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Preparation of Biocompatible Sterically Stabilized Latexes Using Well-Defined Poly(2-(methacryloyloxy)ethyl phosphorylcholine) Macromonomers

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A range of well-defined methacrylic macromonomers based on the biomimetic monomer 2-(methacryloyloxy)ethyl phosphorylcholine (MPC) were synthesized by atom-transfer radical polymerization (ATRP) in alcoholic media using 2-(dimethylamino)ethyl-2-bromoisobutyrylamide. This tertiary amine-functionalized initiator was used to produce homopolymer precursors of various chain lengths via ATRP. These polymerizations were relatively well controlled ($M_w/M_n \leq 1.30$), provided that the target degree of polymerization (DP) did not exceed 30. For higher target DPs, polymerization was only poorly controlled and characterized by broad molecular weight distributions (M_w/M_n = 1.50−2.31). The tertiary amine end-group of each nearly monodisperse homopolymer precursor was then quaternized using 4-vinylbenzyl chloride (4-VBC) to afford the corresponding styrene-functionalized macromonomers. $PMPC_{30}$ macromonomer proved to be an effective reactive steric stabilizer for the formation of polystyrene latexes when employed at 10 w/w % on the basis of the styrene monomer. Nearly monodisperse submicrometer-sized and micrometer-sized latexes were prepared by aqueous emulsion and alcoholic dispersion polymerization, respectively, as judged by scanning electron microscopy and dynamic light scattering studies. In contrast, attempted alcoholic dispersion polymerization conducted either in the presence of the $PMPC_{30}$ homopolymer precursor or in the absence of any macromonomer always resulted in macroscopic precipitation. Such control experiments confirmed the importance of the terminal styrene groups on the macromonomer chains for successful latex formation. FTIR spectroscopy indicated the presence of the $PMPC_{30}$ macromonomer within the polystyrene latex, and XPS studies indicated that these stabilizer chains are located at (or very near) the latex surface, as expected. Using $PMPC_{20}$ and $PMPC_{10}$ macromonomers for the alcoholic dispersion polymerization of styrene led to latexes with substantially broader size distributions compared to those produced using the $PMPC_{30}$ macromonomer under the same conditions. Finally, these new sterically stabilized latexes exhibit excellent freeze−thaw stability and salt tolerance.

Introduction

Macromonomers are polymer chains that contain at least one polymerizable group.[1] There are many literature examples of macromonomers with terminal vinylic groups, which can be used to prepare sterically stabilized latexes,[2] graft copolymers,[3] or "bottle brush" polymers.[4] There are a number of synthesis routes to macromonomers. Commercially available macromonomers such as methoxy-capped poly(ethylene glycol) methacrylate are usually prepared by transesterification of monohydroxy-terminated poly(ethylene glycol) previously prepared by anionic polymerization. Catalytic chain-transfer polymerization (CCTP) can be used to prepare methacrylic macromonomers,[5] but because this approach is based on conventional free radical polymerization only broad molecular weight distributions can be obtained (typically $M_w/M_n > 2.0$). Moreover, the terminal vinyl group produced by CCTP does not exhibit the same copolymerizability as conventional methacrylic monomers.[6] However, CCTP has been recently combined with atom transfer radical polymerization (ATRP) to produce low-polydispersity macromonomers.[7] Both Nagasaki and co-workers[8] and Lascelles et al.[9] reported the preparation of a range of well-defined styrene-functionalized macromonomers via anionic polymerization of tertiary amine methacrylates using potassium 4-vinylbenzyl alkoxide as an initiator. This approach illustrates the general principle that vinylic macromonomers can be synthesized directly with functional initiators provided that the terminal vinyl group does not participate in the chain-growth reaction. Similar selectivity has also been illustrated for vinyl acetate- and vinyl ether-based ATRP initiators.[10,11] ATRP has also been used to produce macromonomers by displacing the terminal halogen atoms from

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the chain ends,[12] although this approach presumably suffers from reduced efficiencies under monomer-starved conditions as a result of side reactions. Another strategy is to use functional initiators to enable postpolymerization derivatization of the polymer chain ends.[13,14] Although this is usually a two-step synthesis, it has the advantage of allowing the efficient incorporation of terminal vinylic groups such as (meth)acrylates or styrene that would otherwise participate in the chain-growth stage. This approach has also been successfully used for anionic polymerization, conventional free radical polymerization, and ATRP.[15,16]

In the present work, we have synthesized near-monodisperse macromonomers based on 2-(methacryloyloxy)ethyl phosphorylcholine (MPC). This zwitterionic biomimetic monomer has been widely used for biocompatible surface coatings in health care applications.[17] Recently, we prepared biocompatible sterically stabilized PMPC latexes using a poly(ethylene glycol) methacrylate stabilizer in alcohol/water mixtures.[18] PMPC-based macromonomers have been reported previously by Ishihara and co-workers.[19,20] These macromonomers were copolymerized with *n*-butyl methacrylate to produce graft copolymers[19] and were also used to prepare sterically stabilized polystyrene latexes.[20] However, they were synthesized by conventional free-radical polymerization and hence were relatively polydisperse. In addition, Sugiyama et al. described the copolymerization of a phosphorylcholine-based, azo-functionalized methacrylic monomer with methyl methacrylate by surfactant-free emulsion polymerization.[21] The resulting latexes resisted protein absorption from aqueous solution, and this resistance could be modulated by UV irradiation. In the present work, a tertiary amine-functionalized ATRP initiator (Figure 1) was synthesized to homopolymerize the MPC monomer with reasonably good control. The terminal tertiary amine groups of these precursors were then quaternized using excess 4-vinylbenzyl chloride to produce a series of well-defined, low-polydispersity styrene-functionalized PMPC macromonomers. These model macromonomers were evaluated as new reactive steric stabilizers for the synthesis of polystyrene latexes via both aqueous emulsion and alcoholic dispersion polymerization. It is also shown that the zwitterionic PMPC stabilizer chains confer excellent freeze−thaw stability and high salt tolerance.

Experimental Section

Materials. 2-(Methacryloyloxy)ethyl phosphorylcholine (MPC, 99.9%) was kindly donated by Biocompatibles (Farnham, UK) and used without further purification. 4-Vinylbenzyl chloride (4-VBC), Cu(I)Cl (99.995%), and 2,2′-bipyridine (bpy, 99%) were all purchased from Aldrich and were used as received. Styrene and *n*-butyl acrylate (Aldrich) were both passed through a column of basic alumina to remove inhibitor and then stored at −20 °C prior to use. 2,2′-Azobisisobutyronitrile (AIBN; BDH), 2,2′-azobis(isobutyramidine) dihydrochloride (AIBA; 97%; Aldrich, U.K.), and ammonium persulfate (APS, Aldrich, U.K.) were used as received. Methanol was purchased from Fisher and 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, and $CDCl_3$) were purchased from Fisher. A poly(vinylidene difluoride) dialysis membrane (Spectra/Por, molecular weight cutoff = 500 000 Da) was also purchased from Fisher.

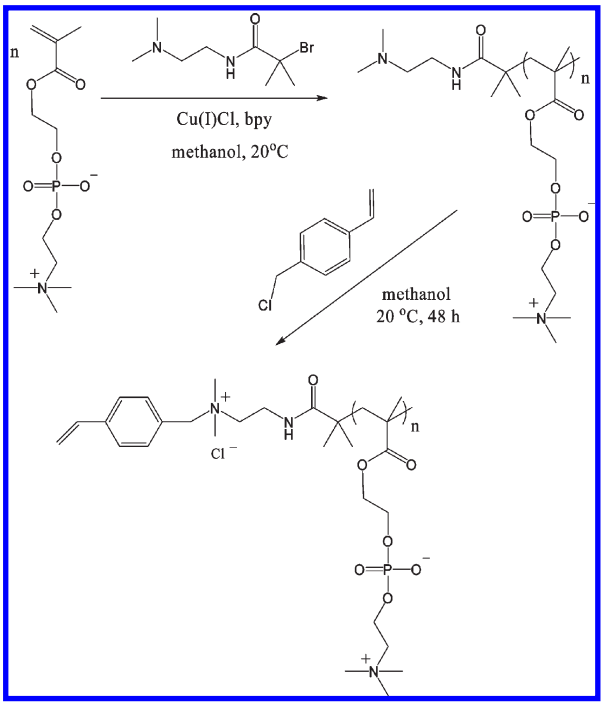

Figure 1. Reaction scheme for the synthesis of well-defined biocompatible PMPC macromonomers: atom-transfer radical polymerization of 2-(methacryloyloxy)-ethyl phosphorylcholine (MPC) in methanol at 20 °C for 6 h, followed by quaternization of the purified PMPC homopolymer using excess 4-vinylbenzyl chloride at 20 °C in methanol for 48 h.

Synthesis of 2-(Dimethylamino)ethyl-2-bromoisobutyrylamide initiator. 2-Dimethylethylenediamine (5.95 g, 0.068 mol), triethylamine (27.27 g, 0.27 mol), and dichloromethane (120 mL) were placed in a 1 L three-necked, round-bottomed flask and purged with nitrogen for 30 min. A white precipitate of triethylammonium bromide was formed on addition of 2-bromoisobutyryl bromide (15.49 g, 0.067 mol) to the reaction mixture, which was stirred for another 5 h. After filtration to remove the precipitate, the solution was dried over $MgSO_4$ and filtered once more, and dichloromethane was removed under reduced pressure to afford a pale-brown liquid. The initiator was used without further purification because ^{1}H NMR analysis confirmed it to be of sufficiently high purity. ^{1}H NMR (400 MHz, CD_3OD): δ 1.88 (6H, s, $2CH_3$), 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 MPC. The polymerization of MPC monomer to afford the $PMPC_{30}$ homopolymer was conducted as follows. 2-(Dimethylamino)ethyl-2-bromoisobutyrylamide initiator (0.134 g, 0.56 mmol), bpy (0.177 g, 1.12 mmol), and MPC (5.00 g, 16.8 mmol; target DP = 30) were weighed into a 25 mL round-bottomed flask and degassed using three vacuum/nitrogen cycles. Methanol (5.13 mL) was degassed separately and transferred into the reaction flask under positive nitrogen pressure. The Cu(I)Cl catalyst (0.055 g, 0.56 mmol) was added quickly to the stirred solution under positive nitrogen pressure, and the reaction

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solution turned dark brown, indicating the onset of polymerization. After 6 h, the reaction solution was diluted with methanol and became blue/green in color, indicating aerial oxidation of the catalyst. The solution was passed through a silica column to remove the spent Cu(II) catalyst. The homopolymer was then dried on a vacuum line overnight to obtain a white powder (93% yield). Syntheses of the $PMPC_{10}$, $PMPC_{20}$, $PMPC_{40}$, and $PMPC_{50}$ homopolymers were each conducted using the same protocol. The target degree of polymerization was adjusted by varying the monomer/initiator molar ratio. The relative molar ratios of [monomer]/[initiator]/[bpy]/[CuCl] in the reaction mixture were *n*:1:2:1, where *n* is the target degree of polymerization.

Quaternization of the PMPC Homopolymer. The $PMPC_{30}$ homopolymer (4.23 g, 0.47 mmol) was dissolved in methanol (13 mL) to afford a 25 wt % solution. To this solution, 4-VBC (0.237 g, 1.41 mmol; 4-VBC/polymer molar ratio = 3:1) was added and stirred at room temperature for 48 h. The excess solvent was removed by rotary evaporation, and the resulting solid was then dissolved in water. The excess 4-VBC was extracted three times with cyclohexane. The aqueous phase was then freeze-dried from water overnight to afford a white powder. The purified macromonomer was characterized by ^{1}H NMR (91% yield). The mean degree of quaternization was calculated by comparing the aromatic styrene signals at δ 7.55−7.70 to the two azamethylene protons due to PMPC at δ 3.61−3.77.

Kinetics of Quaternization of $PMPC_{10}$ for Kinetic Studies. ^{1}H NMR spectroscopy was used to monitor the kinetics of quaternization for various 4-VBC/polymer molar ratios. $PMPC_{10}$ (250 mg, 0.08 mmol) was weighed into a sample vial and dissolved in d_4-methanol (0.75 mL, 25 wt %). 4-VBC (0.037 mL, 0.24 mmol, 3 mol equiv based on tertiary amine end-groups) was added to this stirred solution using a micropipet. This reaction solution was transferred to an NMR tube, and ^{1}H NMR spectra were recorded at hourly intervals. Reactions were also monitored using either 2 or 1 mol equiv of 4-VBC. Degrees of quaternization were calculated by comparing the integrated signal at δ 2.0−2.5 arising from the 2-(dimethylamino)ethyl end-group with the two azamethylene protons at δ 3.6−3.8 due to the MPC repeat units.

$PMPC_{30}$−PS Latex Syntheses via Aqueous Emulsion Polymerization. $PMPC_{30}$ macromonomer (0.50 g) was weighed into a 100 mL round-bottomed flask containing a magnetic flea and dissolved in water (45.0 g), and then styrene (5.0 g) was added. This solution was degassed by five evacuation/nitrogen purge cycles and then heated to 70 °C. Separately, the ammonium persulfate (APS) or AIBA initiator (0.050 g) was dissolved in water (5.0 g) and purged with nitrogen. This solution was then injected into the reaction vessel once the temperature had reached 70 °C (or 60 °C for AIBA). The polymerizing solution turned milky white within 30 min and was stirred for 24 h. The resulting latexes were purified by three centrifugation/redispersion cycles to remove excess macromonomer and any unreacted styrene monomer. In each case, the latex particle diameter was assessed by DLS (before purification) and SEM (after purification). These latexes were also analyzed by ^{1}H NMR, FTIR, XPS, and zeta potential measurements.

$PMPC_{30}$−P(S-BuA) Latex via Aqueous Emulsion Polymerization. $PMPC_{30}$ macromonomer (0.50 g) was weighed into a 100 mL round-bottomed flask containing a magnetic flea and dissolved in water (45.0 g), and then styrene (2.50 g) and *n*-butyl acrylate (2.50 g) were added. This mixture was degassed via five evacuation/nitrogen purge cycles and subsequently heated to 70 °C. Separately, the APS initiator (0.050 g) was dissolved in water (5.0 g), purged with nitrogen, and then injected into the reaction vessel at 70 °C. The polymerizing solution was stirred for 24 h, and the resulting latex was purified by dialysis against water. The latex was assessed by DLS (before purification) and by both SEM and aqueous electrophoresis (after purification). The purified latex was cast into films of approximately 50 μm thickness by drying in plastic molds at room temperature. These films were characterized by XPS measurements.

$PMPC_{30}$−PS Latex Syntheses via Alcoholic Dispersion Polymerization. $PMPC_{30}$ (or $PMPC_{20}$ or $PMPC_{10}$) macromonomer (1.00 g) was weighed into a 250 mL three-necked, round-bottomed flask fitted with a condenser and a nitrogen inlet and dissolved in methanol (100 mL). This solution was purged with nitrogen for 30 min before being heated to 70 °C under a nitrogen blanket. The AIBN initiator (0.100 g) was dissolved in styrene (10.0 g) and purged with nitrogen before being injected into the reaction vessel. The polymerizing solution turned milky white within 1 h and was stirred at 70 °C for 24 h. The above protocol was also used for $PMPC_{10}$ and $PMPC_{20}$ macromonomers and for examining the effect of varying the $PMPC_{30}$ macromonomer concentration. The resulting latexes were purified by three centrifugation/redispersion cycles. In each case, the latex diameter was assessed by DLS (before purification) and SEM (after purification). These latexes were also analyzed by ^{1}H NMR, FTIR, and XPS.

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 $PMPC_{30}$-PS latexes (1.0 mL; 2.0 w/v % solids content) were transferred via a pipet into sample vials to which 1.0 mL aliquots of various aqueous $MgSO_4$ solutions were added (0.02−1.00 M). This dilution produced 1.0% aqueous latex dispersions in 0.01−0.50 M $MgSO_4$. Colloidal (in)stability was judged by visual inspection and confirmed by DLS measurements.

Macromonomer and Latex Characterization. *^{1}H NMR Spectroscopy*. All ^{1}H NMR spectra were recorded in either $CDCl_3$, D_2O, or CD_3OD using a 400 MHz Bruker Avance-400 spectrometer. Dried PMPC-PS latexes were dissolved in 7:1 v/v $CDCl_3/CD_3OD$ for ^{1}H NMR analysis. The integrated intensity of the two azamethylene protons at δ 3.5−3.7 due to the PMPC stabilizer was compared to that of the five aromatic protons due to the styrene residues at δ 6.1−7.2. The dried PMPC-P(S-*n*BuA) latex was dissolved in 3:1 v/v $CDCl_3/CD_3OD$, and the integrated intensity of the nine trimethylammonium protons at δ 2.98−3.14 was compared to that of the five aromatic protons due to the styrene residues at δ 6.1−7.2.

Aqueous GPC. Molecular weights and polydispersities of the PMPC homopolymers were determined by aqueous GPC using two Polymer Laboratories Aquagel-OH 8 mm columns (type 40 first, followed by type 30) in series with a Polymer Laboratories ERC-7515A refractive index detector. The eluent was a solution containing 0.2 M $NaNO_3$ and 0.05 M Trisma buffer at pH 7.0 using a flow rate of 1.0 mL min^{-1}. The GPC columns were calibrated using 10 poly(ethylene oxide) (PEO) homopolymer standards. Data were analyzed using PL Cirrus GPC software (version 2.0) supplied by Polymer Laboratories.

FTIR 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 minutes. 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.

DLS. Dynamic light scattering (DLS; Malvern Zetasizer NanoZS instrument) was used to obtain intensity-average hydrodynamic latex diameters using the Stokes−Einstein equation, which is valid for dilute, noninteracting, perfectly monodisperse spheres. Aqueous 0.01 w/v % latex dispersions were analyzed using disposable cuvettes, and the data were averaged over three consecutive runs. The deionized water used to dilute each latex was ultrafiltered through a 0.20 μm membrane so as to remove extraneous dust.

Disk Centrifuge Photosedimentometry. The weight-average diameter D_w of the polystyrene latexes was measured using

Table 1. ATRP Synthesis of PMPC Homopolymer Precursors with Differing Target Degrees of Polymerization at 20 °C in Methanol[a]

entry no.	target DP	conversion (%)	DP (^{1}H NMR)	M_n (GPC)	M_w/M_n (GPC)
1	10	100	12	8400	1.21
2	20	98	22	11 600	1.28
3	30	100	30	13 100	1.29
4	35	99	45	15 100	1.30
5	40	100	60	17 500	1.97
6	50	99	75	19 400	1.87
7	50[b]	100		18 900	2.31
8	50[c]	100		19 100	2.01

[a] GPC data were obtained using poly(ethylene oxide) calibration standards. [b] Reaction conducted at 50 °C. [c] Reaction initiated at 0 °C and then warmed to 20 °C.

a Brookhaven BI-DCP instrument operating in line-start mode. Samples were prepared by the addition of one drop of latex dispersion to a 3:1 water/methanol mixture (total volume 10 mL). A 15:1 deionized water/methanol mixture was used as the spin fluid. The density of the polystyrene latex particles was taken to be 1.05 g cm^{-3}. This is a reasonable assumption for micrometer-sized latexes, where the thickness of the steric stabilizer layer is negligible compared to the particle diameter. For smaller latexes (typically for diameters of less than 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 the former parameter produces an associated error in the latter.[22]

Aqueous Electrophoresis. Zeta potentials were determined using a Malvern Zetasizer NanoZS instrument equipped with an autotitrator (MPT-2 multipurpose titrator, Malvern Instruments). The solution pH was varied from 2 to 9 in the presence of 1 mM KCl using either dilute NaOH or HCl as required.

SEM. SEM studies were performed using an FEI Sirion field-emission scanning electron microscope. Samples were dried onto adhesive carbon disks and sputter-coated with a thin layer of gold prior to examination using a beam current of 244 μA and a typical operating voltage of 20 kV.

XPS. X-ray photoelectron spectra (XPS) 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} to 10^{-10} mbar. Latex particles were dried onto a silicon wafer and evacuated to ultrahigh vacuum prior to XPS measurements.

Results and Discussion

A summary of the target degrees of polymerization, conversion, molecular weight, and polydispersity of the various PMPC homopolymer precursors synthesized in this study is shown in Table 1. Reasonably good control was achieved for the polymerization of MPC with target DPs of 10, 20, and 30 because the polydispersities of these homopolymers were 1.29 or less and the actual degree of polymerization agreed well with that of the targeted DP, as judged by ^{1}H NMR. GPC traces of these $PMPC_{30}$, $PMPC_{20}$, and $PMPC_{10}$ homopolymer precursors are shown in Figure 2, confirming that the differing degrees of polymerization can easily be distinguished. However, it is clear from Table 1 that there is a marked increase in polydispersity and/or a loss of control if the target DP is greater than 30. For a target DP of 35, the final polydispersity is still relatively low at 1.30, but the actual DP is significantly higher than that targeted, suggesting relatively poor initiation efficiency under these conditions. For higher target DPs, the final polydispersities range from

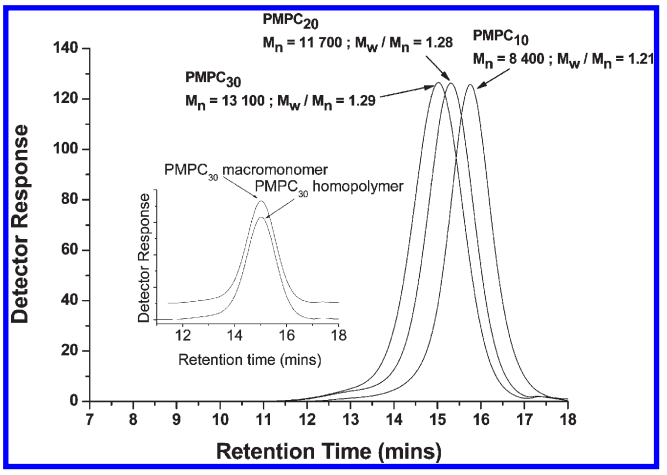

Figure 2. Representative aqueous GPC curves obtained for $PMPC_{10}$, $PMPC_{20}$, and $PMPC_{30}$ homopolymer precursors prepared by ATRP at 20 °C (vs poly(ethylene oxide) calibration standards). The inset compares the GPC trace obtained for the $PMPC_{30}$ homopolymer precursor to that of the corresponding macromonomer.

1.87 to 2.31, and the actual DP is substantially higher than that targeted. Varying the reaction temperature failed to improve the final polydispersities of these higher DP homopolymers (entries 7 and 8 in Table 1). However, a linear evolution of the number-average molecular weight with conversion was observed for the $PMPC_{30}$ synthesis, suggesting that reasonably good living character is obtained under these specific conditions (Figure 3). Although this data set does show a nonzero intercept that may indicate reduced control early in the polymerization, we emphasize that the ^{1}H NMR data confirms that the actual mean DP values are in good agreement with those targeted for the $PMPC_{10}$, $PMPC_{20}$, and $PMPC_{30}$ precursors. In contrast, the corresponding data set obtained for a $PMPC_{50}$ synthesis (Figure S1 in Supporting Information) shows a nonlinear evolution of molecular weight with conversion and the high final polydispersities suggest that only poor control is achieved for this higher DP homopolymer. Additional MPC homopolymerizations using 2-(dimethylamino)-ethyl-2-bromoisobutyrylamide targeting DPs of 30, 40, and 50 were performed several times, and the GPC data proved to be reproducible; the $PMPC_{30}$ precursor was always near-monodisperse (M_w/M_n = 1.2 to 1.3), whereas the $PMPC_{40}$ and $PMPC_{50}$ precursors were invariably polydisperse (M_w/M_n = 1.6 to 2.0). There is some evidence for a high molecular weight tail in the GPC trace for the $PMPC_{50}$ homopolymers, possibly suggesting some termination by combination (Figure S2 in Supporting Information). Currently, we have no convincing explanation for the dramatic loss of living character observed for the higher target DP syntheses, although we note that other workers have reported some difficulties in using amide-based ATRP initiators.[23] Nevertheless, we have shown that near-monodisperse PMPC homopolymers can be obtained for a target DP of up to 30. As we shall see later, this is sufficient to obtain well-defined PMPC macromonomers that allow the preparation of sterically stabilized latexes with enhanced colloidal stabilities.

Macromonomers were synthesized by quaternizing the tertiary amine end-groups of the three well-defined homopolymer precursors ($PMPC_{10}$, $PMPC_{20}$, and $PMPC_{30}$) using excess 4-VBC, as shown in Figure 1. Assigned NMR spectra for the 2-(dimethylamino)ethyl-2-bromoisobutyrylamide initiator, $PMPC_{30}$ homopolymer precursor, and corresponding $PMPC_{30}$ macromonomer

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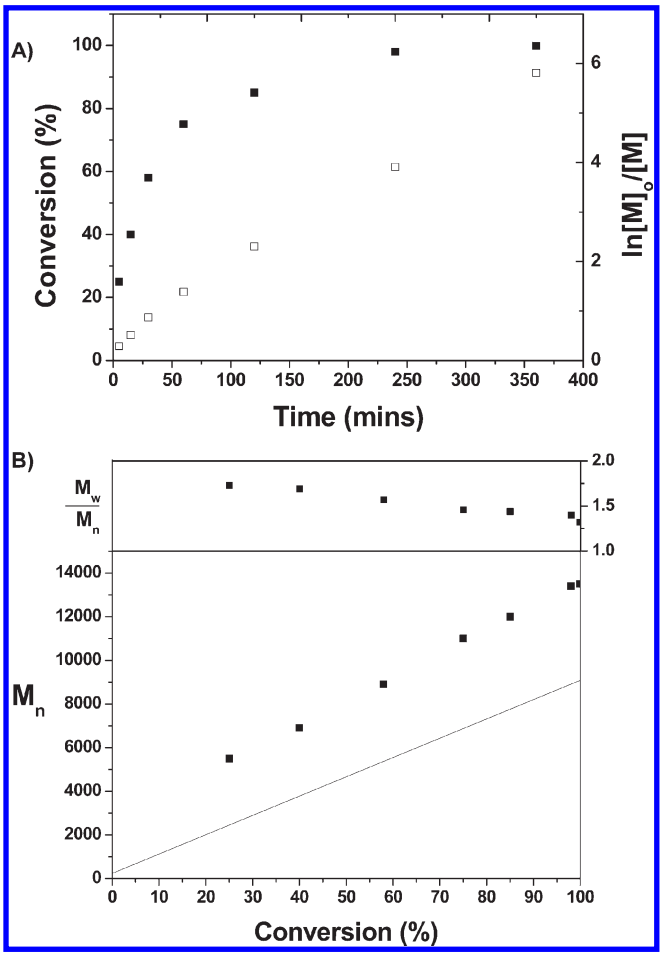

Figure 3. Homopolymerization of MPC in methanol via ATRP at 20 °C: (A) conversion and semilogarithmic plot of monomer concentration vs time data; (B) evolution of the number-average molecular weight and polydispersity with monomer conversion. The solid line represents the theoretical M_n evolution with conversion. Reaction conditions: MPC (10.0 g, 1.13 mmol), methanol (11.0 mL), target DP = 30, relative molar ratios of [I]/[Cu(I)]/[L] = 1:1:2. Aqueous GPC data were obtained using poly(ethylene oxide) calibration standards.

are shown in Figure 4. On quaternization with 4-VBC, NMR shifts are observed for the six dimethyl protons and the two azamethylene protons. The original positions of these two proton signals are shown in the initiator NMR spectrum (Figure 4a), and those of the corresponding homopolymer precursor (Figure 4b) are shown as peaks a and b, respectively. The new positions of these two signals for the quaternized $PMPC_{30}$ macromonomer are shown in Figure 4c. These NMR observations allow the extent of quaternization to be conveniently monitored: the complete disappearance of these initiator end-group signals in the δ 2.2−2.8 region indicates that full quaternization has been achieved. After purification to remove excess 4-VBC, new aromatic and benzylic peaks due to the conjugated 4-vinylbenzyl group are observed in the ^{1}H NMR spectrum (Figure 4c, δ 5.4−7.9). It is perhaps worth emphasizing that the amide-based ATRP initiator is essential for ensuring that these PMPC macromonomers exhibit good hydrolytic stability: our preliminary studies (data not shown) using the corresponding ester-based ATRP initiator indicated that extensive hydrolysis of the quaternized chain ends occurs, even on storage at below ambient temperature.

The amount of 4-VBC required to quaternize the PMPC homopolymer precursors fully was assessed by monitoring this

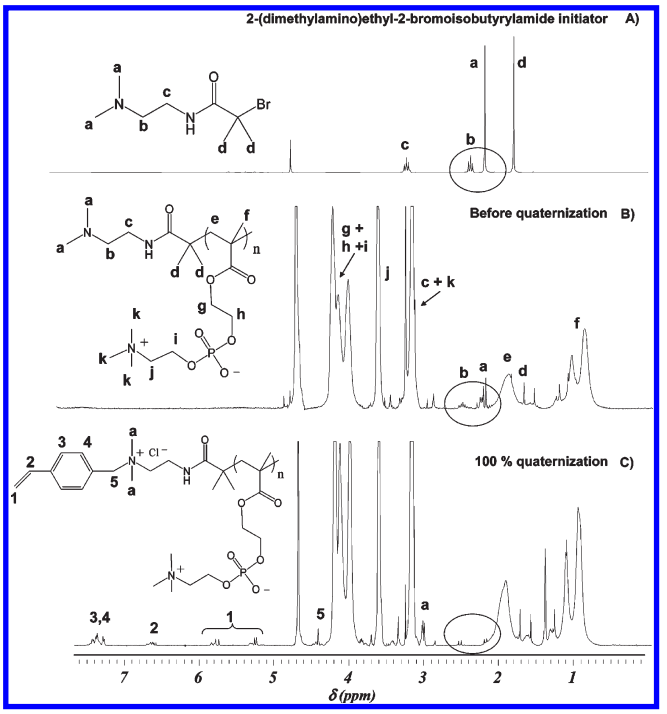

Figure 4. ^{1}H NMR spectra recorded in CD_3OD for (a) 2-(dimethylamino)ethyl-2-bromoisobutyrylamide, (b) $PMPC_{30}$ homopolymer precursor before quaternization, and (c) $PMPC_{30}$ macromonomer after quaternization and purification using a 4-VBC/amine molar ratio of 3:1.

reaction by ^{1}H NMR spectroscopy. The $PMPC_{10}$ homopolymer was used in these kinetic experiments because its relatively low degree of polymerization ensures that its initiator signals are prominent, which aids quantification. The three 4-VBC/$PMPC_{10}$ molar ratios (3:1, 2:1, and 1:1) investigated each allowed full quaternization to be achieved, albeit on differing time scales (Figure 5). The 3:1 molar ratio led to complete quaternization within 14 h, whereas using a 1:1 molar ratio required 72 h at 20 °C. A control experiment was conducted to examine the possible side reaction of 4-VBC with the solvent. No changes were observed in the ^{1}H NMR spectrum of 4-VBC in CD_3OD for up to 72 h at 20 °C, thus confirming that no reaction occurs between 4-VBC and CD_3OD under these conditions. Another possibility is that the 4-VBC might esterify the anionic phosphate groups on the PMPC homopolymer, in addition to quaternizing the desired tertiary amine end-group. Thus, a $PMPC_{30}$ homopolymer containing no terminal tertiary amine group was synthesized using *m*-methylphenyl bromoisobutyrate (MPBr) initiator and mixed with a 3-fold excess of 4-VBC for 72 h in CD_3OD. Again, no change in the ^{1}H NMR spectrum was observed, confirming that no reaction occurs in the absence of terminal tertiary amine groups.

Table 2 summarizes the GPC data obtained for the PMPC homopolymers before and after quaternization, and the inset in Figure 3 compares the GPC molecular weight distributions before and after quaternization of the $PMPC_{30}$ precursor. Quaternization resulted in essentially no difference in the molecular weight distribution, as expected. Moreover, there was essentially no difference between the aqueous GPC curves recorded using UV and refractive index detectors (data not shown), thus confirming that each PMPC chain contained a UV chromophore (i.e., a terminal polymerizable styrenic unit).

Polystyrene latexes were prepared using the PMPC-based macromonomers as reactive steric stabilizers, as illustrated in

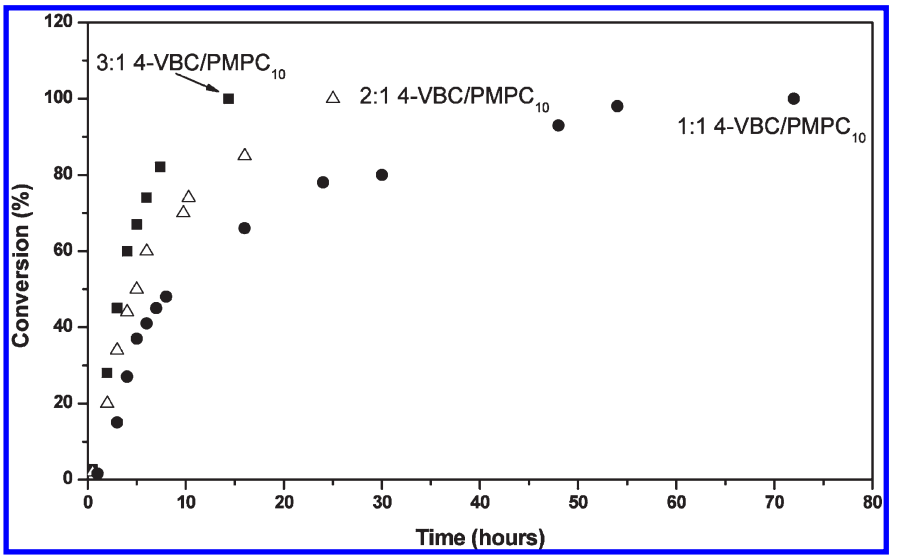

Figure 5. Quaternization of a 25 w/v % $PMPC_{10}$ homopolymer conducted in CD_3OD at 20 °C using 4-VBC/amine molar ratios of 3:1, 2:1, and 1:1.

Table 2. Comparison of GPC Data (vs Poly(ethylene oxide) Calibration Standards) Obtained before Quaternization and after Quaternization (and Purification)

		before quaternization		after quaternization	
target DP	conversion (%)	M_n (g mol^{-1})	M_w/M_n	M_n (g mol^{-1})	M_w/M_n
10	100	8400	1.21	8400	1.22
20	98	11 600	1.28	11 500	1.30
30	100	13 900	1.29	14 000	1.32

Figure 6. A summary of the various latex syntheses conducted using aqueous emulsion polymerization is provided in Table 3. Entries 1, 3, and 5 were prepared using the $PMPC_{30}$ macromonomer, and in each case, very high conversions and narrow particle size distributions were obtained. It is perhaps worth emphasizing that such results are not always observed for surfactant-free macromonomer-only syntheses: in some cases only rather polydisperse latexes are obtained under these conditions.[24] It is also noteworthy that entries 5 and 6 involve the synthesis of film-forming styrene/*n*-butyl acrylate copolymer latexes rather than polystyrene latex. Depending on the precise formulation, it is often possible to obtain colloidally stable latexes via aqueous emulsion polymerization even in the absence of any polymeric or surfactant stabilizer. This proved to be the case in the present study. Thus, polystyrene latexes could be obtained in the absence of any polymeric stabilizer when using the anionic persulfate or cationic AIBA initiators at 70 or 60 °C, respectively. However, these latexes are significantly larger and more polydisperse than those prepared in the presence of the $PMPC_{30}$ macromonomer. This supports the hypothesis that the latter particles are sterically stabilized by the chemically grafted $PMPC_{30}$ macromonomer chains. Latexes prepared in the absence of macromonomer are merely charge-stabilized, with the surface charge originating from the initiator fragments. Given their larger latex diameter and significantly higher polydispersity, this is clearly a much less effective stabilization mechanism under the stated conditions. ^{1}H NMR analysis of the dried latexes allows the calculation of the amount of $PMPC_{30}$ macromonomer incorporated into the latex particles. In the case of aqueous emulsion polymerization, the $PMPC_{30}$ macromonomer comprises 3.7−7.3% of the latex by mass (Table 3). Assuming that all of the macromonomer chains are located on the outside of the latex, this corresponds to an adsorbed amount, Γ, of roughly 1.2−1.3 mg m^{-2}. These adsorbed amounts are approximately constant for all three latexes, as expected.

Alcoholic dispersion polymerization was also used to prepare polystyrene latexes (Table 4). The dispersion polymerization of styrene in alcoholic solution is well documented.[25] Various vinyl-functionalized macromonomers have been used to ensure effective steric stabilization, which is normally a prerequisite for colloid stability under these conditions.[26,27] In the present study, we conducted several control experiments to demonstrate that the macromonomer architecture is essential for producing colloidally stable latex particles. Polymerization of styrene in methanol at 70 °C using an AIBN initiator in the absence of any polymeric stabilizer simply led to macroscopic precipitation, as expected (see entry 10 in Table 4 and also Figure 7). A similar experiment conducted in the presence of the $PMPC_{30}$ homopolymer precursor (i.e., each chain merely has a terminal tertiary amine group, rather than a polymerizable styrene group) also led to precipitation, with little or no colloidal latex being formed (entry 11 in Table 4). In contrast, the polymerization of styrene in the presence of 10 w/v % of the corresponding $PMPC_{30}$ macromonomer led to the production of a near-monodisperse, micrometer-sized polystyrene latex under the same conditions. These results confirm that the presence of a reactive terminal styrenic group is essential for successful latex formation and also suggests that negligible chain transfer to the PMPC precursor occurs (i.e., in situ stabilizer grafting via chain transfer to polymer is not sufficient to ensure colloid stability in this case). However, lowering the stabilizer concentration to 5 w/v % failed to produce a stable latex. This is perhaps understandable given the relatively massive MPC repeat units: a mean DP of 30 corresponds to an M_n of approximately 9000, which means that there are relatively few stabilizer chains per unit mass compared to conventional macromonomers such as commercially available poly(ethylene glycol) monomethacrylates (for which M_n = 1000 or 2000).[22] Syntheses conducted using either the $PMPC_{20}$ or the $PMPC_{10}$ macromonomer at 10 w/v % yielded latexes that were significantly more polydisperse than that

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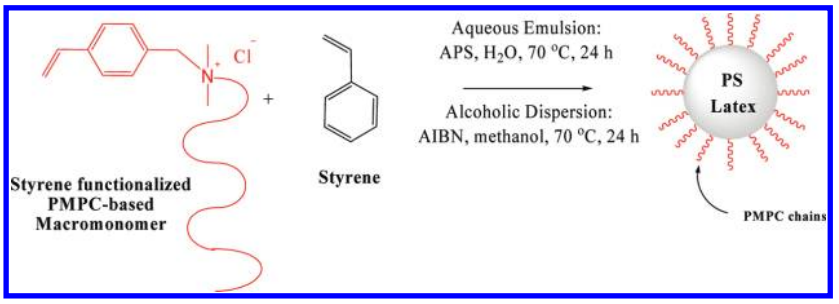

Figure 6. Reaction scheme for the synthesis of sterically stabilized polystyrene latexes by either aqueous emulsion or alcoholic dispersion polymerization using the PMPC-based macromonomer.

Table 3. Emulsion Polymerization of Styrene Showing Initiator and Stabilizer Type and Mean Latex Diameter Determined by DCP, DLS, and SEM[a]

				particle diameter (nm)				
entry no.	stabilizer	initiator type	latex conversion (%)	SEM	DCP	DLS (PDI)	stabilizer content by NMR (wt %)	Γ (mg m^{-2})
1	$PMPC_{30}$ macromonomer	APS	92	170	180 ± 17	191 (0.03)	3.7	1.2[c]
2	no added stabilizer	APS	48	560	580 ± 29	667 (0.05)		
3	$PMPC_{30}$ macromonomer	AIBA	85	95	118 ± 10	114 (0.02)	7.3	1.3[c]
4	no added stabilizer	AIBA	70	200, 750	670 ± 88	1060 (0.10)		
5[b]	$PMPC_{30}$ macromonomer	APS	86			119 (0.04)	5.4	1.2[d]
6[b]	no added stabilizer	APS	37			650 (0.07)		

[a] Reactions were conducted at 60 °C (AIBA) and 70 °C (APS) in water for 24 h using 1.0 wt % initiator and 10 w/v % macromonomer based on the styrene monomer. [b] These two entries are film-forming 1:1 styrene/*n*-butyl acrylate copolymer latexes. [c] Calculated using the SEM diameter. [d] Calculated using the DLS diameter because of the film-forming nature of the copolymer latex.

Table 4. Effect of Stabilizer Type on the Mean Particle Diameter as Determined by DCP, DLS, and SEM for Polystyrene Latexes Prepared via Alcoholic Dispersion Polymerization in Methanol at 70 °C for 24 h Using 1.0 wt % AIBN Initiator Based on the Styrene Monomer

entry no.	stabilizer type	stabilizer (w/v %)	latex conversion (%)	SEM	DCP	DLS	stabilizer content by NMR (wt %)	Γ (mg m^{-2})
7	$PMPC_{30}$ macromonomer	10	100	1020	1080 ± 96	1140 (0.05)	0.7	1.3
8	$PMPC_{20}$ macromonomer	10	100	1090	1120 ± 140	1450 (0.30)	0.4	0.8
9	$PMPC_{10}$ macromonomer	10	100	930	900 ± 100	1120 (0.16)	0.6	1.0
10	no added stabilizer	0	0					
11	$PMPC_{30}$ homopolymer	10	0					
12	$PMPC_{30}$ macromonomer	5	0					

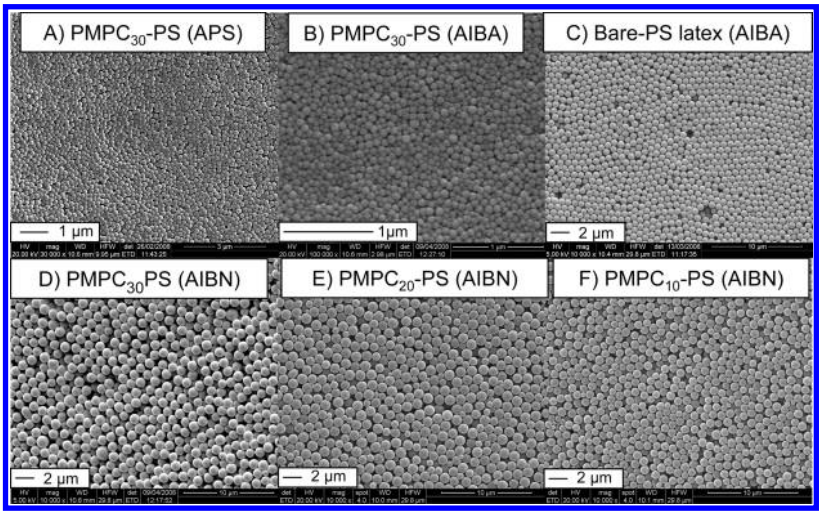

Figure 7. SEM images of selected polystyrene latexes prepared in the presence of $PMPC_{30}$ (A, B, and D), $PMPC_{20}$ (E), and $PMPC_{10}$ (F) macromonomers and a charge-stabilized PS latex control (C) prepared by aqueous emulsion polymerization in the absence of any macromonomer.

produced using the $PMPC_{30}$ macromonomer, but there is no obvious trend between mean latex diameter and macromonomer chain length. ^{1}H NMR spectroscopy was again used to calculate the stabilizer content of the latex. Since alcoholic dispersion polymerization produces much larger latexes (with correspondingly lower specific surface areas), the stabilizer contents were somewhat lower than those prepared by emulsion polymerization (0.4−0.7%, Table 4). This leads to Γ values of between

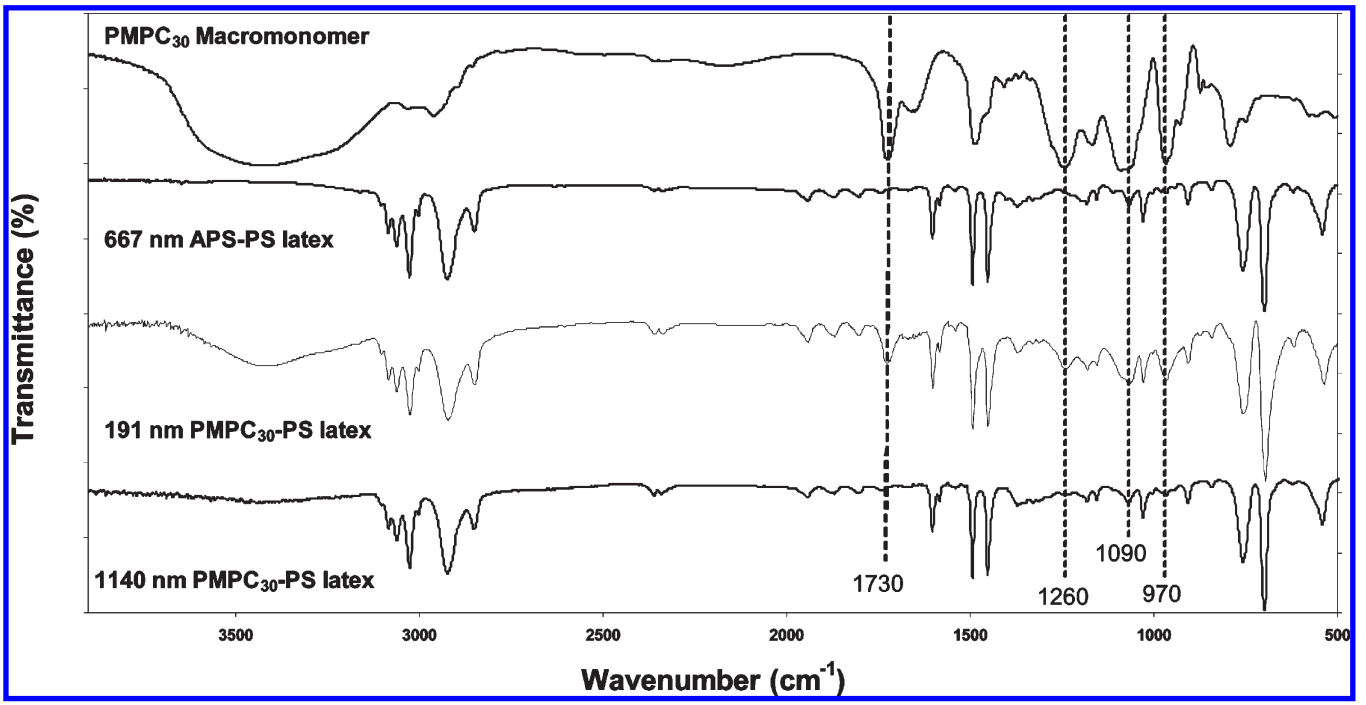

Figure 8. FTIR spectra recorded for the $PMPC_{30}$ macromonomer, a charge-stabilized polystyrene latex prepared by emulsion polymerization in the absence of macromonomer, a polystyrene latex prepared by emulsion polymerization using the $PMPC_{30}$ macromonomer and APS initiator, and a polystyrene latex prepared by alcoholic dispersion polymerization using the $PMPC_{30}$ macromonomer and AIBN initiator.

0.8 and 1.3 mg m^{-2}, which are comparable to those calculated for the three smaller latexes (Table 3). This suggests that our assumption that all of the macromonomer chains are located at the surface of these latexes is likely to be valid.

FTIR spectra were recorded for the $PMPC_{30}$ macromonomer and selected polystyrene latexes (Figure 8). The ester carbonyl stretch due to the PMPC macromonomer is observed at around 1730 cm^{-1}. Characteristic bands also appear at 1260 and 1090 cm^{-1} due to the P=O and P−O−C stretches, respectively, and also at 970 cm^{-1} due to the antisymmetric stretches of the three C−N bonds in the trimethylammonium group,[28] which are consistent with previous FTIR studies of PMPC.[19,20,29] All of these bands are also observed in the spectrum obtained for the polystyrene latex prepared by aqueous emulsion polymerization. This confirms the presence of the PMPC stabilizer (but not its spatial location) in this latex. In contrast, no carbonyl band was observed for the micrometer-sized $PMPC_{30}$-PS latex prepared by alcoholic dispersion polymerization. However, this negative result was not unexpected; the much lower specific surface area of this latex means that its stabilizer content is less than 1% by mass (Table 4), which precludes the detection of the carbonyl band.

Aqueous electrophoresis curves obtained for a charge-stabilized polystyrene latex and several sterically stabilized latexes prepared using the $PMPC_{30}$ macromonomer are shown in Figure 9. As expected, the bare polystyrene latex prepared in the absence of any stabilizer using the cationic AIBA initiator exhibits a positive zeta potential for most of the pH sweep (pH 2−7). In contrast, all of the $PMPC_{30}$-stabilized latexes exhibit much shallower electrophoretic curves with zeta potentials of approximately ±5 mV (and hence very low surface charge).

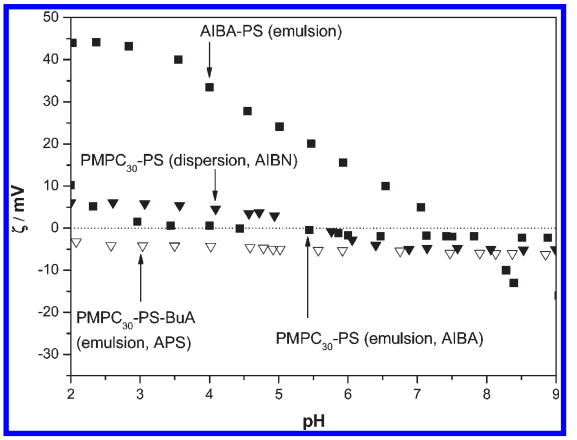

Figure 9. Zeta potential vs pH curves obtained for polystyrene and poly(styrene-*co*-*n*-butyl acrylate) latexes prepared in the presence of the $PMPC_{30}$ macromonomer and also a charge-stabilized polystyrene latex control synthesized in the absence of a macromonomer.

This is not surprising given that the PMPC chains are zwitterionic in nature and therefore have no net charge. Provided that the PMPC stabilizer layer is sufficiently thick, the underlying cationic surface charge (due to the initiator fragments and quaternized macromonomer end-groups) is effectively screened. Therefore, these electrophoretic results are consistent with the $PMPC_{30}$ macromonomer being located at the particle surface. Further evidence is provided by XPS analysis (Table 5). XPS is very surface-specific, with a typical analysis depth of around 2−5 nm. Hence only the near surface of the particles is interrogated. Therefore, if the $PMPC_{30}$ macromonomer lies at the surface of the latex, then XPS should exhibit characteristic N 1s and P 2p signals due to its nitrogen and phosphorus atoms, respectively. These features are indeed observed in the XPS spectra, with the N/

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Table 5. XPS Data Summarizing the Near-Surface Elemental Compositions of the $PMPC_{30}$ Macromonomer, Two Polystyrene Latexes Prepared by Emulsion and Dispersion Polymerization in the Presence of This Macromonomer, and the P(S-nBuA) Film-Forming Latexes Prepared by Emulsion Copolymerization Using This Macromonomer[a]

XPS sample description	% C	% N	% P	% O	% S	N/P	% $PMPC_{30}$ surface coverage
$PMPC_{30}$ macromonomer	73.3	2.7	2.7	21.2		1.0	
charge-stabilized polystyrene latex (prepared with APS initiator)	95.5			4.6	0.4		
$PMPC_{30}$-PS latex (emulsion polymerization, APS initiator)	84.6	1.0	1.1	13.2	0.1	0.9	37
PS precipitate (attempted dispersion polymerization, AIBN initiator)	97.4			2.6			
$PMPC_{30}$-PS latex (dispersion polymerization, AIBN initiator)	83.0	1.4	1.4	14.2		1.0	52
charge-stabilized P(S-BuA) latex film (APS initiator)	89.4			10.6			
$PMPC_{30}$-P(S-BuA) latex film (APS initiator)	90.4			9.6			

[a] A macroscopic precipitate of polystyrene and a charge-stabilized polystyrene latex prepared in the absence of any macromonomer are also included as reference materials.

Table 6. Summary of the Colloidal Stabilities of Various Latexes after Being Subjected to a Single Freeze−Thaw Cycle (at 10 w/v % Solids, Frozen at −20 °C) or the Presence of Varying Amounts of $MgSO_4$ (2.0 w/v % Solids)[a]

		$MgSO_4$ concentration (mol dm^{-3})						
latex type	DLS latex diameter (nm)	0.01	0.05	0.10	0.20	0.30	0.50	freeze−thaw stability (DLS, nm)
APS-PS	667	x	x	x	x	x	x	x (precipitate)
$PMPC_{30}$-PS	191	√	√	√	√	√	√	√ (191)
$PMPC_{30}$-PS	1140	√	√	√	√	√	√	√ (1140)
$PMPC_{20}$-PS	1450	√	√	√	√	√	√	√ (1400)
$PMPC_{10}$-PS	1120	√	√	√	√	√	√	√ (1190)
APS-P(S-BuA)	650	x	x	x	x	x	x	x (precipitate)
$PMPC_{30}$-P(S-BuA)	119	√	√	√	√	√	√	√ (precipitate)

[a] x - Particles are unstable and visibly aggregated. √ - Particles are stable and remain dispersed, with the final DLS latex diameter in nanometers observed after thawing also reported, where applicable.

P atomic ratios being approximately unity (Table 6). Ishihara and co-workers[20] obtained similar XPS results for their PMPC-stabilized polystyrene latexes, although in their case the N/P atomic ratios were not reported. Surprisingly, although aqueous electrophoresis suggests that the $PMPC_{30}$ macromonomer is present at the surface of the $PMPC_{30}$-P(S-BuA) latex, XPS analysis of the latex film does not reveal any characteristic nitrogen or phosphorus signals due to the MPC units. Presumably, this is because the hydrophilic PMPC chains can bury themselves in the low-T_g copolymer film when subjected to the ultrahigh-vacuum conditions required for XPS studies. Similar findings (and conclusions) have been reported by Clarke and co-workers for MPC-based statistical copolymers.[30]

Having demonstrated that the PMPC-based macromonomers are indeed located at the latex surface and thus act as steric stabilizers, we evaluated the latex colloid stability by two methods: a single freeze−thaw cycle and exposure to varying concentrations of $MgSO_4$ (Table 6). A charge-stabilized polystyrene latex control flocculated substantially in just 0.01 M $MgSO_4$ and also failed to redisperse after a freeze−thaw cycle. However, each latex stabilized by the PMPC-based macromonomers (DP = 10, 20, or 30) remained stable at up to 0.50 M $MgSO_4$ and also readily redispersed after freeze−thaw cycles, as judged by DLS. Clearly, the PMPC chains confer substantially enhanced colloidal stability. Good freeze−thaw stability is a typical characteristic of sterically stabilized latexes, but the excellent salt tolerance is presumably due to the zwitterionic nature of the PMPC chains; it is well known that such polybetaines generally exhibit a so-called antipolyelectrolyte effect, whereby they are "salted in" on addition of electrolyte (rather than "salted out" like conventional polyelectrolytes).[31,32]

Conclusions

Novel biocompatible styrene-functionalized macromonomers have been synthesized using a tertiary amine-functional ATRP initiator followed by postpolymerization quaternization using 4-vinylbenzyl chloride. Empirically, we find that there is an upper limit for the target DP of the homopolymer precursors under the conditions investigated in this work: above a target DP of 35, only rather broad molecular weight distributions are obtained ($M_w/M_n > 2.0$), whereas for DP = 10−30 relatively low polydispersity chains are produced ($M_w/M_n < 1.30$) with reasonable control over the target DP. The latter macromonomers were evaluated as reactive polymeric stabilizers for the polymerization of styrene using either aqueous emulsion or alcoholic dispersion formulations. For example, near-monodisperse, sterically stabilized polystyrene latexes of micrometer dimensions are obtained via dispersion polymerization in the presence of the $PMPC_{30}$ macromonomer, whereas only a macroscopic precipitate is observed if a non-quaternized $PMPC_{30}$ homopolymer precursor was utilized. This illustrates the essential role played by the terminal polymerizable styrene group in determining the final particle morphology. Similarly, near-monodisperse polystyrene latexes of around 100−200 nm diameter were obtained via emulsion polymerization using the same $PMPC_{30}$ macromonomer, whereas only polydisperse, charge-stabilized latexes were obtained in the absence of any stabilizer. FTIR, aqueous electrophoresis, and XPS studies confirmed that the chemically-grafted macromonomer is present at (or very near) the surface of the prepared latex particles. The highly hydrated, zwitterionic nature of these PMPC chains confers enhanced colloid stability on these sterically stabilized latexes compared to charge-stabilized latexes. For example, no significant particle aggregation occurs in the presence of up to 0.50 M $MgSO_4$ or after a freeze−thaw cycle at −20 °C.

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Supporting Information Available: Kinetic and molecular weight data obtained for the uncontrolled polymerization of MPC when targeting a mean degree of polymerization of 50. Comparison of GPC curves obtained for near-monodisperse and polydisperse PMPC homopolymer precursors. This material is available free of charge via the Internet at http://pubs.acs.org.