

# Monte Carlo simulations of copolymer adsorption at planar chemically patterned surfaces: Effect of surface domain sizes

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We present results of Monte Carlo simulation studies utilizing the bond fluctuation model in conjunction with single and configurational biased Monte Carlo moves to investigate the adsorption of diblock (A–b–B) and alternating (A–alt–B) copolymers at physically flat surfaces made of an equal number of two chemically different sites, C and D. The adsorption of the copolymer to the surface is driven by the repulsion between the A and B segments along the copolymer and the attraction between the B segments and the D sites on the surface. We address the critical role of the commensurability between the copolymer's monomer sequence distribution and the size and spatial distribution of the surface adsorbing sites on the copolymer adsorption. We show that both copolymer architectures have the ability to recognize the surface motif and transcribe it into the bulk material. Diblock copolymers can transfer the pattern once the heterogeneous domain sizes match the size of the parallel component to the radius of gyration, which is constituted primarily of the adsorbing species. This behavior results from the ability of the diblock copolymer to adopt a brush type conformation. In contrast to the diblocks, copolymers with the alternating sequence distribution are more likely to “zip to” the surface since the adsorbing species are evenly distributed along the copolymer. This chain conformation creates an entropic penalty, which must be alleviated by the formation of loops and tails. These conformational changes endow the alternating copolymer with the ability to recognize patterns with periodicities much less than the parallel component to the radius of gyration, and to invert the pattern as the distance away from the surface is increased.

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## I. INTRODUCTION

Many technologically important applications of polymers involve phenomena associated with copolymer adsorption. These include fiber-filled polymer composites, antireflection coatings, lubricants, adhesives, sensors, structures based on nanoscale patterning and masking, etc.<sup>1–7</sup> In order to further advance these technologies, a better understanding of the key features governing polymer adsorption at surfaces is critical. To this end, there has been a plethora of both theoretical/computational and experimental work investigating the organization of copolymers at planar, chemically homogeneous surfaces and homopolymers at planar, chemically heterogeneous surfaces.<sup>8–25</sup> These reports have provided insight into the basic phenomena governing polymer adsorption. It has now been well established that the driving force for polymer adsorption involves an interplay between (i) the gain in energy due to the adsorption of the binding monomers of the macromolecule to the attractive surface, and (ii) the loss in chain entropy associated with the reduction in the number of possible configurations of the adsorbed chain relative to that of a free chain in the bulk.

In many real systems the substrates onto which copolymers adsorb are not chemically homogeneous. Rather, the surfaces comprise multiple chemical species either due to impurities or by design. These chemical heterogeneities affect the copolymer organization at the substrate/copolymer

interface. Multidimensional systems such as these are often encountered in biological situations, for example: pathogen–host interactions and biopolymer adhesion for transmembrane signaling.<sup>26–33</sup> As with systems containing homogeneous substrates, the adsorption characteristics depend on the adsorption strength, the polymer chain length, and the monomer sequence distribution within the copolymer. However, when a chemically heterogeneous surface is introduced one must also consider the effect of the adsorption strength between each constituent as well as the size, shape, and spatial distribution of the heterogeneous domains on the surface.

We have recently developed a three-dimensional (3D) self-consistent-field (SCF) model of polymer adsorption by extending the 1D SCF scheme of Scheutjens–Fleer.<sup>34,35</sup> We used the 3D SCF model to explore the adsorption of A–B copolymers from an A homopolymer matrix onto planar substrates composed of two chemically distinct sites (C and D), one of which (D) had a preferential affinity for the B segments of the copolymer. The interplay between the spatial distribution of the surface chemical heterogeneities and the monomer sequence distribution in the copolymer was examined for diblock (A–B), triblock (A–B–A, and B–A–B), and alternating (A–alt–B) copolymers. Our results demonstrated that when the chemically heterogeneous motifs on the substrate were detected by the copolymer adsorbing segments, the copolymers were able to transcribe them with high fidelity into three dimensions. The way in which the surface pattern was transferred was dictated primarily by the mono-

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mer sequence distribution. We showed that relative to alternating copolymers, block copolymers were generally more adept in capturing the chemical pattern shape and transcribing it into the polymer mixture.

The aim of this paper is to extend our previous work and analyze the adsorption behavior of A-b-B and A-alt-B copolymers on flat, chemically heterogeneous substrates using Monte Carlo (MC) simulation. Relative to the 3D SCF model, the MC approach provides detailed molecular information about the polymer conformations at the substrate. Also, by utilizing the bond fluctuation model (BFM) any artifacts due to the lattice discretization of the 3D SCF model can be avoided.

## II. THE MC MODEL

All simulations were carried out using the BFM. In the BFM, polymers are represented as connected repeat units residing on a three dimensional cubic lattice. One monomer unit is allowed to occupy a single cube (or eight lattice vertices), and each monomer is connected to another by a predetermined set of bond vectors. The bond vectors are built through all possible permutations and sign inversions of the following vector families:  $\mathbf{P}(2,0,0) \cup \mathbf{P}(2,1,0) \cup \mathbf{P}(2,1,1) \cup \mathbf{P}(2,2,1) \cup \mathbf{P}(3,0,0) \cup \mathbf{P}(3,1,0)$ . These vector sets prevent bond vectors from crossing and monomers from overlapping. A complete description of the model can be found in the original work by Carmesin and Kremer.<sup>36</sup> The benefit to using the BFM is that its high coordination number allows one to closely approximate continuum behavior, while retaining the advantages of lattice models such as integer arithmetic and parallelization.

In conjunction with the BFM we utilize the configurational bias Monte Carlo algorithm (CBMC) of Frenkel, Mooij, and Smit, and a traditional single move Monte Carlo algorithm (SMMC).<sup>37</sup> The CBMC algorithm is a modification of the sampling scheme originally introduced by Rosenbluth and Rosenbluth in the 1950s.<sup>38</sup> The algorithm comprises three general steps. First, a trial conformation is generated to compute the Rosenbluth weight,  $W(n)$ . This step can constitute regrowth of the entire chain or part thereof. Next, the Rosenbluth weight of the old configuration,  $W(o)$ , is determined by retracing the old conformation. Finally, the trial configuration is accepted with a probability of  $\min[1, W(n)/W(o)]$ . The advantage to using this sampling scheme is that at low densities multiple monomer moves can be made per single Monte Carlo step with a relatively good probability of acceptance.

The SMMC algorithm is straightforward in its implementation. A single monomer is chosen at random from a random polymer chain, and its energy,  $E_0$ , is calculated. The monomer is then randomly moved one lattice spacing in any of the six possible directions. A check is made to see if the resulting move retains the constraints set forth by the BFM. If the restrictions are violated the move is rejected. If the constraints are satisfied, then the new energy,  $E_N$ , is calculated and the move is accepted with a probability equal to  $\min[1, \exp\{-\beta(E_N - E_0)\}]$ .

The coupling of the CBMC and SMMC offers two advantages. The CBMC algorithm dramatically increases the

rate of equilibrium conformation sampling at low densities. This allows the polymers to disperse within the simulation box rapidly from the ordered starting configuration. However, as the simulation progresses the SMMC algorithm becomes a necessity because the adsorption process results in high densities at the polymer/surface interface, which substantially reduces the acceptance of the CBMC moves. In fact, simulations that were executed using only the CBMC algorithm never reached equilibrium even after long simulation times.

## III. MOLECULAR PARAMETERS

The simulations presented in this work were carried out on a  $24 \times 24 \times 72$  rectangular lattice with a total polymer volume fraction of 0.22. The system consists of an A-B copolymer bounded in the  $z$  direction by two parallel surfaces, one of which is patterned and the other which remains neutral to all species. All chains in the mixture were 24 monomers long having 12 A monomers and 12 B monomers in either a block copolymer ( $A_{12}$ -b- $B_{12}$ ) or an alternating copolymer ( $A_{12}$ -alt- $B_{12}$ ) sequence distribution. The patterned substrate was set to have a checkerboard pattern comprising C and D domains with domain sizes ranging from  $[1 \times 1]$  to  $[12 \times 12]$ , while the homogeneous surface was composed entirely of C. In all simulations, a square well potential,  $\epsilon_{ij}$ , was used to describe the pairwise interaction between  $i$  and  $j$ . Athermal interactions were used for the A/A, A/C, A/D, B/B, and B/C pairs (i.e.,  $\epsilon_{AA} = \epsilon_{AC} = \epsilon_{AD} = \epsilon_{BB} = \epsilon_{BC} = 0$  kT). A repulsive potential was used for A/B contacts,  $\epsilon_{AB} = 0.1$  kT, and the B/D potential was held constant at  $-0.75$  kT. All interactions were short ranged and limited to the bond vectors  $\mathbf{P}(2,0,0) \cup \mathbf{P}(2,1,0) \cup \mathbf{P}(2,1,1)$ .

The simulations were executed in the following manner. First, two simulation boxes were constructed with different initial configurations. One simulation box was initialized with the copolymers placed in an ordered fashion at the box's center (system I), while the other placed the copolymers at the interface of the heterogeneous surface (system II). Next each system was allowed to disperse the copolymer chains within the simulation box using CBMC moves with A/B repulsions for 10 000 MC steps. Subsequently, the surface interactions were engaged and a transition from CBMC to SMMC was made over the course of 1.0 million attempted moves. During the transition, the probability of attempting a CBMC move over a SMMC move was decreased by 0.10 every 100 000 attempted moves. At this point the CBMC moves were "switched off," and the SMMC moves were used for an additional 1.2 billion moves. During the final 200 million moves, equilibrium conformations were sampled every 50 000 MC steps in order to obtain the desired ensemble averages. Once completed, the ensemble averages for each system's energy and fractional surface coverage were compared to ensure that the systems did in fact reach equilibrium. The ensemble averages were then recalculated using the average between the results of system I and system II. The values between the two systems were systematically within 3% of each other.

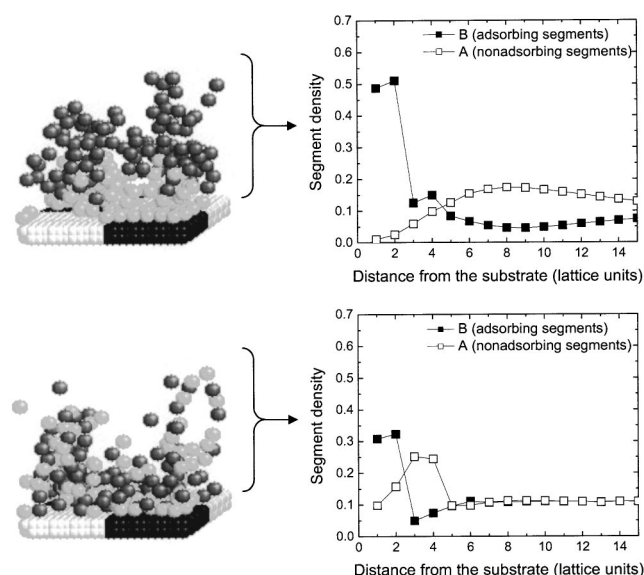


FIG. 1. Three-dimensional profiles of diblock (top) and alternating (bottom) copolymers adsorbed onto a heterogeneous surface with a checkerboard pattern of periodicity  $[12 \times 12]$ . The corresponding segment density profiles for the adsorbing (B, closed symbols) and nonadsorbing (A, open symbols) segments are depicted on the right.

#### IV. RESULTS AND DISCUSSION

The primary focus of this work is to examine the interplay between the monomer sequence distribution within the copolymer and the size and spatial distribution of the adsorbing sites on the flat, chemically heterogeneous surface. In Fig. 1, we show a typical three-dimensional image of the adsorbed polymer chains with the corresponding monomer density profile for both a diblock and an alternating copolymer. In both cases, the surface pattern has a periodicity of  $[12 \times 12]$ . The configurational snapshots show that the diblock copolymer has a high density of B segments (light color along the copolymer) located at the surface of the adsorbing D domains (dark color on the substrate). This density is comparable to that of a polymer melt.<sup>39</sup> Away from this dense interfacial layer, the diblock organizes into a sparse brush comprising the A block, resulting in a depletion layer of the B segments. In contrast to the diblock, the alternating copolymer is only able to maintain a moderate density at the interfacial layer, and the adsorbing segment depletion layer is much sharper. This behavior is a consequence of the conformations adopted by each chain due to the specific monomer sequence distribution. Furthermore, our simulations show no changes in density as a function of the surface domain size for the alternating case. There is, however, a small decrease in the adsorbing segment density for the diblock copolymer as the periodicity of the surface pattern increases, which develops due to a bridging effect. Elaboration of the diblock's ability to form bridges across nonadsorbing surface sites is discussed later in this report.

In order to analyze how the copolymer adsorbs on the heterogeneous substrate, we cannot look at the three-dimensional copolymer density alone. Rather, we section the lattice into  $X$ - $Y$  planes parallel to the substrate and analyze the density profiles of the adsorbing segment in each  $X$ - $Y$

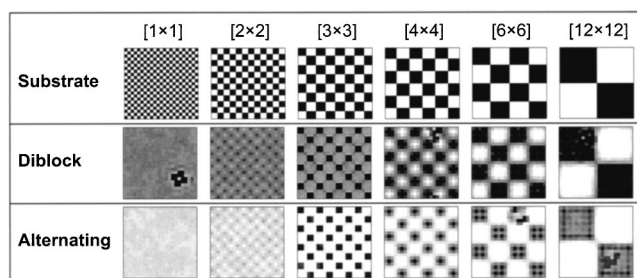


FIG. 2. Planar  $x$ - $y$  dimensional probability density profiles at the substrate interface (i.e.,  $z=1$ ) for the adsorbing B segments of the diblock (middle) and alternating (bottom) copolymer sequences on substrates with different pattern periodicities (top). The black regions on the substrates represent the adsorbing domains (D) and the white regions represent the neutral domains (C). The profiles range from 0 (white) to 1 (black).

plane. This procedure provides a qualitative measure for the substrate pattern recognition. Later in the paper we define a parameter in which we term the pattern transfer parameter. This parameter expresses the ability of the copolymer to recognize the substrate pattern in a quantitative manner.

In Fig. 2 we plot the probability density of the B segments adsorbing onto substrates (top panel) with various pattern periodicities for the diblock (middle panel) and alternating (bottom panel) copolymers. From the data in Fig. 2, both copolymer sequence distributions show signs of recognition at the largest surface periodicity of  $[12 \times 12]$ . As the periodicity of the surface pattern is decreased the recognition for both polymers also decreases. The diblock copolymer's ability to recognize the surface, that is the ability of the adsorbing B segments to organize themselves above D domains only, decreases much more rapidly than in the case of the alternating copolymer. This is due primarily to the large length of the B block. As the surface periodicity decreases, the adsorbing sites become closer to one another allowing for the long run of B segments in the copolymer to bridge across the neighboring non-adsorbing sites. Since the interaction between B segments and C domains is athermal, there is no enthalpic penalty for the B segments to reside above these sites. For the case of A-alt-B, the recognition is maintained at smaller surface periodicities because of the short sequence lengths. Ideally, it is expected that recognition will occur until the surface periodicity becomes less than the sequence length of the copolymer's distribution. This would lead to the expectation that the alternating sequence can recognize surface patterns down to a spatial period of  $[1 \times 1]$ . However, this is clearly not the case. The problem stems from the features of the lattice and not from an energetic standpoint. Recall that in the BFM, the monomers are restricted to a minimum spatial distance of two cells apart, while the adsorbing monomers can feel the effects of the surface in any direction up to  $\sqrt{6}$  cells since each monomer can experience binary interactions only through the vector families  $\mathbf{P}(2,0,0)\mathbf{UP}(2,1,0)\mathbf{UP}(2,1,1)$ . As a consequence of this constraint, an adsorbing segment located a distance of  $\sqrt{6}$  lattice spacings from the surface will feel the effects of a minimum of four adsorbing sites. This results in the copolymer "seeing" the  $[1 \times 1]$  and  $[2 \times 2]$  checkerboard patterns as chemically homogeneous as long as the nonadsorbing surface sites



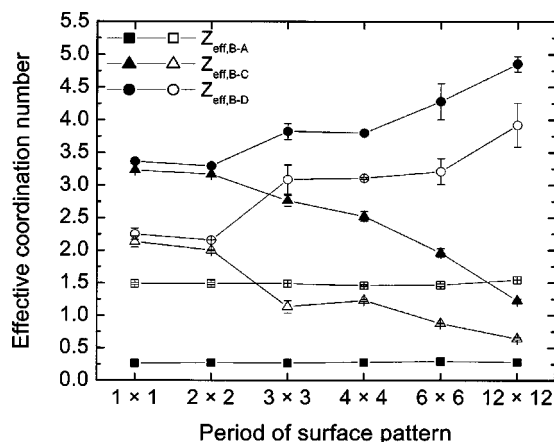


FIG. 3. Effective coordination number for diblock (closed symbols) and alternating (open symbols) monomer sequences for A-B (squares), B-C (triangles), and B-D (circles) binary pairs as a function of the surface pattern periodicity.

remain athermal. Based on this argument one would expect pattern recognition to start occurring on a  $[3 \times 3]$  pattern. This is exactly what our results show.

A convenient way to learn about the interplay between the enthalpic interactions and the spatial distribution of the surface sites is to examine the effective coordination number for individual monomer/surface sites pairs. In Fig. 3, we plot the effective coordination number, defined through a simple counting of nearest neighbors from the vector families  $\mathbf{P}(2,0,0) \cup \mathbf{P}(2,1,0) \cup \mathbf{P}(2,1,1)$ , for A-B, B-C, and B-D binary pairs. The diblock copolymer maintains a higher effective coordination number for the B-D and B-C contacts than the alternating copolymer due to its blocky sequence. However, in both cases the effective coordination number for B-D contacts increases once a pattern periodicity of  $[3 \times 3]$  is reached. Likewise, the number of the B-C contacts decreases once the  $[3 \times 3]$  periodicity is attained. From a qualitative standpoint, one might conclude that pattern recognition initiates once the surface domain size reaches  $[3 \times 3]$ . This is not necessarily true since we define recognition to be ideal when the adsorbing species reside exclusively above adsorbing domains.

To look at the process of pattern recognition more quantitatively we evaluate the so-called pattern transfer parameter (PTP) for each Z plane above the surface. This parameter allows us to account for the B segments that are misplaced from D domains. The PTP was previously defined by Genzer as

$$\text{PTP}(z) = \frac{\frac{\sum_{(x_D, y_D)} \phi^a(x, y, z)}{A_D} - \frac{\sum_{(x_C, y_C)} \phi^a(x, y, z)}{A_C}}{\frac{\sum_{(x, y)} \phi^a(x, y, z)}{A_C + A_D}}, \quad (1)$$

where  $\phi^a(x, y, z)$  is the volume fraction of the adsorbing species at location  $(x, y, z)$  in the lattice and  $A_C$  and  $A_D$  denote the surface areas of the nonadsorbing (C) and adsorbing (D) domains on the surface, respectively.<sup>40</sup> In Eq. (1), the summations in the numerator are carried out over the  $(x, y)$  sites above the D and C domains, while in the denominator

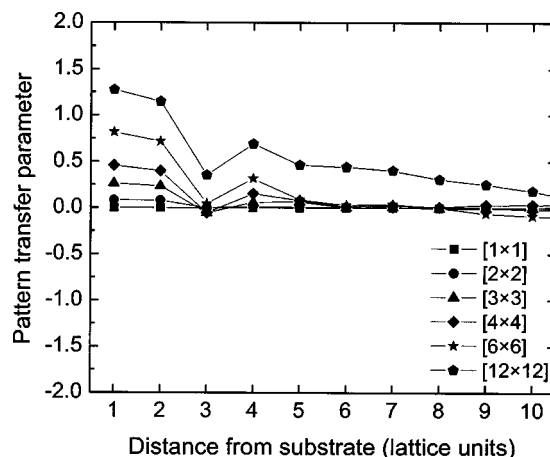


FIG. 4. Pattern transfer parameter of the diblock copolymer for substrate periodicities ranging from  $[1 \times 1]$  to  $[12 \times 12]$ .

the summation is carried out over all surface sites. For this parameter, three distinct values can be defined as benchmarks within a range of  $-2.0$  to  $+2.0$ . A value of  $+2.0$  signifies that the pattern is perfectly replicated by the adsorbing segments of the copolymer for a particular  $x-y$  plane. In contrast, a value of  $-2.0$  results in a perfect inversion of the pattern meaning that the adsorbing segments have replicated the pattern of the nonadsorbing sites. Last, a zero value shows that no recognition occurs and that there is no preference for an adsorbing segment to restrict itself to the pattern of the surface. In Figs. 4 and 5, we plot the PTP as a function of the distance from the substrate for the diblock and alternating copolymers, respectively, for all substrate periodicities studied. There are three trends that can be extracted from these plots. First, as the size of the domains on the surface increases, the PTP also increases for both copolymer sequence distributions. Second, the alternating copolymer not only recognizes the surface, but is also able to invert the surface at three or more lattice spacings from the surface. The last point of interest is the periodicity at which there is a large change in the PTP. For the diblock, this shift is noticeable at a period of  $[6 \times 6]$  and very clear at  $[12 \times 12]$ . The alternating copolymer, however, exhibits this jump at a pat-

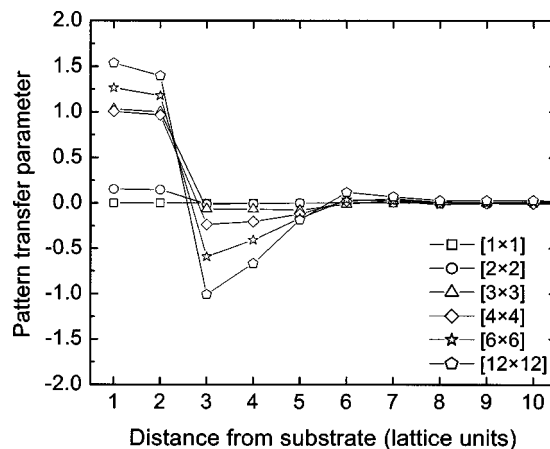


FIG. 5. Pattern transfer parameter of the alternating copolymer for substrate periodicities ranging from  $[1 \times 1]$  to  $[12 \times 12]$ .

tern size of  $[3 \times 3]$ . We have already commented earlier on the lattice effects as to why the alternating copolymer does not show signs of pattern recognition below  $[3 \times 3]$ . One would also expect the diblock copolymer to recognize a surface pattern that is on the same size scale as the radius of gyration,  $R_g$ , of the adsorbing monomer's sequence length, that is, somewhere between  $[3 \times 3]$  and  $[4 \times 4]$ . This is not the case as seen by the PTP.

More information about the copolymer conformations at the heterogeneous substrate can be obtained by evaluating the parallel,  $R_{g,\parallel}$ , and perpendicular,  $R_{g,\perp}$ , components to the radius of gyration, defined as

$$\langle R_{g,\parallel} \rangle^2 = \frac{1}{N} \sum_i (x_i - x_{c.m.})^2 + (y_i - y_{c.m.})^2, \quad (2)$$

$$\langle R_{g,\perp} \rangle^2 = \frac{1}{N} \sum_i (z_i - z_{c.m.})^2, \quad (3)$$

where  $x_i$  is the  $x$  coordinate of the  $i$ th monomer,  $x_{c.m.}$  is the  $x$  component to the center of mass of the polymer,  $y_i$  is the  $y$  coordinate of the  $i$ th monomer,  $y_{c.m.}$  is the  $y$  component to the center of mass of the polymer,  $z_i$  is the  $z$  coordinate of the  $i$ th monomer,  $z_{c.m.}$  is the  $z$  component to the center of mass of the polymer, and  $N$  is the number of monomers in the chain.<sup>41</sup> Despite changes in the substrate's pattern periodicity,  $R_{g,\parallel}$  and  $R_{g,\perp}$  for both diblock and alternating copolymers remain relatively constant. The diblock copolymer maintains its  $R_{g,\parallel}$  and  $R_{g,\perp}$  at  $\approx 5.0 \pm 0.10$  lattice units and  $\approx 4.0 \pm 0.11$  lattice units, respectively. The alternating copolymer has a slightly higher parallel component at  $\approx 5.3 \pm 0.13$  lattice units, and a significantly lower perpendicular component at  $\approx 2.8 \pm 0.15$  lattice units. The large difference in the  $R_{g,\perp}$  is expected since the diblock copolymer adopts a brush conformation. The ratio of  $R_{g,\perp}/R_{g,\parallel}$  ( $\approx 0.81$  for A-b-B and  $\approx 0.54$  for A-alt-B) reveals that the copolymer conformations are greatly deformed at the substrate/melt interface relative to their bulk Gaussian conformation. Similar results have been seen for homopolymers and "proteinlike" copolymers at homogeneous surfaces.<sup>42</sup>

The fact that  $R_{g,\parallel}$  for the diblock copolymer remains relatively constant regardless of the size of the surface periodicity explains why the diblock copolymer does not recognize the surface well until a pattern size of  $[6 \times 6]$  is obtained. It is at this point that the adsorbing segment's sequence length spreads to a length that is commensurate with the size of the adsorbing domains on the surface. The alternating copolymer expands in a similar fashion. However, because of its monomer sequence distribution, A-alt-B is capable of recognizing the pattern at much lower periodicities than the diblock copolymer. Another contributing factor as to why the alternating copolymer has the ability to recognize the surface pattern when the adsorbing domains are small is related to the conformation that the copolymer adopts at the substrate/melt interface. More specifically, it is related to the formation of tails, loops, and trains by the copolymer to form energetically favorable contacts and alleviate the entropic penalties associated with the adsorption.

We have examined three aspects of these formations, which are the number of these specific conformations, the

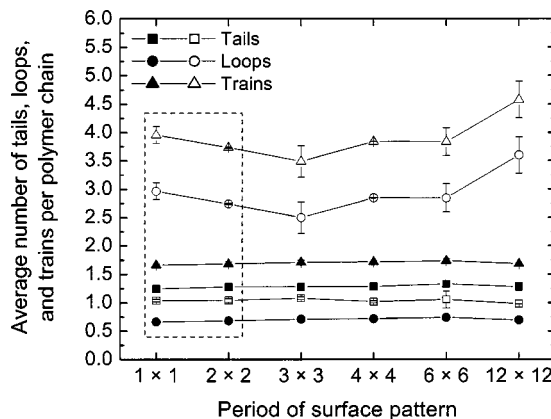


FIG. 6. Average number of tails (squares), loops (circles), and trains (triangles) per adsorbed copolymer chain for diblock (closed symbols) and alternating (open symbols) monomer sequences.

average length of each conformation, and the total length that each conformation contributes to the overall length of the copolymer chain. In Fig. 6 we plot the average number of tails (squares), loops (circles), and trains (triangles) for both the diblock (closed symbols) and alternating (open symbols) copolymers as a function of the substrate periodicity. The diblock copolymer maintains a constant number of loops, tails, and trains for all pattern sizes. The number of each conformation follows what one would expect to see for a typical brush formation. Close to a single train and tail is formed with a small number of loop fluctuations. The alternating copolymer also retains a constant number of tails. But in contrast to the A-b-B case, the number of loops and trains increases once a surface periodicity of  $[6 \times 6]$  is reached. This behavior is related to the spreading size ( $R_{g,\parallel}$ ) of the copolymer on the substrate. The spreading size is now commensurate with the surface domain size such that the copolymer can adsorb completely to a single adsorption domain. In order to alleviate the entropic penalty associated with complete zipping to the surface, the copolymer must form more loops. Note that, as expected, the number of loops is always related to the number of trains (loops = trains - 1). A short commentary is in order to explain the trend of the number of loops and trains below a surface periodicity of  $[3 \times 3]$  for both sequence distributions (boxed area in Fig. 6). The values are somewhat misleading in their trend due to the BFM. As was mentioned prior, the  $[1 \times 1]$  and  $[2 \times 2]$  surfaces are "seen" as homogeneous since the surface periodicity is less than  $\sqrt{6}$ . Because of this, these surfaces are more representative of homogeneous D surfaces of half the surface area. It is for this reason that the slight decrease is seen from a  $[1 \times 1]$  to a  $[3 \times 3]$  periodicity.

In Table I, we give values for the average length of each conformation of tail, loop, and train. These values are maintained over all surface periodicities. The average length of tails for both A-b-B and A-alt-B is relatively high,  $\approx 10$ – $12$ . While this is not surprising for the diblock copolymer, a much smaller length would be expected for the alternating copolymer. This large tail length of the A-alt-B can be explained in two ways. Either the surface density is becoming very high such that the copolymers become too

TABLE I. Average length and total chain length contribution of tails, loops, and trains.

	Average length of			Total chain length contribution of		
	Tails	Loops	Trains	Tails	Loops	Trains
A-b-B	11.46±0.18	1.55±0.24	5.00±0.18	14.71±0.14	1.09±0.17	8.50±0.23
A-alt-B	10.29±0.18	1.93±0.09	2.03±0.08	10.67±0.19	5.57±0.14	7.87±0.11

crowded, thus preventing incoming chains from having the ability to attach to the surface, or the average length of the loops is too small to alleviate the bulk of the entropic frustration. Since this system is almost purely enthalpic, that is to say that there are no strict entropic penalties induced (for example, conformational bond energies), the first explanation is more probable. In fact, the number of adsorbed chains is maintained for each series of alternating copolymer systems and likewise for all diblock copolymer systems. This is because the principle driving force for these systems is to maximize the number of B-D contacts since the attractive force between B-D pairs is much greater than the repulsive force between A-B pairs.

Last, one can look at the total length that each conformation contributes to the length of the chain. These data are also depicted in Table I. In both copolymer sequences, the contribution that each specific conformation has to the overall chain length decreases from tails to trains to loops. The length contributed by trains is approximately the same for both copolymer sequences. This behavior is not surprising since we have already seen that  $R_{g,\parallel}$  is roughly the same for both copolymers. The length of the tails for the diblock copolymer is greater than that for the alternating case due to the ability to form a brush. In the same respect, the total length contributed by loops is greater for the alternating case relative to that of the diblock since the entropic frustration becomes greater with the alternating sequence's tendency to zip to the surface.

## V. CONCLUSIONS

Monte Carlo simulation utilizing the bond fluctuation model in conjunction with single and configurational biased Monte Carlo moves was used to study the adsorption of diblock and alternating copolymers at flat, chemically heterogeneous surfaces. Our results established the critical role of the commensurability between the copolymer's monomer sequence distribution and the size and spatial distribution of the heterogeneous domains on the adsorbing surface. By systematically increasing the spatial distribution of the substrate adsorbing sites, while keeping the overall number of the adsorbing and nonadsorbing sites on the surface unchanged, we have uncovered the conditions at which copolymers with block and alternating sequence distributions recognize the substrate chemical pattern and transfer it from the surface into the bulk. Due to their brushlike conformation at the surface, block copolymers recognize the substrate chemical motif once commensurability between the size of the adsorbing surface domain and the parallel component of the radius of gyration is established. Alternating copolymers, on the other hand, have a tendency to "zip" to the surface because

the adsorbing segments are evenly distributed along the entire length of the chain. This enthalpically driven "zipping" imposes an entropic penalty to the chain which must be alleviated through the formation of loops and tails. These conformational changes give the alternating copolymer the ability to recognize chemical patterns with periodicities much smaller than the parallel component of the radius of gyration and cause the inversion of the chemical pattern with increasing distances from the substrate.

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