

## Copolymer-assisted generation of three-dimensional patterns by replicating two-dimensional substrate motifs

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(Received 21 January 2000; revised manuscript received 8 September 2000; published 19 January 2001)

We use a three-dimensional self-consistent field model to study copolymer adsorption from polymer melts onto chemically heterogeneous substrates. We show that in situations where the copolymer sequence distribution is commensurate with the spatial distribution of the substrate chemical impurities, the two-dimensional substrate pattern gets transcribed into three dimensions and propagates into the polymer mixture. This transference scheme can assist in designing nanostructures that find use in various areas of science and technology.

DOI: 10.1103/PhysRevE.63.022601

PACS number(s): 68.15.+e, 68.35.Md, 68.08.-p, 68.55.-a

Adsorption of polymers at interfaces between the polymer solution (or melt) and a solid nonpolymeric substrate has been a subject of long-standing theoretical and experimental interest [1]. Numerous studies have shed light on the basic physics governing polymer adsorption on chemically homogeneous substrates. However, in most “real world” situations the substrates are not perfectly chemically homogeneous—they may be composed of more than one chemical species or can contain impurities, which will in turn influence the polymer partition on such substrates.

Being motivated mostly by recent experiments on ordering of copolymer melts on chemically heterogeneous substrates [1–4], several theoretical models and computer simulations have recently addressed the adsorption of polymers on chemically heterogeneous substrates [5–12]. While providing a first glimpse at the heterogeneous adsorption phenomena, these studies were limited to just a few specific systems involving homopolymers [5,6], random copolymers [7], and block copolymers [8–12]. The techniques used to study the adsorption on heterogeneous substrates were based primarily on the density-functional theory [5,7,11,12], Monte Carlo simulations [6,8,9], and two-dimensional self-consistent field (SCF) [10] approaches. In this report, a three-dimensional (3D) SCF lattice model is applied to evaluate the density distribution of copolymers of arbitrary monomer sequence distributions adsorbing on substrates with an arbitrary in-plane organization of chemical heterogeneities. We note that this 3D SCF model has several distinct advantages that cannot be achieved simultaneously with any other current 3D computational methods. For example, in 3D SCF one can work with a fully occupied lattice space with only a few limitations on the polymer concentration gradients, the information about chain conformation is available directly from the distribution functions, the calculation does not suffer from “frozen” configurations as in the Monte Carlo techniques, etc.

There are several reports in the literature describing the behavior of copolymers using a multidimensional SCF theory. In particular, Matsen and Schick [13] and Drolet and Fredrickson [14] used multidimensional SCF to explore vari-

ous bulk mesophases in multiblock copolymers. Petera and Muthukumar, and Zhulina and co-workers applied multidimensional SCF to explore the density profile of diblock copolymers near patterned substrates consisting of parallel chemically heterogeneous stripes [10]. In our system, the copolymer bulk concentration is homogeneous; it deviates from its bulk composition only near the substrate/mixture interface. This is in contrast to previous studies [8–12], in which the copolymer melts were ordered also in the bulk (usually lamellae). We show that copolymers whose sequence distribution [15,16] is commensurate with the substrate chemical pattern are capable of recognizing the substrate pattern and can be used to transfer the two-dimensional substrate motif into three dimensions. We claim that this simple assembling methodology based on the recognition of heterogeneous substrates by copolymers and their segment connectivity may assist in the design of a variety of applications including molecular level substrate patterning (or masking) of materials, fabrication of specialty miniature devices, preparation of molecular reaction sites for controlled chemical reactions, etc.

Our model is derived from the one-dimensional version of the SCF scheme introduced by Scheutjens and Fleer (SF SCF) [1]. Unlike the original SF SCF approach, the polymer segment density in our system is not only a function of  $z$ , the coordinate perpendicular to the mixture/substrate interface, but also of  $x$  and  $y$ , the coordinates parallel with the substrate plane. In contrast to 1D and 2D SCF approaches that consider plane and line averages, respectively, we apply a mean-field approximation only at a  $(x,y,z)$  site. Specifically, the segment density at a site  $(x,y,z)$  is derived from the weighted contributions of the site’s nearest neighbors. The computational details of the model have been presented elsewhere [17]. Here we restrict ourselves to just a brief description of the current system.

We consider a mixture of a homopolymer  $A$  (number of segments  $N_{hA}$ ) and a copolymer  $A-B$  (number of segments  $N_c$ ) with  $N_{hA} = 200$ ,  $N_c = 40$  (20 segments of  $A$  and 20 segments of  $B$ ), and the  $A-B$  volume fraction in the mixture, 0.01. The strength of the immiscibility between  $A$  and  $B$  segments is characterized by the Flory-Huggins interaction parameter  $\chi_{AB} = 0.25$ . The calculations have been carried out on a lattice composed of  $24 \times 24 \times 24$  sites with periodic

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boundary conditions applied in each  $(x,y)$  plane; the mixture/substrate interface is located at  $z=1$  and is parallel to the  $(x,y)$  lattice plane. The substrate is composed of two kinds of sites ( $C$ ) and ( $D$ ) that experience different chemical affinities towards  $A$  and  $B$ . The interaction between a polymer segment  $k$  and a substrate site  $m$  is characterized by the interaction energy  $k_B T \chi_{km}^s$ . We consider the substrate/polymer interactions to be of short-range order; thus only the polymer segments directly adjacent to the substrate are under the influence of the external field. By assigning the  $A/C$ ,  $B/C$ , and  $A/D$  interactions to be athermal ( $\chi_{AC}^s = \chi_{BC}^s = \chi_{AD}^s = 0$ ), and those between  $D$  and  $B$  to be attractive ( $\chi_{DB}^s = -0.25$ ), the  $B$  segments of the  $A$ - $B$  copolymer are expected to adsorb preferentially on the  $D$  regions of the substrate while there is no preference for either  $A$  or  $B$  to occupy the  $C$  substrate sites. We keep the number of the  $C$  and  $D$  substrate sites constant (50% each) and vary their spatial distribution on the substrate. Specifically, chemical patterns consisting of ordered arrays of  $C/D$  checkerboards of  $[6 \times 6]$ ,  $[1 \times 1]$ , and [random] periodicities are simulated. The interplay between the spatial distribution of the substrate chemical heterogeneity and the chain sequence distribution is examined for  $A$ - $B$  copolymers with diblock ( $A_{20}$ - $b$ - $B_{20}$ ) and alternating ( $A_{20}$ -alt- $B_{20}$ ) architectures. As demonstrated later, depending on the spatial distribution of the substrate ‘‘impurities’’ and the sequence distribution of the  $A$ - $B$  copolymer, the substrate motif will be recognized by the copolymer and eventually transcribed into the mixture. The volume fractions of the  $k$  segment,  $\phi_k(x,y,z)$ , are evaluated at each lattice site. We note that the total volume fraction profiles of  $A$  and  $B$  segments at the mixture/substrate interface are composed of adsorbed segments,  $\phi_k^a(x,y,z)$  (i.e., at least one polymer segment is adsorbed at the interface) and nonadsorbed segments,  $\phi_k^n(x,y,z)$ . However, in the discussion that follows we only consider  $\phi_k^a(x,y,z)$ .

To quantify the fidelity of the substrate-chemical-pattern transfer, we define the so-called pattern-transfer parameter (PTP) for segment  $k$ ,  $P_k$  as

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

In Eq. (1) the first and second sums in the numerator are carried out over the  $(x,y)$  sites above the  $D$  and  $C$  sites of the substrate, respectively, and  $A_D$  and  $A_C$  denote the substrate areas occupied by the  $D$  and  $C$  substrate sites, respectively (because the numbers of the  $C$  and  $D$  substrate sites are equal in our calculations,  $A_C = A_D$ ). Dividing the numerator by the total polymer volume fraction in layer  $z$  removes the effect of the decreasing concentration of the adsorbed chains with increasing  $z$ . From Eq. (1), the PTP ranges from  $-1$  or  $-100\%$  (perfect negative substrate motif transfer) to  $+1$  or  $+100\%$  (perfect positive substrate motif transfer).

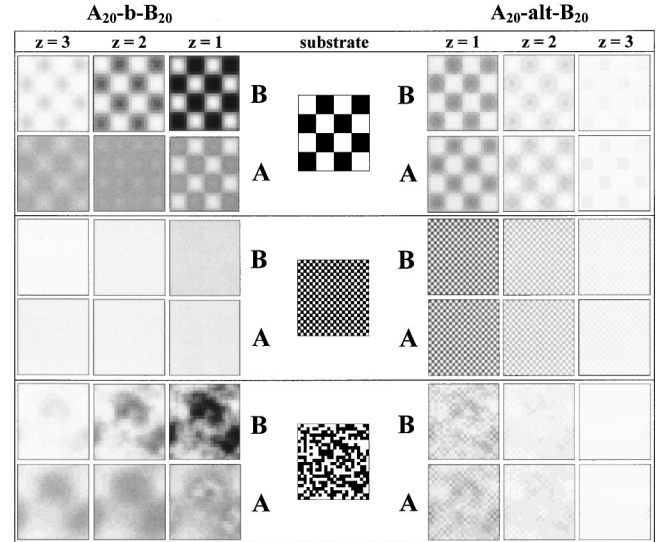


FIG. 1. Volume fraction profile maps of  $B$  segments and  $A$  segments of  $A_{20}$ - $b$ - $B_{20}$  (left panel) and  $A_{20}$ -alt- $B_{20}$  (right panel) copolymers adsorbed at planar substrates composed of  $C/D$  checkerboards with (from top to bottom)  $[6 \times 6]$ ,  $[1 \times 1]$ , and [random] patterns at various distances from the substrate/mixture interface. The white and black regions on the substrate denote the  $C$  and  $D$  substrate sites, respectively. The copolymer segment volume fractions range from 0 (white) to 1 (black).

Figure 1 shows the volume fraction profile maps of  $B$  and  $A$  segments of  $A_{20}$ - $b$ - $B_{20}$  (left panel) and  $A_{20}$ -alt- $B_{20}$  (right panel) copolymers adsorbed at planar substrates composed of  $C/D$  checkerboards with (from top to bottom)  $[6 \times 6]$ ,  $[1 \times 1]$ , and [random] patterns at various distances from the substrate/mixture interface. In Fig. 1, the white and black regions on the substrate denote the  $C$  and  $D$  substrate sites, respectively. The copolymer segment volume fractions range from 0 (white) to 1 (black). A quick visual inspection of Fig. 1 reveals that the sequence of the distribution of  $A$  and  $B$  segments along the copolymer chain determines strongly both the partition of the copolymer at the mixture/substrate interface and the distance through which the substrate pattern is transferred. As already mentioned, the fidelity of the pattern transfer will be evaluated using the pattern transfer parameter defined by Eq. (1).

Figure 1 shows that the spatial distribution of  $B$  in the layer directly adjacent to the  $[6 \times 6]$   $C/D$  checkerboard ( $C$ , white;  $D$ , black) mimics ideally the substrate motif due to the trains of the adsorbing block. As indicated in Fig. 2, the PTP of the  $B$  block of  $A_{20}$ - $b$ - $B_{20}$  is  $\approx +80\%$ . As one moves away from the substrate, the spatial distribution of  $B$  still follows the motif predefined by the substrate (three lattice sites away from the substrate,  $P_B$  is still  $\approx +20\%$ ) but the total amount of  $B$  decreases and eventually dies out at a distance of  $\approx 5$  layers from the substrate. The concentration of  $A$  in  $(x,y)$  planes follows a different pathway, however. While in the first layer the spatial distribution of  $A$  is a mirror image of the substrate pattern ( $P_A \approx -28\%$ ), for  $z > 2$  there is an image inversion of the  $(x,y)$  concentration of  $A$ . This behavior is associated with the formation of an  $A_{20}$ - $b$ - $B_{20}$  copolymer brush, with  $A$  being the nonadsorbing part of the brush that

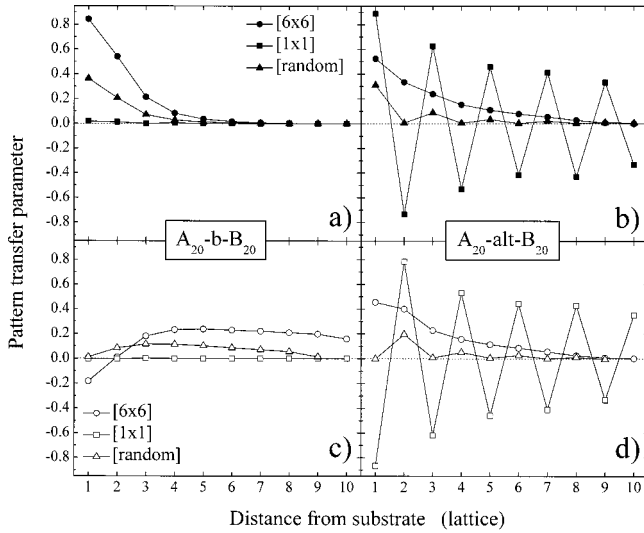


FIG. 2. Pattern transfer parameter for  $B$  segments (closed symbols) and  $A$  segments (open symbols) of  $A_{20}\text{-}b\text{-}B_{20}$  [(a) and (c), respectively] and  $A_{20}\text{-alt-}B_{20}$  copolymers [(b) and (d), respectively] and as a function of the distance from the substrate/mixture interface. The substrate pattern consists of checkerboards bearing  $[6 \times 6]$  (circles),  $[1 \times 1]$  (squares), and [random] (triangles) periodicities.

dangles away from the substrate deep into the mixture ( $P_A \approx +18\%$  even at a distance of 12 layers). Similar behavior observed for the  $[6 \times 6]$  patterns is seen also for the  $[3 \times 3]$  substrate [17], but the effects are weaker because the amount of the  $A_{20}\text{-}b\text{-}B_{20}$  copolymer adsorbing at the substrate/mixture interface decreases as a result of the less favorable spatial distribution of the  $D$  substrate sites. Finally, the substrate pattern information is nearly lost when  $A_{20}\text{-}b\text{-}B_{20}$  copolymers are adsorbing onto the  $[1 \times 1]$  substrate. Because of the strong incommensurability between the substrate chemical pattern and the copolymer sequence distribution, the  $A_{20}\text{-}b\text{-}B_{20}$  copolymer adsorbs at the  $[1 \times 1]$  substrate in the same manner it would do on a chemically homogeneous substrate with an effective interaction  $\chi_{DB}^s \approx -0.125$  [17]. Interesting behavior is detected on the substrate with random distribution of the  $C$  and  $D$  sites [random]. Figure 1 indicates that  $A_{20}\text{-}b\text{-}B_{20}$  detects areas with a small patchiness in the distribution of the  $C$  and  $D$  substrate sites. This in turn gives rise to local nonuniformities in the planar concentration of  $B$  in the close vicinity of the substrate/mixture interface, which decays as one moves away from the substrate. The  $A$  segments directly adjacent to the substrate mirror the distribution of  $B$ . However, at  $z > 1$  the  $A$  block dangles into the mixture forming a polymer brush as observed for the other substrate patterns.

The behavior of  $A_{20}\text{-alt-}B_{20}$  is different from that of  $A_{20}\text{-}b\text{-}B_{20}$ . We start our discussion with the adsorption of  $A_{20}\text{-alt-}B_{20}$  on  $[1 \times 1]$  substrates. The middle part of the right panel of Fig. 1 shows that for  $z=1$ , the  $B$  pattern exactly matches the motif on the substrate while the  $A$  pattern in plane structure is a negative image of the substrate pattern. By moving to  $z=2$ , the situation changes in that the  $B$  and  $A$  ( $x,y$ ) profiles carry the negative and positive imprint, respec-

tively, of the substrate motif. A close inspection of the ( $x,y$ ) profiles in Figs. 2(b) and 2(d) reveals that for  $z=1,3,\dots$ , the  $A$  and  $B$  ( $x,y$ ) profiles are negative and positive images of the substrate motif, respectively, while for  $z=2,\dots$  the situation is reversed. More insight about the pattern transfer can be obtained by evaluating the PTP using Eq. (1). The squares in Fig. 2 show the  $P_B$  (closed) and the  $P_A$  (open), respectively, of the  $A_{20}\text{-alt-}B_{20}$  copolymer on  $[1 \times 1]$  substrates. The data in Fig. 2 indicate that the  $[1 \times 1]$  substrate pattern propagates deep into the polymer mixture—even at a distance of 12 layers away from the substrate, the substrate pattern is transferred with an efficiency of  $\approx +20\%$ . The polymer conformations, determined from the distribution functions, reveal that the  $A_{20}\text{-alt-}B_{20}$  copolymer is “zipped” to the substrate forming a pancakelike structure with a train and tails that extend into the mixture. These tails are in fact responsible for the almost perfect epitaxial transfer of the substrate pattern away from the substrate into the polymer mixture [17]. The high efficiency of the substrate pattern transfer is a consequence of the exact match between the  $A_{20}\text{-alt-}B_{20}$  sequence distribution and the substrate  $[1 \times 1]$  chemical motif. Increasing the substrate pattern causes a mismatch between the chain sequence distribution and the substrate pattern and as a consequence, the  $P_A$  and  $P_B$  decay rather rapidly. Specifically, increase of the checkerboard pattern size to  $[6 \times 6]$  leads to a stronger adsorption of the  $A_{20}\text{-alt-}B_{20}$  copolymer at the mixture/substrate interface. However, in this case, influence of the substrate pattern is almost lost (with the exception of the first two layers closest to the substrate) and the copolymer behaves as a homopolymer on a chemically homogeneous substrate ( $P_A \approx P_B$ ). The volume fraction profile maps of  $B$  and  $A$  blocks of  $A_{20}\text{-alt-}B_{20}$  on the substrate with a [random] pattern are shown in the bottom right part of Fig. 1. Unlike the diblock copolymers (cf. bottom left part of Fig. 1), which preferentially adsorb on the substrate regions with larger patchiness of the  $D$  sites, the random copolymer tends to concentrate outside these  $D$ -rich substrate regions. This happens because the substrate chemical pattern outside these large concentrations of  $D$  substrate sites more closely matches the sequence distribution of the  $B$  stickers along the copolymer. Because the chain is “zipped” to the substrate, the information about the substrate pattern is only preserved up to  $\approx 2$  layers for both  $A$  and  $B$  segments. These concentration-damping effects for  $A_{20}\text{-alt-}B_{20}$  on the [random] substrates can be clearly seen in the behavior of the  $P_B$  and  $P_A$  functions shown by closed triangles and open triangles, respectively, in Fig. 2. Hence, in contrast to the block copolymers that can be applied as “amplifiers” of the substrate chemical patterns, copolymers with alternating sequence distributions can be used to “mask” the substrate “chemical roughness.”

In summary, 3D SCF model was used to show that the copolymer ability to recognize chemical patterns on flat two-dimensional substrates and transcript them with high fidelity into three dimensions depends strongly on the commensurability between the spatial distribution of the substrate “impurities” and the copolymer sequence distribution. Depending on the architecture of the copolymer, the chemical motif

can be imprinted in either a positive or a negative manner. When adsorbed on substrates with a random chemical pattern, block copolymers are capable of detecting small clusters of the substrate adsorption sites; alternating copolymers can successfully suppress the chemical pattern transfer on such random substrates. These simple recognition-assembly concepts presented here can have a great impact on the design of certain classes of materials and structures, many of which cannot be fabricated using any other technique.

This work was supported by the National Science Foundation (CAREER), Grant No. DMR-98-75256 and NCSU Faculty Research & Professional Development Grant. Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The author gratefully acknowledges fruitful discussions with Professor Sanat Kumar (Pennsylvania State University) and Professor Doros Theodorou (University of Patras).

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- [1] G. J. Fleer *et al.*, *Polymers at Interfaces* (Chapman & Hall, New York, 1993).
- [2] J. Heier, E. J. Kramer, S. Walheim, and G. Krausch, *Macromolecules* **30**, 6610 (1997); J. Heier *et al.*, *J. Chem. Phys.* **111**, 11 101 (1999).
- [3] L. Rockford *et al.*, *Phys. Rev. Lett.* **82**, 2602 (1999).
- [4] R. D. Peters *et al.*, *Langmuir* **16**, 4625 (2000).
- [5] D. Andelman and J. F. Joanny, *Macromolecules* **24**, 6040 (1991); G. Huber and T. A. Viglis, *Eur. Phys. J. B* **3**, 217 (1998).
- [6] A. Baumgaertner and M. Muthukumar, *J. Chem. Phys.* **94**, 4062 (1991); K. Sumithra and A. Baumgaertner, *ibid.* **109**, 1540 (1998); M. Muthukumar, *ibid.* **103**, 4723 (1995).
- [7] S. Srebnik, A. K. Chakraborty, and E. I. Shakhnovich, *Phys. Rev. Lett.* **77**, 3157 (1996); D. Bratko, A. K. Chakraborty, and E. I. Shakhnovich, *J. Chem. Phys.* **106**, 1264 (1997); A. K. Chakraborty, E. I. Shakhnovich, and V. S. Pande, *ibid.* **108**, 1683 (1998).
- [8] K. Huang and A. C. Balazs, *Phys. Rev. Lett.* **66**, 620 (1990); A. C. Balazs, K. Huang, and P. McElwain, *Macromolecules* **24**, 714 (1991); A. C. Balazs, M. C. Gempe, and Z. Zhou, *ibid.* **24**, 4918 (1991).
- [9] Q. Wang *et al.*, *J. Chem. Phys.* **112**, 9996 (2000); *Macromolecules* **33**, 4512 (2000).
- [10] D. Petera and M. Muthukumar, *J. Chem. Phys.* **109**, 5101 (1998); A. C. Balazs, C. Singh, and E. Zhulina, *Macromolecules* **31**, 6369 (1998).
- [11] D. Petera and M. Muthukumar, *J. Chem. Phys.* **107**, 9640 (1997); H. Chen and A. Chakraborti, *ibid.* **108**, 6897 (1998); S. K. Nath, P. F. Nealey, and J. J. de Pablo, *ibid.* **110**, 7483 (1999).
- [12] G. G. Pereira, D. R. M. Williams, and A. Chakraborti, *J. Chem. Phys.* **112**, 10 011 (2000), and references therein.
- [13] M. W. Matsen and M. Schick, *Phys. Rev. Lett.* **72**, 2660 (1994).
- [14] F. Drolet and G. H. Fredrickson, *Phys. Rev. Lett.* **83**, 4317 (1999).
- [15] E. A. Zheligovskaya, P. R. Khalatur, and A. R. Khokhlov, *Phys. Rev. E* **59**, 3071 (1999).
- [16] M. Muthukumar, *Proc. Natl. Acad. Sci. U.S.A.* **96**, 11 690 (1999); M. Muthukumar, C. K. Ober, and E. L. Thomas, *Science* **277**, 1225 (1997); M. Muthukumar, *Curr. Opin. Colloid Interface Sci.* **3**, 48 (1998).
- [17] J. Genzer, *Adv. Colloid Interface Sci.* (to be published).