Dispersion Polymerization of Polystyrene Latex Stabilized with Novel Grafted Poly(ethylene glycol) Macromers in 1-Propanol/Water

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ABSTRACT: A novel hydrophilic macromer adapted for chemical grafting has been synthesized. It consists of methyl-end-capped poly(ethylene glycol) functionalized with a urethane terminus. Dispersion polymerization of styrene in an alcohol/water medium in the presence of the macromer allows chemical grafting of the macromer to the surfaces of the developing polystyrene (PS) latex particles. Scanning and transmission electron microscopies confirm the formation of spherical, submicron polystyrene particles. Transmission electron microscopy of films prepared from the latex particles also permits direct visualization of the stabilizing macromer layer grafted on the PS particle surfaces. Data acquired from proton nuclear magnetic resonance reveal a direct correlation between the concentration of macromer in the reaction mixture and the amount grafted to the latex particles. Rheological techniques are employed to (i) discern the stabilization efficacy of the macromer and (ii) identify correlations between latex and flow characteristics.

Introduction

Water-borne colloidal particles are of tremendous use as resins in a wide range of industrial applications, including inks, adhesives, paints, and other coatings. An important property of these latexes is their resistance to flocculation. If a method of countering the natural attractive tendency of the particles is not provided, a latex becomes unstable. Instability and subsequent particle flocculation lead to processing difficulties and inhomogeneity of latex products. Electrostatic stabilization and steric stabilization constitute viable methods by which to neutralize the attractive van der Waals forces between colloidal particles and prevent flocculation. In electrostatic stabilization, ionic surfactants place charged groups on each particle surface so that the particles are stabilized by the resultant interparticle electrostatic potential.[1] Steric stabilization involves grafting or adsorbing a polymer that is partially lyophilic to the surface of a colloidal particle. The lyophilic segments extend into the solvent, thereby creating a stabilizing layer through two thermodynamic effects.[2−4] The first effect is entropic in nature, arising from the loss of configurational freedom associated with interpenetrating stabilizing layers. This contribution to the free energy is always negative. The second effect is an enthalpic one that reflects the change in free energy associated with the partial demixing of chain segments and solvent as the stabilizing layers overlap. The enthalpic contribution can be either positive or negative, depending on the polymer−solvent interaction parameter (χ) for a particular system.

In many latex systems, steric stabilization is more desirable than the less versatile and robust electrostatic stabilization. Some advantages of steric stabilization include pH insensitivity (i.e., the ion concentration does not have to be controlled in order to prevent flocculation), the efficacy of both aqueous and nonaqueous dispersion media, and improved freeze−thaw stability.[5] Steric stabilization also allows for more concentrated stable dispersions. The stabilizing layer thickness can be as small as 3−10 nm for sterically stabilized systems, whereas the layer in electrostatically stabilized systems can be as large as 100 nm due to its diffuse nature. The shorter range of steric interactions permits a higher particle density before the maximum packing fraction, and thus, processable viscosity are exceeded. Increased solids content within a viable viscosity range favors sterically stabilized latex systems for commercial use in printing inks and coatings.

Polymeric stabilizers designed for steric stabilization are anchored to colloidal particles either by grafting (chemical bonding) or by physical adsorption to the particle surface.[6] Grafting is a more effective means of stabilization than physical adsorption, due to the permanence of the particle/stabilizer bond. Relatively few investigators have successfully grafted stabilizing polymer chains directly to latex particles. In most of these studies, short poly(ethylene glycol) (PEG) chains functionalized with an acrylate terminus have been used as the hydrophilic polymeric stabilizer grafted to polystyrene (PS) latexes.[7−13] Bromley,[7] however, reports that the macromer synthesis reaction in which the functional methacrylate group is added becomes inefficient as the molecular weight of the PEG is increased to within the range of effective stability (ca. 2000). Another concern is that the final products of these methacrylate transesterifications are not hydrolytically stable. Using a thiol-functionalized PEG macromer, Bourgeat-Lami and Guyot[14] find that only 15% of the available macromer actually grafts to PS latex particles. Our principal objective in the present study is to identify a synthetic strategy to overcome these difficulties encountered with other types of functionalized PEG macromers. In par-

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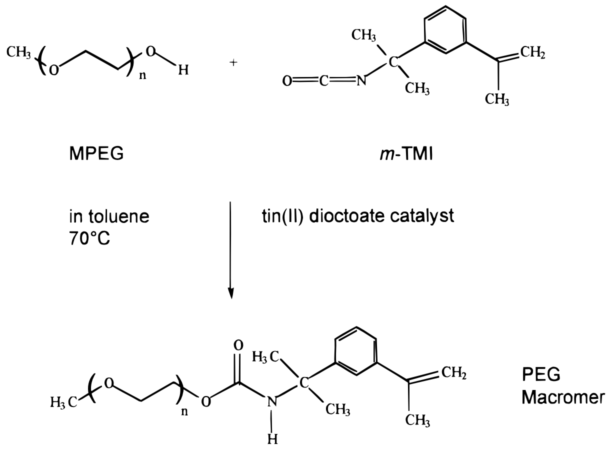

Figure 1. Synthetic scheme used to produce the PEG macromer. Poly(ethylene glycol) methyl ether (MPEG) and 3-isopropenyl-α,α-dimethylbenzyl isocyanate (*m*-TMI) undergo a condensation reaction in toluene at 70 °C.

ticular, we have developed a novel, urethane-functionalized, PEG-based macromer that allows in situ grafting to PS latex particles synthesized through a modified "seed and feed" dispersion polymerization.[7,15] Evidence obtained from proton nuclear magnetic resonance (^{1}H NMR) confirms that the PEG macromers graft fully to PS particles at all macromer concentrations examined. In addition, we evaluate latex stability by rheological methods. Using steady shear rheology, for instance, we have ascertained how the amount of grafted PEG macromer affects latex stability, thereby providing a means by which to optimize process characteristics (flow behavior) on the basis of synthesis parameters (graft concentration).

Experimental Section

Synthesis. *Materials.* Styrene was passed through a column of basic alumina to remove inhibitor. All other materials—poly(ethylene glycol) methyl ether, toluene, tin(II) dioctoate, 3-isopropenyl-α,α-dimethylbenzyl isocyanate, 2-butanone, petroleum ether, 1-propanol, and azobis(isobutyronitrile)—were used as received without further purification. All chemicals were obtained from Aldrich, with the exception of the azobis(isobutyronitrile) (AIBN), which was obtained from Alfa. The deionized (DI) water used in chemical reactions was obtained from a Barnstead water purification system.

Macromer Synthesis. The macromer used in the latex synthesis was prepared from methyl-end-capped poly(ethylene glycol) methyl ether (MPEG) and an unsaturated isocyanate, 3-isopropenyl-α,α-dimethylbenzyl isocyanate (*m*-TMI) (Figure 1). Nominal $\bar{M}_n = 2000$ or 5000 (as reported by Aldrich) MPEG was used to produce two macromers differing in molecular weight and identified as MPEG2000 macromer and MPEG5000 macromer, respectively. A solution of 450 g of MPEG in 50 g of toluene was heated to reflux in a flask equipped with a Dean-Stark trap. (All syntheses were performed under a nitrogen atmosphere and constant stirring.) After complete elimination of water, the solution was allowed to cool to 70 °C, and 0.45 g of tin(II) dioctoate catalyst was added. After the catalyst dissolved, 47.2 g of *m*-TMI was added, and the solution was allowed to reflux for about 2 h. The solution was then allowed to cool to 40 °C and was poured into a pan to set. To remove low molecular weight impurities, the macromer was dissolved in 2-butanone, precipitated in cold petroleum ether, and then vacuum-dried. The precipitation process was repeated to improve purity.

Polystyrene Latex Synthesis. Material characteristics that were varied in the latex preparations included macromer length and macromer/monomer ratio. As an illustrative example of the dispersion polymerization method, the reactor (a three-neck 250 mL glass flask) was charged with 7.2 g of MPEG2000 macromer dissolved in 24.0 g of DI water and 96.0 g of 1-propanol, and the solution was heated to reflux. A solution of 0.238 g of AIBN dissolved in 30.0 g of styrene was prepared, and 20% of this solution was added to the reactor. Within 10 min of adding the styrene solution, the dispersion mixture became slightly cloudy. After 30 min, the dispersion appeared milky white, and the remainder of the styrene/AIBN solution was added dropwise using a syringe pump (kd Scientific) over a 2 h period. After all the styrene/AIBN solution was added, the dispersion was allowed to react for an additional 3 h. Following continued stirring overnight at ambient temperature, the resultant latex possessed a solids content of approximately 20%.

Characterization. *Composition.* Molecular weights of the macromers were measured by gel permeation chromatography (GPC) on a multidetector system consisting of a Waters 2690 separations module with a Waters Styragel HR3 GPC column, a Viscotek T-60 light scattering detector and viscometer, and a Wyatt Technologies Optilab DSP interferometric refractometer. The mobile phase was 1 mL/min HPLC grade tetrahydrofuran (THF), used as-received from Aldrich. Samples were dissolved in THF (10 mg/mL) and 100 μL amounts were injected. The advantage of the multidetector system was that a molecular weight calibration curve generated from a series of standards was not required. Absolute, rather than relative, molecular weight information was consequently obtained. Chemical bonding of the urethane functional group was confirmed by Fourier transform infrared spectrometry (FTIR). Spectra were collected at ambient temperature in chloroform with a Nicolet Magna IR 750 spectrometer. Relative compositions of PS and PEG comprising the latex particles were determined by integrating and comparing characteristic peaks evident in ^{1}H NMR spectra. Samples for analysis were vacuum-dried, dissolved in deuterated chloroform, and tested at ambient temperature in a General Electric GN-300 spectrometer operated at 300 MHz.

Morphology. Field-emission scanning electron microscopy (FESEM) was performed with a JSM-6400F electron microscope. A drop of a highly dilute latex was placed on a silicon substrate. Upon evaporation of water, the particles were sputter-coated with gold, and images were acquired at an accelerating voltage of 1 kV. Transmission electron microscopy (TEM) was conducted using a Zeiss EM902 electron spectroscopic microscope operated at 80 kV at energy-loss settings of 0−100 eV. A liquid-phase staining technique was used to suspend the stabilizing PEG chains in their extended position and provide contrast between the stabilizing layer and the polystyrene core particle. Solutions of osmium tetroxide (OsO_4) in water (2% w/v) were mixed overnight, and latex particles suspended in water were subsequently added until the latex content of the OsO_4 solution was 1%. The OsO_4 reacts with the ether linkage present in PEG, oxidizing the PEG chains and turning them electron dense. (OsO_4 does not react with PS.) The reaction forms cross-links between the oxygen atoms in the OsO_4 and the carbon atoms in the PEO, allowing the OsO_4 to act as both a stain and fixative. After the PEG chains on the latex particles had reacted for 90 min, a drop of the solution was placed on a copper TEM grid, and the liquid was allowed to evaporate. To obtain meaningful particle size distributions, the diameters of about 100 particles in selected latexes were measured with the Image v.1.61 software package (NIH). The thickness of the PEG stabilizing layer was determined by first heating latex particles to 100 °C for 15 min under vacuum to form a contiguous film and then microtoming the film in a Reichert-Jung Ultracut S cryoultramicrotome operated at −100 °C to obtain electron-transparent sections (about 80−90 nm thick). The sections were exposed to the vapor of the OsO_4 solution described above for 90 min to stain the PEG.

Properties. Differential scanning calorimetry (DSC) was performed on selected latexes using a DuPont 910 calorimeter operated under argon. Samples were prepared by vacuum-drying for several days. Measurements of the latexes were acquired from ca. 15 mg samples over a temperature range of

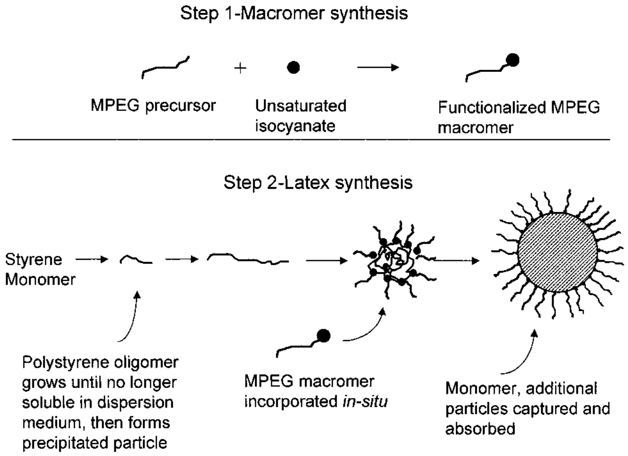

Figure 2. Schematic representation of the procedure to prepare sterically stabilized polystyrene dispersions. Two syntheses are conducted in series: the first is the reaction that produces the functionalized macromer, and the second is the dispersion polymerization that forms the latex particles and grafts the stabilizing macromer to the growing particles in situ.

−50 to 120 °C at a heating rate of 20 °C/min. Rheological tests were conducted on a Rheometrics DSR, a stress-controlled instrument. Stress was applied to the material through a torque placed on the moving portion of the fixture, and the corresponding deformation, or strain, was measured by the shift in the fixture position. Fixtures used in these experiments included a 25 mm diameter cone-and-plate (0.1 rad cone angle), a 40 mm diameter cone-and-plate (0.04 rad cone angle), and a couette, depending on sample viscosity. In these tests, 1-propanol was replaced with DI water through centrifugation (11 000 rpm for up to 2 h, repeated 2−3 times). After each centrifugation, the supernatant was decanted and replaced with water, and the particles were redispersed. The process of mixing each latex thoroughly before loading into the DSR was identical for each test. All reported data, collected at 25 °C, were reproducible to within 10%.

Results and Discussion

Latex Synthesis. Figure 2 is a schematic representation of the two-step procedure that produced our sterically stabilized dispersions investigated in this work. The first synthesis (step 1) corresponds to the condensation reaction that creates the stabilizer—a hydrophilic, PEG-based macromer possessing an unsaturated isocyanate terminal functional group. A unique feature of this work is the use of this isocyanate terminus, which enables the PEG to graft directly to growing PS particles during latex synthesis. Because of the steric hindrance provided by the bulky urethane linkage, this functional group provides excellent hydrolytic stability. Such stability is crucial when long-term storage of a latex product must be considered. The second synthesis (step 2 in Figure 2) refers to the free-radical dispersion polymerization responsible for PS latex formation. Dispersion polymerization occurs by homogeneous nucleation in a three-stage mechanism.[16−18] In the first stage, polymerization is initiated by the decomposition of initiator into free radicals and propagates by the addition of monomer. In the second stage, growth of the oligomeric radical proceeds until a critical chain length is attained. The oligomers then precipitate out of solution, forming an insoluble phase of spherical particles. To prevent particle flocculation, the polymerization may be conducted in the presence of a stabilizing agent, such as an amphiphilic polymer, a nonionic surfactant, or a macromer. During the polymerization, the stabilizing moiety grafts or adsorbs to the small, growing particles. The particles that do not yet have adequate stabilizer coalesce until a critical stabilizer concentration is reached, at which point the particles become sterically stable.[19] At the end of this stage, the particle number is fixed. In the final phase, the small particles serve as nucleation sites, and residual monomer and oligomer are absorbed by the polymer particles, in which they can further polymerize.[20] Any additional particles that begin to form during the third stage are captured and absorbed by existing particles and continue to grow within them.[18]

Table 1. Synthesis Parameters for PEG-Stabilized PS Latexes

latex designation	macromer	macromer concn (wt %/mol % based on styrene)
LD2-001	MPEG2000	6/0.26
LD2-003	MPEG2000	**12/0.53**
LD2-004	MPEG2000	6/0.26 **(1.0 mol % initiator)**
LD2-005	MPEG2000	**18/0.79**
LD2-006	MPEG2000	**15/0.66**
LD5-001	MPEG**5000**	6/**0.11**
LD5-003	MPEG**5000**	**12/0.22**
LD5-004	MPEG**5000**	**18/0.33**
LD5-005	MPEG**5000**	**15/0.27**
LD5-006	MPEG**5000**	**24/0.44**

If a polymeric stabilizer is employed, it is generally added to the dispersion medium at the start of the reaction, and the polymerization is conducted through a semibatch “seed and feed” process. In this method, an aliquot of monomer/initiator solution is added to the stabilizer/dispersion medium. The monomer incorporates the polymeric stabilizer as it polymerizes and forms the seed particles, a process requiring about 30 min. The remainder of the monomer and initiator is then added to the dispersion medium over the course of several hours. The feed rate is generally slow to prevent nonstabilized homopolymer from forming. Unlike syntheses where all reactants are present at their full concentration at the start of the reaction,[14,19,21,22] the seed and feed process produces latexes with higher solids contents and lower particle polydispersity compared to a “one-shot” polymerization.[23] The dispersion medium employed here, a mixture of 1-propanol and water, was selected because preliminary experiments indicated that 1-propanol is more effective than methanol or ethanol in producing a stable latex. Also, the increased solvency of the polymer in a higher alcohol would have decreased the effectiveness of the dispersion polymerization process[24] and hindered removal of the alcohol for water-based applications.

Table 1 lists the polystyrene latexes produced here, as well as their designations. Latex characteristics varied during preparation included macromer length and macromer concentration. Initiator concentrations for all preparations except for LD2-004 are 0.5 mol % on the basis of styrene. The initiator concentration for LD2-004 is 1.0 mol %. Parameters differing from the LD2-001 latex are in bold print in Table 1. All the latexes have been prepared in a dispersion medium composed of 80/20 (w/w) 1-propanol/water. Attempts to use lower alcohol/water ratios (e.g., 60/40) yield unstable latexes, as evidenced by the formation and precipitation of PS particle aggregates during polymerization. One possibility for this observation involves the solubility of PS in the 1-propanol/water mixture.[13] The solubility parameter of PS (17−21 MPa$^{1/2}$) is much closer to that of 1-propanol (24.3 MPa$^{1/2}$) than that of water (47.9

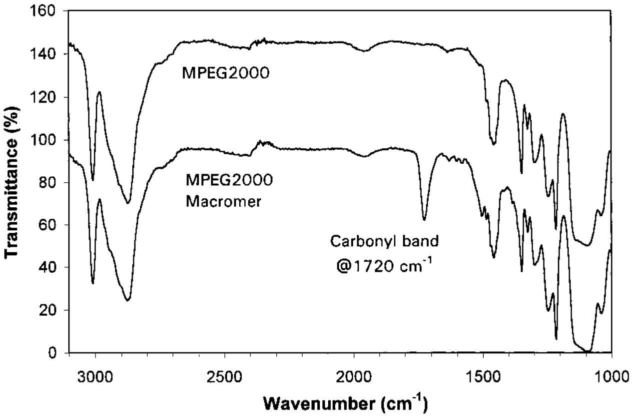

Figure 3. FTIR spectra demonstrating the presence of a carbonyl band at 1720 cm^{-1} in the MPEG2000 macromer. This band provides evidence for incorporation of the urethane functional group. The spectrum for the MPEG2000 precursor is offset for clarity.

MPa$^{1/2}$).[25] A reduction in the solubility of PS in the dispersion medium is accompanied by a decrease in the extent to which PS chains grow during the second stage of homogeneous nucleation before they precipitate. With less 1-propanol in the dispersion medium, PS readily precipitates, possibly before the PS particles can incorporate a sufficient quantity of stabilizing PEG chains.

Another potential cause for latex instability is the effect of the alcohol/water ratio on chain transfer characteristics of the dispersion medium. The alcohol, rather than the water, serves as the chain transfer agent that controls the growth of the polymerizing dispersion particle.[7,25] At a lower alcohol/water ratio, chain transfer is not as effective, and particles may grow too large to ensure adequate surface coverage by the stabilizer, thereby resulting in decreased particle stability. Particle size analysis of unstable latexes, used to ascertain whether the unstable particles are larger or smaller than those in stable latexes, could determine which, if either, of the above mechanisms constitutes a reasonable explanation for the production of unstable latexes. Instability-induced particle aggregation, however, thwarts precise particle size measurement, and the values are not reported here. Instead, ^{1}H NMR analysis confirms that all of the stabilizing PEG macromer was incorporated into the unstable latex particles, implying that the effect of alcohol/water ratio on chain transfer, rather than on PS solubility, is responsible for latex instability. Results obtained from ^{1}H NMR are discussed more fully in the following section.

Latex Characterization. Examination of the MPEG macromer by FTIR reveals the presence of a carbonyl band at 1720 cm^{-1}, as seen in Figure 3. Since this band is not present in the MPEG precursor, its presence in the macromer confirms the addition of the urethane functional group, which contains a C=O bond. (No meaningful spectra at 4000 cm^{-1}, showing the disappearance of hydroxyl groups that accompany carbamate formation, could be observed due to noise.) In addition, GPC provides information regarding molecular weights and macromer purity relative to the MPEG precursor received from the supplier. Results obtained from the multiple-detector GPC system yield the following absolute number-average molecular weight, $\bar{M}_n$, values: 2140 (MPEG2000 precursor), 2360 (MPEG2000 macromer), 5440 (MPEG5000 precursor), and 5680 (MPEG5000 macromer). Since the macromer synthesis only involves the addition of a single isocyanate unit to the end of each PEG chain, the $\bar{M}_n$ and polydispersity index (PDI) of the two polymer precursors are not expected to (and did not) change appreciably as a result of the reaction. In fact, comparison of the PDIs of the macromers with their MPEG precursors indicates that incorporation of the isocyanate group does not affect polydispersity (e.g., the PDI's of both the MPEG2000 macromer and the MPEG2000 precursor are identically 1.08).

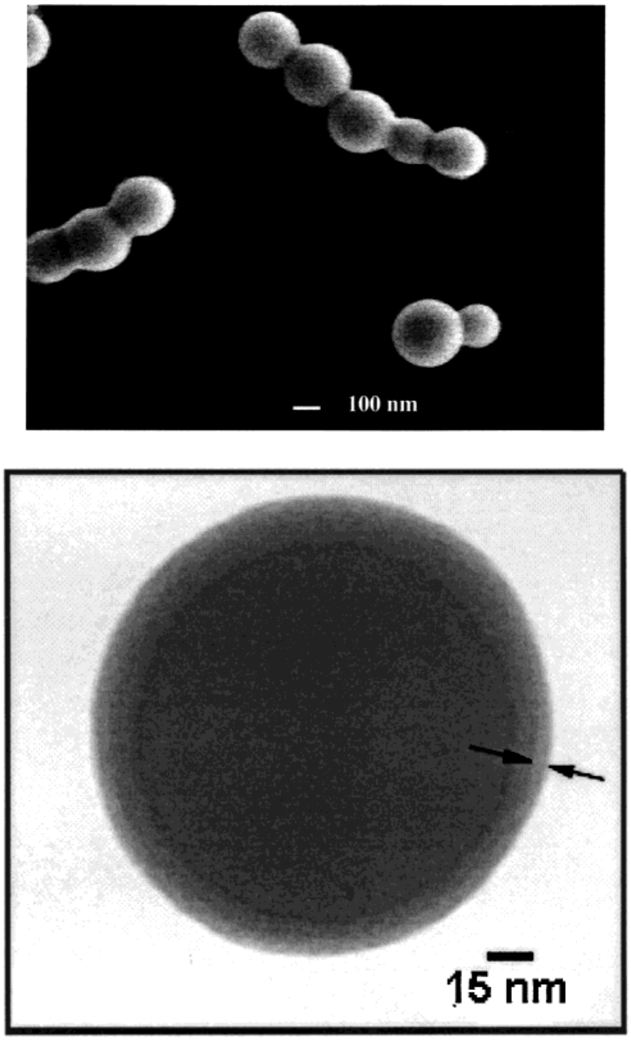

Figure 4. Representative FESEM (a, top) and TEM (b, bottom) micrographs of latex LD5-004 obtained from dilute specimens. The particles appear spherical but in some cases show signs of coalescence during sample preparation. The micrograph in (b) is an enlargement of a single particle and reveals a subtle, but detectable, peripheral PEG layer (see arrow).

Particle morphology has been investigated through the combined use of FESEM and TEM, as shown in Figure 4. A representative secondary electron image of a dilute LD5-004 latex is presented in Figure 4a and demonstrates that the PS particles are, for the most part, spherical. Some of the particles, however, show signs of coalescence due to water evaporation during sample preparation. For comparison, an illustrative TEM micrograph of a high-magnification enlargement of a single particle from latex LD5-004 is displayed in Figure 4b. Quantitative measurements of particle size distribution have been performed by TEM. The particle size distribution obtained from latex LD5-004 is shown

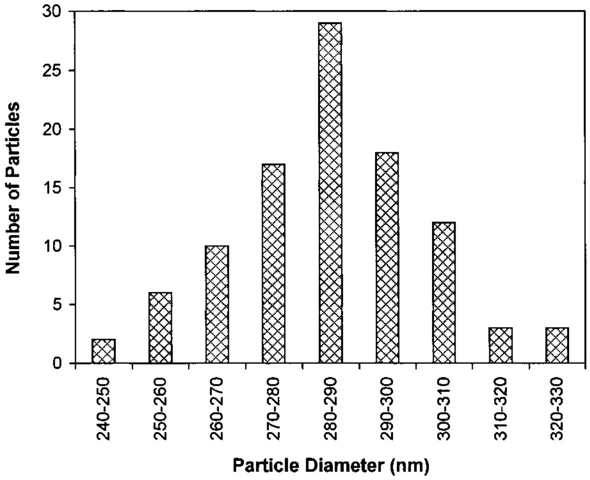

Figure 5. Particle size distribution generated from TEM images of the LD5-004 latex. This relatively narrow distribution is typical for the latexes synthesized here. Values of the mean and standard deviation derived from the size distributions of selected latexes are listed in Table 2.

Table 2. Particle Diameters (nm) of Selected Latexes from TEM Measurements

latex designation	diameter (mean ± std dev)
LD2-001	377 ± 9
LD2-003	327 ± 14
LD2-004	399 ± 10
LD5-003	376 ± 11
LD5-004	285 ± 17

in Figure 5 and reveals that the distribution is relatively narrow (with a mean and standard deviation of 285 and 17 nm, respectively). Average particle sizes of selected latexes are provided in Table 2 to illustrate the range of particle sizes obtained. It must be remembered that the sizes of particles evident in FESEM and TEM images correspond to the PS core, since the stabilizing layer is relatively thin and then collapses onto the particle surface when the dispersion medium is evaporated prior to imaging. As noted elsewhere,[26] the thickness of the stabilizing layer, when collapsed on the particle surface, is negligible. To identify the PEG surface layer, solution staining with OsO_4 has been employed to enhance contrast between PS and PEG. The thin PEG layer is difficult to discern due to the spherical geometry of the particle (which complicates the phase contrast mechanism of image formation). Close examination of images such as the one presented in Figure 4b does, however, reveal a very subtle but detectable peripheral layer (see arrow in Figure) generally measuring less than 5 nm in thickness. As discussed in detail later, this thickness is of the right magnitude for the grafted PEG layers investigated in this work.

Another approach by which to measure the grafted PEG layer utilizes films prepared from stabilized latex particles. Since the short PEG chains are randomly grafted to PS, they are not expected to be highly mobile during film formation at 100 °C, which is just above the measured PS glass transition temperature ($T_g = 93$ °C, according to DSC, for the LD2-001 latex). Two possible reasons exist for the apparently depressed T_g (from nominally 100 °C for high-molecular-weight PS): (i) the PS is plasticized by residual monomer/oligomer or PEG,[27] or (ii) low-molecular weight PS chains comprise the particles. Cross-sectional TEM micrographs of PEG-stabilized latex particles melt-pressed to form a contiguous film are presented in Figure 6a,b. In these images, the PEG layer appears electron-opaque due to selective staining with the vapor of OsO_4(aq). Interpretation of images such as those shown in this figure requires careful consideration. The schematic illustration provided in Figure 6c depicts the geometrical arrangements that could render the images displayed in Figure 6a,b. In Figure 6c, z identifies the direction of the electron beam, t represents the thickness of a sectioned TEM specimen, and λ denotes the length of contact along the z-axis between adjacent particles. In the simplest scenario, λ lies parallel to t. If $\lambda < t$, then scattering from the OsO_4-stained PEG layers on neighboring spherical particles contribute to the final image in such a way to cause the interface between particles to appear diffuse in projection. Note that a comparably diffuse interface is observed when λ is not parallel to z. For quantitation purposes, λ must be nearly parallel to z and should equal or exceed t. In this case, the projected interface will be sharply defined and will likewise be at its thinnest. Only the thinnest interfaces in TEM images must therefore be considered in an effort to quantify the thickness of the PEG layers on these PS latex particles. Analysis of TEM images such as those shown in Figure 6a,b with the NIH Image software package yields a PEG layer thickness of 4.5 ± 0.5 nm in the case of the LD5-006 latex with PEG chains of mass ca. 5000.

Theoretical and experimental studies have found that stabilizing chains on a particle surface exhibit a more extended conformation than do identical polymer chains, which adopt a typical random-coil conformation, in a dilute solution of the same solvent.[28-32] The degree to which the chains are extended depends sensitively on the curvature of the particle surface and the graft density. In the cases of either a low radius of curvature (i.e., relatively large particle radius) or a high graft density, grafted chains are not free to expand along the particle surface and must therefore extend normal to the particle surface to conserve mass. The gyration diameter (D_g) of MPEG5000 in the freely rotating chain limit is estimated from $L(2n/3)^{1/2}$ (where L denotes the length of a repeat unit and n is the number of units per chain) to be about 4 nm. If the PEG layers visible in Figure 6 represent single layers or completely interdigitated bilayers, then each layer should measure ca. 4 nm thick, which agrees favorably with the measured layer thickness reported above.

The average particle sizes listed in Table 2 reveal interesting trends that are directly related to synthesis variables. First, latex particles prepared with a higher macromer concentration possess a smaller diameter, as is seen for latexes LD2-003 and LD5-004. This observation is consistent with the expectation that nucleation begins around the stabilizing chains. An increase in the number of available PEG chains is accompanied by an increase in the number of nucleation sites, resulting in a larger number of particles of smaller diameter.[33] Another explanation for reduced particle size has been offered by Bourgeat-Lami and Guyot.[14] They propose that a larger number of stabilizer molecules can stabilize a large surface area, thereby yielding more particles of smaller size. Second, the particles in latex LD2-004, with a higher initiator concentration (1.0 wt % based on styrene), are larger than those in latex LD2-001 (0.5 wt %). The higher initiator concentration forms more free radicals for polymerization, resulting in more PS chains, but of lower molecular weight.[17,34,35] Since the mechanism of dispersion polymerization requires that

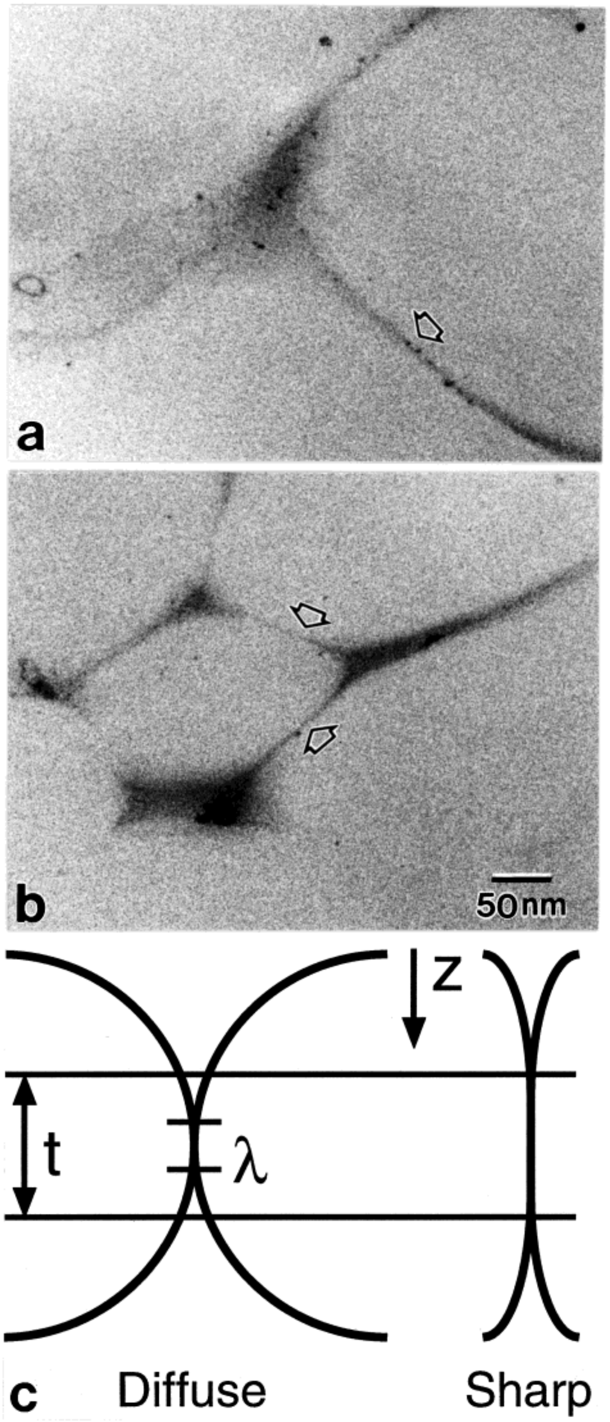

Figure 6. Cross-sectional TEM micrographs (a) and (b) of a melt-pressed film of the latex LD5-006 upon heating for 15 min at 100 °C. The PEG macromer is stained with OsO_4 and appears dark. Note that the PEG forms a contiguous layer and is not dispersed, confirming that the macromer resides primarily on the surfaces of the PS particles. A schematic illustration (c) depicts the geometrical arrangements that could render the images displayed in (a) and (b), where *z* identifies the direction of the electron beam, *t* represents the thickness of a sectioned TEM specimen, and *λ* denotes the length of contact along the *z*-axis between two adjacent particles. Large triangle-shaped features correspond to the intersection of three latex particles and provide no usable information due to the potentially complex geometry associated with such a junction.

the polymer chains reach a critical size prior to nucleation, and since fewer of the chains in the LD2-004 latex attain this size, fewer nucleation sites are available in the LD2-004 latex. Therefore, fewer particles are anticipated to form, but they are larger in diameter.[17,34,35] It should be noted at this juncture that several studies report a slight decrease in latex particle size with increasing initiator concentration.[13,19] Kawaguchi et al.[19] attribute this discrepancy to a difference in the nucleation mechanism in their system of *n*-butyl methacrylate latex particles stabilized with PEG. Third, particle size is not affected significantly by macromer molecular weight, as can be seen by comparing latexes LD2-001 and LD5-003, which possess similar macromer concentrations (mol %) and differ only in macromer molecular weight.

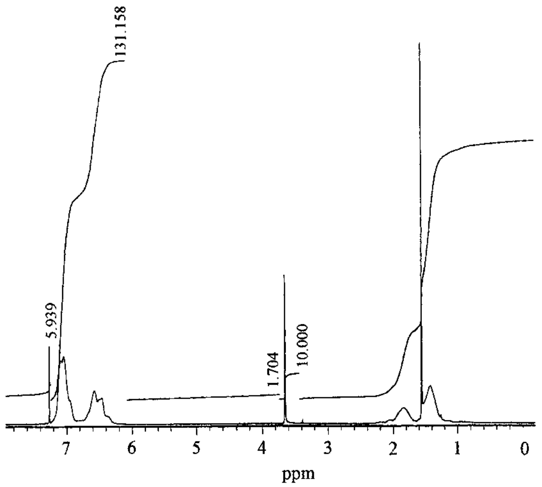

Figure 7. ^{1}H NMR spectrum for latex LD2-001 in which the relative amounts of PS and stabilizer are evident. The two broad peaks between 6 and 7.5 ppm represent the aromatic protons from PS, whereas the narrow peak at 3.6 ppm arises from the methylene protons of PEG. These peaks are used to calculate the graft ratio (eq 1).

In addition to microscopy, two other methods were used to verify PEG grafting. GPC measurements were taken on the centrifuged latex supernatant, and there were no low molecular weight peaks present in the chromatograms that would have indicated significant concentrations of ungrafted macromer. Also, spectra acquired from ^{1}H NMR provide verification that the PEG macromers grafted to the latex particles.[14,22] A typical spectrum is presented in Figure 7, in which chemical shifts are reported in terms of parts per million (ppm) downfield from tetramethylsilane. The two broad peaks located between 6 and 7.5 ppm primarily represent the aromatic protons of PS (and a negligible amount from the isocyanate). (We believe that the signals are broadened by the variation of locations of the protons around the aromatic ring.) The narrow peak at 3.6 ppm arises from the methylene protons of PEG.[36] Integration and normalization of the aromatic and the methylene peaks yield the graft ratio (GR), which is the total ratio of PEG chains to styrene units in the latex particles as calculated from

$$\mathrm{GR} = \frac{\text{5 protons per styrene unit}}{\text{area under styrene proton peaks}} \times \frac{\text{area under EO proton peak}}{\text{4 protons per EO unit}} \times \frac{1}{n_{\mathrm{EO}}} \quad (1)$$

where n_{EO} is the number of ethylene oxide (EO) units per PEG chain—49 for MPEG2000 and 124 for MPEG5000—on the basis of GPC data. Figure 8 shows GR as a function of the concentration of stabilizer

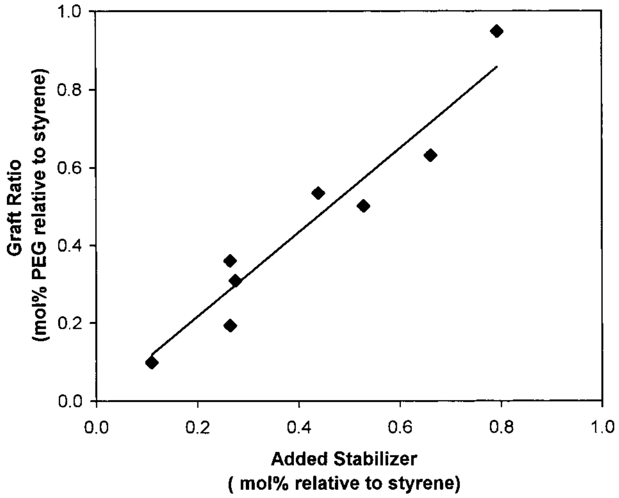

Figure 8. Graft ratio (calculated from ^{1}H NMR data) presented as a function of stabilizer concentration at the onset of the dispersion polymerization. Latexes depicted here employ the MPEG2000 and MPEG5000 macromers. The solid line is a linear fit to all the data.

available to react during the dispersion polymerization. Data collected for the MPEG2000 and the MPEG5000 macromers are included in this figure, which indicates a direct (one-to-one) correlation between stabilizer concentration and GR, even at high stabilizer amounts. This correlation implies that sufficient particle surface is available to accommodate grafting of all the PEG stabilizer. In addition, the absence of vinyl proton peaks that are present between 5 and 6 ppm in the ^{1}H NMR data for the ungrafted macromer (data not shown) supports the implication that no ungrafted macromer remains. Therefore, on the basis of evidence from GPC, ^{1}H NMR, and TEM, we reasonably conclude that most, if not all, of the available PEG macromer is grafted to the PS particles and that the grafting occurs on the particle surfaces. Surface grafting is expected from the dispersion polymerization, since the majority of the hydrophilic PEG chains will tend to migrate to the outer surface of the PS particles to remain in contact with the aqueous dispersion medium.[37]

Numerous studies have synthesized and characterized polymer latexes with a stabilizing layer and have termed the latexes as sterically stable without providing sufficient evidence to support claims of stability.[12-14,22] In the case of the present latex systems, we have employed steady shear rheological measurements to determine stability by analyzing the effect of stabilizer concentration on steady shear viscosity. (Additional steady shear and dynamic rheological analyses of these latexes are detailed elsewhere.[38,39]) The steady shear rate ($\dot{\gamma}$) is measured as a function of shear stress (τ) and the calculated steady shear viscosity (η), and the dependence of η on τ is shown in Figure 9 for two latexes (LD5-003 and LD5-006) at the same particle weight fraction (0.38) but with different macromer concentrations. Particle weight fractions are determined by gravimetric analysis of the latex before and after drying. Both latexes have been stabilized using the MPEG5000 macromer, but LD5-006 possesses 100% more stabilizer than LD5-003 (see Table 1).

Since latex LD5-003 consequently has a lower concentration of MPEG5000 macromer, the surface coverage of PS particles by the stabilizing chains is, most likely, incomplete. (Although at a given bulk stabilizer concentration, particle surface coverage depends on particle size, particle diameter variations must be well over 150 nm before surface coverage is affected sufficiently to exhibit any rheological effects.[40] All latexes synthesized for this study have average particle diameters between 285 and 377 nm.) Therefore, the attractive van der Waals forces of the PS particles of latex LD5-003 are not completely shielded, allowing for small particle clusters, or flocs, to form and impede flow, especially at low shear stresses. The formation of flocs results in a yield stress, which is identified by a significant and abrupt reduction in viscosity as shear stress increases beyond a critical stress (τ_c).[41] At $\tau > \tau_c$, the applied stress either aligns or disperses the flocs to allow unimpeded flow,[42] which appears in Figure 9 to occur in the LD5-003 latex at τ beyond 10 Pa. Latex LD5-006, on the other hand, exhibits Newtonian behavior, in which viscosity is independent of shear stress over the entire τ range examined. The stress-independent behavior of this latex, in contrast to that of the LD5-003 latex, is due to the higher surface coverage by the stabilizer, which effectively prevents flocculation through the steric effects described previously.[2] Latexes stabilized with the MPEG2000 macromer show equivalent flow behavior dependence on surface coverage, indicating that, with appropriate surface coverage, either macromer can provide adequate stability. While Newtonian behavior may be ideal for certain types of coatings, other applications may require the yield stress characteristics of a slightly flocculated system. These rheological results demonstrate that flow behavior can be tuned by changing the system stability, as expressed in terms of graft ratio.

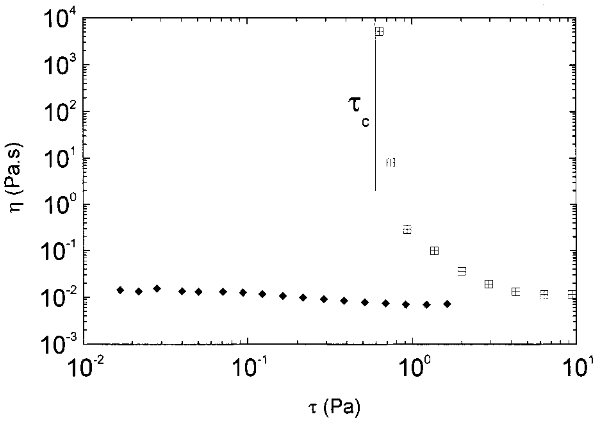

Figure 9. Dependence of steady shear viscosity (η) on shear stress (τ) for latexes LD5-003 (open squares) and LD5-006 (filled diamonds), which differ in graft ratio (see Table 1). Particle flocculation in the LD5-003 latex is due to incomplete surface coverage and promotes a yield stress (τ_c) in the vicinity of 0.6 Pa (vertical line). The LD5-006 latex has a higher graft ratio and exhibits Newtonian behavior. Each latex is measured at a particle weight fraction of 0.38.

As has been indicated earlier, one of the advantages of sterically stabilized latex systems is that they allow for more concentrated stable dispersions when compared with electrostatically stabilized systems. This is illustrated in Figure 10, which compares the high shear viscosity (η_∞) as a function of particle weight fraction (ϕ_w) for a sterically stabilized latex LD2-001 with that of a representative electrostatically stabilized PS latex. The latter, which has been prepared by the surfactant-free emulsion polymerization method of Goodwin et al.,[43] results in a latex stabilized with charged sulfate and chloride groups. The data demonstrate the signifi-

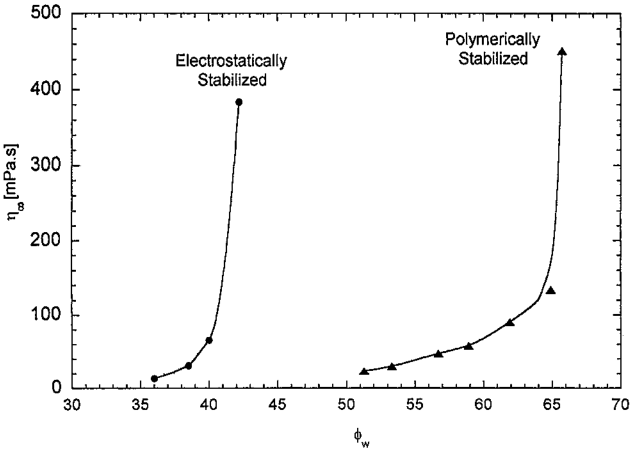

Figure 10. Comparison of the high shear plateau viscosity (η_∞) as a function of particle weight fraction (ϕ_w) of a polymerically stabilized latex system with that of an electrostatically stabilized latex system.

cant difference in the maximum packing fractions of each system: 0.65 for the sterically stabilized system and only 0.42 for the electrostatically stabilized system. The shorter-ranged steric interactions of our system enable more latex particles to pack into the same dispersion volume while maintaining a low viscosity relative to the electrostatically stabilized system. Such high-solids, low-viscosity sterically stabilized systems have strong potential for coating applications where a minimal water content is desired.[38]

Conclusions

A variety of polymer latexes that are sterically stable in a water-based medium have been successfully synthesized. Steric stabilization is achieved through the use of a chemically grafted PEG macromer end-capped with an unsaturated isocyanate. This unsaturated terminus enables in situ grafting of the macromer to the surfaces of PS latex particles as they form during dispersion polymerization. We have shown that the graft ratio could be determined a priori from the macromer concentration at the start of the polymerization. The latex particles exhibit a relatively narrow size distribution, and the average particle size is found to (i) decrease with increasing macromer concentration and (ii) increase with increasing initiator concentration. Electron microscopy images of films produced from the PS latexes verify that the stabilizing layer is present on the particle surfaces. Rheological analyses reveal that stability, and thus flow properties, can be judiciously tailored to a particular application by adjusting the stabilizer graft ratio.

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References and Notes

(1) Barrett, K. E. J. In *Dispersion Polymerization in Organic Media*; Barrett, K. E. J., Ed.; John Wiley and Sons: New York, 1975; p 1.
(2) Napper, D. H. *J. Colloid Interface Sci.* **1977**, *58*, 390.
(3) Hunter, R. J. *Foundations of Colloid Science*; Oxford University Press: New York, 1987; Vol. 1.
(4) Buscall, R.; Ottewill, R. H. In *Polymer Colloids*; Buscall, R., Corner, T., Stageman, J. F., Eds.; Elsevier Applied Science Publishers: New York, 1985; p 141.
(5) Ottewill, R. H.; Satgurunathan, R.; Waite, F. A.; Westby, M. J. *Br. Polym. J.* **1987**, *19*, 435.
(6) Walbridge, D. J. In *Dispersion Polymerization in Organic Media*; Barrett, K. E. J., Ed.; John Wiley and Sons: New York, 1975; p 45.
(7) Bromley, C. W. A. *Colloids Surf.* **1986**, *17*, 1.
(8) Ottewill, R. H.; Satgurunathan, R. *Colloid Polym. Sci.* **1988**, *266*, 547.
(9) Prestidge, C.; Tadros, T. F. *J. Colloid Interface Sci.* **1988**, *124*, 660.
(10) Liang, W.; Tadros, T. F.; Luckham, P. F. *J. Colloid Interface Sci.* **1992**, *153*, 131.
(11) Wesslen, B.; Wesslen, K. B. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3915.
(12) Furuhashi, H.; Kawaguchi, S.; Itsuno, S.; Ito, K. *Colloid Polym. Sci.* **1991**, *275*, 227.
(13) Liu, J.; Gan, L. M.; Chew, C. H.; Quek, C. H.; Gong, H.; Gan, L. H. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3575.
(14) Bourgeat-Lami, E.; Guyot, A. *Colloid Polym. Sci.* **1991**, *275*, 716.
(15) Odian, G. *Principles of Polymerization*; John Wiley and Sons: New York, 1991.
(16) Barrett, K. E. J.; Thomas, H. R. In *Dispersion Polymerization in Organic Media*; Barrett, K. E. J., Ed.; John Wiley and Sons: New York, 1975; p 115.
(17) Paine, A. J.; Luymes, W.; McNulty, J. *Macromolecules* **1990**, *23*, 3104.
(18) Paine, A. J. *Macromolecules* **1990**, *23*, 3109.
(19) Kawaguchi, S.; Winnik, M. A.; Ito, K. *Macromolecules* **1995**, *28*, 1159.
(20) Hansen, F. K.; Ugelstad, J. *J. Polym. Sci., Polym. Chem.* **1978**, *16*, 1953.
(21) Capek, I.; Riza, M.; Akashi, M. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3131.
(22) Liu, J.; Chew, C. H.; Wong, S. Y.; Gan, L. M.; Lin, J.; Tan, K. L. *Polymer* **1998**, *39*, 283.
(23) Thompson, M. W. In *Polymer Colloids*; Buscall, R., Corner, T., Stageman, J. F., Eds.; Elsevier Applied Science Publishers: New York, 1985; p 1.
(24) Barton, J.; Capek, I. *Radical Polymerization in Disperse Systems*; Ellis Horwood: New York, 1994.
(25) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989.
(26) Choi, G. N.; Krieger, I. M. *J. Colloid Interface Sci.* **1986**, *113*, 94.
(27) Haq, Z.; Thompson, L. *Colloid Polym. Sci.* **1982**, *260*, 212.
(28) Dan, N.; Tirrell, M. *Macromolecules* **1992**, *25*, 2890.
(29) de Gennes, P. G. *Adv. Colloid Interface Sci.* **1987**, *27*, 189.
(30) Lin, E. K.; Gast, A. P. *Macromolecules* **1996**, *29*, 390.
(31) Garvey, M. J.; Tadros, T. F.; Vincent, B. *J. Colloid Interface Sci.* **1976**, *55*, 440.
(32) Garvey, M. J.; Tadros, T. F.; Vincent, B. *J. Colloid Interface Sci.* **1974**, *49*, 57.
(33) Tuncel, A.; Kahraman, R.; Piskin, E. *J. Appl. Polym. Sci.* **1993**, *50*, 303.
(34) Tuncel, A.; Kahraman, R.; Piskin, E. *J. Appl. Polym. Sci.* **1994**, *51*, 1485.
(35) Kobayashi, S.; Uyama, H.; Choi, J. H.; Matsumoto, Y. *Polym. Int.* **1993**, *30*, 265.
(36) Szymanski, H. A.; Yelin, R. E. *NMR Band Handbook*; IFI/Plenum: New York, 1968.
(37) Kawaguchi, S.; Winnik, M. A.; Ito, K. *Macromolecules* **1996**, *29*, 4465.
(38) Shay, J. S.; English, R. J.; Khan, S. A. *Polym. Eng. Sci.* **2000**, *40*, 1469.
(39) Shay, J. S. Ph.D. Thesis, North Carolina State University, 1999.
(40) Chow, M. K.; Zukoski, C. F. *J. Rheol.* **1995**, *39*, 33.
(41) Barnes, H. A.; Hutton, J. F.; Walters, K. *An Introduction to Rheology*; Elsevier: New York, 1989.
(42) Macosko, C. W. *Rheology: Principles, Measurements, and Applications*; VCH Publishers: New York, 1994.
(43) Goodwin, J. W.; Hearn, J.; Ho, C. C.; Ottewill, R. H. *Colloids Polym. Sci.* **1974**, *252*, 464.

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