

Soap-free emulsion copolymerisation of styrene with cationic monomer: effect of ethanol as a cosolvent

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Abstract

Soap-free emulsion copolymerisations of styrene with (2-(methacryloyloxy) ethyl) trimethyl ammonium chloride (MATMAC) were performed both in aqueous medium and in the mixture of water and ethanol. On increasing the molar ratio of MATMAC/St from 0/90 to 5/90, the particle size decreased first and then increased in the absence of ethanol, whereas particle size progressively decreased in the presence of ethanol. The addition of ethanol in the polymerisation also influenced the polymerisation kinetics, the charge density of polymer latex particles, agglomeration of primary particles and polymer latex evolution mode. Effects of ethanol on the latex characteristics have been discussed in terms of particle formation mechanism. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Soap-free emulsion polymerisation; Cationic polymer particle; Ethanol

1. Introduction

Latex particles bearing surface charge groups have been widely used as models for fundamental studies or as functional materials for various applications including as chemical additives for papermaking. The main advantage of a soap-free emulsion polymerisation for preparing functional polymer particles over a conventional emulsion polymerisation is that it provides stable latex particles free of added surface-active agents. In order to tailor particle characteristics, soap-free emulsion polymerisations are normally performed in the presence of a small amount of ionic comonomer [1]. The incorporation of ionic monomer units in the copolymer chains can significantly reduce particle size and increase particle surface charge density. However, the presence of ionic comonomer also brings some drawbacks, such as the formation of undesirable water-soluble polyelectrolytes and the possibility of secondary nucleation leading to polydispersity [2,3]. Moreover, only a limited surface charge density is achievable by a batch polymerisation process [2–5]. Seeded polymerisation and semi-continuous process would be more suitable for producing highly charged particles [2,6–8]. Nevertheless,

they still suffer from the formation of a large amount of water-soluble polyelectrolytes [8].

To date, the majority of soap-free emulsion polymerisations have been performed in a water medium, whereas some researchers reported the use of mixtures of water and methanol [9–11]. For soap-free emulsion polymerisation, it is well known that the particle nucleation takes place in the continuous phase and a number of parameters, such as monomer partitioning and particle stability, are dependent on the properties of dispersing medium. Therefore, it is expected that the variation in the composition of dispersing medium would have important consequences on the characteristics of final particles. In a soap-free emulsion copolymerisation of styrene with sodium vinylbenzyl sulfonate, it was reported that the presence of methanol could improve both particle monodispersity and surface charge, but reduce the amount of removable polyelectrolytes [9]. In the current project, cationic latex particles were prepared by soap-free emulsion copolymerisation in the mixture of water and ethanol. The objective is to control the characteristics of polymer particles by varying the properties of dispersing medium. In addition, the influences of ethanol as a cosolvent on the particle formation would provide valuable information for understanding of soap-free emulsion polymerisation mechanism. The results presented in this paper focus on the soap-free emulsion copolymerisation of styrene with a quaternary ammonium comonomer,

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Table 1
A typical polymerisation recipe

| Name | Styrene | MATMAC (75 wt%) | Aqueous V50 (0.08 mol/l) | Water (ml) | Ethanol (ml) |
|--------|---------|-----------------|--------------------------|------------|--------------|
| L50E10 | 37.5 g | 5.54 g | 10 g | 387 | 43 |

(2-(methacryloyloxy) ethyl) trimethyl-ammonium chloride (MATMAC), using a cationic initiator.

2. Experimental

2.1. Materials

Styrene (St) was purchased from Fisher Scientific UK and distilled under reduced pressure prior to polymerisation. 2-(methacryloyloxy) ethyl trimethyl ammonium chloride (MATMAC, 75 wt% aqueous solution) was used as purchased from Sigma–Aldrich. The initiator, 2,2'-azobis(2-methylpropionamide) dihydrochloride (V50) was obtained from Sigma–Aldrich and recrystallised in water–acetone mixture (50/50 wt%). Ethanol (absolute) was used as received from Fisher Scientific UK. Double distilled deionised water was used throughout.

2.2. Polymerisation

Soap-free emulsion polymerisations were conducted using a batch process. All reactants and water, except for the initiator, were initially charged to a 500 ml glass-jacketed reactor fitted with a PTFE-bladed paddle stirrer, four equally spaced baffles, nitrogen inlet, water-cooled reflux condenser and sample taking syringe. Styrene (ca. 0.36 mol), MAPTAC (as 75 wt% aqueous solution, varied from 0.00–0.02 mol) and dispersing medium (430 ml water or mixture of water and ethanol) were initially charged to a 500 ml reactor. The mixture in the reactor was bubbled with nitrogen for about 45 min under 400 rpm agitation. After this, a very slow surface nitrogen flow was maintained and water was pumped through the jacket from a thermostat water bath which was operated at $70 \pm 0.1^\circ\text{C}$. After about 5 min, the initiator in aqueous solution was injected using a glass syringe to start polymerisation. The operation conditions were identical for all polymerisations carried out in this work. A typical polymerisation recipe is presented in Table 1.

2.3. Determination of monomer conversion

Monomer conversions were followed by a gravimetric method. About 4.0 g latex sample was withdrawn from the reactor at various time intervals. Aqueous hydroquinone was then added to stop the post-polymerisation. After evaporation of the most volatile components in a fume cupboard, the samples were finally dried in a vacuum oven to constant weight at 70°C . The styrene conversions

were calculated from the weights of fed monomers and of the dried polymers.

2.4. Latex characterisation

The latexes were cleaned by dialysis against deionised distilled water until the conductivity of the surrounding water reached a constant value.

Particle hydrodynamic diameters were measured by photon correlation spectroscopy (PCS) using a Zetasizer 3000 (Malvern, UK). The measurements were conducted in 1.0 mM NaCl aqueous solution at 25°C , and a z -average diameter of particles was reported. A scanning electron microscope (SEM, SM-300, Topcon, Japan) and a transmission electron microscope (TEM, JEM-100 CX) were employed to observe the particle shape, size and size distribution. The number of particles in unit volume of the latexes (N_p) was calculated by the following equation (Eq. (1)):

$$N_p = \frac{6WC}{\pi\rho Vd^3} \quad (1)$$

Here W is styrene weight (g), C styrene conversion, V volume of dispersing medium (ml), ρ polystyrene density (1.05 g/cm^3) and d is the particle diameter (cm).

Zeta potential of the particles was determined using the same instrument Zetasizer 3000 for PCS measurements. Five repeats were conducted in the mixture of 1.0 mM NaCl aqueous solution with various amount of ethanol which was identical to the amount of ethanol used in polymerisations.

A colloid titration technique was employed to determine the apparent charge density for both particles and water-soluble polyelectrolytes [12]. The dialysed latexes were centrifuged using an Eppendorf Centrifuge 5415 at 14,000 rpm for 8 h. The serums were then decanted and collected. The particles were re-dispersed in deionised distilled water. This cycle was repeated one more time. Finally, the purified particles and the collected serums were titrated with 0.1 and 1.0 mN potassium polyvinyl sulfate (PVSK), respectively. The end point was determined by using toluidine blue-O as colour indicator [13,14]. The charge in the water-soluble polyelectrolytes (E_{poly}) was presented as equivalent mole charge groups per gram of polymer (particles + water-soluble polyelectrolytes). The charge on the particle surface was expressed as equivalent mole of charge groups per gram of particles (E_{pw}) or Coulomb per cm^2 of particle surface (E_{ps}), according to the following equation [5] (Eq. (2)):

$$E_{\text{ps}} = \frac{1}{6} E_{\text{pw}} d \rho F \quad (2)$$

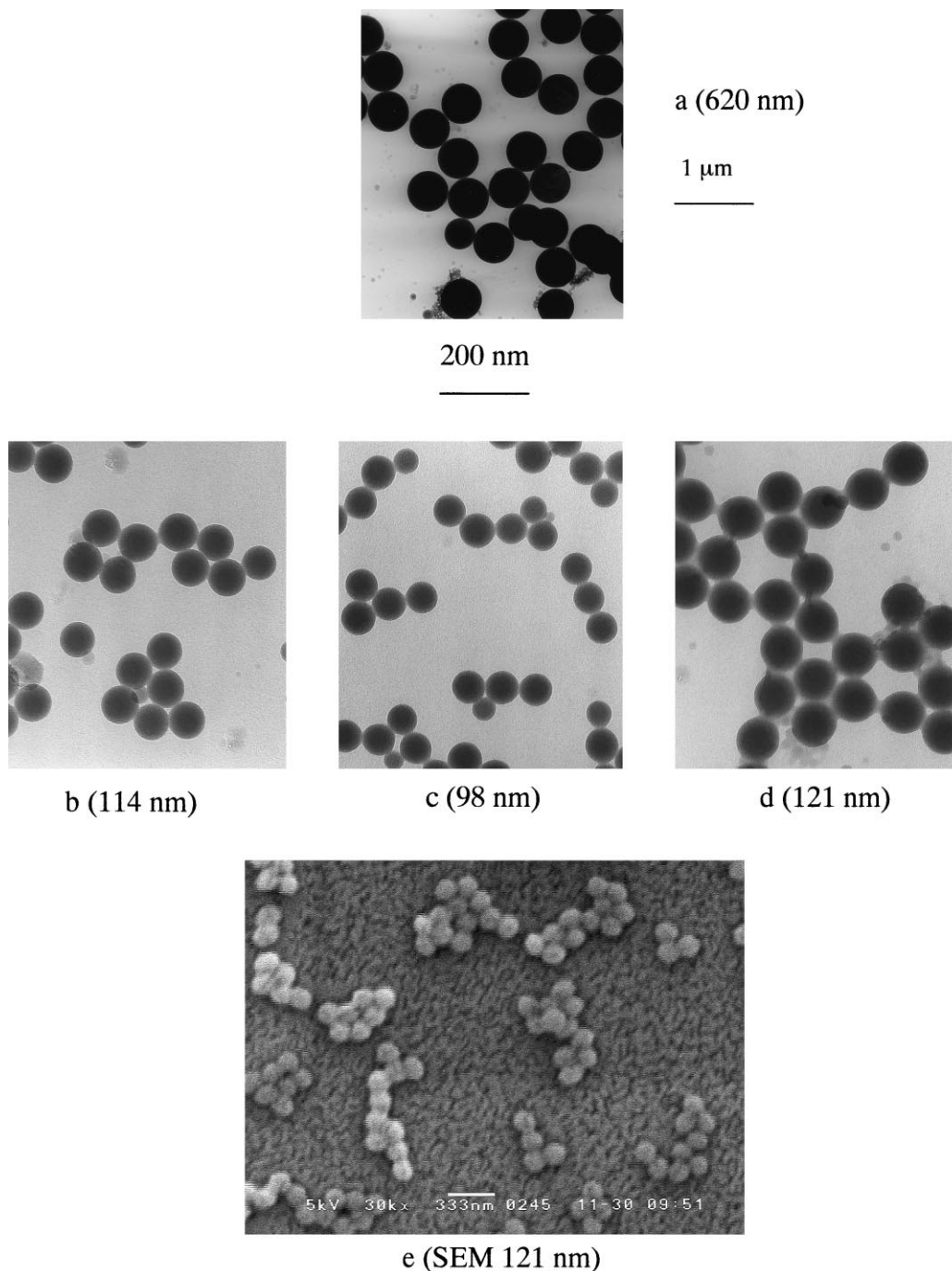


Fig. 1. TEM images and SEM image of particles obtained in the absence of ethanol, hydrodynamic diameters (z-average obtained from Zetasizer 3000) are present in brackets, MATMAC/St (mol/mol): a. 0/90 (TEM); b. 0.5/90 (TEM); c. 1.0/90 (TEM); d. 2.5/90 (TEM); e. 2.5/90 (SEM).

Here F is Faraday constant (9.64×10^4 Coulomb); d and ρ are the same as in Eq. (1). Obviously, E_{ps} is proportional to both E_{pw} and particle diameter d .

3. Results

3.1. Particle size and size distribution

A series of latex particles were prepared by varying the

monomer feed ratio of MATMAC/St from 0/90 to 2.5/90 (mol/mol) in the absence of ethanol. The TEM images of these particles are shown in Fig. 1. All particles are spherical with fairly smooth surface. The sphericity of particles was further approved with a SEM image observation (see Fig. 1(e)). As expected, the copolymerisations with MATMAC generated particles much smaller in size than that obtained by styrene homopolymerisation. However, in the case of copolymerisations, the particle size decreased

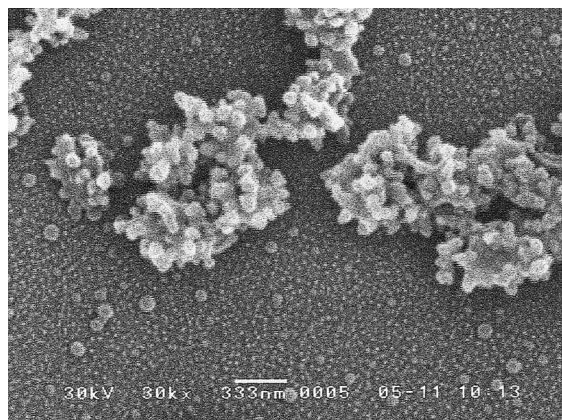


Fig. 2. SEM images of agglomerates. MATMAC/St = 5/90 (mol).

first and then increased with increased ratio of MATMAC/St. The particle hydrodynamic diameters obtained by PCS, which are presented in the brackets in Fig. 1, also show the same trend.

Further increase in the ratio of MATMAC/St to 5/90 (mol/mol) led to the formation of polydisperse latex. The PCS indicated a bimodal size distribution. SEM imaging clearly revealed that large agglomerates accompanied small individual particles (Fig. 2). It is noteworthy that the agglomerates consist of a large number of tiny particles. This implies that the agglomerates could result from the flocculation of primary particles.

In the presence of 20% (vol) ethanol as a cosolvent, soap-free emulsion polymerisations were conducted at various ratios of MATMAC/St. Spherical particles were obtained and no significant agglomerates were observed even at the high ratio of MATMAC/St = 5/90 (Fig. 3). It was found that the particle size progressively decreased as the ratio of MATMAC/St increased, which differs from the case in the absence of ethanol (see Fig. 1). By comparing the TEM images in Figs. 1 and 3 as well as the results in

Table 2 (entries 3, 4, 6 and 7), it can be seen that the particles prepared in the presence of ethanol were larger than the corresponding ones prepared in the absence of ethanol.

Particles were also prepared at the constant ratio of MATMAC/St = 5/90 (mol/mol) in the media containing various ethanol contents. The TEM images and the hydrodynamic diameters of the particles are also showed in Fig. 3. Some agglomerates were found in the latex prepared using 5% (vol) ethanol, which accounts for the large hydrodynamic diameter. However, the agglomerates were hardly observable at higher ethanol contents. Nevertheless, the higher ethanol content tends to produce the latex with larger particle size and broader size distribution.

3.2. Particle surface charge

The surface charge density of the particles (see Table 2) was expressed in two ways: E_{pw} ($\mu\text{eq/g}$) and E_{ps} ($\mu\text{C/cm}^2$). E_{pw} was obtained directly from colloidal titration whereas E_{ps} was calculated from Eq. (2). Both values varied with monomer feed ratio and ethanol content, and agree well with the results reported in the literature for the batch soap-free emulsion copolymerisation of styrene with 3-(methacrylamidinopropyl) trimethyl ammonium chloride [2].

For the particles of styrene homopolymer, the surface charge originated from amidino groups of the initiator fragments. For the copolymerisations, both the quaternised amino groups of MATMAC units and the amidino groups will contribute to the particle stabilisation [5]. In the absence of ethanol, both E_{pw} and E_{ps} increased with increased ratio of MATMAC/St. The same trend was also observed for the copolymerisations in the presence of ethanol (entries 6, 7 and 10 in Table 2). The high value E_{ps} for styrene homopolymer is attributed to its large particle size (approximately six times as high as that of copolymers in diameter). The presence of ethanol in polymerisation tended

Table 2
Latex characteristics

| No. | Sample | MATMAC/St (mol/mol) | Ethanol (vol%) | Hydrodynamic diameter (z-mean nm) | E_{ps} ($\mu\text{C/cm}^2$) | E_{pw} ($\mu\text{eq/g}$) | E_{poly} ($\mu\text{eq/g}$) | A_{poly}^a (%) | Conversion (%) |
|-----|--------|---------------------|----------------|-----------------------------------|---------------------------------|-------------------------------|---------------------------------|------------------|----------------|
| 1 | PS | 0/90 | 0 | 620 | 20.0 | 20.8 | 0 | 0 | 78.1 |
| 2 | L5 | 0.5/90 | 0 | 114 | 12.5 | 65.4 | 1.6 | 2.9 | 99.1 |
| 3 | L10 | 1.0/90 | 0 | 98 | 16.0 | 96.9 | 10.4 | 9.8 | 99.4 |
| 4 | L25 | 2.5/90 | 0 | 121 | 22.3 | 110 | 85.5 | 35.1 | 98.5 |
| 5 | L50 | 5.0/90 | 0 | 298 ^b | –b | 161 | 298 | 61.9 | 98.6 |
| 6 | L10E20 | 1.0/90 | 20 | 160 | 20.7 | 77.0 | 8.7 | 8.0 | 97.6 |
| 7 | L25E20 | 2.5/90 | 20 | 131 | 23.1 | 104 | 72.1 | 28.3 | 99.4 |
| 8 | L50E5 | 5.0/90 | 5 | 106 ^b | –b | 463 | 282 | 58.9 | 98.9 |
| 9 | L50E10 | 5.0/90 | 10 | 86 | 23.1 | 159 | 260 | 53.8 | 99.4 |
| 10 | L50E20 | 5.0/90 | 20 | 103 | 25.4 | 146 | 244 | 50.8 | 99.2 |
| 11 | L50E40 | 5.0/90 | 40 | 131 | 27.6 | 125 | 214 | 45.1 | 99.3 |

^a Percentage of charge in the water-soluble polyelectrolytes over the theoretical charge.

^b Polydispers—consisting of the individual particles and the agglomerates induced by linear polyelectrolytes existed in the system, and difficult to calculate E_{ps} from E_{pw} .

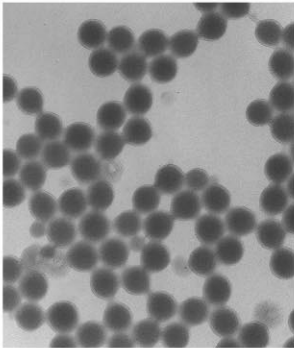

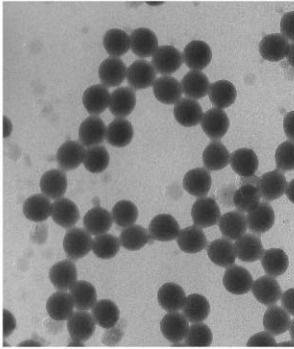
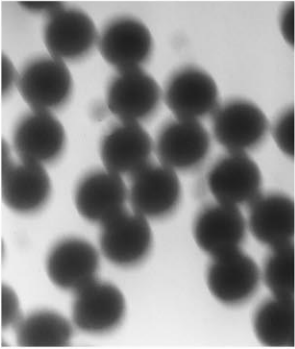
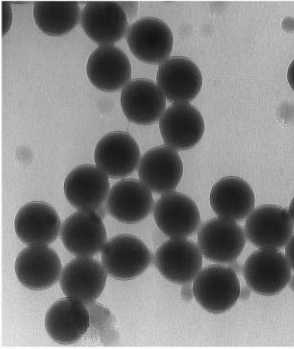
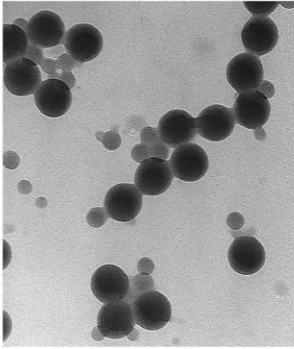
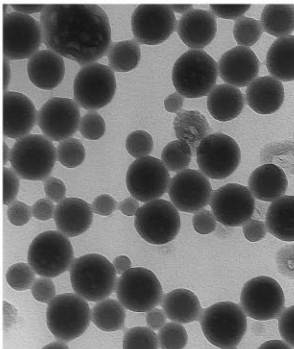
| ethanol content (vol%) | MATMAC/St (mol) | | |
|------------------------|---|---|--|
| | 1.0/90 | 2.5 /90 | 5.0/90 |
| 5 | | |  (106 nm) |
| 10 | |  200 nm |  (86 nm) |
| 20 |  (162 nm) |  (132 nm) |  (103 nm) |
| 40 | | |  (131 nm) |

Fig. 3. TEM images of particles obtained in the presence of ethanol, hydrodynamic diameters (ζ -average obtained from Zetasizer 3000) are present in brackets.

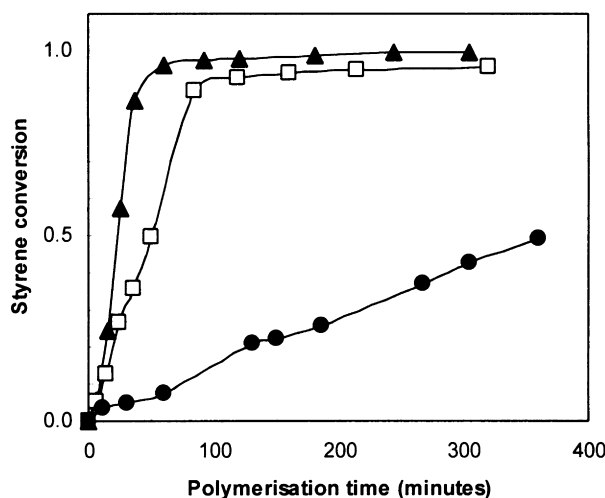


Fig. 4. Styrene conversion curves. (●) styrene homopolymerisation, no ethanol. (□) MATMAC/St = 1.0/90, 20% (vol) ethanol; (▲) MATMAC/St = 1.0/90, no ethanol.

to reduce the total charge of particles (E_{pw}) but increase the particle size and hence the surface charge density E_{ps} , as can be seen by comparing entries 3 and 4 with 6 and 7. At the constant ratio of MATMAC/St = 5/90, E_{pw} progressively decreased, whereas the size and E_{ps} increased, with increased ethanol content from 10–40% (vol) (entries 9–11 in Table 2).

3.3. Water-soluble polyelectrolytes

The formation of water-soluble polyelectrolytes had been reported for the soap-free emulsion copolymerisations in the presence of ionic comonomers [2,3,6–8]. The charges contributed from the water-soluble polyelectrolytes are also presented in Table 2. Because amidino groups can only be present as chain end-groups, the charges in the water-soluble polyelectrolytes must be mainly attributed to the ionic groups of MATMAC units and reflect the amount of polyelectrolytes in the serum. By assuming that complete monomer conversions were achieved and all MATMAC units in the copolymer chains were dissociated, the percentages of charge ($A_{poly}\%$) in the water-soluble polyelectrolytes over the theoretical charge were calculated and are listed in Table 2.

For the copolymerisations in the absence of ethanol, the amount of the water-soluble polyelectrolytes (i.e. $A_{poly}\%$) increased quickly with increased ratio of MATMAC/St. At the ratio of MATMAC/St = 5/90, more than half of the fed MATMAC molecules were incorporated into the water-soluble polyelectrolytes which remained in the latex serum. In contrast, for the copolymerisations in the presence of ethanol, the amount of water-soluble polyelectrolytes formed in latex serum was reduced significantly. For example, at the same constant ratio of MATMAC/St = 5/90, the addition of 20% (vol) ethanol reduced the amount of the polyelectrolytes by more than 10% (see entries 5 and 10).

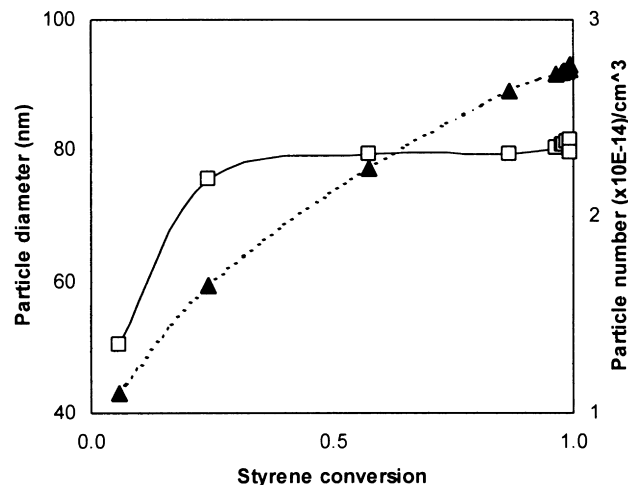


Fig. 5. Variations of particle size and number with styrene conversion in the absence of ethanol. MATMAC/St = 1.0/90 (mol); (▲) Particle diameter (\bar{z} -average) vs. conv.; (□) Particle number vs. conv.

Similar trends were also observed for the other ratios (compare entries 3 and 4 with 6 and 7, respectively). Moreover, the amount of water-soluble polyelectrolytes decreased as ethanol contents increased (see entries 8–11).

3.4. Kinetic study

Fig. 4 shows the styrene conversion curves for the copolymerisations with MATMAC in the absence and in the presence of ethanol. The result of styrene homopolymerisation is also showed for comparison. The copolymerisation with MATMAC drastically accelerated styrene polymerisation rate. This is the common phenomenon in the copolymerisations of styrene with ionic monomers [2,3,8,11,15–17]. Apparently, adding 20% (vol) ethanol to the dispersing medium slightly retarded the rate of styrene consumed in the copolymerisation.

The particle diameters were measured throughout the course of the polymerisations and the variations of particle number with styrene conversion were worked out. The results of particle evolution are showed in Figs. 5 and 6. The particle size increased as polymerisation proceeded both in the absence and the presence of ethanol. However, the addition of ethanol changed the particle evolution mode. For the copolymerisation at the ratio of MATMAC/St = 1/90 in the absence of ethanol, the particle number increased continuously to a constant level at about 40% styrene conversion (Fig. 5). In contrast, for the copolymerisation in the presence of 20% (vol) ethanol, the particle number decreased gradually at the early polymerisation stages and reached a constant value at about 50% styrene conversion (Fig. 6). The latex obtained by the copolymerisation in the absence of ethanol contained about 6 times the number of particles in unit volume than that obtained in the presence of ethanol.

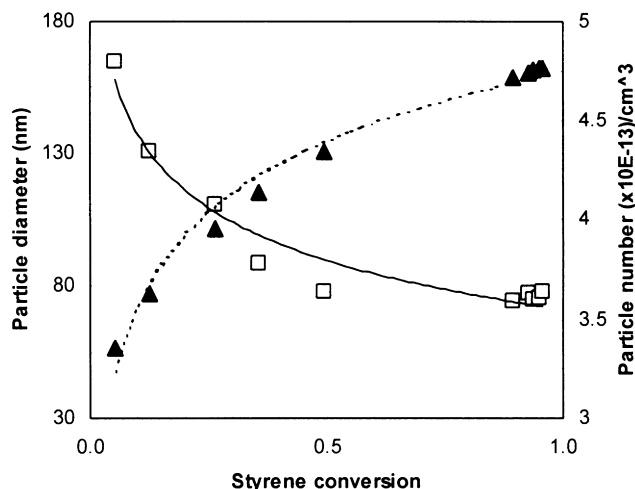


Fig. 6. Variations of particle size and number with styrene conversion in the presence of 20% (vol) ethanol. MATMAC/St = 1.0/90 (mol); (▲) Particle diameter (z -average) vs. conv.; (□) Particle number vs. conv.

3.5. Effect of ethanol on particle zeta-potential

The zeta potential of one type of prepared particles was measured in a series of media containing various contents of ethanol. Fig. 7 shows the results. It is clear that the particles are positively charged. However, the zeta potential decreased with increased ethanol content. This implies a reduction in the electrostatic repulsive energy of the particle surface due to the presence of ethanol in the dispersing medium.

4. Discussion

4.1. Particles obtained in water medium

Unlike a conventional emulsion polymerisation, soap-free emulsion polymerisation generates particles stabilised by covalent bonded ionic groups at the surface. The ionic groups can be introduced by using ionic initiators. Nevertheless, this type of ionic groups can only exist as end-groups and hence, significant coagulation of primary particles normally occurs during the polymerisation, leading to the formation of large particles [18]. By adding an ionic comonomer, the incorporation of the ionic repeat-units in the copolymer chains can effectively enhance the electrostatic stabilisation of the particles. Consequently, particles with smaller size can be obtained [1]. This accounts for the size difference between the MATMAC-containing particles and the styrene homopolymer particles. However, the particle formation in the soap-free emulsion copolymerisation appears to be complex. Higher ionic comonomer concentration does not necessarily lead to the formation of smaller particles. For the copolymerisations in water medium, the smallest particles were obtained at a ratio of MATMAC/St = 1/90. The increase in MATMAC concentration could

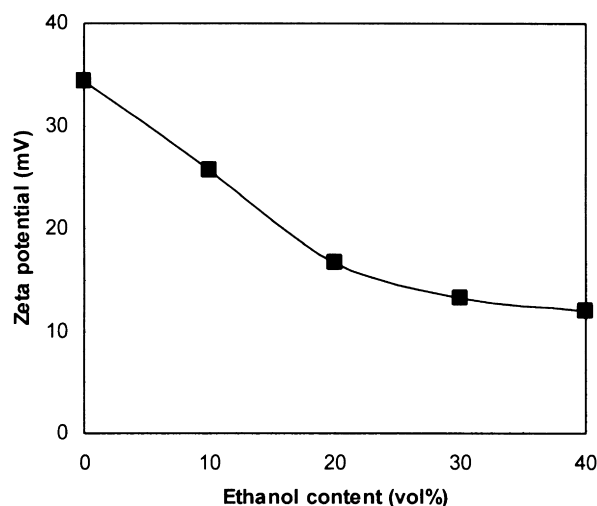


Fig. 7. Variation of zeta potential with ethanol content in dispersing medium latex particle: L25E20.

result in more ionic monomer units incorporated in the copolymer chain, which tends to stabilise the particles via electrostatic repulsion. On the other hand, the increase in ionic strength contributed from the increased fed MATMAC concentration could depress the electrostatic double-layer of the particle surface and induce the coagulation of primary particles [19]. The observed variation of particle size with the ratio of MATMAC/St is probably the combination results of these two factors.

Moreover, a significant amount of agglomerates were formed at a high ratio of MATMAC/St = 5/90. The agglomerates could result from the bridging flocculation of unstable particles by polyelectrolytes (mainly MATMAC homopolymers in this work) existed in the system [3]. The SEM imaging of the agglomerates supports this hypothesis (Fig. 2). The results presented in Table 2 provide further evidence: the charge contributed from the water-soluble polyelectrolytes increased as the fraction of MATMAC in monomer feed increased. The formation of water-soluble polyelectrolytes is due to the fact that some oligoradicals terminate in the continuous phase before they become hydrophobic enough to nucleate or to be captured by the existing particles [2]. The hydrophobicity of a copolymer chain is dependent on both its molecular weight and the chemical composition [17]. A growing oligoradicals consisting of larger fraction of hydrophilic ionic monomer units must have larger critical molecular weight for nucleation or adsorption. In addition, the electrostatic repulsion would make the nucleation and adsorption more difficult. Consequently, the growing oligoradicals could remain in the continuous phase for a longer period and increase the opportunity for the formation of water-soluble polyelectrolytes.

4.2. Effect of ethanol on particle size

In soap-free emulsion polymerisations, particle size is

mainly determined by nucleation rate and particle stability. It is anticipated that the presence of ethanol should increase styrene solubility in the continuous phase and hence, would promote the incorporation of styrene in the copolymerisation that occurred in the continuous phase, provided that the influences on monomer reactivity ratios were negligible [20]. From this point of view, the addition of ethanol and the reduction of the ionic comonomer concentration possess the similar effects on the chemical composition of growing oligoradicals. On the other hand, the solubility of oligomers in the continuous phase would also increase with increased ethanol content [9]. Almog et al. [21] investigated the effects of alcohols on particle formation in the dispersion polymerisations of styrene and of methyl methacrylate. They found that the particle size increased linearly with decreased solubility parameter differences between the polymer and the dispersing media. In the precipitation copolymerisation of acrylamide, acrylic acid and methylene-bisacrylamide in the mixture of alcohols, Kawaguchi et al. [22] also reported a linear relationship between the particle size and the solubility parameters of the dispersing media. In both cases, the increases in particle size were attributed to the retardation of nucleation by increasing the solubility of the oligomers in the dispersing media.

On discussing the oligomer nucleation and adsorption, another important factor must be taken into account; that is, the electrostatic interactions originated from the charge groups. Obviously, an oligomer bearing more charge groups should be more rigid to nucleate or to adsorb on the likely charged particle surfaces. As discussed above, the fraction of MATMAC units in the oligomers could be decreased by adding ethanol. In addition, the dissociation of amidino and the quaternised amino groups is a function of the dielectric constant of the dispersing medium [21,23]. Adding alcohols as cosolvents normally reduces the electrostatic repulsion [9]. This was confirmed by the zeta potential measurements for the latex L25E20 (Fig. 7). Therefore, it is more likely that the presence of ethanol could facilitate the oligomer nucleation and adsorption. Consequently, relatively larger particles were formed at higher ethanol content (see entries 9, 10 and 11 in Table 2).

The faster nucleation might generate more primary particles that then grow to final particles with smaller size [11]. However, at the same extent of monomer conversion, the particle number in the presence of ethanol was less than that in the absence of ethanol (Figs. 6 and 7). This is because the coagulation of nuclei and primary particles was more significant in the former case than that in the latter, which has been clearly indicated by the variations of particle number with styrene conversion. The coagulation of primary particles was enhanced in the presence of ethanol, leading to the formation of relatively large particles.

The overall consumption rate of styrene was reduced by adding ethanol (Fig. 4), although the polymerisation of styrene in the continuous phase was probably enhanced. This is not surprising because of the specific feature of the soap-

free emulsion polymerisation: polymerisation took place simultaneously in the continuous phase and inside the particles [18,24]. The monomer conversion curves showed in Fig. 4 are typical ones of emulsion polymerisation. More particles in the copolymerisation in water medium provided more loci for styrene polymerisation and hence, increased overall styrene consumption rate.

4.3. Effect of ethanol on particle charge density

The particle charge density E_{pw} ($\mu\text{eq/g}$), obtained from colloid titration, only reflects the proportion of charge groups at the particle surface. By comparing the value of E_{pw} with the theoretical amount of charge groups contributed from cationic monomer (supposing complete monomer conversion), the information regarding the burial of charge groups during particle formation can be gained. The decrease in E_{pw} by adding ethanol (Table 2) suggests an increase in buried ionic groups. This is probably attributed to the change in the particle formation modes by the presence of ethanol. In the absence of ethanol, the dissociation of amidino and the quaternised amino groups was high. Therefore, the coagulation was effectively restricted and a continuous nucleation occurred. In contrast, the significant coagulation of primary particles took place in the presence of ethanol due to the reduced electrostatic repulsive energy and hence, resulted in the burial of the ionic groups [25]. The burial of the ionic groups could be more significant at higher ethanol content as indicated by the continuous decrease in E_{pw} on increasing ethanol content.

5. Conclusions

For the soap-free emulsion copolymerisation in water medium, the incorporation of MATMAC repeat-units in the copolymer chains significantly enhanced particle stabilisation and therefore, drastically reduced particle size and size distribution. Nevertheless, the increase in the monomer feed ratio of MATMAC/St resulted in a progressive increase in the amount of water-soluble polyelectrolytes. At the molar ratio of MATMAC/St = 5/90, significant agglomerates were formed probably due to the bridging flocculation of the primary particles by the water-soluble polyelectrolytes.

Using ethanol as a cosolvent effectively restricted the formation of the water-soluble polyelectrolytes. When more than 10% (vol) of ethanol was used, spherical particles without significant agglomerates were successfully obtained at the molar ratio of MATMAC/St = 5/90. The particles obtained in the presence of ethanol were larger than that in the absence of ethanol. These results are probably due to the complex influences of ethanol on both chemical and physical aspects: (1) increasing styrene solubility in the continuous phase and hence, altering the chemical composition of the growing oligoradicals; (2) decreasing electrostatic repulsive forces because of the reduced dielectric

constant of the dispersing media; (3) facilitating the nucleation and the adsorption of the oligomers; and (4) promoting the coagulation of primary particles.

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