Self-Assembly in Thin Films during Copolymerization on Patterned Surfaces

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ABSTRACT: In this work, we use dissipative particle dynamics with chemical reactions to study the question of pattern reproduction by a melt of reacting monomers during polycondensation. We show that it is possible to obtain structures with long-range order using this approach of “patterned polycondensation”. Depending on the incompatibility parameter χ and reaction rate, three main system morphologies are formed: (a) homogeneous systems without separation; (b) systems with long-range order; (c) systems with tendency to macrophase separation; typical block-length distribution for these states are discussed. We show that the region of well-ordered structures moves to the range of higher incompatibility parameter χ and expands upon increasing the reaction rate; possible microscopic explanation of such behavior is proposed. The effect of different film thicknesses and pattern sizes on the structure quality is studied.

INTRODUCTION

Block copolymers attract much interest during the last few decades because of their ability to form well-ordered nano- and microdomains, called microphase separation. Besides well-studied monodisperse block copolymers, mainly diblock copolymers, there is an interest to polydisperse systems. Polydisperse systems are much less studied in theoretic or computer simulation works, but at the same time most of the laboratory experiments deal with polymers with mass distribution far away from delta-function. Usually the wider mass distribution you have—the more available and less expensive your polymer system is. There are many technology applications where block copolymers could be a subject of high demand: lithography masks, new photon materials, media with controlled porosity, proton-conducting materials and many others.1 In addition, there is a great interest to implement blockcopolymer microphase separation to membranes, coatings and different thin films applications. This is because such applications are more technologically developed: there are several powerful methods to fabricate (spincoating, layer-by-layer assembling, Langmuir techniques, etc.) and characterize (transmission electron microscopy, Grazing-incidence small angle scattering, etc.) thin polymer films. During thin films studies, it occurs that many laws known for bulk systems are only partly suitable for thin films of the same polymer. Because of new interactions with substrate and/or free surface, and in some cases because of polymer chains conformational restrictions caused by small film thickness, the behavior of such systems is much more complicated and rich. The most studied types of structure-forming polymer systems in thin films are diblock-copolymers. The main feature of such systems is that it is possible to achieve well-ordered system only over micrometer-scale areas.2,3 Substrate patterning helps to solve this problem and allows establishing of well long-range order.4 Moreover, changing of the pattern parameters could result in formation of different structures.5 Adding homopolymers to the diblock copolymer melt gives a possibility of reproduction of rather complicated surface patterns, for instance bends or jogs.5

However, the commensurability between the surface pattern period and the bulk structure period plays a crucial role in forming a long-range order, so tuning the blend composition is important for achieving defect-free structures on patterned surfaces.4,7,8 Here we would like to address this question from the other side: whether it is possible to create desired thin film morphology during polycondensation in a melt of reacting species. We would like to tune the reaction rate and monomers incompatibility in a way to have a competition between tendency to macrophase separation and irreversible random polycondensation, and finely obtain well-defined microstructure in equilibrium. Most of the papers about living (or “unfrozen”) polymer sequences study single chains. In refs 9 and 10, single macromolecules were studied from hydrophobic and polar groups and the tendency to form block copolymers and core–shell conformations was shown. In ref 11, different regimes of single molecule copolymerization near the patterned surface were studied by computer simulation. However, problem of unfrozen sequences in systems consisting of many chains is not studied in details yet. In our recent work12, we studied a melt of reacting AB-copolymers with annealed sequence in bulk and concluded that microphase separation for such systems is unfavorable. Only macrophase separation was observed while increasing the incompatibility of A and B and varying the

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reaction rate. It should be mentioned that copolymer blends with annealed sequences could be obtained in real experimental systems, for example during exchange reactions (for instance, see ref 13).

Classical theoretical study of such systems is a rather complicated problem, since monomer sequence and polymer conformation change simultaneously. Some information concerning copolymerization models in nonhomogeneous systems can be found in.14,15 There is an interesting study about formation of microphase separated structures in A ⇄ B reacting binary mixtures.16,17 It was shown that depending on about formation of microphase separated structures in A desired for possible applications.

In this study, we focused on structure forming in thin films confined by patterned surfaces. In our work we used coarse-grained computer simulation as a tool to illustrate the idea of desired film morphology creation from a melt of reacting monomers. Partly random sequences near patterned surface were studied by computer simulations in ref 18, authors showed that such strategy could be very useful to replicate surface pattern without fine-tuning of initial polymer composition. In some sense we go further and in this paper we used fully random sequences to present universal and scalable methodology for replication of surface pattern into copolymer film bulk.

**METHODOLOGY**

DPD is a version of the coarse-grained molecular dynamics adapted to polymers and mapped onto the classical lattice Flory–Huggins theory.19–22

Consider an ensemble of particles (beads) obeying Newton’s equations of motion

\[
d\mathbf{r}_i/dt = \mathbf{v}_i, \quad m_i d\mathbf{v}_i/dt = \mathbf{f}_i
\]

\[
\mathbf{f}_i = \sum_{j \neq i} \left( \mathbf{F}_{ij}^b + \mathbf{F}_{ij}^f + \mathbf{F}_{ij}^d + \mathbf{F}_{ij}^\chi \right)
\]

(1)

where \( r_i, m_i, v_i \) are the coordinate, mass, and velocity of an \( i \)-th bead, respectively, \( \mathbf{f}_i \) is the force acting on it. The summation is performed over all other beads within the cutoff radius \( r_c \). Below we assume that all quantities entering eq 1 are dimensionless and for simplicity set \( r_c \) and \( m_i \) for any \( i \) to unity. First two terms in the sum are conservative forces.

Macromolecules are represented in terms of the bead-and-spring model. \( \mathbf{F}_{ij}^b \) is a spring force describing chain connectivity of beads:

\[
\mathbf{F}_{ij}^b = -K(r_{ij} - l) \frac{\mathbf{r}_{ij}}{r_{ij}}
\]

(2)

where \( K \) is a bond stiffness. If beads \( i \) and \( j \) are not connected, then \( \mathbf{F}_{ij}^b = 0 \).

\( \mathbf{F}_{ij}^f \) is a soft core repulsion between \( i \)- and \( j \)-th beads:

\[
\mathbf{F}_{ij}^f = \begin{cases} 
  a_{ij}(1 - r_{ij}/r_g) \mathbf{r}_{ij}/r_{ij}, & r_{ij} \leq 1 \\
  0, & r_{ij} > 1
\end{cases}
\]

(3)

where \( a_{ij} \) is the maximum repulsion between beads \( i \) and \( j \) attained at \( r_r = r_g \). Since \( \mathbf{F}_{ij}^f \) has no singularity at zero distance, a much larger time step than in the standard molecular dynamics could be used.

Other constituents of \( \mathbf{f}_i \) are a random force \( \mathbf{F}_{i}^d \) and a dissipative force \( \mathbf{F}_{i}^\chi \) acting as a heat source and medium friction, respectively. They are taken as prescribed by the Groot-Warren thermostat.22 More detailed description of the simulation methodology could be found somewhere else.23

In all our calculations we used the following parameters: DPD number density \( \rho = 3 \); noise parameter \( \sigma = 3 \); integration time step \( \Delta t = 0.04 \); unpertrubed bond length \( l = 0 \); bond stiffness \( K = 4.0 \) (see (2)); DPD conservative parameter between alike particles \( a_i = 25.0 \) (see (3)).

Patterned by stripes (there were two types of the stripes; these stripes were perpendicular to \( X \) axis) surface from the both sides of the film was used as a template for the desired film structure. Pattern period \( P \) was equal to 11.1, there were \( S \) stripes of each type on the pattern, film thickness was equal to 10. Stripes of the type 1 had strong repulsion from \( B \) monomers and stripes of the type 2 had strong repulsion from \( A \) monomers. In in-plane projections periodic boundary conditions were used. Box size in most of our simulations was equal to \( 55.5 \times 55.5 \times 10 \), which gives approximately 100000 DPD particles. At the initial state, the simulated system was a uniform melt of monomers \( A \) and \( B \) in equimolar composition 1:1.

The same pattern at the both sides of the film was used to avoid effects of interaction with a free surface, which could complicate analysis of the simulation results. However, we believe that this simplification would not impact on our results a lot, and all conclusions made in this work are valid for systems with one free or nonpatterned neutral surface. In our case stripes on the different patterns were parallel to each other, whereas rotation of one of the patterns can give rise to a variety of interesting morphologies.

Every \( \tau \) DPD step chemical reaction step was launched. Irreversible chemical reactions were simulated via the Monte Carlo method described in details in ref 12. In principle, this method is widely used in other DPD studies (see ref 25, for example). The reaction process was performed during all simulation time, however at the large times new bonds were created very seldom since the conversion degree was close to 100%. In our simulations we used \( \tau = 200 \) DPD steps. This number is large enough to ensure local equilibration of the system between consequent reaction steps, and small enough to provide smooth reaction process. In general, there are several methods of introduction of chemical reactions into DPD (for another example see26), but the method we used here seems more suitable for the systems under study. Total simulation time was \( 20 \times 10^6 \) DPD steps which is sufficient for reaction at all rates studied in this work to achieve conversion degree close to 100% and the mean chain length more than 1000 monomer units.

To run simulations we used self-made domain-decomposition parallelized DPD code and performed simulations at MSU supercomputer facilities.27 Each run started independently from the same initial state but with different immiscibility (Flory–Huggins parameter \( \chi \)) and reaction rate (bond formation probability \( P_b \)). Flory–Huggins parameter \( \chi \) was calculated using common expression \( \chi = 0.306/\Delta a_i \) from the work.22

Thus, in our systems competing processes of phase segregation and irreversible cross-linking which was hindering the phase segregation took place simultaneously.
To find the conditions suitable for well-ordered structure formation we performed massive parallel calculation of the systems at a wide range of parameter $\chi$ and at three reaction rates ($P_b = 0.01, 0.03, 0.09$; we call them slow, medium and fast reaction, respectively). It should be mentioned that in this work we deliberately avoid the attempt to model a specific system. Reaction rates used in our simulations are quite high (up to $10^5$ L·mol$^{-1}$·s$^{-1}$, if one takes the DPD space unit equal to 1 nm and the time unit equal to 100 ps), but quantitative estimation of them would depend on the particular system details (coarse-grain level, for example). Moreover, we show that the suitable reaction rates depend on the pattern period (see Results and Discussions). The reaction rates and pattern period that we chose for this study seem to be the most optimal choice for demonstration of the role of the interplay between reaction and diffusion in computer simulations.

RESULTS AND DISCUSSIONS

Depending on the incompatibility parameter, three different final system states were observed (examples of the trough-plane views and density profiles of these states are presented in Figure 1):

(a) Homogeneous state (Figure 1a). At this state parameter $\chi$ is not large enough for the system to undergo phase separation because there are no long enough blocks in the chains sequences. This state is characterized by almost uniform density profile (see Figure 1d).

(b) Lamellar structure (Figure 1b). At some $\chi$-values there is a commensurability between the mean block length $n^*$ (in this case $n^* \approx 8$ monomer units, see below) and the pattern period $D$. This state is characterized by a density profile with well-distinguished periodicity. Number density of beads of type A changes from 0 in the B-rich lamellae to 3 in the A-rich lamellae. This feature could be used as an additional quantitative tool to define structures with a good long-range order (see Figure 1e).

(c) Structure with tendency to macrophase separation (Figure 1c). This happens at largest studied $\chi$-values. Number density profile in this case shows no periodicity (see Figure 1f).

It should be noted here that similar set of states was observed for all studied reaction rates, but lamellar structures with long-range order were found only at medium and fast reaction rates. However, structures of this type could have some defects, for example fluctuating thickness of lamellae or “neck” between two parallel stripes (see Figure 2a). Figure 2b shows positions of short blocks (of length less than 5) for this system. One can see that such blocks are located mainly on the lamellae surfaces, whereas amount of such blocks in the lamellae bulk is vanishingly small. Moreover, density of short blocks near the defects is slightly higher than near the flat surfaces. Excess of...
such blocks could form lamellar thickness fluctuations. In contrary, long blocks (length more than 60; see Figure 2c) are located mostly in the lamellae bulk. We suppose that these blocks are the main reason for defects formation: the equilibrium (Gaussian) coil diameter of such blocks exceeds the lamellar size and the block operates as an additional force to form structure defects. High amount of long blocks close to each other could result in formation of a “neck” defect (see Figure 2, dashed circle); in all studied systems, “neck” defects are formed mainly by big aggregates of long blocks. Such defects appear to be in a steady-state, which could be explained by extremely low mobility of long blocks. In contrast, mobility of small blocks is higher, which allows small thickness fluctuations to evolve over time.

Figure 3 presents the block-length distributions for the systems depicted in Figure 1. One can see that the homogeneous system without long-range order shows clear exponential (Flory-type) distribution with the mean block length smaller than \( n^* = 8 \). The system with partially macrophase separation exhibits two-scale behavior: there are a lot of small blocks and long tail of large blocks; and the mean block length in this case is larger than \( n^* \). It should be noted that this kind of two-scale behavior is typical for phase-separated systems during polycondensation. The system with well-defined structure has more Flory-like distribution, but still amount of short blocks is slightly higher than expected for Flory distribution. This state is characterized by the mean block length equal to \( n^* \).

The same plot on a log–log scale (see Figure 3, inset) shows a very good linear behavior at the range of short blocks both for microphase and macrophase separated systems. This linear behavior corresponds to a power-law distribution with the power index \( \approx -1.1 \). We suppose that the mechanism of formation of such two-scale distribution is the following: during chain growth in partially separated system some fraction of short blocks, located close to the phase surface, was irreversibly connected to beads of the other type, thus fixing the length of these blocks, while many other blocks continued to grow in increasing aggregates of beads of the same type. These “living” blocks, which grow in aggregates, provide Flory-like behavior at the range of long blocks, whereas there are number of “dead” blocks which were formed at the phase surface. However, the question of the slope value is out of the scope of this work and should be discussed elsewhere.

This general behavior of the block-length distribution does not change upon reaction rate varying and depends on the system state only; all obtained block-length distributions look very similar to those presented in Figure 3.

Figure 4 shows the dependence of the mean block length on the incompatibility parameter \( \chi \) at different reaction rates.

Figure 4. Dependence of the mean block length on the incompatibility parameter \( \chi \). Hatching shows the region where structures with minimum number of defects were observed.

Region of minimum of structural defects is marked with hatching. This region corresponds to the mean block length about 8 monomer units.

It should be noted here that in ref 28 we found that random copolymers with mean block length of 8 monomer units could undergo microphase separation to lamellar phase and the resulting lamellar thickness corresponds well with the substrate pattern size \( D = 11.1 \) used in this work. Moreover, we showed that the period of the structure practically does not depend on the incompatibility parameter. It means that to form a structure with period of 11.1 random copolymer melt should have the mean block length about 8 at wide range of parameter \( \chi \), which is confirmed by our simulations in this work.

Figure 4 shows that the region of minimum defects (let us call it “stability window”) moves to the range of higher \( \chi \) and expands upon increasing the reaction rate. Increase of necessary \( \chi \) values could be explained by the presence of two competing processes: phase separation and irreversible random polycondensation. At higher reaction rates there are a lot of short blocks, which are formed at initial steps when there are no large aggregates. It means that to achieve the block lengths typical for the “stability window” one should increase the speed of separation, which could be reached by increasing of \( \chi \). At small reaction rates even minor increase of \( \chi \) over critical point would result in formation of long blocks and lead to the mean block lengths values specific for the “stability window”.

The latter (expanding of the “stability window”) is evident from the hatching region in Figure 4 and is related to the fact that for some particular change of the mean block length the same comparative change of \( \chi \) is needed for all reaction rates. Since the stability region for higher reaction rates is shifted to the range of higher \( \chi \), it leads to expanding of the stability region in absolute values of \( \chi \).

It should be mentioned, however, that random multiblock copolymers need quite high incompatibility to undergo microphase separation. It means that in spite of the presence...
of patterned surfaces, at small reaction rate we did not observe well ordered structures, because incompatibility is not high enough at the region of desired block length (see Figure 4). Moreover, in case of low incompatibility (and low reaction rates) the majority of reaction events proceed at the late stages of segregation, when big aggregates are already in present. As was discussed above, such situation leads to formation of long blocks inside these aggregates, and big amount of short blocks on the surface. This leads to a pronounced two-scale block-length distribution, whereas for higher reaction rates the reaction proceeds mostly before formation of big aggregates, resulting in more "Flory-like" block-length distribution than for low reaction rates at the same mean block length. Big amount of short blocks in the case of slow reaction can lead to a higher surface area and roughness. At the same time, however, too high incompatibilities may result in system "freezing", which could decrease the structure quality.

In order to characterize defects and surface roughness of obtained structures numerically we introduce the following quantity:

$$Q = \frac{P}{P_{id}}, \quad P = \frac{1}{N} \left( \sum_{i=1}^{N} \exp(iqr) \right)^{2}, \quad q = \left( \frac{2\pi}{D}, 0, 0 \right)$$

where $D$ is the pattern period, and $N$ is the number of particles.

Function $P$ as a matter of fact is static structure factor value at one fixed wave vector $q$, which corresponds to the pattern direction. $P_{id}$ is the function value when the film structure is ideal (can be calculated numerically without simulations). Figure 5 shows dependence of the function $Q$ on the incompatibility for different reaction rates. One can see that these dependences confirm our conclusions: values of $\chi$ for maxima of the curves correspond to the "stability region", where the mean block length is about $n^*$ (see Figure 5). Moreover, increasing the reaction rate improves the structure quality by decreasing surface roughness and number of defects. According to the observed structures, a $Q$ value of 0.8 can be considered as the transition point between structures without long-range order and well-ordered structures (i.e., the structures with $Q > 0.8$ have the density profile similar to Figure 1e)

To test the validity of our conclusions we performed additional simulations with different film thicknesses and larger system sizes. At first, we checked the effect of film thickness on the quality of the lamellar structure. To run this test, we chose two additional film thicknesses (5 and 20) preserving the in-plane sizes, and performed our simulations at high reaction rate (0.09) and $\chi$=7.65, which corresponds to the center of the "stability window". Examples of through-plane views, side-plane views, and density profiles compared to the system of thickness 10 are shown in the Figure 6. According to intuitive expectations the lamellar quality is going better upon film thickness decreasing. This fact is clearly seen from the density profiles: for the thin film of thickness 5 density profile shows excellent periodicity with well-distinguished intervals where number density is equal to 0 and 3, which corresponds to the pure B-bead and A-bead phases, respectively. Increase of the film thickness to 10 leads to washing out of the density profile (because of the surface curvature growth), peaks become less sharp, however, there are still regions of pure phases. Further increase of the film thickness results in formation of very curved lamellae; density profile for this case shows no regions of density 0 or 3, which means that the lamellae thickness noticeably fluctuates. The block size distribution in these cases remains similar to that of Figure 3; we do not present it here. Only small decrease in the mean block size upon the film thickness increase was observed, which can be easily explained by an influence of A- and B-rich phases located near the pattern. For thin films this effect is more pronounced since comparative volume of the region which is close to the pattern is higher.

Finally, we checked the stability of observed lamellar structure for films with larger surface area (this is also helpful to exclude presence of box-size effects). After increase of the in-plane sizes to $111 \times 111$ at the same parameters as in the film thickness test we still found well-ordered structure, presented at Figure 7b. The next question is whether lamellar structure of the film remains stable with simultaneous increase of the thickness and pattern period. To test this we doubled all the system dimensions and performed simulations in a box of the size $111 \times 111 \times 20$ (ca. 800000 beads) and the pattern period 22.2. Since this system has bigger pattern period, necessary for ordered structure mean block length must be higher as well. To reach high mean block length values one should increase $\chi$-values and/or decrease reaction rate. Moreover, it is obvious that the "stability window" for such systems is shifted to the region of slower reaction rates, since longer blocks need less incompatibility to segregate. So we chose the reaction rate of 0.01 (which was not high enough for small pattern period) and tested this system over the $\chi$-values between 0 and 15.3 with $\chi$ step 1.02. It turned out that well-ordered structures are formed in this case for the mean block length about 17 and $\chi$-values about 13 (see Figure 7c). Such high values of incompatibility show that reaction rate can be significantly decreased, whereas structure formation can still be possible. However, more comprehensive study of systems with big pattern periods is quite complicated due to the big system sizes and large numbers of particles.

**CONCLUSIONS**

In this work, we used dissipative particle dynamics with chemical reactions to study the question of pattern reproduction by a melt of reacting monomers. Patterned by stripes surface from the both sides of the film was used as a template for the desired film structure. At the initial state, the simulated system was a uniform melt of monomers A and B in

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*Figure 5. Dependence of the quality of pattern replication on the incompatibility for different reaction rates. All curves were smoothed using the adjacent-averaging method. Structures with $Q > 0.8$ can be considered as well-ordered.*
equimolar composition 1:1. We showed that it is possible to obtain structures with good long-range order in such systems. However, in the presence of two concurring processes, irreversible polycondensation and phase separation, behavior of the system might be quite complicated. Depending on the incompatibility parameter $\chi$ and reaction rate, three main system states were observed: (a) homogeneous systems without separation; (b) systems with good long-range order; (c) systems with a tendency to macrophase separation. These states are characterized by different block-length distribution; two-scale block-length distribution behavior for separated systems was observed. The latter can be described by the presence of phase surfaces, which leads to formation of excess of short blocks, and aggregates, which leads to formation of long blocks. It was found that systems with good long-range order always correspond to the mean block length of $n^* = 8$ in our particular case, which can be explained by the commensurability between the surface pattern period and the bulk lamellar period. Structures with good long-range order could have low-scale defects such as fluctuating thickness and “necks” between two neighboring lamellae. It was found that the main reason for formation of such defects is long blocks located within the lamellae.

We found that the region of minimum defects moves to the range of higher incompatibility parameter $\chi$ and expands upon increasing the reaction rate. Moreover, increase of the reaction rate and corresponding rise in $\chi$, which is necessary for reaching the mean block length of $n^*$, result in improvement of the structure quality by decreasing surface roughness and number of defects. However, too high incompatibilities may result in system “freezing”, which could decrease the structure quality.

We also tested stability of our structures for films with different thicknesses, area and pattern period. It was shown that at constant pattern period increase of the film thickness results
in growth of the number of defects. It was also shown that increase of the film area does not change pattern reproduction quality.

Simulation of a system with doubled film thickness and pattern period showed that our general conclusions are valid for this system. It was shown that for such systems reaction rates can be significantly decreased (due to increase of necessary mean block length). This fact is very important since more realistic reaction rates can be used to achieve well-ordered structures; it also shows that the interplay between reaction rate and diffusion speed plays crucial role in our model. Thus, we conclude that the criterion of applicability of this method most probably is the commensurability between film thickness and pattern period.

This could be a good method when there is no need in perfect long-range order. We believe that there is a great potential to use such kind of self-ordering copolymer films to produce polymer solar cells or templates for nanoparticle synthesis, photonic crystals, etc.

We do not consider the question of different pattern morphology here, but we understand that it is a very important question. In general, our system is self-tuning and even nonperiodic and arbitrary patterns should be reproduced if the pattern characteristic length is comparable to the film thickness. But the characterization and analyses of such films would be a much more complicated process.

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**Notes**

The authors declare no competing financial interest.

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