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The effect of acrylic acid amount on the colloidal properties of polystyrene latex

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Abstract Poly(styrene-*co*-acrylic acid) (St/AA) latices were prepared by using a batch soap-free emulsion copolymerisation in non-buffered medium. Polymerisation kinetics, followed by gravimetric method, revealed that increasing AA comonomer concentration was directly proportional to the copolymerisation rate, while adding AA comonomer caused a strong decrease of particle size of final St/AA latex particle without affecting the size distribution. Transmission electron microscopy indicated that the particles were monodispersed and spherical in shape irrespective of AA amount used in the investigated range. The colloidal stability of the latices was increased upon increasing the AA concentration; owing to the electrosteric stabilisation originated from AA-rich layer on the particle surface. In addition, electrophoretic mobility of formed particles versus polymerisation conversion exhibited the constancy of the surface charge density during the polymerisation process and was inferred for discussion of the polymerisation mechanism of this system.

Key words Carboxylated latex · Surfactant-free emulsion polymerisation · Particle size and morphology · Colloidal stability · Electrokinetic properties

Introduction

Polymer microspheres, especially those in submicron-sized range, currently offer useful and suitable solid support in a large number of medical and biological applications such as immunoassay, protein separation and cell sorting [1–3]. For this purpose, many researchers have been dedicated to design and preparing well-defined colloidal polymer particles as a solid support for biologically active macromolecule. The ideal polymer support for latex immunoagglutination should allow the attachment of protein in a controlled manner, resulting in a colloidally stable system with the required surface concentration of immobilised proteins, and retaining a maximum of their biological activity [4,5].

Emulsifier-free emulsion polymerisation, mainly with styrene (St), has been widely used to produce monodisperse polymer microspheres with various functional groups [2,6,7]. Great attention has been paid to synthesis of hydrophilic functional latex with reactive surface group via copolymerisation of St and functional monomer. Among several functional monomers, i.e., carboxyl, amino, hydroxyl, chloromethyl and aldehyde, the most commonly used surface for attachment of protein is carboxyl group, e.g., from acrylic acid (AA) and methacrylic acid (MAA), due to its high stability over time and its well-known chemistry [5]. Results from St/AA and St/MAA copolymers prepared by using a seeded or two-step emulsion copolymerisation method indicated that the reaction behaviour is greatly affected by the type of acid monomer, partition of monomer between the various phases, and locus of polymerisation [8,9]. Potentiometric and conductometric titrations were effectively used to determine the distribution of the acid groups between the aqueous phase, the particle surface and the particle interior, particle stability, and particle generation [10].

The core-shell latex has been also prepared by copolymerisation of AA or MAA with St using a batch or unseeded or one-step emulsion copolymerisation [11,12]. On the basis of the homogeneous nucleation mechanism, the copolymerisation rate increased in the order of AA $<$ MAA due to the fact that MAA is more hydrophobic than AA. The growing chain of MAA in an aqueous phase becomes increasingly less water-soluble and reaches a critical chain length (j_{cr}) or precursor particle with smaller size than AA. Consequently, in the early stage of particle nucleation, the precipitation of St/MAA oligomers, or the chain coming out of solution and forming a primary particle, was easier than that of St/AA. With two different concentrations of AA, it was suggested that more AA in the initial copolymerisation feed yields copolymer microspheres with a higher content of AA [12]. X-rays photoelectron spectroscopy (XPS) and elemental analysis were applied to directly indicate not only the core-shell structure but also the high carboxylic group of St/AA particle surface compared to that of St/MAA.

Since the understanding of the factors affecting the distribution of the carboxylic functionality is very important and is necessary for proper control of the functional group on particle surface, a well characterised St/AA copolymer latex to further use a solid support for malaria protein antigen was focused in this present work. Although seeded copolymerisation significantly increased the number of carboxylic groups on the surface of the St/MAA copolymer microspheres [8], a batch (one step) soap-free emulsion copolymerisation should be suitable to produce a core-shell structure of St/AA particle with various AA contents. Owing to the hydrophobicity of St and hydrophilicity of AA, core-shell particle having polystyrene (PS)-rich core and a surface shell rich in AA could be conveniently produced [12]. The copolymer latex prepared was then characterised in terms of particle size, size distribution and particle morphology. The effect of four AA concentrations on rate of polymerisation, particle size, colloidal stability and surface charge density was investigated. The distribution of carboxylic groups was examined by using conductometric titration. In addition, the electrokinetic properties of particles as a function of polymerisation conversion were explored to obtain further insights on the polymerisation mechanism.

Experimental

Materials

St (Fluka, Purum) and AA anhydrous (Fluka, Purum) were purified by distillation under reduced pressure. The purified monomers were stored at - 25°C until used. Ammonium persulfate (APS, Fluka, Purum), sodium chloride (NaCl, Merck, Analytical), sodium hydroxide (NaOH, Prolabo) and hydrochloric acid (HCl, Prolabo) were used as received. Deionised water (milli-Q) was used throughout the work.

Preparation of styrene/acrylic acid (St/AA) copolymer latex

St/AA copolymer latices were prepared by soap-free emulsion copolymerisation process using APS as an initiator in non-buffered medium. The recipe used for preparing latices is shown in Table 1.

The polymerisation was carried out in a glass reaction vessel equipped with a glass anchor-type propeller connected with mechanical stirrer, condenser, nitrogen inlet and outlet.

Deionised water (190 g) was charged into a 500 ml glass reaction vessel while remaining water was used to dissolve an initiator. After purging with nitrogen for about 1 h while stirring at 350 rpm, the distilled St and AA monomers were added into the reaction vessel. The polymerisation temperature was controlled at 70°C via an external water circulation. The reaction was started by adding an aqueous solution of APS. Polymerisation conversion of St/AA was determined by taking an aliquot of latex (2–3 g) from the reaction vessel and

Table 1 Recipes used for preparing PS and St/AA latices

Latex	M_{H2O} (g)	M_{St} (g)	M_{AA} (g)	M_{APS} (g)	Polymerisation time (h)
PS1	200	20	–	0.1	25
PS2	200	20	–	0.2	25
St/AA1	200	20	3.0	0.1	7
St/AA2	200	20	2.0	0.1	7
St/AA3	200	20	1.4	0.1	7
St/AA4	200	20	0.7	0.1	7

immediately mixed with a small amount of hydroquinone to stop the polymerisation reaction. The conversion was then determined from solid content after drying the latex sample at 120°C.

St/AA copolymer latices obtained were purified in order to remove the residual monomer, electrolyte and water-soluble oligomers by centrifugation with a supraspeed centrifugation (Beckman Coulter; J2-MC) at 12,000 rpm for 30 min. An equal volume of deionised water then replaced the upper serum layer. The process was repeated until the conductivity of supernatant was close to that of the deionised water. In this study, PS latex was also synthesised to use as a control sample.

Particle characterisation

Particle size and size distribution measurements

The hydrodynamic size of latex particles ($\bar{D}_\mathrm{h}$) was determined by coulter counter (Coulter electronics; Hialeah) at room temperature and in 10^{-3} M NaCl concentration. In addition, transmission electron microscopy (TEM) (JEOL; TEM 200-cx) was applied to determine size and size distribution of latex particles in dried state. Number ($\bar{D}_\mathrm{n}$), weight ($\bar{D}_\mathrm{w}$) average diameter, and polydispersity index (PDI) of latex particles were determined from about 150 particles.

Morphological study

TEM was used to investigate the morphology of latex particle. A drop of very dilute latex was placed on a 300 mesh carbon-coated copper grid and then the excess amount of fluid was removed by using filter paper.

Colloidal stability

The extent of particle aggregation in the dispersion (N_τ) was estimated from the wavelength dependence of turbidity [13], i.e.

$$N_\tau = -\left(\frac{d\log\tau}{d\log\lambda}\right), \tag{1}$$

where τ is turbidity of sample and λ is wavelength. A given amount of polymer particles was added into various NaCl solutions (10^{-5} to 3 M) to obtain 0.005% w/w. The mixture was stored at 20°C for 1 h before measuring the turbidity variation versus the wavelength ranging 400 to 700 nm using UV-vis spectrophotometer (Monaco; SAFAS; UVmc^2).

Surface charge titration

To determine surface charge density (σ) of St/AA latex particle, the conductometric back titration was performed on 1 ml of cleaned latex in 50 ml of milli-Q water at 20°C. The excess amount of 1 M NaOH solution was firstly added into the latex. Back titration was started when 0.01 M HCl was automatically dropped into the latex via piston burette (Titronic universal; SCHOTT) while gently stir. The change in conductivity value of latex was measured by conductimeter and pH meter 4330 (JENWAY) equipped with glass conductivity cell ($K=1$). The number of microequivalents of acid groups per gram ([COOH]) was given as follows:

$$[\mathrm{COOH}] = \frac{V_\mathrm{HCl}\cdot M_\mathrm{HCl}\cdot 10^{-3}}{\text{Mass of latex(g)}\cdot\text{Solid content}}\quad(\mu\mathrm{eg/g}), \tag{2}$$

where, V_HCl and M_HCl are volume of HCl at equivalent point (ml) and concentration of HCl (M), respectively. The surface charge density (σ) of latex was calculated from Eq. 3

$$\sigma = \frac{\rho}{6}\cdot D_\mathrm{h}\cdot[\mathrm{COOH}]\cdot N_\mathrm{A}\cdot e\quad\left(\mu\mathrm{C/cm^2}\right), \tag{3}$$

where ρ is density of polymer (1.045 g/cm^3 for PS), D_h is hydrodynamic diameter of particle (cm), N_A is Avogadro's number (6.02205×10^{23} mol^{-1}), and e is electronic charge in coulombs (1.60219×10^{-19} C).

Electrophoretic mobility measurement

The experiment was performed with Zeta Sizer (Malvern; 3000HS) in 1 mM NaCl solution with pHs ranging from 3 to 8. In the measurement, NaCl solution was filtered through 0.22 μM filter to remove impurities before being mixed with the latex sample and then injected into the sample chamber at 20°C. All measurements were repeated at least five times.

Results and discussion

By using soap-free emulsion copolymerisation for preparation of polymer microsphere bearing reactive groups, hydrophilic monomer tends to locate on the particle surface and, therefore, provides stability of the particles [11]. A kinetic study of a series of the carboxylated latices prepared by varying the AA concentration added in the polymerisation system was first investigated. Then the colloidal properties and morphology of all latices were examined.

Effect of the AA comonomer concentration on polymerisation kinetics

The influence of AA content on the copolymerisation rate of St with AA is reported in Fig. 1.

It was clearly observed that the conversions increased with increasing polymerisation time in St/AA1, St/AA2 and St/AA3 latices whereas those in the St/AA4 having small amount of AA was slightly increased similar to the PS latex. From the slopes, it could be pointed out that the rate of polymerisation performed in the St/AA was higher than that of PS and the AA concentration was directly proportional to the rate of polymerisation as previously reported [12]. An explanation based on the homogeneous nucleation mechanism can be put forward that the increase in the polymerisation rate is influenced by the increased number of primary particles formed in aqueous phase in the early step of nucleation [14]. It is well known that persulfate radicals induce polymerisation of monomer dissolved in the aqueous phase, resulting in oligomer radicals. As the oligoradicals reach a j_{cr}, they precipitate and agglomerate to form primary particles. Particle growth continues inside the particles, which maintain their stability from the hydrophilic shell provided also by the carboxyl groups, which concentrate at the particle/water interface. From this explanation, the higher rate of copolymer particle having higher AA concentration due to the increase in rate of formation of oligomers or oligoradicals to some extent in the aqueous phase resulted in more primary particles and, hence, more polymer particles; the more primary particles, the faster the polymerisation rate. The data of St/AA1 (3 g of AA) and St/AA2 (2 g of AA) agreed well with those containing the same compositions formerly reported [12]. Based on the same principle, the previous work also indicated that the St/AA system had lower polymerisation rate and lower total conversion than those in the St/MAA (at the acid monomers content of 3 g). The more hydrophobic MAA could easily form oligoradicals in water and, hence, provide higher number of primary particles which subsequently, became swollen with St. Since the polymerisation mainly took place in the swollen St polymer particles, the copolymerisation rate or total conversion was determined by the polymerisation or conversion of St. To confirm this hypothesis, the study on the other two St/AA systems having low AA contents, i.e., St/AA3, St/AA4 and PS latices was extended in our research. As expected, the lower copolymerisation rate and lower conversion were observed. The smaller amount of water soluble AA possibly caused the lower number and/or shorter chain of oligoradicals generated from the reaction of persulfate radicals with monomer in aqueous phase. The short oligomer chains, less than j_{cr}, would not be able to be hydrophobic enough for effective aggregation to form primary particles within the observed polymerisation time, i.e., 7 h of the systems with low AA in St/AA4 and without AA in PS latices. In the latter case the higher concentration of APS might be needed to efficiently prepare PS latex via soap-free emulsion polymerisation [15,16].

Since the initial slope of conversion-time curves provides copolymerisation rate (R_p) of St and AA. A plot of R_p versus AA concentration is presented in Fig. 2. Results confirmed that the rate of polymerisation linearly increased, with increasing AA content. The higher AA content in the system, the more oligoradicals formed, resulting in the larger amount of primary particles.

Based on Eq. 4, the rate of polymerisation (R_p) at any instant is given by the product of the concentration of active particles ($[P^{\cdot}]$) and propagation rate constant (k_p) [17] is expressed as:

$$R_p = k_p[M][P^{\cdot}], \qquad (4)$$

where [M] is the monomer concentration in the particles. It was attributed that the carboxylic acid monomer

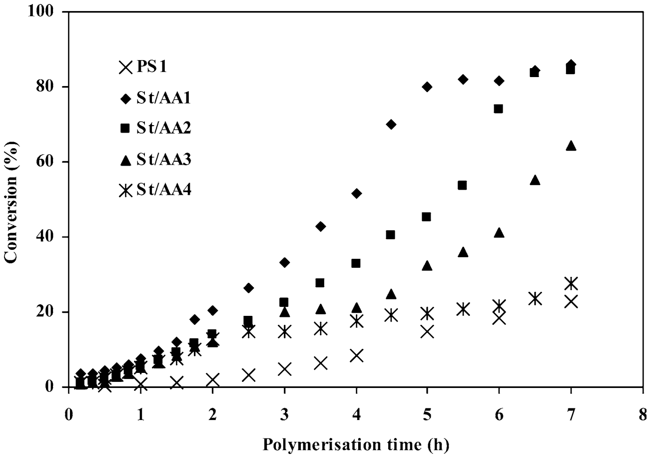

Fig. 1 Conversion-time curves of PS and St/AA latices

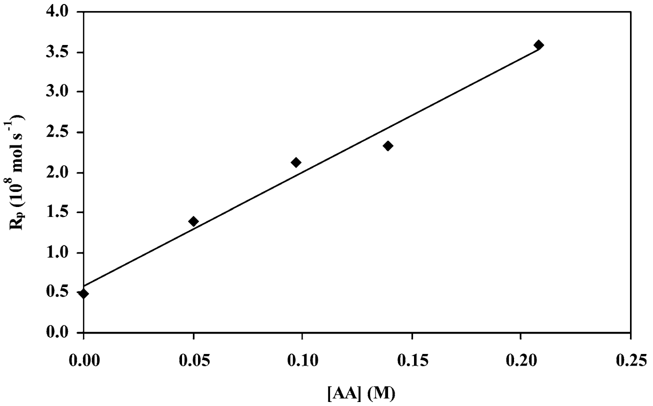

Fig. 2 Copolymerisation rate (R_p) versus AA concentration

causing an increased number of reaction loci and, consequently, increased rate of polymerisation. The relationship between R_p and particle number (N_p) has been derived as

$$R_p = k_p \frac{\bar{n} N_p}{N_A} [M], \tag{5}$$

where $\bar{n}$ is the average radical number in the particles and N_A is the Avogadro's number.

The hydrodynamic diameter of PS and St/AA latex particles, determined from the light scattering technique, as a function of AA concentrations are shown in Fig. 3.

The particle size was inversely proportional to the AA concentration. The size of St/AA latex particles was smaller than that of PS latex as generally observed in soap-free emulsion polymerisation of St with functional comonomer [6]. It was explained that the presence of higher amount of ionic functional monomer caused the greater number of formed primary particles. Due to the same amount of St in all formulations used, the quantity of St swollen in the larger number of primary particles was lower. With several highly reactive and water-soluble functional monomers, some authors reported an increased particle size coupled with a broadening of size distribution at relatively high functional monomer concentration [18,19]. It was described by the formation of high level of polyelectrolytes, which might cause bridging flocculation of growing particle [20–22]. However, this tendency was not observed in the AA concentration range investigated in this study.

In order to gain the additional insight in the mechanism of copolymerisation between St and AA, the values of hydrodynamic diameter were plotted as a function of conversion$^{1/3}$. If we assumed that polymer mass is equal to conversion (monomer-to-polymer) and the density (ρ) of PS is constant, the hydrodynamic diameter (D_h) can be related to the conversion via the following equation.

$$D_h \approx \left[\frac{1}{N_P}\right]^{1/3} \text{Conversion}^{1/3}, \tag{6}$$

where N_p is the particle number. Figure 4 shows the variation of hydrodynamic diameter versus conversion$^{1/3}$.

It was observed that while the hydrodynamic diameter depended linearly on conversion$^{1/3}$, N_p is almost constant during the polymerisation process. It could be concluded from the result that no secondary nucleation occurred when the polymerisation proceeded. In addition, it was confirmed that no particle coalescence took place during the polymerisation. The size of primary particle stabilised with efficient ionic surface charges growing due to the diffusion of residual monomer from monomer droplet and aqueous phase.

Morphological study

TEM provided the direct evidence of morphology of PS and St/AA microspheres and the micrographs are shown in Fig. 5.

From TEM micrographs, it was clearly seen that particles in all latices are spherical in shape. Polydispersity index (PDI) of St/AA latex particles was close to 1, reflecting the narrow size distribution of the elaborated latices. Table 2 presents the characteristics of the latices. The diameter of St/AA latex in the dried state ($\bar{D}_n$), from TEM, was slightly smaller than that obtained from the light scattering method due to the shrinkage of hydrophilic poly(acrylic acid) (PAA) layer on latex surface.

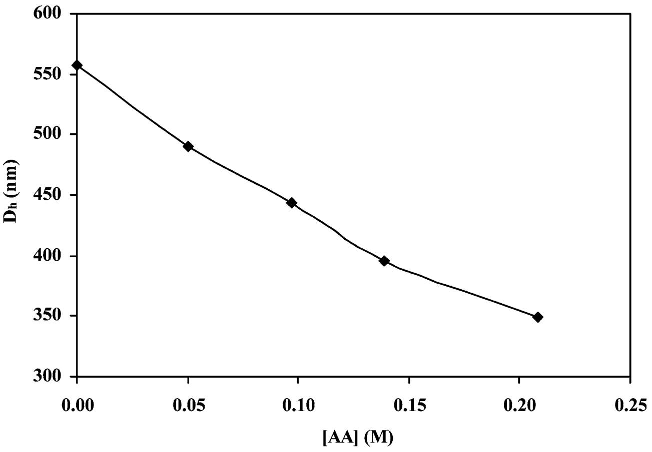

Fig. 3 Dependence of hydrodynamic diameter on AA concentrations used in the polymerisation recipe

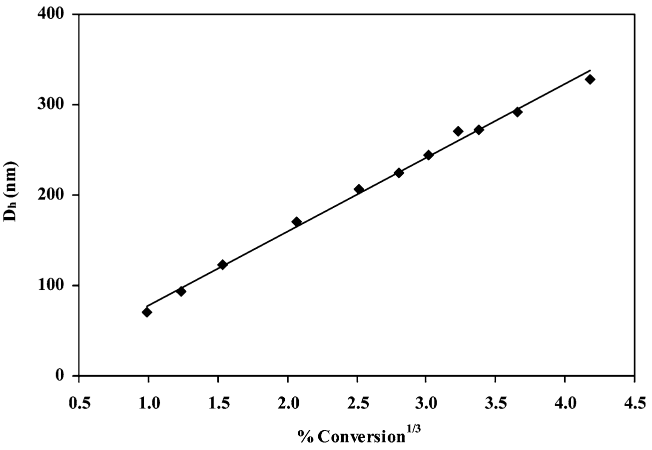

Fig. 4 Variation of hydrodynamic diameter of St/AA1 latex versus %conversion$^{1/3}$

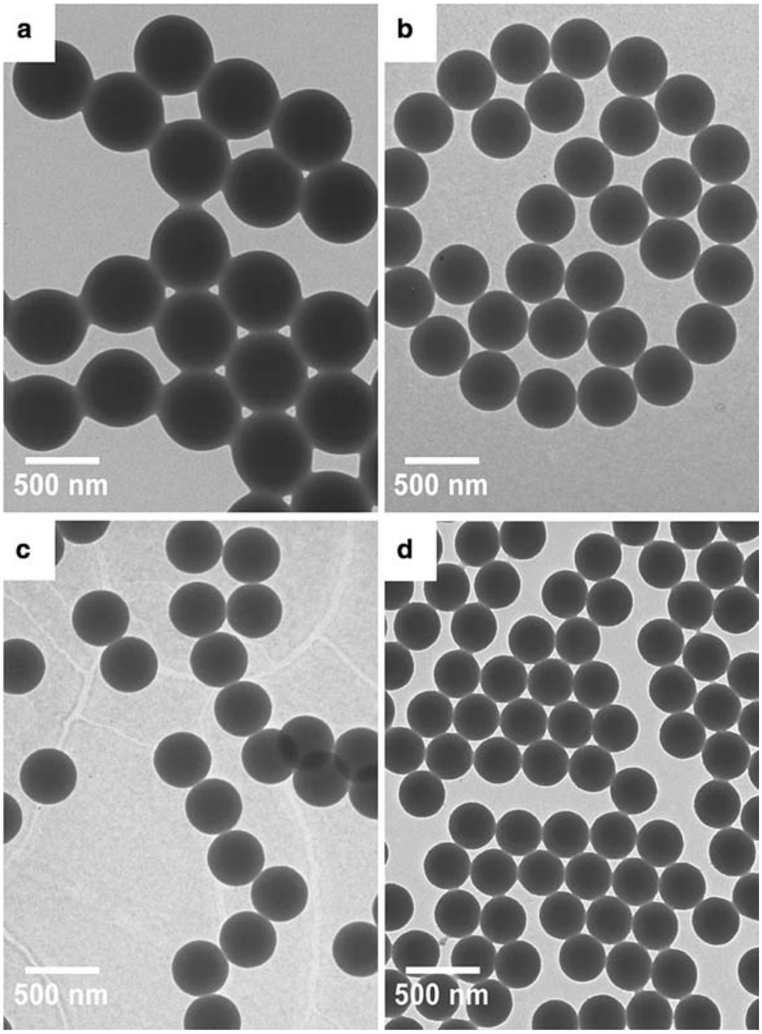

Fig. 5 TEM micrographs of PS and St/AA latex particles. **a** PS2 **b** St/AA3 **c** St/AA2 **d** St/AA1

Table 2 Hydrodynamic size ($\bar{D}_h$), number average diameter ($\bar{D}_n$), weight average diameter ($\bar{D}_w$), and polydispersity index (PDI) for PS and St/AA latices

Latex	$\bar{D}_h$ (nm)	SD[a]	$\bar{D}_n$ (nm)	$\bar{D}_w$(nm)	PDI
PS2	512	49	514	515	1.0014
St/AA1	349	21	335	336	1.0003
St/AA2	396	15	378	378	1.0008
St/AA3	411	33	403	403	1.0007
St/AA4	490	29	–	–	–

[a] Standard deviation

Colloid stability study

Turbidity-wavelength measurement, which is a sensitive method for detecting aggregation in dispersion, was used in this work. Flocculation is detected by a decrease in the magnitude of N_τ, i.e. the value of N_τ decreases suddenly when aggregation takes place. The effect of NaCl concentration on N_τ in which are observed the two domains—the stable and the unstable—are clearly presented in Fig. 6.

In the case of St/AA latices, N_τ was not significantly changed in broad range of NaCl concentrations until 1 M, whereas the drastical decrease of N_τ value was observed at approximately 0.1 M NaCl solution in the PS latex. Thus, the coagulation concentration (CC) of St/AA and PS latices were approximately 1 M and 0.1 M NaCl, respectively. In the vicinity of CC, the particles are less charged and, consequently, the colloidal stability is drastically reduced. The higher CC value of St/AA latex reflected, therefore, that the colloidal

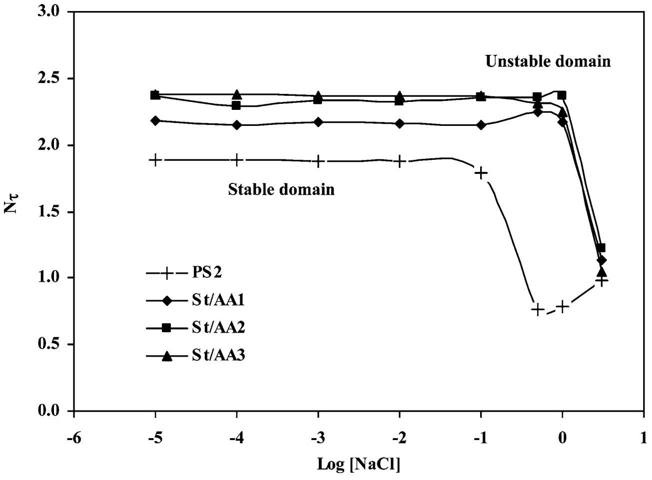

Fig. 6 N_τ as a function of NaCl concentration at 20°C

stability in electrolyte medium of the St/AA latices was higher than that of PS, possibly due to steric stabilisation of PAA.

Surface charge titration

The surface charge density, representing the amount of ionised groups existing on the latex surface, of purified St/AA copolymer latex particle was determined by conductometric back titration using 0.01 M HCl as the titrant. The surface charge density values are shown in Table 3.

Obviously, the charges on St/AA particles were induced by the APS initiator and carboxylic acid groups originated from AA. The surface charge density decreased with decreasing AA concentration, while the amount of initiator was kept constant. By taking into account of the cross-sectional area of each COOH group calculated by Huheey [23] which was equal to 9 Å^2, the St/AA1 particle could be considered as core-shell morphology carrying more than one COOH group monolayer. On the contrary, less than monolayer of carboxyl groups was presented on St/AA2 and St/AA3 particle surface. In this case, it seemed that some copolymers of St and AA tended to protrude out from the surface of PS core into aqueous phase giving the surface as a fuzzy aspect [24]. These results established that the surface morphology of St/AA particles could be controlled by changing the concentration of AA comonomer in the polymerisation recipe.

Table 3 Number of microequivalents of acid groups per gram ([COOH]) and surface charge density (σ) of PS and St/AA latices from conductometric back titration

Latex	[COOH] (μeq/g)	σ(μC/cm^2)	Surface area occupied by a surface carboxyl group (Å^2)
PS2	5 ± 2	4 ± 2	–
St/AA1	484 ± 16	271 ± 9	5.7
St/AA2	174 ± 7	116 ± 5	13.8
St/AA3	105 ± 1	73 ± 1	22.1

In addition, the surface area occupied by a surface of carboxyl group for each St/AA latex was much smaller than the molecular area of 48 Å^2 previously reported for sodium dodecyl sulphate (SDS) on the surface particle of PS latex [25]. Consequently, it could be concluded that the St/AA latices were sufficiently stabilised by the presence of carboxyl groups on particle surface.

Electrokinetic study

For electrokinetic study, electrophoretic mobility of latices was measured as a function of pH at low ionic strength (1 mM NaCl solution). The results obtained for all latices are shown in Fig. 7.

The values of electrophoretic mobility (μ_e) of the latices were negative in pH ranging from 3 to 8, which was derived from the strong acidic groups ($-SO_4^-$, p $K_A \approx 0.00$) and weakly acidic groups (-COOH, p $K_A \approx 4.75$) [26] originated from initiator and AA, if added, respectively. The drastical decrease of μ_e values when increasing pH until pH 5 (close to p K_A of –COOH) was not observed as formerly reported [27]. It might be due to: (1) the $[SO_4^-]/[COO^-]$ ratio on the particle surface and (2) the presence of water soluble layer PAA shell on the particle surface which affected the slipping plane position by inducing shifts away from the latex surface. It was reported that PS latex prepared by soap-free emulsion polymerisation with different buffer conditions exhibited the difference in surface charge density [28].

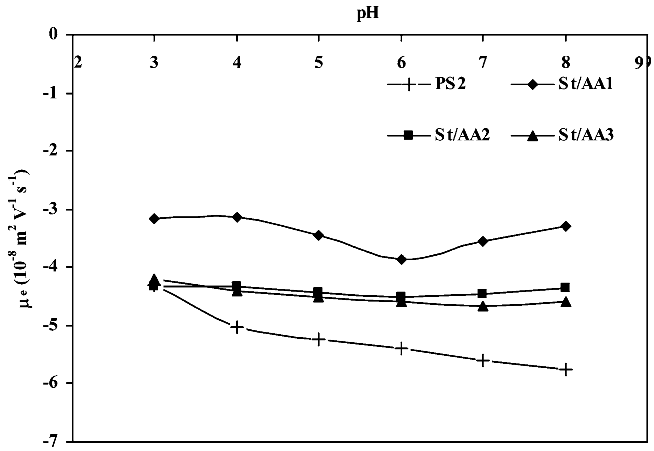

Fig. 7 Electrophoretic mobility as a function of pH for PS and St/AA latices

The presence of chain-end sulfate group would more or less screen the presence of carboxyl group [29].

To obtain further insight in the polymerisation mechanism, the electrophoretic mobility was measured as a function of polymerisation conversion. Figure 8 shows the plot of electrophoretic mobility versus conversion of St/AA1 latex.

It was observed that μ_e rapidly increased at low conversion (until ~5% conversion) and then gradually increased until 40% conversion before reaching constant value. This result implied that the particle formation or nucleation period was quickly completed within 5% conversion. It should be stated that the nucleation period normally varies in the range 2–15% conversion depending on the initiation rate and water solubility of monomer used [17]. The distribution of St monomer is almost in monomer droplet due to its poor water solubility, and some of St can be captured in the polymer particle, while AA functional monomer dissolved in aqueous phase. The polymerisation continued owing to the fact that monomer diffused from monomer droplet and aqueous phase to replace the consumed one leading to a small change in μ_e values until 40% conversion. At the end of polymerisation, μ_e was not significantly changed, since monomer droplets were no longer present.

In addition, it was possible to obtain direct information on the charge density of latex particle via electrophoretic mobility measurement. The surface charge density in the shear plane (σ_ς) can be estimated from the relationship between the surface potential (Ψ_o) and the surface charge density based on the Helmholtz and Gouy-Chapman equation for higher potential and spherical interface [30].

$$\sigma_\varsigma = \left(\frac{\varepsilon_o \varepsilon_r nkT}{Ze}\right)\left[2\sinh\left(\frac{Ze\psi_o}{2kT}\right) + \frac{4}{\kappa R}\tanh\left(\frac{Ze\psi_o}{4kT}\right)\right], \tag{7}$$

where ε_o is the vacuum permittivity, ϵ_r is the dielectric constant of bulk fluid, n is the electrolyte concentration expressed in ion/m^3, Z is the valency of the ion, T is the absolute temperature, k is the Boltzman's constant, e is the electron charge, κ is the inverse of the Debye length, and R is the particle radius. If κ is equal to 0.1 nm^{-1} for 1 mM NaCl solution [31], it could be assumed that the electrophoretic mobility (μ_e) related to surface charge density and particle size via the approximated equation, i.e., $\mu_e \approx \sigma_\varsigma[0.1R/0.1R + 1]$. The values of μ_e are then plotted versus $\left[\frac{0.1R}{0.1R+1}\right]$ as shown in Fig. 9. The linear relationship was obtained which indicated that the surface charge density at shear plane was constant during the polymerisation. It could be stated that the particle size and number of charge on surface increased as the polymerisation proceeded.

Conclusions

Monodispersed and spherical carboxylic containing latices were successfully prepared by batch soap-free emulsion copolymerisation of St and AA. The presence of small amount of AA concentration strongly affected emulsion copolymerisation rate, final particle size, colloidal stability and surface charge density. Due to the hydrophilic character of AA, the formation of primary particle and nucleation period were more rapid than those in the system having only St leading on one hand to the enhancement of the initial polymerisation rate and, on the other hand, the diminishing of the final

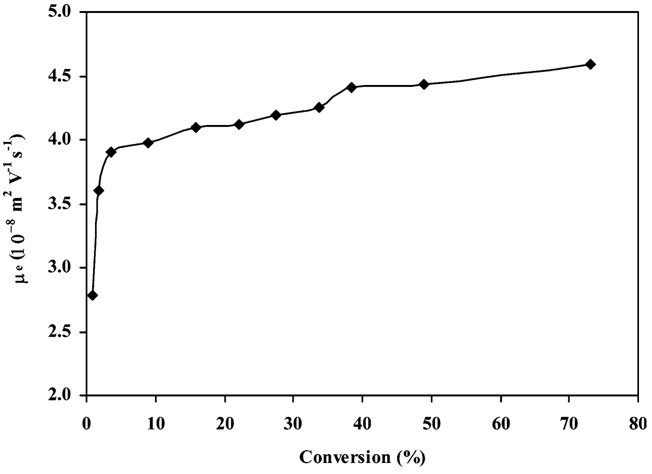

Fig. 8 Electrophoretic mobility (absolute value) versus conversion of St/AA1 latex

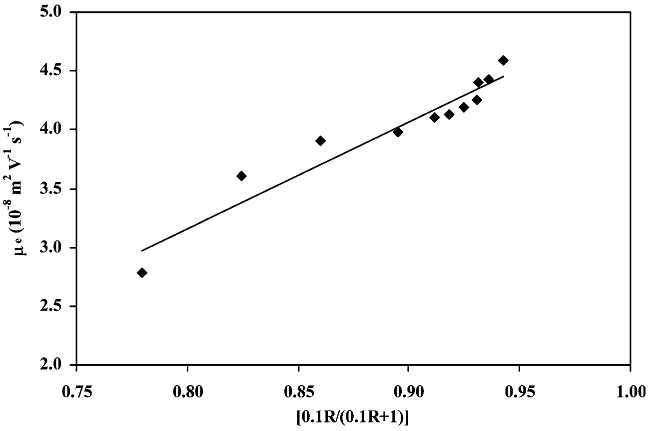

Fig. 9 Electrophoretic mobility (absolute value) versus [0.1R/(0.1R + 1)]

particle size. The constant particle number during the polymerisation reaction and the low value of PDI confirmed the shorter nucleation period compared to the particle growth interval as well as the absence of secondary nucleation and particle coalescence. After nucleation period (with about 5% conversion), the primary particle, stabilised with sufficient ionic groups originated from initiator and AA, grew and became latex particle with using the rest of monomer in monomer droplet and aqueous phase. Colloidal stability and surface charge density of the prepared particles were found to increase with increasing AA concentration. The presence of PAA chain around the St/AA particles provided latex stability also via electrosteric stabilisation. The preparation of PS latex using charge monomer in the polymerisation system led to the formation of polymer chains mainly located at the particle surface. This was confirmed from the large values of surface charge density of St/AA latices obtained from conductometric titration. It is interesting to observe the constancy of the surface charge density of the particles during the polymerisation process, which explains the increase of the number of charge as the particles surface increases.

Such well-defined St/AA latex particles will be applied as a solid support for malaria protein immobilisation. The immunolatex prepared will therefore be used in immunological study and diagnostic test.

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References

1. Kawaguchi H (1993) In: Tsuruta T, Hayashi T, Kataoka K, Ishihara K, Kimura Y (eds) Biomedical applications of polymeric materials. CRC press, Boca Raton, FL, pp 299–324
2. Lee CF, Young TH, Huang YH, Chiu WY (2000) Polymer 41:8565
3. Elaissari A, Rodrigue M, Meunier F, Herve C (2001) J Magn Magn Mater 225:127
4. Ortega-Vinuesa JL, Bastos-Gonzalez D (2001) J Biomater Sci Polymer Edn 12(4):379
5. Molina-Bolivar JA, Galisteo-Gonzalez F (2004) In: Elaissari A (ed) Colloidal biomolecules, biomaterials, and biomedical applications. Marcel Dekker, Inc., New York, pp 53–101
6. Ganachaud F, Sauzedde F, Elaissari A, Pichot C (1997) J Appl Polym Sci 65:2315
7. Lui Z, Xiao H (2000) Polymer 41:7023
8. Shoaf GL, Poehlein GW (1991) J Appl Polym Sci 42:1213
9. Wang ST, Poehlein GW (1993) J Appl Polym Sci 50:2173
10. Slawinski M, Meuldijk J, Van Herk AM, German AL (2000) J Appl Polym Sci 78:875
11. Wang PH, Pan CY (2001) Colloid Polym Sci 279(1):98
12. Wang PH, Pan CY (2002) Colloid Polym Sci 280(2): 152
13. Long JA, Osmond DWJ, Vincent B (1973) J Colloid Interface Sci 42(3):545
14. Fitch RM (1997) Polymer colloids: a comprehensive introduction, Academic Press, New York, pp 8
15. Tauer K, Kuhn I (1995) Macromolecules 28:2236
16. Kuhn I, Tauer K (1995) Macromolecules 28:8122
17. Odian G (1991) Principle of polymerization, 3rd edn. John Wiley, New York, pp 335–348
18. Schild RL, El-Aasser MS, Poehlein GW, Vanderhoff JW (1978) In: Becher P, Yudenfreund MN (eds) Emulsion latexes and dispersions, Marcel Dekker, New York, pp 99–128
19. Liu LJ, Kriegger IM (1981) J Polym Sci Polym Chem Ed 19:3031
20. Delair T, Pichot C, Mandrand B (1994) Colloid Polym Sci 272(1):72
21. Delair T, Marguet V, Pichot C, Mandrand B (1994) Colloid Polym Sci 272(8):962
22. Feeney PJ, Napper DH, Gilbert RG (1984) Macromolecules 17: 2520
23. Huheey JE (1978) Inorganic chemistry. Harper & Row, New York, pp 846
24. Lock MR (1989) Preparation and characterization of acrylate latexes containing dicarboxylic acid comonomers, Ph.D. Thesis, Lehigh University
25. Vanderhoff JW, van den Hul HJ (1973) J Macromol Sci Chem 7(3):677
26. Zwetsloot JPH, Leyte JC (1994) J Colloid Interface Sci 163:362
27. Bastos-Gonzalez D, Hidalgo-Alvarez R, De Las Nieves FJ (1996) J Colloid Interface Sci 177(2):372
28. Furusawa K (1982) Bull Chem Soc Jpn 55:48
29. Santos AM, Elaissari A, Martinho JMG, Pichot C (2004) Colloid Polym Sci 282:661
30. Hunter RJ (1981) Zeta potential in colloid science principles and applications. Academic, London, pp. 335
31. Hiemenz PC, Rajagopalan R (1997) Principles of colloid and surface chemistry, 3rd edn. Marcel Dekker, New York