ROLE OF ACETONE IN THE FORMATION OF HIGHLY DISPERSED CATIONIC POLYSTYRENE NANOPARTICLES

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Dedicated to Prof. Leon Gradoń on the occasion of his 70th birthday

A modified emulsion polymerisation synthesis route for preparing highly dispersed cationic polystyrene (PS) nanoparticles is reported. The combined use of 2,2′-azobis[2-(2-imidazolin-2-yl)propane] di-hydrochloride (VA-044) as the initiator and acetone/water as the solvent medium afforded successful synthesis of cationic PS particles as small as 31 nm in diameter. A formation mechanism for the preparation of PS nanoparticles was proposed, whereby the occurrence of rapid acetone diffusion caused spontaneous rupture of emulsion droplets into smaller droplets. Additionally, acetone helped to reduce the surface tension and increase the solubility of styrene, thus inhibiting aggregation and coagulation among the particles. In contrast, VA-044 initiator could effectively regulate the stability of the PS nanoparticles including both the surface charge and size. Other reaction parameters i.e. VA-044 concentration and reaction time were examined to establish the optimum polymerisation conditions.

Keywords: diffusion, emulsion, nanoparticle, polystyrene, solubility

1. INTRODUCTION

Polystyrene (PS) nanoparticles, both anionic and cationic, have attracted much interest owing to their excellent properties such as low density, high hydrophobicity, large specific surface area, good mechanical and chemical stability (Ernawati et al., 2016; Liu et al., 2012; Nandiyanto et al., 2008; Nandiyanto et al., 2012). They have many potential applications as templates, calibration standards, film coatings, ink toners, or polymer fillers, or in chromatographic separation and drug delivery (Chou et al., 2014; Li et al., 2011; Shibuya et al., 2014; Tadros, 2013). The size and distribution of PS particle are considered to be the most important parameters that succeeded in these applications (Abadi et al., 2015; Camli et al., 2010). Hence, how to synthesize and control highly dispersed PS particles with the size around 50 nm or less becomes a critical issue.

Numerous polymerisation methods, including dispersion, suspension, miniemulsion, microemulsion, and living radical polymerisation, have been used for preparing PS nanoparticles (Liu et al., 2014; Rao and Geckeler, 2011; Sood, 2004). Among these methods, the emulsion method is widely used because of its rapid polymerisation rate, high conversion, and environmental friendly and readily scalable characteristics (Chou and Chiu, 2013; Liu et al., 2014). In an emulsion system, to control the stability and to reduce the size of PS particle, high amount of surfactant (up to 20 wt%) and/or emulsifier are often required (Ishii et al., 2014; Maiti and Mc Grother, 2004). It is because of the adsorbed surfactant

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molecules at the oil-water (O/W) interface which can effectively reduce the O/W interfacial tension, further against the droplet coalescence and increase the emulsion stability. However, the use of high level amount of surfactant is often not acceptable as it leaves uncommon residues in products and contaminants in the reaction medium which have to be removed. Moreover, particle coagulation also readily occurs during the emulsion process and becomes the major drawback of this method.

The addition of co-solvents such as alcohols, acetone and some organic solvents into emulsion system also played an important role in controlling formation and size of PS particle (Kim et al., 2010). For instance, the synthesis of anionic PS nanoparticles using potassium persulfate as the initiator and acetone/water as the mixture solvent medium was reported for the first time by Okubo and co-workers (Okubo et al., 1981). Acetone was used to increase the solubility of styrene in the aqueous-phase system. This approach could effectively prevent particle coagulation and generate small PS particles. Subsequent research has enabled the successful preparation of smaller anionic PS particles (50 nm) via a microwave-assisted emulsion polymerisation process (Ngai and Wu, 2005). Additionally, a detailed study of the nucleation and growth mechanism of anionic PS particles has been reported (Li et al., 2012). Besides anionic PS nanoparticles, cationic PS particles are as important, particularly as a template material in the design of nanostructures (Balgis et al., 2012; Balgis et al., 2014; Ogi et al., 2014). However, to our knowledge, the synthesis of cationic PS particles with controllable size of less than 50 nm is rarely reported.

The present study reports an improved synthesis route for the preparation of highly dispersed cationic PS nanoparticles as small as 31 nm in diameter by the combined use of acetone/water as the mixture solvent medium and 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride as the cationic initiator. Acetone was selected as a co-solvent because of its rapid diffusion characteristic and ability to promote the formation of small droplets in an emulsion system. 2,2′-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride was used to control both the surface charge and size of the particles.

2. EXPERIMENTAL

2.1. Materials

Monomer styrene (99%, Kanto Chemical Co., Inc., Japan) was purified using sodium hydroxide (NaOH) prior to use. Cationic initiator 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044; 99%) was obtained from Wako Pure Chemical Industries, Ltd. (Japan). Acetone (99%, Kanto Chemical Co., Inc.) and ultra-pure water were used as a mixture solvent medium without further purification.

2.2. Preparation of cationic PS particles

The reaction set-up consisted of a 300-mL three-neck round-bottom flask equipped with a stirrer (the rotation speed was adjusted to 700 rpm), a reflux condenser, a heating jacket to control the temperature, a temperature controller, and a nitrogen (N_2) gas source. The polymerisation process was performed as follows. Ultra-pure water and acetone at known compositions were introduced into the reactor vessel and heated at 60°C under N_2 atmosphere for 30 min. After the reaction temperature and oxygen-free conditions were attained, styrene and VA-044 were added simultaneously. The acetone-to-water mass ratio and VA-044 concentration were varied from 0 to 2.33 and 0.0048 to 0.0193 mol L^{-1}, respectively. The reaction time was varied from 2 to 14 h. Other parameters i.e., styrene concentration and reaction temperature were maintained at 9.24 mol L^{-1} and 60°C, respectively. The polymerisation conditions are given in Table 1. After polymerisation, acetone was removed by heating at 60 °C for 3 h. The samples were then dried in a vacuum oven at 60 °C overnight prior to calculating total solid content (TSC).

2.3. Characterisation

The morphology of the prepared particles was observed by scanning electron microscopy (SEM; Hitachi S-5000, Japan; operating at 20 kV) and transmission electron microscopy (TEM; JEM-3000F, JEOL, Japan; operating at 300 kV). To obtain the average diameter and size distribution of the particles, more than 200 particles ($\Sigma n_i = 200$) were statistically examined. The hydrodynamic diameter (D_h) distribution of the PS particles was determined using dynamic light scattering (DLS). For the measurement, colloidal PS particle suspensions were diluted with deionised water and sonicated for 1 h at room temperature. The zeta potential (ζ) of the particles was measured on a Zetasizer (Malvern Instruments, Nano ZS, UK). The surface tension of PS particles in colloidal solution was measured using a surface tensiometer (KF14001139, Japan; operating at 100 V). Hence, for the measurement of surface tension, the use of VA-044 initiator was negligible.

3. RESULTS AND DISCUSSION

3.1. Influence of acetone-to-water mass ratio on PS particle size

The effect of the acetone-to-water mass ratio on the surface charge of the PS nanoparticles was examined by measuring the zeta potential of the PS samples. Positively charged PS particles, with zeta potentials of approximately +43 to +47 mV, were obtained for the PS samples prepared with varying acetone-to-water mass ratios as given in Table 1. No significant changes in the zeta potential values of the PS samples were obtained with increasing acetone-to-water mass ratios.

Table 1. Polymerisation conditions employed for the synthesis of the cationic polystyrene particles

Sample	C_{VA-044}[a] (mol L^{-1})	Acetone/ water mass ratio	VA-044/ styrene mass ratio (g/g)	Reaction time (h)	R_h (DLS) (nm)	D_p (SEM) (nm)	Zeta potential (ζ) (mV)	TSC [b] (wt.%)
CPS1	0.0064	0	0.055	8	330	272	+43	7.4
CPS2	0.0064	0.28	0.055	8	192	163	+45	6.4
CPS3	0.0064	0.67	0.055	8	101	88	+46	4.1
CPS4	0.0064	1.04	0.055	8	47	35	+47	3.6
CPS5	0.0064	1.50	0.055	8	44	31	+48	2.4
CPS6	0.0064	1.86	0.055	8	-	coagulated	+46	-
CPS7	0.0064	2.33	0.055	8	-	coagulated	+47	-
CPS8	0.0064	> 2.33	0.055	8	-	no particle	+47	-
CPS9	0.0064	1.04	0.055	2	41	32	+45	0.6
CPS10	0.0064	1.04	0.055	4	43	33	+46	1.5
CPS11	0.0064	1.04	0.055	6	44	34	+48	3.2
CPS12	0.0064	1.04	0.055	10	46	42	+47	3.7
CPS13	0.0064	1.04	0.055	12	48	45	+48	3.8
CPS14	0.0064	1.04	0.055	14	55	48	+49	3.9
CPS15	0.0048	1.50	0.041	8	coagulated	coagulated	+41	-
CPS16	0.0091	1.50	0.077	8	46	33	+46	2.2
CPS17	0.0128	1.50	0.112	8	47	35	+48	2.3
CPS18	0.0193	1.50	0.167	8	48	37	+49	2.4

The concentration of styrene was kept constant at 9.24 mol L^{-1}.
[a] Initial concentration of VA-044 initiator in mixture solution system.
[b] TSC was determined using a gravimetric method and calculated as follows

Additionally, the effect of varying the acetone-to-water mass ratio from 0 to 2.33 on the average diameter of the PS particles was examined. (Other parameters namely, the concentration of styrene and VA-044 initiator, reaction time, and reaction temperature were kept constant.). The results are shown in Fig. 1 and summarised in Table 1.
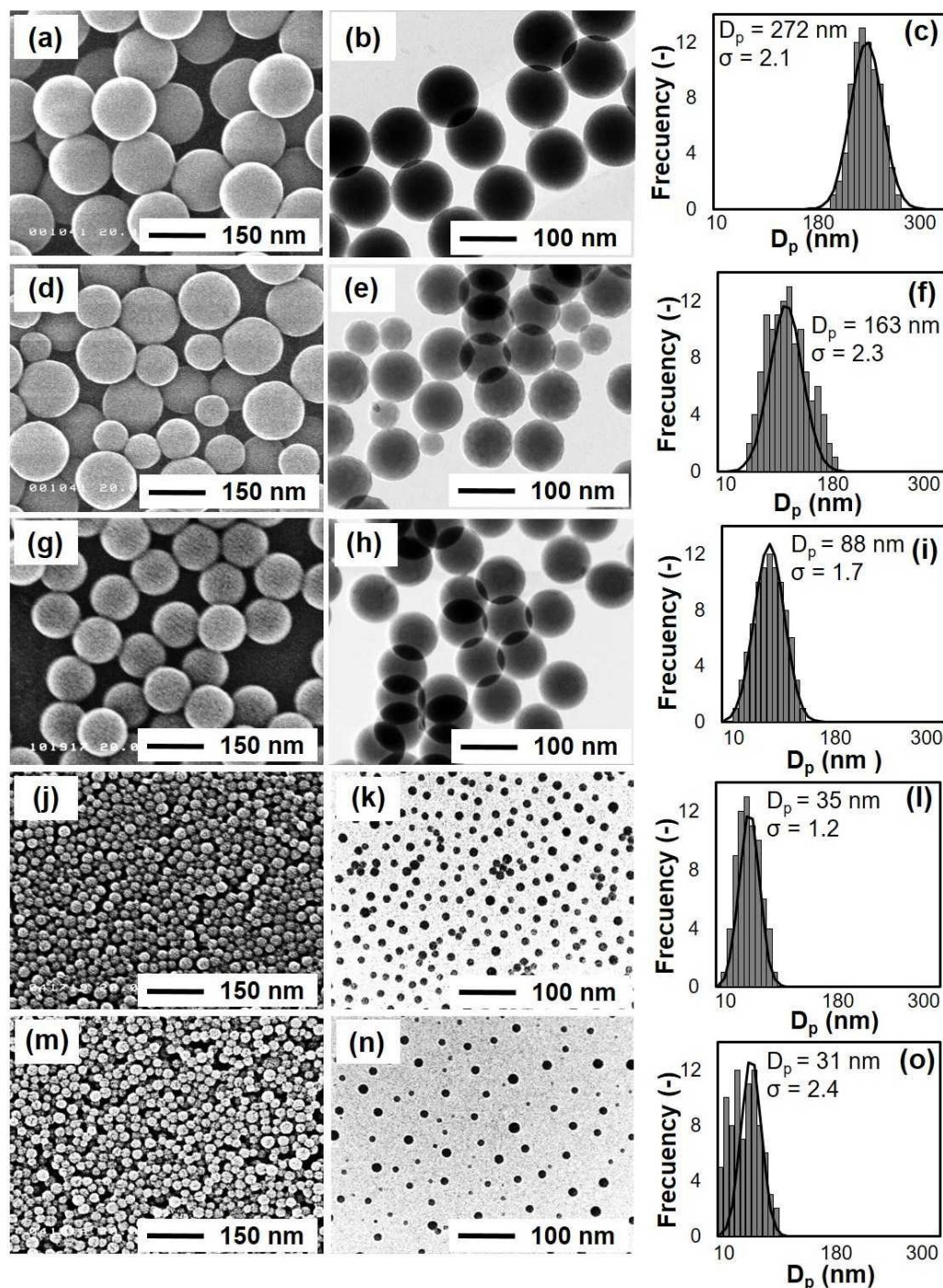

Fig. 1. SEM and TEM images, and size distribution profiles of the PS particles prepared at different acetone-to-water mass ratios of (a, b, c) 0, (d, e, f) 0.28, (g, h, i) 0.67, (j, k, l) 1.04, and (m, n, o) 1.50. Other parameters were kept constant: VA-044 initiator-to-styrene mass ratio, 0.055; reaction temperature, 60 °C; and reaction time, 8 h

$$S(wt\%) = \left(\frac{W_1}{W_2} \right) \tag{1}$$

where W_1 and W_2 are the weights of the dried and wet PS samples, respectively.

Large cationic PS particles of ~272 nm were obtained in the absence of acetone (Fig. 1(a)). The particle size could be significantly reduced to 31 nm when the acetone-to-water mass ratio was increased to 1.50. It is well known that high-polarity solvents, such as acetone, can form small droplets owing to rapid diffusion of the solvent (Ganachaud and Katz, 2005; Horn and Rieger, 2001; Legrand et al., 2007). The emulsion droplets formed upon addition of the styrene monomer to the acetone/water mixture solvent medium. Acetone quickly diffused and spread into the styrene monomer, subsequently leading to rupture of styrene into small droplets. By assuming that one PS particle is formed in each emulsion droplet, the particles shrink after evaporation of acetone, resulting in the formation of PS nanoparticles (Gradon et al., 2004). Thus, a good correlation between the initial droplet size and final size of the PS particles can be expected. According to this concept, the role of acetone on the formation of the cationic PS nanoparticle is illustrated in Fig. 2.
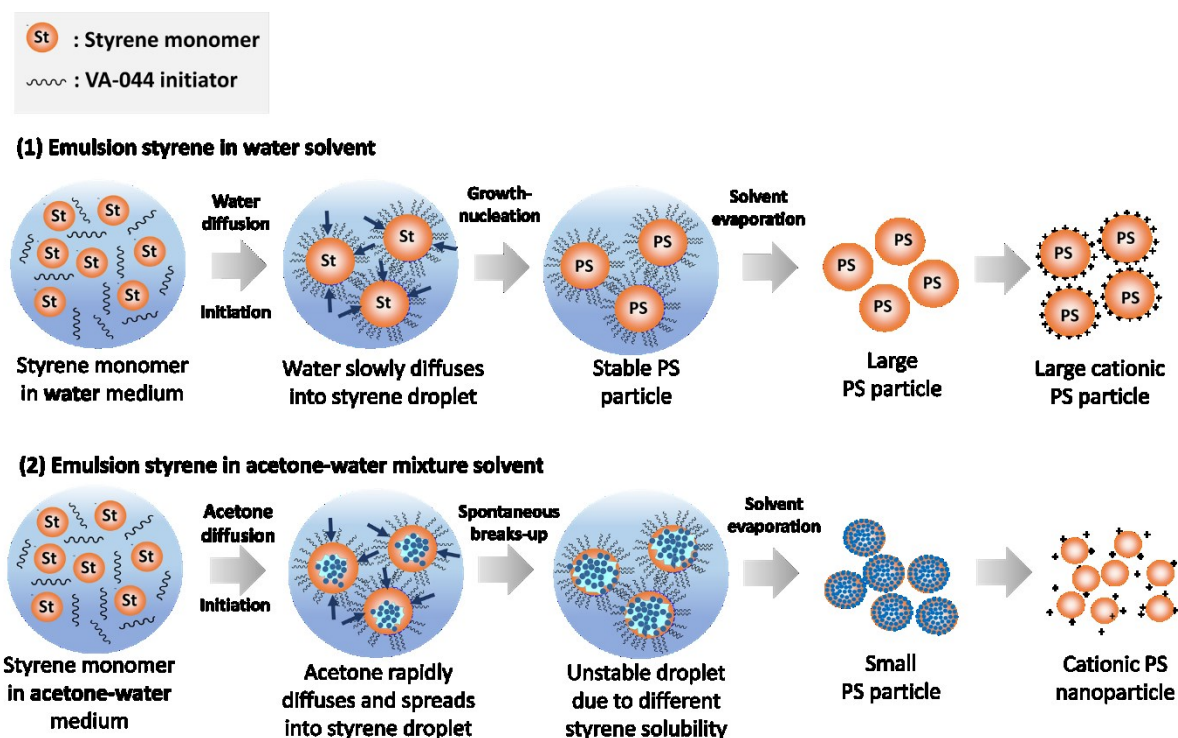

Fig. 2. Schematic of the formation of the cationic PS nanoparticles influenced by differences in the diffusion rate of acetone in the emulsion system

The solvent diffusion phenomenon, which causes spontaneous rupture of droplets, depends on the mass ratio of acetone to water. In the presence of water medium only, droplet rupture is slower owing to the slower diffusion rate of water (when compared with that of acetone), thereby resulting in the formation of large droplets. In contrast, when acetone is added to the emulsion system, emulsion droplets can readily break into small droplets owing to rapid diffusion of acetone.

Based on the proposed mechanism in Fig. 2, rapid diffusion of acetone, which promotes the formation of small cationic PS particles, was successfully attained when the mass ratio of acetone to water was 1.50 (Fig. 1(m, n, o)). In contrast, when the mass ratio of acetone to water was greater than 1.50, particle coagulation occurred (Fig. A.1(a, b), *APPENDICES*); the results are summarised in Table 1. Particle coagulation, observed at acetone-to-water mass ratios of 1.86 and 2.33, occurred because the equilibrium solubility of styrene was surpassed. Furthermore, the increase in the diffusion of acetone, while the amount of styrene monomer was constant, likely led to increased particle collision events and gelling effects. Further increases in the acetone-to-water mass ratios to above 2.33 did not generate any PS nanoparticles. Styrene monomers tend to dissolve in acetone rather than in aqueous phase, thereby accelerating the diffusion process. Consequently, the formation of particle nuclei becomes difficult

because of the imbalance in the hydrophobic and hydrophilic properties of the different solvents involved in the system.

As noted, the droplet size was mainly influenced by the acetone/water composition, diffusion and shrinkage processes. The size of PS particles could be adjusted by controlling the mass ratio of the acetone/water mixture solvent. With increasing acetone contents, the diffusion of acetone becomes rapid and the extent of shrinkage of the particle becomes greater owing to the evaporation of more acetone molecules. Both processes synergistically reduce the diameter of PS particles.

In the present system, the rapid diffusion of acetone has important roles in instigating spontaneous droplet break-up and preventing particle re-coalescence, thereby generating PS nanoparticles. However, the balanced mass ratio between acetone and water should be properly maintained; excessive amounts of acetone will result in increased supersaturation of styrene, thus impeding the subsequent growth and nucleation of emulsion droplets, consequently impeding the formation of PS nanoparticles.

Moreover, as previously reported, the effect of interfacial phenomena during diffusion contributes to the formation of nanoparticles (Natu et al., 2015). In this work, a similar trend was observed as represented by the effect of increasing acetone-to-water mass ratios on the solubility of styrene and the reduction of surface tension (Figs. 3 and 4).

Figure 3 shows that a high acetone content reduced the surface tension of the emulsion system, consequently inducing a reduction in the particle size. (The surface tension of acetone is lower than that of water). Specifically, when the acetone-to-water mass ratio was 1.50, a low interfacial tension of 32.73 N m^{-1} was attained. As the interfacial tension of the aqueous phase was decreased further by increasing the content of acetone, the affinity and/or electrostatic force between the initiator and the PS particle surface was not as high as the affinity among the initiator molecules. Consequently, the initiator molecules were loosely packed on the PS particle surface, and the degree of particle dispersion become high owing to the enhanced solubility of styrene, thereby promoting the formation of PS nanoparticles.
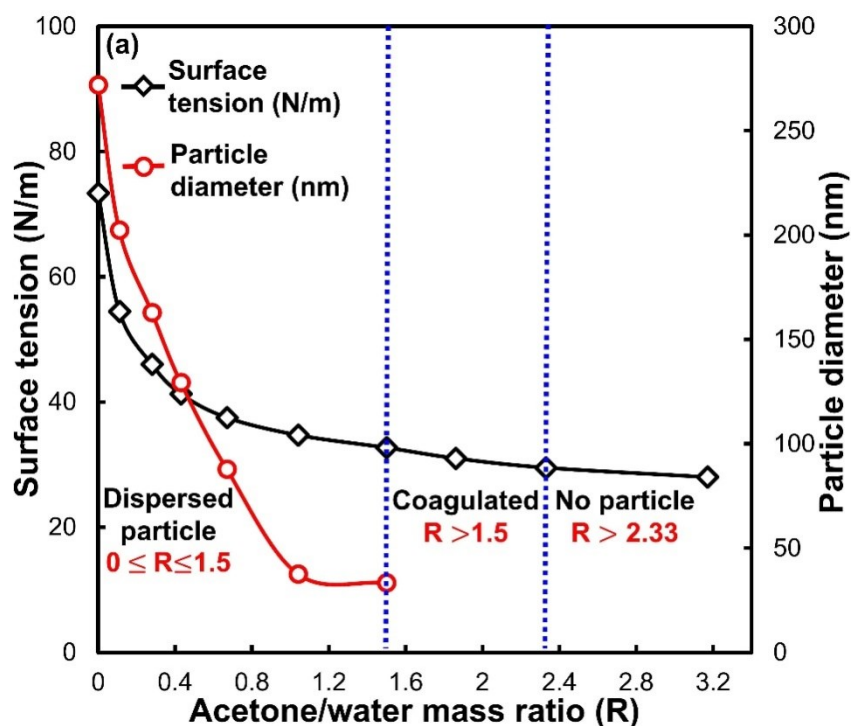

Fig. 3. Influence of the acetone/water composition on the average diameter of the PS particles and surface tension of the emulsion system

Figure 4 shows the relationship between the acetone/water composition and the surface tension and the solubility parameter of styrene in the mixture solvent system, which was evaluated by using the model established by Beerbower et al. (1971):

$$\sum \delta^2 = \delta_d^2 + 0.632\delta_p^2 + 0.632\delta_h^2 = 13.9\left(\frac{1}{V_m}\right)^{1/3}\gamma_L \text{ (for non-alcohols)} \tag{2}$$

The experimental data were then linearly fitted using the model established by Koenhen and Smolders (1975):

$$\sum \delta^2 = \delta_d^2 + \delta_p^2 = 13.5\left(\frac{1}{V_m}\right)^{1/3}\gamma_L \text{ (for all substances)} \tag{3}$$
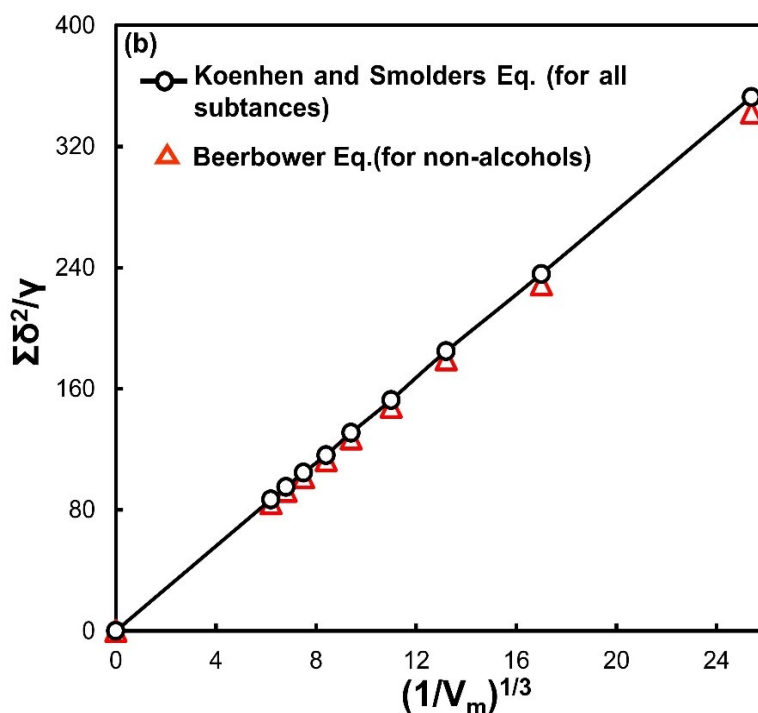

Fig. 4. Correlation between the acetone-water composition to the surface tension and the solubility parameter of styrene in the mixture solvent system calculated using the Beerbower model (1971) and fitted using the Koenhen-Smolders equation model (1975)

As deduced from these calculations, increasing the acetone-to-water mass ratio increased the solubility of styrene and reduced the interfacial tension of the solution system simultaneously. Furthermore, it enabled the formation of a homogenous mixture emulsion system and an increased number of particle nuclei, while preventing aggregation and coagulation among the particles, consequently leading to the formation of small PS particles.

3.2. Influence of VA-044 initiator concentration on PS particles size and zeta potential

The effect of VA-044 concentration on the average size and zeta potential of the prepared PS particles was evaluated. The polymerisation process was performed at varying VA-044 concentrations from 0.0048 to 0.0193 mol L^{-1}, while other parameters i.e., styrene concentration, acetone-to-water mass ratio, reaction time, and reaction temperature were kept constant. The results are given in Fig. 5 and summarised in Table 1.

As observed from the SEM and TEM images in Fig. 5, the VA-044 concentration had a slight effect on the particle size. The size of PS particles increased slightly from 33 from 37 nm with increasing VA-044 concentrations from 0.0091 to 0.0193 mol L^{-1}. As reported, the formation of considerably larger PS particles is expected by increasing the VA-044 concentration (Lee et al., 2010; Nandiyanto et al., 2014). However, the trend obtained herein differed from that previously reported using excessively high VA-044 concentrations and did not have a significant effect on the size of the particles; only a small difference in the particle size was observed. This result indicated that when a high VA-044 concentration was used, both the consumption and initiation rates of the styrene monomers increased simultaneously.
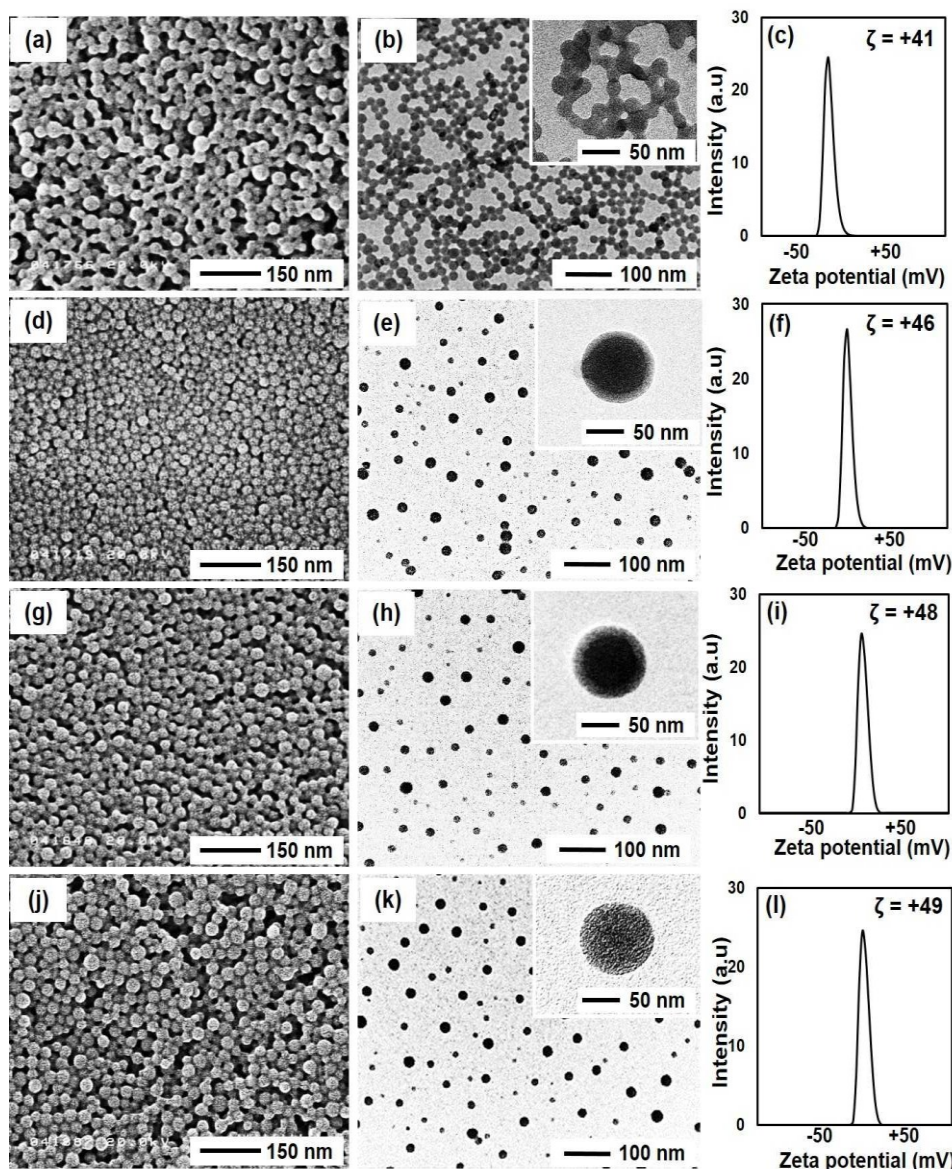

Fig. 5. SEM and TEM images, and zeta potential distribution (ζ) of the PS particles prepared at various VA-044 concentrations of (a, b, c) 0.0048, (d, e, f) 0.0091, (g, h, i) 0.0129, and (j, k, l) 0.0193 mol L^{-1}. Other parameters were kept constant: acetone-to-water mass ratio, 1.50; styrene, 9.24 mol L^{-1}; reaction temperature, 60 °C; and reaction time, 8 h

As the amount of styrene monomers was constant, the number of styrene units that could be attacked by the initiator was limited by the solubility of the monomer itself. This promoted the uncontrolled formation of free-radical initiators, thereby generating particle nuclei. In contrast, using excessively low VA-044 concentrations did not impact on the formation of PS particles as shown in Fig. 5(a). This is due to the low initiation and consumption rates of the styrene monomers in the emulsion system.

Likewise, the zeta potential of PS particles increased slightly from +41 to +50 mV with increasing VA-044 concentrations. This result implied that the presence of VA-044 initiator stabilised the emulsion system by a combined electrostatic and attractive force mechanism. To investigate the effect of increasing VA-044 concentrations on the stability of PS particles, D_h of PS particles in aqueous medium was evaluated as shown in Fig. 6.

Figure 6(a) shows that the D_h of cationic PS nanoparticles, as measured by DLS, was ~50 nm. The diameter of the particles, as measured by SEM, was 30 nm. The smaller size determined by SEM was related to the shrinkage of the particles upon drying for the measurement.

The principle of DLS for D_h particle measurement depends on the measuring of fluctuation intensity caused by interference of laser light that is scattered by diffusing particles. The evolution time of these fluctuations depends on the particle movement caused by Brownian motion, as well as the size of particle (Hirschle et al.,2016). Hence, it is possible to observe the correlation between the force at distance, $G(\text{г})$, of colloidal PS particles and lag time, (г).

Force at distance is also called as the first-order autocorrelation function $G(\text{г})$. This parameter describes temporal aggregated formation and/or coagulation of particles in a particular orientation within scattering light. At short time, the system is nearly stationary and the value of the correlation function is approximately equal to unity (1). Due to the random nature (i.e., Brownian motion effect), at longer time, the force appeared in the system, meaning that the system with the initial state approaches zero. On the other hand, lag time (г) describes the required time to reach a steady-state of particle size distribution (PSD) which is determined as a function of the relative rates of coagulation (Holthoff et al., 1996). Herein, the intensity of $G(\text{г})$ represents the degree of interaction between interfacial PS particles in the colloidal system that is controlled by regulating the VA-044 concentration. As observed in Fig. 6(b), at short lag times (<50 µs), the $G(\text{г})$ intensity changed slightly with increasing VA-044 concentrations from 0.0048 to 0.0193 mol L^{-1} (inset of Fig. 6(b)). This result revealed that by using VA-044 initiator, the nucleation and growth rates of particles could be greatly suppressed, thereby affording control over the formation of smaller PS particles without any coagulation. This result agreed with the results of previous reports (Ito et al., 2002; Shibuya et al., 2014). The authors reported high electron density and strong hydration capabilities of VA-044 initiator that resulted in weak adsorption between particle interfaces. Thus, VA-044 initiator has potential in preventing the formation of large particles through coagulation.

3.3. Influence of reaction time on the yield and PS particles size

The effect of reaction time on the size of PS particles was evaluated, and the results are shown in Fig. 7.

Figure 7 shows that the size of PS particles increased slightly from 32 to 48 nm when the reaction time increased from 2 to 14 h. The PS particles grew continuously during the early stages of the reaction (2–8 h), after which the growth rate became steady. These results revealed that as the reaction time increased, the monomer concentration in the emulsion system decreased continually as it was converted into an oligomer and a polymer. The growth of PS particles decreased slowly, and then stopped. Using a short reaction time of 2 h produced small PS particles of ~32 nm in size. PS nanoparticles with controllable sizes of <50 nm were also obtained when the reaction time was increased from 8 to 14 h (Table 1). This result shows that the reaction time is important for controlling the size of PS particles. The effect of the reaction time on D_h of PS particles was also evaluated by DLS, and the results are shown in Fig. S2. Based on the DLS results, the size of PS particles could be controlled to less than 60 nm even under prolonged polymerization ($t = 14$ h).
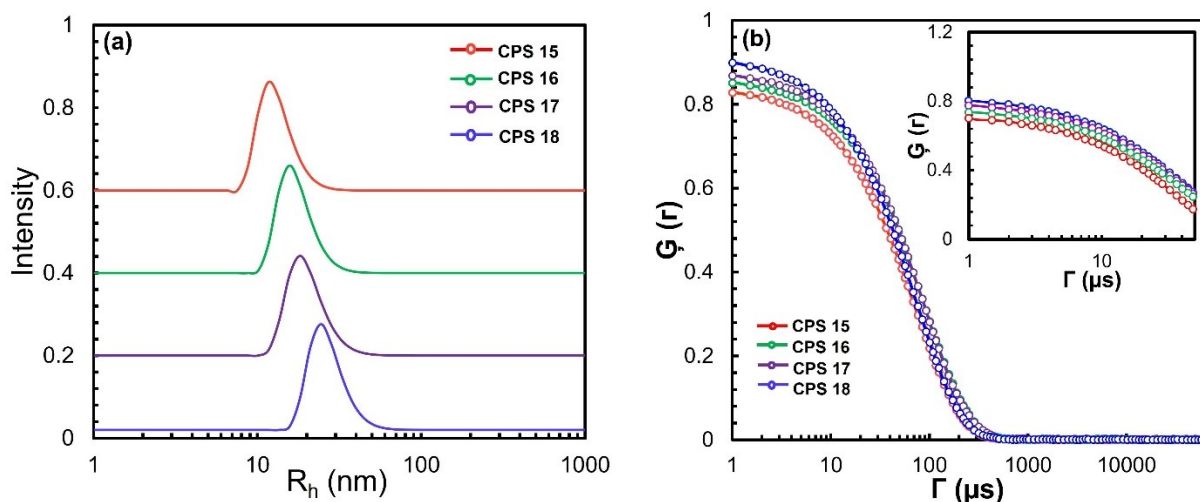
Fig. 6. (a) Hydrodynamic diameter (R_h) distributions of the colloidal PS particles measured by DLS. (b) Force at distance, $G(\Gamma)$, of the colloidal PS particles as a function of lag time, (Γ). The inset shows an enlarged view at the shorter lag-time intervals. The synthesis condition of representative PS sample was summarised in Table 1
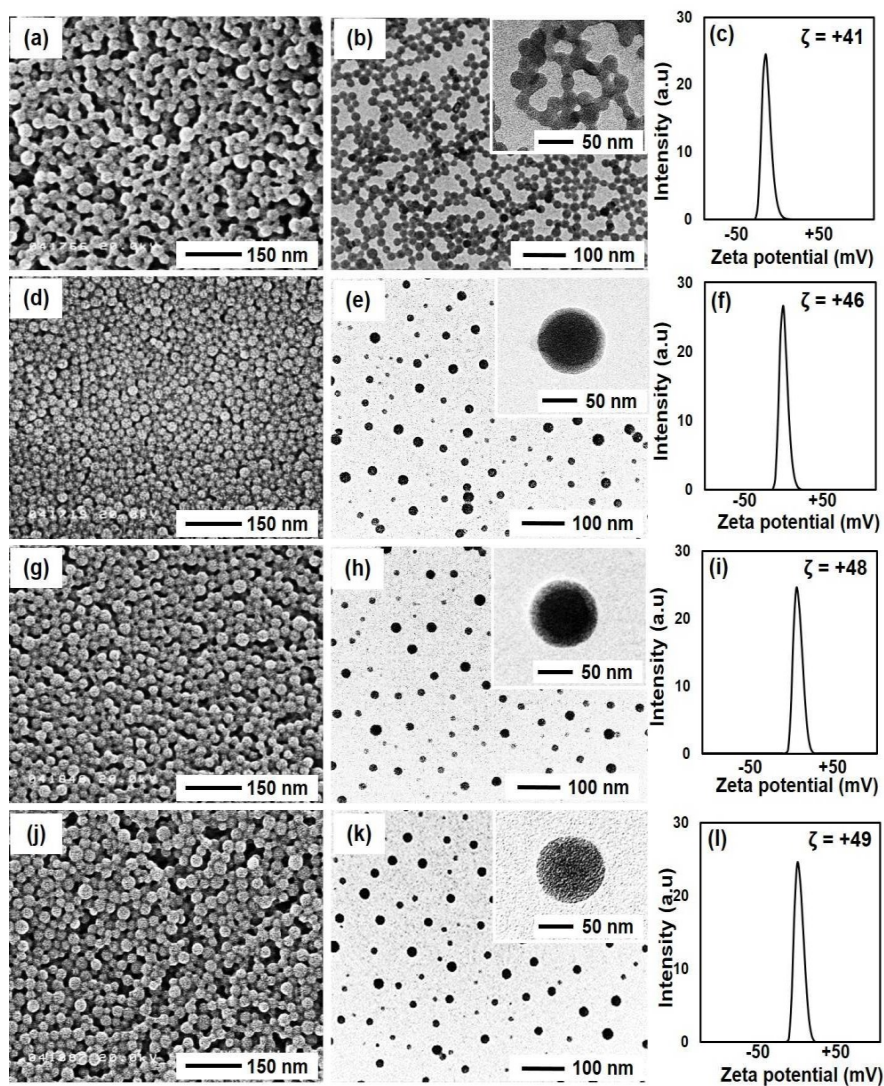

Fig. 7. SEM images and associated size distribution profiles of the PS particles prepared under different reaction times of (a, b) 2, (c, d) 4, (e, f) 10, (g, h) 12, and (i, j) 14 h. Other reaction parameters were kept in constant: acetone-to-water and VA-044 initiator-to-styrene mass ratio, 1.04 and 0.055, respectively; reaction temperature, 60 °C

3. CONCLUSIONS

Highly dispersed cationic PS nanoparticles were successfully synthesised via a modified emulsion polymerisation method. Specifically, the combined use of VA-044 initiator and acetone/water mixture solvent enabled the preparation of cationic PS nanoparticles with enhanced stability and controllable sizes of ~31 nm. Moreover, highly dispersed cationic PS nanoparticles could be obtained using high styrene concentrations without any added surfactant. The optimum polymerisation condition was achieved by using VA-044 initiator concentration of 0.0064 mol L^{-1}, acetone-to-water mass ratio of 1.50, reaction time of 8 h, styrene concentration of 9.24 mol L^{-1}, and reaction temperature of 60 °C. The addition of acetone increased the solubility of styrene and reduced the surface tension between the PS particle surface and aqueous phase. Additionally, rapid diffusion of acetone contributed to the formation of small droplets in the emulsion system, further enabling the formation of PS nanoparticles. The VA-044 initiator could effectively control the stability of both the surface charge and size of PS particles. This study provides important insights and a new methodology for further research and application, especially for preparing polymer nanoparticles via a convenient, low-temperature, and chemical handling process.

SYMBOLS

D_h	hydrodynamic diameter
$G(e)$	first-order autocorrelation function (force at distance of the colloidal PS particle)
Σn_i	total number of PS particles counted from SEM results
t	reaction time
V_m	average molar volume of styrene based on the mole fraction of acetone to water
Z	zeta potential of colloidal PS particles

Greek symbols

γ_L	gradient surface tension between the PS surface and acetone in aqueous phase system
Γ	lag time
δ_d	solubility parameter owing to dispersion forces
δ_p	solubility parameter owing to polarity
δ_h	solubility parameter owing to hydrogen bonding (donor–acceptor interactions)
$\Sigma \delta^2$	total solubility of styrene in acetone-water mixture medium

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APPENDICES

A1. Influence of high acetone-to-water mass ratio on the formation of PS particles

SEM images of the PS nanoparticles prepared at high acetone-to-water mass ratios and R_h distribution profiles evaluated by DLS.
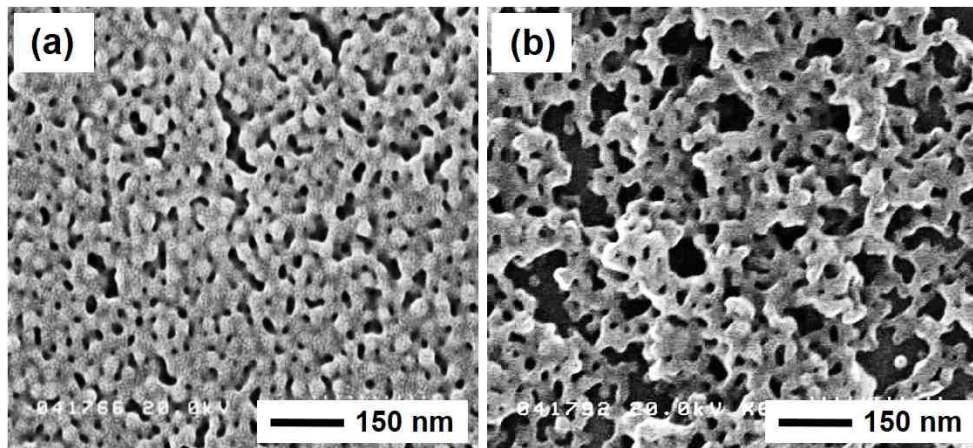
Fig. A.1. SEM images of the PS particles prepared at different acetone-to-water mass ratios of (a) 1.86 and (b) 2.33. Other parameters were kept constant: VA-044 initiator-to-styrene mass ratio, 0.055; reaction temperature, 60 °C; and reaction time, 8 h

A2. Hydrodynamic diameter (D_h) distribution of the prepared PS particles as a function of reaction time
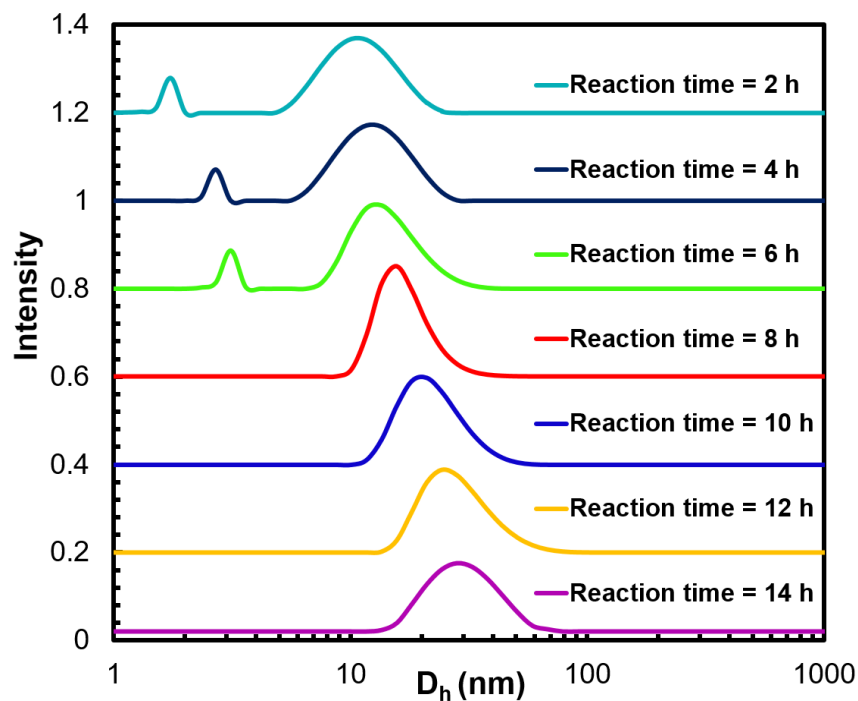

Fig. A.2. Hydrodynamic diameter (D_h) distribution profiles of the PS particles in aqueous medium measured by DLS. The colloidal PS samples were diluted in ultra-pure water prior to characterisation.