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Formation of Grafted Macromolecular Assemblies with a Gradual Variation of Molecular Weight on Solid Substrates

Michael R. Tomlinson and Jan Genzer*

Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905

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The development of new polymeric materials and structures relies primarily on controlled polymerizations, chain growth polymerizations that proceed without irreversible chain transfer, and chain termination. Recent advances in living radical polymerizations have led to the advancement of robust and simple polymerization methodologies. In particular, atom transfer radical polymerization (ATRP), pioneered by Sawamoto[1] and Matyjaszewski,[2] provides a convenient means of synthesizing end-functionalized and body-functionalized polymers, thereby enabling the synthesis of a variety of polymer architectures, including block copolymers, multiarmed stars, hyperbranched polymers, and polymer combs with well-defined composition and relatively low molecular weight polydispersities.[3] Many types of monomers including acrylates, methacrylates, styrenes, vinylpyridines, acrylonitrile, and acrylamides have been polymerized successfully via ATRP.

Continuous molecular gradients represent chief tools for combinatorial chemistry and materials science.[4,5] These multivariant methods enable systematic variation of one or more physicochemical properties, thus enabling systematic exploration of the broad parameter space, improved efficiency, and lower cost.[6] Surface-tethered polymer structures represent an effective means of tuning the physicochemical properties of substrates. Recently, techniques, involving the patterning of polymer layers grafted to the substrate, have been developed that utilize ATRP.[7−14] The latter group of technologies is based on selectively decorating the material surfaces with polymerization initiators and then performing the polymerization directly on the surface ("grafting from"). In this Communication we report on creating surface-grafted layers with a gradual variation of polymer molecular weight (or length). We use ATRP of methyl methacrylate (MMA) from water/methanol solution. Previous reports indicated that such polymerization proceeds rapidly even at a room temperature.[11,15]

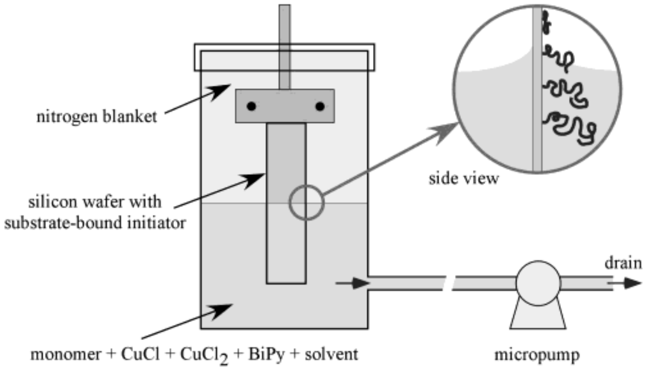

Figure 1. Schematic of the apparatus for creating surface-grafted polymer assemblies with a gradient in molecular weight. The chamber is loaded with a solution comprising a monomer, bipyridine, $CuCl_2$, and the solvent. The chamber is then purged with nitrogen in order to remove oxygen. CuCl is added, and the silicon wafer, covered with a chemisorbed ATRP initiator, is lowered into the solution. During the reaction, the micropump removes the solution from the chamber causing a steady decrease in the vertical position of the three-phase (substrate/solution/inert) contact line. The profile (including the "steepness") of the polymer brush length gradient on the substrate can be controlled by varying the removal rate.

Surface-bound macromolecular assemblies with position-dependent molecular weight were prepared in a custom-designed apparatus shown schematically in Figure 1. Silicon wafer ($\approx 1 \times 5$ cm) was first covered with (11-(2-bromo-2-methyl)propionyloxy)undecyltri-

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* Corresponding author: e-mail Jan_Genzer@ncsu.edu; Tel +1-919-515-2069.

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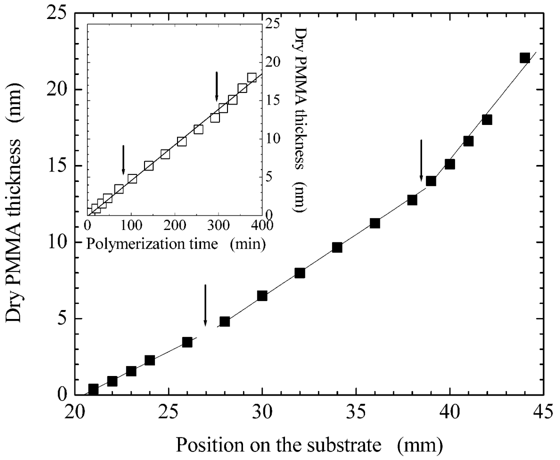

Figure 2. Dry poly(methyl methacrylate) thickness as a function of the position on the silica substrate. The polymerization of methyl methacrylate (MMA) was carried out at room temperature using 32.7 g of MMA, 25.5 g of methanol, 7.0 g of deionized water, 2.06 g of bipyridine, 0.66 g of CuCl, and 0.04 g of $CuCl_2$. The inset shows the dry poly(methyl methacrylate) thickness as a function of the polymerization time. The arrows mark instances where the drain speed of the polymerization solution from the chamber was decreased relative to the previous drain speed. The lines are meant to guide the eye.

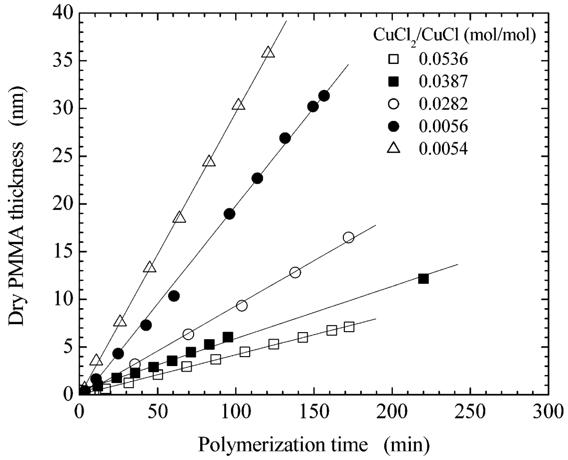

Figure 3. Dry poly(methyl methacrylate) thickness as a function of the polymerization time for various $CuCl_2$/CuCl ratios: 0.0536 (□), 0.0387 (■), 0.0282 (○), 0.0056 (●), and 0.0054 (△). The amounts of methyl methacrylate, methanol, deionized water, bipyridine, and CuCl were the same as those indicated in Figure 2. The lines are linear fits to the data.

chlorosilane (BMPUS), which served as an initiator for the ATRP.[16] Experiments using variable-angle spectroscopic ellipsometry (VASE, J.A. Woollam, Co.) confirmed that only a monolayer of BMPUS was formed on the substrate and that the BMPUS molecules were homogeneously distributed on the substrate. The polymerization of MMA was carried out at room temperature using 32.7 g of MMA, 25.5 g of methanol (MeOH), 7.0 g of deionized water, 2.06 g of bipyridine (BiPy), 0.66 g of CuCl, and 0.04 g of $CuCl_2$. Tubing, attached at the bottom of the chamber, is connected to a micropump, which controls the solution flow rate removal from the chamber. Figure 2 shows the dry thickness of PMMA (measured by VASE) as a function of the position on the substrate. The inset shows the dependence of the dry PMMA thickness on the polymerization time. The data in the inset demonstrate that the brush thickness increases linearly with polymerization time, in accord with previous reports.[2,11] We tested the effect of varying the volumetric flow of the drained solution on the polymer properties along the substrate. The arrows in Figure 2 mark the instances where the solution removal speed was reduced relative to the previous drain rate. As apparent from the data in Figure 2, changing the drain speed of the solution from the chamber does not affect the polymerization rate (defined as the slope of the dry polymer thickness vs polymerization time; see discussion below) but influences the “steepness” of the gradient. This behavior is a result of the large excess of MMA in the polymerization solution.

Figure 3 depicts the dry PMMA thickness as a function of the polymerization time for various $CuCl_2$/CuCl ratios. In this set of experiments we used the same quantities of MMA, MeOH, H_2O, BiPy, and CuCl and varied the amount of $CuCl_2$. The results in Figure 3 reveal that the dry thickness of the surface-anchored PMMA increases linearly with increasing polymerization time. Moreover, this increase is more rapid for smaller $CuCl_2$/CuCl ratios. This finding is not surprising given the nature of the reaction. The key reaction in ATRP is the reversible activation−deactivation process using metal (M)/ligand (L) complexes[2,3]

$$\mathrm{P{-}X + M^{I}X/2L \underset{k_d}{\overset{k_a}{\rightleftharpoons}} P^{*} + M^{II}X_2/2L} \qquad (1)$$

where k_a and k_d are the rate constants for activation and deactivation, respectively, M is usually Cu, and X is Cl or Br. The propagating radical, P*, produced by the halogen atom transfer from P−X to the $M^{I}X/2L$ complex, will undergo polymerization until it is deactivated by the $M^{II}X_2/2L$ complex. The quick speed of the activation−deactivation cycles compared to the rate of polymerization and the low concentration of the active species (relative to the P−X ones) results in polymers with narrow polydispersities. MCl_2 may be added to the reaction mixture to regulate the reaction rate and chain polydispersity. The combinatorial design of our system is conveniently suited for such studies because it allows for complete probing of the anchored polymer properties and studying the polymerization kinetics in confined geometries.

More insight into the ATRP polymerization on solid substrates can be obtained by evaluating the polymerization rate as a function of the $CuCl_2$/CuCl ratio. Matyjaszewski and co-workers established that the rate of ATRP polymerization, R_p, is given by eq 2[2,3]

$$R_p = k_p \frac{k_a}{k_d}[\mathrm{PMMA - Cl}][\mathrm{MMA}]\frac{[\mathrm{CuCl}]}{[\mathrm{CuCl_2}]} \qquad (2)$$

where k_p is the rate constant for propagation, [PMMA−Cl] is the concentration of the growing ends of the grafted polymer, [MMA] is the concentration of the free monomer in the solution, and [CuCl] and [$CuCl_2$] are the concentrations of CuCl and $CuCl_2$, respectively. The dry thickness of PMMA on the substrate, h, is related to the polymer molecular weight, M_{PMMA}, through eq 3

$$h = M_{\mathrm{PMMA}}\frac{\sigma}{\rho_{\mathrm{PMMA}}N_{\mathrm{A}}} \qquad (3)$$

where σ is the polymer grafting density, ρ_{PMMA} is the PMMA density, and N_A is Avogadro’s number. Recog-

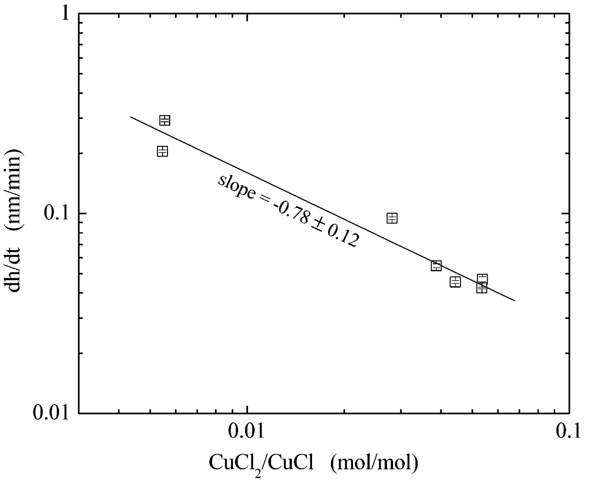

Figure 4. Change of the dry poly(methyl methacrylate) thickness with polymerization time (dh/dt) as a function of the CuCl$_2$/CuCl ratio. The dh/dt values were obtained by fitting the experimental values of h vs t in Figure 3.

nizing that $R_p \sim dh/dt$ and lumping the terms that stay constant during the polymerization, one arrives at eq 4

$$\frac{dh}{dt} \sim \left(\frac{[\mathrm{CuCl_2}]}{[\mathrm{Cu}]}\right)^{-1} \tag{4}$$

Figure 4 depicts the dh/dt obtained by fitting the dry thickness vs polymerization time data (cf. Figure 3) as a function of the CuCl$_2$/CuCl ratio. By fitting the data to a line on the logarithmic scale, we obtain an exponent of $\approx -0.78 \pm 0.12$. This value is a slightly lower than the exponent predicted by the scaling argument presented in eq 4. There are multiple factors that may influence the absolute value of the exponent. First, the slope (=dh/dt) is extremely sensitive to the amount of CuCl$_2$ at very low CuCl$_2$ concentrations (cf. Figure 3). Second, the scaling argument in eq 4 is derived from the ATRP polymerization rate that has been derived for bulk polymerization and does not take into account any constraints due to confinement effects. Third, at low CuCl$_2$ content the ATRP polymerization proceeds quite rapidly (cf. Figure 3), and the nature of the reaction is less controlled relative to the situations at higher CuCl$_2$ concentrations.

We envision that this simple technology can lead to several key advancements in the field of thin polymer films. In addition to the ability of monitoring the kinetics of polymerization on a single sample, this technique can be utilized to generate complex polymer assemblies, such as block copolymers with gradually variable block lengths.[17] These can in turn be utilized as position-dependent sensors. Moreover, when combined with the method of preparing surface-bound polymers with gradients in grafting density,[14] one can generate substrates with orthogonal variation of molecular weight and grafting density. The latter set of structures will enable a convenient means of protein separation and will facilitate multivariant studies of molecular and macromolecular adsorption.

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