JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

Simultaneous Bulk- and Surface-Initiated Controlled Radical Polymerization from Planar Substrates

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Supporting Information

ABSTRACT: We employ Monte Carlo computer simulations to investigate the simultaneous controlled radical polymerization in solution and from a flat surface. The bulk polymers grow at faster rates and possess narrower molecular weight distribution than polymers initiated from flat, impenetrable surfaces. The rate of surface-initiated polymerization depends on the density of initiator sites. Our results provide evidence that the assumption that the molecular weight of surface-initiated polymers is equal to that of polymers grown in bulk, invoked often in determining the grafting density of surface-bound polymers, is generally invalid.

Surface-initiated controlled radical polymerization (SI-CRP) from planar substrates has been employed widely to produce substrate-anchored polymers with high grafting densities.[1−13] Despite widespread use of this methodology, there is a lack of direct experimental characterization of the molecular weight (M_n) and polydispersity index (PDI) of surface-bound polymers grown by SI-CRP. The lack of experimental data is mainly due to difficulties associated with measuring M_n and PDI, as it typically requires cleaving the polymers from the surface and probing them with size-exclusion chromatography (SEC). Unfortunately, the amount of polymer cleaved from planar substrates is low, resulting in prohibitive uncertainties in the SEC data.

A method to estimate M_n and PDI of the surface-grown polymers implemented frequently involves simultaneous polymerization on the surface and in bulk (cf. Figure 1). This approach allows for the characterization of the surface layer by assuming that the rates of polymerization and the resulting M_n and PDI of both classes of polymers are similar. Furthermore, by combining the average molecular weight of the surface-grown polymer ($\langle N\rangle_s$) thus obtained and the dry thickness of the polymer layer (h), one can estimate the polymer grafting density (σ):

$$\sigma = \frac{h\rho N_a}{\langle N\rangle_s} \tag{1}$$

where ρ is the bulk density of the polymers and N_a is Avogadro's number. Experimental attempts to verify these assumptions have provided mixed results.[6,14−18] Although some researchers[6] reported similar surface and bulk ($\langle N\rangle_b$) average molecular weights and PDI, others[17] observed significant differences between the M_n and PDI of these polymer populations. We show herein that $\langle N\rangle_s$ depends on σ, and that in eq 1 the assumption that $\langle N\rangle_s = \langle N\rangle_b$ should not be invoked if accurate estimates of σ are needed.

Previously, we employed Monte Carlo (MC) computer simulations to compare the properties of either bulk or surface polymers synthesized independently.[19,20] We demonstrated that polymers grown from flat surfaces exhibit higher PDIs relative to polymers initiated in bulk solutions under identical reaction conditions. In this Communication, we report on how the competitive growth between surface and bulk polymers affects their polymerization rates and PDIs. We show that the validity of the assumption that polymers initiated in bulk and on flat surfaces exhibit similar growth characteristics is limited; it depends on σ and the fraction of surface-bound (η) initiators.

Our methodology has been described previously.[19,20] We employ MC simulations based on the bond fluctuation model[21] and define the probability that a monomer near an active chain-end reacts. By neglecting any chain transfer or termination reaction, we model a true "living" polymerization process. To approximate the behavior seen in CRPs, polymer chains in our simulation can adopt either active or dormant states. Both chain states are allowed to move about the lattice, but only the active chains undergo propagation reaction. In order to probe systematically the effect of σ and η, we vary the lateral ($L_x = L_y$) and perpendicular (L_z) dimensions of the lattice while keeping constant the lattice volume, the total number of initiators ($I_o = 400$), the number of monomers ($M_o = 25\,000$), and the probabilities of the individual reaction events. We define a Monte Carlo time step (MCTS) as the number of MC steps needed so that, on average, every bead in the simulation undergoes an attempted move. Because we alter the dimensions of the simulation cell when we vary σ and η, it is necessary to truncate some data sets at low conversion values. Details on the truncation, the simulation parameters, and the initial configurations are available in the Supporting Information.

Recall that the polymerization rate can be written as

$$r_p = k_p[\mathrm{P}^\bullet][\mathrm{M}] \tag{2}$$

where k_p is the rate constant due to propagation, and $[\mathrm{P}^\bullet]$ and $[\mathrm{M}]$ are the concentrations of active radical chains and monomer, respectively. Equation 2 assumes implicitly that the system is well mixed and that both concentrations are invariant with the spatial location in the reaction vessel. For surface-initiated polymerization, the assumption of good mixing may break down if, for example, the kinetics of the reaction is faster than the diffusion time of monomer to the surface, or if simultaneous polymerization of

Received: August 29, 2011
Published: October 06, 2011

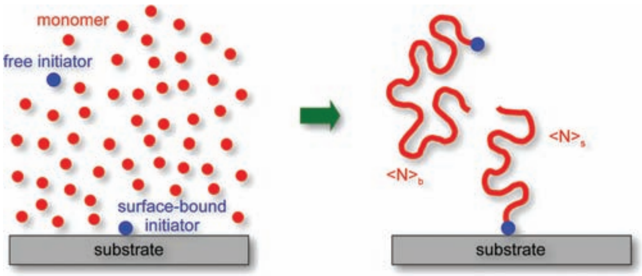

Figure 1. Schematic depicting simultaneous bulk- and surface-initiated polymerization.

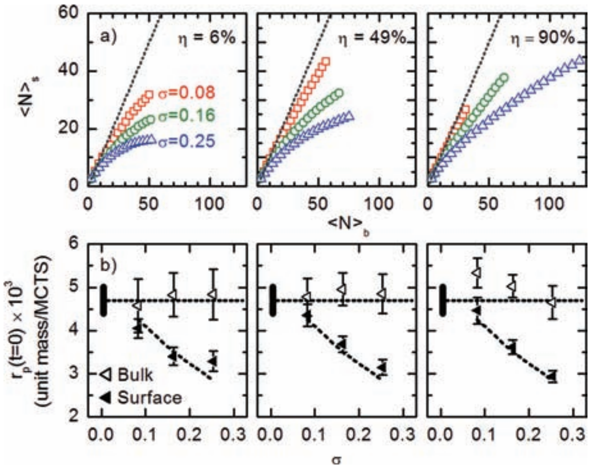

Figure 2. (a) Average molecular weight of the surface polymers as a function of the same quantity for bulk polymers at three values of the fraction of surface polymers. The gray dotted line represents the $\langle N \rangle_b = \langle N \rangle_s$ case. (b) Initial rate of polymerization for both surface and bulk polymers. The dotted lines represent the pure bulk and surface cases. The thick black line is the error of the pure bulk measurement.

bulk and surface polymers takes place in the system and the concentration of monomers in solution decreases substantially.

The data in Figure 2a show that, for all systems studied, $\langle N \rangle_b > \langle N \rangle_s$, invalidating the assumption of equal molecular weights of bulk and surface polymers. Furthermore, this difference increases with increasing σ and decreases with increasing η. At high values of σ, the rate of surface polymerization relative to the bulk decreases for two reasons. First, the presence of the surface prevents monomer delivery to the chain ends from all directions, thus reducing effectively [M] near the active chain ends. Second, the growing polymer layer may hide a fraction of the chain ends, thus reducing the effective concentration of monomers near the active ends.[20] Any surface-initiated polymerization scheme exhibits the latter effect to a certain extent. Polymerizing from flat surfaces therefore leads to an effective reduction of one or both concentration terms in eq 2.

If the growth rates of surface- and bulk-initiated polymers were identical, our results would be independent of η, since no matter where the polymers are located they would grow at the same pace. However, our results reveal that the relative molecular weights between surface- and bulk-initiated polymers depend on η (cf. Figure 2a). At low η the system consists primarily of faster-growing bulk polymers (Figure 2b) that compete with each other for the available monomers. They consume the monomers quickly, decreasing the monomer concentration and resulting in a quick plateau in $\langle N \rangle_s$. As η increases, the bulk polymers have to compete less with each other and more with the slower-growing surface-initiated polymers for the available monomers. The competition with slower-growing polymers leads to higher $\langle N \rangle_b$ than for the low η case. At higher η, the smaller number of faster-growing bulk polymers results in slower monomer consumption and increased availability of monomers for the surface polymers. The net effect is an increase in both $\langle N \rangle_b$ and $\langle N \rangle_s$ with increasing η.

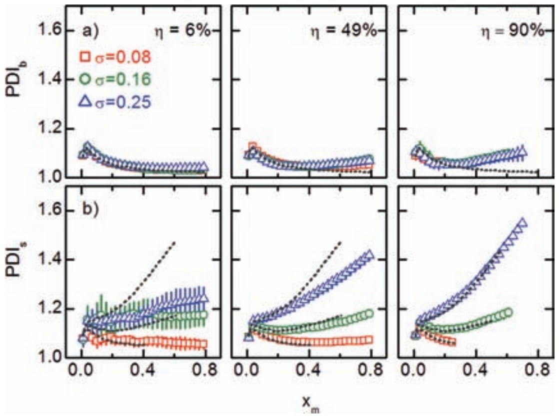

Figure 3. Polydispersity index for (a) bulk and (b) surface polymers as a function of the monomer conversion. The dotted lines represent (a) the η = 0% PDI and (b) the η = 100% PDI.

Experimentally, conflicting results on $\langle N \rangle_s$ and $\langle N \rangle_b$ for polymers grown simultaneously from surfaces and in solution have been reported; invariably they correspond to either the $\eta \ll 1\%$ (free initiator) or the $\eta = 100\%$ (no free initiator) case. When $\eta = 100\%$, no comparison to our results is possible because no bulk polymerization data are available. For $\eta \ll 1\%$, Koylu et al.[22] and Devaux et al.[23] reported lower molecular weight for the solution polymers than for the grafted ones, in disagreement with our results. When polymerization occurred from curved substrate, Husseman et al.[24] reported similar solution and grafted molecular weights ($\eta \ll 0.01\%$). Pasetto et al.[17] provided the most thorough experimental study of the issues discussed here, exploring the whole range of η values, and found $\langle N \rangle_b > \langle N \rangle_s$ in all cases. Gorman et al.[18] did not polymerize simultaneously but noted that identical polymerization solutions yielded lower molecular weights for cleaved polymers than for solution-grown ones.

In addition to differences in the average molecular weights of the bulk and surface polymer populations, changes in η and σ also affect their PDI$_s$ (cf. Figure 3). At high values of η and low values of σ, PDI$_b$ is comparable to PDI$_s$. As σ increases, PDI$_s$ increases, whereas PDI$_b$ remains unchanged. As σ increases, the crowding between growing surface chains increases. Any disparity in chain lengths results in the longer chains disrupting the delivery of monomers to nearby shorter chains.[20] This results in a difference in the polymerization rates of surface-initiated polymers as a function of their chain length, with longer chains growing at a faster rate (higher monomer availability).

We have shown herein that the polymerization rates and the PDIs of polymers initiated simultaneously in bulk and on a flat, impenetrable surface depend strongly on the polymer grafting density and the ratio of bulk to surface polymers. Our results reveal that the practice of polymerizing simultaneously bulk and surface polymers and assuming that both polymer populations possess equal average molecular weights is generally not valid and should be invoked with great caution and under conditions where η is controlled. The dependence of the average molecular weight on the grafting density precludes the use of eq 1 for precise estimation of σ.

ASSOCIATED CONTENT

Supporting Information. Input parameters for the simulations; initialization procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work was supported by the National Science Foundation (Grant No. DMR-0906572).

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