

# Computer Modeling of Reversible Adsorption of Head-to-Tail Associating Polymers

Elena E. Dormidontova and Chun-Chung Chen

Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106

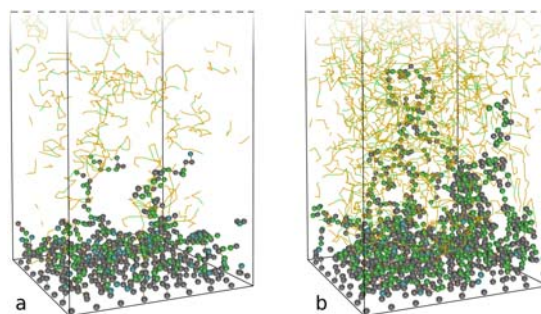
## INTRODUCTION

Using reversibly associated polymers for surface applications has attracted considerable attention recently due to their self-healing properties.<sup>1-4</sup> Among reversibly associated polymers, there is a variety of novel end-to-tail associated polymers, which can be used for film formation. In so far there were only a couple of reports<sup>4</sup> concerning thick films of pyridine carboxylic acids based on intermolecular head-to-tail hydrogen bonding. It has been shown that the observed self-assembled structures at the surfaces replicate the structures observed in solid state and the quality of the film strongly depends on the method of film preparation and chemical architecture of the hydrogen bonded sites.<sup>4</sup> The behavior of head-to-tail associating polymers have also started to attract the attention of theorists,<sup>1-3</sup> however most of them considered freely adsorbed polymers. Thus, Schmitt and co-authors<sup>1</sup> and later Milchev and Landau<sup>3</sup> concluded that confined living polymers, flexible and especially rigid, are able to re-arrange their molecular weight distribution. In more recent papers dealing with freely adsorbed supramolecular polymers, Besseling and co-authors found that, depending on the association energy, the thickness of the depletion layer increases with concentration in the dilute regime, followed by a decrease in more concentrated solutions.<sup>2</sup> Ring formation and the polymer brush regime have not been considered in these papers.<sup>1-3</sup> The present research is aimed to overcome these deficiencies by studying polymer brushes of head-to-tail associated polymers. Since polymer chain length varies as a function of the association rate (which depends on concentration, energy of association and so on), such polymer brushes are expected to behave quite differently compared to traditional brushes. Associated polymer brushes should be able to adjust their length to optimize chain conformation in the layer as well as the thickness of the layer.

## COMPUTATIONAL

**Model.** We employ Monte Carlo (MC) simulations (bond-fluctuation model<sup>7,8</sup>) to study polymer brushes formed by reversible associated polymers, shown in **Figure 1**. Each oligomer contained  $N$  monomer units including one donor and one acceptor end-group for reversible association. We also have uniformly attached  $\sigma S$  oligomers of four monomer units each to the surface of size  $S = 64 \times 64$ . Each anchored oligomer ended by an acceptor unit similar to that of oligomers in bulk. All oligomers were placed on a 3 dimensional cubic lattice with periodic boundary conditions in two dimensions corresponding to the surface plane ( $x, y$ ). In the direction perpendicular to the surface,  $z$ , we assumed the constant chemical potential of the free oligomers, i.e. all oligomers were confined to  $0 < z < L_z = 128$ , however the number oligomers was not fixed. To maintain a constant bulk concentration of oligomers we kept constant number of oligomers within a buffer zone at the top of the box ( $L_z - 4 \leq z < L_z$ ) and allowed oligomers to move from that area to compensate for the change in concentration by removing or adding an oligomer next to the top of the box every  $s = 128$  MC time steps, when necessary.

In framework of the bond fluctuation model the distance between any two monomers can be no less than twice of the cell size,  $2a$ . Furthermore, for any pair of monomers that are bonded, covalently or by reversible association, the distance between the two must have one of the values  $2a, 5^{1/2}a, 6^{1/2}a, 7^{1/2}a$ , or  $10^{1/2}a$ . This amounts to a total of 108 possible bond vectors in 3D. This model corresponds to the good solvent conditions where the radius of gyration for a free oligomer scales as  $R_g \propto N^{0.55}$  with the number of monomers in an oligomer,  $N$ . We did not assume any interactions between the oligomers or solvent and the surface, apart from the excluded volume and end-group interactions.



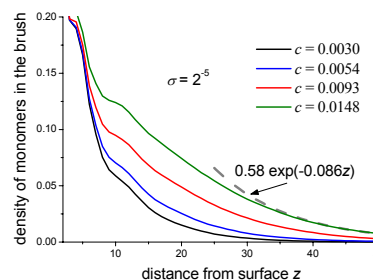
**Figure 1.** Example of MC simulation for adsorbed layers of self-assembling polymers with low  $c = 0.003$  (a) and high  $c = 0.0092$  (b) bulk concentration at grafting density  $\sigma = 2^{-6}$ .

We assumed the backbones of oligomers to be absolutely flexible, so there is no penalty for bending any of the chemical bonds connecting the monomer units of an oligomer. Reversible interactions between donor and acceptor groups are orientationally specific, therefore, there will be a penalty,  $E_{st} = K(1 - \cos\theta)$ , for bending a reversible bond, where  $\theta$  is the angle characterizing deviation from linearity. In our simulations, we choose the rigidity constant  $K = 5kT$ . This rigidity constant results in the same contribution to the partition function as restricting the bond angle to the range  $\theta \leq \theta_c \approx 37^\circ$  and amounts to a loss of entropy per reversible association of  $\Delta S \approx 2.3$ .

**Simulation procedure.** For each realization of the system we started with some number of anchored oligomers on the surface and some concentration of oligomers in bulk. To equilibrate the system we randomly choose a movable monomer and a direction for the movement and determine its acceptance with the Metropolis algorithm<sup>9</sup>. Following a moving attempt for a donor end-group, a new bonding configuration is chosen from all possible ones (bonding with one of the free acceptors within bonding distance or not forming a bond at all) with probabilities weighted by their respective Boltzmann factors. We repeated such monomer moves, reversible bonds updates and corresponding adjustment of free oligomers in the buffer region for no less than  $2^{21} \approx 2 \times 10^6$  MC time steps to equilibrate the system. Then, the distribution of number of free oligomers associated to each anchored oligomer as well as the density profiles as functions of distance from the surface are calculated and averaged over multiple system configurations.

## RESULTS AND DISCUSSION

We have performed a series of MC simulations for the fixed density of adsorbing sites,  $\sigma = 2^{-5}$  and varying the bulk concentration of oligomers. Similar to the adsorption of regular polymers, a smaller bulk concentration of oligomers produces a sparser layer of adsorbed associated polymers as is seen in **Figure 1**. In the case of a larger concentration of oligomers in the bulk, the adsorbed layer is relatively dense and thick, so it can be considered as a polymer brush. However in contrast to regular polymer brushes, the monomer density profile does not follow the parabolic form (**Figure 2**).



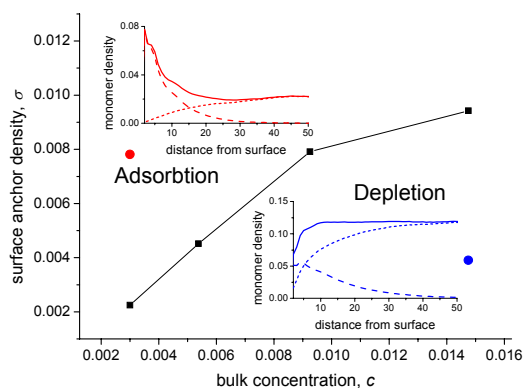
**Figure 2.** Density profile for reversibly associated polymers adsorbed to the surface.

The density of monomers approaches a relatively high level near the surface due to attached first layer of oligomers and it decreases away from the surface, going through a plateau corresponding to the second and third layer of reversibly attached oligomers. Far away from the surface the density profile decays exponentially according to  $\varphi(z) = B(\sigma)\exp[-A(c)z]$  law. For a constant density of adsorbing sites the  $B$  prefactor remains the same for all bulk concentrations,  $c$ , considered, whereas the decay rate changes with  $c$  according to the **Table 1**

**Table 1. Decay rate,  $A$ , for the brush density profile formed by oligomers of various bulk concentration  $c$ .**

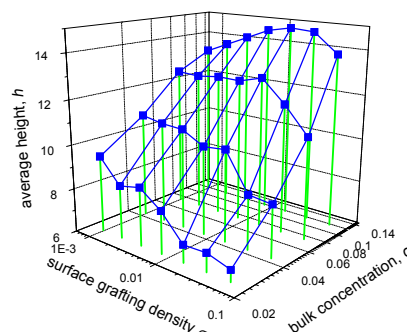
Bulk concentration, $c$	0.0030	0.0054	0.0093	0.0148
Decay rate, $A$	0.1449	0.1149	0.0995	0.087

As is seen from the **Table 1** and **Figure 2** lower bulk concentration results in a lower density of monomers in the brush and in a more rapid decay of the density with the distance from the surface. The unusual density profile of monomers in the adsorbed layer is likely to be caused by the considerable polydispersity of chains in the bulk<sup>5,6</sup> typical for "living" polymers. Comparing the chain length distribution in the bulk and in the adsorbed polymer brush we found that the probability to find a shorter chain in the adsorbed layer exceeds that in the bulk. Therefore, end-to-tail associated polymers produces polymer layers noticeably distinct from that of traditional polymer brushes both because of the larger polydispersity and the capability of self-adjusting to the layer conditions. The high responsiveness of reversibly associated polymers to external condition allows their properties to be manipulated. For instance, an increase in the association energy of donor-acceptor interactions (which can be achieved chemically or by a temperature decrease) results in considerable increase of the monomer density and thickness of the layer.



**Figure 3.** Adsorption/depletion conditions as a function of grafting density and bulk concentration of reversibly end-associating polymers.

The overall effect of the surface on associated oligomers in the bulk can be considered as an attraction if the density of polymer near the surface is higher than the bulk density and is repulsive otherwise. Since adsorption of end-to-tail associating polymers to the surface has some common features with both grafted polymer brushes and freely adsorbing chains, the effect of the surface depends on both grafting density of the first oligomer layer and bulk density of free oligomers. As is seen from **Figure 3**, a low concentration of oligomers requires also a low density of adsorption sites for oligomers to adsorb on the surface. With an increase in bulk oligomer concentration the critical density of adsorption sites that ensures overall absorption of polymer on the surface increases nearly linearly, tending to some leveling off at higher oligomer concentrations. The observed effect is connected to the fact that higher oligomer concentration in bulk implies larger average chain length for which excluded volume effect near the surface is stronger than for shorter chains. Therefore it requires larger density of adsorption sites to ensure polymer adsorption to the surface.



**Figure 4.** Average height for adsorbed polymer layer as a function of grafting density  $\sigma$  and concentration  $c$ .

Using the results for the density profile we have also calculated the average height of the adsorbed polymer layer,

$$h = \int z\varphi(z)dz / \int \varphi(z)dz.$$

The result of these calculations is shown in **Figure 4**. As discussed above, increasing the oligomer concentration in the bulk results in a more dense adsorbed layer of higher thickness. This tendency persists for any density of grafting sites considered. The increase in the grafting density has a less obvious effect. For relatively low bulk oligomer concentration, increasing the grafting density results in the decrease of the average height of the brush. The main reason for this is the decrease of the average length of the chain attached to the surface to avoid extra stretching caused by the decrease in the area per chain. For a larger bulk oligomer concentration the height of the brush remains constant or slightly increases with increasing grafting density and only when sufficiently high density of adsorption sites is reached the height of the brush starts to decrease. The difference in the behavior of oligomers at low and high bulk concentration is a consequence of the fact that for high oligomer density produces longer chains in bulk with their large excluded volume for which the surface remains repulsive until there is a relatively high density of grafting. Until that moment an additional chain adsorption and stretching occurs, resulting in an increase of the average brush height. When the number of grafting sites becomes large enough to consider the surface as attractive a further increase in the grafting density results in the decrease in average chain length (similar to the case of low oligomer concentration) and the height of the layer decreases as well.

#### ACKNOWLEDGEMENTS

This work was supported by the Biomimetic and Bioactive Polymers Program of Case Western Reserve University (OBR Challenge, CSE RC 00-01).

#### REFERENCES

- Schmitt, V.; Lequeux, F.; Marques, C.M. *J. Phys. III* **1993**, 3, 891.
- (a) van der Gucht, J.; Besseling, N.A.M.; Stuart, M.A.C. *J. Am. Chem. Soc.* **2002**, 124, 6202. (b) van der Gucht, J.; Besseling, N.A.M. *Phys. Rev. E* **2002**, 65, 051801.
- Milchev, A.; Landau, D.P. *J. Chem. Phys.* **1996**, 104, 9161.
- (a) O'Shea, J.N.; Luo, Y.; Schnadt, J.; Patthey, L.; Hillesheimer, H.; Krempasky, J.; Nordlund, D.; Nagasono, M.; Bruehwiler, P.A.; Mårtensson, N. *Surface Science* **2001**, 486, 157. (b) O'Shea, J.N.; Schnadt, J.; Bruehwiler, P.A.; Hillesheimer, H.; Mårtensson, N.; Patthey, L.; Krempasky, J.; Wang, C.K.; Luo, Y.; Agren, H. *J. Phys. Chem. B* **2001**, 105, 1917.
- Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1989**, 22, 853.
- Chakrabarti, A.; Toralt, R. *Macromolecules* **1990**, 23, 2016.
- Carmesin, I.; Kremer, K. *Macromolecules* **1988**, 21, 2819.
- Deutsch, H.P.; Binder, K. *J. Chem. Phys.* **1991**, 94, 2294.
- Metropolis, N.; Rosenbluth, A.W.; Rosenbluth, M.N.; Teller, A.H.; Teller, E. *J. Chem. Phys.* **1953**, 21, 1087.