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Polymer Adsorption on Chemically Heterogeneous Substrates

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ABSTRACT: Using Monte Carlo simulations, we investigated the adsorption of an A homopolymer and various AB copolymers onto chemically heterogeneous substrates. The substrates contain random arrangements of two different molecules: S1 and S2. The A monomers are strongly attracted to the S1 sites, while the A–S2 and B–surface interactions are weak in nature. The ratio of the S1/S2 surface sites is varied, and we determine how changing the fraction of S1 binding sites affects the properties of the adsorbed polymer films. To determine if the pattern of the S1's and S2's affects polymer adsorption, we examined a random and ordered arrangement of the surface sites. The results show that the arrangement of these sites influences the spatial distribution of the polymeric units on the surface. We also demonstrate that under certain circumstances AB copolymers are more effective at coating S1 surface domains than isolated A monomers. The results aid in tailoring polymers to yield films that display the desired characteristics on heterogeneous surfaces.

Introduction

The performance of polymer films, coatings, and polymer–ceramic and -metal composites depends in large part on the ability of polymers to adsorb and subsequently adhere to a substrate. Numerous studies have been undertaken to investigate the adsorption of homopolymers and copolymers on chemically uniform surfaces.[1-20] Substrates, however, may be composed of more than one chemical species or can contain impurities that arise from contamination or corrosion. Recently, we used Monte Carlo simulations[21] and self-consistent-field lattice calculations[22] to initiate fundamental studies of copolymer adsorption from solution onto chemically heterogeneous surfaces. In these studies, the surface contained equal amounts of two distinct materials, S1 and S2. Holding the ratio of the S1/S2 sites fixed, we determined how varying the morphology of the S1 and S2 domains on the surface affects the adsorption properties of copolymers.[21] We also established how varying the copolymer–surface interaction energies and chain architecture affects adsorption on surfaces containing fixed strips of S1 and S2.[22]

In this paper, we use Monte Carlo simulations to vary the ratio of S1/S2 surface sites and, for each value of this ratio, to contrast the surface adsorption of an A homopolymer and three different AB copolymers. Here, the A's are assumed to be attracted to the S1 sites, while the B's do not have a strong attraction to either the S1 or S2 components. Thus, the A–S1 interaction anchors the chains onto the surface. This situation will arise, for example, if the A's and S1 sites are hydrophobic, the B's are hydrophilic, and the solvent above the substrate is an aqueous medium. The model is also appropriate in the case where A and S1 are oppositely charged (and thus, are attracted through an electrostatic interaction) and all the other species are neutral.

Our goal in these investigations is 2-fold: first, to determine how varying the fraction of S1 on the surface affects the adsorption of the polymers onto the substrate, and, second, to determine if there is an optimal copolymer architecture that will provide the most uniform coverage of this heterogeneous surface.

It is anticipated that the actual arrangement of the S1/S2 sites on the surface will also affect the manner in which the polymers bind to the interface. In order to investigate this issue, we compare the results for a case where a finite fraction of S1 sites are randomly distributed on an S2 matrix with the case where the same fraction of S1 sites form a distinct pattern on the S2 interface.

Finally, using this patterned surface as the substrate, we compare the surface coverage provided by isolated A particles and polymer chains containing varying concentrations of A sites. This experiment is performed for various values of the A–surface interaction energy. The aim is to determine whether, and under what conditions, there is an advantage to using polymeric species when attempting to maximize the selective coverage of specific surface regions.

These studies are carried out by using Monte Carlo computer simulations that we developed to investigate the adsorption of copolymers onto a variety of interfaces.[18-21] Through this technique, we can precisely and independently vary such factors as the concentration and arrangement of the different surface sites, the sequence distribution of the monomers in the copolymer, and the monomer–surface interaction energies. The molecular weight, molecular weight distribution, and concentration of polymers in the solution above the substrate can also be precisely specified. Another advantage of the method is that the calculations will yield not only the total surface coverage but also the specific fraction of A and B units that lie on both S1 and S2 sites.

The results of these calculations will aid in tailoring copolymers for two diverse applications: either for coatings that provide a uniform coverage of nonuniform substrates or for films in which specific monomers are localized onto particular domains on the surface. Below, we detail the way in which the simulations are performed and present our results.

The Model

The simulation takes place in a cubic lattice that is 50 × 50 × 50 lattice sites in size. The $Z = 0$ plane represents the adsorbing wall. At the outset, the concentration and arrangement of the S1 and S2 lattice sites on this surface are specified. In these studies, we consider cases where the ratio of S1/S2 sites is less than or equal to 1, as well as the situation where the surface is composed entirely of S1 molecules. In the former examples, a specified number of S1 sites are randomly dispersed on a matrix of S2 molecules. Once the surface is specified, 20 self-avoiding random-walk chains are placed at random locations in the cube. The length and the sequence distribution of the chains are also fixed at the beginning of the simulation.

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In a given run, all the polymers have the same structure, and in all the runs, the chains are 33 lattice sites in length.

The chains are allowed to diffuse throughout this volume. In particular, one of the chains in the system is chosen at random, and one of the beads in this chain is randomly selected. The chain is "wiggled" about this bead via the algorithm for chain dynamics developed by Verdier and Stockmayer[23] and Hilhorst and Deutch.[24] Then the entire chain is translated one lattice site in one of six possible directions (to be picked at random). All attempted moves obey the excluded-volume criteria.

These free chains continue to diffuse until an A site (or "sticker") is one lattice unit above an S1 surface site. Then, the A bead remains bound at this location (for a finite number of time steps, see below), while the remainder of the chain is free to wiggle about this point of attachment. Whenever any subsequent A bead is one unit above an S1 site, it binds at the location, thus modeling the strong affinity between an A monomer and the S1 species. The intervening units in the copolymer are still allowed to wiggle about the points of attachment (under the constraint that the chain does not break apart at any time). Thus, if an A segment comes in contact with an S2 surface site or if a B segment comes in contact with either an S1 or S2 site, these species can wiggle away from such surface locations in a later move. This aspect of the program models the weak A–S2 and B–surface interaction.

Whenever a free chain becomes bound to the surface, a new chain is added at a random location in the solution above the adsorbing surface. Thus, the number of free chains in the solution remains constant throughout the simulation.

In this set of simulations, we assume that the binding between an A bead and an S1 site is reversible. Specifically, when a bound chain is randomly selected from all the chains in the system and, furthermore, an S1-bound A is picked from the units on the chain, the single A sticker is allowed to wiggle off this site with a specified probability *P*. In these studies we have arbitrarily set *P* equal to 0.1. Only a single A bead is allowed to desorb from S1 per unit time step: if the wiggling motion also causes continguous A units to desorb from S1 sites, the move is rejected. On the other hand, if A sites are simultaneously desorbed from S2 sites or if B sites are simultaneously desorbed in the course of the wiggle, the move is accepted. These rules model the fact that the chain is anchored to the surface through the strong A–S1 bonds.

When a particular A bead desorbs from an S1 site, it may wiggle back to a surface position in a subsequent move and, thus, once again become bound. When a chain does desorb, it is translated in a direction to be picked at random: either in the four directions parallel to the interface or one lattice site vertically up or one lattice site vertically down. In the latter case, the chain can again become bound to the surface. If, on the other hand, the chain remains free, the chain furthest from the *Z* = 0 wall is removed from the box. This ensures that the number of free chains in solution remains constant at 20.

Initially, the chains can desorb without significant hindrance from the other adsorbed chains. As the surface becomes more crowded, steric hindrance from neighboring chains will make desorption more and more difficult.

The simulations were run for 10–30 million time steps, that is, until the surface has effectively become saturated and the surface coverage reaches a plateau value (see Figure 1). (Specifically, we run the simulation until three consecutive values, measured at 1 million time step intervals, all differ by less than 1%.) The values in the subsequent figures and tables, which characterize the surface properties of the polymers, are taken from this plateau region. Two independent runs were performed for each case that was examined, and the results represent the averages of the values that were obtained from the two trials. (For each *particular* S1/S2 ratio that was investigated, the *same* random surface was used in both trials.)

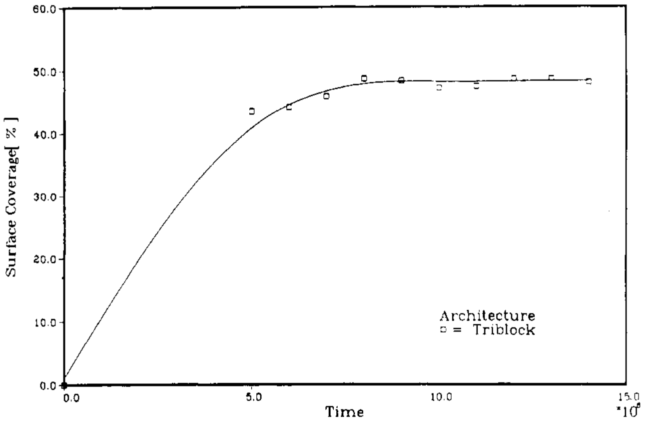

Figure 1. Surface coverage versus time for the triblock architecture.

In all these investigations, we are focusing our attention on the nature of the polymer–surface interaction. Thus, we neglect chain–chain interactions in the solution and between free and adsorbed chains. Such interactions can be neglected when the energy of interaction between the surface and the polymer is much greater than the interaction between individual polymers. It is for this scenario that our simulations are most appropriate.

Results and Discussion

Five different surfaces containing various percentages of S1 sites were examined. In particular, 10%, 16%, 30%, and 50% of the total surface sites were S1's randomly dispersed on the remaining S2 material. A surface containing 100% S1's was also examined. Along with the A homopolymer, three distinct copolymer sequence distributions were investigated: an alternating, triblock, and diblock structure. The alternating chain contains 17 A's and 16 B's that are arranged in an ABABAB... sequence. The triblock is composed of two A blocks, of eight sites each, on either side of an intervening segment of 17 B's: the $A_8B_{17}A_8$ structure. The diblock is formed from a block of 17 A's followed by a block of 16 B's, or $A_{17}B_{16}$. By maintaining the number of A's and B's approximately the same in all of the copolymer structures, we can clearly distinguish the effect of the sequence distribution of the monomers on the adsorption behavior.

Figure 2 and Table I show the total surface coverage (the *total* number of polymer sites lying in the *Z* = 1 plane divided by the area of the surface) provided by the different polymer solutions for the various surfaces examined. Table I also contains the percentage of A's (B's) in the bound chains that are in direct contact with the surface (both S1 and S2 sites). This number is calculated as

$$f_J = \frac{\text{total number of } J \text{ beads on surface}}{\text{number of bound chains} \times \text{number of } J\text{'s per chain}} \qquad (1)$$

where *J* is A or B.

Table II shows the average number and length of the "trains", "loops", and "tails" that exist in a given adsorbed chain. The terms refer to the different configurations that are present in these chains: a train is composed of

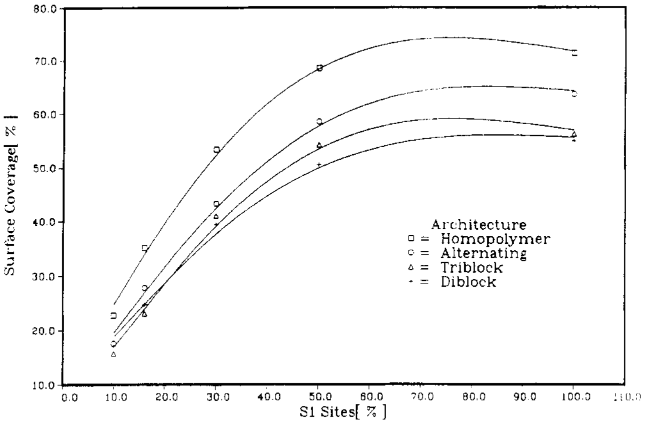

Figure 2. Percent surface coverage provided by the four polymers for the various surfaces examined. The horizontal axis displays the percentage of S1 sites on the S2 matrix.

contiguous beads that lie directly on the surface, a loop lies between two trains and extends away from the surface, and a tail rises into the solution and does not return to the wall. These data are given for all the architectures on the various surfaces examined. (To obtain the number of each configuration in a chain, we summed the total number of trains, loops, and tails and then divided by the number of bound chains. To calculate the length of each structure, we summed the total number of beads that are in each configuration and then divided by the total number of beads in all the bound chains.)

For the pure S1 surface, the highest surface coverage is provided by the homopolymer. The alternating copolymer yields a somewhat lower coverage, and the two block architectures give the lowest values. This implies that the way in which the noninteracting B comonomers are arranged in the chain affects the surface activity of the copolymer. Specifically, when the number of A–B contacts is high, A's that bind to the surface can drag contiguous B's down onto the wall, which then contribute to the overall surface coverage. (Note the high values of f_B in Table I for the alternating chains.) In the block cases, however, the long B segments form loops and tails that extend into the solution and away from the interface (see Table II). Thus, these segments do not contribute to the surface coverage.

If we now consider the surface that contains 50% of the noninteracting S2 sites, an unexpected result is found. Namely, in reducing the percentage of S1 sites from 100 to 50, the surface coverages provided by the various polymers are affected by only a few percent. As noted above, the S1 sites are randomly distributed on the wall. At a 50% level, on average, every other site is S1 in nature. Consequently, the average distance between S1 sites has only been reduced from one to two lattices sites in this alteration of the surface. Furthermore, the homopolymer, alternating, and triblock have "sticky" A's at both ends; thus, they can readily span the noninteracting sites. In addition, the entire chain length can come in contact with the wall and the intervening units will bind to the surface. In particular, A's and B's that lie pinned between S1-bound A units, can be "pulled" onto neighboring S2 sites. As can be seen in Table I, though the number of A–S1 and B–S1 interactions decreases (in going from the 100% to 50% case), the number of new A–S2 and B–S2 contacts partially compensates for this loss. (Due to the increased number of A–S2 contacts, the values of f_A are higher for the 50% S1 surface than for the 100% S1 wall.)

These observations are supported by the data in Table II. The configurations of all the various polymers (including the diblock) change in going from the 100% to 50% S1 surface. The chains now contain a higher number of shorter trains and loops. The net result is that the number of beads in trains increases, while the number in loops decreases. In essense, the chains are "stretched out" along the surface in order to optimize the number of A–S1 contacts.

As the number of S1 sites is reduced below 50%, the decrease in surface coverage becomes more dramatic. In going from 50% to 10% S1, the average spacing between the S1's increases from 2 to 10 lattice sites. Now, large S2 domains begin to appear on the interface, making it more difficult for chains to bind to the wall. Table I reveals the large decrease in the number of bound chains as the number of S1 sites is reduced.

Further insight into the adsorption properties of copolymers on heterogeneous surfaces can be gained from examining the spatial distributions of the A's and B's within the adsorbed layer. These distributions are displayed in parts a–d of Figure 3 for each polymer architecture on the surfaces containing 100%, 50%, 30%, and 10% S1 sites, respectively. The percentages in the histograms are calculated from the data in Table I through the equation

$$\% \text{ of } J \text{ on } SK = \frac{\text{number of } J \text{ beads on } SK}{\text{total number of polymer beads on the surface}} \tag{2}$$

where J can be A or B and K can be 1 or 2.

As can be seen by comparing parts a and b of Figure 3, reducing the S1 sites by 50% reduces the number of A–S1 contacts particularly for the homopolymer, triblock, and diblock architectures. In these polymers, adsorption of one A brings neighboring A's down on the surface, which may bind to the wall in contiguous segments or trains (see Table II). Since the S1's are randomly interspersed among the S2's, this behavior causes a high fraction of A's to lie atop the S2 sites.

Since each A sticker is separated by a B in the alternating structure, it is difficult to form long trains along the surface (see Table II). Rather, the chains form a large number of loops between A–S1 contacts. Thus, introducing a random distribution of 50% S2 sites does not effect the surface distribution of the A's for this architecture as dramatically as for the other examples. Since the A's bind preferentially to the S1's, the B's in the alternating copolymer will be primarily localized on the S2 sites when they come in contact with the surface.

An important conclusion emerges from the above discussion and from comparing Figures 2 and 3b. While the total surface coverage provided by the alternating and triblock copolymers is comparable for the 50% S1 surface, Figure 3b indicates that the type of coating provided by these chains will, in fact, be quite different. In particular, the S2 sites are primarily covered by B's for the alternating case, while the S2's are primarily coated by A's in the triblock example.

Another surprising result is that the spatial distribution of the A's and B's on the surface is quite similar for the triblock and diblock architectures. The similarities in Figure 3b can be attributed to changes in the conformation of the triblocks. A particular advantage of the triblock structure is that while one end is pinned to the wall, the other end can slide along the surface until the number of A–S1 contacts is maximized. This process can continue until the total number of such contacts is maximized for *both* ends. The net result is that the number of A's in trains increases, while the number of B's on the surface

Table I[a]

fraction of S1 sites	A–S1	A–S2	B–S1	B–S2	total beads	no. of chains	surface coverage, %	FA, %	FB, %
Homopolymer									
10	161.0	383.0	0.0	0.0	544.0	42	22.7	39.3	0.0
16	301.0	542.0	0.0	0.0	823.0	76	35.1	33.6	0.0
30	590.5	691.0	0.0	0.0	1281.5	77	53.4	50.4	0.0
50	999.5	648.5	0.0	0.0	1648.0	101	68.6	49.4	0.0
100	1715.5	0.0	0.0	0.0	1715.5	113	71.4	46.0	0.0
Alternating									
10	106.2	114.3	14.5	184.8	419.8	36	17.5	36.0	34.6
16	194.5	54.0	40.5	279.5	668.5	50	27.8	29.2	40.0
30	353.1	188.3	110.5	386.7	1038.6	65	43.3	49.0	47.8
50	575.9	166.1	262.3	413.7	1408.0	90	58.6	48.5	46.9
100	801.5	0.0	729.5	0.0	1531.0	112	63.7	42.1	40.7
Triblock									
10	117.8	178.1	3.6	76.7	376.2	38	15.7	48.7	12.4
16	220.0	241.5	5.0	88.0	554.5	52	23.1	55.5	10.5
30	475.5	375.7	24.8	109.5	985.5	82	41.0	64.9	9.6
50	792.3	357.5	60.1	93.4	1303.3	105	54.3	68.4	8.5
100	1155.5	0.0	196.0	0.0	1351.5	114	56.3	63.4	10.1
Diblock									
10	137.3	235.8	2.4	34.2	409.7	38	17.1	57.8	6.0
16	230.5	327.0	3.0	32.5	592.5	53	24.7	61.9	4.2
30	469.5	421.4	8.6	46.0	945.0	78	39.4	67.2	4.4
50	791.2	370.4	17.0	37.4	1216.0	93	50.6	73.4	3.7
100	1248.0	0.0	72.0	0.0	1320.0	111	55.0	66.1	4.1

[a] The maximum standard deviation on all values is within ±9.0%.

Table II[a]

fraction of S1 sites	trains per chain	train length (A, B)	loops per chain	loop length (A, B)	tails per chain	tail length (A, B)
Homopolymer						
10	2.92	4.40 (4.40, 0.00)	1.98	4.36 (4.36, 0.00)	1.05	10.98 (10.98, 0.00)
16	3.48	4.36 (4.36, 0.00)	2.50	4.11 (4.11, 0.00)	1.00	7.53 (7.53, 0.00)
30	4.29	4.00 (4.00, 0.00)	3.36	3.98 (3.98, 0.00)	0.56	4.26 (4.26, 0.00)
50	3.81	4.29 (4.29, 0.00)	2.86	5.23 (5.23, 0.00)	0.37	4.66 (4.66, 0.00)
100	2.92	5.20 (5.20, 0.00)	1.92	9.01 (9.01, 0.00)	0.17	3.24 (3.24, 0.00)
Alternating						
10	2.53	4.44 (2.34, 2.10)	1.56	5.32 (2.64, 2.68)	1.15	11.72 (6.05, 5.67)
16	3.11	4.28 (2.22, 2.06)	2.19	4.45 (2.23, 2.22)	1.06	9.37 (4.87, 4.50)
30	4.08	3.90 (2.02, 1.88)	3.16	3.98 (1.99, 1.99)	0.56	7.84 (4.16, 3.68)
50	4.58	3.43 (1.78, 1.65)	3.62	4.09 (2.08, 2.01)	0.33	8.44 (4.42, 4.02)
100	3.97	3.45 (1.80, 1.65)	2.98	6.20 (3.16, 3.04)	0.11	7.92 (4.14, 3.78)
Triblock						
10	2.20	4.26 (3.51, 0.75)	1.28	8.04 (1.80, 6.24)	1.14	11.62 (5.18, 6.44)
16	2.23	4.76 (3.96, 0.80)	1.28	9.35 (1.83, 7.52)	0.93	11.17 (5.13, 6.04)
30	2.83	4.28 (3.70, 0.58)	1.86	9.14 (1.91, 7.23)	0.54	7.53 (3.71, 3.82)
50	2.76	4.51 (3.98, 0.53)	1.79	10.36 (2.27, 8.09)	0.30	6.94 (3.19, 3.75)
100	2.46	4.80 (4.11, 0.69)	1.46	13.89 (3.79, 10.10)	0.11	8.51 (3.56, 4.95)
Diblock						
10	1.90	5.66 (5.16, 0.50)	0.94	4.17 (3.03, 1.14)	1.29	14.22 (3.35, 10.87)
16	2.01	5.60 (5.27, 0.32)	1.04	3.41 (2.66, 0.75)	1.35	13.46 (2.68, 10.78)
30	2.41	5.02 (4.74, 0.28)	1.43	2.87 (2.52, 0.35)	1.24	13.57 (1.59, 11.98)
50	2.26	5.81 (5.56, 0.25)	1.29	2.92 (2.48, 0.44)	1.13	14.32 (1.10, 13.22)
100	2.00	6.53 (6.18, 0.35)	1.01	4.70 (4.36, 0.34)	1.04	14.64 (0.23, 14.41)

[a] The maximum standard deviation on all values is within ±10.0%.

decreases (see Table II). As a consequence, the histograms for these tri- and diblocks appear similar in nature.

Finally, we note that while the homopolymer yields a higher surface coverage than the tri- and diblocks, the spatial distribution of the polymeric units on the 50% S1 surface for these architectures is remarkably similar. This is due to the fact that the homopolymer binds in loops (and to a lesser extent tails), not just long trains that lie along the surface.[11,12] In particular, from Table I, we see that only 46% and 49% of the A's on all the bound homopolymers lie on the surface for the 100% and 50% S1 surface, respectively. From Table II, it is clear that the remainder of the A's lie in loops (and tails) that extend away from the wall. Thus, the homopolymer does not provide a significantly more *uniform* coverage of the 50/50 surface than the tri- and diblock copolymers.

By comparing parts b–d of Figure 3, we can determine how these adsorption patterns shift as the concentration of S1 sites on the surface is decreased. In agreement with intuition, the fraction of A's bound to S1 decreases as the fraction of S1 binding sites decreases. It is worth noting that, even on the 10% and 16% S1 surfaces (Figures 3d and 5d), A's sticking to S1's still constitute a significant fraction of all the molecules on the surface. Thus, the sticky A's can locate the small number of randomly dispersed binding sites. In addition, as the percentage of

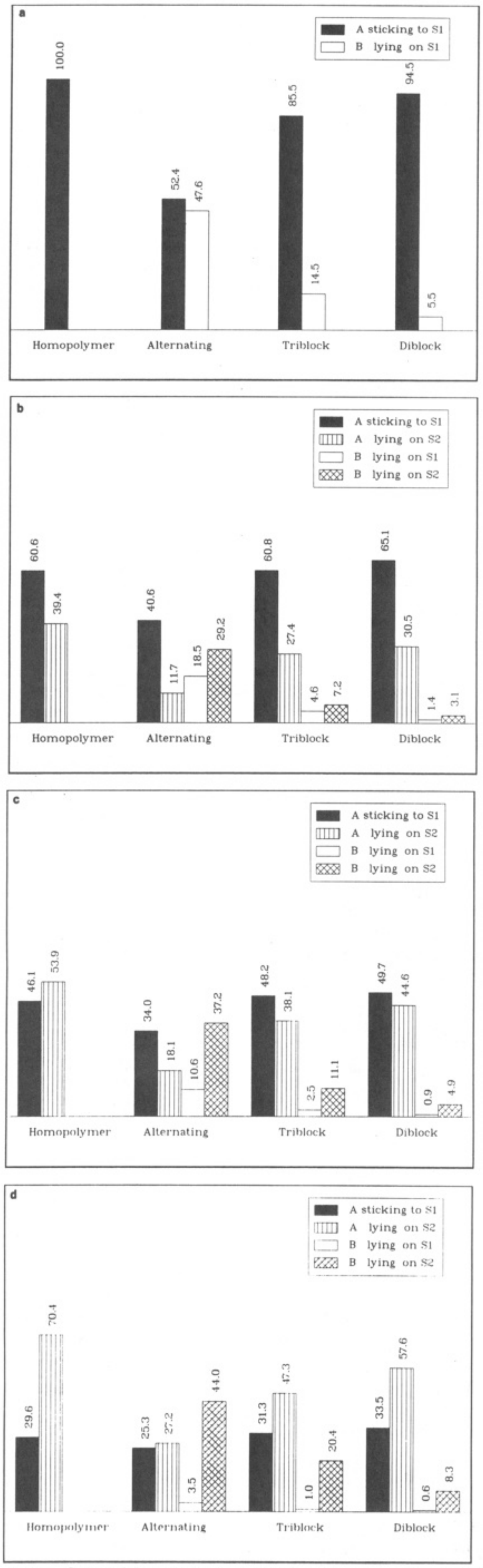

Figure 3. Spacial distribution of the A and B sites on the surfaces containing (a) 100%, (b) 50%, (c) 30%, and (d) 10% S1 surface sites.

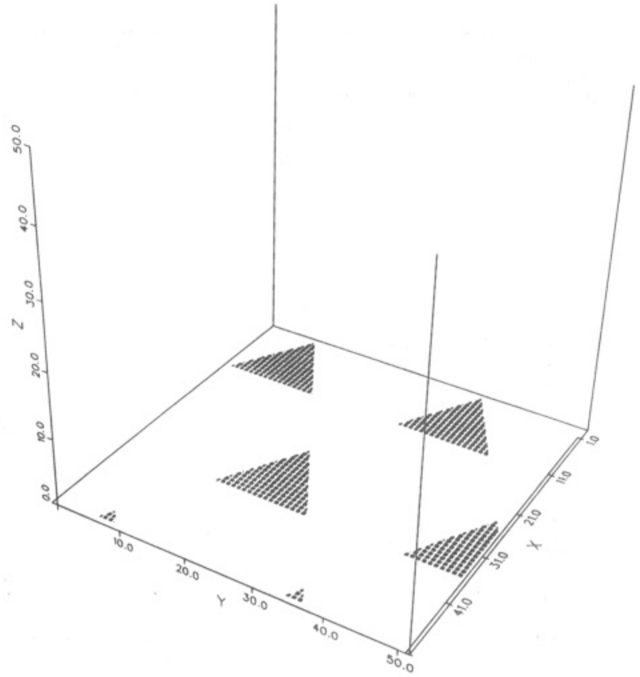

Figure 4. View of the patterned substrate. The shaded areas represent the S1 sites. The surface is 16% S1 and 84% S2. Periodic boundary conditions are applied along the edges of the wall.

S1's is lowered to 10 or 16, the percentage of A's on the S1's is essentially comparable for all architecture. At such a low concentration of binding sites, only two of four A's on each chain will bind to the S1 sites (as can be calculated from Table I). Since the sites are randomly dispersed and there are large S2 domains, the chains bind to S1's that are in close proximity. This constrains all chains to occupy comparably small areas on the surface. In effect, the polymers now bind with a significant fraction of the chain extending into the solution.

Further evidence for this behavior is seen in Table II. Below 50% to 30% S1 sites, the number of beads in trains and loops decreases, while the number in tails increases significantly for all the polymers examined. (This again indicates that the chains occupy a smaller area directly on the surface.) With such a high fraction of beads in tails, differences due to variations in molecular architecture are seen to decrease.

Random versus Ordered Surface Sites. To determine if the underlying pattern of S1 and S2 sites affects the mode of copolymer adsorption, we examined two surfaces in which the S1 concentrations were identical (16%); however, in one case these sites were randomly dispersed (as in the above examples) and in the other case, the S1's were arranged in a regular geometric pattern (see Figure 4). In the latter scenario, the S1's are arranged in uniform triangles that are regularly spaced on the S2 matrix. By viewing parts a and b of Figure 5, it is clear that there are large differences in the spatial distributions of the polymers on the two surfaces.

The adsorption properties of the homopolymer and tri- and diblock copolymers on the two distinct surfaces are particularly different. Since the ordered surface contains well-defined S1 domains, the A blocks can efficiently bind to and cover these regions (see Figure 5b and Table III). Since fewer S1 sites have S2 neighbors in the regularly patterned surface, far fewer A's bind to S2 sites. These characteristics are evident for all three architectures. (We note that the average radius of gyration of these chains is less than the spacing between the triangles on the patterned

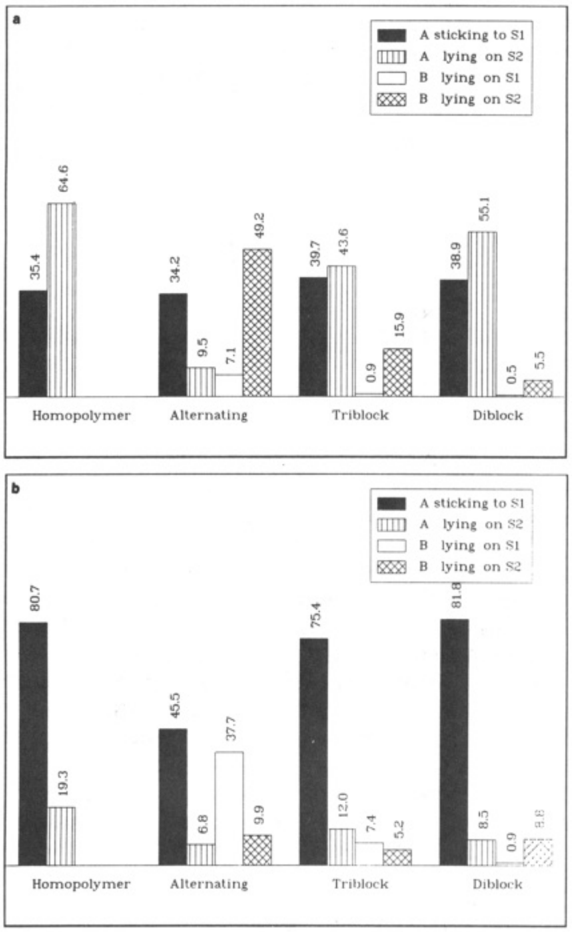

Figure 5. Spacial distribution of the A and B sites on the surfaces containing a random (a) and patterned (b) arrangement of the 16% S1 sites.

surface. Thus, the polymers bind to one particular S1 region and do not span between the triangles.)

Additional differences are evident when comparing the behavior of the triblocks on both surfaces. The triblock has two "sticky feet"; consequently, B's that are in proximity of either block can be dragged down onto the interface. Since, the A's are localized on the S1 domains in the ordered surface, B's that are brought in contact with the wall are more likely to lie above S1 sites than S2 locations. Thus, the percentages of B's on S1 is enhanced and the number of B's on S2 is subsequently less for the geometrically patterned interface. (For the diblock, which has only one "sticky foot", this effect is less pronounced.)

The alternating copolymer also shows differences in adsorption behavior between the two surfaces. The most dramatic difference is the high percentage of B's on the S1 sites in the ordered surface. Again, since the A's are localized above the triangular S1 domains, these species will force the intervening B's to lie in close proximity. The number of A–B contacts is highest for the alternating copolymer; thus, this architecture exhibits the highest fraction of B's that are dragged down onto this region. Forced to lie on the S1 sites, there are fewer B's available for covering the S2 sites, as can be seen in the Figure 5b. Since, a high fraction of B's now cover S1 locations, fewer sites are available for A–S1 interactions. Thus, the number of A–S1 interactions is not as dramatically enhanced in going from the random to ordered surface as in the case of the blocky architectures, where the B's do not intervene to such a large extent.

From Table III, it is clear that the total number of chains bound to the ordered interface (and subsequently, the overall surface coverage) is significantly less than the number bound to the random surface. In the former case, the chains pack densely about the S1 sites (as can be seen from the spatial distribution data noted above). This dense brush of chains sterically hinders other copolymers from approaching the S1 domain and effectively diminishes the number of chains on the surface. When the inhomogeneities are randomly dispersed, the chains are also more dispersed on the interface and, therefore, are less effective at sterically hindering incoming copolymers. Consequently, more chains can access the available binding sites.

These calculations represent the first computational demonstration that the actual arrangement of the different surface sites affects the surface adsorption of these copolymers. The above results (see Table III) indicate that the homopolymer and blocky copolymers are highly efficient at covering finite-sized S1 surface regions. This behavior can prove particularly advantageous if the coating of specific surface domains is desired.

Polymers versus Particles. In addition to comparing the adsorption characteristics of different polymers, it is of significant interest to contrast the binding properties of chains and particles. In particular, we examine whether the copolymers or isolated A particles will provide a higher coverage of the S1 region. Our aim is to probe under what conditions there is an advantage to "stringing" the A's into a chain versus utilizing isolated monomers in order to coat specific surface domains. To investigate this behavior, we carried out simulations for the adsorption of particles and various polymers on the ordered surface shown in Figure 4.

At the onset of the simulation for particle adsorption, 600 A sites are placed at random locations in the cubic lattice above the $Z = 0$ plane. This represents a concentration of 4.8×10^{-3} particles/unit volume. The simulation proceeds as noted in The Model section; however, the particles diffuse via translations and are not wiggled. In addition, we now vary the probability that an A unit will stick to the surface when it comes in contact with an S1 site. While this parameter was set equal to 1.0 in the previous studies, its value is altered from 0.1 to 1.0 in these calculations. To ensure that a high fraction of particles will remain bound to the surface, the probability that an A site leaves the wall has been reduced to 0.0001.

In order to compare systems that contain the same total number of A's, the polymer simulation is modified so that a fixed number of chains are placed into the box at the onset of the simulation and no further chains are added in the simulation. In particular, the chain length is now fixed at 20 lattices sites, and we consider the cases where the chains are composed of 25%, 50%, and 75% A's. Thus, in the first case, 120 chains are placed in the box, in the second case 60 identical copolymers are introduced onto the lattice, and, finally, in the last instance 40 chains are used. In this way, all simulations (polymers and particles) involve the identical number of stickers. In the first copolymer example, the A's constitute every fourth bead, in the second case, the A's alternate with the B's, and in the last situation, three A's follow a single B along the length of the chain. As in the case of the particles, we now specify the sticking probability between the A's and the S1's, and the reversing probability, P, has been set at 0.0001.

Parts a and b of Figure 6 display the differences in the binding behavior between the various copolymers and particles. For a high A–S1 sticking probability, the particles are uniformly more efficient at covering the S1 domain than the various copolymers. As may be expected,

Table III[a]

	A-S1	A-S2	B-S1	B-S2	total beads	no. of chains	surface coverage, %	S1 coverage, %
				Random Surface				
homopolymer	301.0	542.0	0.0	0.0	843.0	76.0	35.1	78.4
alternating	194.5	154.0	40.5	279.5	668.5	70.0	27.8	50.5
triblock	220.0	241.5	5.0	88.0	554.5	72.0	23.1	57.3
diblock	230.5	327.0	3.0	32.0	592.5	73.0	24.6	60.0
				Patterned Surface				
homopolymer	357.1	88.2	0.0	0.0	445.3	26.5	17.8	90.9
alternating	165.7	24.8	137.3	36.0	363.8	24.5	14.6	42.2
triblock	291.4	46.5	28.4	20.0	386.3	33.0	15.5	74.1
diblock	331.0	34.2	3.7	35.7	404.6	33.0	16.2	84.2

[a] The maximum standard deviation on all values is within ±9.0%.

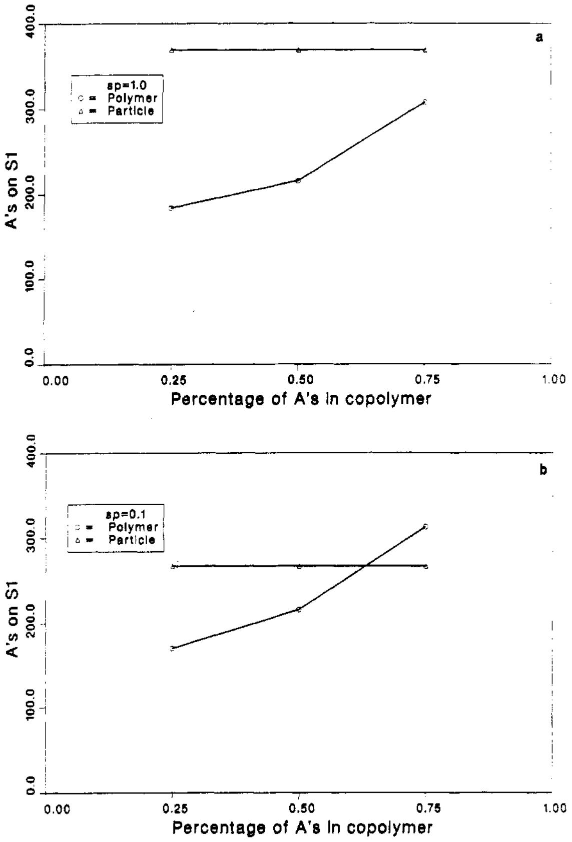

Figure 6. Number of A sites on S1 versus the fraction of A's in the copolymer. The sticking probability, SP, is equal to 1.0 in a and 0.1 in b. The straight line in both graphs displays the behavior for the particles.

the greatest difference between the polymers and particles occurs when the copolymer contains the lowest fraction of A's. In this instance, the intervening B's prevent the A's from accessing the S1 sites.

On the other hand, when the A-S1 sticking probability is reduced to 0.1, we see a crossover in the binding characteristics (Figure 6b). When the copolymers contain more than 65% of A units, they are more efficient at covering the S1 domain than the isolated particles, despite the fact that they contain a finite fraction of B's. At a lower sticking probability, the particles are less likely to stick to the surface; however, when an A on a chain finally sticks, it brings the contiguous A's into contact with the interface. Once the A's in the copolymer bind, it is also more difficult for this string of molecules to be peeled away from the S1 domain. Thus, for monomers that have a low surface affinity there is a considerable advantage to polymerizing these units if these molecules are to be used in coating specific regions on chemically heterogeneous surfaces.

Conclusions

We have used a Monte Carlo model on a cubic lattice for our simulations. The qualitative agreement between our previous work[20] and that of Evers et al.[13] highlights two important features. First, since good agreement was obtained between these Monte Carlo simulations and the self-consistent-field lattice calculations, the fundamental conclusions are not method-dependent. Second, since a hexagonal lattice was used in the latter work, agreement between the two models also indicates that the conclusions are independent of the nature of the lattice.

Here, we examined the adsorption properties of an A homopolymer and three distinct AB copolymers on chemically heterogeneous surfaces containing various random distributions of S1 and S2 sites. Reducing the fraction of S1 binding sites from 100% to 50% does not appreciably affect the total surface coverage provided by the homopolymer or the alternating and tri- and diblock copolymers. These results have important implications about the concentration of binding sites that are necessary to ensure a high surface coverage. In particular, if impurities occur at random locations on the interface, the total surface coverage provided by these polymeric films will not be significantly diminished until the concentration of impurity sites exceeds 50% of the surface. (Here, we are assuming that the size of a monomer is comparable to the size of an impurity site.)

On the other hand, since the number of strong A-S1 contacts is reduced by 30% to 40% (see Table I), the adhesion between the substrates and the polymer films will be significantly affected by decreasing the number of S1 sites.

The histograms in Figure 3b reveal another surprising finding: the homopolymer and tri- and diblock copolymers provide a comparable distribution of molecules on the 50% S1 substrate. In all cases, approximately 60% of the A's lie on S1 sites, while 30-40% lie on the S2 material. This phenomenon is due to the fact that a significant fraction of the homopolymer A's lie in loops and tails rather than trains along the surface. Thus, covering this substrate with a homopolymer will *not* yield a more uniform layer of A's directly on the surface than covering the substrate with the triblock or diblock copolymer. Coating the surface with these chains will yield the same spatial distribution of A's throughout the interface, which will, to a large degree, mask the presence of the underlying impurities.

For the alternating copolymers, the A's are fairly segregated on the S1's, while the B's are primarily localized on the S2's in the surfaces containing 16-50% S1's. Thus, coating such heterogeneous surfaces with the alternating copolymer will create films that contain domains rich in A and regions rich in B. The adsorbed surface layer will essentially mirror the heterogeneities that are present in the substrate.

The differences in the adsorption properties of the various copolymers indicate that the adhesion between the copolymers and the heterogeneous substrate will also be different for the blocky and alternating chains. Since a higher fraction of the strong A–S1 bonds are formed through the adsorption of the blocky chains, it is expected that the adhesion between these copolymers and the substrate is stronger than that in the alternating copolymer case. Though the alternating copolymers provide a slightly higher surface coverage, a high fraction of the polymer surface contacts involve the weaker A–S2 or B–surface interactions, which would not significantly contribute to adhering the chains to the interface.

We also found that the arrangement of the different chemical species in the substrate greatly influences the spatial distribution of the polymeric units on the surface. With the number of S1's held fixed, we examined a random and ordered arrangement of the surface sites. The spatial distributions of the A and B molecules on the two surfaces are different for all the polymers examined. In the patterned substrate, the A's are highly localized on the S1 regions of the surface. Our previous studies[21,22] have also shown that adsorption on ordered heterogeneous substrates results in the segregation of chains onto specific surface domains.

Finally, we demonstrated that under certain circumstances AB copolymer are more effective at coating the S1 surface sites than isolated A monomers, despite the fact that the copolymer contains the nonreactive B units.

The above results help establish design criteria for tailoring copolymer chains to yield polymeric films that display the desired characteristics on heterogeneous surfaces.

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