Use of Block Copolymer Stabilizers for the Dispersion Polymerization of Styrene in Alcoholic Media

F. L. Baines,*,† S. Dionisio, N. C. Billingham, and S. P. Armes*

School of Chemistry and Molecular Sciences, University of Sussex,
Falmer, Brighton BN1 9QJ, U.K.

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ABSTRACT: Near-monodisperse micrometer-sized polystyrene particles were produced by dispersion polymerization in alcoholic media using poly(2-(dimethylamino)ethyl methacrylate-*b*-alkyl methacrylate) copolymer stabilizers. The effect of varying stabilizer concentration, copolymer composition, solvent, and reaction temperature on latex particle size was investigated. A maximum particle size of 2.8 μm was found for 1-butanol in a series of alcoholic solvents ranging from methanol to 1-octanol. As expected, the particle size decreased slightly with increasing stabilizer concentration; however, varying the copolymer composition had, surprisingly, little or no effect on particle size. As the polymerization temperature was increased, the size and polydispersity of the latexes increased.

Introduction

There has been substantial interest in the preparation of polymer particles of narrow particle size distribution since the work by Vanderhoff and Bradford (reported in ref 1) on the synthesis of monodisperse polystyrene particles. The majority of studies have focused on particles of submicrometer dimensions prepared using emulsion polymerization. However, in the last two decades, there has been increasing interest in the synthesis of micrometer-sized polystyrene or poly(methyl methacrylate) (PMMA) latexes in either nonpolar[2] or polar media *via* dispersion polymerization.[3−6] Dispersion polymerization, which is a modified precipitation polymerization, was invented by workers at ICI.[2,7] In a dispersion polymerization, the initial mixture (which contains monomer, solvent, initiator, and stabilizer) is homogeneous. The precipitating polymer is obtained in the form of microscopic sterically stabilized latex particles. The key component is the stabilizer, which can be a block or graft copolymer, a polymer carrying a polymerizable group, or a homopolymer.

Most stabilizers examined to date have been commercial polymers of broad molecular weight distribution, such as poly(*N*-vinyl pyrrolidone)[6,8] (PVP), methacrylate polymers,[9] and various cellulose derivatives.[7,10] It is believed[4,9] that, in many cases, they participate in the free-radical polymerization and become chemically grafted (rather than merely physically adsorbed) onto the latex particles Indeed, in some cases, reactive (co)polymers that contain pendant polymerizable groups have been shown to be particularly effective stabilizers.

Ober *et al.*[10] produced micrometer-sized polystyrene particles using hydroxypropylcellulose (HPC; M_w = 100 000) as a stabilizer in ethanol. They found that the stabilizer concentration had little effect on particle size or polydispersity. They also examined the effect of using different alcohols as the dispersion medium. Polymerizations were carried out in methanol, ethanol, and 2-methyl-2-propanol. Particle size increased from methanol to ethanol to 2-methyl-2-propanol; for polymerizations in 2-methyl-2-propanol, the latex size distribution was much wider. Paine *et al.* studied the effect of reaction parameters on latex particle size and molecular weight in PVP-stabilized reactions of styrene in polar solvents.[6] They produced monodisperse latex particles in the size range 1−18 μm. Smaller particles were obtained at higher stabilizer concentrations and molecular weights and decreasing initiator concentrations. An inverse correlation between latex particle size and polymer molecular weight was reported, with the largest particles having the lowest molecular weights. Similar effects of reaction parameters on particle size were observed for PVP-stabilized PMMA latexes in alcoholic media. For example, Shen *et al.*[8] prepared PMMA particles ranging in diameter from 2 to 10 μm. Particle size was found to increase with increasing polymerization temperature, initiator concentration, and solvency of the dispersion medium. Larger particles were also favored at increased stabilizer concentrations and molecular weights.

There have been few papers describing the use of near-monodisperse, well-defined polymeric stabilizers in dispersion polymerization. Dawkins and co-workers described the use of poly(styrene-*b*-ethylene-*co*-propylene)[11−13] and poly(styrene-*b*-dimethylsiloxane)[14−16] stabilizers for the preparation of PMMA and poly(vinyl acetate) dispersions in nonpolar media. Poly(styrene-*b*-dimethylsiloxane) (PS-*b*-PDMS) copolymers were used to stabilize PMMA particles polymerized in *n*-alkanes.[16] The insoluble PS blocks were adsorbed onto the PMMA particles, while the PDMS blocks were well-solvated and provided a thick protective layer against flocculation *via* a steric stabilization mechanism. The sizes of the latexes ranged from 100 to 800 nm, depending on reaction conditions. Larger particle sizes were obtained at higher monomer concentration, decreasing stabilizer concentration, and decreasing molecular weight of the soluble PDMS block. Stejskal and co-workers have described the use of poly(styrene-*b*-ethylene-*co*-propylene) copolymers for stabilizing PMMA dispersions in *n*-decane.[17−19] Schneider and Malhaupt[20] have prepared "living" polystyrene particles with average diameters varying between 0.5 and 3.8 μm *via sec*-butyllithium-initiated anionic dispersion polymerization of styrene in hexane using poly(styrene-*b*-4-(trimethylsilyl)styrene) as the steric stabilizer. The influences of block copolymer concentration, polymerization temperature, and monomer concentration on latex particle size and mo-

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* Authors to whom correspondence should be addressed.

† Present address: Dow Corning Ltd., Cardiff Road, Barry, S. Glamorgan CF63 2YL, U.K.

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lecular weight were investigated. Similar studies were reported by Awan *et al.*[21] for the polymerization of styrene in *n*-hexane using poly(styrene-*b*-butadiene) copolymer stabilizers.

There have been relatively few reports describing the use of block copolymer stabilizers for dispersion polymerization in polar media. Terada *et al.* polymerized styrene in the presence of polydisperse poly(styrene-*b*-vinyl acetate) (PS-*b*-PVAc) block copolymers and their partially hydrolyzed derivatives in ethanol.[22] Poly(vinyl acetate) (PVAc) homopolymer and partially hydrolyzed PVAc failed to prevent coagulation during the course of the polymerization. On the other hand, Dawkins *et al.*[23] demonstrated the effectiveness of partially hydrolyzed PVAc as a steric stabilizer in the dispersion polymerization of styrene in alcoholic media. The polymeric stabilizer was produced by alkaline hydrolysis, which results in a "blocky" structure for the copolymer. Polystyrene particles in the range 0.5–3.0 μm were produced by controlling the solvent polarity of the dispersion medium. When ethanol/methanol (50:50 w/w) mixtures were used, larger particles were formed than in methanol alone. However, glycerol/methanol (25:75 w/w) mixtures produced particles that were significantly smaller than those polymerized in methanol. These observations were rationalized in terms of the solvency of the diluent for the growing polystyrene chain. The glycerol/methanol diluent had the lowest solvency for polystyrene and so produced the smallest particles. Winnik and co-workers have investigated a series of poly(styrene-*b*-ethylene oxide) copolymers as steric stabilizers for the dispersion polymerization of styrene in methanol.[24] As far as we are aware, these stabilizers are the first well-defined block copolymer stabilizers to be used in polar media. The effects of stabilizer molecular weight, stabilizer/anchor ratio, and stabilizer concentration were examined. Large monodisperse polystyrene particles (~2 μm) were obtained when a low molecular weight copolymer stabilizer was used. Bimodal distributions were found with high molecular weight copolymer stabilizers, indicating that polymerization of styrene probably takes place within micelles (leading to submicrometer particles) as well as in the continuous phase.

Recently, we synthesized[25] a series of hydrophilic–hydrophobic block copolymers of 2-(dimethylamino)ethyl methacrylate and various alkyl methacrylates using group-transfer polymerization (GTP). Provided that the hydrophobic alkyl methacrylate block is not too long, these copolymers are water-soluble or water-dispersible and show complex micellization behavior.[26] They are also soluble in alcohols as unimers rather than micelles. In this work, we describe the use of these poly(2-(dimethylamino)ethyl methacrylate-*b*-alkyl methacrylate) copolymer stabilizers for the dispersion polymerization of styrene in alcoholic media.

Experimental Section

(A) Copolymer Synthesis. Materials. All reagents were purchased from Aldrich Chemical Co., unless otherwise stated. Tetrahydrofuran (Fisons) was initially dried over sodium wire and then refluxed over potassium for 3 days. It was stored over 4 Å molecular sieves and transferred into the reaction vessel *via* a double-tipped needle. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS) was distilled and stored at −5 °C in a graduated flask. All monomers were passed down a basic alumina column to remove the hydroquinone monomethyl ether inhibitor. Octyl methacrylate (Fluorochem) was stirred over calcium hydride and then decanted and stirred with bis(dimethylamino)methylsilane (ABCR). All other monomers were dried by stirring over calcium hydride for 24 h, stored at −20 °C, and freshly distilled prior to use. Tetrabutylammonium bibenzoate (TBABB) was prepared according to by the method of Dicker *et al.*[27]

The preparation of a poly(2-(dimethylamino)ethyl methacrylate-*b*-methyl methacrylate) (PDMAEMA-*b*-MMA) copolymer serves as a typical example for the block copolymer synthesis: TBABB (10 mg, 2 mol % based on initiator) and MTS (0.20 mL) were added to THF (100 mL) at room temperature. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) (18.0 mL) was added dropwise at an approximate rate of 1 mL min^{-1} *via* a canulla to this stirred solution. The reaction mixture was left stirring at room temperature until the exotherm had abated (usually 90 min); a homopolymer sample was then extracted for GPC analysis prior to the addition of the methyl methacrylate (MMA) (3.0 mL). Again the reaction mixture was left to stir for 1 h, and then the polymerization was quenched by the addition of methanol (2 mL). The copolymer was recovered by removing the solvent using a rotary evaporator and then drying *in vacuo* for 2 days at room temperature. This procedure gives a copolymer containing 79 mol % DMAEMA with an M_n of ~21 000 by GPC (see below). Copolymers of differing compositions were produced by varying the amount of MMA added. Different molecular weights were obtained by varying the comonomer/initiator ratio. All copolymerizations gave quantitative (>99%) yields, and the polymers were shown to be free of residual monomer by both GPC and ^{1}H NMR. For convenience, a shorthand notation was used to define the block copolymer compositions: the first number indicates the DMAEMA content, and the second number indicates the alkyl methacrylate content. Thus, in the above example, a 79:21 block copolymer was synthesized.

Copolymer Characterization. Molecular weights and molecular weight distributions were determined using gel permeation chromatography (GPC). The GPC equipment consisted of a refractive index detector and two PLgel 5 μm mixed D columns. Calibration was carried out using PMMA standards (Polymer Laboratories), ranging from $M_p = 2010$ to $M_p = 53000$. The eluent was THF (HPLC grade; stabilized with butylated hydroxytoluene) at a flow rate of 1 mL min^{-1}. Mark–Houwink parameters were not available for the copolymers. Thus, all molecular weights are reported as PMMA equivalents. The DMAEMA content of the block copolymers was determined by ^{1}H NMR spectroscopy using a Bruker AC-P 250 MHz instrument and $CDCl_3$ as the solvent. The composition of the copolymers containing DMAEMA and MMA was determined by comparing the peak integral at δ 2.2, corresponding to the dimethylamino protons, to the peak integral at δ 3.55, due to the methoxy protons of MMA. All copolymer compositions were subsequently confirmed by elemental microanalysis (reduced nitrogen contents relative to PDMAEMA homopolymer).

(B) Polystyrene Latexes: Synthesis and Characterization. Materials. All solvents were used as received. Methanol, ethanol, 1-propanol and 1-butanol were purchased from Fisons, and 1-pentanol, 1-hexanol, and 1-octanol were purchased from Aldrich. Styrene and methyl methacrylate (Aldrich) were purified by passing through a neutral alumina column to remove the hydroquinone monomethyl ether inhibitor. Azoisobutyronitrile (AIBN) (BDH Chemicals Ltd.) was used as received. Block copolymer stabilizers were prepared as described earlier and used without further purification.

Latex Synthesis. To create a hydrophobic surface, all glassware was treated with a 10% v/v solution of dichlorodimethylsilane (Aldrich) in dichloromethane (Fisons) prior to use. Reactions were carried out in a 100 mL round-bottom flask fitted with a magnetic stir bar and a water-cooled condenser. The general procedure used to prepare all the polystyrene latexes was as follows. The block copolymer stabilizer (0.50–2.00 g) was dissolved in 50 mL of alcohol and left to stir under nitrogen for 1 h in an oil bath (50–70 °C). A mixture of styrene monomer (5.0 g) and initiator (AIBN, 50 mg) was then added. The reaction was left to stir for 24 h, after which the latex was centrifuged, and the particles were redispersed in methanol.

Table 1. Molecular Weight, Copolymer Composition, and Polydispersity of the Poly(2-(dimethylamino)ethyl methacrylate-*b*-alkyl methacrylate) Stabilizers

alkyl methacrylate	DMAEMA content (mol%) theor	obsd[a]	M_n of block copolymer theor	obsd[b]	M_w/M_n[b]
methyl	83.5	85	19 000	23 800	1.10
methyl	79	80	19 900	19 600	1.14
methyl	70	67	21 700	24 300	1.10
methyl	59	59	24 600	23 800	1.13
ethyl	79	83	20 300	21 800	1.08
n-butyl	79	81	21 100	22 600	1.11
n-octyl	79	80	22 200	18 100	1.10

[a] As determined by ^{1}H NMR spectroscopy. [b] As determined by GPC using PMMA standards.

Effect of Stabilizer Composition. Syntheses were carried out using either a PDMAEMA homopolymer or a range of PDMAEMA-*b*-MMA copolymers containing 59−85 mol % DMAEMA, as determined by ^{1}H NMR spectroscopy. The formulation for each preparation was 0.50 g of stabilizer, 5.0 g of styrene, 50 mg of AIBN, and 50.0 mL of ethanol. All polymerizations were performed at 60 °C.

Effect of Alkyl Methacrylate Type. All experiments were performed at 60 °C with 0.50 g of stabilizer, 50.0 mL of ethanol, 50 mg of AIBN, and 5.0 g of styrene. Block copolymers of PDMAEMA with methyl, ethyl, *n*-butyl, and *n*-octyl methacrylate were used as stabilizers. Each of the four stabilizers contained ~80 mol % DMAEMA and had an overall number-average molecular weight of approximately ~20 000.

Effect of Copolymer Stabilizer Concentration. All experiments were performed at 60 °C in ethanol (50.0 mL). A 59:41 PDMAEMA-*b*-MMA stabilizer with an overall number-average molecular weight of ~24 000 was used, and stabilizer concentrations were varied over the range 0.5−4.0 w/v %.

Effect of Solvent Type. All experiments were carried out at 60 °C using a 59:41 PDMAEMA-*b*-MMA stabilizer with a number-average molecular weight of ~24 000 g mol^{-1}. The solvents used were methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-octanol. The formulation used for each polymerization was 0.50 g of stabilizer, 50.0 mL of alcohol, 50 mg of AIBN and 5.0 of g styrene.

Effect of Reaction Temperature. All experiments were carried out using 1.0 w/v % of a 59:41 PDMAEMA-*b*-MMA stabilizer with a number-average molecular weight of ~24 000. The solvent used was 1-butanol. Polymerizations were carried out at 50, 60, and 70 ± 1 °C.

Disk Centrifuge Photosedimentometry (DCP). DCP was used to assess the particle size and polydispersity of the polystyrene latexes. All experiments were carried out using a Brookhaven BI-DCP instrument, operating in the line start mode. Samples for DCP analysis were prepared by adding a few drops of the alcoholic latex mixture to 3 mL of a 1:2 v/v % methanol/water mixture. The centrifuge rate was adjusted depending on the size of the particles being measured. Typically, centrifugation rates of around 2000 to 3000 rpm were used for samples greater than 1 μm in diameter. A particle density of 1.05 g cm^{-3} was used for the polystyrene latex particles.

Scanning Electron Microscopy (SEM). SEM measurements were made using a Leica Stereoscan 420 instrument. Samples were prepared by casting latex from methanol solutions onto aluminum SEM stubs. All samples were sputter-coated with gold prior to examination in order to minimize sample charging.

FTIR Spectroscopy. FTIR spectra were recorded using a Nicolet Magna 550 (Series II) spectrometer at 4 cm^{-1} resolution. The dried latex was dispersed in KBr disks prior to examination.

Results and Discussion

The characteristics of our block copolymers are summarized in Table 1. Good agreement was observed between theoretical and observed GPC molecular weights. All stabilizers have low polydispersities (M_w/M_n < 1.15), which is typical for GTP (co)polymers. There was good agreement between the theoretical copolymer compositions and those determined by ^{1}H NMR spectroscopy, which is not surprising in view of the high conversions achieved.

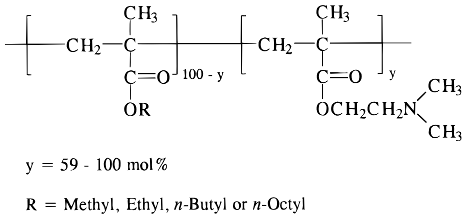

Figure 1. Structure of PDMAEMA-*b*-alkyl methacrylate copolymer stabilizers.

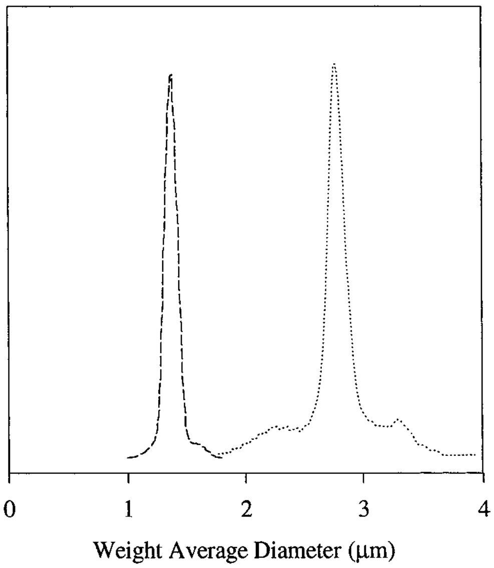

Figure 2. Typical weight-average particle size distribution curves of polystyrene latexes prepared in methanol (- - -) and 1-butanol (···) obtained using the disk centrifuge.

The PDMAEMA-*b*-alkyl methacrylate copolymers and PDMAEMA homopolymers were used as stabilizers in the dispersion polymerization of styrene (Figure 1). In most cases, colloidally stable dispersions were obtained, and disk centrifuge photosedimentometry (DCP) was used to assess their particle size distribution. This technique is not usually applied to sterically stabilized latex particles because the solvated stabilizer layer leads to considerable uncertainty regarding their effective particle density, which is an important input parameter for DCP. However, for the micrometer-sized latexes studied here, the stabilizer layer (*d*) is so thin relative to the particle diameter (typically $d = 10-20$ nm) that it was considered to be a negligible source of error. Indeed, excellent agreement was always obtained between the DCP data and electron microscopy studies. Given its inherent high resolution and rapid analysis times (typically 10−20 min/sample), we adopted DCP as our standard particle sizing technique. While DCP confirmed that most syntheses produced latexes that were near-monodisperse with respect to particle size (see Figure 2), GPC analysis showed that the polystyrene had a broad molecular weight distribution (M_w/M_n ~2), as expected from a free-radical polymerization (see Figure 3).

Typical FTIR spectra of a PDMAEMA-*b*-MMA-stabilized polystyrene latex and polystyrene are shown in Figure 4. The latex spectrum is essentially identical

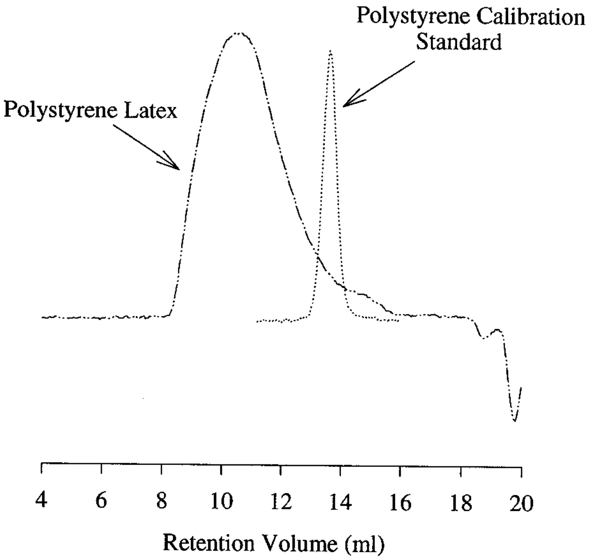

Figure 3. Typical GPC chromatogram of polystyrene produced during dispersion polymerization.

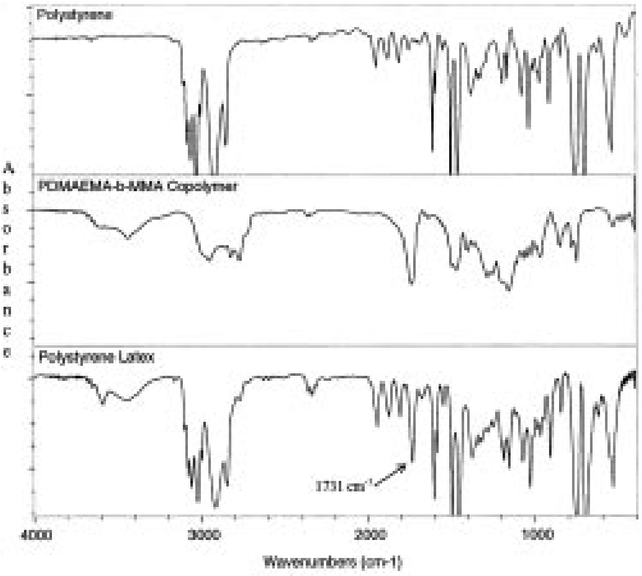

Figure 4. FTIR spectra of polystyrene, a PDMAEMA-*b*-MMA copolymer, and a polystyrene latex.

to that of polystyrene, but there is an additional weak absorption at 1731 cm^{-1}. This is attributable to the carbonyl ester(s) of the stabilizer, thus confirming the presence of this component.

The usual requirement for AB block copolymer stabilizers is that the A blocks (*e.g.*, PMMA) are preferentially contained in the precipitating polymer and act as anchors for the B blocks (*e.g.*, PDMAEMA), which are swollen by the diluent and extend away from the particle surface (see Figure 5). This layer of B blocks provides a protective barrier against flocculation. Lower alcohols are poor solvents for poly(alkyl methacrylates), although Fox and co-workers[28] have reported that low molecular weight PMMA is soluble in lower alcohols. PDMAEMA is readily soluble in lower alcohols at the polymer molecular weights used here. In our previous work,[26] we have shown that the PDMAEMA-*b*-MMA copolymer stabilizers used here are molecularly dissolved in methanol. Furthermore, ^{1}H NMR spectroscopy studies in methanol-d_4 indicated that the PMMA component was solvated. Thus, the alkyl methacrylate anchor component may be in a relatively poor solvent, but it is nevertheless reasonably well-solvated, probably because only relatively short PMMA chain lengths are involved.

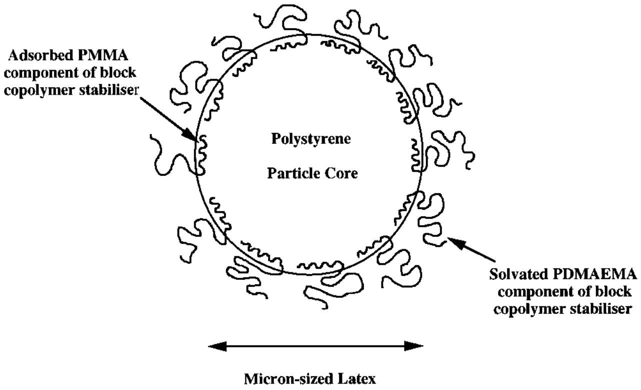

Figure 5. Schematic representation of a polystyrene latex particle stabilized by an adsorbed layer of PDMAEMA-*b*-MMA copolymer.

Table 2. Effect of Stabilizer Composition on Polystyrene Latex Formation and Particle Size

reaction no.	stabilizer composition (DMAEMA content, mol %)	stabilizer molecular weight	weight-average diameter by DCP (μm)
L27	100	17 900	precipitate
L26	85	23 800	1.59 ± 0.17
L24	80	19 600	1.31 ± 0.13
L23	67	24 300	1.45 ± 0.14
S3	59	23 800	1.58 ± 0.08

Effect of Stabilizer Composition. The results for latexes produced using a series of PDMAEMA-*b*-MMA copolymer stabilizers with varying MMA contents are summarized in Table 2. All experiments were carried out in ethanol at 60 °C. PDMAEMA homopolymer (M_n 17 900) was ineffective as a stabilizer; only a macroscopic polystyrene precipitate was obtained. This control experiment confirms the importance of the MMA component in the stabilizer as an anchor group.

All the stabilizers examined in this study had PDMAEMA as the major component, with compositions ranging from 85:15 to 59:41. Within this range near-monodisperse latexes were formed in each case, but varying the copolymer composition had little effect on particle size. All latexes had weight-average diameters in the range 1.45 ± 0.15 μm. The block copolymers had similar PDMAEMA block lengths and variable PMMA block lengths. Since the role of the PMMA block is presumably to be to anchor the soluble PDMAEMA blocks, which provide the steric stabilization, it is perhaps not unreasonable that the PMMA block length had relatively little effect on the particle size. A study of copolymers with fixed PMMA block length and variable PDMAEMA block length might prove interesting. An increase in the soluble block length would stabilize a greater surface area; thus, smaller particles might be expected.

It has been suggested[29] that the most efficient stabilizers have a molar ratio of anchor to soluble block in the range of 0.33–3. However, we find that block copolymers containing as little as 15 mol % PMMA, the anchor block, are efficient stabilizers. Similarly, Ober has reported that block copolymers containing as little as 10 mol % anchor component can act as effective steric stabilizers.[9] This author claimed that the anchor block

Table 3. Effect of Varying the Alkyl Chain Length of the Alkyl Methacrylate Anchor Group in the Copolymer Stabilizer on the Particle Size of the Polystyrene Latex

reaction no.	alkyl methacrylate	stabilizer comopsition (DMAEMA content, mol %)	stabilizer molecular weight	weight-average diameter by DCP (μm)
L24	methyl	80	19 600	1.31 ± 0.13
S13	ethyl	83	21 800	2.23 ± 0.30[a]
S12	*n*-butyl	81	22 600	1.27 ± 0.11[a]
S15	*n*-octyl	80	18 100	precipitate

[a] Some coagulum was also observed in these syntheses.

of the stabilizer should be compatible with the particle core. However, our study suggests that this is not an essential requirement.

It is noteworthy that Stejskal *et al.*[18] have successfully prepared PMMA dispersions in decane using poly(styrene-*b*-ethylene-*co*-propylene) copolymer stabilizers. Since PS is known to be virtually immiscible with PMMA, the anchor component of the stabilizer is incompatible with the polymer particles, and precipitation of the PMMA might have been predicted. Stejskal *et al.* suggested that the locus of the dispersion polymerization was actually inside the monomer-swollen micelles formed by the block copolymer, thus leading to the formation of submicrometer latex particles. Winnik *et al.*[24] studied the dispersion polymerization of styrene using poly(ethylene oxide-*b*-styrene) in alcohols, a system in which the anchor block is compatible with the polymer formed. All of their stabilizers were found to form micelles in methanol. When low molecular weight copolymer stabilizers were used (~10 000−20 000), relatively monodisperse micrometer-sized particles were obtained. In contrast, when higher molecular weight copolymers (>40 000) were used as stabilizers, only polydisperse submicrometer particles (analogous in size to those prepared by Stejskal *et al.*[18]) were formed. These results were rationalized in terms of the equilibrium between the copolymer micelles and unimers. Micelles of low molecular weight copolymers can undergo relatively rapid exchange with unimers, making the unimers available to act as a steric stabilizer for the precipitating polystyrene phase. In contrast, micelles formed by high molecular weight copolymers are slow to exchange with unimers, so polymerization of the styrene takes place within micelles, leading to the formation of submicrometer particles, as observed by Stejskal *et al.*

In an earlier study,[26] we showed that the PDMAEMA-*b*-MMA copolymers used in this work do not form micelles in alcohols but are molecularly dissolved. Thus, our styrene polymerization is a true dispersion polymerization; the precipitating polystyrene particles are stabilized by adsorption of block copolymer unimers, even though polystyrene and PMMA are incompatible.

Effect of Alkyl Methacrylate Type. DMAEMA was copolymerized with methyl, ethyl, *n*-butyl, or *n*-octyl methacrylate in order to examine the effect of the hydrophobicity of the anchor group of the copolymer stabilizer (see Table 3). Each of these block copolymers contained ~80 mol % DMAEMA and 20 mol % alkyl methacrylate. The block copolymer containing DMAEMA and *n*-octyl methacrylate did not promote the formation of stable latex particles; instead, only precipitate was formed. Block copolymers of DMAEMA with methyl, ethyl, and *n*-butyl methacrylate each produced stable latexes. Some precipitate (as well as latex particles) was observed when block copolymers containing ethyl or *n*-butyl methacrylate were utilized. It is probable that the observed reduction in stabilizer efficiency with increasing hydrophobicity of the alkyl methacrylate anchor component is related to the increasing incompatibility of the stabilizer with the polystyrene surface.

Table 4. Effect of Increasing Copolymer Stabilizer Concentration on the Particle Size of the Polystyrene Latex

reaction no.	stabilizer concn (w/v %)	weight-average diameter by DCP (μm)
L34	0.5	1.78 ± 0.15[a]
S3	1.0	1.58 ± 0.08
L28	2.0	1.46 ± 0.06
S16	4.0	1.40 ± 0.05

[a] Some coagulum was also observed in this synthesis.

Table 5. Effect of Varying the Alkyl Chain Length of the Alcohol Solvent on the Particle Size of the Polystyrene Latex

reaction no.	solvent	weight-average diameter of PS latex by DCP (μm)
S4	methanol	1.38 ± 0.08
S3	ethanol	1.58 ± 0.08
S1	1-propanol	1.97 ± 0.28
S2	1-butanol	2.80 ± 0.31
S9	1-pentanol	1.54 ± 0.11
S13	1-hexanol	0.93 ± 0.13
S7	1-octanol	0.70 ± 0.05

Effect of Stabilizer Concentration. The stabilizer concentration of a 59:41 PDMAEMA-*b*-MMA copolymer was varied from 0.5 to 4.0 w/v %. As the stabilizer concentration was increased, the size of the latex particles decreased slightly (see Table 4). This trend of decreasing particle size with increasing stabilizer concentration was observed by other workers.[6,7,11,14] For example, Dawkins and co-workers reported the use of both poly(styrene-*b*-dimethylsiloxane)[14−16] and poly(styrene-*b*-ethylene-*co*propylene)[11−13] copolymers as stabilizers for the dispersion polymerization of styrene. In both systems, higher stabilizer concentrations led to smaller latexes.

Effect of Solvent Type. The effect of solvent was investigated by polymerization of styrene in the presence of a 59:41 PDMAEMA-*b*-MMA stabilizer. All reactions were carried out at 60 °C in alcohol solutions. The alkyl chain length of the alcohol was varied from methanol to 1-octanol. As seen in Table 5 and Figures 6 and 7, the weight-average particle diameter of the latexes increased from 1.38 μm in methanol up to a maximum of 2.80 μm in 1-butanol and then decreased to 0.70 μm in 1-octanol.

Paine *et al.*[6] observed similar results in the dispersion polymerization of styrene using a PVP stabilizer. The effect of solvent was tested using straight-chain alcohols ranging from methanol to 1-decanol in ethanol/water mixtures containing from 80 to 100 vol % ethanol. Particle size increased from 1.16 μm in ethanol/water to 4−4.5 μm in 1-butanol and then decreased to 1.64 μm in 1-decanol. Lok and Ober[4] also investigated the effect of solvent in the polymerization of styrene using cellulosic stabilizers. They found that the particle size increased from 1.11 μm in methanol to 1.40 μm in ethanol up to 2.27 μm in 1-butanol.

The fact that narrow size distribution latexes are formed in these polymerizations indicates that nucleation of particles at low conversions controls particle

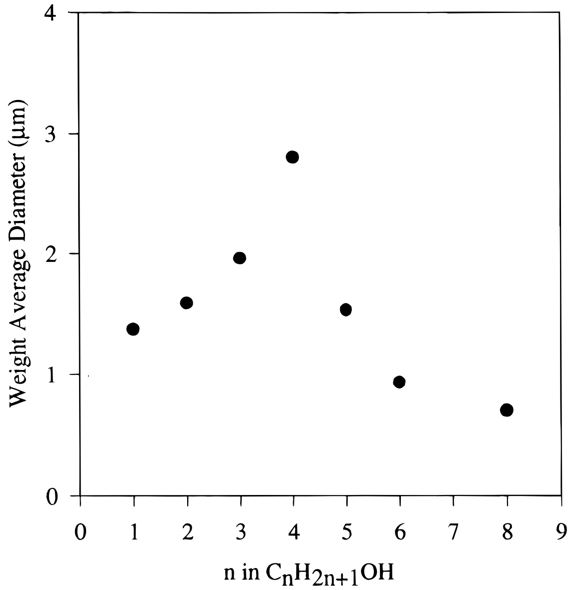

Figure 6. Effect of solvent type on latex particle size.

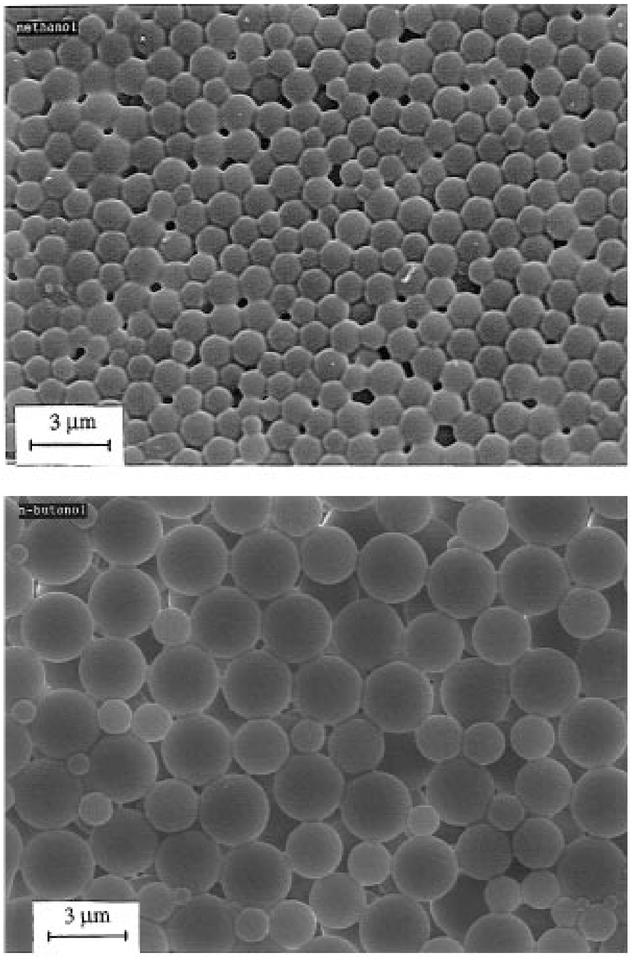

Figure 7. Scanning electron micrographs of polystyrene particles produced by dispersion polymerization using methanol (top) and 1-butanol (bottom) as diluents.

Table 6. Effect of Increasing Reaction Temperature on the Particle Size of the Polystyrene Latex

reaction no.	reaction temp (°C)	weight-average diameter by DCP (μm)
S6	50	2.05 ± 0.08
S2	60	2.80 ± 0.31
S8	70	polydisperse

size; once the initial nucleation has occurred the probability of forming more particles is low compared to that of growth of existing particles, and a narrow distribution latex is formed. Thus, larger particles will be produced under conditions where phase separation is delayed to higher conversions, leading to a smaller number of larger nuclei, and increasing particle size should be favored by increasing compatibility between the solvent and the polystyrene/stabilizer complex.

In their work, Lok and Ober[4] proposed that the particle sizes could be broadly correlated with the solubility parameter of the initial polymerization mixture, though quantitative correlations between different solvent types were not possible. A recent paper by Dawkins *et al.* proposed a similar explanation for particle size effects.[23] They used partially hydrolyzed poly(vinyl acetates) as steric stabilizers for polymerization of styrene in alcohols. Polymerizations carried out in glycerol/methanol mixtures produced 0.6−1.2 μm sized particles, compared to 2.0 μm in methanol and 2.2−2.7 μm in ethanol/methanol mixtures. They suggested that, as the solvent power of the reaction medium for the growing polymer chain increases, a smaller number of nuclei precipitate at the start of the polymerization, and so larger particles are formed.

In contrast, Paine *et al.*[6] suggested that the maximum in particle size in their PVP-stabilized reaction was due to a close match of solubility parameters between 1-butanol and the stabilizer. In a related paper,[32] Paine analyzed particle sizes in styrene polymerization stabilized with HPC and concluded that the maximum occurs when there is the best match in both polar and nonpolar contributions of the solubility parameter of the reaction mixture with those of the stabilizer. He concluded that the solvating power of the reaction mixture for the stabilizer is the important factor.

Our data do not allow us to resolve the question of whether the stabilizer or the polymer is the more important species in size control, since the range of solvents is small and the complex solubility parameters of PDMAEMA are not available. However, a comparison of our data with those of Paine *et al.*[6,32] shows that the largest latex particles are produced in 1-butanol for our stabilizers, PVP and HPC. Since these are very different polymers, it is tempting to conclude that the solvent power of the medium for polystyrene is more important than that for the stabilizer.

Effect of Reaction Temperature. The effect of reaction temperature was investigated by carrying out polymerizations in the presence of a 59:41 PDMAEMA-*b*-MMA stabilizer, at three temperatures: 50, 60, and 70 °C. All reactions were carried out in 1-butanol since this solvent has a relatively high boiling point (118 °C). As reported in Table 6, the reactions carried out at 50 and 60 °C both had fairly narrow size distributions, with the particle size increasing from 2.05 μm at 50 °C to 2.8 μm at 60 °C. El-Aasser and co-workers[8] have observed a similar trend in the dispersion polymerization of methyl methacrylate in alcoholic media using a PVP stabilizer. In their study, the PMMA particle size increased from 2.8 μm at 50 °C up to 3.2 μm at 55 °C and 4.0 μm at 60 °C. This increase in particle diameter with increasing temperature was attributed to (1) an increase in the critical chain length due to the increase in the solvency of the continuous phase, (2) an increase in the concentration of precipitated oligomer chains due to increases in both the decomposition rate of the initiator and the propagation rate of oligomer radicals, and (3) a decrease in the viscosity of the continuous phase. In principle, all of these factors can contribute to an increase in particle size. In our study, it was found that the size distribution of the latex particles increases with increasing temperature, and at 70 °C, a polystyrene latex of very broad size distribution was produced. Ober *et al.* investigated the dispersion polymerization of styrene in methyl cellosolve–ethanol media using a cellulosic stabilizer.[30] They also found that the polydispersity of the particles increased at higher temperatures, from 0.5–3.5 μm at 55 °C to 1.5–9 μm at 70 °C.

Latex Colloid Stability. The polystyrene latex particles synthesized in the present study become irreversibly flocculated if redispersed in deionized water. Originally, we believed that the block copolymer stabilizer became desorbed from the surface of the latex particles, inevitably leading to flocculation of the latex particles. However, the flocculated latex becomes restabilized upon addition of dilute HCl. This reversibility indicates that the copolymer stabilizer remained adsorbed onto the latex particles and that the poor latex stability in deionized water is simply due to the collapse of the steric stabilizer layer in this medium. This suggests that deionized water is a poorer solvent than methanol for the PDMAEMA component. Moreover, the latex particles can be successfully redispersed directly into dilute HCl, presumably since the PDMAEMA component becomes protonated and therefore more extended (a thicker steric stabilizer layer) in this medium. Similar acid–base reversible flocculation behavior has been reported for polyelectrolyte-stabilized polypyrrole particles.[31]

Conclusions

We have demonstrated that PDMAEMA-*b*-MMA copolymers are effective steric stabilizers for the dispersion polymerization of styrene. Variation of the DMAEMA content of the copolymers produced relatively little change in latex particle size, at least within the composition range studied here. Block copolymers comprising DMAEMA and either ethyl, *n*-butyl or *n*-octyl methacrylate were also investigated. With the exception of the PDMAEMA-*b*-octyl methacrylate block, these copolymers proved to be effective steric stabilizers. As the concentration of block copolymer stabilizer was increased, the latex particle size decreased slightly. However, latexes in the size range 0.7–2.8 μm could be easily obtained by varying the composition of the diluent, with a maximum particle size being obtained for 1-butanol. As the polymerization temperature was increased, the particle size and polydispersity of the latexes generally increased. Our results indicate that block copolymers can be effective steric stabilizers, even in a medium that is initially a good solvent for both block components. However, control experiments using PDMAEMA homopolymer indicate that the PMMA component is essential for effective steric stabilization.

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