Macromolecules **2004,** *37,* 1319−1323

One-Step Batch Synthesis of High Solids Monodisperse Styrene/Glycidyl Methacrylate and Styrene/Methacrylic Acid Emulsion Copolymers

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Received July 12, 2003; Revised Manuscript Received November 11, 2003

ABSTRACT: Surfactant-free emulsion copolymerizations of styrene (St) with glycidyl methacrylate (GMA) and styrene (St) with methacrylic acid (MAA), initiated by either potassium or ammonium persulfate, have been carried out to assess the possibility of making monodisperse latices of relatively high solids content (∼30−50 wt %) in a one-step batch process. Evaluation of the effect of the functional comonomer content in the range 2−40 wt % and the latex solids content in the range 2−33 wt % has allowed identification of compositions which do indeed allow monodisperse particles to be prepared at solid contents up to 33 wt % in a one-pot process. In addition, a monodisperse sample with both epoxy and carboxylic acid functionalities has been successfully prepared at 33 wt % solids contents.

Introduction

In the course of our continuing work on novel polymer supports[1] and their exploitation, we required some functional monodisperse latex particles as starting materials. Styrene/glycidyl methacrylate and styrene/methacrylic acid copolymers seemed ideal candidates for us, and we were aware that monodisperse latex particles were accessible via controlled surfactant-free polymerizations.[2] Furthermore, the high cost of commercially available monodisperse samples encouraged us to develop our own synthetic methodologies. Interestingly, the literature relevant to our particular targets[3−5] suggested that very narrow particle size distributions could be best maintained in a one-step process by working at low solids content, typically less than 10 wt %. Since our demands were for much higher solids content than these, our initial strategy was to follow the literature precedent for synthesizing monodisperse systems and to generate increased solids by removal of water by for example centrifugation and decantation. However, we required relatively large quantities of latex particles (∼50 g) and hence needed to centrifuge large volumes of emulsions generally at very high speeds in a large centrifuge. In the event this strategy proved tedious, prompting us to examine the possibility of producing higher solids monodisperse latex particles in a one-step batch process. We were encouraged to believe that this might be possible by a report of semibatch emulsion copolymerizations of butyl acrylate and (meth)acrylic acid which yielded final solids contents of ∼40 wt % of particles with a relatively narrow size polydispersity index.[6] No images of these products were shown, however. Other monodisperse samples up to 40 wt % and narrow polydisperse samples up to 55 wt % have also been reported for other systems exploiting a dilute monodisperse latex seed.[7−9]

Experimental Section

Materials. Styrene (St), methacrylic acid (MAA), and glycidyl methacrylate (GMA) were from Aldrich and were distilled and stored at 8 °C. The water used was distilled following deionization. All other materials were of analytical grade and were used as supplied.

Surfactant-Free Emulsion Polymerizations. These were carried out as follows. Purified water (150 or 175 mL) was added to a four-necked jacketed glass reactor (250 mL) fitted with a nitrogen bubbler, an overhead D-shaped stirrer paddle, and a condenser. Nitrogen was bubbled through the water until the system reach thermal equilibrium at the desired reaction temperature, heat being supplied by circulating appropriately thermostated hot water through the reactor jacket. Appropriate masses of each comonomer (St and GMA or St and MMA) were then added to target the solids content (wt %) of the desired latex (e.g., 33% solids content requires 37.13 g of St and 12.38 g of MAA in 150 mL of water). The mixture was stirred vigorously at 430 rpm while being purged with nitrogen for 15 min. The required quantity of initiator dissolved in a small known amount of water was then added, and the flow of nitrogen reduced through the bubbler to minimize the stripping of monomer from the reaction mixture. No additional salts or buffer were added. The stirrer speed was adjusted to 350 rpm, and the mixture was then left at constant temperature for 24 h before it was cooled to room temperature and the milky fluid filtered through glass wool to remove any coagulum.

For the St/GMA copolymers the reaction temperature was 65 °C and the initiator used was potassium persulfate (2.07×10^{-3} M), and for the St/MAA copolymers the reaction temperature was 70 °C and the initiator was ammonium persulfate (1.40×10^{-3} M).

Latex Characterization. A sample of each latex was centrifuged at 9000 rpm for 30 min and then washed with distilled water. After repetition of this the particles were dried overnight in a vacuum oven at 50 °C. The size and superficial morphology of the latex particles were estimated by transmission electron microscopy (TEM) using a JEOL 1200 microscope. FTIR spectra were recorded on a Perkin-Elmer Spectrum 1 employing a diamond compression cell. Elemental microanalyses were carried out on a Perkin-Elmer 2400 elemental analyzer.

Results and Discussion

Surfactant-Free Polymerizations. Previous work[3,4] on surfactant-free emulsion copolymerization of St and GMA showed that the particle morphology and size and size distribution are influenced by many factors including the concentration of initiator, the ionic strength of

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10.1021/ma030380j CCC: $27.50

Table 1. St/GMA and St/MAA Latex Copolymer Compositions[a]

latex	comonomer feed (wt %) St	comonomer feed (wt %) GMA	comonomer feed (wt %) MAA	copolymer composition (wt %)[b] St	copolymer composition (wt %)[b] GMA	copolymer composition (wt %)[b] MAA	particle size (nm)[c]
1	98	2		93	7		250
2	84.5	15.5		80	20		270
3	60	40		58	42		310
4	98		2	86		14	185
5	90		10	81		19	150
6	75		25	71		29	140
7	60		40	57		43	120

[a] 11% solids content. [b] Determined from C and H wt %. [c] ±10 nm estimated from TEM micrographs.

the aqueous phase, the comonomer concentration, and the ratio of comonomers. GMA contents from ~15 to 72 wt % and solids content from ~4 to 12 wt % were examined. On the basis of this work and our need for small emulsion particles, we chose potassium persulfate as the initiator used at a concentration of 2.07×10^{-3} M, GMA contents of 2−40° wt %, and solids content of 2−33 wt %. Earlier work[5] with St and MAA copolymers employed ~10 wt % MAA and a solids content of ~11 wt %. Guided by this, we chose ammonium persulfate as the initiator used at a concentration of 1.40×10^{-3} M, and we extended the MAA composition range to 2−40 wt % and the solids content to 2−33 wt %. We restricted our studies to an upper limit of 33 wt % solids content because preliminary experiments demonstrated that the viscosity of latices with solids content above ~33 wt % was too high for the application we had planned for these materials. We also anticipated that levels of coagulum might become unacceptable at much higher solids content.

In all cases the emulsion polymerizations appeared superficially successful to the naked eye, and the level of coagulum was consistently very low for latices up 11 wt % solids content. For the 25 wt % targeted solids content ~4 g of coagulum was recovered from ~40 g of monomers, and for the 33 wt % target ~5 g of coagulum was obtained from ~50 g of monomers. The targeted solids content were therefore reasonably well met. The copolymer composition was estimated from the experimentally determined wt % C and H, and the results for a series of copolymer latices each prepared with 11 wt % solids content are shown in Table 1. The correlation with the feed compositions is much better at the higher GMA and MAA contents than at the lower levels, with the elemental microanalysis derived data for the lower compositions always being higher than the feed values. This most likely arises from residues of water in the products. This would be expected to reduce the apparent wt % C and hence enhance the apparent GMA or MAA content. Bearing in mind the likely error in assessing the copolymer composition from these data, the correlation with the comonomer feed values is relatively good, and certainly the trends in targeted compositions are clearly visible. Analysis of the FTIR spectra of these copolymers allowed an independent assessment of the compositional data. For the St/GMA copolymers the carbonyl band at 1728 cm^{-1} was taken as indicative of the GMA content and the bands at 1453 and 1493 cm^{-1} as characteristic of the St content. The respective absorbance values of these bands are shown in Table 2. Similarly, the band at 1698 cm^{-1} in the spectra of the St/MAA copolymers was taken as indicative of the MAA content, and the respective intensity ratios with the St bands are also shown in Table 2. While these data do not show a direct proportionality between the GMA and MAA content in respective St copolymers and the corresponding intensity ratios of the characteristic FTIR bands, the trends in composition are clearly indicated and provide confirmatory evidence for the incorporation of each of the methacrylic comonomers. In the case of the St/MAA copolymers titration of the carboxylic acid functionalities would allow a more quantitative correlation as would ^{1}H NMR spectroscopic analysis of a solubilized sample. Likewise, chemical analysis of the epoxide content in the St/GMA copolymers might be more accurate via reaction with an amine, though some epoxy groups may be consumed during polymerization with formation of a cross-linked architecture.

Particle Morphology Evaluation by TEM. Figure 1 shows the TEM images of latices 1−7 prepared with 11 wt % solids content. For the St/GMA copolymers 1−3 though the particle diameters are reasonably uniform in each case, latex 1 with 2 wt % GMA and latex 3 with 40 wt % GMA are not perfectly spherical and indeed in the latter case appear to have a rough surface. However, latex 2 with 15.5 wt % GMA contains perfectly smooth and spherical particles. These results parallel those reported earlier.[4] For the St/MAA copolymer latices 4−7 again the particle diameters are reasonably uniform, and again the smoothest and most spherical materials are present in latices 5 and 6 with intermediate MAA contents of 10 and 25 wt %. Latex 4 with 2 wt % MAA has particles with a relatively irregular morphology, and latex 7 with 40 wt % MAA shows some evidence of the loss of perfect spherical symmetry in its particles.

Particle Size Variation. Very interesting variations in particle diameter, measured directly from the TEM images, arise with both sets of copolymers. In the case of the St/GMA system the particle diameter rises linearly with wt % GMA, and for the St/MAA system the particle diameter falls linearly with wt % MAA (Figure 2). The increase in diameter with GMA content is difficult to rationalize. A higher GMA content would provide a higher polar content in the latex which might be expected to favor stabilization of smaller particles, especially if some hydrolysis of epoxide groups occurs as may indeed be possible. However, free radical ring opening of a low level of epoxide groups during emulsion polymerization is also possible, potentially introducing cross-links and this may be of significance in controlling the particle size. The observed trend is however in

Table 2. FTIR Spectral Data for St/GMA and St/MAA Latex Copolymers[a]

latex	GMA feed/found (wt %)	intensity ratio FTIR bands 1728/1493 cm^{-1}	intensity ratio FTIR bands 1728/1453 cm^{-1}	latex	MAA feed/found (wt %)	intensity ratio FTIR bands 1698/1493 cm^{-1}	intensity ratio FTIR bands 1698/1453 cm^{-1}
1	2/7	0.71	0.68	4	2/14	0.48	0.48
2	15.5/20	1.13	1.06	5	10/19	0.97	0.97
3	40/42	1.33	1.16	6	25/29	1.08	1.07
				7	40/43	1.21	1.08

[a] 11 wt % solids content.

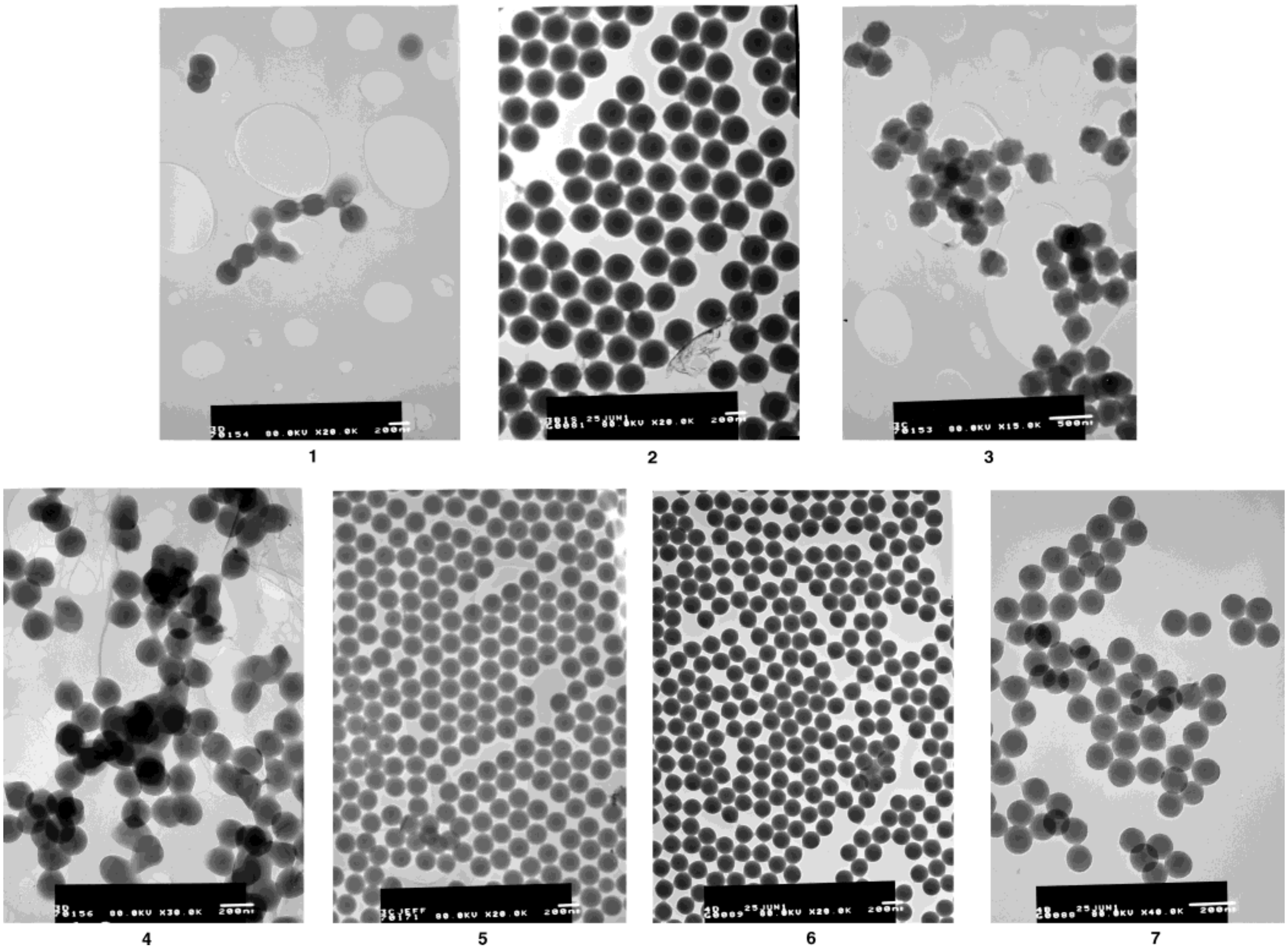

Figure 1. Transmission electron micrographs of latices 1−7 prepared with 11 wt % solids (see Table 1). Bar shows the scale in each case.

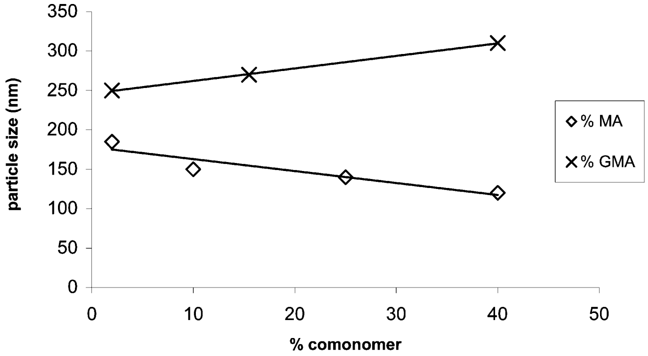

Figure 2. Variation of latex particle diameter with wt % of GMA and MAA in feeds of St/GMA and St/MAA surfactant-free emulsion polmerisation of 11 wt % solids content.

agreement with earlier work involving GMA[4] and is similar to the behavior observed with monodisperse homopolystyrene latices.[2] The fall in size of particles with increase in MAA content is more readily rationalized and probably arises because the carboxylic acid groups in the MAA segments provide enhanced stabilization of smaller particles. Overall, the different behavior of GMA and MAA containing latices allows particles to be prepared over the size range 120−310 nm (Table 1).

Effects of Solids Content. For our own particular needs, to be reported in due course, the solids content was a key parameter, with our target being to produce monodisperse latices with as high a solids content as possible while retaining reasonably low viscosity. Repeating the syntheses of the most uniform latices produced at 11 wt % solids (i.e., latices 2 (GMA 15.5 wt %), 5 (MMA 10 wt %), and 6 (MAA 25 wt %)), each at a solids content of 33 wt %, yielded the latex particles 8−10 shown in Figure 3. Latex 8 with 15.5 wt % GMA shows a broadening in particle size distribution (320−640 nm) and likewise latex 9 with 10 wt % MAA yields particles in the range 145−430 nm. However, latex 10 with 25 wt % MAA is essentially monodisperse (200 ± 10 nm) albeit that there is evidence of some loss of a perfectly spherical morphology.

Since the St/MAA copolymer with 25 wt % MAA yields particles with diameter of 140 nm at 11 wt % solids and 200 nm at 33 wt % solids, it was of interest to prepare latices of other solid content with the same MAA content. Accordingly, latices 11−13 were prepared at 2, 5, and 25 wt % solids content each with an MAA content of 25 wt %. All three of these proved to be monodisperse (Figure 4) with particle sizes of respectively 95, 125, and 155 ± 10 nm. Once again therefore a linear relationship emerges this time in the variation of particle diameter with latex solids content for copolymers of St/MAA with 25 wt % MAA (Figure 5). These data yield an empirical relationship for the diameter, d, of

$$d = 2.77 \times (\text{wt \% solids content}) + 101$$

Interestingly, a similar increase in particle size with

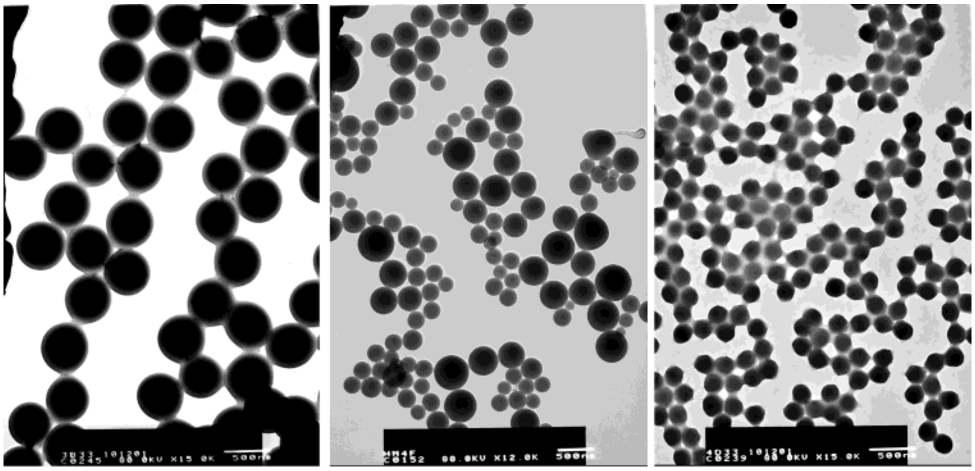
8 9 10

Figure 3. Transmission electron micrographs of St/GMA latex 8 with 15.5 wt % GMA and St/MAA latices 9 and 10 with 10 and 25 wt % MAA, respectively, each prepared with 33 wt % solids content. Bar shows the scale in each case.

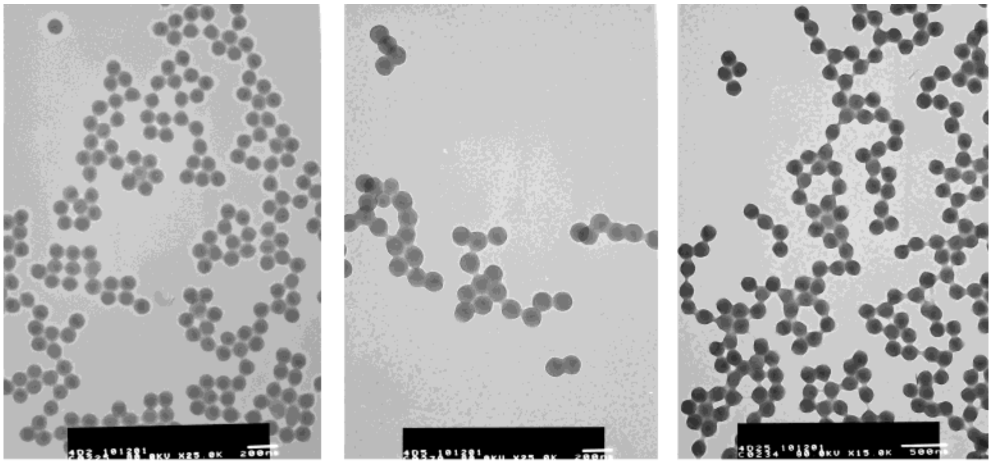
11 12 13

Figure 4. Transmission electron micrographs of St/MAA latices 11−13 with 25 wt % MAA and solids content respectively of 2, 5, and 25 wt %

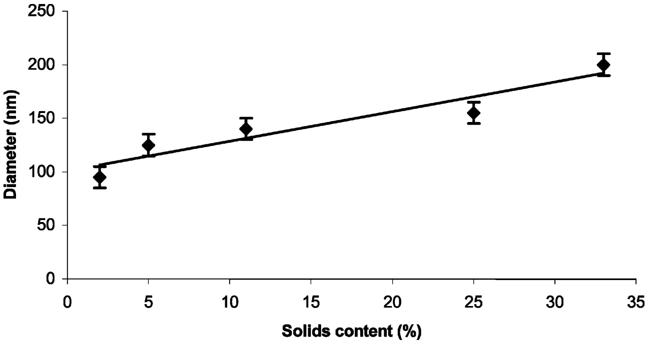

Figure 5. Variation of latex particle diameter with solids content in St/MAA (MAA 25 wt %) surfactant-free emulsion polymerizations.

solids content has also been reported for GMA-containing latices.[4]

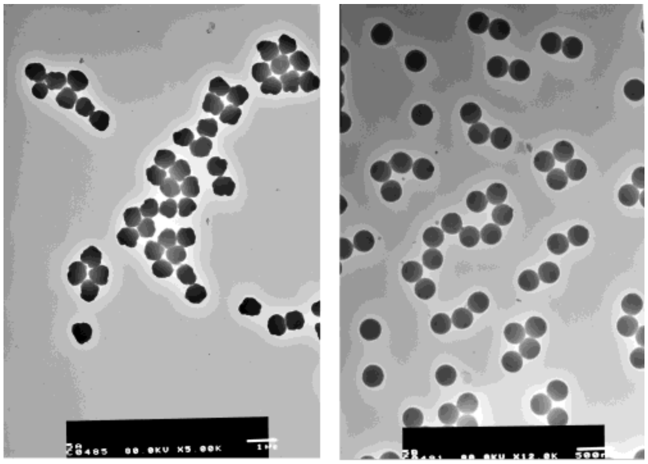
14 15

Figure 6. Transmission electron micrographs of St/MMA/GMA difunctional latex 14 with 12.5 wt % MAA and 12.5 wt % GMA and latex 15 with 5 wt % MAA and 20 wt % GMA each prepared in surfactant-free emulsion polymerizations with 33 wt % solids content.

Difunctional Latex. Since both epoxy and carboxylic acid function containing monodisperse latices were prepared at high solids contents, it was of interest to assess whether a difunctional species could also be prepared with a narrow particle size distribution and at high solids. Accordingly, latices 14 and 15 were prepared with compositions St/MAA/GMA of 75/12.5/12.5 and 75/5/20 wt % each at 33 wt % solids content (Figure 6). Latex 14 was of rather narrow particle size distribution (625 ± 10 nm) but had an irregular morphology. Latex 15 was smaller, monodisperse (250 ± 10 nm), and with good spherical symmetry. The presence of both methacrylate comonomers in the copolymer was shown in the FTIR spectrum of the product, and such materials offer considerable scope for further chemical modification.

Conclusions

St/GMA and St/MAA copolymer latices have been prepared in one-step batch surfactant-free emulsion polymerizations. Copolymer compositions in the range 2−40 wt % of methacrylate comonomers have been explored, along with variations in solids content between 2 and 33 wt %. With appropriate compositions monodisperse emulsion particles can be obtained even at a solids content of 33 wt %. Latex particle diameter increases linearly with GMA content and decreases linearly with MAA content, in polymerizations performed at 11 wt % solids content. St/MAA latices with 25 wt % MAA show a linear increase of particle diameter with solids content up to 33 wt %. Finally, monodisperse St/MAA/GMA difunctional latices can be prepared at 33 wt % solids content by appropriate choice of MAA and GMA feed.

The ability to synthesize monodisperse latices at high solids content in a simple one-step batch procedure provides a convenient source of concentrated particles of uniform size for exploitation in solid support applications. We will report further in this context in due course.

Acknowledgment. We thank Dr. D. W. McComb for arranging the TEM analyses, and we acknowledge the receipt of a postdoctoral fellowship from Amersham Biosciences for H.M.

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MA030380J