Macromolecules **2002,** *35,* 4247−4257

Synthesis and Characterization of Polymer Brushes of Poly(*N*,*N*-dimethylacrylamide) from Polystyrene Latex by Aqueous Atom Transfer Radical Polymerization

K. N. Jayachandran,[†] Aniko Takacs-Cox,[†] and Donald E. Brooks*,[†,‡]

Department of Pathology and Laboratory Medicine and Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 2B5

Received September 20, 2001; Revised Manuscript Received March 14, 2002

ABSTRACT: Negatively charged polystyrene latex was synthesized, and a copolymer shell of 2-(methyl-2′-chloropropionato)ethyl acrylate (HEA-Cl) and styrene was added, from which poly(*N*,*N*-dimethylacrylamide) (PDMA) was polymerized by atom transfer radical polymerization in aqueous suspension at room temperature. Increasing monomer concentration in the presence of CuCl or CuBr and one of three ligands (*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), and tris[2-(dimethylamino)ethyl]amine (Me_6TREN)) produced grafts whose molecular weight increased to over 600 000 and polydispersities in the range of 1.3−1.8, determined from chains recovered following cleavage by base. Hydrodynamic brush thicknesses were 70−800 nm, and average chain separations, calculated from M_n and the mass of polymer recovered per particle, varied from 4.0 to 1.1 nm. Very high grafting densities were achieved with good molecular weight control, the highest densities yet reported for high molecular weight polymer chains grown from a surface. Control of the polymerization was improved by addition of Cu(II) to enhance deactivation of free radicals, by including a low concentration of exogenous hydrophobic initiator at high monomer concentration and by reducing latex concentration. Increasing the concentration of exogenous initiator reduced graft thickness but eliminated control over the polydispersity. The unusual conditions required for optimization of the reaction and the observation of decreasing chain separation as M_n increased were explained by invoking a model of the particle surface that took into account the finite depth and high copolymer concentration of the region in which chains were initiated and particularly the fixed charges due to the sulfate initiator of shell copolymerization.

Introduction

Control of the surface properties of solid materials is central to many areas of research and numerous commercially important technologies, ranging from biotechnology and biomaterials to advanced microelectronics.[1,2] Grafting polymer chains with single points of attachment at one end to a surface can produce “polymer brushes”, chains of which are extended by virtue of being separated by less than their unconstrained diameter. These provide one intriguing method of providing such control.[3−5] Originally, polymer brushes were prepared by the adsorption of a block copolymer to the surface, but the noncovalent nature of the grafting made this a risky strategy.[6,7] Other methods include the “grafting to” technique,[3,8] in which preformed polymer chains in solution are tethered to the surface. This method does not allow high-density brushes to be formed, in general, due to the exclusion of chains as the graft density grows. However, the molecular weight distribution can be excellent since polymer fractions with narrow molecular weight distributions can be used. The other approach, in principle more versatile, is the “grafting from” technique,[9−29] in which polymerization is initiated from initiators coupled covalently to the surface. One should be able to grow very high-density polymer brushes on a substrate using the latter method, if proper conditions are employed.

The characteristics of polymer brushes have been analyzed using a variety of theoretical and experimental methods that are now fairly well established.[30−32] The brush height and grafting density are two important parameters controlling the polymer brush properties.[32] To precisely manipulate the surface properties, one needs to control the grafting density, molecular weight, and brush height.

Several methods have been used to grow polymer chains from a surface, including radical,[10−12] anionic,[13] cationic,[14−16] ring-opening,[17] ring-opening metathesis,[18,19] and atom transfer radical polymerization (ATRP).[20−29] The use of controlled/living polymerization for surface polymerization should be optimal because such methods afford good control over the molecular weight, molecular weight distributions, and structure of the resulting polymer.[33] Atom transfer radical polymerization in organic systems tolerates a variety of reaction conditions and monomers and has been reported for a number of surfaces. Recently, there has been growing interest in aqueous ATRP[29,34,35] which is able to produce water-soluble polymers at room temperature. Its attraction lies in its simplicity, robustness, its ability to produce narrowly distributed polymer chains, and the possibility of synthesizing controlled block copolymers. Aqueous ATRP is difficult to apply successfully to surface grafting reactions, however. Standard conditions used successfully in ATRP solution reactions do not provide good control over polymerization from flat surfaces or large silica particles.[21,24,27,28] The lack of control is evidenced by a large increase in graft thickness over a short time and poor initiating

---

[†] Department of Pathology and Laboratory Medicine.

[‡] Department of Chemistry.

* Address to which correspondence should be addressed: phone (604) 822-7081; Fax (604) 822-7635; e-mail don@pathology.ubc.ca.

10.1021/ma011651y CCC: $22.00

efficiency. Usually addition of a deactivator or free external initiator is used to control the polymerization.

The chemistry of grafting from latex particles is a relatively new but developing area.[36−40] Conventional radical polymerization is inefficient in this application due to unwanted radical coupling or disproportionation, chain termination that occurs at diffusion-controlled rates, and difficulty in controlling film thickness and grafting density. The alternative technique of ATRP ought to allow for more precise manipulation of surface properties of grafted latex particles. The well-known benefits of ATRP—the protected growing ends and the low and stationary concentration of growing radicals maintained by fast dynamic equilibrium between the active and dormant species—should allow much better control of the polymerization.

The present report describes a detailed investigation of the grafting of poly(*N*,*N*-dimethylacrylamide) from negatively charged polystyrene latex to which a copolymer shell of styrene and ATRP initiator has been added. A variety of ligands and reaction conditions are explored. The results define conditions for grafting of well-controlled brushes of unprecedented molecular weight and chain density. We also provide a model that emphasizes the role of the surface properties of the particle in determining the characteristics of the reactions observed, particularly the role played by electrostatic interactions between the surface and the ligand/catalyst complexes that control polymerization.

Experimental Section

All commercial reagents were purchased from Aldrich and used without further purification. Analytical TLC was performed on commercial Whatman flexible plates coated with 250 μm thick silica gel. Styrene (Aldrich, 99%) was first washed with a 1% NaOH solution and then distilled under reduced pressure. *N*,*N*-Dimethylacrylamide (DMA) (Aldrich, 99%)was purified by vacuum distillation and stored under argon at −80 °C until use. Three ligands, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (Aldrich, 97%), and tris[2-(dimethylamino)ethyl]amine (Me_6-TREN), prepared by one-step synthesis[41] from tris(2-aminoethyl)amine (Aldrich, 96%) were used. Methyl 2-bromopropionate (Aldrich, 98%) and methyl 2-chloropropionate (Aldrich, 97%) were used as external initiators. Once distilled water was further purified using a Milli-Q Plus water purification system (Millipore Corp., Bedford, MA). Nuclear magnetic resonance was performed on a Bruker Avance 300 NMR spectrometer using deuterated solvents ($CDCl_3$, Cambridge Isotope Laboratories, 99.8% D) with the solvent peak as a reference. Reverse-phase HPLC analysis was done on a Hitachi model L-6210 HPLC fitted with a L-4200 UV−vis detector and a Lichrospher 60 RP-select B reverse-phase column from Merck, at $\lambda = 235$ nm using aqueous 0.1% trifluoroacetic acid (TFA) solution as the mobile phase at a flow rate of 4 mL/min at 22 ^{o}C. Gel permeation chromatography (GPC) for molecular weight determinations was carried out on a Waters 2690 separation module fitted with a DAWN EOS multiangle laser light scattering detector from Wyatt Technology Corp. with 18 detectors placed at different angles (laser wavelength $\lambda =$ 690 nm) and a refractive index detector from Viscotek Corp. operated at $\lambda = 620$ nm. Aqueous 0.1 N $NaNO_3$ solution was used as the mobile phase at a flow rate of 0.8 mL/min. Aliquots of 200 μL of the polymer solution were injected through Ultrahydrogel columns at 22 °C (guard column, Ultrahydrogel linear with bead size 6−13 μm, elution range 10^3−5×10^6 Da and Ultrahydrogel 120 with bead size 6 μm, elution range 150−5×10^3 Da connected in series; from Waters). Particle size measurements (i.e., measurements of the hydrodynamic diameter distribution of particle suspensions) were carried out on a Beckman Coulter N4 Plus particle size analyzer. Dispersed particles were allowed to thermally equilibrate for 5 min and then measurements taken at 20 °C. Analyses were performed using the software supplied by the manufacturer. UV−vis spectra were recorded on a Hewlett-Packard 8450A UV/vis spectrometer at 22 °C.

Synthesis of 2-(Methyl 2′-chloropropionato)ethyl Acrylate (HEA-Cl). The 2-chloropropionyl chloride (0.1968 mol, Aldrich, 97%,) and triethylamine (Fisher, 99%, 0.2140 mol) were added dropwise to the cold solution of 2-hydroxyethyl acrylate (0.1789 mol, Aldrich, 96%) in DCM at 0 °C over a period of 2 h. The reaction was continued at 0 °C for 4 h and left overnight at room temperature. The formation of the product was monitored by TLC. The precipitated triethylamine hydrochloride was filtered. The reaction mixture was washed successively with 0.1 N HCl, saturated sodium bicarbonate solution, and distilled water. The organic layer was dried over anhydrous sodium sulfate, and the solvent was evaporated in a rotary evaporator. The product was vacuum distilled (yield 71%) and characterized by ^{1}H NMR ($CDCl_3$). $C\mathbf{H}_3{-}CHCl{-}$ $\delta = 1.95$ (d, 3H), $CH_3{-}C\mathbf{H}Cl{-}$, $\delta = 4.15{-}4.3$ (m, 1H), $-O-C\mathbf{H}_2-C\mathbf{H}_2-O-$ $\delta = 4.2$ (s, 4H), $C\mathbf{H}_2{=}CH{-}$ $\delta = 5.95$ (d, 1H), $CH_2{=}C\mathbf{H}{-}$ $\delta = 6.05$ (t, 1H), $C\mathbf{H}_2{=}CH{-}$ $\delta = 6.2$ (d, 1H).

Synthesis of Water-Soluble Initiator (2-Hydroxyethyl 2′-Bromopropionate). The 2-bromopropionyl bromide (0.2316 mol, Aldrich, 97%) was added dropwise to a cold solution of ethylene glycol (5.47 mol, Aldrich, anhydrous) and triethylamine (0.2342 mol, Fisher, 99%) at 0 °C for a period of 2 h. The reaction was continued at 0 °C for another 2 h and then heated to 40 °C for 5 h. The reaction mixture was cooled, added to 500 mL of water, and extracted with chloroform three times, and then the chloroform layer was washed successively with dilute HCl, saturated $NaHCO_3$, and water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to provide the product. The product was vacuum-distilled (yield 81%) and characterized by ^{1}H NMR ($CDCl_3$): $C\mathbf{H}_3{-}CHBr{-}$ $\delta = 1.95$ (d, 3H), $-CH_2-C\mathbf{H}_2-OH$ δ −3.95 (t, 2H), $-C\mathbf{H}_2-CH_2-OH$ δ −4.15 (t, 2H), $CH_3{-}C\mathbf{H}Br{-}$ δ −4.17−4.25 (m, 1H).

Polystyrene Seed Latex. Narrow, dispersed polystyrene (PS) seed latex was synthesized by surfactant-free polymerization of styrene (0.333 mol), water (720 g), NaCl (0.870 g), and potassium persulfate (KPS) (0.002 mol) at 70 °C for 24 h under an argon atmosphere. A stirring rate of 350 rpm was used for the experiment. The latex suspension was cleaned by dialysis (1 week) against distilled water with daily changes and repeated centrifugation (5 times) and serum replacement. The solid content of the suspension was determined by freeze-drying. The hydrodynamic particle diameter was 551 nm as determined using the particle size analyzer.

Shell Growth Polymerization: Synthesis of ATRP Initiator Layer. A suspension of PS latex particles (3.33 wt %, 155 g) was heated to 70 °C with stirring at 350 rpm, degassed, and purged with argon. Styrene (25.3 mmol) and HEA-Cl (8.5 mmol) were added successively to the suspension in a 10 min interval. The initiator solution (0.37 mmol of KPS in 20 mL of water, degassed) was added after 5 min. The reaction was continued for 6 h, and the latex was cleaned by dialysis against water for 1 week and five cycles of centrifugation and resuspension. The solid content was determined by freeze-drying.

The surface initiator concentration was calculated from a conductometric titration of saponified latex as follows.[36] The latex (2 g) was stirred with 1 mL of 2 N NaOH for 36 h at room temperature. The suspension was multiply centrifuged, the pellet was resuspended in distilled water acidified with 0.1 N HCl, and the centrifugation and redispersion were continued until the pH was 7.0. Conductometric titration with 0.04 N NaOH (standardized using potassium hydrogen phthalate) gave total negative charge on the surface, the sum of the sulfate surface charge and the carboxyl groups produced from hydrolysis of the initiator. The surface charge of the latex was determined from the conductometric titration of unhydrolyzed latex; the difference between the two values gave the surface concentration of the initiator. The surface concentration of the initiator was 1.72×10^{-5} mol/g or 2.01×10^{-6} mol/m^2 (specific area = 8.568 m^2/g) of the latex, implying ~9 Å apparent separation between the initiator sites, assuming they were arranged in a two-dimensional square lattice; the titrated negative surface charge concentration unhydrolyzed was 0.275×10^{-5} mol/g or 3.2×10^{-7} mol/m^2 of latex. Particle size measurement showed an increment of 118 nm (from 551 to 669 nm) in diameter for the latex carrying the shell compared to the original latex and a narrow size distribution. A concentration calculation from ^1H NMR spectra (freeze-dried sample dissolved in $CDCl_3$) showed the amount of initiator present in the shell was much greater than the number of molecules accessible to conductometric titration (the value from ^1H NMR was 6.74×10^{-4} mol/g of the latex) and was comparable to the amount of HEA-Cl polymerized in the reaction.

Atom Transfer Radical Polymerization from Latex. *General Method for Grafting of Poly(N,N-dimethylacrylamide).* All the reactions were performed in a glovebox filled with argon due to the sensitivity of the Cu(I) complex to air. A suspension of latex (22 g) carrying the ATRP initiator layer was degassed for 2.5 h by continuous vacuum and argon cycles and transferred to the glovebox. Brij-35 (nonionic surfactant) (0.035 g, 0.16 wt %) was added to the suspension and stirred for 5 min. (Reactions without the addition of the surfactant produced initial latex aggregation that was not reversed upon grafting of large amounts of polymer.) For most reactions (unless otherwise stated) we used CuX (X = Br, Cl) and ligand at 9 times the titratable surface initiator molar content (determined by conductometric titration as described above), CuX_2 (X = Br or Cl) at 15 mol % of Cu(I), and Cu powder at 8 times the Cu(II) concentration (all are in mole ratio). For a typical reaction, DMA (2 mmol) was stirred with HMTETA (19 μmol), CuCl (16 μmol), $CuCl_2$ (2.4 μmol), and Cu powder (19 μmol) for 3 min to form a solution; 3.5 g of Brij-35 stabilized shell latex (3.0 wt %) was added to this under stirring at room temperature (22 °C). The reaction was continued for 12 h and monomer conversion determined by analyzing the supernatant solution by reverse-phase HPLC. The grafted latex was cleaned by repeated sequential centrifugation and resuspension in water, $NaHSO_3$ solution (50 mmol), and water to remove adsorbed copper complexes for 8−10 cycles until there was no detectable amount of polymer/monomer/catalyst in the supernatant.

Grafting Reactions Varying Monomer Concentration, Ligands, and Copper Salts. Three ligands, PMDETA, HMTETA, and Me_6TREN, were used for ATRP grafting reactions. A latex suspension (3.5 g, 3 wt %) was added to a stirred solution of monomer/catalyst (Cu(I)X/CuX_2/ligand; X = Cl or Br) at room temperature; Cu(I)X:ligand was at a 1:2 mole ratio for PMDETA and 1:1 mole ratio for HMTETA and Me_6TREN. Monomer concentration was varied from 1.47% to 10.29 wt %. The remaining procedures and other reaction conditions were applied following the general reaction scheme described above. In the case of the external initiator addition, the free initiators were added to the latex before addition to the monomer/catalyst solution. Increments in the addition of Cu(II) were done by adding the calculated amount of $CuCl_2$ to the monomer/catalyst solution at the beginning of the reaction. Latex concentration was changed by changing the solid content of the latex suspension.

Analysis of the Grafted Latex. The grafted latex was characterized by hydrodynamic size measurements utilizing the particle size analyzer and by analysis of the polymer released by hydrolysis. Characterization of the polymer chains (molecular weight, molecular weight distribution, mass of the grafted chains per unit area of latex, and radius of gyration, R_g) grown from the PS surface was performed by cleaving off the chains as follows. A known amount of grafted latex (2 g) was stirred with 1 mL of 2 N NaOH (final concentration ~ 0.7 mol/L) until no change in the amount released was detected (2 weeks). The supernatant and the washings were collected and analyzed by GPC. The value of dn/dc of the PDMA in the mobile phase calculated at 620 nm was 0.150 mL/g and was used for determining molecular weight parameters. Aliquots of 200 μL of the polymer solution were injected through the two Ultrahydrogel columns at 22 °C. The mass of polymer in the cleaved solution was determined using a calibrated RI detector and confirmed by independent absorbance measurements utilizing a PDMA calibration curve at 235 nm (for selected samples). Both approaches agreed to within ±1.5%, with no systematic differences between the methods.

Measurement of Association of the Copper/Ligand Complex with the Latex. A suspension of latex (15 g, 3 wt %) was degassed for 2.5 h by continuous vacuum and argon cycles and transferred to the glovebox. Brij-35 (0.024 g, 0.16 wt %) was added to the suspension and stirred for 5 min. Solutions of the copper(I) complex of different ligands were made in water inside the glovebox and added to 1 g of the latex suspension. A duplicate and control set (no latex) were also done. The suspension was stirred for 5 min and centrifuged. The supernatants were collected, and all samples were taken outside the glovebox and exposed to air for 3 h. The absorbance of the solutions was measured, and concentrations were calculated from calibration curves for each of the complexes. The amount of copper complex associated with the latex surface was calculated from the difference in complex concentration between the control and experimental samples.

Results and Discussion

The PS latex carrying immobilized initiator was stable over time and provided an excellent surface for studies of aqueous grafting reactions by ATRP. We examined a large set of conditions in seeking those that provided good grafts, the selection of which was based initially on those developed for solution ATRP reactions. We found considerable differences in the optimal conditions for polymerization from initiator immobilized on the latex surface.

Following grafting, the volume of the sedimented latex pellets expanded significantly as the monomer concentration was increased, and the apparent particle size increased dramatically. Grafted latex was very difficult to centrifuge for the two highest monomer concentrations studied, as the suspensions were very viscous due to the high particle volume fraction. The increase in particle size is due to grafted chains decreasing the particle diffusion constant, which is interpreted as being caused by a uniform increase in particle diameter. We refer to the difference between the grafted and bare latex diameters as the hydrodynamic thickness (HT) of the grafted layer. Its determination is independent of the molecular properties of the released grafted chains, which are determined by light scattering following chromatography of the cleaved chains.

Figure 1 shows the molecular weight of the grafted polymer as a function of monomer concentration at a latex concentration of 3 wt % for three ligands (HMTETA, PMDETA, and Me_6TREN) with either CuBr or CuCl as the catalyst. The expected M_n increase with monomer concentration at constant initiator concentration is observed for HMTETA and PMDETA, although the molecular weights differ significantly, but not for Me_6TREN systems. There is little dependence on the anion used. Table 1 contains additional data from these experiments, including the measured radius of gyration of the cleaved chains (R_g) and the number of chains per unit area (N_a), calculated from the total mass of graft released per unit area of latex and M_n. Assuming a square lattice of grafted chains the average chain separation (D) is given by $N_a^{-1/2}$. The ratio D/R_g is also given; $D/R_g < 2$ implies adjacent chains interact and extend to form brushes, the more so the smaller the value. Figure 2 gives the polydispersities for the same materials. The Me_6TREN reactions are quite uncon-

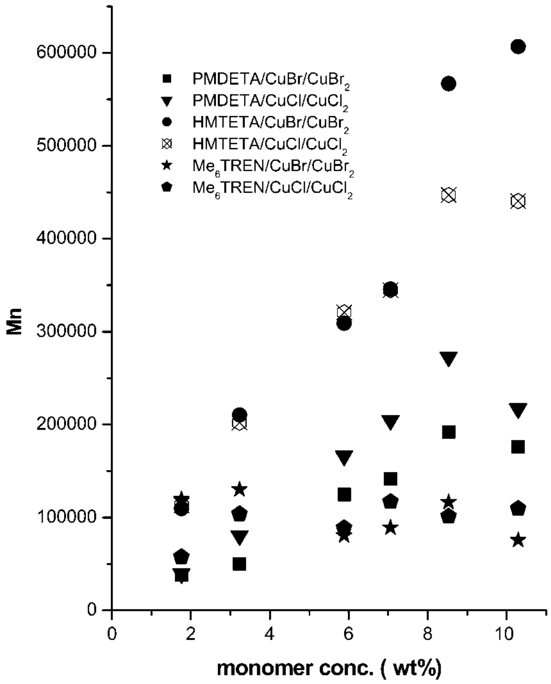


Figure 1. Effect of monomer concentration on molecular weight of the cleaved PDMA from grafted latex measured by GPC-LS. Experimental conditions: 3.5 g of 3 wt % suspension of latex, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA 32 μmol), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA 16 μmol), tris[2-(dimethylamino)ethyl]amine (Me_6-TREN 16 μmol), CuCl/CuBr (16 μmol), $CuCl_2$, $CuBr_2$/HMTETA, PMDETA, Me_6TREN (2.4 μmol), copper powder (19 μmol) at 22 °C. Surface initiator concentration: 1.72×10^{-5} mol/g.

Table 1. Effect of Monomer Concentration on Radius of Gyration (R_g), Distance between the Chains (D), and Number of Moles Chains Grafted per Unit Area[a]

catalyst	monomer concn (wt %)	R_g (nm)	chains grafted (mol/m^2) × 10^7	D/R_g
PMDETA/CuBr/$CuBr_2$	1.47	7.90	1.16	0.478
	2.94	10.0	2.90	0.238
	4.41	14.6	3.35	0.152
	5.88	17.9	6.51	0.089
	8.23	21.2	6.12	0.077
	10.3	21.0	10.9	0.058
HMTETA/CuBr/$CuBr_2$	1.47	13.7	1.55	0.247
	2.94	22.8	1.67	0.132
	4.41	28.7	2.34	0.089
	5.88	30.6	2.32	0.082
	8.23	40.6	2.12	0.066
	10.3	41.9	2.12	0.061
PMDETA/CuCl/$CuCl_2$	1.47	7.00	1.07	0.562
	2.94	12.4	3.2	0.183
	4.41	19.0	3.28	0.118
	5.88	19.8	3.65	0.107
	8.23	23.9	6.92	0.064
	10.3	22.3	13.1	0.050
HMTETA/CuCl/$CuCl_2$	1.47	13.6	1.92	0.214
	2.94	18.6	2.19	0.146
	4.41	25.4	2.55	0.099
	5.88	26.0	2.60	0.096
	8.23	33.5	3.65	0.063
	10.3	32.8	4.48	0.058

[a] Experimental conditions: 3.5 g of 3 wt % suspension of latex: Cu(I)complex (16 μmol), Cu(II) complex (2.4 μmol), Cu powder (19 μmol), reaction temperature 22 °C. Surface initiator concentration = 1.72×10^{-5} mol/g latex.

trolled. The polydispersity index (PDI = M_w/M_n) is reasonably narrow for the other two ligands, however, and use of CuCl rather than CuBr reduces PDI when PMDETA is the ligand but not when HMTETA is utilized. The hydrodynamic thickness values, HT, of the grafted layers produced by ligands HMTETA and PMDETA in the experiments described in the previous figures are provided in Figure 3. Again, there are differences associated with the ligands but little dependence on the Cu(I) anion, consistent with the M_n data.

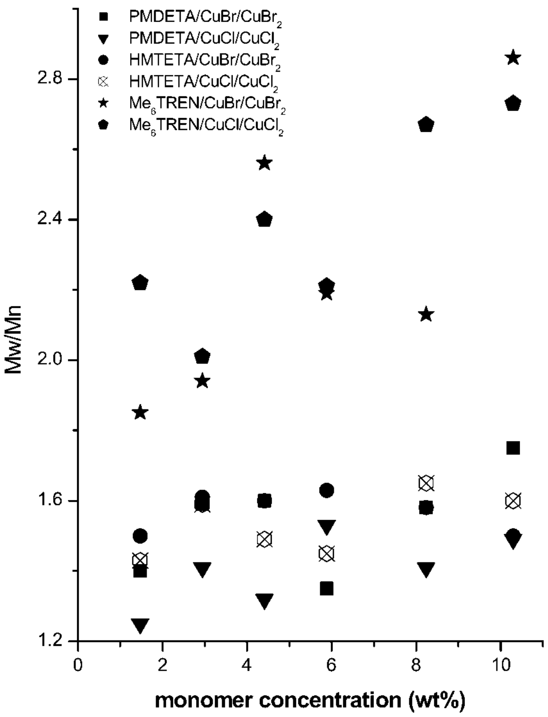


Figure 2. Effect of monomer concentration on the molecular weight distribution of cleaved PDMA grafts by GPC-LS. Samples and experimental conditions as in Figure 1.

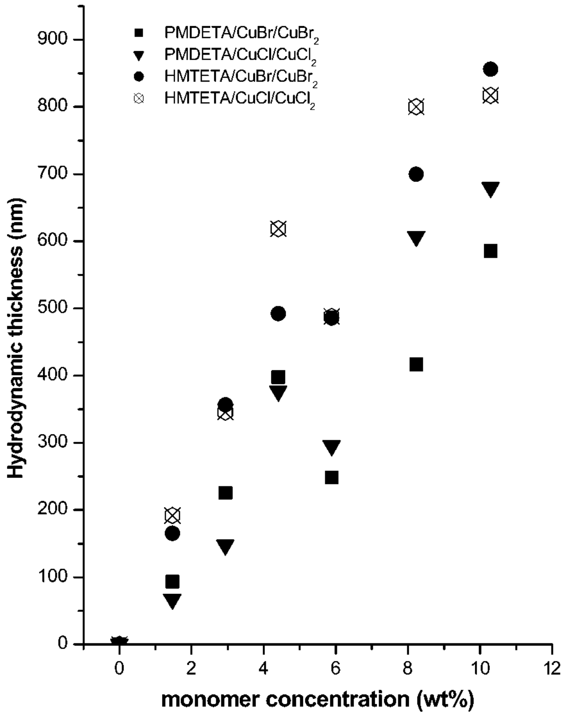


Figure 3. Effect of monomer concentration on hydrodynamic thickness of the grafted polymer latex measured by particle size analysis. Samples and experimental conditions as in Figure 1.

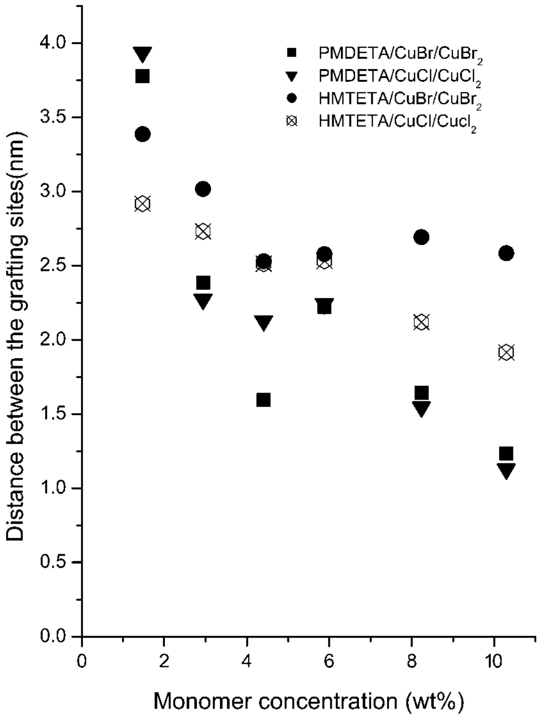


Figure 4. Effect of monomer concentration on distance between the grafting site (D) for the PDMA grafted latex. Samples and experimental conditions as in Figure 1.

The average chain separation distances on the surface (D) are shown in Figure 4. In all cases these decrease with increasing monomer concentration, despite the increases in M_n. The initiation efficiency, calculated as the fraction of titratable initiation sites occupied by chains, was ≤65% for all experiments performed in this study.

The above results show significant differences between the characteristics of the grafting reactions and the results anticipated from solution ATRP chemistry.[42,43] The strong dependence on the nature of the ligand, for instance, is very different for solution reactions with this monomer, where control of the polymerization observed occurs in the order Me6TREN/CuBr > HMTETA/CuBr ~ PMDETA/CuBr, whereas we find HMTETA/CuBr > PMDETA/CuBr > Me6TREN/CuBr for our grafting reactions (Figures 1 and 2). Another striking difference between the grafting and solution reactions is the increase in number of chains grafted per bead as the monomer concentration is increased, whereas the solution reaction would initiate a constant number of chains per unit volume at constant initiator concentration. To explain these differences, we invoke the model illustrated in Figure 5.

Model of the Surface Region. The copolymer shell consists of styrene:HEA-Cl in a feed ratio of 3:1; we expect a random copolymer based on a calculation utilizing reactivity ratios for styrene (R1 = 0.66) and *n*-butyl acrylate (R2 = 0.19), a comonomer structurally related to our initiator at 60 °C,[44] and the number of moles of the styrene and HEA-Cl used. From the microstructure equation we calculated[45] the probability of a diad of the acrylate to be 6.1% and a triad to be 0.4%, while styrene diad, triads, and tetrads have probablilities of 114%, 73%, and 47%, respectively. Hence, it is very likely a random distribution of initiator occurs throughout the copolymer. While the styrene is hydrophobic, the initiator is much more hydrophilic due to the ester oxygens, so the structure of the copolymer should be somewhat open in an aqueous environment. Hence, water-soluble reagents could have access to more than just the surface of the particle, penetrating some distance into the shell. To estimate the degree of penetration, we compare the initiator concentration obtained by titration of the particle in situ, described in the Experimental Section, with that from ^{1}H NMR measurements made on the solubilized particle. The ratio obtained is 0.0255 (titrated surface initiator concentration/total initiator concentration = 1.72×10^{-5} mol g^{-1}/6.74×10^{-4} mol g^{-1}). We assume that the initiator is distributed uniformly throughout the shell, implying that only 2.55% of the shell is accessible to the NaOH solution used in the titration measurement. The total thickness of the shell, determined by comparing the hydrodynamic diameter of the seed particle with the seed carrying the shell, is 59 nm. Hence, assuming a layer with uniform properties accessible to aqueous reagents, its thickness is estimated to be 0.0255 × 59 nm = 1.51 nm or approximately 15 Å.

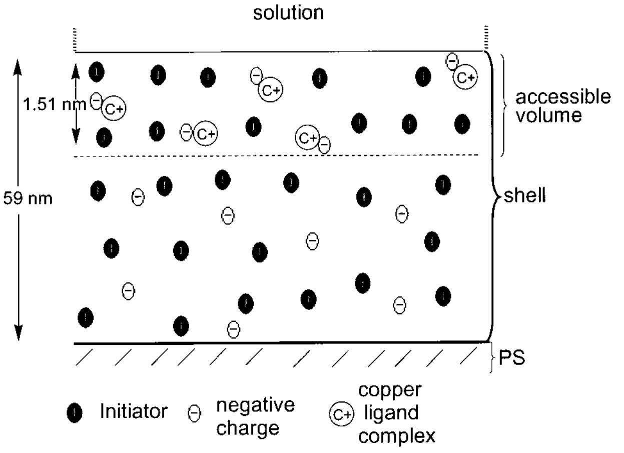


Figure 5. Model of the surface region; not to scale.

From conversion measurements we also know the ratio of the total mass of polymer in the shell to that in the same number of seed particles is 0.545. Knowing the radii of the bead (275 nm) and (bead + shell) (334 nm), the copolymer concentration in the shell is calculated to be 0.73 g/cm^3. Assuming a density of ~1.0 for the copolymer provides a model for the surface region accessible to aqueous reagents as a layer only about 27% water ~15 Å thick containing a very high concentration of chains (~73% concentration). Within this region the ATRP grafting reaction must take place since the monomer and ligand/catalyst complex are water-soluble. Titration of the surface charge before hydrolysis gives the sulfate concentration in the surface region as 2.75×10^{-6} mol/g latex which, when distributed in the surface region, translates to a volumetric concentration of 213 mmol/L negatively charged sulfate groups in this region of the shell. Similarly, the average concentration of surface initiator is calculated to be 1.33 mol/L in this region of the shell.

The amount of complex associated with the particles when they are spun down has been measured as described in the Experimental Section, albeit at a 9-fold lower concentration than used in the grafting chemistry (Table 2). The data implies an increased concentration of ligand is present in the volume of the latex shell accessible to aqueous reagents. In addition, because the ligand/Cu(I) complex is the only cation present, it will

Table 2. Association of Copper Complex with Negatively Charged Latex and Equilibrium Solution Concentration at 22 °C (Measured at ~1:1 Surface Initiator Concentration to Complex Mole Ratio)[a]

complex	surface associated complex concn (mol/m^2) × 10^7	equilib concn (mol/L) × 10^4
PMDETA/CuBr	5.68	367
PMDETA/CuCl	6.37	421
HMTETA/CuBr	6.28	296
HMTETA/CuCl	4.72	195
Me6Tren/CuBr	4.84	401
Me6Tren/CuCl	2.64	392

[a] Thickness of the surface layer is taken as 1.51 nm. Surface concentration of initiator = 1.72×10^{-5} mol/g of latex = 2.01×10^{-6} mol/m^2. The suspension volumes used differed among experiments, which causes the differences among the equilibrium concentrations.

distribute adjacent to the shell out into solution to form the diffuse double layer. The counterions associated with each species will also distribute and contribute to the double layer. The characteristic thickness of this region can be calculated from the ionic strength in the solution; it is the inverse of the Debye−Hückel parameter[46] and has the value for our conditions, assuming a nominal ligand/Cu(I) concentration of 2.7 mmol/L under reaction conditions, of ~75 Å. The cations will not be distributed uniformly; the majority will collect within the surface region to neutralize the fixed surface charges in the copolymer, which have a concentration of 213 mmol/L, the remainder collecting in the double layer. This concentration is much lower than the initiator concentration of 1.33 mol/L within the shell, so the reactions will be carried out under conditions of limiting ligand/Cu(I) concentration, not at the usual 1:1 mole ratio typical of solution reactions.[47] Increasing the bulk ligand/Cu(I) concentration would not change this condition materially because if a concentration higher than the fixed negative charge were to accumulate within the shell, the sign of the net charge would change and the positive ligand complexes would be repelled electrostatically. The only way to alter this would be to change the charge density in the copolymer.

Because the local ligand concentration around the initiators is relatively low, when the reaction starts, not all initiators can react with a ligand/Cu(I) and begin the ATRP process. As an oligomer is formed and extends outside the shell region, it will tend to compete less for ligand retained within the shell, allowing initiation of new chains from previously unreacted initiator. This effect will slow the initiation rate and possibly increase the polydispersity index relative to a pure solution reaction.

Although the ligand complex is at a lower mole ratio with respect to initiator than would be used in solution, its surface concentration is nonetheless strongly concentrated with respect to the solution concentration, which is of the order of 2.7 mmol/L under reaction conditions. This is caused by the fixed negative charge in the surface region of the shell due to the terminal sulfate groups from the initiation of the shell copolymer. Reactions performed on positively charged latex and with varying ionic strength (to be published elsewhere) are consistent with this conclusion. Since all ligand/Cu(I) complexes carry the same charge, the differences in distribution behavior illustrated in Table 7 must be due to secondary interactions between the complexes and the shell, involving properties such as relative hydrophobicity or hydrated size. The small differences between systems containing Br$^-$ and Cl$^-$ as the counterion to the ligand/Cu(I) complex reflect their secondary involvement in the ion distribution and species differences in their interaction with the components of the shell.

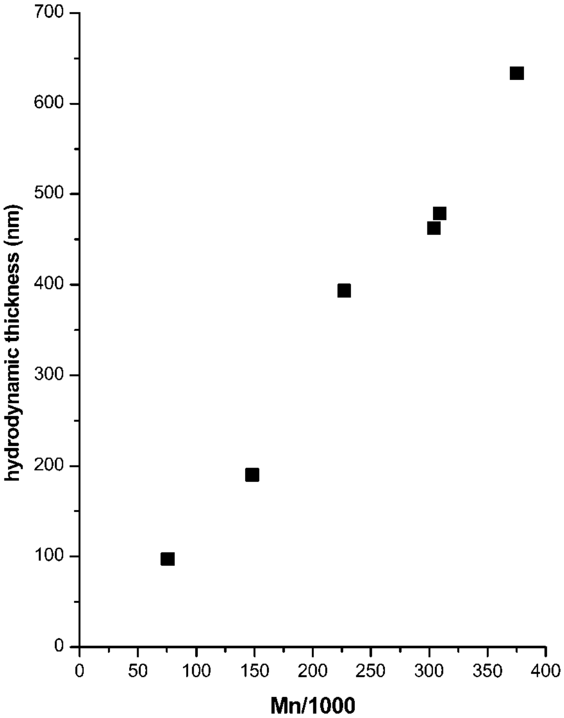
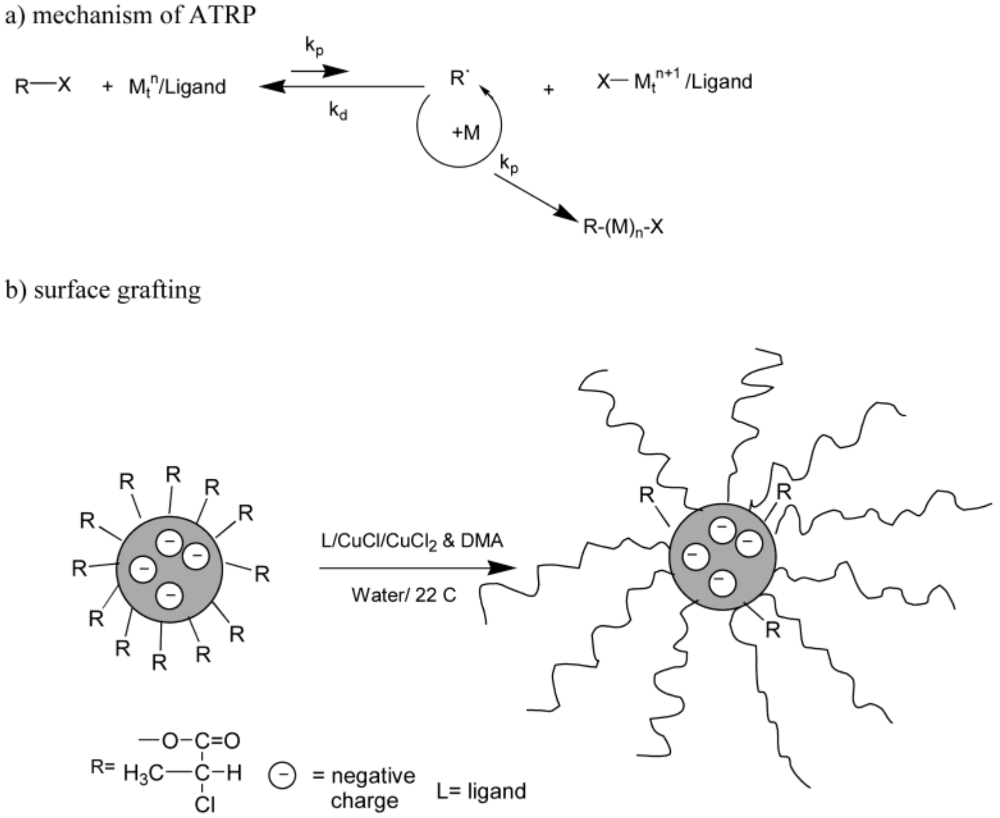


Figure 6. Variation of brush hydrodynamic thickness with molecular weight of the cleaved PDMA from grafted latex measured by GPC-LS at constant monomer concentration (5.9 wt %). Experimental conditions: 3.5 g of 3 wt % suspension of latex; catalyst 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA)/CuCl (16 μmol), copper powder (19 μmol), concentration of HMTETA/CuCl$_2$ complex is varied with respect of HMTETA/CuCl complex at 22 °C. Surface initiator concentration 1.72×10^{-5} mol/g.

Characteristics and Determinants of the Grafted Polymer Layer. Two overall features of the results illustrated are the generally high molecular weights and the high surface concentrations achieved for the grafted layers. The values of D/R_g (Table 1) are in some cases the lowest reported to date, and the M_n values reach values that are higher than those described previously. The chains are very extended, as evidenced by the large values of HT and particularly by the parallel between M_n and HT in many of the systems examined (Figure 6). Hence, the grafts behave as true brushes and are of inherent interest for their potential as a model system for this condition.

There are significant differences between the characteristics of the polymerization reactions in the present system and results obtained by ATRP in solution, due to the presence of the surface, its charge, and the high copolymer concentration present in the volume in which chain initiation takes place. While we do not know the detailed structure of the shell and the initiator distribution present within it, we do know that only a small fraction of the ester groups comprising the initiator are accessible to saponification by NaOH. It could be argued that all of the accessible initiating groups are on the surface of the particle, but the fact that so much remains inaccessible to aqueous reagents makes such stratification unlikely. Hence, it seems likely that the grafted

Scheme 1. Schematic Representation of (a) Mechanism of ATRP and (b) Surface Grafting onto PS Latex



chains are initiated from relatively immobile groups in the interstices between the copolymer chains making up the outer region of the shell. While the copper complex will be maintained at its local concentration by electrostatic effects, monomer must diffuse into this region for chains to grow. This diffusion will likely be hindered by the high copolymer chain concentration around the initiation sites. Yet, if the chain is to grow, this is the only way in which monomer can add to the immobile initiation site. This property is likely to have a strong effect on the nature of the chain initiation reactions that lead to the grafts observed. Moreover, since initiation takes place in such a low solvent fraction, concentration effects of all reactants will be more pronounced.

Once the chains have been initiated and oligomers formed, the growing chains will extend into the bulk solution. Under these conditions further polymerization will take place increasingly like a pure solution reaction as the end of the growing chain becomes more mobile and able to sample a larger volume of solution.

The principal results in Figures 1−4 can be understood qualitatively on the basis of the model described above. The increase in both molecular weight and number of chains initiated per unit area as monomer is increased follows from a picture in which, at low monomer concentration and constant relatively low ligand/Cu(I), formation of free radicals occurs only on a fraction of the initiators on the surface as a result of the activation reaction (Scheme 1). At low monomer concentration, not all of these sites can react rapidly with monomer. Replenishment of the depleted monomer is also slow in the region of chain formation due to impeded diffusion in the surface layer. Hence, transfer of a free radical to either the solvent or potentially to the ligand can occur. For instance, the rate constant for chain transfer to water has been reported as 2×10^{-7} while that to triethylamine is 4×10^{-2}.[44] Since triethylamine is not unrelated to the structure of the ligands used here, such transfer seems possible. Chain transfer to either produces a diffusible species that would diffuse out of the surface layer and undergo the normal ATRP reaction cycle in solution. Ungrafted chains are therefore at their highest concentration under conditions of low monomer concentration (Table 3). The chain transfer must occur early in the polymerization reaction since the molecular weights are higher than the grafted chains, consistent with their initial formation in the surface region. The solution reaction is very poorly controlled, however, and the solution reaction proceeds more rapidly than grafting. As the monomer concentration is increased, the probability of monomer reacting with the free radical on an activated initiator increases, resulting in an increased number of chains grafted and

Table 3. Surface Polymerization and Solution Polymerization[a]

	surface polymerization		solution polymerization	
monomer concn (wt %)	M_n (M_w/M_n)	% polymer grafted to total	M_n (M_w/M_n)	% solution polymerized to total
1.47	39 500 (1.25)	18.0	62 800 (1.74)	82.0
2.94	80 400 (1.41)	45.1	88 500 (2.26)	54.9
4.41	166 000 (1.53)	51.1	224 000 (2.53)	48.9
5.88	205 000 (1.32)	60.0	261 000 (2.31)	39.7
8.23	273 000 (1.41)	ND	504 000 (1.97)	ND[c]
10.3	217 000 (1.49)	ND	714 000 (1.95)	ND

[a] The total amount of polymer formed is calculated from conversion of the monomer and the solution polymerized amount is calculated from the difference between the grafted amount and total. [b] Experimental conditions: 3.5 g of 3 wt % suspension of latex, PMDETA (32 μmol) or CuCl (16 μmol), CuCl$_2$/ PMDETA (2.4 μmol), copper powder (19 μmol) at 22 °C. Surface initiator concentration: 1.72×10^{-5} mol/g. [c] ND = not determined.

a decrease in the number of ungrafted chains formed, as observed.

In a normal solution reaction monomer diffusion is not restricted, and the initiator/ligand/Cu(I) complex, at higher concentration, can diffuse sufficiently that this effect is not seen. The number of chains initiated in solution polymerization is roughly constant with increase in monomer concentration at constant initiator concentration. The molecular weight increases with increased monomer concentration in both cases by the usual mechanism, since the initiator concentration remains constant.

We do not know the reasons for the differences in M_n, HT, and D observed when different ligands are used. Their surface concentrations likely do not differ significantly under reaction conditions, since at a lower concentration there is little difference measured (Table 2), with the exception of the Me$_6$TREN. Also, the concentration is largely controlled by the fixed negative charge in the shell, as discussed above. While the relative reactivity of these ligands is known in bulk polymerization[42,43] of this monomer, we have no data on their behavior in water at room temperature. Hence, the most likely explanation for the differences seen lies in their inherent reactivity under the conditions of low solvent volume fraction and low concentration with respect to initiator used in our experiments.

Control over the molecular weight distribution of the grafts was not particularly good in the reactions illustrated in Figures 1−4. Reactions in the presence of Me$_6$TREN were poorly controlled, PDI reaching ~2.8 at the highest monomer concentrations. This ligand is the most reactive in organic solution polymerization with a fast activation rate and relatively slow deactivation, resulting in poorly controlled polymerization.[42,48] Because of this, and the low graft molecular weights, no further work was done with this ligand. Of the other two ligands, PMDETA gave generally better control than HMTETA, and PDI was lower in the CuCl system than in CuBr. The relative differences among these conditions are not consistent with the ligand surface concentrations measured so other factors must be involved.

In solution and surface ATRP reactions, it has been shown that addition of low concentrations of Cu(II) can increase control of the reaction, reducing PDI.[21,24,42] Addition of Cu(II) deactivates the free radical and reduces the propagation rate. The data in Figure 7 show that as the Cu(II) concentration is increased in our system, the graft M_n decrease strongly, as expected, and that PDI also decreases to <1.4 when the Cu(II):Cu(I) mole ratio exceeds ~0.50. These are much higher concentrations than are used to improve control in solution reactions and surface polymerizations.[21,24,42] In terms of our model, this can be explained by the lower propagation rate reducing the effect of hindered monomer diffusion in the surface region. Cu(II) will be enriched even more than Cu(I) in this region due to its higher positive charge, enhancing deactivation. In the absence of added deactivating agent, local monomer depletion leads to chain transfer to solvent or ligand. The Cu(II) slows the rate at which the chain propagates, allowing more time for monomer diffusion between addition reactions.

The number of chains initiated per unit area, as reflected by the interchain separation D, remains roughly constant as the Cu(II) concentration is increased (Figure 8). For this data set, when the graft thickness, HT, is plotted against M_n, the straight line in Figure 7 results, clearly showing that these grafts are true brushes. Despite their proximity (D ~ 2.5 nm), chains from ~ 75 000 to 375 000 Da grow from the surface initiators, with most of them characterized by PDI ~ 1.4 under the conditions employed.

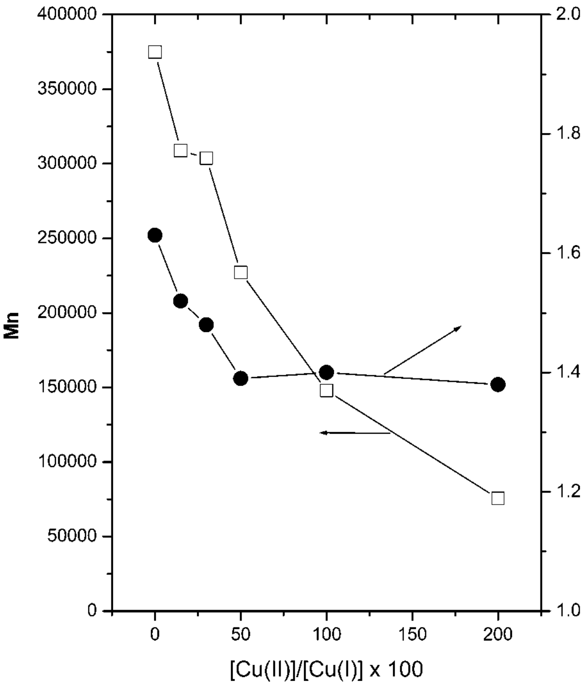


Figure 7. Effect of concentrated of CuCl$_2$ on the molecular weight and polydispersity of the cleaved PDMA from grafted latex measured by GPC-LS. Experimental conditions are as in Figure 6.

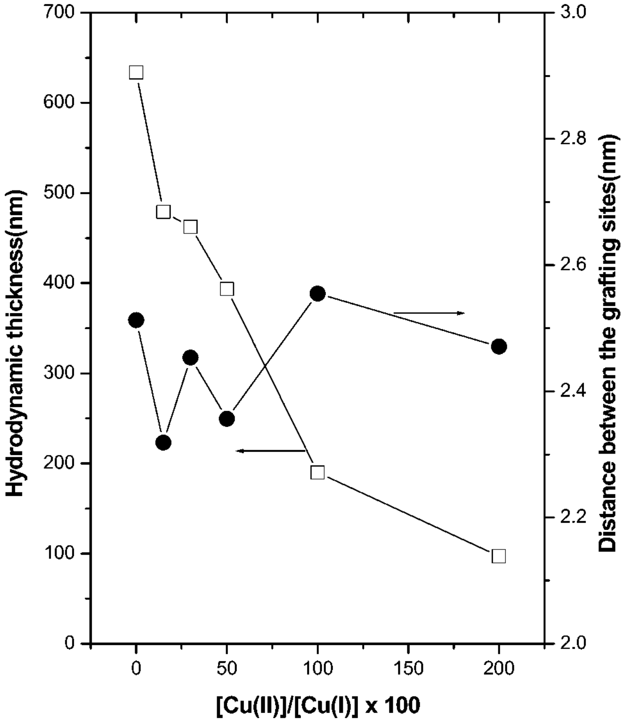


Figure 8. Effect of concentration of CuCl$_2$ on the hydrodynamic thickness and distance between the grafting sites at constant monomer concentration (5.9 wt %). Experimental conditions are as in Figure 6.

Table 4. Effect of External Initiator (Water-Soluble; 2-Hydroxyethyl 2′-Bromopropionate) at Constant Concentration of 0.675 μmol/mL[a]

catalyst	monomer concn (wt %)	M_n	M_w/M_n	distance between the grafting sites (nm)
PMDETA/CuBr/CuBr$_2$	4.70	19 500	1.7	2.38
	5.88	26 700	2.04	2.95
	8.23	40 500	2.22	2.67
	10.3	46 300	2.01	1.67
HMTETA/CuBr/CuBr$_2$	2.94	61 800	1.74	5.23
	4.70	122 000	2.02	2.81
	5.88	163 000	1.99	3.43
	8.23	270 000	1.72	2.08
	10.3	297 000	1.73	3.00

[a] Experimental conditions: 3.5 g of 3 wt % latex: PMDETA (32 μmol)/CuBr (16 μmol) or HMTETA/CuBr (16 μmol), CuBr$_2$/HMTETA/PMDETA (2.4 μmol), copper powder (19 μmol). Temperature 22 °C. Surface concentration of initiator = 1.72×10^{-5} mol/g of latex.

The surface initiator concentration and chain density allow initiation efficiencies to be calculated. These reach values of up to 65% at high monomer concentration, and chain separations approach the average distance between initiators. This efficiency compares to values of 7−25% reported for other surface polymerization reactions in organic solvents.[5,24,49,50] The lower efficiency in these nonaqueous systems is likely due to the low local mole ratio of ligand to surface intitiator, as no mechanism for concentrating the ligand−metal complex from the bulk phase would be present in systems in which electrostatic attraction was absent.

Another approach to controlling the molecular weight and polydispersity and obviating the effects of impurities is to include exogenous initiators in the reaction.[20,24,27] We therefore examined the effects of addition of both a water-soluble and oil-soluble initiator, to determine the effects of limiting mobile initiator to the surface phase. Table 4 shows the results of adding the hydrophilic initiator. The M_n was reduced, as expected since more total chains were initiated, but the control was worse, PDI rising to >2.0 for both ligands. Presumably the additional initiation of chains in the aqueous phase in the shell exacerbated the dependence on monomer diffusion, and the effects of the restriction appear as a worsening of control over the graft. Under the conditions employed PMDETA was much less effective at grafting than HMTETA, for reasons that are unclear.

The hydrophobic initiator's effects should be limited to the interface between the shell and solution. It also reduced M_n for the graft, as seen in Figure 9 (corresponding values for HT and D are given in Table 5), and the PDI decreased as monomer concentration was increased at relatively low levels of exogenous initiator (5 μmol). However, as the initiator concentration was increased at constant monomer concentration (8.25 w%), although M_n decreased smoothly, control was abruptly lost above ∼1×10^{-5} M initiator (Figure 10; data for HT and D are in Table 6). Use of such an approach is therefore not an effective way to control graft molecular weight or thickness.

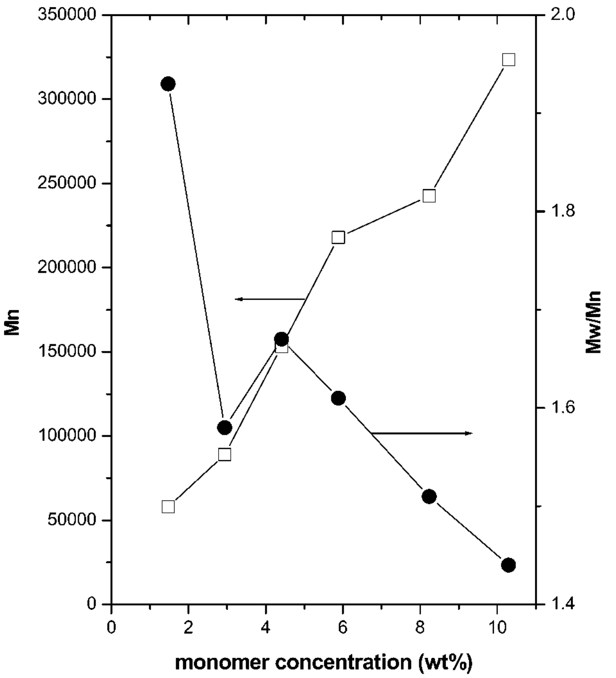


Figure 9. Variation with monomer concentration of M_n and M_w/M_n of the cleaved PDMA from grafted polymer latex measured by GPC-LS in the presence of externally added initiator methyl 2-chloropropionate. Experimental conditions: 3.5 g of 3 wt % suspension of latex, catalyst 1,1,4,7,-10,10-hexamethyltriethylenetetramine (HMTETA)/CuBr (16 μmol), HMTETA/CuBr$_2$ (2.4 μmol), Cu powder (19 μmol), and methyl 2-chloropropionate at 0.794 μmol/mL concentration at 22 °C. Surface initiator concentration 1.72×10^{-5} mol/g.

Table 5. Effect of External Initiator (Oil-Soluble; Methyl 2-Chloropropionate) at Constant Concentration of 0.794 μmol/mL[a]

monomer concn (wt %)	distance between the grafting sites (nm)	hydrodynamic thickness (nm)
1.47	6.76	449
2.94	3.47	418
4.41	3.18	321
5.88	3.04	287
8.23	2.83	161
10.3	2.87	51

[a] Copper complex used was HMTETA/CuBr. Experimental conditions: 3.5 g of 3 wt % suspension of latex, catalyst HMTETA/CuBr (16 μmol), HMTETA/CuBr$_2$ (2.4 μmol), Cu powder (19 μmol), and methyl 2-chloropropionate at 0.794 μmol/mL concentration at 22 °C. Surface concentration of initiator = 1.72×10^{-5} mol/g latex.

Another parameter that is available for manipulation is the total latex concentration. Since the local initiator in the shell is at a constant average surface concentration, varying the number of latex particles per unit volume varies the total amount of initiator available (Figures 11 and 12, Table 7). At low latex concentration (1.5 wt %; Figure 11; corresponding values of HT and D are in Table 7), M_n increases as expected as monomer concentration is increased. Unlike the situation at 3 wt % of latex (Figure 2), the polydispersity index is initially high and decreases as monomer levels are raised, precipitously so for the PMDETA system. When 6 wt % latex is used (Figure 12; corresponding values of HT and D are in Table 7), the opposite trend is seen in that PDI for both ligands increases with monomer concentration. As would be expected, at the lower latex and total initiator concentration, the grafts reached higher M_n values than at 4 times the concentration. However, the difference was relatively small (750 000 maximum for HMTETA at1.5 wt % latex vs 550 000 at 6 wt % latex), much less than the factor of ∼4 expected for an equivalent solution reaction, again underlining the unique behavior of immobilized initiators and limited complex concentration in the surface region.

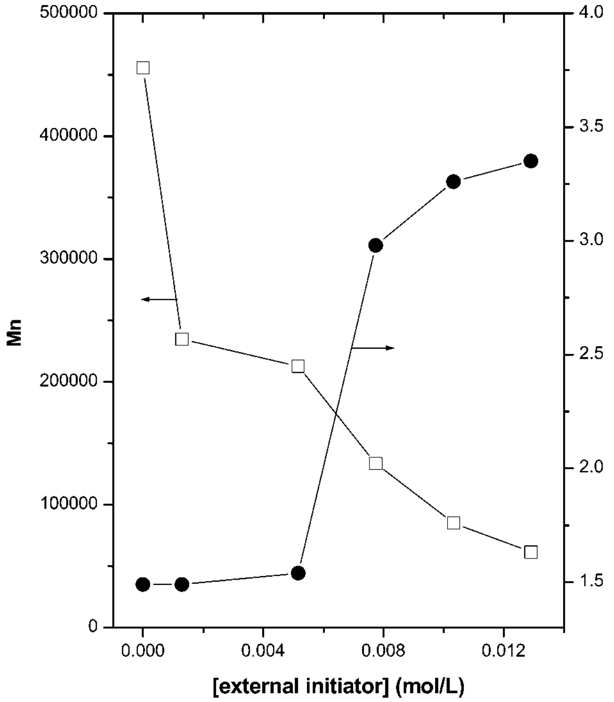


Figure 10. Variation with concentration of oil-soluble external initiator methyl 2-chloropropionate of M_n and M_w/M_n of the cleaved PDMA from grafted polymer latex measured by GPC-LS at constant monomer concentration (8.23 wt %). Experimental conditions: 3.5 g of 3 wt % latex, catalyst HMTETA/CuBr (16 μmol), HMTETA/CuBr$_2$ (2.4 μmol), Cu powder (19 μmol) at 22 °C. Surface initiator concentration 1.72×10^{-5} mol/ g.

Table 6. Effect of Concentration of External Initiator, Methyl 2-Chloropropionate, at Constant Concentration of Monomer (8.23 wt %)[a]

external initiator concn (mol/L) x 10^5	distance between grafting sites (nm)	hydrodynamic thickness (nm)
0	2.46	680
129	2.43	415
516	2.71	396
774	3.33	369
1032	4.20	233
1290	4.69	131

[a] Experimental conditions: 3.5 g of 3 wt % latex, catalyst HMTETA/CuBr (16 μmol), HMTETA/CuBr$_2$ (2.4 μmol), Cu powder (19 μmol) at 22 °C. Surface concentration of initiator = 1.72×10^{-5} mol/g latex.

The local conditions in the shell at the onset of the reaction should be the same for both low and high latex concentrations, since the local initial initiator, monomer, and ligand/Cu(I) concentration will be the same for each particle. Hence, the same number of chains per unit area should be initiated in each case, which is what is observed within experimental variation (Table 7). As monomer is incorporated, however, monomer depletion from the bulk will influence the polymerization more in the high latex condition than in the low, due to the difference in total number of chains initiated (Figure 12). The most obvious difference between the two conditions occurs in the variation of PDI with monomer concentration for PMDETA systems, where control is quite variable, relative to the HMTETA systems.

Table 7. Effect of Concentration of Latex on Distance between the Chains (*D*) and Hydrodynamic Thickness (HT) for Two Complexes: (PMDETA/CuCl) and (HMTETA/CuCl)[a]

		latex concn 1.5 wt %		latex concn 6.0 wt %	
catalyst	monomer concn (wt %)	*D* (nm)	HT (nm)	*D* (nm)	HT (nm)
PMDETA/CuCl/CuCl$_2$	1.47	3.80	17.5	3.32	14.7
	2.94	2.73	103	2.67	149
	4.41	1.84	93	1.68	205
	5.88	2.41	95	1.39	247
	8.23	1.90	512	1.47	409
	10.3	1.30	689	1.38	525
HMTETA/CuCl/CuCl$_2$	1.47	3.60	241	3.72	71
	2.94	3.05	271	3.44	402
	4.41	2.87	514	2.99	540
	5.88	2.93	623	3.09	628
	8.23	2.79	761	3.15	754
	10.3	2.46	799	3.20	764

[a] Experimental conditions: 3.5 g of 3 wt % latex: PMDETA (32 μM)/CuCl (16 μmol) or HMTETA/CuCl (16 μmol), CuCl$_2$/HMTETA/PMDETA (2.4 μmol), copper powder (19 μmol). Temperature 22 °C. Surface concentration of initiator = 1.72×10^{-5} mol/g of latex.

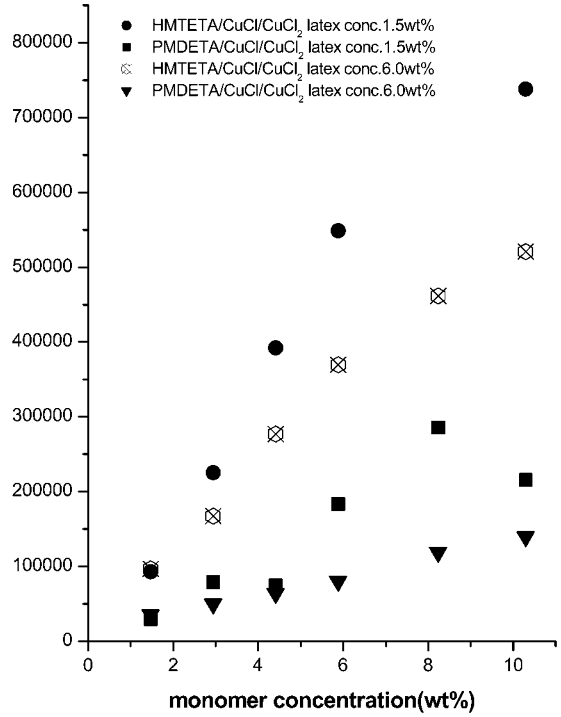


Figure 11. Variation with monomer concentration of molecular weight of cleaved PDMA from grafted latex measured by GPC-LS at different latex concentrations. Experimental conditions: 3.5 g of 3 wt % latex: *N*,*N*,*N'*,*N'*,*N''*-pentamethyldiethylenetriamine (PMDETA (32 μmol)/CuCl (16 μmol) or 1,1,4,7,-10,10-hexamethyltriethylenetetramine (HMTETA)/CuCl (16 μmol), CuCl$_2$/HMTETA/PMDETA (2.4 μmol), copper powder (19 μmol). Temperature 22 °C. Surface initiator concentration 1.72×10^{-5} mol/g.

In this work we have found a number of ways to control the thickness of the grafted polymer layer. The hydrodynamic thickness (brush height) was found to be sensitive to monomer concentration, presence of an exogenous hydrophobic initiator, latex concentration, and particularly addition of Cu(II) in the reaction medium. Appropriate selection of Cu(II) concentration produced conditions in which the brush thickness varied linearly with molecular weight of the graft.

Summary

We describe a systematic investigation of the role of monomer concentration, ligand type, Cu(I) anion, added Cu(II), exogenous initiators soluble in either water or

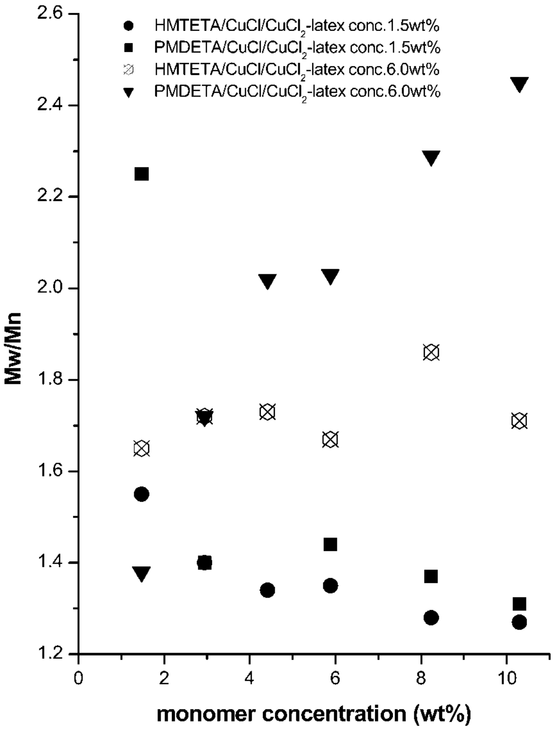


Figure 12. Variation with monomer concentration of molecular weight distribution of cleaved PDMA from grafted latex measured by GPC-LS at different latex concentrations. Experimental conditions are as in Figure 11.

oil, and latex concentration on the polymerization of *N*,*N*-dimethylacrylamide from surface initiators on polystyrene latex by aqueous ATRP. All grafting reactions were carried out at room temperature. Conditions that provided good control over the molecular weight distribution (PDI down to < 1.25), chain separation as low as $D \geq 1.1$ nm), and graft thicknesses (HT up to 800 nm) are described. True brushes were routinely obtained, with very extended configurations of the chains and molecular weights up to ∼750 000. It was possible to achieve average grafted chain separations as low as ∼5% of R_g of the unconstrained polymer. Control was optimized by inclusion of a high mole ratio of Cu(II):Cu(I), use of a low total surface area of latex, and choice of ligand. There were large differences between characteristics of these surface-initiated reactions and those obtained in solution. A model of the surface is presented that allows qualitative mechanisms to be proposed for most of the features observed.

Acknowledgment. We thank the Canadian Institutes of Health Research for support.

References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31.
(2) Milner, S. T. *Science* **1991**, *251*, 905.
(3) Mansky, P.; Liu. Y.; Huang, E.; Russell, T. P.; Hawker, C. J. *Science* **1997**, *275*, 1458.
(4) Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. *J. Am. Chem. Soc.* **2000**, *122*, 2407.
(5) Shah, R. R.; Merreceyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597.
(6) Hadziioznnou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.
(7) Fytas, G.; Anastasizdis, S. H.; Seghrouchni, R.; Vlassopoulos, D.; Li, J.; Factor, B. J.; Theobald, W.; Toprakcioglu, C. *Science* **1996**, *274*, 2041.
(8) Mir, Y.; Auroy, P.; Auvray, L. *Phys. Rev. Lett.* **1995**, *75*, 1863.
(9) Hertler, W. R.; Sogah, D. Y.; Boettcher, F. P. *Macromolecules* **1990**, *23*, 1264.
(10) Prucker, O.; Ruhe, J. *Macromolecules* **1998**, *31*, 592.
(11) Prucker, O.; Ruhe, J. *Macromolecules* **1998**, *31*, 602.
(12) de Boer, B.; Simon, H. K.; Werts, M. P. L.; Van der Vegte, E. W.; Hadziioannou, G. *Macromolecules* **2000**, *33*, 349.
(13) Jordan, R.; Ulman, A.; Kang, J. F.; Rafailovich, M. H.; Sokolov, J. *J. Am. Chem. Soc.* **1999**, *121*, 1016.
(14) Ingall, M. D. K.; Honeyman, C. H.; Mercure, J. V.; Bianconi, P. A.; Kunz, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 3607.
(15) Zhao, B.; Brittain, W. J. *J. Am. Chem. Soc.* **1999**, *121*, 3557.
(16) Jordan, R.; Ulman, A. *J. Am. Chem. Soc.* **1998**, *120*, 243.
(17) Husseman, M.; Mecerreyes, D.; Hawker, C. J.; Hedrick, J. L.; Shah, R.; Abbott, N. L *Angew. Chem., Int. Ed.* **1999**, *38*, 647.
(18) Buchmeiser, M. R.; Sinner, F.; Mupa, M.; Wurst, K. *Macromolecules* **2000**, *33*, 32.
(19) Juang, A.; Scherman, O. A.; Grubbs, R. H.; Lewis, N. S. *Langmuir* **2000**, *17*, 1321, 2001.
(20) Zhao, B.; Brittain, W. J. *Macromolecules* **2000**, *33*, 8813.
(21) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716.
(22) Kim, J.; Bruening, M. L.; Baker G. L. *J. Am. Chem. Soc.* **2000**, *122*, 7616.
(23) Wu, T.; Efimenko, K.; Genzer, J. *Macromolecules* **2001**, *34*, 684.
(24) von Werne, T.; Patten, T. E. *J. Am. Chem. Soc.* **2001**, *123*, 7497.
(25) Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **1998**, *31*, 5934.
(26) Huang, X.; Wirth, M. J. *Macromolecules* **1999**, *32*, 1694.
(27) Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Herdrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424.
(28) Huang, W. X.; Kim, J. B.; Bruening, M. L.; Baker, G. L. *Macromolecules* **2002**, *35*, 1175.
(29) Perruchot, C.; Khan, M. A.; Kamitsi, A.; Armes, S. P.; von Werne, T.; Patten, T. E. *Langmuir* **2001**, *17*, 4479.
(30) de Gennes, P. G. *J. Phys.* (*Paris*) **1976**, *37*, 1445; *Macromolecules* **1980**, *13*, 1069.
(31) Alexander, S. J. *J. Phys.* (*Paris*) **1977**, *38*, 983.
(32) Fleer, G. J. Cohen Sutart, M. A.; Scheutjens, J. M. H. M.; Cosgrov, T.; Vincent, B. *Polymers at Intefaces*; Chapman & Hall: London, 1993.
(33) Webster, O. W. *Science* **1991**, *251*, 887.
(34) Wang, X. S.; Jackson, R. A.; Armes, S. P. *Macromolecules* **2000**, *33*, 255.
(35) Wang, X. S.; Lascelles, S. F.; Jackson, R. A.; Armes, S. P. *Chem. Commun.* **1999**, 1817.
(36) Hritcu, D.; Muller, W.; Brooks, D. E. *Macromolecules* **1999**, *32*, 565.
(37) Brooks, D. E.; Haynes, C. A.; Hritcu, D.; Steels, B. M.; Muller, W. *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 7064.
(38) Guo, X.; Weiss, A.; Ballauff, M. *Macromolecules* **1999**, *32*, 6043.
(39) Guerrrinni, M. M.; Charleux, B.; Vairon, J. P. *Macromol. Rapid Commun.* **2000**, *21*, 669.
(40) Guo, X.; Ballauff, M. *Lanumuir* **2000**, *16*, 8719.
(41) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966**, *5*, 41.
(42) Teodorescu, M.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4826.
(43) Rademacher, J. J.; Baum, M.; Pallack, M. E.; Brittain, W. J.; Simonsick, W. J., Jr. *Macromolecules* **2000**, *33*, 284.
(44) Brandrup, J., Immergut, E. H., Eds.; *Polymer Handbook*; John Wiley & Sons: New York, 1989.
(45) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991; Chapter 6.
(46) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry;* Marcel Dekker: New York, 1977; Chapter 9.
(47) Teodorescu, M.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2000**, *21*, 190.
(48) Xia, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5958.
(49) Yamamoto, S.; Ejaz, M.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2000**, *33*, 5608.
(50) Zhao, B.; Brittain, W. J. *Macromolecules* **2000**, *33*, 342.

MA011651Y