Macromolecules **2003,** *36,* 591−598

Synthesis of Poly(*N*,*N*-dimethylacrylamide) Brushes from Charged Polymeric Surfaces by Aqueous ATRP: Effect of Surface Initiator Concentration

Jayachandran N. Kizhakkedathu[†] **and Donald E. Brooks***[,†,‡]

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

Received August 15, 2002; Revised Manuscript Received December 2, 2002

ABSTRACT: We have synthesized polystyrene shell latex (PSL) surfaces with different initiator concentrations by changing the feed ratio of styrene to 2-(methyl-2′-chloropropionato)ethyl acrylate (HEA−Cl) in a series of shell-growth copolymerization reactions. Surfaces were characterized by conductometric titration of saponified and nonsaponified functionalized PSL to give the surface charge and initiator concentrations accessible to aqueous reagents and by ^{1}H NMR methods. Poly(*N*,*N*-dimethylacrylamide) brushes were grafted from the functionalized surfaces by aqueous atom transfer radical polymerization and the dependence of molecular weight and chain density determined as a function of monomer concentration, ligand type, and surface initiator concentration by analyzing the chains cleaved from the PSL by saponification. M_n varies linearly with monomer concentration for most systems, and grafting density is roughly independent of monomer concentration except at the highest initiator concentration. Very high molecular weights were obtained at low initiator concentration, up to $M_n \sim 1.2 \times 10^6$ with $M_w/M_n < 1.3$; chain separations down to 1.1 nm and brush thicknesses to ~800 nm were found. Grafting density varies as (initiator surface concentration)$^{2.6}$. The surface charge density also varies among the latexes synthesized and seems to play a role in this strong dependence on surface initiator concentration, perhaps by partially immobilizing the positively charged catalyst complex.

Introduction

Controlling the properties of surfaces by attaching polymer chains has relevance to many fields, including reduction of protein adsorption,[1] polymer electronics,[2] and wetting control and colloidal stability.[3] The properties of polymer chains tethered at high surface concentrations, known as polymer brushes, depend on many factors: monomer type, molecular weights of the grafted chains, graft density, and thickness of the grafted polymer layer. Several techniques have been used for grafting polymers to surfaces,[4−21] the most versatile being surface-initiated "grafting from" polymerization as high grafting densities and molecular weights can be achieved. Surface-initiated living polymerizations have been applied to modify the properties of different substrates.[7−21] Atom transfer radical polymerization (ATRP) in particular has been used successfully to synthesize well-defined polymer layers on the surface of a variety of substrates.[12−21] This technique can be applied to many different experimental paradigms and monomers. Recently, the aqueous ATRP technique has been used to grow hydrophilic polymer layers of unprecedented thickness and surface density.[17−21]

Huck et al.[22] and Yamamoto et al.[23] have shown that the grafting density of brushes can be changed by varying the initiator density on silica surfaces. Recently, we used surface-initiated ATRP to generate thick poly(*N*,*N*-dimethylacrylamide) layers on the surface of negatively charged polystyrene shell latex (PSL). This system showed an unexpected increase in grafting density with increasing monomer concentration[17] at high surface initiator concentration. This observation has led us to synthesize a series of latex preparations with varying initiator surface concentration and to study their polymerization behavior.

The PSL surface is a good model system with which to study the mechanism of surface-initiated polymerization due to the large surface area, narrow size distribution, and the synthetic control over surface properties offered by surfactant-free latex synthesis. We have shown elsewhere that the PSL surface in water is very different from a silica surface.[17] The PSL surface is charged and largely hydrophobic under our experimental conditions, the monomer is hydrophilic and neutral, and the surface region carries an ion concentration gradient due to the electrical double layer. Since the catalyst used is positively charged, it accumulates in the double layer to provide a much higher concentration in the surface region than is present in the bulk solution. This makes the surface polymerization reaction quite complex.

This paper reports the synthesis and characterization of polystyrene shell latexes with varying initiator density and the use of this latex in aqueous ATRP to synthesize poly(*N*,*N*-dimethylacrylamide) brushes of varying surface concentration and chain length. We describe the dependence of molecular weight, grafting density, and hydrodynamic layer thickness of the brushes on initiator surface density and on feed monomer concentration. In particular, the nonlinear dependence of grafted chain density on initiator surface concentration is discussed in terms of a model of the surface polymerization reaction.

Experimental Section

All commercial reagents were purchased from Aldrich and used without further purification except as noted below.

[†] Department of Pathology and Laboratory Medicine.

[‡] Department of Chemistry.

[*] Corresponding author: phone (604) 822-7081; Fax (604) 822-7635; e-mail don.brooks@ubc.ca.

10.1021/ma021337j CCC: $25.00

Table 1. Reaction Conditions for the Functionalization of Latex Particles by Shell-Growth Polymerization[a]

latex code	seed latex (g)[b]	styrene (mol)	HEA−Cl (mol) $\times 10^5$ [c]	KPS (mol) $\times 10^5$ [d]	HD (nm)[e]
L1	166	0.019	2.42	23	509
L2	166	0.016	9.71	23	509
L3	166	0.016	48.5	23	509
L4	166	0.016	97.5	23	509
L5	265	0.025	784	37	559

[a] Temperature of the polymerization 70 °C. [b] Mass of 3.3 wt % suspension in water. [c] 2-(Methyl-2′-chloropropionato)ethyl acrylate (HEA−Cl). [d] Potassium persulfate. [e] Hydrodynamic diameter of seed latex determined by particle size analyzer.

Styrene (Aldrich, 99%) was first washed with a 1% NaOH solution, dried, 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. *N*,*N*,*N*′,*N*′,*N*″-Pentamethyldiethylenetriamine (Aldrich, 99%) (PMDETA) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (Aldrich, 97%) (HMTETA) were used as such. 2-(Methyl-2′-chloropropionato)ethyl acrylate (HEA−Cl) was synthesized by following our earlier report.[17] Once distilled water was further purified using a Milli-Q Plus water purification system (Millipore Corp., Bedford, MA) and was used for all experiments. 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 analyses for monomer conversion measurements were 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, with detection at $\lambda = 236$ nm using aqueous 0.1% trifluoroacetic acid (TFA) solution as the mobile phase at a flow rate of 4 mL/min at 22 °C. Molecular weights were determined by gel permeation chromatography (GPC) on a Waters 2690 separation module fitted with a DAWN EOS multiangle laser light scattering (MALLS) 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 $10^3 - 5 \times 10^6$ Da and Ultrahydrogel 120 with bead size 6 μm, elution range $150 - 5 \times 10^3$ Da connected in series; from Waters). The value of d*n*/d*c* for PDMA in the mobile phase was determined at $\lambda = 620$ nm to be 0.150 mL/g and was used for determining molecular weight parameters. 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. Size analyses were performed using the software supplied by the manufacturer. Conductometric titrations were done on a YSI model 35 conductance meter and 3403 cell with platinum electrode at 25 °C. A syringe pump (Harvard Instruments) was used to inject dilute NaOH at constant flow rate of 0.0102 mL/min.

Two sets of narrowly dispersed polystyrene seed latex (PS seed latex) were synthesized by surfactant-free emulsion polymerization of styrene and characterized by reported procedures.[17] The hydrodynamic sizes of the latex particles were 509 and 559 nm (Table 1).

Shell Growth Polymerization: Synthesis of the ATRP Initiator Layer. An aqueous suspension of PS seed latex particles (3.33 wt %, 265 g) was heated to 70 °C with stirring at 350 rpm, degassed, and purged with argon. Styrene (2.6 g, 0.025 mol) and 2-(methyl-2′-chloropropionato)ethyl acrylate (HEA−Cl) (1.62 g, 0.0078 mol) were added successively to the suspension 10 min apart, and shell polymerization was initiated with potassium persulfate (KPS) (0.100 g, 0.37 mmol in 20 mL of water, degassed) 5 min later. The reaction was continued for 6 h, then the latex was cleaned by dialysis against water for 1 week with frequent changes in water followed by five cycles of centrifugation and resuspension. The solid content was determined by freeze-drying. Four other shell latexes were also synthesized by varying the ratio of styrene to HEA−Cl. The reaction conditions and amounts of reagents used in the shell growth polymerizations are given in Table 1; the size distributions, demonstrating monodispersity, are provided in the Supporting Information.

Atom Transfer Radical Polymerization from Latex. General Method for Grafting of Poly(*N*,*N*-dimethylacrylamide) (PDMA). All reactions were performed in a glovebox filled with argon due to the sensitivity of the Cu(I) complex to air. We followed the general methods of polymerization reported in our earlier communication.[17] A suspension of latex (22 g, 3 wt %) 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. For a typical reaction, DMA (0.35 g, 3.5 mM) was stirred with HMTETA (4.7 mg, 20 μM), CuCl (1.6 mg, 16 μM), $CuCl_2$ (0.3 mg, 2.4 μM), and Cu powder (1.2 mg, 19 μM) for 3 min to form a solution; 3.5 g (3% w/w) of degassed Brij-35 stabilized PSL L5 was added to this under stirring at room temperature (22 °C). The reaction was continued for 12 h, and monomer conversion was 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 mM), and water to remove adsorbed copper complexes for 8−10 cycles until there was no detectable amount of polymer, monomer, or catalyst in the supernatant. Different series of experiments were conducted by changing the catalyst, monomer concentration, and surface initiator concentration (different shell latexes). The same concentrations of catalyst and latex were used for all grafting reactions when other latexes were employed.

Analysis of the Shell and PDMA Grafted Latex. Shell latex was analyzed for hydrodynamic size, surface initiator concentration, and surface charge density. The accessible surface initiator concentration was calculated from a conductometric titration of saponified latex as reported earlier.[5,17] For a typical case, the latex L5 (2 g) was stirred with 1 mL of 2 N NaOH for 36 h at room temperature. The suspension was 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. Latex surface charge 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 initiator for L5 was $(2.00 \pm 0.10) \times 10^{-6}$ mol/m^2 (specific area = 8.568 m^2/g) of 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 $(2.75 \pm 0.14) \times 10^{-7}$ mol/m^2 of latex. For latexes with lower surface initiator concentrations we used more latex for conductometric titrations to provide data reproducible to ±5%. Particle size measurement showed an increment of 110 nm (from 559 to 669 nm) in diameter for latex L5 carrying the shell compared to the original latex and a narrow size distribution. The total concentration of HEA−Cl incorporated into the latex was determined from ^{1}H NMR spectra of the freeze-dried samples dissolved in $CDCl_3$ utilizing the peaks at 4.1−4.3 ppm which are characteristic of HEA−Cl. From the ratio of the intensities of peaks at 4.1−4.3 ppm ($-O-CH_2-CH_2-O-$ and $-CHCl-$) and peaks of aromatic protons from polystyrene (6.7−7.2 ppm), the mole percent of HEA−Cl present in the latex was calculated (6.74 mol/g of latex for L5). The depth of the region accessible to aqueous reagents was estimated by multiplying the shell thickness by the ratio of the titratable to total initiator surface concentration, since titration only detects

Table 2. Characteristics of the Functionalized Latexes

latex code	feed concn HEA−Cl[a] (mol/g× 10^5)	concn HEA−Cl (from ^{1}H NMR) (mol/g × 10^5)	surface concn of HEA−Cl[b] mol/m^2× 10^7	surface concn of HEA−Cl[b] area/initiator (nm^2)	surface charge concn[b] mol/m^2× 10^7	surface charge concn[b] area/charge (nm^2)	HD[c] (nm)	shell[d] (nm)	AT[e] (nm)
L1	0.32	low	0.50	32.80	5.78	2.85	576	34	5.2
L2	1.35	low	2.11	8.13	4.99	3.29	578	35	5.2
L3	6.67	low	2.81	5.92	2.17	7.58	578	35	1.4
L4	13.2	16.9	4.47	3.72	2.17	7.47	586	39	1.3
L5	59.9	67.3	20.00	0.83	2.75	5.19	669	55	1.6

[a] Calculated from the total amount of PS solid, styrene, and HEA−Cl added; HEA−Cl = 2-(methyl-2′-chloropropionato)ethyl acrylate. [b] By conductometric titration. [c] Hydrodynamic diameter. [d] Shell thickness = half the increase in HD when the shell added. [e] Estimate of depth of region accessible to aqueous reagents.

those groups that react with water-borne reagents. The hydrodynamic size, surface initiator concentration, surface charge, and ^{1}H NMR concentration values for the other latexes are given in Table 2.

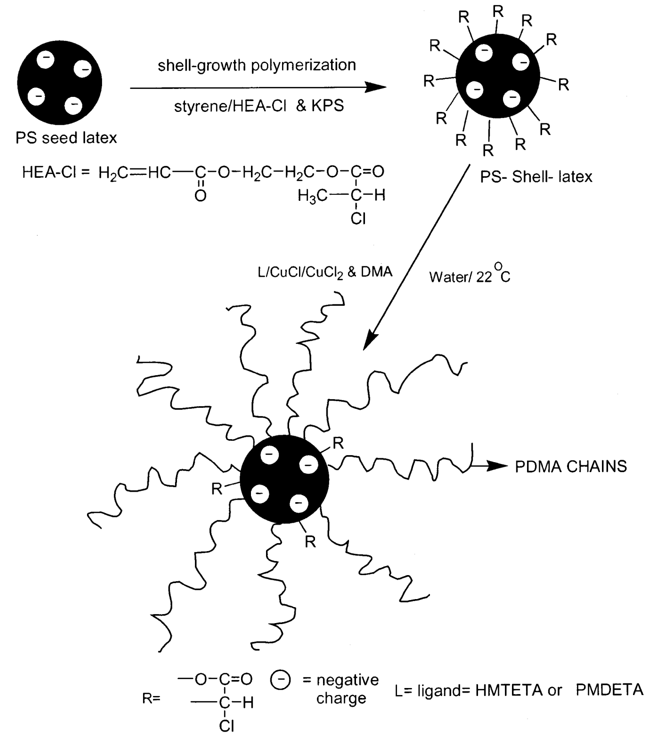
The grafted latex was characterized by hydrodynamic size measurements utilizing the particle size analyzer and by analysis of the polymer released by hydrolysis. We define the difference between the grafted and shell latex radii to be the hydrodynamic thickness (HT) of the grafted layer. Characterization 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 surface was performed by quantitative cleavage of the chains and analysis by GPC-MALLS as reported earlier.[17] 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 washings were collected and analyzed by GPC. The mass of polymer in solution following cleavage was determined using a calibrated RI detector.

Results and Discussion

Synthesis and Characterization of PSL Carrying Shells with Different Surface Concentrations of ATRP Initiator. We have already reported the synthesis of an ATRP initiator-functionalized monomer, 2-(2′-chloromethylpropionato)ethyl acrylate (HEA−Cl), for use in copolymerization with styrene.[17] We have also reported the synthesis and characterization of a well-defined initiator layer on the surface of PS seed latex by shell-growth polymerization[17] in which we copolymerized styrene and HEA−Cl on the surface of seed PS seed latex. In the present report we have extended this method to vary the concentration of ATRP initiator on the surface by diluting the ATRP initiator-functionalized monomer with styrene in the initial monomer feed to produce five different latexes, L1 to L5. Table 1 gives the experimental conditions we employed. A schematic representation of the modification of the latex surface is given in Scheme 1. Attempts to prepare surfaces using a lower feed ratio than illustrated (higher HEA−Cl) were unsuccessful due to aggregation of the latex during polymerization. All the polymerizations reported were successful in producing narrowly dispersed ATRP functionalized latex, evidenced by the unimodal peaks in the size measurements (shown in Supporting Information) and the dominance of single particles when suspensions were viewed under a microscope (results not shown).

^{1}H NMR measurements on functionalized latex provide the total amount of HEA−Cl incorporated into the latex. All the latexes had peaks at 4.1−4.3 ppm, characteristic of HEA−Cl, showing successful functionalization. This technique was successful only in the cases of L4 and L5 as the other preparations have very low concentrations of HEA−Cl, which produces an unacceptable error in the calculation.

Scheme 1. Schematic Representation of Surface Functionalization and Aqueous ATRP on Polystyrene Latex Particles



We described earlier the use of conductometric titration for the surface characterization of functionalized latexes.[5,17] It is a powerful technique for determination of the functionality present on the polystyrene latex surface that is accessible to aqueous reagents.[24] Conductometric titrations were done on saponified (to hydrolyze HEA−Cl and produce a titratable COO$^-$ function) and unsaponified shell latexes. The latter allows titration of the charged sulfonic acid groups produced by the potassium persulfate (KPS) initiator used for shell polymerization. The combination allows the surface initiator concentration and charge density to be calculated. We have found that the saponification procedure used here reduces the titratable sulfate surface concentration by at most the sum of the uncertainties in the two measurements, making any decrease insignificant. The surface initiator concentration, charge density, area per initiator molecule, area per charge, and hydrodynamic diameters of the latex carrying the shell are given in Table 2.

The surface concentration of ATRP initiator decreases with decreasing amounts of HEA−Cl in the monomer feed, as expected, but Figure 1 shows that the titratable surface initiator concentration is not linear with the

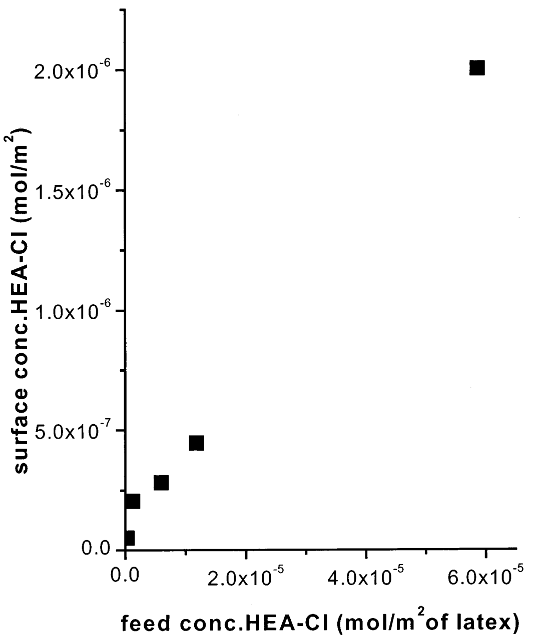


Figure 1. Concentration of water-accessible 2-(methyl-2′-chloropropionato)ethyl acrylate (HEA−Cl) (ATRP initiator) concentration on the surface of PS shell latex with feed concentration in the shell-growth polymerization. Surface concentrations of initiators were calculated from duplicate conductometric titrations of saponified latex; the observed variability in each value was smaller than the symbol dimensions.

amount of functional monomer in the feed. The initial slope (points for L1 and L2) is higher than that observed at higher feed concentrations of HEA−Cl. Comparing the initiator concentration in the feed (normalized to the amount of latex present) with the total calculated from ^{1}H NMR shows that at the highest two feed concentrations (L4 and L5) essentially all of the ATRP initiator monomer is incorporated into the surface layer. Assuming this is true at low concentrations, the initial steep slope seen in Figure 1 implies that more of the total surface-associated initiator is accessible to the water-soluble titration reagents at low surface concentrations than at high. The small difference between the feed concentration and ^{1}H NMR concentration is due to experimental uncertainty in the ^{1}H NMR values due to the large mole percent of polystyrene present in the shell latex.

Table 2 also provides data for the area per charge associated with the shell copolymerization initiator, KPS. At the two lowest HEA−Cl concentrations (L1 and L2) the area per charge is relatively low, implying lower molecular weights for the shell copolymer under these conditions, since each sulfonic acid is an end group for a chain.[25] These copolymers, formed at high styrene: HEA−Cl ratios, will be more hydrophobic than at lower ratios, which likely affects how the shell interacts with the very hydrophobic surface of the PS seed latex. Earlier calculations have shown[17] that these two monomers should form random copolymers rather than blocks of each monomer for shell latex L5. With a feed ratio of ∼3:1 for styrene:HEA−Cl for latex L5, we expect a random copolymer based on a calculation utilizing reactivity ratios for styrene ($r_1 = 0.66$) and *n*-butyl acrylate ($r_2 = 0.19$), a comonomer structurally related to our initiator, at 60 °C.[26] From the microstructure equation we calculated[27] 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 probabilities of 114%, 73%, and 47%, respectively. Since the other latex preparations contain lower HEA−Cl concentrations, in all cases we expect a random distribution of ATRP initiator over the latex surface rather than a patchy layer.

As we have suggested earlier,[17] the data in Table 2 can be used to estimate the thickness of the region of the initiator-containing shell accessible to aqueous reagents if it is assumed that HEA−Cl is distributed uniformly throughout the volume of the copolymer shell. Shell thicknesses, given by the difference between the diameters of the shell bearing and seed latex, are shown in Table 2. The depths accessible to aqueous reagents are also given in Table 2. The two shells with the lowest HEA−Cl concentrations, L1 and L2, show much more water accessibility than L3−L5, which carry higher initiator concentrations. Table 2 also shows that L1 and L2 have much higher surface charge densities than the other three shells. The more accessible structure of shells L1 and L2 may be due to the higher concentration of heavily hydrated sulfonic acid residues and the electrostatic repulsion between adjacent residues. The latter would be significant under the conditions of very low ionic strength at which the shell is formed, since the dimensions of the electrical double layer would exceed the average charge separation in the shell.[28] The consistency of the picture that emerges, based on two independent measurements (sulfonic acid and initiator titrations), supports the assumption of a relatively uniform distribution of initiator throughout the shell on which the accessibility calculation rests.

Aqueous Atom Transfer Radical Polymerization on Surfaces. A schematic representation of the surface-initiated ATRP is shown in Scheme 1. Tables 3 and 4 provide the values for M_n, M_w/M_n (PDI), surface density of grafted chains, the ratio of the average distance between chains to the radius of gyration of the grafted chains (D/R_g), and hydrodynamic thickness for the latexes carrying five different surface concentrations of initiator at three monomer concentrations using two ligands. The saponification reactions in all cases produced latex with diameters indistinguishable from the original shelled latex (i.e., within 2%), so saponification was quantitative by this measure. However, because a low concentration of chains of unknown molecular weight could still be left on the surface, the values for chain concentration in Tables 2 and 3 should be considered lower limits, and small uncertainties in M_n and PDI are possible from this source.

Figure 2 shows the dependence of M_n on monomer concentration for the five latexes using HMTETA/CuCl. In general, M_n increases roughly linearly with monomer concentration at constant surface initiator concentration for all but the highest surface initiator value (L5), which shows a much weaker dependence. Control is quite good (PDI = 1.25−1.44) for all but L5 (PDI = 1.49−1.6). M_n increases as the initiator concentration decreases at constant monomer concentration. At the lowest initiator surface concentrations the molecular weights achieved are very high ($>1.2 \times 10^6$) with reasonable PDI values. These M_n values are the highest reported for ATRP from surfaces. Data for PMDETA are comparable (Table 4), but in general the M_n values are somewhat lower, as reported previously for high surface initiator concentrations.[17] This is one of the many differences between surface-initiated ATRP and solution ATRP as in the

Table 3. M_n, M_w/M_n (PDI), Surface Density of Polymer Chains per Unit Area, D/R_g, and Hydrodynamic Thickness of Polymer Layers Grafted from Different Latex Using PMDETA/CuCl as Catalyst at Three Monomer Concentrations[a]

	5.9 wt %[c]					8.24 wt %[c]					10.3 wt %[c]				
latex	M_n × 10^{-3}	PDI	no. chains (mol/m^2) × 10^9	D/R_g[b]	HT (nm)	M_n × 10^{-3}	PDI	no. chains (mol/m^2) × 10^9	D/R_g	HT (nm)	M_n × 10^{-3}	PDI	no. chains (mol/m^2) × 10^9	D/R_g	HT (nm)
L1					0.5	523	1.43	0.60	1.86	26	1364	2.01			2.5
L2	238	1.42	10.21	0.67	61	358	1.38	11.5	0.50	184	438	1.47	9.28	0.48	256
L3	213	1.59	5.51	0.70	70	341	1.5	5.55	0.56	105	414	1.48	6.20	0.49	143
L4	271	1.5	16.9	0.38	141	477	1.5	16.0	0.30	217	275	1.76	18.0	0.32	177
L5	204	1.32	366	0.11	377	272	1.41	693	0.06	607	217	1.49	1359	0.05	680

[a] Experimental conditions: 3.5 g of 3 wt % suspension of latex, N,N,N′,N′,N″-pentamethyldiethylene triamine (PMDETA, 32 μmol), CuCl (16 μmol), $CuCl_2$/PMDETA (2.4 μmol), and copper powder (19 μmol) at 22 °C. Reaction time: 24 h for latexes L1–L4 and 12 h for latex L5. Surface initiator concentration is varied from latex L1 to L5 and is in the order L5 > L4 > L3 > L2 > L1 is given in Table 2. [b] D = distance between the grafted chains and R_g = radius of gyration. [c] Monomer concentration.

Table 4. M_n, M_w/M_n (PDI), Surface Density of Polymer Chains per Unit Area, D/R_g, and Hydrodynamic Thickness of the Polymer Layer Grafted on to Different Latex Using HMTETA/CuCl as Catalyst at Three Monomer Concentrations[a]

	5.9 wt %[c]					8.24 wt %[c]					10.3 wt %[c]				
latex	M_n × 10^{-3}	PDI	no. chains (mol/m^2) × 10^9	D/R_g[b]	HT (nm)	M_n × 10^{-3}	PDI	no. chains (mol/m^2) × 10^9	D/R_g	HT (nm)	M_n × 10^{-3}	PDI	no. chains (mol/m^2) × 10^9	D/R_g	HT (nm)
L1	750	1.25	0.90	1.35	55	901	1.50	1.14	1.06	68	1130	1.55	1.06	1.01	139
L2	534	1.44	13.1	0.38	312	735	1.39	10.5	0.37	374	1102	1.36	13.4	0.27	513
L3	661	1.35	62.2	0.39	217	1046	1.36	73.1	0.27	347	1257	1.29	64.1	0.27	354
L4	385	1.36	173	0.33	194	678	1.34	216	0.20	338	981	1.36	176	0.18	442
L5	345	1.49	261	0.10	619	447	1.65	367	0.18	800	441	1.60	449	0.06	817

[a] Experimental conditions: 3.5 g of 3 wt % suspension of latex, 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 20 μmol), CuCl (16 μmol), $CuCl_2$ (2.4 μmol), and copper powder (19 μmol) at 22 °C. Reaction time: 24 h for latexes L1–L4 and 12 h for latex L5. Surface initiator concentration is varied from latex L1 to L5 and is in the order L5 > L4 > L3 > L2 > L1 is given in Table 2 [b] D = distance between the grafted chains and R_g = radius of gyration. [c] Monomer concentration.

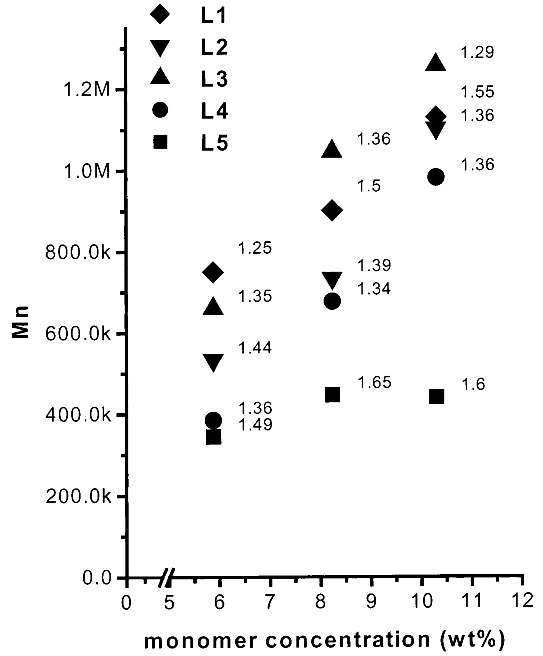


Figure 2. Effect of monomer concentration on molecular weight of the cleaved PDMA from different grafted latexes measured by GPC-MALLS; M_w/M_n for each polymer is given as a label for each point. Experimental conditions: 3.5 g of 3 wt % suspension of latex, 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 20 μmol) CuCl (16 μmol), $CuCl_2$ (2.4 μmol), and copper powder (19 μmol) at 22 °C. Reaction time: 24 h for latexes L1–L4 and 12 h for latex L5. Surface initiator concentration varies from latex L1 to L5 and is in the order L5 > L4 > L3 > L2 > L1; values are given in Table 2.

latter case the molecular weight is directly proportional to monomer concentration and independent of catalyst type.

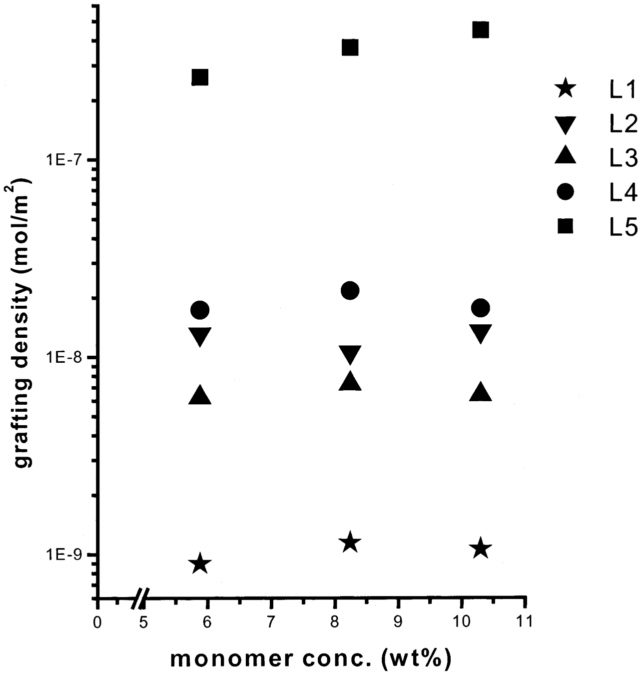


Figure 3. Effect of monomer concentration on the grafting density of PDMA for latexes L1–L5 carrying different surface initiator concentrations. Surface initiator concentration is in the order L5 > L4 > L3 > L2 > L1 and is given in Table 2. Experimental conditions are as in Figure 2

Figure 3 illustrates the dependence of the density of grafted chains (i.e., number of moles of PDMA grafted per unit area) on monomer concentration for L1–L5 with HMTETA as ligand. For the four lower surface initiator concentrations L1–L4 the graft density is independent of monomer concentration while at the highest surface initiator concentration the surface den-

Table 5. Initiator Efficiency at Three Monomer Concentrations for Different Latex Surfaces[a]

		initiator efficiency (%)[b]		
catalyst	latex	5.88 wt %[c]	8.23 wt %[c]	10.3 wt %[c]
PMDETA/CuCl	L1	ND	1.2	ND
	L2	4.8	5.5	4.4
	L3	2.0	2.0	2.2
	L4	3.8	3.6	4.0
	L5	18.3	34.6	65.2
HMTETA/CuCl	L1	1.8	2.3	2.1
	L2	6.4	5.2	6.7
	L3	2.2	2.6	2.3
	L4	3.9	4.9	3.9
	L5	13.0	18.3	22.4

[a] ND = not determined, PMDETA = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine, HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine. [b] Initiator efficiency is calculated as the number of chains of polymer grafted from the surface divided by the amount of initiator initially accessible on the surface. [c] Monomer concentration.

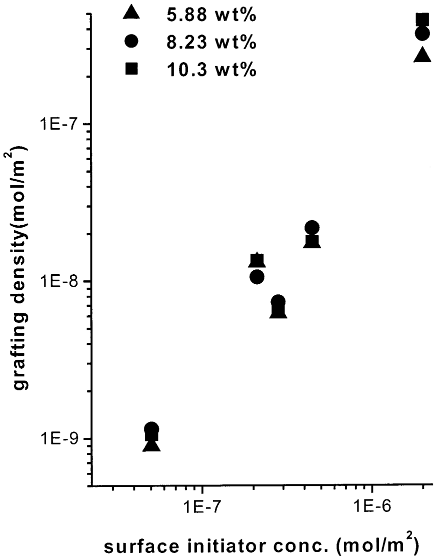


Figure 4. Effect of surface initiator concentration on the grafting density of PDMA from latex as a function of monomer concentration. Experimental conditions are the same as in Figure 2.

sity increases somewhat with increasing monomer. This is also true in the PMDETA systems. Hence, the number of chains successfully initiated does not depend on the local monomer concentration for most of the systems examined. While this is the expected result for solution ATRP, the data in Table 5 demonstrate again the great difference in the surface-initiated case, in that for L1−L4 only a few percent of the titratable initiators are reacted. The only exception is the surface carrying the highest initiator concentration, L5, where the initiation efficiency varies from 18 to 65%, depending on monomer concentration and ligand present. The value of 65% for PMDETA at 10.3% monomer is the highest value yet reported for a surface-initiated ATRP. These data are consistent with other reports on surface-initiated polymerization[12,22,29] and show that surface initiation is not quantitative.

In considering the properties of L5 that might influence initiation efficiency the relatively high hydrophilicity suggests itself. The hydrophilic groups in the surface region consist of the sulfonic acid and HEA−Cl groups. Table 2 shows that the sum of their surface concentrations is roughly constant ($\sim(5-7.3) \times 10^{-7}$ mol/m^2) for latexes L1−L4, but for L5 it is $\sim 23 \times 10^{-7}$ mol/m^2. It may be that the relative hydrophobicity of L1−L4 plays a role in initiation by affecting reagent access to the initiators, or the much higher local concentration of initiator on L5 may simply allow a more efficient reaction to occur within the surface region.

While in most cases grafting density increases with increasing surface initiator concentration, L2 and L3 are reversed in order in this regard (Figure 3). L2 has a much higher surface charge than L3, while only a small difference in initiator concentration is present, so it may be that the ligand concentrating effect of the higher surface charge dominates over the slightly higher initiator concentration on L3 in this instance.

All of these experiments were carried out at relatively high monomer concentrations compared to those in our earlier report[17] in order to minimize the probability of chain transfer to catalyst complex or solvent as we showed this reaction was reduced at higher monomer concentrations.[17] At these higher concentrations monomer depletion effects should also be minimized near the surface as the chains initiate and begin to grow.

Figure 4 illustrates the dependence of graft density on surface initiator concentration, plotted as a log−log plot to capture the magnitude of the variation. The figure and Table 3 show that there is a very strong dependence of chain density on initiator concentration. The graft density varies by over a factor of 1000 while the surface initiator concentration varies by a factor of only ~34. Figure 4 shows that the relationship is essentially linear on the log−log plot, with only a small spread associated with monomer concentration effects. The plot has an average slope of 2.6 ± 1.5, implying that the graft density varies as [initiator]$^{2.6}$, a highly nonlinear relationship.

As we have discussed previously, surface initiation in this system is complex because of the fixed negative charge, polystyrene hydrophobicity, low solvent concentration, and high chain density in the region in which the initiator is accessible to aqueous reagents.[17] Estimates of the depth of this region are given in Table 2. The most important influence on the initiation reaction, however, seems to be the presence of the charged sulfonic acid groups in the surface region which form the termini of the shell copolymers. These groups must be neutralized by ions from solution, in this case the positively charged Cu(I) and Cu(II) complexed with ligand, as there are no other ions in the system.

We know little about the nature of the interaction between the sulfonic acids and the positively charged complexes, particularly in the presence of low water activity and high surface hydrophobicity. It is possible that the interaction could either enhance or inhibit the initiation reaction. For instance, the concentration of negative surface charge in the surface region is much higher than the average Cu(I) or Cu(II) concentration in solution. Since the surface phase must be electrically neutral, the surface region will be concentrated in the two cations relative to the bulk solution. The high local concentration of complex in principle could enhance the initiation rate relative to a case in which surface charge was lower or absent, in which case increasing surface charge would increase initiation. On the other hand, since the ionic strength of the medium is quite low, the positively charged catalyst complexes could associate strongly with the sulfonic acid groups and be less

Table 6. Comparison of Solution Polymer and Graft Polymer for Latex L4[a]

	monomer concn (wt %)	graft polymer M_w	graft polymer M_w/M_n	solution polymer M_w	solution polymer M_w/M_n
PMDETA/CuCl	5.88	407 000	1.50	420 000	2.14
	8.23	674 000	1.41	614 000	2.05
	10.3	486 000	1.76	484 000	1.69
HMTETA/CuCl	5.88	524 000	1.36	521 000	1.90
	8.23	908 000	1.34	974 000	1.58
	10.3	1 334 000	1.36	1 307 000	2.17

[a] PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine; HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine.

available to initiate radical formation on the HEA−Cl groups than in a less negative or electrically neutral environment. Increasing surface charge would then tend to inhibit initiation, all other factors being equal. Since both the initiator and monomer are electrically neutral, electrostatic factors will not directly affect their reactions.

The data in Figure 4 show that the latexes differ very significantly in the magnitude of the chain densities achieved. The three factors expected to determine these values are the monomer concentration, initiator surface concentration, and the surface charge (assuming constant ligand and Cu(I) and Cu(II) concentrations, as is the case here). The monomer concentration has very little effect. The ∼34-fold change in surface concentration of initiator produced >1000-fold change in chain density, suggesting the remaining factor, the charge density, also plays a role. As was discussed above, the charge density varies throughout the latex series (Table 2) because it is determined by properties of the copolymerization reactions that form the surface initiator layers. It is a difficult parameter to vary independently. In general, it decreases through the series L1−L5 as the initiator concentration increases so the correlation is that lower surface charge is associated with higher graft density, suggesting an inverse relationship between the two parameters. If the ratio of initiator concentration to surface charge is calculated, it varies by a factor of ∼72 through the series, a larger range than the initiator itself, providing some degree of support for this concept. Of the two potential mechanisms associated with the surface charge, then, that in which it acts to reduce the availability of Cu(I)/Cu(II) complex for reaction with initiator or free radicals seems the more likely from this indirect evidence.

In our previous discussion of the surface model,[17] we pointed out the role of chain transfer to solvent or ligand, finding that more occurred at low monomer concentration when latex with a high initiator concentration was used. In the present work we have not been able to measure the fraction of conversion that went into solution polymerization, but in one case we have analyzed the molecular weight properties of the grafted and solution polymers formed, shown in Table 6 for latex L4. The chains released from the grafted surface and those recovered directly from solution before cleavage have very similar molecular weights, although the polydispersity is greater for the solution reaction. The similarity in molecular weights strongly suggests that chain transfer has occurred very early in the reaction, most likely when the initiator first reacts with a catalyst complex and forms a free radical, as discussed elsewhere.[17] Control over the solution polymer is poorer than that for the released graft because reaction conditions have been optimized for the grafts, not the free solution product.

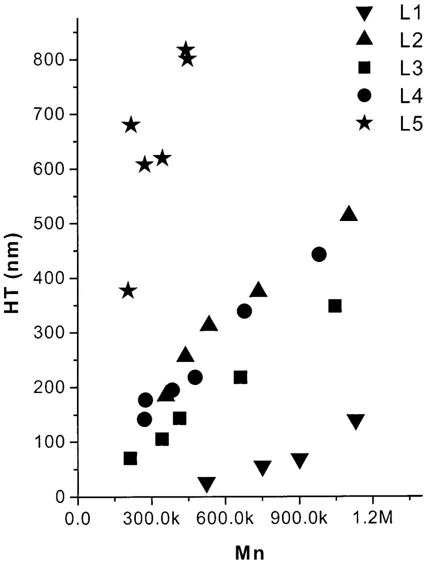


Figure 5. Variation of brush hydrodynamic thickness with molecular weight of grafted PDMA cleaved from different latexes measured by GPC-MALLS. Hydrodynamic thicknesses were obtained by particle size analysis; experimental conditions as in Figure 2 and Table 3.

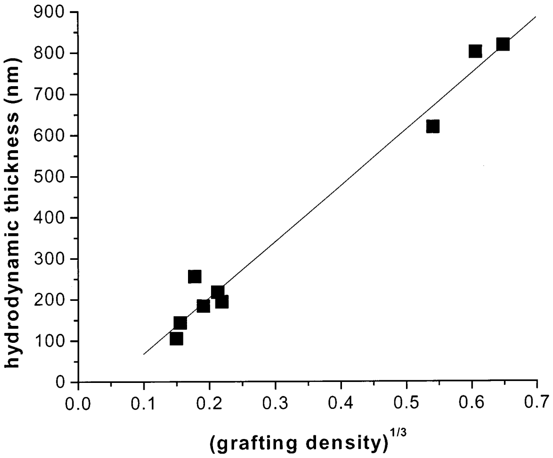


Figure 6. Variation of hydrodynamic thickness with (grafting density)$^{1/3}$; experimental conditions as for Figure 2 and Table 3. Least-squares best-fit line is shown.

The data in Tables 3 and 4 indicate that for all the cases illustrated chain separation is less than twice the radius of gyration of the released chain, implying that a brush conformation dominates on the surface. Theoretical predictions for the extension of the chains away from the surface state that the brush extension ought to depend on both the molecular weight and the chain density. At constant chain density the extension is predicted to vary linearly with molecular weight, and at constant molecular weight the extension should vary as the cube root of the chain density.[30−32] These two predictions are tested in Figures 5 and 6, utilizing the hydrodynamic thickness, as determined from the change in diffusion constant of the shell latex as chains are added, as the measure of brush extension. Both predictions are supported quite well, particularly the dependence on graft density, despite a variation in molecular weight from point to point over the range 350 000−

450 000. The graft density is not constant for L5; thus, the hydrodynamic thickness in Figure 5 is somewhat less linear with M_n in this case. For L2, L3, and L4 the grafting density remains almost constant, and the plots are reasonably linear, as predicted. The data for Ll appear to be nonlinear as well, perhaps because for these chains the ratio of average separation to radius of gyration D/R_g lies in the range $2 > D/R_g > 1$. While this is formally in the brush regime,[30,31] some mushroom character would be expected to be present on statistical grounds, which may explain some of the nonlinearity observed. The differences in slope seen in Figure 5 are due to the chain density dependence, which obeys the predicted cube root behavior quite well at intermediate M_n values, despite small variations in M_n for the points illustrated.

Summary

We have successfully synthesized PSL surfaces with different initiator concentrations by changing the feed ratio of styrene to HEA−Cl in a series of shell-growth copolymerizations. The surface concentration of initiator accessible to aqueous reagents does not directly reflect the monomer feed ratio, particularly at low initiator concentrations. We have delineated the dependence of aqueous ATRP grafting of PDMA on the surface concentration of initiator. We find a highly nonlinear dependence of chain density on surface concentration of initiator but a very weak dependence on monomer concentration. The surface charge density seems to play a role in this dependence, chain density increasing at lower charge densities. This suggests that the catalyst complex, while strongly increased in concentration relative to the bulk solution, may be associated with the sulfonic acid groups making up the surface charge, reducing access to surface initiation sites. The molecular weight of the grafts and the properties of the grafted polymer layer can be tuned by controlling the initiator concentration on the surface. With this approach we have synthesized well-characterized polymer layers with M_n up to 1.2×10^6, interchain separations from >50 nm to as low as 1.1 nm, and hydrodynamic thicknesses from a few nanometers to ~800 nm.

Acknowledgment. We thank the Canadian Institutes of Health Research, The National Science and Engineering Research Council of Canada, and the Canada Foundation for Innovation for financial support.

Supporting Information Available: Unimodal analysis results from N4 Plus particle size analyzer for shell latexes L1 to L5. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Delamarche, E.; Benard, A.; Schmid, H.; Bietsch, A.; Michel, B.; Biwbuyxk, H. A. *J. Am. Chem. Soc.* **1998**, *120*, 500.
(2) Niu, Q. J.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 667.
(3) Milner, S. T. *Science* **1991**, *251*, 905.
(4) Tran, Y.; Auroy, P. *J. Am. Chem. Soc.* **2001**, *123*, 3644.
(5) Hritcu, D.; Muller, W.; Brooks, D. E. *Macromolecules* **1999**, *32*, 565.
(6) Prucker, O.; Ruhe, J. *Macromolecules* **1998**, *31*, 592.
(7) von Werne, T.; Patten, T. E. *J. Am. Chem. Soc.* **2001**, *123*, 7497.
(8) 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.
(9) Jordan, R.; Ulman, A.; Kang, J. F.; Rafailovich, M. H.; Sokolov, J. *J. Am. Chem. Soc.* **1999**, *121*, 1016.
(10) Ingall, M. D. K.; Honeyman, C. H.; Mercure, J. V.; Bianconi, P. A.; Kunz, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 3607.
(11) Jordan, R.; Ulman, A. *J. Am. Chem. Soc.* **1998**, *120*, 243.
(12) Zhao, B.; Brittain, W. J. *Macromolecules* **2000**, *33*, 8813.
(13) Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **1998**, *31*, 5934.
(14) Kim, J.; Bruening, M. L.; Baker, G. L. *J. Am. Chem. Soc.* **2000**, *122*, 7616.
(15) Guerrrinni, M. M.; Charleux, B.; Vairon, J. P. *Macromol. Rapid Commun.* **2000**, *21*, 669.
(16) Perruchot, C.; Khan, M. A.; Kamitsi, A.; Armes, S. P.; von Werne, T.; Patten, T. E. *Langmuir* **2001**, *17*, 4479.
(17) Jayachandran, K. N.; Takacs-Cox, A.; Brooks, D. E. *Macromolecules* **2002**, *35*, 4247. (b) Jayachandran, K. N.; Takacs-Cox, A.; Brooks, D. E. *Macromolecules* **2002**, *35*, 6070.
(18) Xiao, D.; Wirth, M. J. *Macromolecules* **2002**, *35*, 2919.
(19) Huang, W. X.; Kim, J. B.; Bruening, M. L.; Baker, G. L. *Macromolecules* **2002**, *35*, 1175.
(20) Jones, D. M.; Huck, W. T. S. *Adv. Mater.* **2001**, *13*, 1256.
(21) Bontempo, D.; Tirelli, N.; Masci, G.; Crescenzi, V.; Hubbell, J. A. *Macromol. Rapid Commun.* **2002**, *23*, 417.
(22) Jones, D. M.; Brown, A. A.; Huck, W. T. S. *Langmuir* **2002**, *18*, 1265.
(23) Yamamoto, S.; Ejaz, M.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2000**, *33*, 5608.
(24) Goodall, A. R.; Hearn, J.; Wilkinson, M. C. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1019.
(25) Van den Hul, H. J.; Vanderhoff, J. W. *Br. Polym. J.* **1970**, *2*, 121.
(26) Brandrup, J., Immergut, E. H., Eds.; *Polymer Handbook*; John Wiley & Sons: New York, 1989.
(27) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991.
(28) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1991.
(29) 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.
(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.

MA021337J