



# Comparison of chain-growth polymerization in solution versus on surface using reactive coarse-grained simulations



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## ABSTRACT

We developed a reactive coarse-grained model for chain-growth polymerization to study the chain length distribution of polymers grafted from a surface as compared to those grown in solution. The surface-initiated polymer chains exhibit a markedly broader distribution of chain lengths (larger dispersity) and slower chain growth kinetics as compared to the solution phase process. Two key factors that cause deviation from ideal grafting are identified: (1) the formation of chain “loops” with both termini attached to the substrate *via* recombination and (2) the “starvation” effect, in which the live chain ends of short polymers are sterically shielded from monomers by the presence of longer neighboring chains. Both effects are markedly amplified with increasing initiator surface density, thus limiting the density of high molecular weight chains grafted from the surface. Whereas the “loop” effect is absent in systems that are very strictly “living” (no termination), the starvation effect is likely operative in most real systems. Taken together, these results suggest a theoretical limit on the density of polymer brushes that can form on surfaces by a “grafting-from” technique, based on the kinetics of the chain-growth polymerization process.

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## 1. Introduction

Polymer brushes have recently attracted enormous scientific and commercial interest in a wide range of fields, including drug delivery [1,2], biosensing [3,4], anti-biofouling [5,6], patterned surface architecture [7,8], nanomaterials dispersion control [9,10], and stimuli-responsive materials [11,12]. Unlike conventional polymer films in which the chains are chemisorbed or physisorbed onto substrates in an uncontrolled manner, polymer brushes are well-defined single macromolecular layers formed by covalent attachment of the polymer terminal chain end to the substrate. High grafting density in polymer brushes induces a considerable degree of chain extension, thus giving rise to their unique properties [13,14].

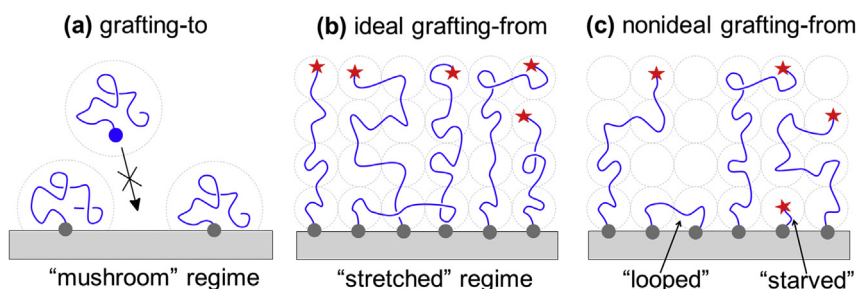
There are two fundamental approaches employed to synthesize polymer brushes: grafting-to [15] and grafting-from Refs. [16–19]. In the grafting-to approach (Fig. 1 a), premade polymer chains are covalently linked to a substrate by a chemical reaction between the terminal chain end and a reactive site on the substrate surface. This

strategy suffers from low grafting density due to the excluded volume effect. The ideal grafting-from (Fig. 1 b) approach, however, fundamentally overcomes this limitation *via* directly growing polymer chains from initiation sites bound to the substrate.

A variety of synthetic routes, including free radical [9,20–22], ionic [23], ring-opening [24,25], and controlled chain-growth polymerization [26] may be employed in the grafting-from approach. In particular, surface-initiated atom transfer radical polymerization (SI-ATRP) [27,28] is widely employed since it putatively yields brushes with high grafting density, well-controlled thickness, and relatively narrow molecular weight distribution (MWD) with low chain length dispersity ( $\bar{\Phi}$ ) [29]. Direct experimental characterization of the MWD and  $\bar{\Phi}$  for synthesized polymer brushes is extremely challenging due to the vanishingly small amount of polymer formed at the 2D interface in these experiments. Still, one successful attempt has been recently reported [30]. Most commonly, researchers circumvent this limitation by assuming that the MWD of a polymer synthesized in the solution phase without a surface, under otherwise identical conditions, is identical to that of the polymer brushes grown on a surface. Some experimental studies justified this approach in reporting similar [31], or nearly identical [32] MWD and  $\bar{\Phi}$  for polymers grown in solution and from substrates. However, other experimental studies

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**Fig. 1.** (a) In the "grafting-to" approach, surface chain density is limited by the hydrodynamic spheres. (b) In the ideal "grafting-from" case, surface chain density reaches the maximum described by Gennes [38]. (c) Deviations from ideality may arise from loop defects and/or nascent chain starvation effects.

[30,33–35] found much higher  $\bar{D}$  for surface-initiated polymer brushes as compared to solution phase polymers. Moreover, recent simulation results [29,36,37] also found broader MWD in the case of SI-ATRP which further casts doubt on the assumption that polymers from solution phase and surface-initiated syntheses possess identical MWDs.

Uncontrolled surface-initiated chain-growth polymerization [9,20–22], albeit less precise than "living" polymerization, is in fact one of the most industrially employed polymerization techniques for polymer brush fabrication due to its technical simplicity and robustness, especially in applications where complex polymer architectures are not strictly required [39–41]. Characterization of the structure of these polymer brushes is equally as important and challenging as those using controlled chain-growth polymerization techniques.

Due to the aforementioned experimental limitations on structural characterization, computer simulations have become invaluable tools because time-dependent information and monomer-level insight into the polymerization process are readily accessible. Simulation methods including Monte Carlo (MC) [29,36,37,42] and dissipative particle dynamics (DPD) [43] have been carried out to study the controlled solution phase and surface-initiated chain-growth polymerization. Such studies consistently point out that the MWD of surface-initiated grown polymers could differ markedly from that grown in the solution phase due to the "starvation" effect, in which the live chain ends of short polymers are sterically shielded from monomers in solution by the presence of longer neighboring chains.

The common strategy to simulate polymerization reactions therein involves checking the proximity of monomers to the propagating chain end at regular time step intervals, randomly selecting one monomer for reversible/irreversible addition with a given probability, and then redefining the terminal monomer as the new propagating chain end, thus having the advantage of good controllability of polymerization process [43,44]. One concern with this approach might be the specific criteria to create bonds must be specified *a priori* (usually set as constants) despite the fact that bond formation varies drastically with local temperature, pressure, and monomer concentration. Moreover, the sudden creation of new bonds will lead to a drastic change of forces of the involved particles. Such sudden variation of interatomic forces may disrupt the dynamics of the simulation so that the diffusivity cannot be reliably measured, and undesired local heating might be induced. In addition, there remains a relative dearth of computational literature on the MWD, and its dependence on grafting density, for polymer brushes growth by uncontrolled chain-growth techniques.

To that end, we herein present a *reactive* coarse-grained model for chain-growth polymerization using MD simulations, by modifications to our previous reactive force field [45] on step-growth polymerization. This is a completely different methodology to

simulate chain-growth polymerization, which does not rely on any MC operations of bond creation/deletion as was employed in other existing models. Instead, chain propagation and termination are purely powered by the *reactive* force field developed in this model. The main goal of this study is to directly compare the chain length distributions between polymers grown in solution phase and surface-initiated polymer brushes. We report that the distribution of chain length depends sensitively on the initiator loading. Most importantly, the surface-initiated system yields considerably higher dispersity ( $\bar{D}$ ) as compared to solution phase system, mainly due to the larger fraction of low molecular weight chains in the case of surface-initiated polymer brushes. As shown in Fig. 1 (c), the short chains arise from two concurrent phenomena: (1) recombination of chains during the early stage of polymerization to form "looped" chains, and (2) the steric "screening" of monomers from nascent chains imposed by neighboring long chains to form "starved" chains. Moreover, both of these effects are markedly amplified with increasing initiator surface density, thus imposing an upper limit on the grafting density of polymer chains. Our work further reinvigorates the substantial experimental challenge to characterize polymer brushes synthesized *via* surface-initiated polymerization.

## 2. Simulation model and method

### 2.1. Rationale of the chain-growth polymer model

The coarse-grained model for simulating chain-growth polymerization is based on our previous step-growth polymerization (SGP) model [45] in which linear polymer chains are synthesized *via in silico* polymerization reaction of generic monomer particles. Generally, the SGP model is a binary system with bi-functional A and B particles (identical particle attributes except the particle type) that exhibit pair-wise interactions. The heterobonds (A-B) are attractive and homobonds (A-A or B-B) are repulsive. The bi-functionality of each particle is achieved by adjusting the length and magnitude of the homobond repulsion. Thus, each particle can only potentially bond two other particles (of the opposite type) and thus results in linear chain molecules. The detailed model description is available in our previous paper [45]. Herein, we maintain the basic framework of the SGP model to simulate chain-growth polymerization. In this case, however, A and B particles are nonreactive unless activated by a specific "radical" species. In other words, A and B particles are expected to have two states: dormant and reactive. A simple scheme to achieve this is to introduce a "patch" particle such that the dormant state is when the patch particle shields the A or B particle, while bare A or B particle is the reactive state.

There are four fundamental particle types in this model: monomers (A and B), patches (P), and initiators (AT) (Fig. 2). Similar

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