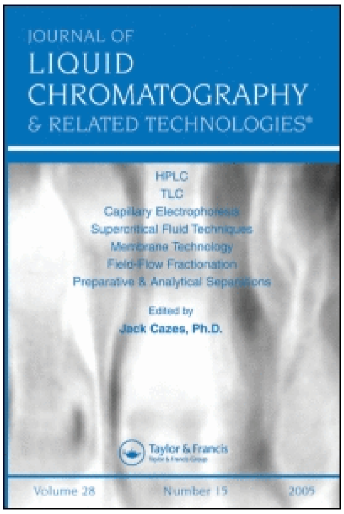

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Abstract: A gravitational field-flow fractionation (GrFFF) was employed to study the influence of various reaction parameters in emulsion polymerization on size distribution of polymeric latex beads. Micron-sized polystyrene (PS) latex beads were synthesized by conventional emulsion polymerization. The reaction parameters such as the stirring rate (rpm), reaction time, concentration of azobisisobutyronitrile (AIBN) and polyvinylpyrrolidone (PVP), were systematically varied. Then the PS beads were analyzed by GrFFF for size determination. It was found that the mean diameter and the size distribution of the PS latex beads change as some of the reaction parameters change. No clear trends were observed in the mean diameter and the coefficient of variation (CV) with the stirring rate in the range of 60 to 300 rpm, or with the reaction time in the range of 13 to 24 hrs. A clear trend of increase in the mean diameter with the AIBN concentration was observed, suggesting the particle size can be controlled by varying the AIBN concentration without affecting the size distribution much. It was also found that the mean diameter tends to decrease as the PVP concentration increases while the CV tends to increase. Results obtained from GrFFF were compared with those obtained from photon-correlation spectroscopy (PCS) and optical microscopy (OM).

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Keywords: Emulsion polymerization, Gravitational field flow fractionation (GrFFF), Mean diameter, Polystyrene (PS) latex beads, Reaction parameters, Size distribution

INTRODUCTION

Micronized polymeric latex beads are widely used in various industries including ink, filtration systems, nebulizers, spraying systems, and powder coating, etc. It is well known that the mean size and the size distribution of the polymeric latex beads affect their physical and chemical properties.[1,2]

Developing a method for controlled synthesis of micron-sized polymeric particles has long been the subject of extensive work. Emulsion polymerization is a long established method, which is still widely used in various industries. However, preparation of micron-sized polymeric latex beads having a desired morphology, size, and structure by emulsion polymerization is not simple due to some difficulties, such as coagulation of the latex beads and formation of the second generation particles during the synthesis. Still, the emulsion polymerization method remains to be popular as it allows preparation of various types of structural and functional polymeric particles.

Many sizing techniques are available for polymeric latex beads. They include light scattering (such as photon correlation spectroscopy, PCS) and microscopy. Separation techniques such as hydrodynamic chromatography (HC) and field-flow fractionation (FFF) are particularly useful for determination of the size distribution as well as the mean size.

Gravitational field-flow fractionation (GrFFF), a member of FFF family, is a separation technique that is applicable to separation and characterization of micron-sized particles ranging about 2∼50 μm in diameter, and thus is useful for size analysis of micron-sized polymeric beads. GrFFF has been employed for the separation of various types of micron-sized particles including some inorganic particles,[3,4] cells,[5–7] starch granules,[8,9] silica gel particles,[10,11] polymer latexes,[12,13] and fine coal particles and residues from coal liquefaction.[14]

In this study, micron-sized polystyrene (PS) latex beads were synthesized by emulsion polymerization with systematic variation of reaction parameters, such as the stirring rate (rpm), reaction time, concentrations of azobisisobutyronitrile (AIBN) and polyvinylpyrrolidone (PVP). Then the emulsion polymerized PS micro beads were analyzed by GrFFF for a quick and easy measurement of the mean size and the size distribution. The aim of this work is to investigate the capability of GrFFF for size analysis of polymeric latex beads and to study the relationship between the size and size distribution vs. reaction parameters.

THEORY

In GrFFF, the retention time, t_r of particles having diameter, d, is given by:[15]

$$t_r = \frac{wt^o}{3\gamma d} \tag{1}$$

where w is the channel thickness and t^o the channel void time. γ is a dimensionless "steric correction factor", whose detailed discussion seems to be beyond the scope of this paper.[16–19]

Due to the uncertainty in γ, the size analysis by GrFFF usually requires calibration. From Equation 1,

$$\log t_r = -S_d \log d + \log A \tag{2}$$

is obtained,[20–22] where A is the extrapolated elution time of a particle of unit diameter. Generally the plot of log t_r vs. log d is used as the calibration plot in size analysis by GrFFF. The size based selectivity, S_d, is the slope of the calibration plot, and is a measure of the resolving power of a separation system. S_d is defined by:[23,24]

$$S_d = \left| \frac{d \log t_R}{d \log d} \right| \tag{3}$$

Assuming the band broadening is negligible, a GrFFF fractogram can then be transformed into the size distribution by:[25]

$$m(d) = c(t_r)\, \dot{V} \left| \frac{dt_r}{dd} \right| = c(t_r)\, \dot{V}\, S_d t_{r1} \left(\frac{t_r}{t_{r1}} \right)^{(s_d+1)/s_d} \tag{4}$$

where m(d) is the mass-based size distribution, c(t_r) the fractogram signal (detector response), and V the volumetric flow rate (in mL/min) through the channel. The size distribution obtained by Eq. (4) is the mass based size distribution. The number-based size distribution can be obtained by the same equation with c(t_r) replaced by $\frac{c(t_r)}{d^2}$.[25]

EXPERIMENTAL

Materials

Polystyrene latex standards having nominal diameters of 4 and 7 μm were purchased from Duke Scientific Corp. (Palo Alto, CA, USA), 8 and 12 μm from Fluka AG (Steinheim, Germany).

Synthesis of Polystyrene Latex Beads

Micron-sized polystyrene (PS) latex beads were synthesized by emulsion polymerization with azobisisobutyronitrile (AIBN) purchased from Sigma-Aldrich (St. Louis, MO, USA), as an initiator, and polyvinyl pyrrolidone (PVP) purchased from Junsei Chemical Corp. (Tokyo, Japan), as a dispersant agent. One of the four reaction parameters (stirring rate, concentration of AIBN, concentration of PVP, and the reaction time) were varied, with the other three parameters kept constant, yielding four groups of PS beads. For example, the A group samples were obtained by varying the stirring rate, while the other three parameters were fixed constant. The reaction conditions used in this study are summarized in Table 1. In all cases, 66.23 mL of styrene monomer was added to 152.8 mL of ethanol with the other reagents. Before polymerization, the emulsion was purged with N_2. Then the reaction system was heated to 70°C while stirring. After 1 hour of stirring, the mixture was mixed with 250 mL of methanol, and then stirred again for 24 hours (for D group samples the reaction time was varied from 13 to 24 hrs). Next, the reaction mixture was stored in an oven for 24 hour at 60°C to evaporate the solvent.

Gravitational Field-Flow Fractionation (GrFFF)

The GrFFF system was assembled in our laboratory in the similar manner as described in previous reports.[3–14] An overhead transparency sheet having the thickness of 165 μm was used as the spacer. The channel dimensions were 2 cm wide and 50 cm long. The channel void volume measured from the retention volume of acetone was 1.6 mL. The spacer was clamped between two pieces of acryl blocks. Particle suspensions were directly injected into the channel with a 50 μL Hamilton hypodermic syringe (Reno,

Table 1. Reaction conditions used for emulsion polymerization of polystyrene latex beads in this study

Sample	Stirring rate (rpm)	AIBN (g)	PVP (g)	Reaction time (hr)
Group A	Varied from 60 to 300	0.6	4	24
Group B	70	Varied from 0.1 to 1.0	4	24
Group C	70	0.6	Varied from 1.0 to 10.0	24
Group D	70	0.6	4	Varied from 13 to 24

Nevada, USA) through a rubber septum. A Younglin SP930D isocratic pump (Anyang, Korea) was employed to deliver the carrier solution. The PS latex beads were monitored by a Younglin M720 UV detector operating at the wave length of 254 nm. The injection volume was kept constant at 20 μL with the injection flow of 0.3 mL/min. The carrier liquid was doubly distilled water containing 0.05% (w/v) sodium dodecyl sulfate (SDS) and 0.02% (w/v) sodium azide in all experiments. Both SDS and sodium azide were purchased from Sigma Aldrich (St. Louis, MO, USA).

Photon Correlation Spectroscopy (PCS)

The PCS used in this study was a Malvern 4700C (Worcestershire, UK) equipped with a He-Ne laser (632.8 nm) as the light source. Experimental parameters were: viscosity = 0.009 cp, refractive index = 1.33. The collection angle was 90°C.

RESULT AND DISCUSSION

Separation of Polystyrene Latex Standards by GrFFF

Figure 1(a) shows GrFFF fractograms of 4, 7, 8, and 12 μm PS standards obtained at three different flow rates. Plots of log t_r vs. log d are also shown for each flow rate at Figure 1(b). It is seen that, as the flow rate increases, the retention time gradually decreases as shown in Figure 1(a), and the slope of the log t_r vs. log d plot (and thus the size based selectivity, S_d) increases as shown in Figure 1(b). The S_d measured at the flow rate of 1.0, 1.5, and 2.0 were 0.40, 0.51, and 0.72, respectively. This suggests higher resolving power is obtained at a shorter period of time as the flow rate increases. The flow rate of 2 mL/min was used for all size analysis of the PS latex beads synthesized in this study.

At the flow rate above 2 mL/min, the log t_r vs. log d plot tends to deviate from linearity due to stronger influence by the lift forces, which may cause the size analysis by GrFFF to be less accurate.[18,19]

Size Analysis of Emulsion Polymerized PS Latex Beads by GrFFF

Figures 2–5 show GrFFF fractograms obtained at 2 mL/min, and the mass and number based size distributions measured for the PS beads in Group A, B, C, and D, respectively. It is seen in Figures 2–5 that all PS beads synthesized in this study have rather broad size distributions ranging in diameters from 3 to about 15 μm for both the mass and number based distributions. As a measure of the broadness of the size

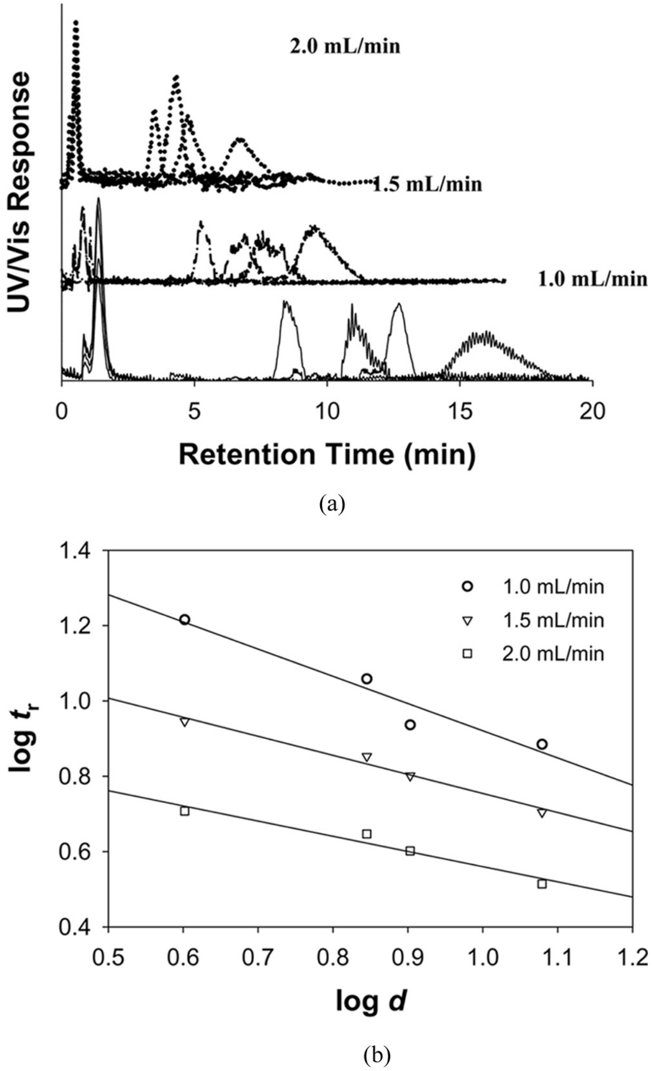
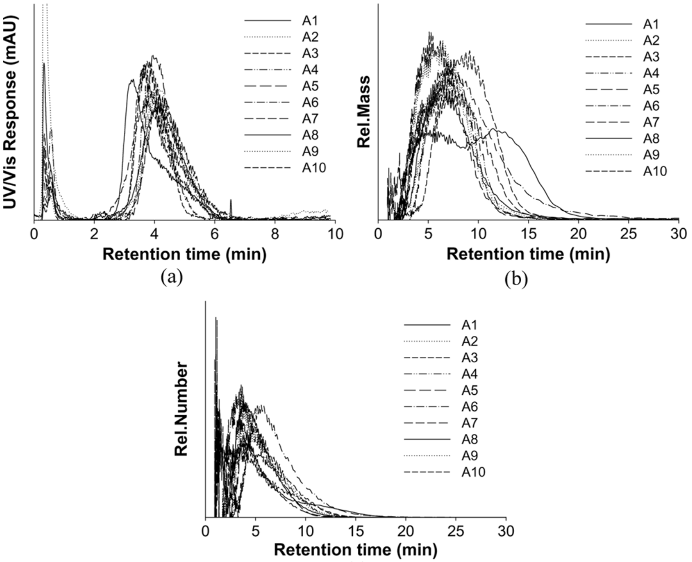


Figure 1. GrFFF fractograms of 4, 7, 8, and 12 μm PS standards obtained at three different flow rates (a) and plots of log t_r vs. log d for each flow rate (b).

distributions, CV was determined by:

$$\mathrm{CV}(\%) = (S/\bar{x}) \times 100$$

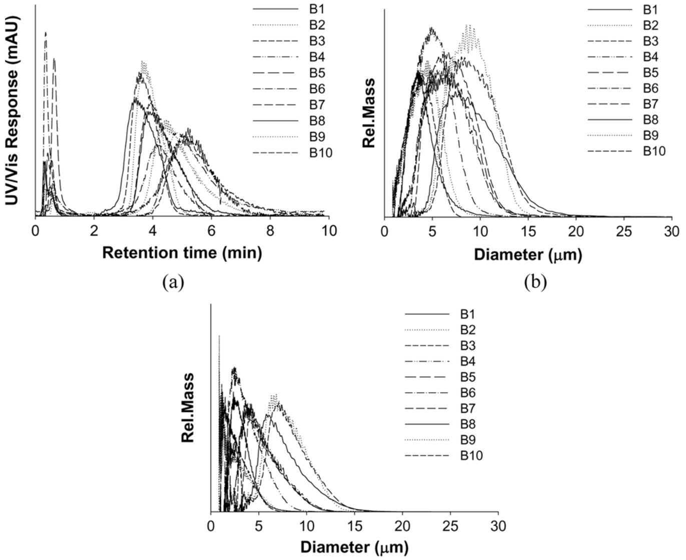
where s is the standard deviation, $\bar{x}$ is the mean value. The mean diameters and the coefficient of variations (CV) determined from the mass and the number based size distributions are listed in Table 2.



(a) (b)

(c)

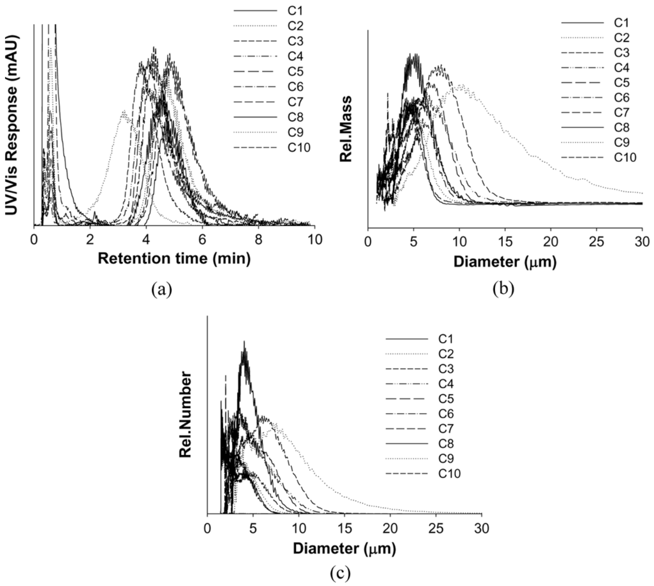
Figure 2. GrFFF fractograms of PS beads in group A (a) and their mass based (b) and number based (c) size distributions obtained at flow rate of 2 mL/min.



(a) (b)

(c)

Figure 3. GrFFF fractograms of PS beads in group-B (a) and their mass based (b) and number based (c) size distributions obtained at flow rate of 2 mL/min.

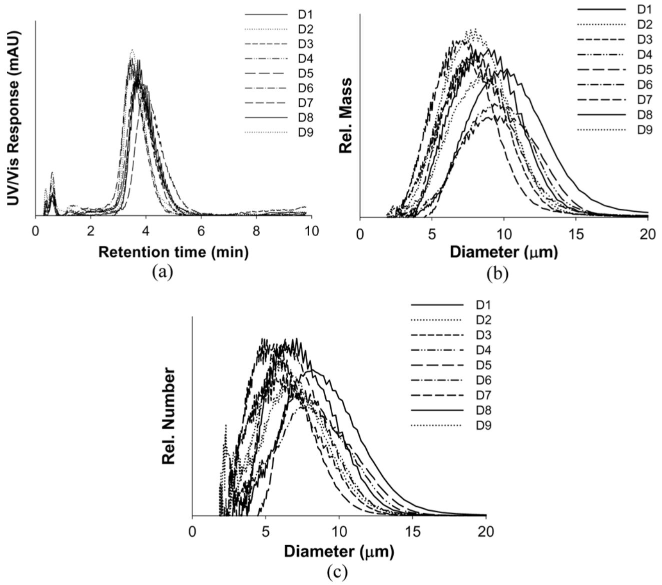


(a)

(b)

(c)

Figure 4. GrFFF fractograms of PS beads in group C (a) and their mass based (b) and number based (c) size distributions obtained at flow rate of 2 mL/min.



(a)

(b)

(c)

Figure 5. GrFFF fractograms of PS beads in group D (a) and their mass based (b) and number based (c) size distributions obtained at flow rate of 2 mL/min.

Table 2. Mean sizes and CV's of mass- and number-based size distributions of four groups of PS beads

Sample		$d_{\mathrm{mean,mass}}{}^{a}$	$\mathrm{CV}_{\mathrm{mass}}{}^{b}$	$d_{\mathrm{mean,no}}{}^{c}$	$\mathrm{CV}_{\mathrm{no}}{}^{d}$
Group A					
A1	Stirring rate (rpm) = 60	7.22	4.28	5.74	5.84
A2	70	5.85	3.13	4.42	3.70
A3	90	6.15	4.72	4.71	5.97
A4	100	5.25	3.26	3.66	5.95
A5	110	7.72	1.95	6.11	4.35
A6	130	5.39	2.11	4.71	5.50
A7	160	5.66	2.20	3.94	6.22
A8	200	6.69	1.45	4.68	5.80
A9	250	6.46	1.62	5.22	4.69
A10	300	7.27	2.74	4.75	4.11
Group B					
B1	AIBN (g) = 0.1	3.53	3.42	2.85	3.06
B2	0.2	3.11	6.61	1.82	2.98
B3	0.3	3.04	0.28	2.09	0.49
B4	0.4	4.26	0.46	3.06	2.71
B5	0.5	5.78	3.26	3.79	5.13
B6	0.6	5.85	3.13	4.43	3.70
B7	0.7	6.39	2.20	4.86	1.15
B8	0.8	8.22	0.09	6.88	0.52
B9	0.9	8.05	3.52	7.12	4.07
B10	1.0	8.68	1.22	7.42	9.91
Group C					
C1	PVP (g) = 1.0	4.97	1.53	4.37	2.58
C2	2.0	11.03	2.83	7.22	4.62
C3	3.0	7.36	4.14	5.48	5.69
C4	4.0	5.85	3.13	4.42	3.70
C5	5.0	5.29	2.03	3.50	5.45
C6	6.0	3.80	4.21	2.26	7.47
C7	7.0	3.86	6.20	2.99	8.85
C8	8.0	3.88	8.82	2.97	9.81
C9	9.0	4.59	9.29	3.39	13.78
C10	10.0	4.41	10.28	2.40	15.66
Group D					
D1	Reaction time (h) = 13.0	8.95	4.99	7.90	1.97
D2	14.0	8.88	0.60	7.86	0.83
D3	15.0	8.57	3.28	7.57	3.24
D4	15.5	9.12	0.34	8.11	2.33
D5	16.0	8.01	1.04	7.14	0.43
D6	16.5	9.14	5.54	7.73	2.44

(*Continued*)

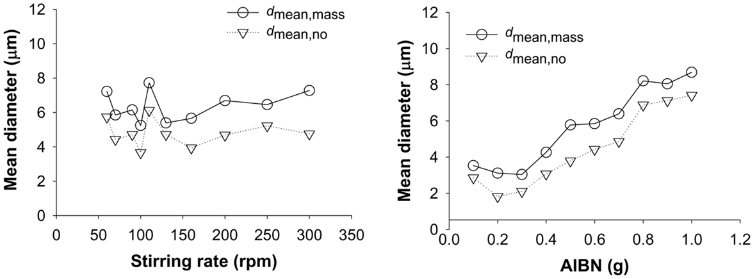
Table 2. Continued

Sample		$d_{\mathrm{mean,mass}}$[a]	$\mathrm{CV}_{\mathrm{mass}}$[b]	$d_{\mathrm{mean,no}}$[c]	$\mathrm{CV}_{\mathrm{no}}$[d]
D7	17.0	9.15	4.96	8.07	4.13
D8	18.0	8.90	2.42	7.70	0.97
D9	24.0	5.85	3.13	4.43	3.70

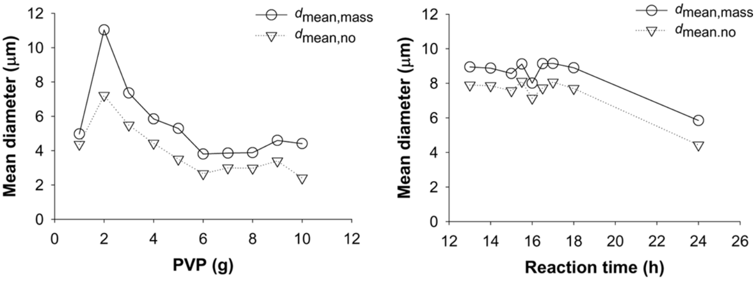
[a] mean diameter.
[b] CV of mass-based size distribution.
[c] mean diameter.
[d] CV of number-based size distribution.

Effects of the four reaction parameters on the mean diameters and CV's are shown in Figures 6 and 7, respectively. As shown in Figure 6(a), no particular trends were observed in the mean diameters with the stirring rate in the range of 60 to 300 rpm. Similar results were observed for CV as shown in Figure 7(a).

Clear trends of increase in the mean sizes with the AIBN concentration was observed as shown in Figure 6(b). On the other hand, no

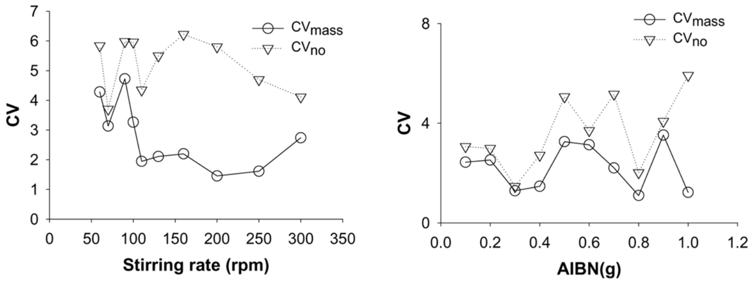


(a) **Group A** (b) **Group B**



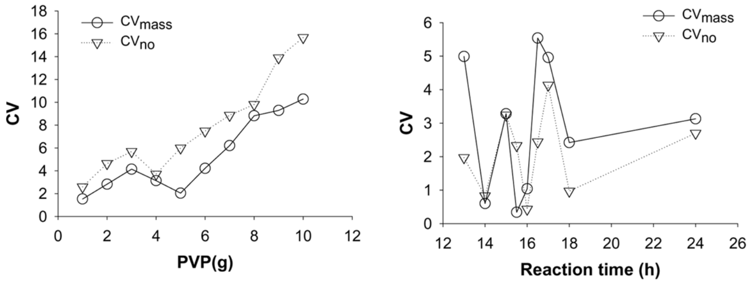
(c) **Group C** (d) **Group D**

Figure 6. Effect of stirring rate (a), concentration of AIBN (b), concentration of PVP (c), and reaction time (d) on mean diameter of emulsion polymerized PS beads.



(a) **Group A**

(b) **Group B**



(c) **Group C**

(d) **Group D**

Figure 7. Effect of stirring rate (a), concentration of AIBN (b), concentration of PVP (c), and reaction time (d) on CV of emulsion polymerized PS beads.

particular trends were observed in CV with the AIBN concentration as shown in Figure 7(b). This finding agrees with the results reported previously,[26] that the size increases with the initiator concentration. These results suggest the particle size can be adjusted by controlling the AIBN concentration without affecting the broadness of the size distribution much.

As shown in Figure 6(c), the mean sizes of both the mass and number based size distributions tend to decrease as the PVP concentration increases, while the CV tends to increase as shown in Figure 7(c). Among the four reaction parameters, the PVP concentration is the only one that affects CV with a clear trend. Results indicate the PVP concentration needs to be kept as low as possible to obtain polymer beads with narrow size distribution. As shown in Figure 6(d) and 7(d), no particular trends were observed in the mean diameter and CV with the reaction time.

Figure 8 shows the size distributions obtained for the same sample (A5) by three different methods: GrFFF, photon-correlation spectroscopy (PCS), and optical microscopy (OM). The GrFFF result was obtained by converting the fractogram to the number based size distribution as explained above. The results from PCS and OM are presented in

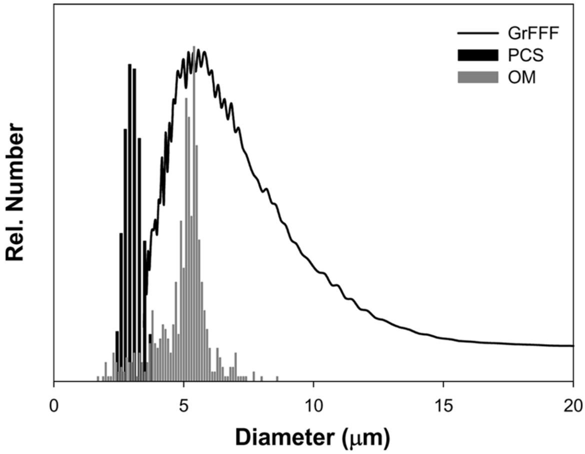


Figure 8. Size distributions determined by GrFFF, PCS and OM for PS beads A5.

histograms. Among the results from the three different methods, the OM result could be considered to be the most accurate as long as the population of the measured particles is large enough to make the histogram continuous. For the OM measurement shown in Figure 8, 622 particles were measured, which required a few hours to complete. It is noted that the OM histogram is still not continuous. The mean diameter obtained by OM was 5.0 μm. The mean diameter from GrFFF was 6.1 μm, which is closer to the OM data than the PCS data (3.1 μm). Similar results were observed for other PS latex beads.

PCS is widely used for measuring the particle size in the range from a few nanometers up to a few micrometers. Usually PCS provides accurate sizes for particles having relatively narrow size distributions.[27] It has been reported, however, that the size measurements by PCS may not be accurate for particles whose size distributions are broad or sultimodal.[28,29]

It is noted in Figure 8, that the size distribution obtained by GrFFF is significantly broader that that by OM, probably due to the zone broadening during separation in the GrFFF channel. The zone broadening must be kept as low as possible because it could cause the GrFFF result to be inaccurate.

CONCLUSION

Results show GrFFF is a useful tool for size analysis of micron-sized latex beads. GrFFF provides some advantages over existing techniques, such as PCS or OM. GrFFF analysis is much faster (less than 10 min) than OM (a few hours at least), and GrFFF data may be more accurate than PCS data, particularly for those having broad size distributions. Unlike PCS or OM, GrFFF provides separation of the particles, allowing collection of a slice of the fractogram for further in depth analysis. Also GrFFF is less expensive to set up, and easy to operate.

It is noted that the size data reported in this study may not be accurate because of the zone-broadening. Particular care must be taken to minimize the zone broadening to make the GrFFF data more reliable.

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