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Layering Phase Separation of Densely Grafted Diblock Copolymers

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ABSTRACT: Phase separation of symmetric diblock copolymers end-grafted to a wall is studied using a Monte Carlo simulation. The nearest-neighbor repulsion between the two types of monomers is quenched from $\chi = 0$ to $\chi = 1$ for chains of length $N = 100$ at near-melt densities. We present evidence that the two monomer species vertically segregate to form a three-layer structure that is uniform in the grafting plane. This is qualitatively different from a binary mixture of grafted homopolymers, which laterally segregates to form a structure with concentration modulated in the grafting plane at a scale of the side-to-side fluctuation distance.

An important way to modify a surface is to chemically bond polymer chain ends to it.[1] In general, when polymer chains are grafted to the surface at high densities, steric interactions cause strong chain stretching normal to the wall.[2] The resulting grafted layer will have a constant density ϕ near the wall; the density will fall to zero beyond a characteristic height $h \sim Na^3\sigma/\phi$ where a is the statistical monomer size (typically about 5 Å) and σ is the grafting density. The length of the individual chains that is not consumed by the stretching contributes to fluctuations on the scale of $\lambda \sim (N - h/a)^{1/2}a$ from side to side.

If such a brush is composed of two sufficiently immiscible monomers (A and B), it will separate into domains, each of which is rich in one species. However, conventional bulk phase separation[3] is disallowed in this case since the chain ends are permanently attached to specific points on the substrate. This constraint introduces a competition between two possible ordered states.[4] The first takes advantage of the side-to-side chain fluctuations and is characterized by a modulation or "rippling" of the concentration in the plane with a ripple wavelength of order the side-to-side chain fluctuation distance. The second possible structure consists of alternating layers parallel to the wall with a thickness comparable to h. If "layering" is to occur, then in the *absence* of demixing interactions, fluctuations in concentration in the vertical direction over a distance h must be sufficiently strong to overwhelm the in-plane concentration fluctuations due to the side-to-side chain fluctuations over the shorter distance λ.[4]

If we suppose that a contact between an A and a B monomer costs an enthalpy χk_BT, then in each of these cases, the ordering achieves an enthalpic gain of order $k_BT\chi N$ per chain and imparts an entropic loss of k_BT per chain. The scale for the entropic loss may be understood by noting that the two ordering modes both involve constraint of one degree of freedom and hence a free energy cost of order k_BT per chain: layering requires localization of an end in either the upper or lower region of the layer, while rippling requires the end to be splayed to one side a distance of order λ. Both structures require $\chi N \approx 1$ to order.

The precise χN at which the mixed (uniform concentration) state is unstable to the formation of ripples and layers has been computed for melt conditions in the limit $N \to \infty$,[4] using the random-phase approximation (RPA). For mixed grafted A and B homopolymers, the leading instability toward ripples requires $\chi N \approx 4.5$, preempting the layering instability which is located at $\chi N = 8.0$ (for reference we note that a symmetric bulk homopolymer blend separates at $\chi N = 2$ [5]). The rather large difference between the calculated critical χN for layers and ripples suggests that little or no fluctuation toward layering should be observed as one goes through the transition. Recently Dong[6] carried out an analysis of the strong-segregation regime of grafted homopolymers and concluded that ripples continue to be stable for $\chi N \gg 4.5$. These results are consistent with the equilibrium state adopted by the A–B homopolymer system with $\chi N = 100$ studied in MC simulation,[7] where a strongly segregated rippled phase was observed. In those simulations, the vertical profiles of A and B monomers were nearly identical; i.e., no layering fluctuations were observed. Lai[8] observed qualitatively the same behavior at lower densities.

In the case of symmetric end-grafted diblocks (where the A and the B ends of the diblocks are grafted with equal probability), RPA calculations provide a rather different picture.[9,10] While rippling remains the leading instability at $\chi N = 5.2$, a layering instability occurs for nearly the same interaction strength, $\chi N = 5.5$. Per polymer, and thus per ordering degree of freedom, there is only a fraction of k_BT free energy difference between the two modes of ordering at the transition, and we thus expect layering fluctuations as one passes through the rippling transition. Because crystal phases in two dimensions (i.e., rippling) are suppressed by fluctuations[11] somewhat more than Ising-like transitions (i.e., layering), layering might even be the leading transition in this case. Small differences between the RPA theory and any realization of it, experimental or numerical (e.g., finite-N corrections, solvent quality, etc.), could conceivably overwhelm the small 7% difference between the critical χN's for layering and rippling to make layering the leading instability for grafted diblocks. Alternatively, a rippled structure might be stable only for low values of χN; at large χN there could be a

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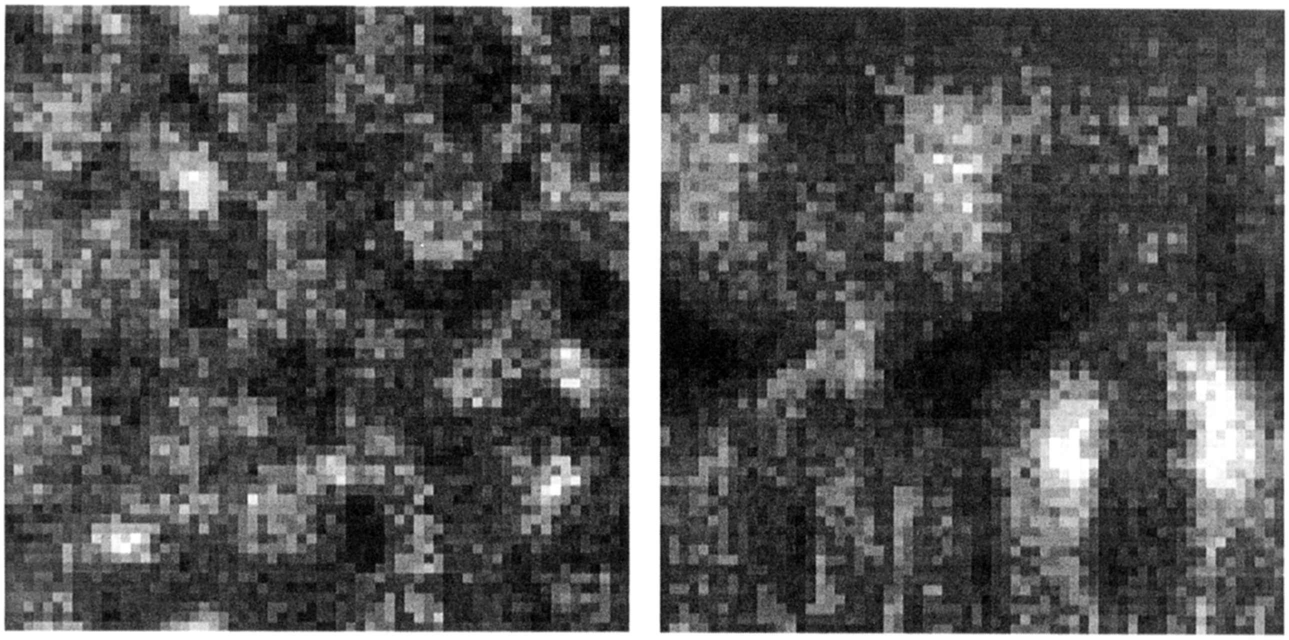

Figure 1. Two-dimensional projections of the grafted block copolymer system. The left-hand figure is a projection perpendicular to the wall into the $x-y$ plane. The domains characteristic of the rippled phase are visible. The right-hand figure is a projection along the wall into the $x-z$ plane. Correlated columns associated with rippling are present, but an A-rich layer surrounded by B-rich layers is also obvious.

transition to a layered state. For diblocks with a grafted block that is 30% of the total molecule, the RPA theory indicates that the layering χN is even nearer to the χN required for rippling than for the symmetrical (50%) diblock case studied here.

The RPA theory for diblocks also indicates that the ordering involves formation of a three-layer structure (ABA or BAB as one goes vertically through the layer).[9,10] This follows from the shape of the eigenfunction associated with the unstable rippling mode at $\chi N = 5.2$, which is of the form $f(z)\cos(kx)$ where x is in-plane distance, $k \approx 2.39N^{-1/2}$, and $f(z)$ is a function with two zeroes at $z = 0.2h$ and $z = 0.7h$. The vertical eigenfunction associated with the $k = 0$ layering instability at $\chi N = 5.5$ has the same two-zero structure. No strong-segregation calculations have been done for rippled structures of grafted diblocks.

The idea that various effects could tilt the free energy balance in favor of layering, and knowledge of current experimental efforts focusing on fabrication of grafted multiblock copolymers,[12] led us to carrying out large-scale computer simulations of grafted diblocks. Additional practical motivation for this work was that layering might have technological importance for construction of coatings with bistable or sensitively controllable chemical, optical, adhesive, or other surface properties.[4,13,14]

In our simulations, the diblock copolymers are modeled as self- and mutually avoiding random walks of two types of monomers, A and B. Each monomer occupies one site of a simple cubic lattice, and its adjacent monomers in the chain are sited at nearest-neighbor sites on the lattice. The $L \times L \times N$ lattice, with $L = 64$, has periodic boundary conditions in the x and y directions and a noninteracting, impenetrable wall at $z = 0$. The chains are $N = 100$ long and are not affected by the system edge at $z = 99$. The excluded-volume criterion is implemented by allowing only one monomer to occupy each site on the lattice.

Simulated grafted chains were generated by randomly selecting 1228 grafting sites alternating between A and B ends, giving a total grafting density of $\sigma = 0.30$. Monomers $n = 1, ..., 49$ along the chain are taken to be of the same type as the grafted monomer, $n = 1$, while $n = 50, ..., 100$ are taken to be of the other type. This sort of mixed grafting could be experimentally created using an ABCAB multiblock where C is chemically bonded to the surface.

Due to the high grafting density, the chains are placed in a fully stretched configuration which is then artificially relaxed (using kinetic rules that do not obey detailed balance) at the beginning of the simulation. The chains are then equilibrated at infinite temperature ($\chi = 0$) through one- and two-monomer motions, kink-jumps and crankshafts, for 187 500 Monte Carlo steps per monomer (MCM). The moves are made by randomly picking a chain and monomer. Moves are rejected only because of the excluded-volume criterion, and crankshafts are attempted only where kink-jumps are not allowed. As the system relaxes, the total monomer density near the wall approaches 0.70 and falls off rapidly for $z > 50$. Monte Carlo simulations at these monomer densities have been shown to correspond to melt conditions.

After this equilibration process, at time $t = 0$, we suppose that a deep temperature quench is made so that neighboring A and B monomers are suddenly subject to strong demixing interactions. This is modeled by introducing a repulsive nearest-neighbor A−B interaction, $\epsilon = 1.0k_BT$. The energy is accounted for via the Metropolis algorithm: to the excluded-volume criterion we add the stipulation that a move that lowers the system energy is accepted while a move that increases the energy by an amount ΔE is accepted with probability $\exp(-\Delta E/k_BT)$. The simulation is still limited to one- and two-monomer motions, and the grafted monomers are immobile at all times.

The simulation is carried out with these interactions to time $t = 1\,325\,000$ MCM. Figure 1 contains two projections of the system at this time: (a) is a projection along the z axis into the $x-y$ plane and (b) is a projection along the y axis into the $x-z$ plane. The pattern in

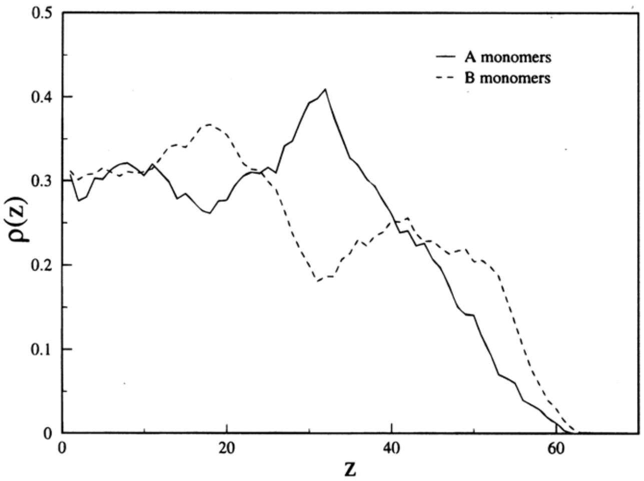

Figure 2. Density profiles for A and B monomers perpendicular to grafting surface at latest simulation time. Two B-rich layers with an A-rich layer between them are evident. The total density profile has not changed from its prequench form.

Figure 1a is suggestive of in-plane separation that is correlated in the z direction and is reminiscent of the rippled structures observed in monomer density projections of demixed grafted homopolymers.[7] However, an important feature of Figure 1b is a strong concentration of A at $z \sim 35$ across the entire system, flanked above and below by regions of excess B. Strong layering fluctuations of this sort (excess of one species at a given z across the entire system) were never observed in our previous study of grafted homopolymers. This three-layer structure is similar to the demixing profile obtained from the RPA theory.

The three-layer structure may be quantitatively displayed using the monomer density profiles at the latest simulation time, $\rho_I(z)$ where I = A or B, presented in Figure 2. Near the wall, where the system is strongly constrained by the immobile grafts, there is little separation. At larger z, the grafted layer has begun to separate into two B-rich layers with an A-rich layer in between. Inspection of the density profiles for several times suggests that a buildup of A monomer occurs at $z \sim 35$ from early times. As the system evolves, this layer intensifies but does not appear to shift in z. The total monomer density profile at all times remains similar to the prequench profile, suggesting that no expansion or contraction of the grafted copolymer layer is taking place. A similar separation can be seen in the free chain ends, whose distribution appears in Figure 3. From this distribution it also appears that the A ends are concentrated at the top of the A-rich layer, while the B-end distribution is bimodal. When the quench occurs, there is a small shift to higher z, on the order of 5 lattice units, in the total end distribution.

The in-plane structure of the grafted system is conveniently studied using a Fourier transformation of the monomer occupancy, where sites are assigned a value of $\psi = 1$ for A monomer occupancy, $\psi = -1$ for B monomer occupancy, and $\psi = 0$ for a vacancy. A structure factor for in-plane density fluctuations at height z is

$$S(k,z,t) = \sum_{k<|\vec{k}'|<k+1} \{|\sum_{x,y} \exp(i\vec{k}'\cdot\vec{r})\psi(\vec{r},t)|^2\} \quad (1)$$

where the sum over x and y is the fast Fourier transform and the sum over k denotes circular averaging. This particular structure factor would be difficult to realize experimentally as scattering from a particular height z is hard to achieve. However, some of the information contained in it would be accessible in a conventional scattering experiment where the scatterers couple differently to contrast at different heights in the layer. This type of structure factor is central to our study, as it will allow a clear distinction to be drawn between rippled and layered structures.

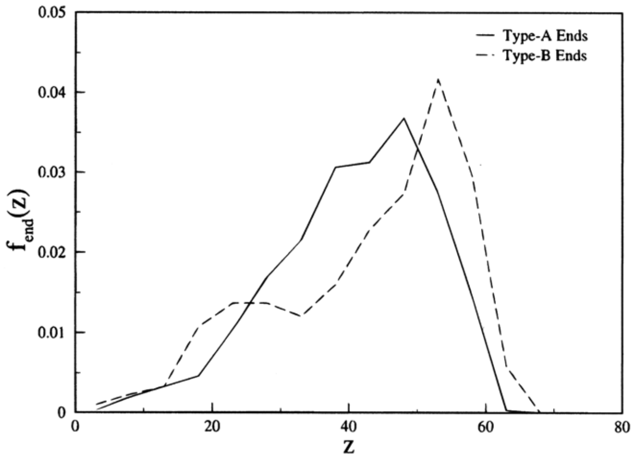

Figure 3. Distribution of free chain ends. The separation in chain ends matches that seen for the density profiles. Comparison with Figure 2 suggests free A ends prefer the top of the A-rich layer.

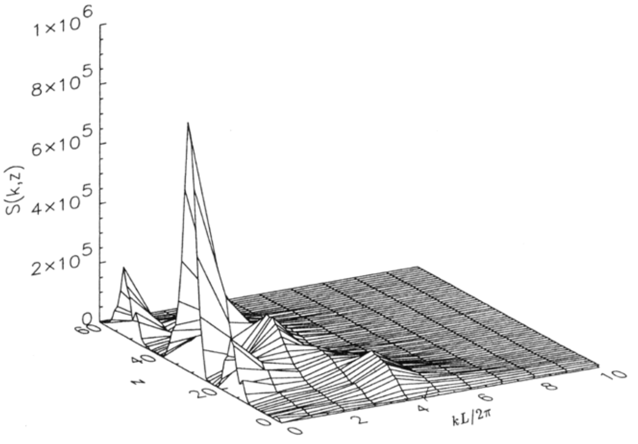

Figure 4. Three-dimensional graph of single-height structure factor $S(k,z)$ for the grafted block copolymer system at the latest simulation time. Peaks at $k \neq 0$ indicate rippling for small z. Away from the wall, however, the largest peak occurring at $k = 0$ is a consequence of layering.

This structure factor for grafted diblock copolymers at t = 1325000 MCM is presented in Figure 4 as a function of both k and z. Peaks at $k = 0$ occur for layers with an abundance of one type of monomer relative to the other and indicate layering, while peaks at $k \neq 0$ reflect correlations associated with rippling. The large peaks at $k = 0$ seen here correspond to the layers indicated by the density profiles. In addition, Figure 4 reveals that there are ripple-like modulations in the monomer density near the wall (for small z the peak is at $k \neq 0$), but also that the structure factor at nonzero wavenumber decays with increasing distance z from the wall. This should be compared with Figure 5, the corresponding structure factor for the latest time of a N = 100 A–B homopolymer simulation. For homopolymers, a robust peak is always observed for $k \neq 0$, except for the largest z, where the brush thins out and there can be large A–B fluctuations. For homopolymers, the

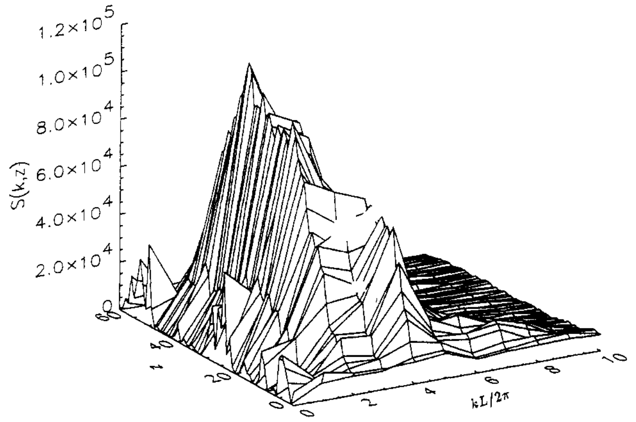

Figure 5. Single-height structure factor $S(k,z)$, for our previous homopolymer simulation (ref 7) at t = 400 000 MCM, presented for comparison with Figure 4. The peak occurs for $k \neq 0$ at all z since no layering occurs in this system. Some layering occurs at the top edge where the monomer density goes to zero.

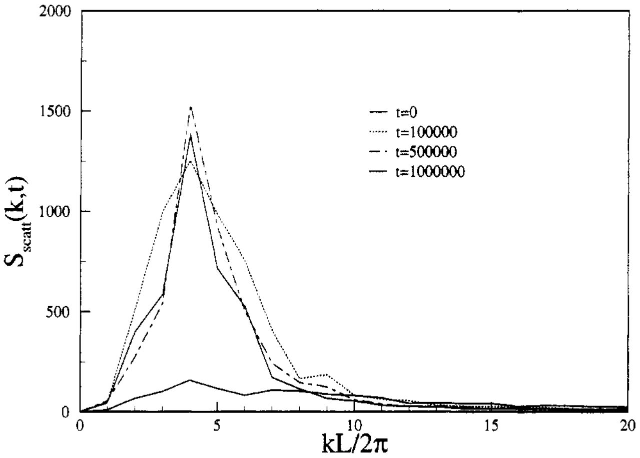

Figure 6. Circularly averaged structure factor in planes parallel to the grafting surface. The peak corresponds to the side-to-side fluctuations of grafted chains and does not move with time. At first the peak strengthens with time, but at the latest simulation times it is slowly decreasing in height.

monomer density is strongly modulated, or rippled, throughout the layer.

One might wonder what would be observed for scattering from in-plane concentration fluctuations (assuming that the probe is scattered by the A−B contrast) with momentum transfer in the grafting plane:

$$S_{\mathrm{scatt}}(k,t) = \sum_{k<|\vec{k}'|<k+1} \frac{1}{z_{\max}} \Big| \sum_{x,y,z} \exp(i\vec{k}'\cdot\vec{r})\psi(\vec{r},t)\Big|^2 \quad (2)$$

where the wavevectors lie only in the $x-y$ plane and the sum over z is simply an average. S_{scatt} at $k = 0$ is fixed because of conservation of the total number of A and B monomers. Because of this, the difference between layering (characterized by a $k = 0$ order parameter) and rippling is not as clear for this structure as it is for S.[15]

In Figure 6 we show S_{scatt} for grafted diblock copolymers at several different times. Before the quench there is a broad peak that intensities immediately after the quench but does not shift to the left or the right, which is similar to what is observed during rippling.[7] By averaging over the system at different times, we estimate the wavevector of the peak to be $Lk/2\pi = 3.87 \pm 0.01$ ($ak = 0.380 \pm 0.001$), which corresponds to the equilibrium side-to-side fluctuations of the stretched, grafted chains. At times beyond t = 500 000 MCM, the magnitude of this peak slowly decreases.[15]

In our previous study of rippling of mixed grafted homopolymers, we observed a strong peak in $S_{\mathrm{scatt}}(k,t)$ to appear and saturate at $k^* \approx 1/N^{1/2}$.[7] In the present study of grafted diblock copolymers, we observe a slightly different peak evolution. A peak appears at roughly $k^* \approx 1/N^{1/2}$ and grows over time scales of order 10^5 MCM. However, beyond 500 000 MCM, we observe a decrease in the peak height due to lateral broadening of the phase-separated region. Even though monomers are correlated at large length scales in most of the layers, some lateral scattering at short wavelengths remains because near the grafting surface the chains are constrained by the immobile grafts. A slow decrease in the scattering intensity at k^* is an observable signature of the formation of a phase-separated layer structure. Eventually, the scattering at k^* should approach a plateau value corresponding to the scattering from the modulated region near the grafting wall where the chains are forced to mix.

Our conclusion is that, immediately after a thermal quench of grafted diblock copolymers, lateral modulation develops at a length scale on the order of the side-to-side chain fluctuations, λ. Examination of the phase separation at different heights at later times reveals that the modulation predominantly remains near the grafted wall where the chains are forced to mix together; away from the wall there is vertical segregation—layering. Our structure factor study indicates that this layering is a $k = 0$ phase transition, and thus the lateral layer domain size should coarsen with time. Since the layering order parameter (essentially the choice of exposure of A or B monomer at the layer surface) is not conserved, one expects the layering domains to grow in lateral size as the square root of time after the quench.

Although the RPA theory predicts that a rippled phase should be the leading instability, it also predicts that there is a competing layering instability at nearly the same χN. Our results indicate that, under some conditions, layering may become the stable state for grafted diblocks. We note however that much longer runs are necessary for a complete resolution of this issue. An interesting possibility is that the quenched disorder of the grafting may play some role in stabilizing layering or rippling; such effects should be strongest for short grafted chains. We also observe layering in an on-going study of simulated annealing in grafted diblocks. The results of the annealing study, which include studies of mixed asymmetric grafted diblocks, will be reported elsewhere: preliminary results indicate that layering is the equilibrium state for $\chi = 1$ across a range of diblock compositions.

A distinctive signature of the layering of grafted diblocks is the ABA/BAB structure, which is in qualitative agreement with the vertical structure associated with the instability predicted by the RPA theory. This unique structure might be probed in a reflectivity experiment[16] or by use of ion-scattering depth-profiling techniques.[17] If atomic force microscopy could be done with A−B contrast sensitivity[18] (e.g., due to dielectric contrast differences), perhaps the in-plane domain structure, which should be characterized by a length scale that can grow indefinitely, could be visualized.

In experimental situations, the grafting surface may have some preference toward one or the other components of the copolymers. However, for meltlike densities in the strong-segregation regime, the surface energy per chain (for substrate–monomer interactions of strength comparable to that of the monomer–monomer demixing interactions) will be a small fraction of the demixing interaction energy per chain. Thus, surface interactions will be important immediately adjacent to the substrate, but for long grafted chains, the remainder of the layer will adopt a state reminiscent of the system with no surface interactions. A role for surface interactions to play is that of a symmetry-breaking field which will select one of the two layered structures. If the affinity of A or B domains for the exposed surface region could be modified, for example by use of poor solvents with different repulsive interactions with the A and B segments, perhaps the whole layer could be physiochemically "switched" between BAB and ABA structures.

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