in Figures 6 and 7, respectively (only styrene conversion is presented in Fig. 7 because the DADMAC conversion was not obtained). The hydrodynamic diameter of DADMAC-containing particles increased gradually as polymerization proceeded. The SEM imaging also revealed that the particles grew continuously with time. In contrast, the mean size of the VBTMAC-containing particles remained constant in a wide range of monomer conversion. The SEM imaging throughout the course of polymerization observed a complex morphology of the particles. The latex consisted of individual particles with a

Table IV Characteristics of Polymer Particles Initiated by KPS

QACM	St : QACM (molar ratio)	Hydrodynamic Diameter (nm)	Electrophoretic Mobility ($\mu\text{mcm/Vs}$)	Zeta Potential (mV)	Surface Charge Density ($\mu\text{eq/g}$)
—	9 : 0	342	-2.66	-33.5	—
MATMAC	9 : 1	234	3.75	47.3	92.4
VBTMAC	9 : 1	215	3.98	50.2	85.6

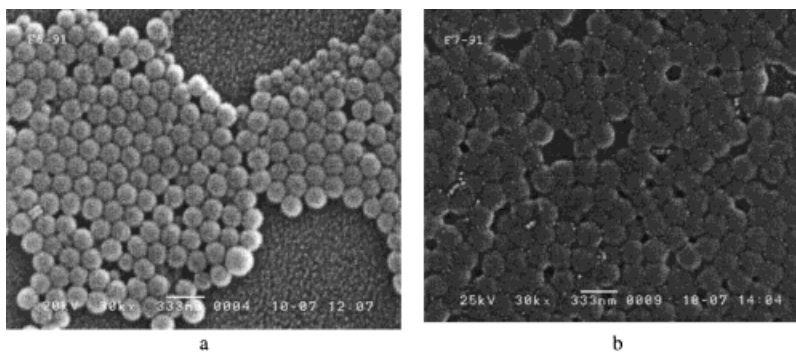


Figure 5 SEM images of bipolymer particles using KPS initiator. (a) VBTMAC-containing particles; (b) MATMAC-containing particles.

broad size distribution and some large agglomerates. The continuous particle growth was not observed in this case. The hydrodynamic diameter of MATMAC-containing particles increased with total monomer conversion. However, the mean size of the nonaggregated particles varied little (Fig. 8). SEM imaging observed no large particles in the final latex. The combination of PCS and SEM results suggests a continuous nucleation mechanism for the binary copolymerizations of styrene with VBTMAC and with MATMAC, using V50 as initiator. Similar phenomena were also reported by other researchers.^{17,18}

Figure 9 shows the variation of hydrodynamic diameter of the VBTMAC-containing particles initiated by KPS with total monomer conversion. The particles progressively grew with increased total monomer conversion to a final size much larger than the corresponding particles obtained by using V50 initiator. The different behaviors in

particle evolution between the two binary copolymerizations using the different initiators confirm the important role of initiator nature in particle formation.

Ternary Copolymerizations in the Presence of Acrylamide

Latexes of terpolymers were prepared by ternary copolymerizations using acrylamide as a second comonomer and V50 as initiator. The results of particle characterization are presented in Table V. Figure 10 shows the SEM images of the final particles. The MAPTAC-containing terpolymer particles possess very similar characteristics to the corresponding particles obtained by binary copolymerization. In the cases of using VBTMAC and MATMAC, however, the hydrodynamic diameters of the terpolymer particles are much smaller than those of the corresponding ones obtained by

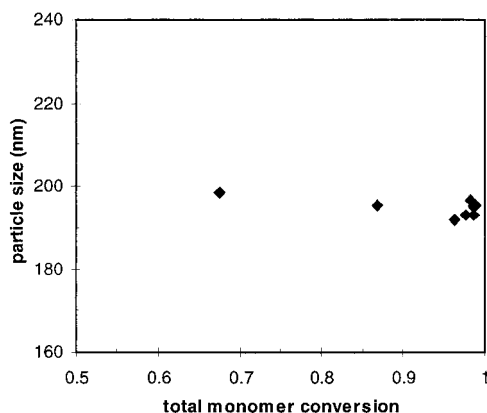


Figure 6 Variation of particle size with total monomer conversion for binary copolymerization with VBTMAC using V50 initiator.

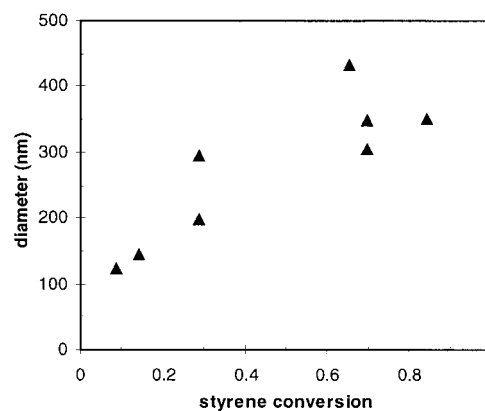


Figure 7 Variation of particle size with styrene conversion for binary copolymerization with DADMAC using V50 initiator.

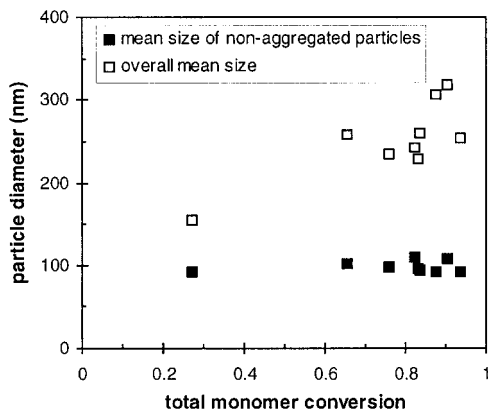


Figure 8 Variation of particle size with total monomer conversion for binary copolymerization with MATMAC using V50 initiator.

binary copolymerizations. From the SEM images, it is clear that the reduction in the hydrodynamic particle diameter is due to the disappearance of the agglomerates in the ternary copolymerizations, rather than the real decrease in the size of individual particles. This implies that the incorporation of AAM repeat-unit reduced the particle agglomeration. In the case of using DADMAC, ternary copolymerization generated smaller particles than binary copolymerization. This also suggests that the presence of AAM repeat-unit in the copolymer chains could have effects on particle formation.

DISCUSSION

Mechanism for Particle Formation

For an emulsifier-free emulsion homopolymerization of styrene initiated by an ionic initiator, it is well established that the nucleation occurs in the aqueous phase. The driving force for nucleation is the increase in the hydrophobicity of the growing oligomeric radicals as their chains propagated. Once they reach a critical chain length, the oligomeric radicals would precipitate to form nuclei (homogeneous nucleation)¹⁹ or become surface active to form micelles (micellar nucleation).^{2,20} These nuclei or micelles could be swollen by styrene molecules and consequently grow by three possible ways: 1) coagulation; 2) capture of newly formed oligomers or of dead polymer molecules from the aqueous phase; and 3) polymerization of absorbed styrene inside them. The particle stabilization is solely attributed to the electrostatic

forces of the ionic end-groups that originated from the ionic initiator fragments and were located at the particle surface. The coagulation and the capture of oligomers/polymers enhance the particle stabilization because of the increase in particle surface-charge density, whereas the further polymerization inside the particles generates more unstable surfaces and, in turn, promotes the former two processes. In an extreme case, the rate of capture of oligomers was high enough so that no more new nuclei or micelles form in the aqueous phase and thus nucleation ends. After that, the particle size increased with monomer conversion whereas the particle number remained constant (two-stage mechanism).²

In the case of emulsifier-free emulsion copolymerization of styrene with an ionic monomer, the presence of the ionic monomer repeat-unit along the copolymer chains could make the mechanism for particle formation more complicated. Firstly, the incorporation of ionic monomer into the growing oligomeric radicals must have an influence on nucleation process. Because the repeat-units of the ionic monomers are highly hydrophilic (most ionic homopolymers are water-soluble), the hydrophilic-hydrophobic property of the growing oligomeric radicals is not only dependent on their chain lengths (that is the case in styrene homopolymerization), but also on their chemical compositions. In this case, homogeneous nucleation is more likely to occur because of the random distribution of the two kinds of monomer repeat-units.^{5,6,11,21} Therefore, it is reasonable to postulate that the nucleation only occurs when a certain molar fraction of styrene has been incorporated into the copolymer chains. The

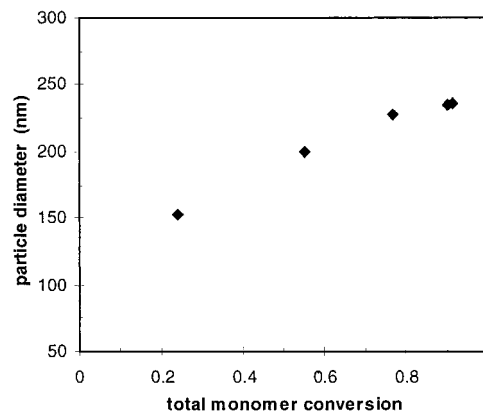


Figure 9 Variation of particle size with monomer conversion for binary copolymerization with VBTMAC using KPS initiator.

Table V Characteristics of Terpolymer Particles Initiated by V50

QACM	St : QACM : AAM (molar ratio)	Hydrodynamic Diameter (nm)	Electrophoretic Mobility ($\mu\text{mcm/Vs}$)	Zeta Potential (mV)	Surface Charge Density ($\mu\text{eq/g}$)
DADMAC	9 : 1 : 2	256	3.62	45.9	20.4
MAPTAC	9 : 1 : 2	168	6.53	44.5	102.8
MATMAC	9 : 1 : 2	124	3.46	4.36	**
VBTMAC	9 : 1 : 2	130	4.07	51.4	**

** Not obtained due to difficulty in elimination of water-soluble polyelectrolytes by repetitive centrifugation-redispersion.

chemical composition of copolymer chains can be a function of a number of factors, including the reactivity ratios and the concentrations of the monomers. The higher the reactivity ratio or concentration of an ionic monomer, the faster its molecules incorporate into the growing oligomeric radicals. At an extreme, the incorporation of the ionic monomer was so fast that the growing oligomeric radicals remained very high in hydrophilicity and consequently water-soluble polyelectrolytes were formed.¹⁸ Secondly, the presence of the ionic monomer repeat-units at particle surfaces must contribute to particle electrostatic stabilization. Indeed, final particle size normally decreases with increased ionic monomer concentra-

tion in a certain range.^{4,5,10,11,21} This has been attributed to the restriction in the particle growth due to the significant increase in the particle surface-charge density.^{7,11,22} The presence of more ionic groups at particle surfaces certainly enhances the electrostatic repulsive forces between the particles and hence, the coagulation of primary particles would be restricted. Moreover, the capture of oligomers by the existing particles would be less significant than that in the styrene homopolymerization because of the electrostatic repulsion between the highly surface-charged particles and the oligomers with ionic groups along their chains. Furthermore, if the particle surface-charge density is high enough, the elec-

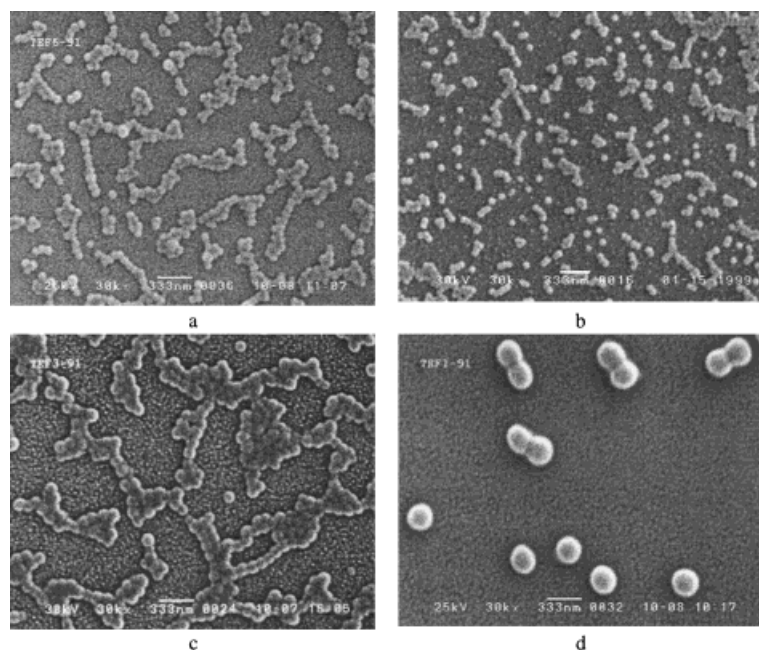


Figure 10 SEM images of terpolymer particles using V50 initiator. (a) VBTMAC-containing particles; (b) MATMAC-containing particles; (c) MAPTAC-containing particles; (d) DADMAC-containing particles.

trostatic layer at the particle surface could prevent likely charged primary free radicals (generated in aqueous phase) from entering. As a result, the polymerization of styrene inside the particles could be also restricted.¹⁷

Effect of Cationic Monomers

Because the current four types of QACMs have the same quaternary ammonium cationic group, each repeat-unit of them is supposed to have almost identical contribution to particle stabilization. In addition, although there might be slight differences in hydrophilicity between the four types of QACM repeat-units, the variation in the hydrophilic-hydrophobic property of the oligomer/copolymer chains would be predominantly determined by the molar fraction of the incorporated QACM units. Therefore, the differences in the characteristics of final particles between the four binary copolymerizations must be mainly attributed to their different copolymerization behaviors.

The favorable polymerization of styrene in the binary copolymerizations probably resulted in a quick built up of styrene sequences in the growing oligomer chains (see Figs. 1 and 2). Therefore, the hydrophobicity of the growing oligomeric radicals would increase as chain propagation proceeded. However, the incorporation rate of the hydrophilic repeat-units varied with the QACMs. Both the polymerization kinetics and the particle characterization suggest that the incorporation of DADMAC repeat-unit was probably very slow. Therefore, the electrostatic stabilization resulting from the DADMAC repeat-unit could be small and hence, the particle formation would proceed in a very similar way to that for the styrene homopolymerization.

In the cases of copolymerizations with VBTMAC and with MATMAC, both styrene and the QACM molecules incorporated rapidly into the copolymer chains. As discussed in the preceding section, the precipitated nuclei could soon develop to stable mature particles and further particle growth could be effectively restricted because of the remarkable enhancement in particle electrostatic stabilization. Consequently, the final particles were much smaller in size but with higher surface-charge density than the styrene homopolymer particles. On the other hand, the growing oligomeric radicals must be more hydrophilic than the ones containing solely styrene repeat-unit with the same chain length. There-

fore, the QACM-containing oligomers probably have longer critical chain length for nucleation than the styrene oligomers. This could result in a prolonged nucleation period and lead to the formation of a large amount of polyelectrolytes in the system. The results in Table III provide such evidence, i.e., the amount of water-soluble polyelectrolytes increases with increased initial MATMAC concentration. Obviously, higher initial MATMAC concentration resulted in faster incorporation of its repeat-unit into the copolymer chains and hence, more water-soluble polyelectrolytes were formed. If the newly formed propagating polyelectrolytes were not captured by the existing particles, they could grow large enough to nucleate independently, leading to a continuous nucleation. This probably contributed to some extent to the particle polydispersity as reported by Kim et al.¹² The presence of large amount of polyelectrolytes could also result in the formation of agglomerates, through a mechanism of bridging flocculation, as proposed by Guillaume et al.¹⁸ Moreover, the QACM molecules, especially at relatively high concentration, might act as electrolyte and as such would facilitate primary particle coagulation by reducing the electrostatic repulsive forces. This probably account for the variation of particle size with initial MATMAC concentration (see Table III).

The copolymerization with MAPTAC was in an intermediate situation. Although MAPTAC successfully incorporated into the copolymer chains, it polymerized at a rate significantly lower than styrene did. Therefore, the influence of the cationic repeat-unit on nucleation and particle growth would be less significant in this case than in the copolymerizations with VBTMAC and with MATMAC, but more pronounced than in the copolymerization with DADMAC. Indeed, the MAPTAC-containing particles were much smaller than the particles obtained by the copolymerization with DADMAC, but larger than the VBTMAC-containing and MATMAC-containing particles. However, no significant agglomerates were formed.

Effect of Initiator Nature

Kawaguchi et al.²³ reported the influence of initiator nature on particle characteristics in the emulsifier-free emulsion copolymerization of styrene with a nonionic monomer, N-(hydroxymethyl)-acrylamide. The final particles obtained by using KPS were slightly larger than when using

2,2'-azobis(2-amidinopropane) hydrochloride. The authors found that the contribution of the cationic initiator fragments to particle stabilization was insignificant. Therefore, they proposed that more particles could be generated in the case of using the cationic initiator, on the assumption that weak electrostatic repulsive forces might enhance the precipitation of growing oligomeric radicals. When using V50 initiator, the present results indicate a pronounced increase in particle surface-charge density by the presence of VBTMAC repeat-unit at the particle surfaces (see Table II). In the case of using KPS as an anionic initiator, the VBTMAC-containing particles also possess positively charged surfaces (Table IV). This indicates that the contribution to the electrostatic stabilization at the particle surface was predominantly from the VBTMAC repeat-unit, rather than from the fragments of KPS. This is not surprising because each copolymer chain probably contains a number of VBTMAC repeat-unit but only one or two KPS end-group(s). Therefore, the effect of initiator nature on particle formation can not be simply attributed to the different ability of the two kinds of initiator fragments at the particle surface to stabilize the particles. Nevertheless, the differences in both particle evolution and the final particle size between the copolymerizations using the two different initiators indicate an important role of initiator nature in particle formation. As discussed above, the particle growth could be effectively restricted in the copolymerization with VBTMAC using V50 initiator. In the case of using KPS initiator, however, the progressive increase in particle size with monomer conversion suggests that the particle growth could continue until the end of polymerization. Because of their relatively high inner hydrophobicity, particles could be swollen by residual styrene. The polymerization inside these particles would take place as soon as the free radicals had entered. For the copolymerization using V50 initiator, both the particle surface and the primary free radicals are positively charged and hence, the electrostatic repulsive forces could successfully prevent the primary free radicals from entering the particles. In contrast, the primary free radicals derived from the decomposition of KPS are negatively charged. Therefore, they could easily diffuse into the particle and consequently initiate polymerization of styrene inside. As reported in the literature,² the polymerization inside the particles could be faster than in the aqueous phase. The styrene molecules transferred from the styrene droplets, through

the aqueous phase, into the particles. The particles therefore increased in size and at the same time acquired more oligomers from the aqueous phase to stabilize their unstable surfaces. This process could proceed until all styrene droplets had disappeared. Finally, the particles reached a size much larger than the particles obtained by using V50.

Role of Acrylamide

The effective copolymerization of styrene with acrylamide and the ability of acrylamide repeat-unit for particle stabilization have been reported by Ohtsuka et al.²⁴ This could explain the difference in final particle size between the DADMAC-containing terpolymer particles and the corresponding particles produced by the binary copolymerization. For the VBTMAC-containing and MATMAC-containing systems, however, the reason for the suppression of agglomeration by the presence of acrylamide seems more complicated. In the emulsifier-free emulsion binary copolymerization of styrene with acrylamide, it was reported that acrylamide was highly reactive and preferentially polymerised in the aqueous phase at the early polymerization stages.²⁴ This led to the formation of a large amount of water-soluble copolymer containing up to about 75% acrylamide repeat-unit. For the current ternary copolymerizations, the presence of acrylamide increased the total amount of hydrophilic monomer whereas the initial styrene concentration in the aqueous phase would be hardly changed. Therefore, it was anticipated that more hydrophilic oligomers/copolymers would be formed in the ternary copolymerizations than in the binary copolymerizations. If their subsequent adsorption onto the particle surfaces took place, these oligomer/copolymer chains would result in more significant agglomeration via bridging flocculation. One possibility is that most of the acrylamide molecules polymerized at the very early stage of polymerization to form a polyacrylamide-rich layer around the growing primary particles ensuring steric stabilization and hence, the agglomeration of unstable particles was effectively suppressed. More detailed research is required to obtain better understanding on the observed phenomena.

CONCLUSIONS

Cationic polymer microparticles have been successfully obtained by emulsifier-free emulsion co-

polymerizations of styrene with different types of QACMs. The reactivity of the QACMs in the copolymerization with styrene had crucial effects on the final particle characteristics. The faster incorporation of the QACM repeat-units into copolymer chains led to the formation of smaller final particles. However, agglomeration of tiny unstable particles could occur at high QACM concentration, leading to polydispersity. Nevertheless, the agglomeration could be prevented by lowering the initial QACM concentration. Alternation of the cationic initiator V50 to the anionic initiator KPS resulted in a large increase in the size of final individual particles. Adding acrylamide as a second comonomer induced various changes to the different copolymerization systems. For the copolymer containing a low fraction of the cationic monomer repeat-unit (St/DADMAC/AAM system), the incorporation of acrylamide into the copolymer chains reduced the final particle size possibly by an enhancement in particle stabilization. In the cases of copolymer containing a high fraction of the cationic monomer repeat-units (St/VBTMAC/AAM and St/MATMAC/AAM systems), the presence of acrylamide suppressed the formation of agglomerates.

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