Monte Carlo Simulation of Bidisperse Melt Polymer Brushes

Visit Vao-soongnern

Laboratory of Computational and Applied Polymer Science
School of Chemistry, Institute of Science, Suranaree University of Technology,
Nakhon Ratchasima 30000 THAILAND

ABSTRACT

Considerable research efforts have recently gone into the study of the nanostructure and physical properties of polymers end-grafted onto a solid surface. These systems are known as polymer brushes for sufficiently high polymer densities. Interfaces between polymers and solids play a key role in many industrial applications as adhesives, colloidal stabilizers, and lubricants. Establishing quantitative relations between chemical constitution and macroscopic properties of such systems and predicting their structure and properties is highly desirable, because this can tremendously facilitate the rational design of various surface modification systems suitable for real application. In experimental situations, polydispersity is an often unavoidable feature, which greatly affects the brush structure and can actually be used to tailor specific brush structures and properties. Unfortunately, experimental observations of brushes available at present are not so sensitive to the details of structure, but are concerned mainly with more global brush properties, such as brush thickness or force profiles via brush deformation. On the other hand, computer simulations can provide very detailed information from the level of effective monomer to macroscopic quantities. Detailed information like the polymer chain trajectory, fluctuation etc. can conveniently be obtained in a computer simulation. Unfortunately, little simulation work has been performed for chains with chemically realistic architectures.

In this work, a novel computer simulation technique capable of probing the structure of the interface between the solid substrate and grafted polymer melts at a prescribed grafting density was developed. This simulation allows us to obtain detailed information about the conformational, structural, and thermodynamic properties near the solid substrate, while avoiding many of the assumptions invoked in the mesoscopic, SCF models, in analytical brush theories and past simulations of bead-spring or ideal chains. Using the second-nearest neighbor lattice, coarse-grained models of bidisperse polyethylene brushes have been studied using Monte Carlo simulations of grafted polymer melts. Each chain containing N ethylene units, with $30 \leq N \leq 60$. The total number of available surface sites is 40x40 (surface area = 86.6 nm^2). We choose periodic boundary conditions in the x and y directions, while the two boundary in z direction (at $z = 1$ and $z = M$, where $M > N$) are treated as hard impenetrable walls. The grafting density (σ) is from 0.92 to 1.85 nm^{-2} (80 to 160 chains). RIS formalism is used to model the short-range intramolecular interactions of PE chains. Long-range intra- and intermolecular interaction among nonbonded units are incorporated into the simulations using the Lennard-Jones potential for ethylene units with $\varepsilon/k_B = 185$ K and $\sigma = 0.44$ nm. Single bead and pivot moves on the lattice are accepted according to the Metropolis MC algorithm. Results reported in this work is for the system of fixed σ.

Profiles of monomer density and free end density, chain linear dimensions, bond orientation, and average monomer position along a chain were studied. For distribution of density, the profile for the shorter chains are denser when the longer chains are grafted. Interestingly, the overall melt density increases at all regions. The total density for bimodal brush also shows a slightly negative slope which is different from a flat density profile from the case of a monodisperse brush. This negative slope is more prominent as N_L get longer at fixed σ. The end bead profiles for short components become narrower and the maxima move closer to the graft wall as a function of the length of the longer chains. Our MC data for finite chain lengths also indicate significant chain end interpenetrations into the outer sublayer which is about the same of the long ends into the inner sublayer. The maxima of end bead profiles are located close to the boundary between two sublayers and this may be the reason that a considerable amount of shorter/longer chain ends are able to penetrate into the outer/inner layer. Compared to the monodisperse brush, this maximum point is located at smaller z at the same length and coverage. The orientation of the bonds induced by grafting shows that the curvature of $<\cos \theta_i>$ for shorter chain are less aligned perpendicular to the wall if longer chains were grafted. In addition, short chains are less stretched when compared to the monodisperse brush. The portion of long chain in the outer sublayers are less crowned and it is more stretched. For the inner sublayers, the curvature of $<\cos \theta_i>$ for longer chains are almost the same.

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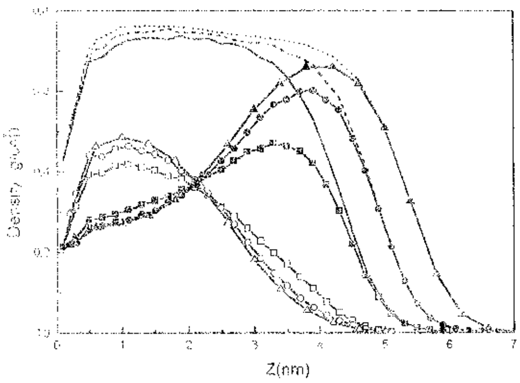

Figure 1: Density profiles for bidisperse brushes of fixed grafting density with varying long chain length (160 chains of C_{60} mixed with C_{80}, C_{100} and C_{120}, from left to right)

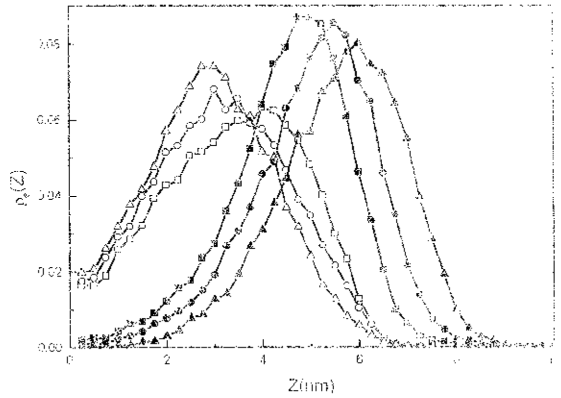

Figure 2: Free end distribution for bidisperse brushes of fixed grafting density with varying long chain length (160 chains of C_{60} mixed with C_{80}, C_{100} and C_{120}, from left to right)

References

References

1. A. Halperin, M. Tirrell and T. P. Lodge, *Adv. Polym. Sci.* 100, 31, (1991)
2. S. T. Milner, *Science* 251, 905, (1991)
3. V. Vao-soongnern, *J. Nanosci and Nanotech*, (2006), *in press*.