# Surface Initiation of Living Radical Polymerization for Growth of Tethered Chains of Low Polydispersity

**X. Huang and M. J. Wirth***

*Department of Chemistry & Biochemistry, University of Delaware, Newark, Delaware 19716*

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## Introduction

Tethered polymer chains on surfaces are of fundamental interest[1] and are important for chemical separations, sensors, and composite materials, where the ability to control the thickness of the polymer film on the nanometer scale is important. One method of controlling the molecular weight of tethered polymers is to graft living polymers synthesized in solution.[2,3] While this provides precise control of molecular weight, the molar coverage decreases with increasing molecular weight, sacrificing control of film thickness. A second method is to grow the polymer layer by layer;[4−7] however, this becomes laborious for thick films and is not applicable to a wide range of functional groups. Hyperbranched polymers provide a novel means of performing surface polymerization,[8] although the scheme is also not generally applicable. There is a need for a generally applicable means of preparing uniform films of tethered polymer chains on surface with controlled molecular weight and film thickness.

Surface-initiated living polymerization is promising as a new means of controlling growth of tethered polymer chains because the ends of the chains would remain reactive, potentially allowing indefinite molecular weight and film thickness, both controlled through monomer concentration. This is expected from the growth rate of polymer chains, $-\mathrm{d[M]/d}t$, which is first order in both monomer concentration, [M], and radical concentration, [R•].

$$-\mathrm{d[M]/d}t = k[\mathrm{M}][\mathrm{R}^\bullet] \qquad (1)$$

In the absence of termination reactions, which is the hallmark of living polymerization, [R•] is constant. Thus, surface-initiated living polymerization is expected to give both a molecular weight and a film thickness that increase in proportion to the monomer concentration for a fixed reaction time. Recently, it has been demonstrated that living cationic polymerization can be initiated on a surface, giving a 100 Å film of poly(*N*-propionylethylenimine).[9] The grafting density and molecular weight distribution have not yet been characterized in this case. Previously, surface-initiated cationic living polymerization of poly(*p*-methoxystyrene) was carried out on silica;[10] however, the polymerization was not restricted to the surface.

We describe the surface-initiated living radical polymerization of acrylamide on silica gel, illustrated in Scheme 1. The design of this reaction scheme is based on advances in the atom-transfer radical polymerization of styrene and methacrylate in bulk and solution, where polymers with controlled molecular weight and narrow polydispersity have been prepared.[11−17] This living radical polymerization relies on the equilibrium between the dormant and active chain ends, with the equilibrium preferring the dormant species, as illustrated in the first step of Scheme 1.

The surface initiator in this case is benzyl chloride in a self-assembled monolayer made from 1-trichlorosily-2-(*m*-*p*-chloromethylphenyl)ethane, and the surface is silica. The low concentration of radical minimizes chain termination and transfer reactions. Acrylamide then reacts with the surface-bound radical. We have previously shown that a film of 100 Å in thickness can be grown by this scheme on porous silica having an average pore diameter of 860 Å, without blocking the pores.[18] This confirms that the polymerization is restricted to the surface. We have further shown by infrared spectroscopy that the film thickness is proportional to monomer concentration over the range 0−100 Å, and we have shown by atomic force microscopy that the 100 Å film has a root-mean-square roughness of only 5 Å.[19] These characteristics support the notion that the polymerization is living; however, the steric hindrance among the tethered polymer chains could act to terminate chain growth. A characterization of the molecular weight distribution is thus needed for a more complete understanding, and this characterization is presented here for the film at its thickest extreme.

## Experimental Section

Acrylamide (electrophoresis grade, 99.9% minimum) and *N*,*N*-dimethylformamide were purchased from Fisher Scientific. 2,2′-Dipyridyl (bpy) (99+%) and copper(I) chloride (98+%) were from Aldrich. 1-Trichlorosily-2-(*m*-*p*-chloromethylphenyl)-ethane was from United Chemical Technology, Inc. All chemicals were used as received. Pure water (18 MΩ cm) was obtained using a Barnstead E-pure system.

The atom-transfer polymerization of acrylamide was carried out in solution using DMF as the solvent at 130°. A 24 h reaction time was used for a 0.01 M concentration of benzyl chloride and a 1.75 M concentration of acrylamide. The MALDI mass spectrometer used was a Finnigan MAT Vision 2000 (HEMEL Hempstead, England). The polyacrylamide was dissolved in pure water to make 0.5 mg/mL solution. 2,5-Dihydroxybenzoic acid, which was used as the matrix, was dissolved in pure water to prepare a 10 mg/mL solution. The polyacrylamide and matrix solutions were mixed by 1:1 volume ratio. A 1 $\mu$L aliquot of the mixed solution was spotted on the gold-coated sample plate and dried in air. Mass spectra were obtained in the reflectron mode operated at 5 kV ion acceleration and 20 kV postacceleration.

Polyacrylamide films were grown on porous silica gel obtained from YMC, Inc. (mean particle diameter = 5 $\mu$m, mean pore diameter = 860 Å, and surface area = 36 $m^2/g$). The procedures were the same as before,[18] with a 40 h reaction time in 130° DMF, and a 5 M concentration of acrylamide, which was chosen to give a film thickness on the order of 100 Å.[19] To cleave the polymer chains, the polyacrylamide-coated porous silica was mixed with 10% (W/W) HF in a 50 mL round flask and stirred for 2.0 h. Then the mixture was neutralized by adding sodium carbonate and filtered to remove the silica particles. Microanalysis of the silica particles before and after the HF treatment confirmed that all organic material had been removed. The aqueous filtrate of cleaved polyacrylamide was analyzed by GPC, which avoids the possibility of fractionation.

The GPC was performed using a Perkin-Elmer LC-100 pump, a Hitachi AS-4000 auto sampler, a Perkin-Elmer LC-

* Corresponding author.

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**Scheme 1**

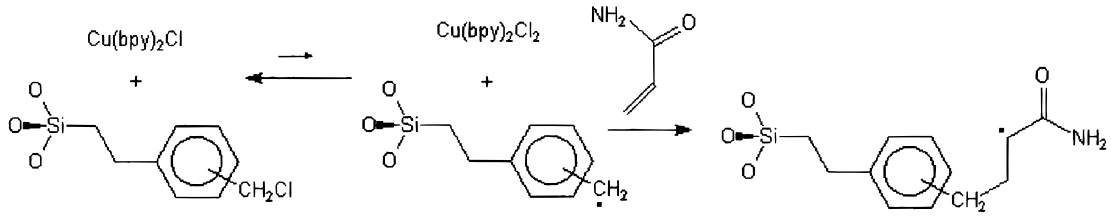


**Table 1. Summary of Molecular Weight and Polydispersity Indices (PDI) for the Polymer Standards and the Surface-Initiated Polymer; for the Latter, the Percent Carbon from Microanalysis and the Surface Molar Density Are Shown**

| polyacrylamide | $M_n$ | $M_w$ | PDI | % carbon | density ($\mu$mol/m$^2$) | $M_n$/[acrylamide] (kD/M) |
|---|---|---|---|---|---|---|
| 10 kD standard | 7 600 | 11 530 | 1.52 | | | |
| 15 kD standard | 12 800 | 15 500 | 1.21 | | | |
| 20 kD standard | 13 700 | 21 900 | 1.60 | | | |
| surface, 4.3 M | 13 100 | 17 030 | 1.30 | 9.9 | 0.24 | 2.3 |
| surface, 4.5 M | 13 550 | 15 580 | 1.15 | 10.4 | 0.24 | 2.3 |
| surface, 5.1 M | 15 200 | 17 480 | 1.15 | 11.9 | 0.24 | 2.3 |

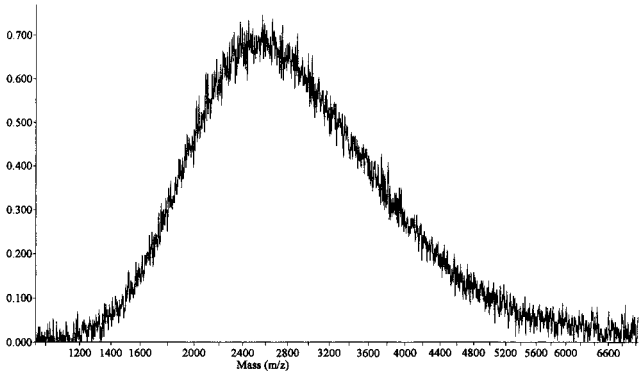


**Figure 1.** MALDI mass spectrum of polyacrylamide prepared in solution by atom-transfer living radical polymerization. $M_n$ = 2949, $M_w$ = 3283, and PDI = 1.11.

30 RI detector, and a TSK-Gel column from TOSOHAAS. The flow rate was 0.8 mL/min. Three polyacrylamide standards (10K, 15K, and 20K) were from American Polymer Standard Corp. All the samples were prepared in E-pure water, and the concentration was 2.0 mg/mL.

## Results and Discussion

The MALDI spectrum of the polyacrylamide made by polymerization in solution is shown in Figure 1. The calculated polydispersity index is 1.11, establishing that a narrow molecular weight distribution is achieved in solution under the conditions used for the surface-initiated polymerization.

The gel permeation chromatograms of commercial polyacrylamide standards are shown in Figure 1a−c. The narrow chromatogram of Figure 1b owes to the sample being fractionated by the supplier to reduce its molecular weight distribution. The chromatograms for three samples of cleaved surface-initiated polyacrylamide, prepared at different monomer concentrations, are shown in Figure 2d−f. The sample made using 5.1 M acrylamide gave a film thickness of 100 Å.[19] The chromatograms show that the cleaved polyacrylamide samples give narrower chromatograms than the commercial standards that had no prior fractionation. The molecular weights and polydispersity indices for the three standards and the three samples are summarized in Table 1. The number-average molecular weights for the cleaved polymers span the range of 13−15 kD, comparable to the range of the standards.

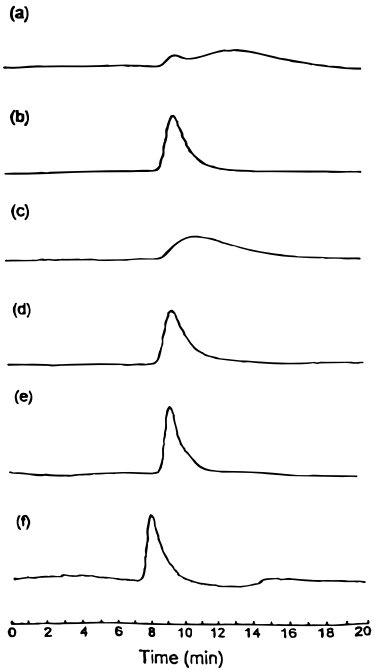


**Figure 2.** Gel permeation chromatograms of polyacrylamide samples: (a−c) commercial standards of 11.5, 15.5, and 21.9 kDa, respectively; (d−f) cleaved polymer from surface-initiated polymerization, using 4.3, 4.5, and 5.1 M acrylamide, respectively.

The polydispersity indices are consistent with what is expected from living polymerization (PDI < 1.5) for all three of the cleaved samples. The ratio $M_n$/[acrylamide], included in Table 1, is the same in each case, indicating that the film growth is reproducible. The percent carbon (% C) for each of the samples before HF treatment is listed in Table 1. The % C can be combined with the average molecular weight to calculate the average chain density, which is shown in Table 1 to be 0.2 $\mu$mol/m$^2$ in each case. This is comparable to chain densities reported for grafted living polymers[2,3] and is low enough to accommodate two successive gauche conformations of the carbon backbone. Conformational disorder is probably a factor in governing the chain density.

The narrow molecular weight distribution, combined with the previous result showing the proportionality between film thickness and monomer concentration,

supports the conclusion that living polymerization occurs for these films. This means that the living ends of the chains must be sterically accessible for reaction on the time scale of the film growth. While some termination of chains due to steric inaccessibility might be occurring, the lack of any tail in the chromatogram toward high molecular weight indicates that steric inaccessibility is not a significant factor. The gel permeation chromatograms thus provide critical data to establish that the film growth occurs through living polymerization.

The ability to control film thickness through monomer concentration for a fixed reaction time will facilitate the use of polymer films in nanomaterials. Since the ends of the chain are living, alternate layers of polymer films having different chemical, electronic, or optical properties could be grown. The silica/polymer composites prepared here have the potential to combine the advantage of silica gel (high separation efficiency) with the advantage of polymer resins (chemical inertness) for purification of biotechnology products and recovery of wastewater, both of which are presently performed inefficiently by polymer resins. The results suggest the ability to prescribe a molecular weight through the experimentally controllable monomer concentration. Possible applications are discussed in a review paper.[20] Since the date our work was completed, another means was reported for growing polymer chains on surfaces by atom-transfer polymerization.[21] This work employed an immobilized monolayer of chlorosulfonylphenyl groups on a silicon wafer, and it was demonstrated that films of poly(methyl methacrylate) could be controlled in thickness. A greater variety of initiators for growth of polymer chains from surfaces will broaden the number of applications possible.

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