Latex Syntheses Using Novel Tertiary Amine Methacrylate-Based Macromonomers Prepared by Oxyanionic Polymerization

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ABSTRACT: Recently, Nagasaki et al. [*Macromol. Rapid Commun.* **1997**, *18*, 827−835] reported that certain heteroatom methacrylate monomers such as 2-(diethylamino)ethyl methacrylate (DEAEMA) can be polymerized at room temperature using oxyanionic initiators such as potassium ethoxide. Furthermore, functional initiators such as potassium 4-vinylbenzyl alcoholate produced styrene-functionalized macromonomers. We have utilized this chemistry to synthesize a range of novel, well-defined water-soluble macromonomers based on 2-(dimethylamino)ethyl methacrylate (DMAEMA) and other tertiary amine methacrylates. These macromonomers were typically contaminated with small amounts of residual initiator, but this could be easily removed by precipitation into *n*-hexane. NMR and GPC studies confirmed that each poly(DMAEMA) chain had a polymerizable styrene end group. Selected macromonomers were used to prepare submicrometer-sized and micrometer-sized polystyrene latexes via aqueous emulsion and nonaqueous dispersion polymerization, respectively. The terminal functional group participates in the styrene polymerization, leading to chemical grafting of the macromonomer onto the outside of the latex particles. The presence of the stabilizer in the latexes was confirmed by FTIR spectroscopy and nitrogen microanalyses. The adsorbed amount of macromonomer varied between 0.5 and 4.6 mg m^{-2}. The first examples of well-defined, sulfobetaine-based macromonomers were obtained by derivatizing selected DMAEMA macromonomers with 1,3-propane sultone. One of these macromonomers proved to be an effective steric stabilizer for the synthesis of polystyrene latexes at high electrolyte concentration (1.0 M NaCl).

Introduction

Macromonomers are polymers that contain a single, usually terminal, polymerizable group. They are useful for the synthesis of graft copolymers and sterically stabilized latexes.[1] Hydrophilic macromonomers are of particular interest for the synthesis of water-borne latexes. Literature examples include nonionic macromonomers based on poly(ethylene oxide),[2−7] poly(*N*-vinylpyrrolidone),[2,8] and poly(vinyl alcohol).[9]

Macromonomers based on polyelectrolytes have also received attention. For example, Ishizu and co-workers[10] recently described the synthesis of styrenic-functionalized poly(acrylic acid) using a degradative chain transfer agent, followed by end-capping with 4-chloromethylstyrene. These macromonomers were then copolymerized with methyl methacrylate to produce poly(acrylic acid)-stabilized poly(methyl methacrylate) latex particles. The same group also reported the synthesis of poly(methacrylic acid) macromonomers of narrower molecular weight distribution by capping living poly(*tert*-butyl methacrylate) anionic chains with 4-chloromethylstyrene, followed by removal of the *tert*-butyl protecting groups via hydrolysis.[11]

Well-defined macromonomers of narrow molecular weight distribution are best prepared via living polymerization chemistry using functional initiators.[1] This approach generally guarantees that each polymer chain has a terminal polymerizable group (i.e., the macromonomer functionality is unity) and usually involves fewer synthetic steps than other routes. Classical anionic polymerization,[12−15] "group transfer" polymerization,[16] living cationic polymerization,[17] and, most recently, living free radical polymerization[18,19] have all been utilized to prepare well-defined macromonomers.

Very recently, Nagasaki et al. reported[20] the synthesis of poly[2-(diethylamino)ethyl methacrylate] macromonomers using potassium 4-vinylbenzyl alcoholate as a functional initiator. Such oxyanionic initiators do not normally polymerize methacrylate monomers: the Japanese group attributed their unexpected success to complexation of the potassium counterion with the nitrogen heteroatom of the (2-diethylamino)ethyl methacrylate. However, this explanation remains speculative; the precise mechanism for this polymerization has not yet been established. Nevertheless, polymerization of the tertiary amine methacrylate monomer proceeded at or above ambient temperature to produce well-defined macromonomers (M_w/M_n < 1.30) containing a single polymerizable styrenic unit per chain. Since the tertiary amine groups can be protonated at low pH, this cationic macromonomer is complementary to the anionic, carboxylic acid-based macromonomers reported by Ishizu and co-workers.[10,11]

In the present work we investigated the scope and limitations of the Nagasaki chemistry, which we have termed "oxyanionic" polymerization. Various functional alcoholate initiators have been utilized in order to produce a range of novel macromonomers based on three tertiary amine methacrylates: 2-(dimethylamino)ethyl methacrylate, 2-(diisopropylamino)ethyl methacrylate, and 2-(*N*-morpholino)ethyl methacrylate (see Figure 1). The efficacy of these tertiary amine methacrylate-based macromonomers as reactive polymeric stabilizers for polystyrene latex syntheses via both aqueous emulsion and nonaqueous dispersion polymerization is demonstrated.

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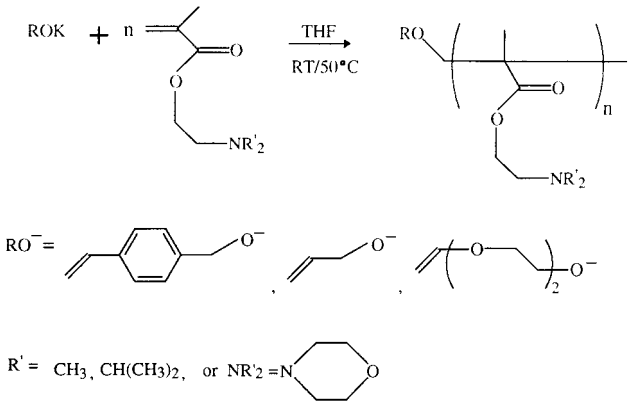

Figure 1. Reaction scheme for the synthesis of tertiary amine methacrylate-based macromonomers via oxyanion-mediated polymerization with functional initiators.

Experimental Section

Materials. Unless otherwise stated, materials were obtained from Aldrich and used without further purification. Tetrahydrofuran (THF) was dried over sodium wire and then refluxed over potassium metal for 3 days prior to use. It was collected and stored over molecular sieves under dry nitrogen. Allyl alcohol and di(ethylene glycol) vinyl ether were distilled and stored under nitrogen at −15 °C prior to use. 4-Vinylbenzyl alcohol (VBA), kindly donated by Seimi Chemical Co., Japan, was distilled from CaH_2 and stored under nitrogen in a solution of dry THF. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) was passed through a column of activated basic alumina, stored over CaH_2 for 24 h, and distilled immediately prior to use.

Macromonomer Synthesis. A flame-dried 100 mL round-bottomed flask was filled with dry nitrogen and then weighed. KH was added as a 35 wt % dispersion in mineral oil under a purge of nitrogen. Dry THF was added via a double-tipped needle, and the resulting dispersion was briefly stirred before being allowed to sediment. The THF was then removed using a double-tipped needle. This washing procedure was repeated twice, and then the flask was evacuated to remove the remaining THF. When the solvent was completely removed, the flask was refilled with dry nitrogen and weighed again to determine the amount of KH (0.023 mol). Approximately 60 mL of THF and a dry magnetic flea were then added to the flask, and the dispersion was cooled to 0 °C. A stoichiometric amount of 4-vinylbenzyl alcohol (as a solution in THF) was then added to the stirred dispersion, and the resulting solution was maintained at 0 °C for 30 min, before warming to room temperature. DMAEMA monomer (7.4 mL) was then added quickly via a double-tipped needle, and the polymerization was left for 30 min before addition of a small amount of methanol to terminate the reaction. The macromonomer was purified by repeated precipitation into cold *n*-hexane, followed by filtration and drying under vacuum at room temperature overnight. Typical final yields of purified macromonomer were around 90%.

Betainization of Macromonomers. The required amount of macromonomer (8.09 g, M_n = 4800 g mol^{-1}) was added to a round-bottomed flask, and 250 mL of THF was added together with a magnetic flea. Then 1,3-propane sultone (5 mL, 20 mol % excess) was added to the stirred solution at 25 °C. Gelation occurred overnight, and the reaction was terminated after 24 h. THF was removed by rotary evaporation, and the betainized macromonomer was redissolved in the minimum volume of deionized water. The polymer was precipitated from this aqueous solution into THF. This procedure was repeated twice to ensure complete removal of 1,3-propane sultone.

Emulsion and Dispersion Polymerizations. For aqueous emulsion polymerizations the macromonomer stabilizer (0.25−0.50 g) was dissolved in dilute hydrochloric acid (pH 2, 50 mL) and heated to 60 °C under nitrogen with magnetic stirring. The reaction was purged with nitrogen for a further hour, and then styrene (5.0 g) was added. Stirring was continued for a further 10 min to emulsify the monomer. A solution of $K_2S_2O_8$ (0.050 g in 2 mL of water) was added and the reaction allowed to proceed for 24 h. After cooling to room temperature, the reaction mixture was purified by three centrifugation−redispersion cycles, with successive supernatants being replaced by deionized water. The "high salt" emulsion polymerization using the sulfobetainized macromonomer was carried out in the same way, except 1 M NaCl was used in place of the aqueous HCl. Alcoholic dispersion polymerizations were also carried out similarly, except that after the nitrogen purge a solution of azoisobutyronitrile (AIBN) predissolved in styrene monomer was added. Again, reactions were allowed to proceed for 24 h and were cleaned up via centrifugation−redispersion cycles as described above.

Gel Permeation Chromatography (GPC). GPC studies were carried out using a Perkin-Elmer instrument with an LC 25 RI detector and a Knauer UV detector (λ = 254 nm) in series, with a PLgel 3 μm Mixed "E" column (Polymer Labs). HPLC grade THF was used as the eluent at a flow rate of 1 mL min^{-1}. Chromatographs were analyzed using four poly(methyl methacrylate) calibration standards (ranging from 400 to 29 400 g mol^{-1}).

Nuclear Magnetic Resonance Spectroscopy (NMR). Spectra (averaged over 16 scans) were obtained using a Bruker AC-P250 Fourier transform spectrometer using $CDCl_3$ as solvent.

Disk Centrifuge Photosedimentometry. The latex size distributions were assessed using disk centrifuge photosedimentometry (DCP). Samples were prepared by addition of one drop of the latex dispersion to a 2:1 water:methanol mixture. All measurements were carried out using a Brookhaven BI-DCP instrument, operating in the line start mode. A particle density of 1.05 g cm^{-3} was assumed for the polystyrene latex particles. For the micrometer-sized particles this is a reasonable assumption, since the steric stabilizer thickness is negligible compared to the particle diameter. For smaller latex particles (i.e., <300 nm), however, the stabilizer layer thickness (ca. 5−10 nm) is significant. Thus, an inherent error in the particle density, and hence in the particle diameter calculated by the DCP, is incurred.

Scanning Electron Microscopy (SEM). SEM measurements were made using a Leica Stereoscan 420 instrument. The dried latex was deposited onto an aluminum stub, followed by sputter-coating with a thin overlayer of gold prior to examination.

Results and Discussion

Macromonomer Syntheses. The synthesis of macromonomers via vinyl-functionalized initiators requires highly selective polymerization chemistry. Thus, the monomer residues that form the macromonomer main chain must be polymerized under conditions that do not lead to copolymerization of the terminal vinyl functionality; otherwise, cross-linked graft copolymers will be obtained, rather than well-defined linear macromonomers. Since styrene cannot be polymerized by oxyanions, this criterion is fulfilled for the potassium 4-vinylbenzyl alcoholate/tertiary amine methacrylate combination utilized in the present work. It is also well-known that vinyl ethers and allyl monomers cannot be polymerized by anionic polymerization, so we examined the potassium alcoholate salts of di(ethylene glycol) vinyl ether and of allyl alcohol as functional initiators. These latter initiators also produced well-defined vinyl ether- and allyl-terminated tertiary amine methacrylate macromonomers, as expected.

Nagasaki et al. reported the polymerization of both 2-(trialkylsiloxy)ethyl methacrylates[21] (ProHEMAs) and 2-(diethylamino)ethyl methacrylate[20] (DEAEMA) using various potassium alcoholates as initiators. They proposed that the donor atom in these monomers increased

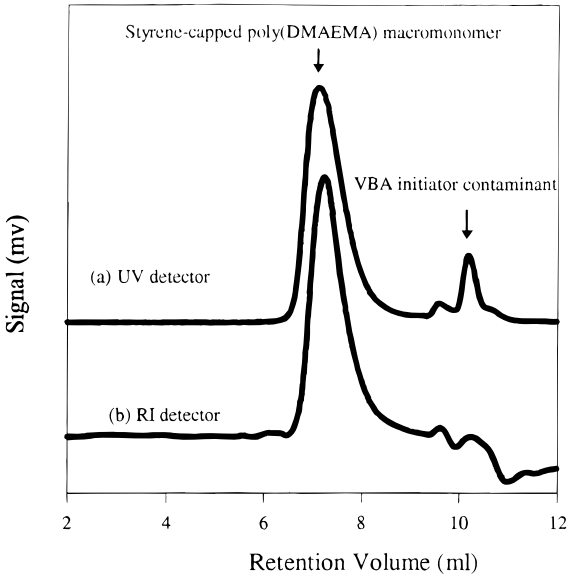

Figure 2. GPC curves for poly(DMAEMA) macromonomer M5: (a) using a UV detector set at 254 nm, (b) using an RI detector.

the nucleophilicity of the alkoxide ion by chelation of the alkali metal cation.[21] In these syntheses a yellow coloration was noted on addition of the monomer to the reaction solution. We also observed this coloration in the present study. Nagasaki et al. used a potassium naphthalene complex for the in situ production of the potassium 4-vinylbenzyl alcoholate. In our study we preferred to use KH, which quantitatively converts the hydroxy groups into alkoxides with the liberation of hydrogen. This avoids the possibility of naphthalene contamination of the final macromonomer. However, addition of excess KH should be avoided, since our control experiments indicated that this reagent can initiate the polymerization of tertiary amine methacrylate monomers.

GPC analyses (both UV and RI detectors) of the reaction solution after termination with methanol shows that, in addition to the macromonomer, a low molecular weight contaminant is present. Figure 2 shows the GPC curves obtained for macromonomer M5 using the RI and UV detectors, respectively. The UV detector was set at a wavelength of 254 nm, which corresponds to the absorption maximum for the terminal styrene groups. The UV GPC trace clearly indicates the presence of a low molecular weight species. This is residual VBA initiator, which is present only at low concentration (undetectable by the RI detector but observed using the more sensitive UV detector). Perhaps the most important result from the GPC studies is that the UV and RI chromatograms directly overlay for each macromonomer (Figure 2). Thus, each polymer chain has a reactive styrene unit at one end; i.e., well-defined macromonomers have been synthesized, as expected. Like Nagasaki et al., we found that carrying out polymerizations of tertiary amine methacrylates at above ambient temperatures resulted in lower polydispersities.[20] For example, the synthesis conditions for macromonomers M1 and M2 were identical except for the reaction temperatures (see Table 1). Macromonomer M2 (synthesized at 50 °C) had a polydispersity index (PI) of 1.28, whereas macromonomer M1 (synthesized at 20 °C) had a PI of 1.34. A similar trend was also observed for macromonomers M4 and M5.

From Table 1, it is clear that the macromonomer molecular weights determined by GPC (vs poly(methyl methacrylate) standards) are always higher than the target molecular weight. This suggests inefficient initiation, which is consistent with the VBA contamination observed in the UV−GPC trace and also explains the imprecise molecular weight control. Poly(DMAEMA) is soluble in many common solvents but insoluble in cold *n*-hexane (−15 °C). However, VBA is soluble under these conditions; thus, we were able to reduce the level of VBA contamination substantially by repeated precipitation into cold *n*-hexane. Figure 3, for example, shows the UV chromatograms for macromonomer M5 (a) prior to cleanup and (b) after two precipitations into cold *n*-hexane. Clearly VBA contamination has been significantly reduced.

A useful method for the accurate determination of absolute molecular weights is end-group analysis using NMR spectroscopy. Figure 4a shows an NMR spectrum of macromonomer M1. Signals due to the vinyl protons of the styrenic end group are clearly visible at δ 6.6, 5.7, and 5.2. A comparison of the peak integrals obtained for these signals with those associated with the DMAEMA residues (e.g., at δ 4.0, due to the oxymethylene protons adjacent to the ester group) allows an absolute number-average molecular weight of 8600 g mol^{-1} to be calculated. Such NMR-derived molecular weights were generally in reasonably good agreement (within experimental error) with the GPC data. It should be noted that the NMR method assumes that the macromonomer is completely free from low molecular weight contamination. Prior to removal of the excess VBA contaminant, the NMR analysis indicated a much lower molecular weight than that found by GPC analysis. Indeed, as might be expected, analysis of the NMR spectra of unpurified macromonomers appeared to indicate that the target molecular weight had been achieved. Nagasaki et al. also observed higher molecular weights than expected from monomer/initiator ratios; however, these workers demonstrated better molecular weight control than we were able to achieve. No VBA contamination problems were reported by the Japanese group, but apparently only a refractive index detector was used in this earlier study.[20]

As shown in Table 1, the potassium salts of allyl alcohol and di(ethylene glycol)vinyl ether have also been used to initiate the polymerization of DMAEMA, resulting in macromonomers M6 and M7, respectively. These initiators allow the synthesis of macromonomers with polymerizable allylic or vinyl ether end groups. The crude macromonomers are also contaminated with low levels of residual initiator which can again be removed by precipitation in *n*-hexane. NMR spectra of representative allylic- and vinyl ether-ended macromonomers are shown in Figure 4b,c. End-group analysis based on relative peak integrals indicated number-average molecular weights of 5400 and 2900 g mol^{-1}, respectively.

Scope and Limitations of Oxyanionic Polymerization. In addition to demonstrating the oxyanionic polymerization of DMAEMA with a range of functional initiators, we also evaluated other heteroatom monomers. Two other tertiary amine methacrylates, 2-(*N*-morpholino)ethyl methacrylate (MEMA) and 2-(diisopropylamino)ethyl methacrylate (DIPAEMA), were successfully polymerized (see entries M8 and M9 respectively in Table 1). In contrast, we were unable to polymerize 2-tetrahydropyranyl methacrylate (THPMA)

Table 1. GPC Results for a Series of Tertiary Amine Methacrylate-Based Macromonomers Synthesized by Oxyanionic Polymerization Using Various Functional Initiators

macromonomer ID	initiator	monomer	temp (°C)	target M_n	measd M_n[a]	M_w/M_n[a]
M1	VBA[b]	DMAEMA	20	7200	10000	1.34
M2	VBA	DMAEMA	50	7200	10300	1.28
M3	VBA	DMAEMA	20	5100	8600	1.24
M4	VBA	DMAEMA	20	3000	8000	1.30
M5	VBA	DMAEMA	50	3000	6400	1.22
M6	AA[c]	DMAEMA	20	2900	6200	1.24
M7	DEGVE[d]	DMAEMA	20	2800	4300	1.17
M8	VBA	MEMA[e]	50	5600	5900	1.29
M9	VBA	DIPAEMA[f]	50	3000	6200	1.24

[a] Determined by GPC (using PMMA standards, RI detector, THF eluent). [b] VBA = 4-vinylbenzyl alcohol. [c] AA = allyl alcohol. [d] DEGVE = di(ethylene glycol) vinyl ether. [e] MEMA = (*N*-morpholino)ethyl methacrylate. [f] DIPAEMA = 2-(diisopropylamino)ethyl methacrylate.

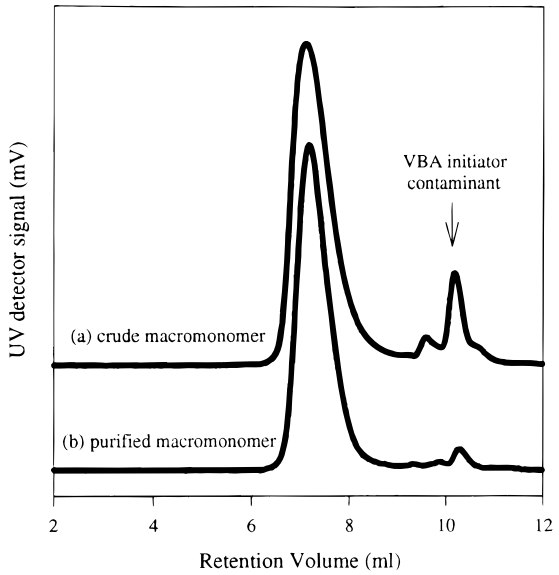

Figure 3. UV−GPC curves for macromonomer M5 before (a) and after (b) precipitation into *n*-hexane.

via oxyanionic polymerization. The THPMA monomer may not be suitable for efficient chelation of the potassium cation because the oxygen heteroatom is in a slightly different position compared to the ProHEMA's reported by Nagasaki et al. Similarly, no polymerization was obtained for oligoethylene glycol methacrylate monomethyl ether, possibly for the same reason. In addition, attempted polymerization of 2-(dimethylamino)ethyl *acrylate* (DMAEA) was unsuccessful at 25 °C. This unexpected negative result may be due to the relatively acidic α-hydrogen on this monomer, which can often lead to side reactions during acrylate polymerizations at ambient temperature.[22] It is possible that subambient temperatures (<25 °C) may be beneficial for the oxyanionic polymerization of acrylates. Attempts to use counterions other than potassium were also unsuccessful. Thus, in our hands, DMAEMA could not be polymerized with *sodium* 4-vinylbenzyl alcoholate in THF at 25 °C. Remarkably, methyl methacrylate was polymerized at 25 °C using the potassium 4-vinylbenzyl alcoholate initiator. However, an induction time of almost 10 min was observed, and GPC analysis indicated that this polymerization was uncontrolled, since only a very broad molecular weight distribution was obtained ($M_w/M_n > 2.5$).

Latex Syntheses. Liu et al. reported the synthesis of a series of polystyrene latexes in the presence of a methacrylate-terminated poly(ethylene oxide) (PEO) stabilizer via dispersion polymerization.[23] It was found that this macromonomer typically accounted for approximately 4.8 wt % of the final polystyrene latex, as judged from the NMR spectra of latexes dissolved in $CDCl_3$. This value corresponds to an adsorbed amount of macromonomer (Γ) of approximately 2.10 mg m^{-2}. Cosgrove and Ryan also used methacrylate-terminated PEO stabilizers in polystyrene latex syntheses.[24] These workers calculated Γ to lie between 1.0 and 4.0 mg m^{-2}, depending on the synthesis conditions.

Chen et al.[25] described the synthesis of styrene-functionalized poly(*N*-isopropylacrylamide) [poly(NIPAM)] macromonomers via a two-step process using conventional free-radical chemistry. Consequently, only rather ill-defined macromonomers were obtained, with relatively high polydispersities (PI > 2.0), and only 70−80% of the polyNIPAM chains had terminal styrenic groups. Nevertheless, these macromonomers were effective stabilizers for the dispersion polymerization of styrene in ethanol (albeit at relatively high stabilizer concentrations of ≈20 wt %). Like poly(DMAEMA), poly(NIPAM) also displays inverse temperature solubility,[26] and Chen et al. were able to demonstrate reversible flocculation of their poly(NIPAM)-stabilized latexes by varying the temperature of the aqueous dispersion. A Japanese group led by Okubo has recently claimed that polystyrene latexes coated with a cross-linked overlayer of poly(DMAEMA) may have various biomedical applications.[27]

In the present work the efficacy of the styrene-terminated poly(DMAEMA) macromonomers as reactive stabilizers for the synthesis of polystyrene latexes was explored. Two routes were investigated: aqueous emulsion polymerization and alcoholic dispersion polymerization. It is well-known that poly(DMAEMA) exhibits inverse-temperature solubility. Cloud points of 35−45 °C are observed at around pH 8, depending on molecular weight.[28−31] Thus, for the emulsion polymerizations, it was necessary to adjust the acidity of the aqueous solution to around pH 2 to prevent precipitation of the poly(DMAEMA) macromonomer at the styrene polymerization temperature of 60 °C. Under these conditions the DMAEMA residues are fully protonated,[32] and the macromonomer exists as a water-soluble cationic polyelectrolyte at all temperatures up to 100 °C.

The results for all of our latex syntheses via dispersion and emulsion polymerizations are summarized in Table 2. A control experiment in the absence of macromonomer produced a large amount of polystyrene coagulum, as well as some monodisperse charge-stabilized latex (entry L1). An emulsion polymerization carried out using 5 wt % stabilizer based on monomer (entry L2) resulted in much smaller latex particles with a relatively broad particle size distribution (PSD), as

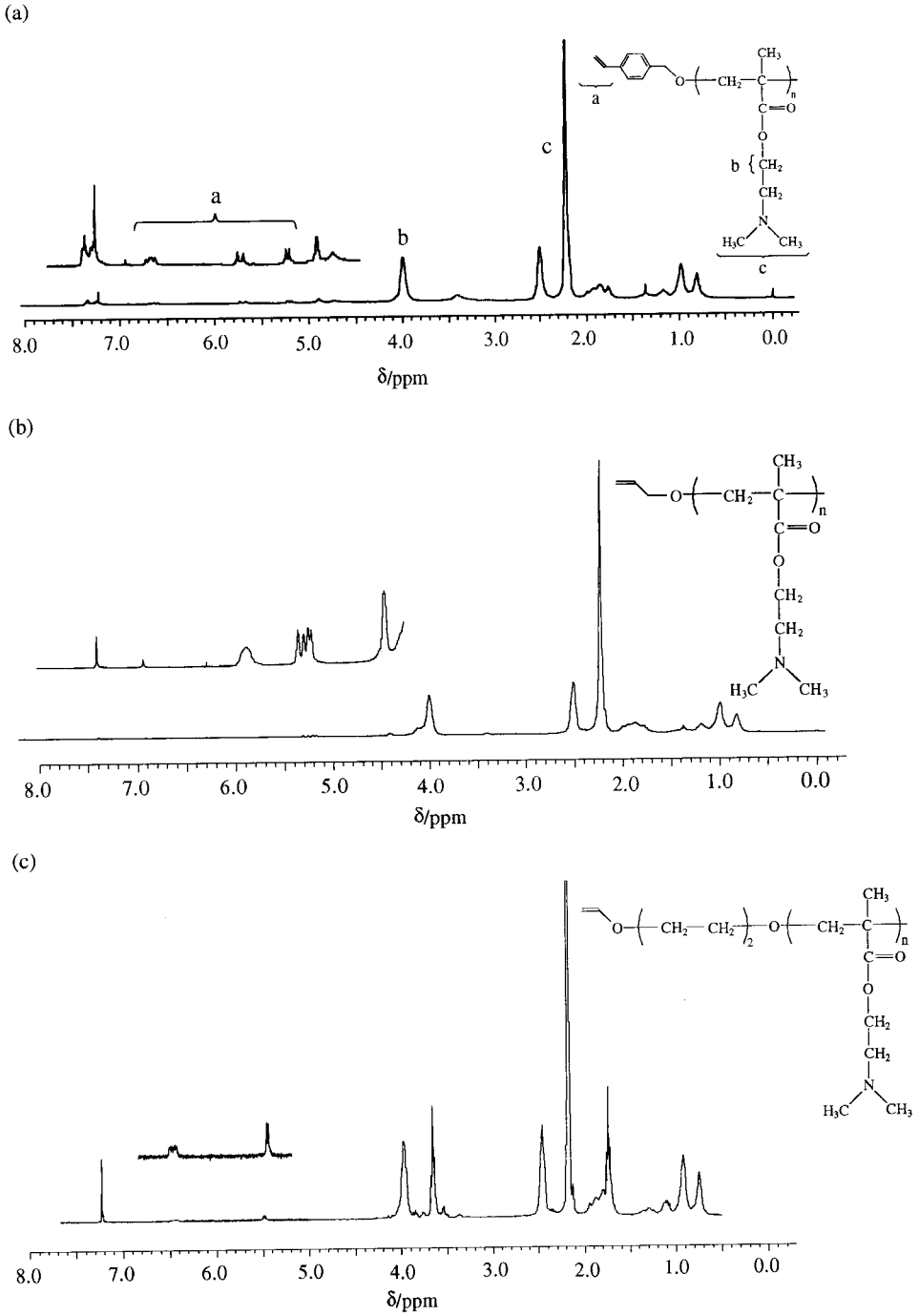

Figure 4. ^{1}H NMR spectra of (a) macromonomer M1, (b) macromonomer M6, and (c) macromonomer M7.

judged by DCP. This macromonomer concentration was barely adequate for latex stabilization, since a significant amount of coagulum was also obtained. Increasing the stabilizer concentration to 10 wt % produced a latex with a narrower size distribution (see entry L3) and no coagulum. Similar trends have been observed for macromonomer-based latex syntheses carried out under emulsion polymerization conditions and also for block copolymer[33] and homopolymer stabilizers,[34,35] under dispersion polymerization conditions.

Using the nitrogen content of the macromonomer as a reference, nitrogen microanalyses of the dried latexes showed that the poly(DMAEMA) macromonomer was present in the polystyrene particles at between 2.0 and 12.0 wt %. These values are in reasonable agreement with those of Liu et al.[23] However, there is no correlation between the initial macromonomer concentration, macromonomer content of the latexes, and latex diameter. From nitrogen microanalyses, it is also possible to calculate the fraction of initial macromonomer actually incorporated into the latex. Typically, 20−40% of the stabilizer chains originally present in the reaction solution became incorporated into the final latex particles.

Similarly, using the number-average diameters of the latexes (from DCP analysis) and their stabilizer contents (summarized in Table 2), it is possible to calculate Γ values for the latex particles. In this calculation it is assumed that all of the macromonomer is present at the latex surface.[24] As can be seen from Table 2, the Γ values are in the range 0.6−4.1 mg m^{-2}. Despite the differences in stabilizer type and polymerizable end group, our

Table 2. Particle Size and Stabilizer Contents of Polystyrene Latexes Synthesized via Either Aqueous Emulsion or Alcoholic Dispersion Polymerization Using a Styrene-Functionalized DMAEMA Macromonomer (M5, See Table 1)

latex ID	stabilizer concn (wt % based on styrene)	reaction solvent	wt-avg particle diameter[a] (nm)	nitrogen microanalysis (wt %)	stabilizer content of polymer (wt %)	Γ^b (mg m^{-2})
L1	0.0	0.01 M HCl	683 ± 30[c]	0.00	0.0	-
L2	5.0	0.01 M HCl	260 ± 160[c]	0.90	12.0	4.1
L3	10.0	0.01 M HCl	190 ± 30	0.15	2.0	0.6
L4	5.0	methanol	1010 ± 360	0.18	2.4	3.8
L5	5.0	*n*-propanol	1130 ± 360	0.13	1.7	2.8
L6	5.0	*n*-butanol	1140 ± 230	0.12	1.6	2.9
L7	5.0	*n*-heptanol	940 ± 190	0.14	1.9	2.8
L8	10.0	methanol	810 ± 390	0.23	3.1	3.1
L9	10.0	*n*-propanol	480 ± 50	0.25	3.3	2.7
L10	10.0	*n*-butanol	510 ± 130	0.17	2.3	1.8

[a] Determined by disk centrifuge photosedimentometry. [b] Calculated using nitrogen microanalytical data and D_n values from DCP. [c] Some coagulum was obtained in addition to the latex particles.

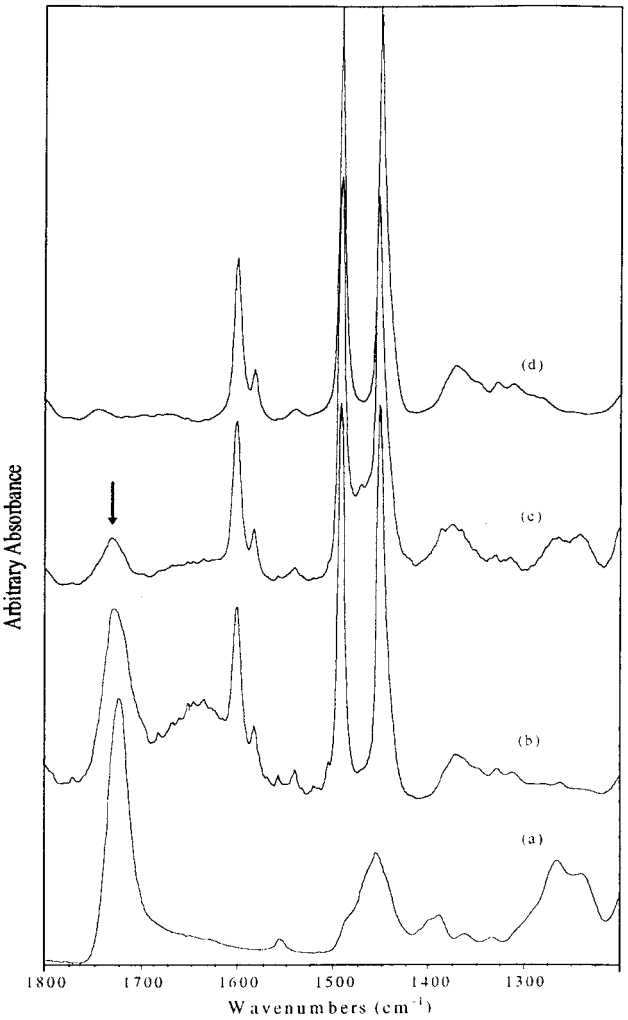

Figure 5. FTIR spectra of (a) a poly(DMAEMA) macromonomer (M5), (b) a polystyrene latex prepared by emulsion polymerization (L2), (c) a polystyrene latex prepared by dispersion polymerization (L9), and (d) a charge-stabilized polystyrene latex (L1).

results are in good agreement with those of Liu et al.[23] and of Cosgrove and Ryan.[24]

The presence of the macromonomer stabilizer in the latex particles after the centrifugation−redispersion cycles was also confirmed by FTIR spectroscopy. Figure 5 shows the IR spectra for poly(DMAEMA) macromonomer M5, latex L2, latex L9, and the charge-stabilized polystyrene latex L1. The 1730 cm^{-1} band due to the ester carbonyl of the DMAEMA residues is clearly visible in the IR spectrum of the macromonomer (spectrum A). This band is also present in the IR spectra of latexes L2 and L9 (spectra B and C, respectively). As expected, this feature is more prominent for latex L2, which has a smaller mean particle diameter, and hence is expected to have a higher stabilizer content (confirmed by nitrogen microanalyses). The IR spectrum (spectrum D) of the charge-stabilized polystyrene latex prepared in the absence of any macromonomer stabilizer (L1) is included for comparison and confirms the expected absence of this band. FTIR spectroscopy also provided some evidence for macromonomer grafting. Thus, one of the polystyrene latexes (L8) was dissolved in THF and precipitated into water. The precipitate was isolated by filtration and washed with copious amounts of methanol. The IR spectrum of the recovered dried latex was compared to that of the original latex (not shown). The relative intensity of the ester carbonyl band due to the DMAEMA residues of the macromonomer compared to the PS bands was unchanged, indicating that the macromonomer was chemically grafted to the polystyrene. If the macromonomer had been only physically adsorbed onto the polystyrene particles, precipitation of the dissolved latex into water followed by methanol washing should have reduced its macromonomer content significantly, since both water and methanol are good solvents for poly(DMAEMA).

For the alcoholic dispersion polymerizations it was found that 5 wt % stabilizer concentrations yielded dispersions which, although colloidally stable, had quite broad PSDs. Increasing the initial macromonomer concentration to 10 wt % gave smaller latexes with narrower PSDs for a given alcohol. This is illustrated in Figure 6, which shows the DCP curves for two latexes synthesized in methanol at initial macromonomer concentrations of 10 wt % (curve A, latex L8) and 5 wt % (curve B, latex L4). Both PSDs have long "tails" to 3.0 μm diameter, indicating either weak flocculation or a relatively broad PSD. SEM studies suggested that this "tailing" is due to weak flocculation, since no latex particles as large as 1.5−3.0 μm were observed (see Figure 7a,b). The particle morphology is surprisingly ill-defined; although the particles are approximately spherical, their surfaces are somewhat rough. All latexes synthesized in alcoholic media displayed this unusual morphology. It was also noted that surface roughness appeared to increase with increasing alkyl chain length of the alcohol. Thus, latex L7, synthesized in *n*-heptanol, had a particularly rough morphology (see Figure 7d). This is most likely due to some unidentified property of the macromonomer, since polystyrene latexes synthesized under the same conditions (monomer and initiator concentrations, solvent, temperature, etc.) with a wide

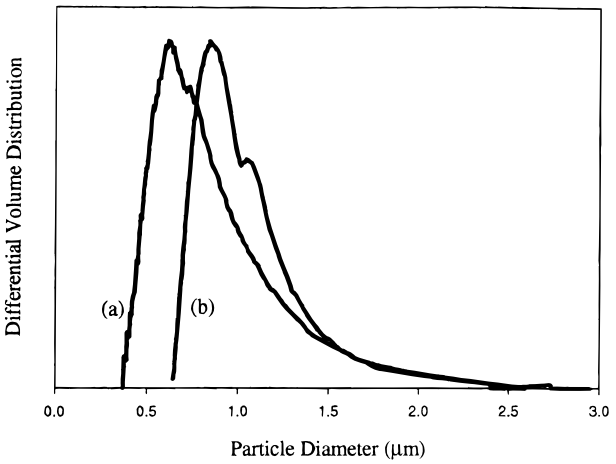

Figure 6. Weight-average particle size distribution curves obtained using the disk centrifuge for poly(DMAEMA)-stabilized polystyrene latexes synthesized by dispersion polymerization in methanol using (a) 10% stabilizer (latex L8) and (b) 5% stabilizer (latex L4).

range of other polymeric stabilizers [e.g., homopolymers, statistical and block copolymers] invariably have smooth spherical morphologies.[33−36]

Changing the alkyl chain length of the alcoholic solvent has surprisingly little effect on the polystyrene latex diameter (see Table 2). This is in contrast to the work of Baines et al., who employed DMAEMA−methyl methacrylate block copolymers as stabilizers for the dispersion polymerization of styrene.[33] As the solvent was changed systematically from methanol to *n*-butanol, an increase in particle size was observed, followed by a reduction in particle size for higher alcohols up to *n*-octanol. These observations are in good agreement with those reported by other workers, and it has been proposed that the final particle size is largely determined by the solvent power of the reaction medium for the growing polystyrene−stabilizer complex.[34,35] These earlier studies were carried out using both block copolymers and homopolymer stabilizers, and therefore it seemed reasonable to assume that our new macromonomers would follow the same general trends with respect to solvent type, concentration effects, etc. We have no satisfactory explanation for the various anomalies reported herein for our macromonomer stabilizers.

We also evaluated an allyl-terminated stabilizer (macromonomer M6) for the dispersion polymerization of styrene. At 5 wt % stabilizer concentration, stable latexes were not obtained. At 10 wt % stabilizer concentration, latexes with bimodal PSDs were obtained. These latter syntheses also produced some coagulum. These problems were encountered regardless of the alcoholic solvent. The poor stabilizer performance of the allyl-terminated DMAEMA macromonomer is most likely due to the poor copolymerizability of the allyl group with styrene.

Latex Syntheses Using Betaine Macromonomers. We recently reported the quantitative betainization of DMAEMA residues in both homopolymers[37] and a range of DMAEMA-based block[38] and statistical[39] copolymers using 1,3-propane sultone. The DMAEMA macromonomers reported herein can be similarly derivatized. For example, a styrene-terminated poly(DMAEMA) macromonomer (macromonomer M3) was converted to the corresponding polysulfobetaine. Elemental microanalyses indicated a S/N ratio of 0.98 ± 0.06, which confirmed that essentially all the DMAEMA residues had reacted. We believe that this is the first example of a well-defined polysulfobetaine macromonomer. It is worth emphasizing that the 2-(diethylamino)ethyl methacrylate-based macromonomers described by Nagasaki et al. are much more difficult to derivatize *quantitatively* with 1,3-propane sultone.[31] This macromonomer was evaluated as a steric stabilizer for the aqueous emulsion polymerization of styrene at pH 2. Although stable dispersions were formed in each case, there was no evidence of the 1730 cm^{-1} band characteristic of the DMAEMA residues in the IR spectra of these latexes. Furthermore, rapid flocculation was observed upon addition of low levels of electrolyte. Thus, we had succeeded in synthesizing only charge-stabilized, rather than the expected sterically stabilized, latex particles. (The surface charge originates from the persulfate anions of the initiator.) Higher initial concentrations (up to 20 wt %) of betainized macromonomer gave similar results. Thus, we concluded that the styrenic end group of the betainized macromonomer does not participate effectively in the in-situ styrene polymerization. Since it is relatively hydrophobic, the styrene end group may prefer to remain within the polysulfobetaine random coil rather than the aqueous solution, which would make it less accessible for in-situ grafting. It is well-known that polybetaines are more soluble in the presence of salt, due to the so-called "anti-polyelectrolyte effect".[40] Thus, latex syntheses were also attempted in the presence of 1.0 M NaCl. Again, efficient stabilizer grafting did not occur, and this time only macroscopic precipitation of polystyrene was observed (since the charge stabilization mechanism is ineffective at high ionic strength).

To further investigate the grafting efficiency, a DE-GVE-functionalized macromonomer (M7 in Table 1) was derivatized with 1,3-propane sultone (see Figure 8). Elemental microanalyses indicated a S/N ratio of 0.96 ± 0.06, again confirming that all the DMAEMA residues had reacted. The resulting vinyl ether-functionalized betaine macromonomer was evaluated as a steric stabilizer. The vinyl ether end group is much more hydrophilic than the styrene end group and therefore much more likely to be available for in-situ grafting in aqueous solution, but its copolymerizability with styrene was considered to be less than ideal. At 10% stabilizer concentration, a stable polystyrene latex was obtained in 1.0 M NaCl at 60 °C. Inspection of the purified latex by SEM showed spherical, approximately micrometer-sized polystyrene particles (see Figure 9a). The synthesis was repeated at 20% stabilizer concentration, and again spherical polystyrene latex particles were obtained, this time with a mean diameter of around 450 nm (see Figure 9b). As far as we are aware, this is the first example of a polybetaine macromonomer being used to prepare latexes in high salt media. Given the failure of the styrene-functionalized sulfobetaine macromonomer, it seems that a relatively hydrophilic polymerizable group is a prerequisite for such syntheses.

Conclusions

A new range of water-soluble macromonomers based on 2-(dialkylamino)ethyl methacrylates have been synthesized with styrenic, allylic, or vinyl ether end groups via oxyanionic polymerization. The as-synthesized macromonomers are contaminated with excess initiator,

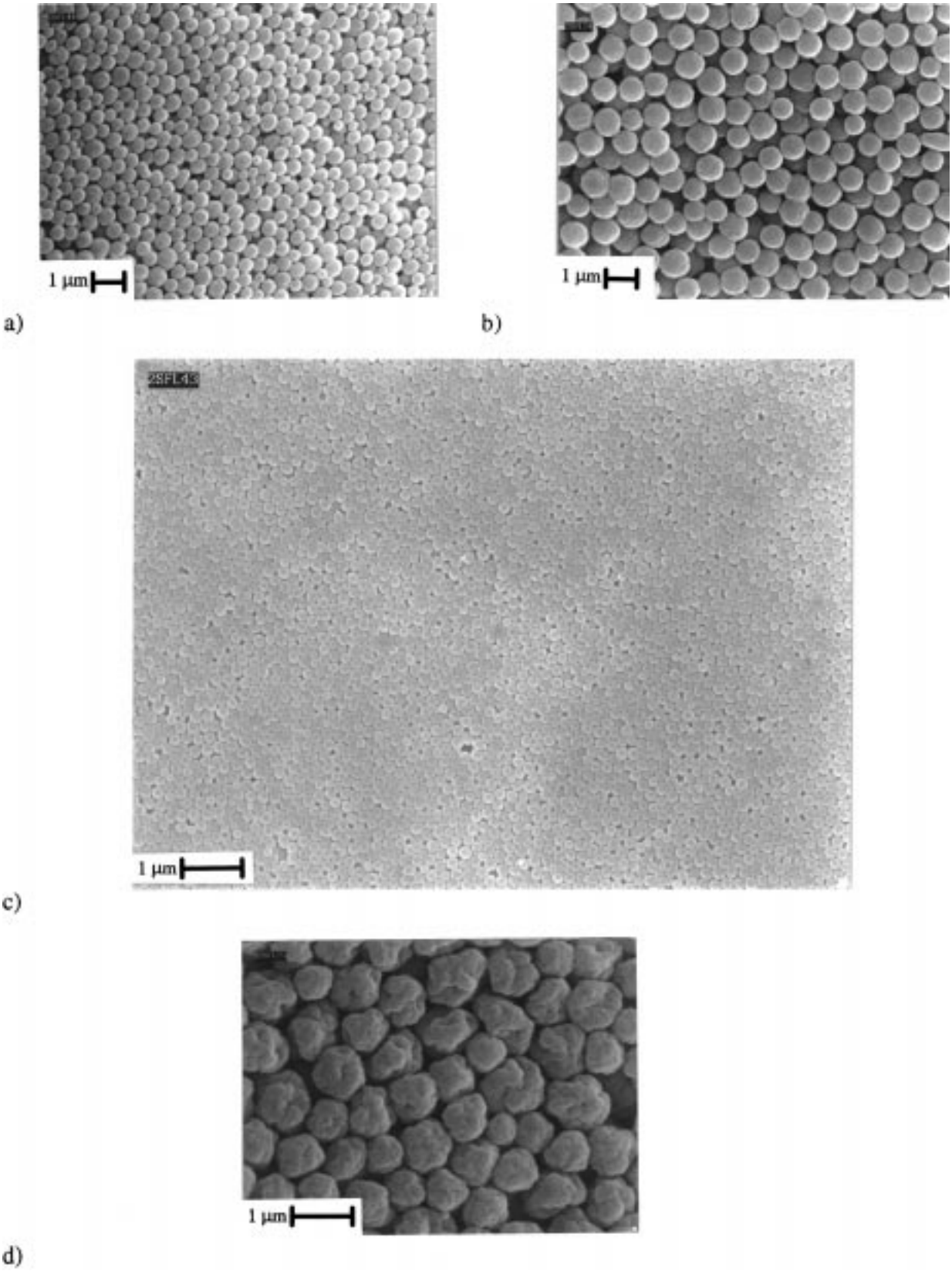

Figure 7. Scanning electron micrographs of poly(DMAEMA)-stabilized polystyrene latex synthesized by (a) dispersion polymerization in methanol using 10% stabilizer (L8), (b) dispersion polymerization in methanol using 5% stabilizer (L4), (c) by emulsion polymerization using 10% stabilizer (L3), and (d) dispersion polymerization using *n*-heptanol (L7).

which can be removed easily by precipitation into *n*-hexane. Attempts to polymerize other monomers containing oxygen heteroatoms, such as 2-tetrahydropyranyl methacrylate or an oligoethylene glycol methacrylate monomethyl ether, were not successful. Similarly, 2-(dimethylamino)ethyl acrylate could not be polymerized at 25 °C.

Styrene-terminated poly(DMAEMA) macromonomers can be used in both the emulsion and dispersion polymerization of styrene to produce sterically stabilized

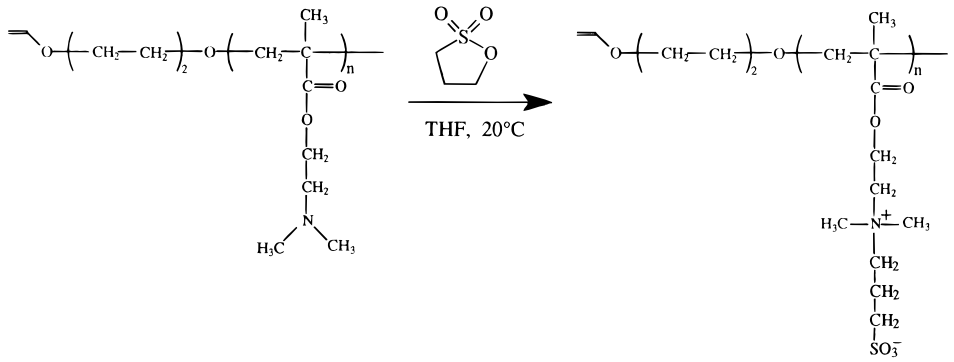

Figure 8. Reaction scheme for the betainization of macromonomer M7 using 1,3-propane sultone.

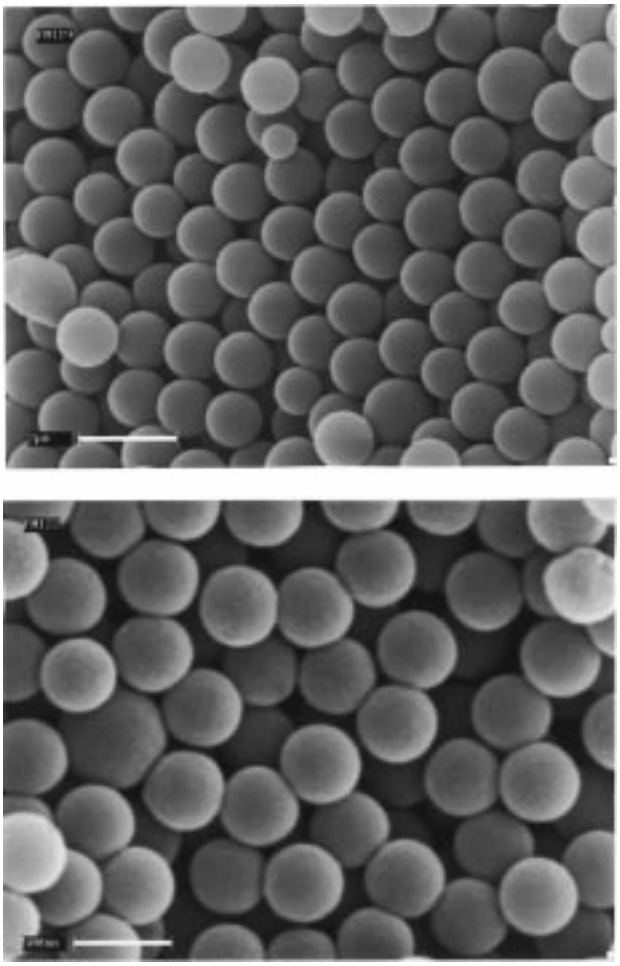

Figure 9. Scanning electron micrographs of a betaine macromonomer-stabilized polystyrene latex synthesized by aqueous emulsion polymerization in 1.0 M NaCl at 60 °C using (a, top) 10% stabilizer and (b, bottom) 20% stabilizer. Stable latexes were only obtained with the hydrophilic di(ethylene glycol) vinyl ether-functionalized macromonomer; the more hydrophobic styrene-functionalized macromonomer did not prove to be an effective steric stabilizer.

polystyrene latexes. Latexes of 190−260 nm diameter are obtained in aqueous media, whereas micrometer-sized latexes are obtained in alcoholic media. The latter particles have an unusually rough surface morphology. Nitrogen microanalyses and FTIR spectroscopy studies confirmed that the macromonomer stabilizers are incorporated into the latex particles, as expected. The DMAEMA macromonomers can also be quantitatively derivatized to produce the first examples of well-defined sulfobetaine macromonomers. A styrene-functionalized sulfobetaine macromonomer was ineffective as a steric stabilizer for the aqueous emulsion polymerization of styrene, even at concentrations as high as 20 wt % based on styrene monomer. However, a polybetaine macromonomer functionalized with a more hydrophilic diethylene glycol vinyl ether group could be used to prepare colloidally stable polystyrene latexes at relatively high electrolyte concentrations (1.0 M NaCl).

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