Communications to the Editor

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

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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 Sawamoto1 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 polydisperisities.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 Surface-bound macromolecular assemblies with position-dependent molecular weight were prepared in a custom-designed apparatus shown schematically in Figure 1. Silicon wafer (≈1 × 5 cm) was first covered with (11-(2-bromo-2-methyl)propionyloxy)undecyltri-

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chlorosilane (BMPUS), which served as an initiator for the ATRP. 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, 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 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.

As apparent from the data in Figure 2, changing the solution removal speed was reduced relative to the previous drain rate. 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$_2$O, 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

$$P-X + M^{1/2L} \frac{k_a}{k_d} P^* + M^{1/2L}$$

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$^{1/2L}$ complex, will undergo polymerization until it is deactivated by the M$^{1/2L}$ 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

$$R_p = \frac{k_p}{k_d}[PMMA - Cl][MMA][CuCl] \frac{[CuCl]}{[CuCl}_2]$$

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

$$h = \frac{M_{PMMA}}{\rho_{PMMA}} \frac{\sigma}{N_A}$$

where $\sigma$ is the polymer grafting density, $\rho_{PMMA}$ is the PMMA density, and $N_A$ is Avogadro’s number. Recog-
As position-dependent sensors. Moreover, when combined with the method of preparing surface-bound polymers with gradients in grafting density, 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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References and Notes