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Synthesis of Sterically-Stabilized Latexes Using Well-Defined Poly(glycerol monomethacrylate) Macromonomers

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ABSTRACT: A range of well-defined methacrylic macromonomers based on glycerol monomethacrylate (GMA) has been synthesized by atom transfer radical polymerization (ATRP) in alcoholic media using an *N*-(dimethylamino)ethyl-2-bromoisobutyrylamide initiator. This tertiary amine-functionalized initiator was used to produce six homopolymer precursors with target degrees of polymerization of 20, 30, 40, 50, 60, and 70 via ATRP. These polymerizations proceeded to very high conversions (> 95%) and afforded relatively low polydispersities ($M_w/M_n \leq 1.33$). The tertiary amine end groups were then quaternized using 4-vinylbenzyl chloride (4-VBC) to afford the corresponding near-monodisperse styrene-functionalized PGMA macromonomers. These PGMA macromonomers were evaluated as reactive steric stabilizers for latex syntheses. Near-monodisperse submicrometer-sized and micrometer-sized polystyrene latexes were obtained by aqueous emulsion and alcoholic dispersion polymerization, respectively, as judged by scanning electron microscopy and dynamic light scattering studies. Attempted latex syntheses conducted in the absence of any macromonomer invariably resulted in macroscopic precipitation under dispersion polymerization conditions, with no evidence of latex formation. Higher molecular weight macromonomers (DP = 40 or 50) generally gave smaller, more monodisperse particles compared with the lower molecular weight macromonomers (DP = 20 or 30). Latex syntheses conducted in the presence of the $PGMA_{50}$ homopolymer precursor produced particles with significantly larger diameters than those prepared with the corresponding styrene-functionalized $PGMA_{50}$ macromonomer. Such control experiments confirmed the importance of having terminal styrene groups on the macromonomer chains for successful latex formation. FT-IR spectroscopy indicated the presence of the $PGMA_{50}$ macromonomer within the polystyrene latex and XPS studies indicated that these stabilizer chains are located at (or very near) the latex surface, as expected. Finally, approximately micrometer-sized latexes can be produced by aqueous dispersion polymerization of 2-hydroxypropyl methacrylate in the presence of the $PGMA_{50}$ macromonomer.

Introduction

Polymer latexes have a wide range of commercial applications ranging from coatings and adhesives to binders and foams.[1] Conventional surfactants such as sodium dodecyl sulfate are commonly used as stabilizers to prepare such latexes.[2] However, such physically adsorbed small molecules are relatively mobile and tend to migrate toward interfaces within latex films.[3,4] This phenomenon can be detrimental to the physical properties of such films.[5] The problem of surfactant migration can be solved by the use of polymerizable surfactants or macromonomers, which become chemically grafted onto latex particles during polymerization.[6] The benefits of reactive stabilizers in heterophase polymerization have been known for some time.[7,8] Such sterically-stabilized latexes are particularly resistant toward destabilization induced by high shear or electrolyte addition and typically exhibit good freeze−thaw stability.[9,10]

There are two general routes to vinyl-capped macromonomers. The first route involves using a suitable vinyl-functionalized initiator, and the second route is based on the postpolymerization modification of the polymer chain ends. The former route was exploited by Lascelles et al.,[11] who conducted the oxyanionic polymerization of tertiary amine methacrylates in THF using a potassium 4-vinylbenzyl alkoxide initiator. Similarly, atom transfer radical polymerization (ATRP) has been used to prepare both hydrophilic and hydrophobic macromonomers using allyl-, vinyl acetate-, and vinyl ether-based initiators.[12−14] Although the use of vinyl-functionalized initiators offers an attractive one-pot route to macromonomers, the choice of vinyl group is often rather limited because it must not participate in the polymerization. A potentially more versatile route is postpolymerization modification of the polymer chain ends, allowing for a larger range of different macromonomers. For example, ATRP has been used to prepare macromonomers by postpolymerization reaction of the terminal bromine group with either acrylic or methacrylic groups.[15] An alternative strategy is to modify the initiator group in a second step after the in situ polymerization, so as to afford a polymerizable end group.[16−21] This approach clearly requires facile chemistry but can lead to higher efficiencies than those achieved by substitution of terminal halogen atoms because the fidelity of the halogen functionality is often compromised under monomer-starved conditions. Recently, we reported the preparation of macromonomers by a combination of ATRP and click chemistry.[22] An azido α-functionalized ATRP initiator was used to produce well-defined homopolymers with terminal azide functionality. These homopolymer precursors were then efficiently clicked using either propargyl methacrylate or propargyl acrylate to yield near-monodisperse (meth)acrylate-capped macromonomers. Other research groups have reported similar syntheses.[23,24]

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Very recently, we reported the preparation of polystyrene latexes using near-monodisperse macromonomers ($M_w/M_n \approx 1.2$ to 1.3) based on a biomimetic monomer, 2-(methacryloyloxy)ethyl phosphorylcholine (MPC).[25] The synthesis of these well-defined MPC-based macromonomers involved two steps: (i) ATRP of MPC using a tertiary amine-functionalized initiator and (ii) quaternization of the tertiary amine chain ends using excess 4-vinylbenzyl chloride (4-VBC) in methanol at room temperature. However, this strategy only proved to be effective for relatively low molecular weight (target degree of polymerization < 35) macromonomers: if higher molecular weight macromonomers (target degree of polymerization > 40) were targeted, then substantial loss of control during the ATRP of MPC was observed and only rather polydisperse precursors were obtained ($M_w/M_n \approx 1.6$ to 2.0). In the present work, we have extended this macromonomer route to include a second hydrophilic methacrylic monomer, glycerol monomethacrylate (GMA). We have previously polymerized GMA to high conversions with reasonable control ($M_w/M_n < 1.30$) via ATRP in methanol at 20 °C.[26]

PGMA chains are known to be good anchoring blocks for the synthesis of sterically-stabilized magnetite nanoparticles.[27] GMA has also been used for the synthesis of various types of shell cross-linked (SCL) micelles.[28] In this context, PGMA blocks can be readily cross-linked with divinyl sulfone in aqueous alkaline solution or converted into polyacid blocks via esterification using succinic anhydride.[29] PGMA can also act as the coronal steric stabilizer of SCL micelles.[30] In addition, Rimmer and coworkers have utilized the highly hydrophilic character of GMA for the preparation of biocompatible amphiphilic hydrogel networks.[31] Unlike the unexpected synthetic limitations observed for the MPC-based macromonomers previously reported,[25] in the present work, we demonstrate good control over the ATRP of GMA for target degrees of polymerization ranging from 20 to 70. The resulting series of six near-monodisperse PGMA macromonomers was evaluated for the synthesis of sterically-stabilized polystyrene latex using either aqueous emulsion or alcoholic dispersion polymerization and also for the synthesis of sterically-stabilized poly(2-hydroxypropyl methacrylate) latex using aqueous dispersion polymerization.

Experimental Details

Materials. GMA and 2-hydroxypropyl methacrylate were kindly donated by Cognis Performance Chemicals (Hythe, U.K.) and used without further purification. 4-Vinylbenzyl chloride (90%), Cu(I)Cl (99.995%), and 2,2′-bipyridine (bpy, 99%) were purchased from Aldrich and were used as received. Styrene (Aldrich) was passed through a column of basic alumina to remove inhibitor and then stored at −20 °C prior to use. 2,2′-Azobisisobutyronitrile (AIBN; BDH) and 2,2′-azobis(isobutyramidine) dihydrochloride (AIBA; 97%; Aldrich, U.K.) were used as received. Methanol was purchased from Fisher and was used as received. Deionized water was used in all experiments. Silica gel 60 (0.0632−0.2 mm) was obtained from Merck (Darmstadt, Germany). NMR solvents (D_2O, CD_3OD, $CDCl_3$, and d_5-pyridine) were purchased from Fisher.

Synthesis of 2-(Dimethylamino)ethyl-2-bromoisobutyrylamide ATRP Initiator. *N*,*N*-Dimethylethylenediamine (6.00 g, 0.068 mol), triethylamine (27.27 g, 0.27 mol), and dichloromethane (120 mL) were placed in a 500 mL three-necked round-bottomed flask and purged with nitrogen for 30 min. A white precipitate of triethylammonium bromide was formed upon the addition of 2-bromoisobutyryl bromide (15.49 g, 0.067 mol) to this reaction mixture, which was stirred for a further 5 h at 20 °C. The precipitate was removed by filtration, and the reaction solution was washed three times with $NaHCO_3$ solution and dried over $MgSO_4$. The dichloromethane was removed under reduced pressure to afford a pale-brown liquid (11.5 g; 72% yield). ^{1}H NMR (400 MHz, CD_3OD, δ): 1.88 (6H, s, 2 × CH_3), 2.26 (6H, s, $N(CH_3)_2$), 2.45 (2H, t, $J = 7.0$ Hz, $(CH_3)_2NCH_2$), 3.31 (2H, t, $J = 7.0$ Hz, $CH_2NHCOO(CH_3)_2Br$).

Homopolymerization of GMA via ATRP. 2-(Dimethylamino)-ethyl-2-bromoisobutyrylamide (0.300 g, 1.25 mmol), bpy (0.390 g, 2.5 mmol), and GMA (10.0 g, 62.4 mmol) were weighed into a 25 mL round-bottomed flask and degassed. Methanol (12 mL) was degassed and transferred to the reaction solution under nitrogen. The Cu(I)Cl catalyst (0.120 g, 1.25 mmol) was added to the stirred solution, which turned dark brown, indicating the onset of polymerization. After 24 h, the reaction solution was diluted with methanol and passed through a silica column to remove the spent Cu(II) catalyst. The product was then dried on a vacuum line overnight to afford a white powder (8.0 g; 77% yield).

Quaternization of PGMA Homopolymer Precursor. The $PGMA_{50}$ homopolymer (7.00 g, 0.85 mmol) was dissolved in methanol (20 mL). 4-Vinylbenzyl chloride (0.430 g, 2.55 mmol; 4-VBC/polymer molar ratio = 3:1) was added, and the reaction solution was stirred at room temperature for 48 h. The excess solvent was removed under reduced pressure, and the resulting solid was dissolved in water. The excess 4-vinylbenzyl chloride was extracted three times with cyclohexane. The aqueous solution was then freeze-dried from water overnight to afford a white powder (6.0 g; 84% yield).

Aqueous Emulsion Polymerization of Styrene. $PGMA_{50}$ macromonomer (0.50 g) was weighed in a 100 mL round-bottomed flask and dissolved in water (44.5 g). This solution was purged with nitrogen for 30 min before being heated to 70 °C under a nitrogen blanket. The AIBN initiator (0.050 g) was dissolved in styrene (5.0 g) and purged with nitrogen before being injected into the reaction vessel. The solution turned milky white within 1 h and was stirred for 24 h at 70 °C. The latexes were purified by three centrifugation/redispersion cycles, replacing each successive supernatant with pure water.

Alcoholic Dispersion Polymerization of Styrene. $PGMA_{50}$ macromonomer (0.50 g) was weighed into a 100 mL three-necked round-bottomed flask fitted with a condenser and nitrogen inlet and dissolved in 44.5 g of a 90:10 mixture of methanol/water. This solution was purged with nitrogen for 30 min before being heated to 70 °C under a nitrogen blanket. AIBN initiator (0.050 g) was dissolved in styrene (5.00 g) and purged with nitrogen before being injected into the reaction vessel. The solution turned milky white within 1 h and was stirred for 24 h at 70 °C. The latexes were purified by three centrifugation/redispersion cycles replacing each successive supernatant with the methanol/water mixture, followed by an additional three redispersion cycles using pure water.

Aqueous Dispersion Polymerization of 2-Hydroxypropyl Methacrylate. $PGMA_{50}$ macromonomer (0.50 g) was placed into a 100 mL round-bottomed flask, along with HPMA monomer (5.00 g) and water (44.5 g). The reaction vessel was degassed by five evacuation/nitrogen purge cycles and subsequently heated to 70 °C. AIBA initiator (0.050 g) was dissolved in water (5.0 g) and purged with nitrogen before being injected into the reaction vessel at 70 °C. The reaction turned milky white within 1 h and was stirred for 24 h before being allowed to cool to room temperature. The resulting PHPMA latexes were purified by three centrifugation/redispersion cycles, replacing each successive supernatant with deionized water.

Freeze−Thaw and Salt Stability Experiments. Selected PMPC-PS latexes (10.0 w/v % solids content) were frozen at −20 °C and then allowed to thaw at room temperature. Flocculation was judged by visual inspection and confirmed by DLS measurements. Various PGMA-PS latexes (1.0 mL; 2.0 w/v % solids content) were transferred via pipet to sample vials to which 1.0 mL aliquots of various aqueous $MgSO_4$ solutions were added (0.02 to 1.00 M). This dilution produced 1.0% aqueous latex dispersions in 0.01 to 0.50 M $MgSO_4$. Colloidal (in)stability was again judged by visual inspection and confirmed by DLS measurements.

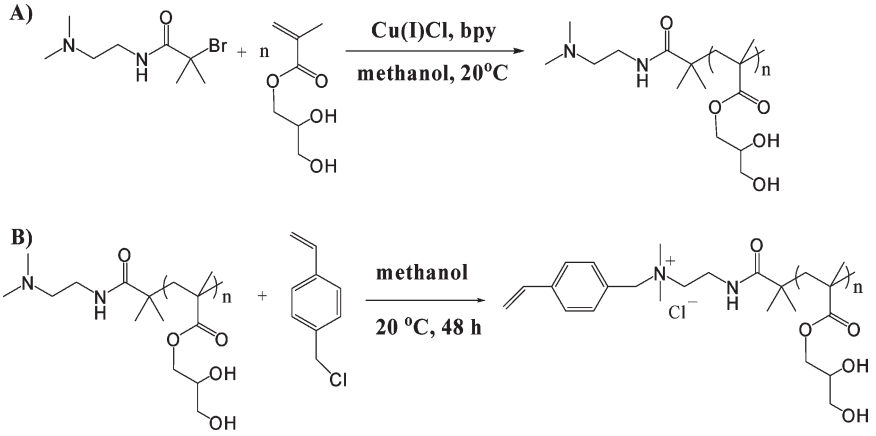

Figure 1. Two-step synthesis of $PGMA_n$ macromonomers: (a) ATRP of GMA monomer at 20 °C in methanol for 16−24 h; (b) postpolymerization quaternization of tertiary amine end groups with 4-vinylbenzyl chloride at 20 °C.

Table 1. Conversion and Molecular Weight Data for PGMA Homopolymer Precursors Synthesized at 20 °C in Methanol and the Degrees of Quaternization for the Corresponding $PGMA_n$ Macromonomers Achieved Using 4-VBC in Methanol in 20 °C (4-VBC/Amine Molar Ratio = 3.0 in Each Case)[a]

target DP	conversion (%)	DP (NMR)	M_n (GPC)	M_w/M_n (GPC)	degree of quaternization (%)
20	100	22	20 000	1.19	99
30	100	32	32 000	1.27	100
40	100	38	41 700	1.25	99
50	99	53	49 000	1.21	100
60	100	62	57 700	1.24	100
70	100	72	64 700	1.33	100

[a] GPC data were obtained using poly(methyl methacrylate) standards.

Polymer Characterization

^{1}H NMR Spectroscopy. All ^{1}H NMR spectra were recorded in $CDCl_3$, D_2O, CD_3OD, or d_5-pyridine using a 400 MHz Bruker Avance-400 spectrometer.

FT-IR Spectroscopy. Each sample (1.0 mg) was ground up with 150 mg of KBr to afford a fine powder and compressed into a pellet by applying a pelletization pressure of 8 tonnes for 10 min. The FTIR spectra were recorded using a Nicolet Magna (series II) spectrometer at 4.0 cm^{-1} resolution, and 64 scans were recorded per spectrum.

Gel Permeation Chromatography (GPC). The molecular weights and polydispersities of the $PGMA_n$ homopolymer precursors were determined by DMF GPC at 70 °C. The GPC setup comprised three Polymer Laboratories PL gel 10 μm MIXED-B columns in series with a Viscotek TriSEC model 302 refractive detector. The flow rate was 1.0 mL min^{-1}, and the mobile phase contained 10 mmol LiBr. Ten near-monodisperse poly(methyl methacrylate) standards (M_p = 2000−300 000 g mol^{-1}) were used for calibration. Data were analyzed using Viscotek TriSEC 3.0 software.

Dynamic Light Scattering (DLS). The intensity-average hydrodynamic diameter of each latex was obtained by DLS using a Malvern Zetasizer NanoZS instrument. Aqueous solutions of 0.01 w/v % latex were analyzed using disposable plastic cuvettes, and results were averaged over three consecutive runs. Deionized water used to dilute each latex was ultrafiltered through a 0.20 μm membrane to remove dust.

Disk Centrifuge Photosedimentometry (DCP). The weight-average diameters (D_w) of the polystyrene latexes were measured using a CPS disk centrifuge photosedimentometer model number DC24000. Samples of ~0.1% (0.10 mL) were injected in an aqueous spin fluid consisting of a sucrose gradient (15 mL). The gradient for polystyrene samples was from 2 to 8% sucrose, whereas the gradient used for the PHPMA sample was 4−12% sucrose. The density of the polystyrene latex particles was taken to be 1.05 g cm^{-3}, whereas that of the PHPMA latex was taken to be 1.17 g cm^{-3}. This is a reasonable assumption for latex diameters of ~1 μm, where the thickness of the steric stabilizer layer is negligible compared with the particle size. For smaller latexes (particularly for diameters of <200 nm), the stabilizer layer thickness becomes significant, resulting in a reduction in the effective particle density. Because an accurate particle density is required when calculating the weight-average particle diameter, D_w, any uncertainty in density produces an associated error in D_w.[32]

Scanning Electron Microscopy (SEM). SEM studies were performed using a FEI Sirion field emission scanning electron microscope at a beam current of 244 μA and an operating voltage of 5 kV. Samples were dried onto aluminum stubs and sputter-coated with a thin layer of gold prior to examination to prevent sample charging. Mean latex diameters were estimated by counting at least 100 particles.

X-ray Photoelectron Spectroscopy (XPS). XPS spectra were acquired using a Kratos Axis ULTRA "DLD" X-ray photoelectron spectrometer equipped with a monochromatic Al−Kα X-ray source ($h\nu$ = 1486.6 eV) and operating at a base pressure of 10^{-8}−10^{-10} mbar. Latex particles were dried on indium foil prior to XPS measurements.

Results and Discussion

The two-step synthesis route used in this study to obtain well-defined PGMA-based macromonomers is outlined in Figure 1.

Various $PGMA_n$ homopolymer precursors were prepared with target degrees of polymerization, n, ranging from 20 to 70. (See Table 1.) Good molecular weight control was achieved for the targeted homopolymers, with the actual degree of polymerization calculated from ^{1}H NMR lying close to that targeted. The associated experimental error is estimated to be around ±5% for lower values of n, increasing to approximately ±10% for higher degrees of polymerization.

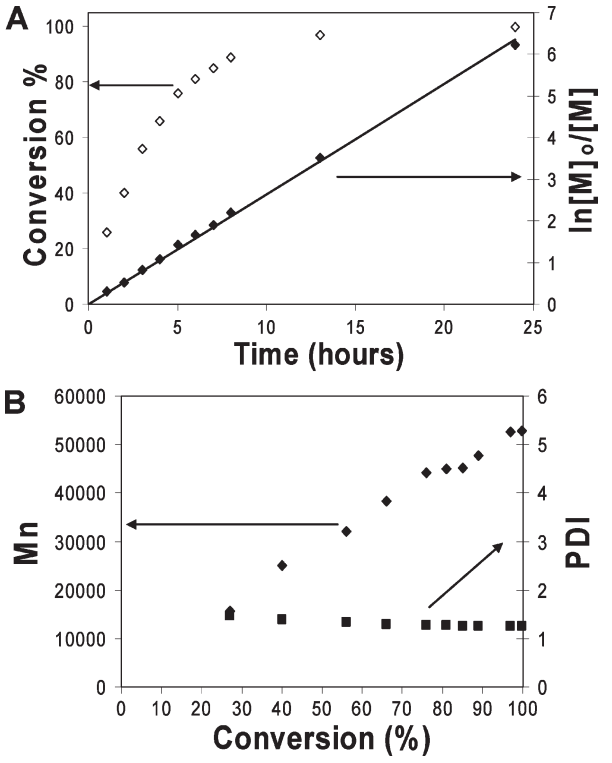

Figure 2. (a) Conversion versus time and semilogarithmic plot and (b) evolution of M_n and polydispersity versus conversion for the homopolymerization of GMA at 20 °C in methanol for 24 h. Reaction conditions: [GMA]/[initiator]/[CuCl]/[bpy] 50:1:1:2.

The polymerization kinetics was first order with respect to the monomer, and the linear evolution of molecular weight with conversion indicates that these homopolymerizations possess good living character, as expected, see Figure 2. This is in marked contrast with the results recently reported by our group for the synthesis of PMPC macromonomers, where good control over the ATRP of MPC using the 2-(dimethylamino)ethyl-2-bromoisobutyrylamide initiator was demonstrated only for relatively low degrees of polymerization.[25] The molecular weight distribution of each $PGMA_n$ homopolymer was unimodal. (See Figure 3.) It is particularly noteworthy that low polydispersities were obtained for higher target degrees of polymerization (40 to 70) because this was found to be a significant limitation of the synthesis of the analogous MPC-based macromonomers using the same two-step route.[25]

Well-defined macromonomers based on all six of the $PGMA_n$ homopolymers were synthesized, as shown in Figure 1. Assigned ^{1}H NMR spectra for the 2-(dimethylamino)ethyl-2-bromoisobutyrylamide initiator, the $PGMA_{20}$ homopolymer precursor, and the corresponding $PGMA_{20}$ macromonomer are shown in Figure 4. Quaternization of the precursor with 4-VBC leads to distinct shifts in the NMR signals due to the six dimethylamino and two adjacent azamethylene protons in the initiator from δ 2.5 and δ 2.7 to δ 3.2 and δ 3.4. (See Figure 4.) When 100% quaternization is achieved, the original initiator end-group signals are no longer visible at δ 2.5 to 2.7. After purification to remove excess 4-VBC, new aromatic, benzylic, and vinyl signals due to the 4-vinylbenzyl group can be observed at δ 5.2−7.7, thus confirming successful quaternization. Again, quantification of the actual degrees of quaternization (using the more prominent aromatic signals) is somewhat problematic given the relatively low sensitivity of NMR spectroscopy. Nevertheless, in all cases, the signals at δ 2.5 and δ 2.7 due to the original (nonquaternized) initiator end groups completely disappear, suggesting that at least 98% quaternization was achieved for each of the $PGMA_n$ macromonomers.

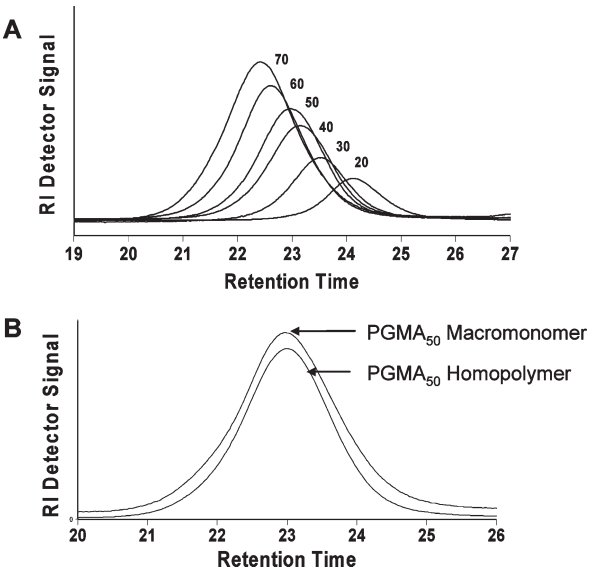

Figure 3. (a) Representative GPC curves for $PGMA_n$ homopolymer precursors prepared by ATRP at 20 °C (vs PMMA standards). (b) Comparison of the GPC traces obtained for $PGMA_{50}$ homopolymer and $PGMA_{50}$ macromonomer. Quaternization using 4-vinylbenzyl chloride under mild conditions clearly has no deleterious effect on the molecular weight distribution.

These PGMA-based macromonomers were evaluated as potential reactive steric stabilizers for latex syntheses, as illustrated in Figure 5. Three routes were employed to prepare PGMA-stabilized polystyrene (PS) and poly(2-hydroxypropyl methacrylate) (PHPMA) particles. PGMA-PS latexes were prepared by both aqueous emulsion and alcoholic dispersion polymerization, producing mean diameters of approximately 100−200 and 1100 nm, respectively. PGMA-PHPMA latexes of 700−1000 nm were also successfully prepared by aqueous dispersion polymerization. Tables 2−4 summarize all of these latex syntheses using PGMA macromonomers of varying chain lengths as well as the results of various control experiments conducted in the absence of any macromonomer or in the presence of a nonquaternized $PGMA_{50}$ homopolymer precursor. Representative SEM images of the $PGMA_{50}$-PS and $PGMA_{50}$-PHPMA latexes are shown in Figure 6.

PGMA macromonomers with DP 20, 30, 40, or 50 were utilized in aqueous emulsion polymerization. In each case, colloidally stable sterically-stabilized latexes were obtained. However, in some cases, it proved difficult to correlate the final latex diameter with the synthesis parameters because of incomplete monomer conversions. Therefore, we decided to focus on just the $PGMA_{50}$ macromonomer for such syntheses. Table 2 shows the particle size data for the aqueous emulsion polymerization of styrene at 70 °C using the AIBN initiator in the presence of the $PGMA_{50}$ macromonomer. Oil-soluble initiators such as AIBN are rarely used in aqueous emulsion polymerization. However, we found empirically that AIBN, which has rather limited water solubility, gave the best results in our latex syntheses. Attempted emulsion polymerization with water-soluble initiators such as ammonium persulfate or 2,2′-azobis(isobutyramidine) dihydrochloride (AIBA) invariably led to highly flocculated particles. In this regard, these PGMA macromonomers appear to be less versatile than the PMPC macromonomers previously reported.[25] $PGMA_{50}$-PS latexes of ~100 nm in diameter were produced with polydispersities of 0.03 and 0.09, as judged by dynamic light scattering (DLS). For these smaller latexes, there is some discrepancy between the intensity-average and weight-average diameters reported by DLS and

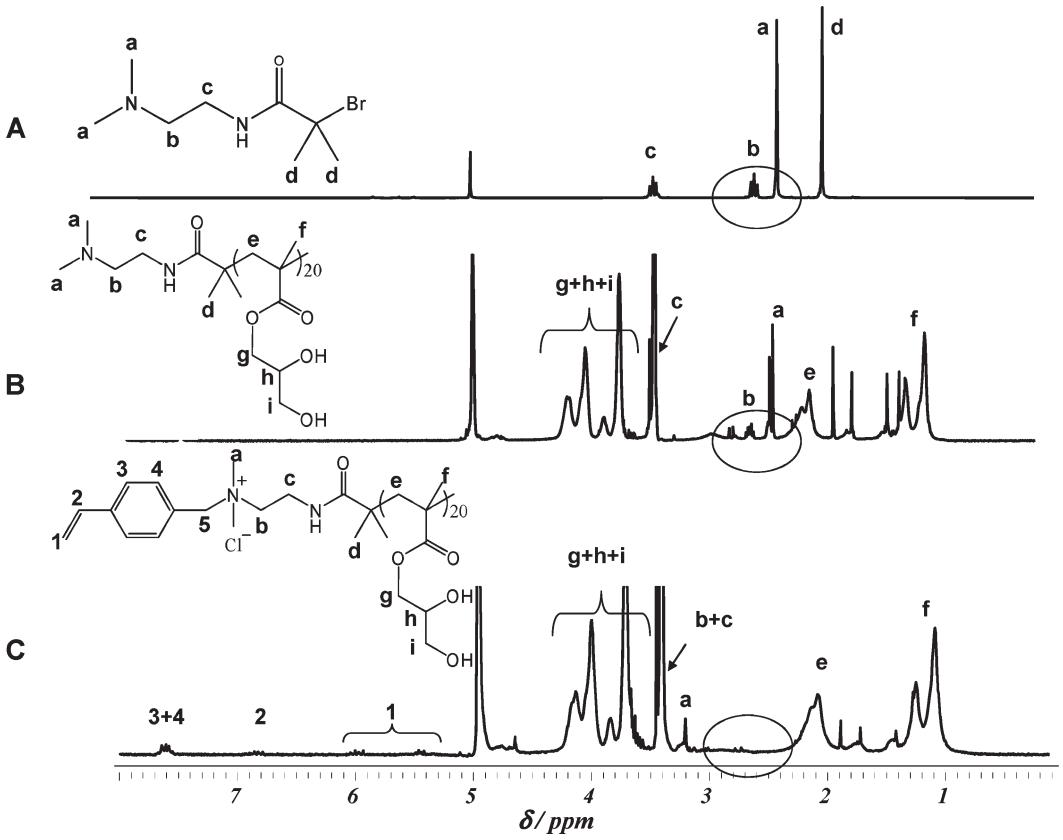

Figure 4. ^{1}H NMR spectra recorded in CD_3OD for: (a) 2-(dimethylamino)ethyl-2-bromoisobutyrylamide initiator, (b) $PGMA_{20}$ homopolymer precursor prior to quaternization, and (c) fully quaternized $PGMA_{20}$ macromonomer.

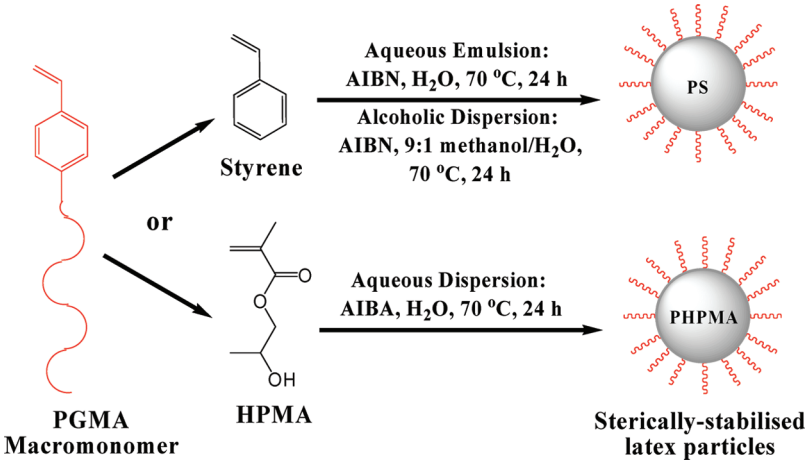

Figure 5. Reaction scheme for the synthesis of PGMA-stabilized polystyrene latex via both aqueous emulsion and alcoholic dispersion polymerization and poly(2-hydroxypropyl methacrylate) latex via aqueous dispersion polymerization.

Table 2. Latex Yield, Particle Size Data, and Stabilizer Contents for $PGMA_n$-PS Latexes Prepared by Aqueous Emulsion Polymerization Using 10.0 w/v % Stabilizer Based on Styrene at 70 °C in Water with AIBN for 24 h[a]

entry no.	stabilizer type	initial stabilizer concentration w/v %	latex yield %	SEM diameter (nm)	DCP diameter (nm)	DLS diameter (nm) (PDI)	stabilizer content w/w %	Γ mg m^{-2}
1	none	0	0					
2	$PGMA_{50}$ homopolymer	10	12	546	580 ± 100	641 (0.17)	1.25	1.3
3	$PGMA_{50}$ macromonomer	10	69	90	163 ± 40	120 (0.03)	9.4	1.8
4	$PGMA_{50}$ macromonomer	20	95	88	133 ± 39	130 (0.09)	19.8	3.8

[a] Size distributions were determined by disk centrifuge photosedimentometry (DCP) and dynamic light scattering (DLS). Latex yields were determined by gravimetry and stabilizer contents were determined by analyzing latexes dissolved in d_5-pyridine using ^{1}H NMR spectroscopy.

DCP, respectively. This is because the former values should always be higher than the latter for any latex size distribution with a finite width. However, for latex diameters of < 200 nm, the thickness of the hydrated $PGMA_{50}$ stabilizer layer becomes significant relative to the mean particle diameter, resulting in a substantial reduction in the effective particle density. Because an

Table 3. Latex Yield and Particle Size Data for Selected $PGMA_n$-PS Latexes Prepared by Alcoholic Dispersion Polymerization Using 10 wt % Stabilizer Based on Styrene at 70 °C for 24 h in 9:1 Methanol/Water Using AIBN Initiator[a]

entry no.	stabilizer type	latex yield (%)	SEM diameter (nm)	DCP diameter (nm)	DLS diameter (nm) (PDI)
1	none	0			
2	$PGMA_{50}$ homopolymer	50	2700	2760 ± 521	2800 (0.32)
3	$PGMA_{20}$ macromonomer	90	1300	1599 ± 640	1840 (0.40)
4	$PGMA_{30}$ macromonomer	85	910	1085 ± 76	1100 (0.15)
5	$PGMA_{40}$ macromonomer	100	900	990 ± 105	1100 (0.10)
6	$PGMA_{50}$ macromonomer	100	980	980 ± 106	1100 (0.03)

[a] SEM: scanning electron microscopy, DCP: disk centrifuge photosedimentometry, DLS: dynamic light scattering; latex yields determined by gravimetry.

Table 4. Latex Yield and Particle Size Data for Selected $PGMA_n$-PHPMA Latexes Prepared by Aqueous Dispersion Polymerization Using 10 wt % Stabilizer Based on HPMA at 70 °C for 24 h in Water Using AIBA Initiator[a]

entry no.	stabilizer type	latex yield (%)	SEM diameter (nm)	DCP diameter (nm)	DLS diameter (nm) (PDI)
1	none	0			
2	$PGMA_{50}$ homopolymer	0			
3	$PGMA_{20}$ macromonomer	86	1020	1036 ± 164	1490 (0.37)
4	$PGMA_{30}$ macromonomer	99	765	790 ± 145	950 (0.09)
5	$PGMA_{40}$ macromonomer	100	720	744 ± 100	1110 (0.14)
6	$PGMA_{50}$ macromonomer	100	855	880 ± 143	1070 (0.06)

[a] SEM: scanning electron microscopy, DCP: disk centrifuge photosedimentometry, DLS: dynamic light scattering; latex yields determined by gravimetry.

Table 5. Colloid Stability of Selected Latexes in the Presence of Added Salt and after One Freeze−Thaw Cycle at −20 °C[a]

latex type	DLS diameter before freeze−thaw (nm)	DLS diameter after freeze−thaw (nm)	$MgSO_4$ concentration/M					
			0.01	0.05	0.10	0.20	0.30	0.50
AIBA-PS	667	aggregation	×	×	×	×	×	×
$PGMA_{20}$-PS	1840	1971	*	*	*	*	*	*
$PGMA_{30}$-PS	1100	1990	*	*	*	*	*	*
$PGMA_{40}$-PS	1110	1200	*	*	*	*	*	*
$PGMA_{50}$-PS	120	120	*	*	*	*	*	*
$PGMA_{50}$-PS	1100	1200	*	*	*	*	*	*
$PGMA_{50}$-PHPMA	1070	1108	*	*	*	*	*	*

[a] × indicates substantial particle aggregation (coagulation); * indicates no change in DLS diameter within experimental error.

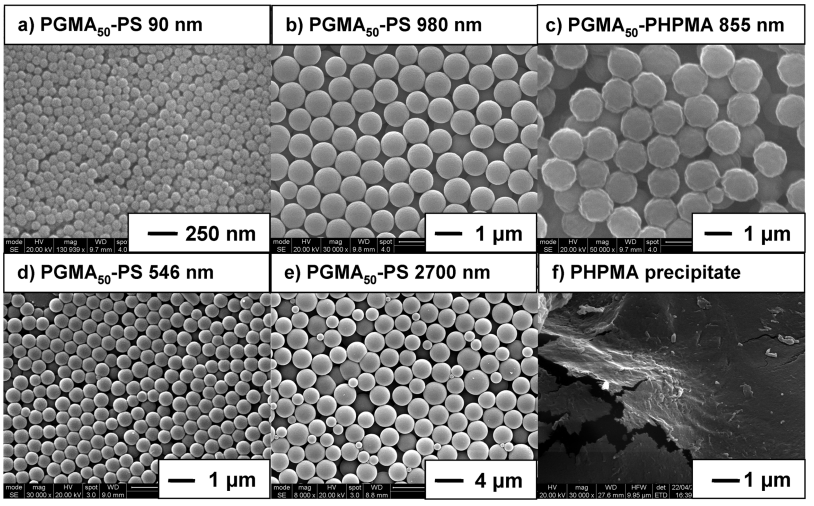

Figure 6. Scanning electron micrographs of latexes prepared using the $PGMA_{50}$ macromonomer by (a) aqueous emulsion (entry 6, Table 2), (b) alcoholic dispersion (entry 6, Table 4), and (c) aqueous dispersion polymerization (entry 6, Table 5). (d,e) (entry 2 in Table 2 and entry 2 in Table 4, respectively) Latexes synthesized using the corresponding $PGMA_{50}$ homopolymer precursor. (f) Amorphous PHPMA precipitate obtained in the attempted aqueous dispersion polymerization of 2-hydroxypropyl methacrylate in the presence of the $PGMA_{50}$ homopolymer precursor (entry 2, Table 5).

accurate particle density is required for DCP analysis, any uncertainty in the particle density produces an associated error, as previously discussed by Cairns et al.[32] In summary, the DLS data shown in Table 2 are all reliable, but the DCP data are subject to significant systematic errors, particularly for the smaller latexes. This interpretation is supported by the relatively small latex diameters indicated by SEM studies. It is emphasized that this error becomes negligible for all of the larger latexes shown in Tables 3 and 4. As expected, a control experiment conducted in the absence of any stabilizer led to gross precipitation

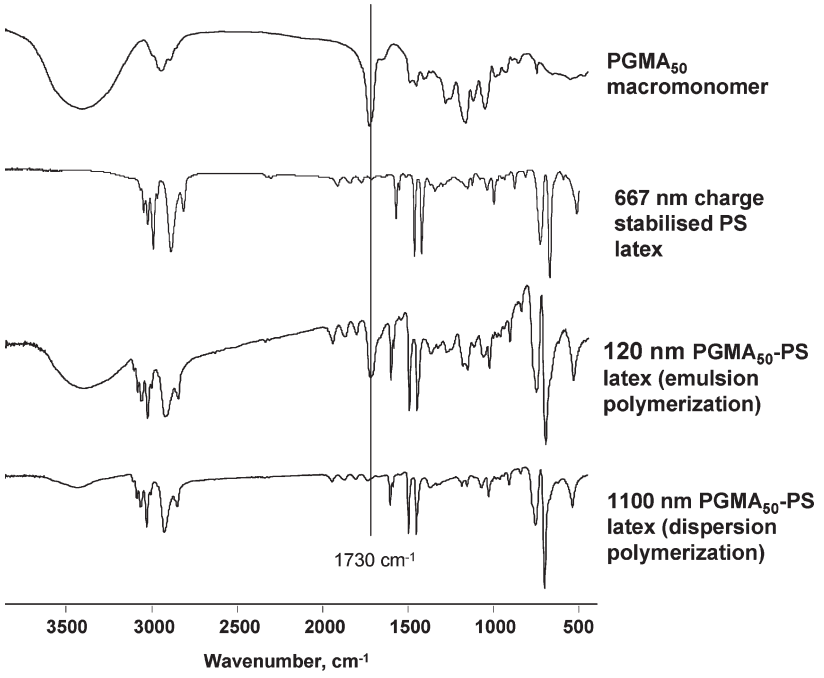

Figure 7. FT-IR spectra recorded for $PGMA_{50}$ macromonomer, charge-stabilized polystyrene latex prepared in the absence of any macromonomer and two $PGMA_{50}$-stabilized polystyrene latexes prepared by aqueous emulsion and alcoholic dispersion polymerization, respectively. Note the prominent carbonyl ester band at ~1730 cm^{-1} observed for the spectrum of the 120 nm $PGMA_{50}$-stabilized polystyrene latex. This band is barely detectable in the 1100 nm $PGMA_{50}$-stabilized polystyrene latex since its stabilizer content is much lower.

with no latex formation; charge-stabilized PS latex particles cannot be formed under such conditions because of the non-ionic nature of the AIBN initiator. A second control experiment conducted in the presence of the $PGMA_{50}$ homopolymer precursor produced mainly coagulum with a small fraction of a significantly larger, more polydisperse latex compared with that formed in the presence of macromonomer (compare entry 2 with entries 3 and 4 in Table 2). This obvious difference in size is highlighted by SEM when comparing Figure 6a and 6d. These control experiments demonstrate that macromonomers (rather than homopolymer precursors) are essential for producing small, uniform latexes because the former stabilizers confer much more efficient steric stabilization. ^{1}H NMR analysis of the dried latexes allows calculation of the amount of PGMA macromonomer or homopolymer incorporated into the latex particles. The stabilizer content ranges from 1.25 to 19.8 w/w % of the latex by mass (Table 2), depending on the type and amount of stabilizer used. Assuming that all of the $PGMA_{50}$ chains are located on the outside of the latex, this corresponds to an adsorbed amount, Γ, of approximately 1.3−3.8 mg m^{-2}. The lowest stabilizer content (1.25 w/w %) was obtained when the homopolymer precursor was used. This is consistent with the relatively poor grafting expected from this stabilizer because it lacks a polymerizable group. In contrast, when the $PGMA_{50}$ macromonomer was used, significantly higher stabilizer contents and corresponding absorbed amounts were observed, as expected. This is attributed to the polymerizable nature of the macromonomer chains, which allows much more efficient grafting onto the latexes.

Alcoholic dispersion polymerization in a 9:1 methanol/water mixture was successfully used to prepared larger, micrometer-sized polystyrene latexes, see Table 3. Although no definite trend was observed between mean particle diameter and macromonomer chain length by DLS, a small reduction in particle diameter was observed by DCP when the mean degree of polymerization of the macromonomer was increased from 20 to 50. There is also a concomitant reduction in latex polydispersity, and the $PGMA_{50}$ macromonomer produced the most uniform particles, see entry 6 in Table 3. A control experiment conducted in the absence of any macromonomer led to gross precipitation with essentially no latex formation, and much larger (~2800 nm) latex particles were produced in the presence of the $PGMA_{50}$ homopolymer precursor, albeit with a latex yield of only 40% (the rest being coagulum, see entries 1 and 2 in Table 3 and the SEM image in Figure 6e).

Table 4 summarizes the results obtained for the synthesis of PGMA-PHPMA latexes by aqueous dispersion polymerization. Such particles are rather unusual because the steric stabilizer and the latex core both contain hydroxyl functionality. In this case, no particular trend was observed between latex particle diameter and macromonomer chain length, but the $PGMA_{50}$ macromonomer again produced more monodisperse particles. Control experiments conducted either in the absence of any macromonomer or in the presence of the $PGMA_{50}$ homopolymer precursor both led to gross precipitation of PHPMA, as expected, see entries 1 and 2 in Table 4 and the SEM image in Figure 6f. This confirms the importance of the polymerizable styrenic group on the macromonomer chain to confer effective steric stabilization.

FT-IR spectra were recorded for the $PGMA_{50}$ macromonomer, selected $PGMA_{50}$-stabilized polystyrene latexes, and a polystyrene precipitate. The distinctive ester carbonyl stretch due to the GMA repeat units of the macromonomer chains is observed at ~1730 cm^{-1}. (See Figure 7.) The same band appears in the $PGMA_{50}$-stabilized polystyrene latex prepared by aqueous emulsion polymerization. This confirms the presence of the PGMA stabilizer in this latex, but does not provide any information regarding its spatial location. It is perhaps noteworthy that this carbonyl band is barely observed in the much larger $PGMA_{50}$-PS latex prepared by alcoholic dispersion polymerization. However, this negative result was not unexpected because of the much lower stabilizer content of this latex (< 1 wt %).

Further evidence of the presence of the PGMA chains being incorporated into these latexes is provided by aqueous electrophoresis and XPS analysis (Figures 8 and 9); both are surface-specific techniques. Aqueous electrophoresis shows that the $PGMA_{50}$-PS latexes display only a relatively modest change in ζ potential (±10 mV) as a function of pH; much

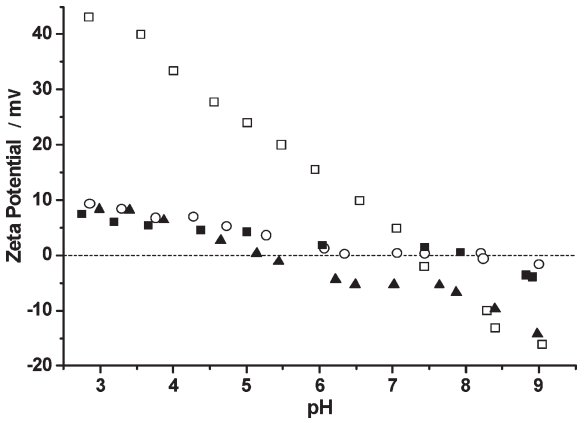

Figure 8. Aqueous electrophoresis curves observed for a 1100 nm $PGMA_{50}$-PS latex (▲), 120 nm $PGMA_{50}$ (■), a $PGMA_{50}$-PHPMA latex (○), and also a 667 nm charge-stabilized PS latex prepared in the absence of macromonomer using a cationic azo initiator AIBA (□). The presence of the nonionic PGMA chains effectively shields the underlying cationic surface charge.

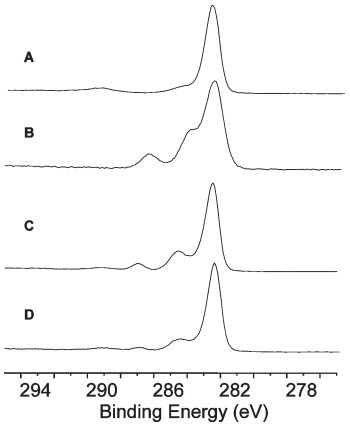

Figure 9. XPS core-line C1s spectra for (a) a polystyrene precipitate prepared in the absence of macromonomer, (b) the $PGMA_{50}$ macromonomer, and (c,d) the 120 and 1100 nm $PGMA_{50}$-PS latexes, respectively. There is clear evidence of C−O and C=O species in the latter two spectra, which confirms the presence of the PGMA chains at the surface of each latex.

larger changes are observed for a cationic charge-stabilized PS latex examined under the same conditions. This indicates that the nonionic $PGMA_{50}$ stabilizer chains are located at the latex surface and effectively shield the underlying cationic charge that arises from the quaternized amine end group.

Comparing the X-ray photoelectron spectra recorded in the C1s region for the $PGMA_{50}$ macromonomer, the precipitated polystyrene homopolymer, and both $PGMA_{50}$-PS latexes, it is clear that the $PGMA_{50}$ macromonomer is present in both latexes, see Figure 9. Moreover, because XPS has a typical analysis depth of ~2−8 nm, the PGMA stabilizer chains must be located at (or very near) the latex surface. It is also possible to estimate the surface coverage of the $PGMA_{50}$ chains on the latex particles using the O1s signals due to the ester groups in the PGMA macromonomer because no such signals are observed for the precipitated polystyrene homopolymer (data not shown). Using this approach, surface coverages of 44 and 53% are estimated for $PGMA_{50}$-PS latexes prepared by aqueous emulsion and alcoholic dispersion polymerization, respectively. Unfortunately, because of the similar chemical structures of PGMA and PHPMA, it was not possible to confirm directly the presence of the PGMA macromonomer chains in the PHPMA latexes by FT-IR, ^{1}H NMR, or XPS. However, the aqueous electrophoretic data again indicate very low ζ potentials over a wide pH range, which suggests that the surface charge from the underlying cationic AIBA initiator fragments is effectively screened by the non-ionic PGMA chains.

Having demonstrated that the PGMA-based macromonomers are indeed located at the latex surface and thus act as steric stabilizers, the colloid stability of selected latexes was evaluated by two methods: (i) a single freeze−thaw cycle at −20 °C and (ii) addition of varying concentrations of $MgSO_4$, see Table 5. A charge-stabilized polystyrene latex flocculated substantially upon the addition of just 0.01 M $MgSO_4$ and also failed to redisperse after a freeze−thaw cycle. However, each latex stabilized using the $PGMA_n$-based macromonomers (where n = 20, 30, 40, or 50) remained stable at up to 0.50 M $MgSO_4$ and also readily redispersed after a freeze−thaw cycle, as judged by DLS. Clearly, the chemically-grafted PGMA stabilizer chains confer substantially enhanced colloidal stability, as expected for sterically-stabilized latexes.

Conclusions

A series of well-defined styrene-functionalized poly(glycerol monomethacrylate)-based macromonomers have been synthesized by combining the use of a tertiary amine-functional ATRP initiator with postpolymerization quaternization using 4-vinylbenzyl chloride. Target degrees of polymerization can be systematically varied from 20 to 70 with good molecular weight control and relatively low polydispersities ($M_w/M_n \leq 1.33$). Selected hydrophilic macromonomers were evaluated as reactive polymeric stabilizers for the polymerization of styrene and HPMA under either emulsion or dispersion conditions. Near-monodisperse, sterically-stabilized polystyrene latexes of micrometer dimensions were obtained via dispersion polymerization in the presence of the $PGMA_{50}$ macromonomers, whereas only flocculated, poorly defined particles were observed if a nonquaternized $PGMA_{50}$ homopolymer precursor was utilized. Also, macroscopic precipitation occurred in the absence of any stabilizer. This serves to illustrate the essential role played by the terminal polymerizable styrene group in determining the final particle morphology. Near-monodisperse polystyrene latexes of ~120 nm diameter were also obtained via emulsion polymerization using the same macromonomer. Varying the molecular weight of the macromonomer affected the latex particle size distribution; more uniform particles were achieved in the presence of higher molecular weight macromonomers. FT-IR studies confirmed the presence of the stabilizer in the smaller latexes, and XPS studies indicated that the chemically-grafted macromonomer was present at (or very near) the latex surface, as expected. Compared with a charge-stabilized polystyrene latex, these sterically-stabilized latexes proved to be highly resistant to the addition of electrolyte, as expected. Finally, the tolerance of these new sterically-stabilized latexes toward freeze−thaw cycling was enhanced for higher molecular weight macromonomers.

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