

## Monodisperse Polystyrene Microspheres: Studies on the Effects of Reaction Parameters on Particle Diameter and Colloidal Stability

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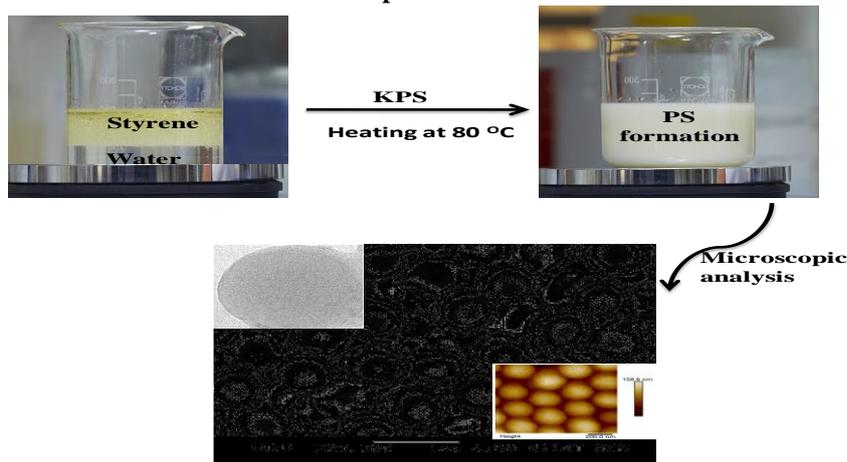
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### Abstract

The synthesis of highly monodisperse polystyrene (PS) microspheres via surfactant-free emulsion polymerization process was successfully carried out. Various reaction conditions such as initiator amount, monomer amount, reaction temperature and stirring speed were varied with a view to studying the effects of these polymerization parameters on the particle diameter and colloidal stability of the synthesized PS microspheres. Microscopic analysis revealed that the as-synthesized particles are spherical in shape without any form of agglomeration. Thermo-gravimetric analyzer (TGA) analysis revealed that the prepared PS sample completely degrades at 465 °C. DLS analysis showed a reduction in the average particle diameters of the as-synthesized PS microspheres as the reaction temperature, stirring speed and initiator amount increased, whereas an increase in average particle diameter was observed with increased monomer amount. Zeta-potential values ranging from -30.10 mV to -39.50 mV, which is indicative of stable colloidal dispersion of particles, were seen for all the synthesized PS samples.

**Keywords:** Monodisperse; Colloidal Stability; Polystyrene Microspheres; Average Particle Diameter

### Graphical abstract



### Introduction

Monodispersed polymer colloidal spheres have attracted numerous attentions because of

their amazing applications in areas such as diagnostics, combinatorial synthesis and drug delivery (Zhang et al. 2003). Among the

myriad of polymers that have been previously used in the preparation of polymers with monodisperse colloidal particles, polystyrene (PS) is considered to be very valuable due to its low water absorbing property, rigidity and low production costs (Yoon et al. 2006). Many practical applications such as storage, catalytic and packaging applications have been achieved in the industry using this polymer (Yohanala et al. 2015). However, obtaining PS colloidal spheres with a good level of monodispersity can be very challenging as the end product usually comes out polydispersed. Attaining a monodispersed PS spheres is more valuable than a polydispersed PS because of applications such as instrument calibration standards, standards for the determination of pore size, the efficiency of filters, column packing material for chromatographic separation and support materials for biochemicals (Yoon et al. 2006, Zhang et al. 2003). Achieving each of the aforementioned applications can be facilitated by taking factors such as morphology of the particles and the surface characteristics, the particle size and its distribution among other numerous factors into consideration during the synthesis stages of the PS spheres. A previous study has synthesized monodispersed PS spheres with amazing unique properties via emulsion polymerization, with and without the presence of a surfactant (Telford et al. 2013).

The main disadvantage of the use of a surfactant is that the emulsifier is adsorbed at the interface of the PS particles. The complete removal of the adsorbed emulsifier can be quite difficult as one can never be too sure that all emulsifier molecules in the interface of the polymer have been removed completely after washing with water (Zhang et al. 2009). This setback has made surfactant-free emulsion polymerization a very valuable method in the preparation of polymer particles with micron range sizes and narrow size distributions. Based on the fact that emulsion polymerization in the presence of surfactant is considered a more conventional technique than surfactant-free emulsion polymerization, the particle

formation mechanism is possibly well understood than that of polymerization in the absence of surfactant; hence the need to optimize reaction conditions aimed at controlling the particle size and its distribution, polydispersity and particle stability of the PS microspheres (Zhang et al. 2009). Monodispersed polymer latex has previously been prepared via surfactant-free emulsion polymerization method and the effects of certain reaction conditions such as polymerization time, ionic strength, the concentration of the ionic copolymer, initiator concentration were studied (Choi et al. 2002, Fang et al. 2010). However, these research works did not examine the effects of the aforementioned reaction conditions on the colloidal stability of the particles.

In this study, micro size monodispersed polystyrene (PS) colloidal spheres were successfully prepared via surfactant-free emulsion polymerization process. Various reaction conditions such as initiator amount, monomer amount, reaction temperature and stirring speed were varied with a view to determining the effects of these reaction conditions on the average particle diameter, dispersity and colloidal stability of the polystyrene spheres.

## **Materials and Methods**

### **Chemicals**

Styrene, sodium hydroxide, pure nitrogen gas, de-ionized water and potassium persulfate (kps), were all purchased from Sigma-Aldrich and were of analytical grade.

### **Experimental procedure**

Samples of colloidal polystyrene (PS) spheres were synthesized using the surfactant-free emulsion polymerization method as described by a published procedure (Yohanala et al. 2015). The styrene used was washed using 1 M sodium hydroxide solution to remove the inhibitor present. The styrene layer was removed and washed with de-ionized (DI) water for another four times. 1.36 g (13.05 mmol) of styrene was measured and then

added to 15 g (833.3 mmol) of distilled water in a two-neck reaction flask and agitated with a magnetic stirrer (700 rpm). The reaction vessel was maintained at a temperature of 80 °C. At the same time, pure nitrogen was injected into the system. After the system was left to stand for 15 minutes to completely purge the vessel of oxygen, 0.05 g of potassium per-sulphate (0.185 mmol) was added drop-wise to start the polymerization process under a nitrogen atmosphere for another 7 hours. After centrifugation, the

colloidal particles sediment at the bottom and the top layer of clear solvent (de-ionized water) were poured away. This was repeated for a few times to ensure that the colloidal suspension was free of any unreacted reagent. The polystyrene (PS) spheres with various diameters were similarly prepared by changing the monomer concentrations, reaction temperature, stirring speed and initiator concentration while leaving all other reaction conditions constant as depicted in Table 1.

**Table 1:** Reaction parameters used during the preparation of polystyrene

Sample names/codes	Reaction temperature (°C)	Monomer amount (mmol)	Initiator amount (mmol)	Stirring speed (Rpm)
PS <sub>1</sub>	80.0	13.056	0.185	700
PS <sub>2</sub>	80.0	17.400	0.185	700
PS <sub>3</sub>	60.0	13.056	0.185	700
PS <sub>4</sub>	80.0	13.056	0.185	900
PS <sub>5</sub>	80.0	13.056	0.185	400
PS <sub>6</sub>	80.0	13.056	0.074	700
PS <sub>7</sub>	80.0	13.056	0.222	700
PS <sub>8</sub>	80.0	13.056	0.296	700
PS <sub>9</sub>	80.0	13.056	0.370	700

### Characterization techniques

Scanning electron microscope (JEOL-JSM 5600 LV) and atomic force microscope in the tapping mode (Bruker Multimode, Germany) were used to evaluate the morphology of PS microspheres. An FT-IR spectrometer (Perkin-Elmer Series Spectrometer) was used to determine the functional groups of the polystyrene (PS) samples. Powder X-ray diffraction patterns of PS samples were taken using a PANalytical EMPYREAN instrument equipped with reference radiation of Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) at an operating voltage of 45 kV. Thermo-gravimetric analyzer, TA Q50 was used to examine the thermal stability of the polystyrene samples under a nitrogen gas atmosphere at a heating rate of 10 °C/min. The Raman scattering (SERS) activity was evaluated using WI-Tec Raman microscope (Germany, alpha 300R). Dynamic Light Scattering (DLS) (Nano-Zetasizer, Malvern

Instruments) was used to determine the average particle size and size distribution (polydispersity index (PDI) of the PS samples at 25 °C, under the scattering angle of 173° at 6333 nm wavelength. The zeta-potentials of the synthesized PS samples were determined using Zeta-Sizer (Malvern Instruments).

### Results and Discussion

#### Functional groups, thermal stability and XRD analysis of the synthesized PS sample

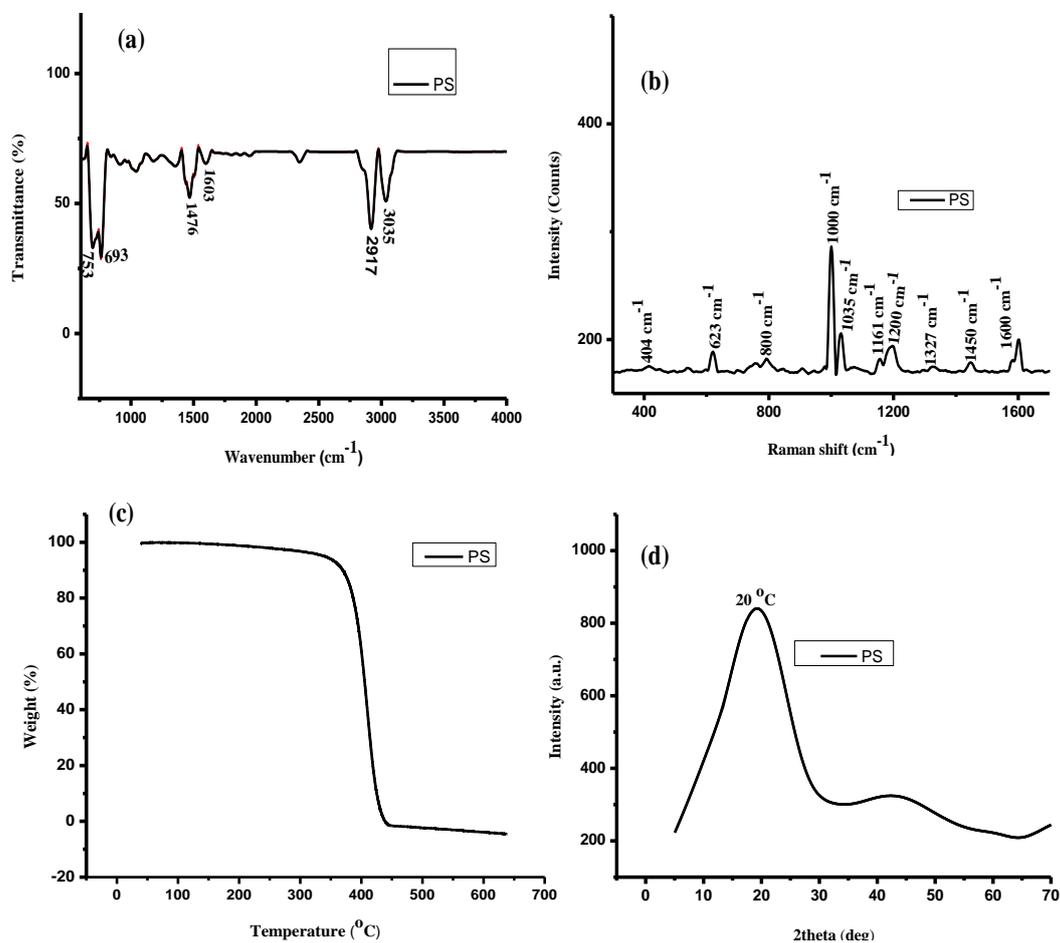
Figure 1(a) shows the different functional groups in the synthesized polystyrene sample revealed by FT-IR analysis. Aromatic C-H and C=C stretching vibrations can be respectively assigned to 1476 cm<sup>-1</sup> and 1603 cm<sup>-1</sup> wave numbers (Ifijen et al. 2019). The existence of these wavenumbers shows that the synthesized PS is aromatic in nature (Fang et al. 2010). The absorbance peaks at 753 cm<sup>-1</sup> and 693 cm<sup>-1</sup> can be attributed to the presence of C-H

out-of-plane bending vibration. Symmetric/asymmetric -C-H-bending/stretching vibration in methylene and benzene groups can be assigned to the pronounced peaks at 2917  $\text{cm}^{-1}$  and 3035  $\text{cm}^{-1}$ , respectively. The functional groups observed from the as-synthesized PS according to the band of FTIR absorbance peaks are in line with works of literature (León-Bermúdez and Salazar 2008).

To further confirm that the synthesized compound is polystyrene, Raman spectrometric analysis was carried out on the as-synthesized compound. Figure 1b shows the vibrational, rotational, and other low-frequency modes of the synthesized PS<sub>1</sub> sample. The peak at 1035  $\text{cm}^{-1}$  has been reported by a previous study to be the characteristic Raman peak for PS (Schmälzlin et al. 2014). The intense Raman band at 1000  $\text{cm}^{-1}$  can be attributed to the symmetrical ring breathing frequency in the phenyl ring (Liang and Krimm 1958). The Raman band at 623  $\text{cm}^{-1}$  can be linked to the components of the degenerate mode in monosubstituted benzene units in polystyrene (Brack et al. 2004). The low-intensity Raman band at 800  $\text{cm}^{-1}$  can be attributed to carbon-carbon (C-C) vibrations. The hydrogen-bending modes in the phenyl ring can be traced to the Raman bands at 1161  $\text{cm}^{-1}$  and 1200  $\text{cm}^{-1}$ . CH and CH<sub>2</sub> modes can be assigned to the Raman

bands at 1327  $\text{cm}^{-1}$  and 1450  $\text{cm}^{-1}$ , respectively. The Raman band at 402  $\text{cm}^{-1}$  can be linked to the presence of skeletal modes of a planar zig-zag carbon chain. The emergence of Raman band at 1600  $\text{cm}^{-1}$  can be traced to the vibrational modes, involving mainly quadrant stretching of the ring C-C bonds having a small interaction with C-H in-plane bending modes in the polystyrene chain (Colthrup et al. 1990).

To determine if the as-synthesized PS<sub>1</sub> sample can be applied in an application that will require material to be thermally stable, the influence of heating rate on the thermal decomposition of polystyrene (PS<sub>1</sub>) sample was evaluated. Figure 1c displays the generated TGA results of PS microspheres at a 10 °C/min heating rate. An almost constant degradation rate from 0 °C to 358 °C was observed by the spectra. However, a further increase in heating temperature from 358 °C to 383 °C led to a rapid weight loss of 15% as signified by the steep nature of the curve. The degradation in the weight of the PS was observed to increase in a continuous manner until the heating temperature reached 465 °C. The total loss in weight estimated during this period is 85%. The as-synthesized PS was therefore shown to be completely degraded at 465 °C according to the TGA analysis.

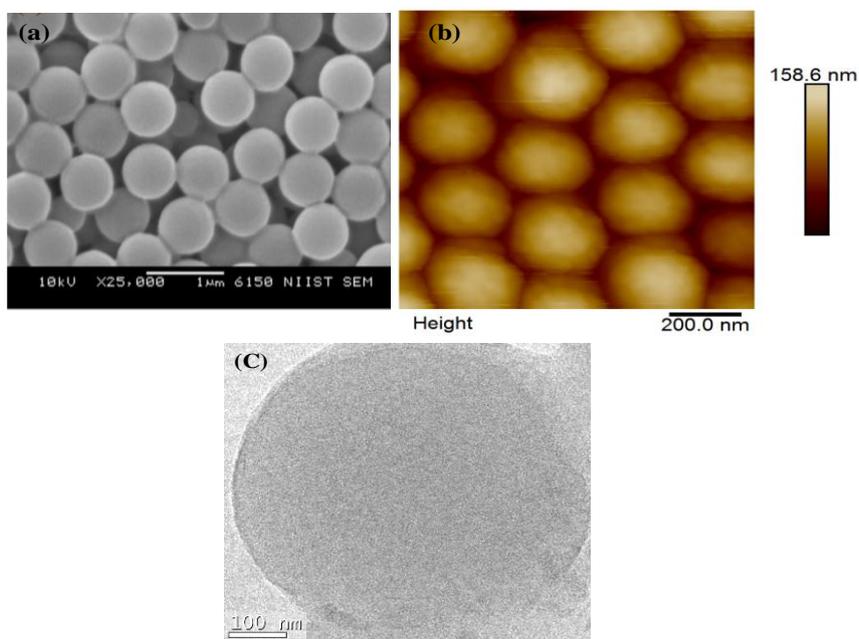


**Figure 1:** (a) FTIR spectrum (b) Raman spectrum (c) TGA curve (d) XRD patterns of polystyrene (PS).

The XRD pattern of the synthesized polystyrene ( $\text{PS}_1$ ) sample is shown in Figure 1d. The observed broad diffraction peak at position  $2\theta$  is equal to  $20^{\circ}$ . This indicates that the synthesized PS sample is highly amorphous in nature (Fang et al. 2010).

#### Morphology of the synthesized PS sample

The morphology of the as-synthesized  $\text{PS}_1$  was examined using scanning electron microscope (SEM) and atomic force microscope (AFM). Figure 2 depicts the scanning electron and atomic force micrographs of the prepared  $\text{PS}_1$  sample.



**Figure 2:** (a) SEM (b) AFM (c) TEM of PS microspheres.

The prepared particles were seen to be spherical in shape with even size distribution without any form of agglomeration. The average particle diameter of the synthesized PS<sub>1</sub> colloidal particles according to SEM and AFM analysis were estimated to be about 541 nm and 551 nm, respectively. These values are very close to the average particle diameter of 577.6 nm obtained by the DLS analysis in Table 2. The fact that DLS measures the hydrodynamic size of particles may be attributed to the slight difference seen in the average particle diameter by the SEM, AFM and DLS analysis. 41 nm and 9.11 nm were respectively estimated to be the particle height and surface roughness of the synthesized PS<sub>1</sub> colloidal particles.

The as-synthesized PS sample was also examined using transmission electron microscope. Figure 2(c) showed the TEM micrograph of the synthesized PS. The result revealed spherical shaped particle which was in agreement to the results from the scanning electron microscope (SEM) and atomic force microscope (AFM) (Figure 2(c)).

#### **Effects of monomer amounts**

The styrene monomer amounts were varied between 13.056 mmol and 17.400 mmol in order to study the effects of the increase in monomer amounts on the average particle diameter, polydispersity index and zeta-potential of as-synthesized PS sample. Table 2 shows the impacts of the size distribution reports by intensity, polydispersity index and zeta-potential of polystyrene particles on styrene monomer amounts which were added before the initiation of polymerization (Figure 3). Average particle diameters of 577.6 nm and 632 nm were respectively obtained for PS<sub>1</sub> and PS<sub>2</sub> microspheres (Table 2). This showed that there was an increase in the average particle diameter of the synthesized PS as the monomer amounts increased. The observed increase in size could be attributed to the decrease in concentration difference between the monomer and aqueous phase caused by the increased monomer amount (Choi et al. 2002). This would lead to a corresponding decrease in the rate of diffusion of the oil phase styrene

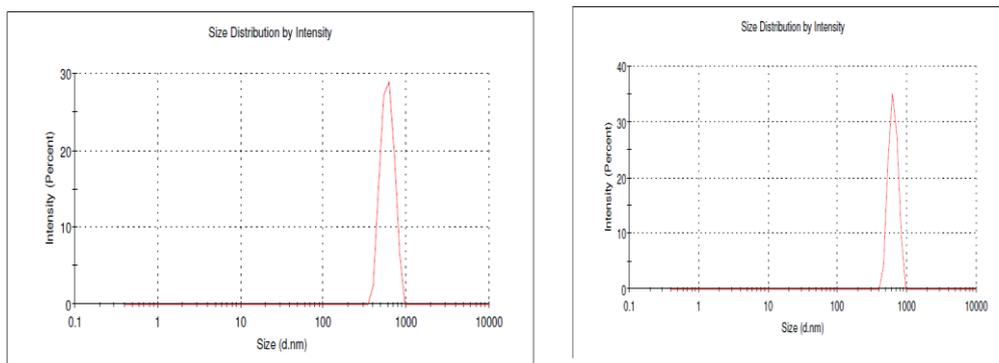
monomer into the aqueous phase, thereby decreasing the partially dissolved monomer; making most of it exist as an oil-phase monomer rather than an aqueous phase monomer. Based on the fact that the aqueous-phase monomer is easily attacked by the initiator (KPS) (Yamamoto et al. 2006), the rate of consumption of the aqueous-phase

monomer was, therefore, faster than the rate of diffusion of the monomer (from oil to aqueous phase) (Yamamoto et al. 2006). This could, in turn, limit the available active monomer and the nucleation stage (Nandiyanto et al. 2012) and thereby, increase the particle size (Yamamoto et al. 2006).

**Table 2:** Polystyrene spheres under different monomer amounts

	PS <sub>1</sub> (17.400 mmol)	PS <sub>2</sub> (13.056 mmol)
Average particle diameter (nm)	577.6	632.0
Polydispersity Index (PDI)	0.006	0.164
Zeta-potential (mV)	-36.60	-38.20

	Size (d.nm...)	% Intensity:	St Dev (d.n...		Size (d.nm...)	% Intensity:	St Dev (d.n...		
<b>(a)</b>	Z-Average (d.nm): 577.6	Peak 1: 596.3	100.0	106.2	<b>(b)</b>	Z-Average (d.nm): 632.0	Peak 1: 635.1	100.0	95.67
	Pdl: 0.006	Peak 2: 0.000	0.0	0.000		Pdl: 0.164	Peak 2: 0.000	0.0	0.000
	Intercept: 0.953	Peak 3: 0.000	0.0	0.000		Intercept: 0.918	Peak 3: 0.000	0.0	0.000
	Result quality <b>Good</b>					Result quality <b>Refer to quality report</b>			



**Figure 3:** Size distribution report by intensity of (a) PS<sub>1</sub> and (b) PS<sub>2</sub>-different monomer amounts.

Previous studies have used the polydispersity index (PDI) as an indicator of the particle size distribution (Masarudin et al. 2015). Samples with a wider range of particle sizes have higher PDI values, while samples consisting of evenly sized particles have lower PDI values (Masarudin et al. 2015). The low polydispersity index (PDI) of < 0.2 (0.006, 0.164) showed narrow size distributions for the obtained PS samples. However, the sample prepared using the higher monomer concentration showed better monodispersity compared to the PS prepared with the lower

monomer concentration. The colloidal dispersion of both polystyrene samples (PS<sub>1</sub> and PS<sub>2</sub>) was observed to be very stable. However, a slightly more improved stable colloidal dispersion was observed for PS<sub>2</sub> sample (-38.20 mV) when compared to PS<sub>1</sub> sample (-36.60 mV) (Hanaor et al. 2012, Che Hak et al. 2018).

### Effect of temperature

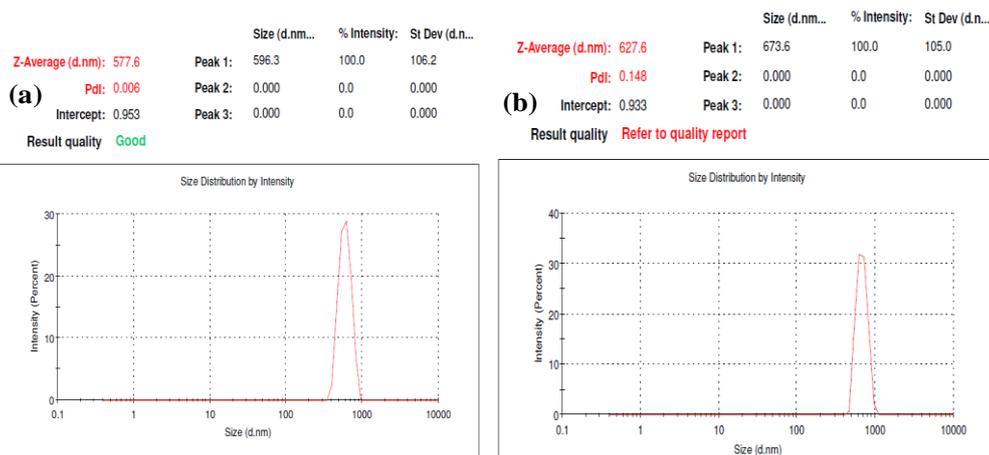
Table 3 shows the effect of reaction temperature on the average particle diameter, monodispersity and zeta-potential of the

particle sizes of PS microspheres (Figure 4). The reaction temperature (80 °C) used in the synthesis of PS<sub>1</sub> sample was decreased to 60 °C for the preparation of PS<sub>3</sub>. The size distribution report by intensity obtained by the dynamic light scattering results (Table 2) showed an increase in average particle diameter from 577.6 nm to 627.6 nm as the reaction temperature decreased. This was assumed to be due to the concentration of primary free radicals produced by the KPS initiator, which is a function of the reaction

temperature. A lesser amount of free radicals were produced in a long time at a lower temperature, compared to a higher temperature, and therefore, resulted in less primary nuclei and larger particle size. Polydispersity index/zeta-potentials of 0.006/–38.20 mV and 0.148/–33.80 mV were respectively obtained for PS<sub>1</sub> and PS<sub>3</sub>. This is an indication that a more monodispersed and stable colloidal solution was obtained at a higher temperature of 80 °C than at 60 °C (Masarudin et al. 2015).

**Table 3:** Polystyrene spheres under different reaction temperature conditions

	PS <sub>1</sub> (80 °C)	PS <sub>3</sub> (60 °C)
Average particle diameter (nm)	577.6	627.6
Polydispersity Index (PDI)	0.006	0.148
Zeta-potential (mV)	–38.20	–33.80



**Figure 4:** Size distribution report by intensity of (a) PS<sub>1</sub> and (b) PS<sub>3</sub> under different reaction temperature.

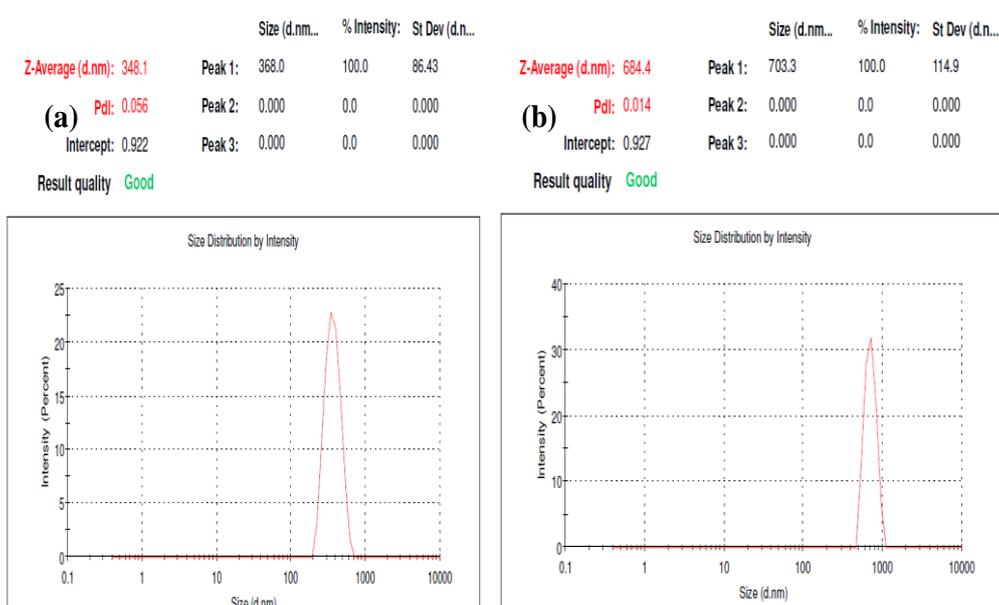
**Effects of stirring speed**

To study the effects of stirring speed on the particle sizes of PS microspheres, PS<sub>4</sub> and PS<sub>5</sub> samples were prepared using stirring speeds of 900 rpm and 400 rpm. The results (Table 4) placed the average particle diameters of both PS microspheres at about 348.1 nm and 684.4 nm, respectively (Figure 5). This showed that a decrease in stirring speed (from 900 rpm to 400 rpm) led to an increase in the average particle diameter of the prepared polystyrene

microspheres from 348.1 nm to 684.4 nm. This could be as a result of the low diffusion rate of monomer droplets into the aqueous phase caused by the decreased stirring speed. This may have led to a low rate of monomer emulsification that resulted in slower consumption rate of the monomer species and inhibition of the nucleation stage, leading to an increase in the average particle diameter of the PS colloidal microspheres.

**Table 4:** Average particle diameter and polydispersity index of polystyrene spheres under different stirring speeds

	PS <sub>4</sub> (900 rpm)	PS <sub>5</sub> (400 rpm)
Average particle diameter (nm)	348.1	684.4
Polydispersity Index (PDI)	0.056	0.014
Zeta-potential (mV)	-39.50	-38.23

**Figure 5:** Size distribution report by intensity of (a) PS<sub>4</sub> and (b) PS<sub>5</sub> under different stirring speeds.

The polydispersity index (PDI) values of 0.056 and 0.014 obtained for the prepared PS samples (Table 4) suggest very narrow size distributions (Masarudin et al. 2015). However, the stirring speed of 900 rpm resulted in more monodispersed PS microspheres.

The zeta potentials of -39.50 mV and -38.23 mV observed for PS samples (Table 4) show that the force of electrostatic repulsion in the particles of both samples surpassed their attractive forces and thus have a higher tendency to resist any possible agglomeration that can arise between them (Hanaor et al. 2012, Masarudin et al. 2015). The PS prepared

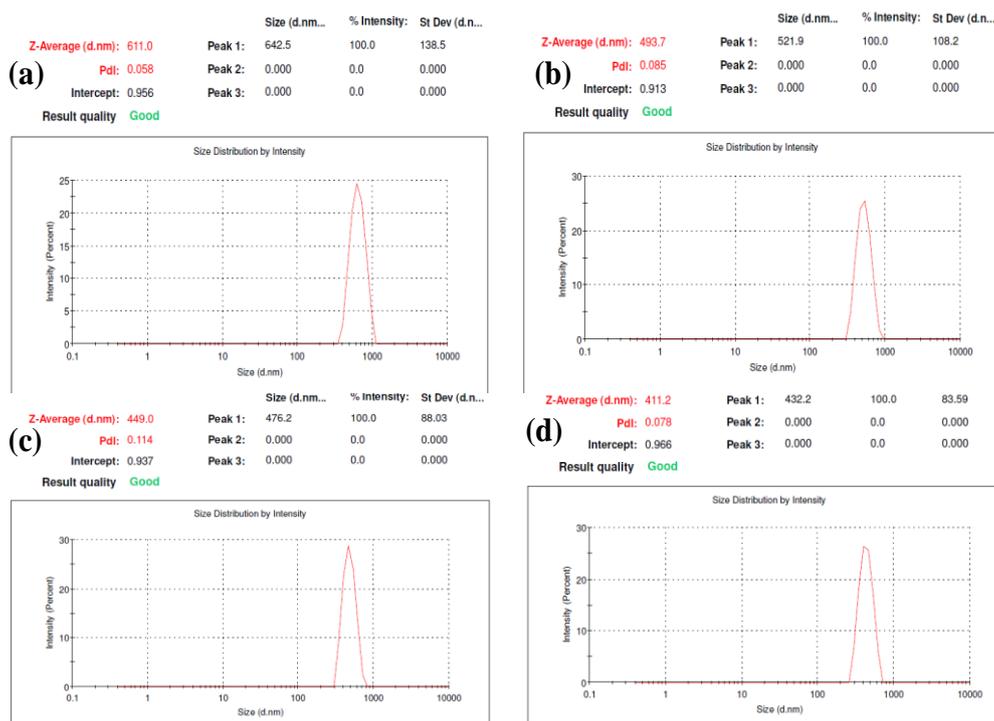
under a higher stirring speed (900 rpm) was observed to possess a slightly better stable colloidal dispersion.

#### Effects of initiator amount

The effects of an increase in initiator amounts on the particle sizes of PS samples were examined by varying the initiator amounts (0.074 mmol, 0.222 mmol, 0.296 mmol and 0.370 mmol) while leaving all other reaction conditions constant. Table 5 shows the impacts of varying initiator amounts on the particle sizes, polydispersity index and zeta potentials of PS microspheres (Figure 6).

**Table 5:** Average particle diameter and polydispersity index of polystyrene spheres under different initiation concentrations.

	PS <sub>6</sub> (0.074 mmol)	PS <sub>7</sub> (0.222 mmol)	PS <sub>8</sub> (0.296 mmol)	PS <sub>9</sub> (0.370 mmol)
Average particle diameter (nm)	611.0	493.7	449.0	411.2
Polydispersity Index (PDI)	0.058	0.085	0.114	0.078
Zeta-potential (mV)	-38.92	-33.66	-30.10	-37.90



**Figure 6:** Size distribution report by intensity of (a) PS<sub>6</sub> (b) PS<sub>7</sub> (c) PS<sub>8</sub> and (d) PS<sub>9</sub> under different initiation concentrations.

The average particle sizes of PS<sub>6</sub>, PS<sub>7</sub>, PS<sub>8</sub> and PS<sub>9</sub> were found to be 611, 493.7, 449 and 411.2 nm, respectively. This trend shows a decrease in the average particle diameter of the PS microspheres as the initiator concentrations increased. This may be attributed to the increased rate of polymerization process brought about by increasing the initiator concentrations, which led to a shorter nucleation period and therefore, a decrease in the particle sizes (Gorsd et al. 2012). The polydispersity index (PDI) of << 0.1 (0.058, 0.085, 0.114 and 0.078) obtained for PS<sub>6</sub>, PS<sub>7</sub>,

PS<sub>8</sub> and PS<sub>9</sub> showed that the ultimate latex particles of the PS samples have relatively narrow particle size distributions (Masarudin et al. 2015). The as-synthesized PS<sub>6</sub>, PS<sub>7</sub>, PS<sub>8</sub> and PS<sub>9</sub> respectively have zeta potentials of -38.92 mV, -33.60 mV, -30.10 mV and -37.90 mV (Table 5). The results show that all the synthesized PS samples have good colloidal stability (Masarudin et al. 2015, Hanaor et al. 2012). However, the PS synthesized using the lowest amount of initiator was observed to be the most stable.

## Conclusion

Surfactant-free emulsion polymerization was successfully used to prepare monodisperse polystyrene colloidal microspheres with different particle sizes by altering the amount of monomer, reaction temperature, stirring speed and the amount of initiator. The results showed a reduction in the particle sizes of the PS colloidal microspheres as the reaction temperature, stirring speed and initiator concentration increased, whereas the average particle sizes increased with increase in monomer concentrations. Variations in these polymerization parameters should be closely monitored to produce particles with a monodisperse size distribution and desired particle diameter.

## Competing Interests

Authors declare that no competing interests exist.

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