AIP | The Journal of Chemical Physics

Multiblock copolymers prepared by patterned modification: Analytical theory and computer simulations

E. N. Govorun, A. A. Gavrilov, and A. V. Chertovich

Citation: The Journal of Chemical Physics **142**, 204903 (2015); doi: 10.1063/1.4921685
View online: http://dx.doi.org/10.1063/1.4921685
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/142/20?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS **142**, 204903 (2015)

Multiblock copolymers prepared by patterned modification: Analytical theory and computer simulations

E. N. Govorun,[a] A. A. Gavrilov, and A. V. Chertovich
Faculty of Physics, Lomonosov Moscow State University, Leninskie Gory 1-2, Moscow 119991, Russia

(Received 20 February 2015; accepted 14 May 2015; published online 27 May 2015)

We describe a special type of multiblock copolymers which are synthesized by a hypothetic procedure of the modification of monomer units in a polymer melt according to a certain geometrical criterion. In particular, we explore the case of lamellar-like structures: the sequence statistics of the resulting multiblock copolymers is described and their ability to self-assemble is studied. It is found that the block-size distribution $P(k)$ for such random copolymers contains a large fraction of short blocks with the asymptotic dependence $\sim k^{-3/2}$, where k is the block size. A characteristic feature of such multiblock copolymers is their extremely high block-size polydispersity with the polydispersity index being proportional to the space period of the modification. The morphological behavior of such copolymers is simulated by means of dissipative particle dynamics. A stable self-assembled lamellar structure is observed, but the domain size appears to be sufficiently larger than the initial pattern period. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4921685]

I. INTRODUCTION

Self-assembling in block copolymer systems has attracted a great interest in recent decades; a number of applications have been proposed in the literature, ranging from lithography to biosensors and many others.[1] For many years, researchers focused on the synthesis and characterization of mostly monodisperse diblock copolymers,[2] but now more and more studies are turning to polydisperse and even random block-copolymers. Recently, the effect of polydispersity on the phase behavior of multiblock copolymers has been actively studied in experiments, theory, and computer simulations.[3–11] Block-size variability is no more considered as a non-desirable property of synthetic polymers; on the contrary, it is regarded now as a tool to control the morphological phase behavior.[12,13]

Polydisperse block copolymers can be obtained via blending copolymers with different molecular weights or as a product of polymerization or polycondensation reactions. The first route was used, for example, by Noro, Matsushita, Takano *et al.* for obtaining poly(styrene-*b*-2-vinylpyridine) (PS-PVP) diblock and poly(styrene-*b*-2-vinylpyridine-*b*-styrene) (PS-PVP-PS) triblock copolymers.[14–17] The second method has been employed in a number of investigations on diblock and triblock copolymers[18–22] and recently by Lee and Bates for direct synthesis of alternating and random multiblock copolymers.[3] In the latter work, the morphology and thermal and mechanical properties of multiblock copolymers were studied: lamellar and bicontinuous-like morphologies were found, and tensile tests of the material demonstrated much higher toughness compared to the analogous poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymers. The copolymers which contained large amount of blocks with very high polydispersity index (3-6.5) revealed a bicontinuous-like morphology that in the authors' opinion inhibits the development of crazes in the sample under strain. Li *et al.*[4] used chain shuttling chemistry to synthesize polydisperse olefin block copolymers. Domain spacing of the observed lamellar morphologies was five times larger than that in equivalent monodisperse block copolymers. It should be noted that despite their promising properties, there are not so many works on experimental investigation of random multiblock copolymers, mainly due to the difficulties associated with the experimental characterization of such systems.

The theoretical investigation of the phase behavior of multiblock copolymers began from the work of de Gennes,[23] in which the stability of an AB copolymer melt was studied for regular and polydisperse multiblock copolymers. After that, the order-disorder transition for different types of polydisperse multiblock copolymers including correlated random copolymers (with the Markovian unit sequences along their chains) was thoroughly investigated using the weak segregation theory.[24–32] The common conclusion is that the structure period increases with increasing polydispersity.

Computer simulations including, in particular, the dissipative particle dynamics (DPD) methods prove to be an excellent tool for studying phase behavior of both linear copolymers[33–36] and copolymers with more complex architectures.[37] In our previous works,[5–7] we studied phase behavior of a melt of random copolymers and showed that they can undergo a transition to a lamellar state, the period of which shows only a weak dependence on the incompatibility parameter.

The design of copolymer sequences according to geometrical criteria was proposed for polymer globules with a modified surface layer (so-called protein-like copolymers). The resulting solvable polymer globules with mostly polar surfaces were studied by means of computer simulations, theory, and experiments.[38–43] In the case of small amount of polar units at the surface, using mean-field theory, it was found that the macromolecules with designed protein-like sequences form

---

[a] Author to whom correspondence should be addressed. Electronic mail: govorun@polly.phys.msu.ru.

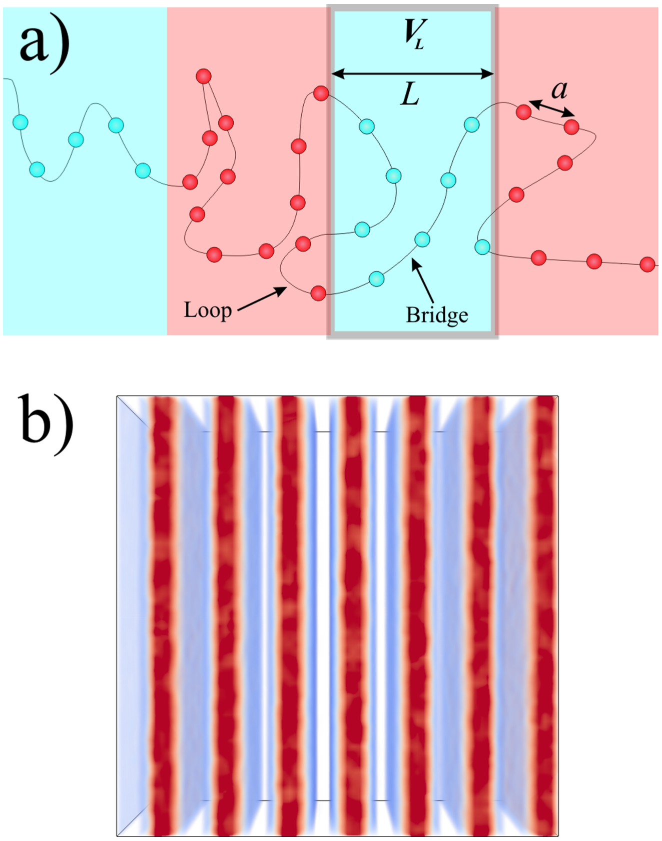

FIG. 1. A schematic representation of the sequence modification procedure (a) and a simulation box after the modification (b).

more stable globules than those with regular sequences.[41] Although the lowest free energy was provided by another sequence type (copolymer chain consisting of one long and many short hydrophobic blocks separated by polar units), its value is very close to that of the protein-like copolymers. Similar idea of sequence design can find other applications, in particular, for preparing multiblock copolymers capable of microphase separation, which is investigated in this study.

In the present paper, a special type of random multiblock copolymers, which are neither characterized by the Markovian unit sequence nor obtained by a procedure of the premade blocks coupling, is considered. We imaginarily introduce a periodic lamellar structure in a homopolymer melt and assign A or B type to monomer units according to the layer type they are located in (Fig. 1(a)). Homopolymers thus become multiblock copolymers with AB monomer unit sequences corresponding to their "parent" conformations in the melt. Assuming that macromolecules have random conformations in a homopolymer melt (the Flory theorem), the probability distribution of block sizes is calculated using the approaches of statistical physics of macromolecules. If one introduces repulsion between A and B monomers, a microphase separated state can be expected in equilibrium. We check this hypothesis using DPD computer simulations by analyzing the evolution of such "pattern-modified" random multiblock copolymers (Fig. 1(b)) of 50:50 composition from the "parent" lamellar and preliminary homogenized states.

II. THE MODEL AND METHODOLOGY

A. Analytical model

Let us consider a layer V_L of the thickness L in a polymer melt and suppose that all monomer units in the layer V_L have a type A, whereas the monomer units in neighbor layers have a type B (see Fig. 1(a)). Conformations of polymer chains in a melt can be described as ideal Gaussian coils (the Flory theorem); therefore, each A-block can be considered as a random walk trajectory terminated at the each of two layer boundary planes. We assume that all macromolecules are very long, i.e., for any macromolecule $Na^2 >> L^2$, where N is the number of monomer units (statistical segments) in a chain, each unit has a size a; it means that the probability to find a chain end inside a layer is negligible.

Let us introduce a coordinate system $\{x,y,z\}$, where the axis x is perpendicular to the layer confined between the planes $x = 0$ and $x = L$. Let $P_A(k)$ be the probability distribution for an A-block consisting of k monomer units. This distribution is determined by the chain conformation: the type of monomer units changes at the planes $x = 0$ and $x = L$ when moving along a polymer chain. The chain conformations can be described by a diffusion-type equation for the Green function $G_A(\mathbf{r},k|\mathbf{r}_0)$ of an A-block consisting of k statistical segments of length a with the beginning at the point $\mathbf{r}_0 = (x_0, y_0, z_0)$ and the end at the point $\mathbf{r} = (x, y, z)$ in the layer,[44,45]

$$\frac{\partial}{\partial k} G_A(\mathbf{r},k|\mathbf{r}_0) = \frac{a^2}{6}\Delta G_A(\mathbf{r},k|\mathbf{r}_0), \quad \mathbf{r},\mathbf{r}_0 \in V_L, \tag{1}$$

Δ is the Laplacian with respect to $\mathbf{r}$. The initial condition is

$$G_A(\mathbf{r},0|\mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0) \tag{2}$$

and the boundary conditions are

$$G_A(\mathbf{r},k|\mathbf{r}_0)|_{x=0} = G_A(\mathbf{r},k|\mathbf{r}_0)|_{x=L} = 0. \tag{3}$$

The zero boundary conditions determine the termination of an A-block when it touches the planes $x = 0$ and $x = L$, which corresponds to the problem of first return in statistics and has been previously used for the calculation of the block-size distribution of protein-like copolymers.[40]

The solution of Eq. (1) with the conditions (2) and (3) can be represented as the product

$$G_A(\mathbf{r},k|\mathbf{r}_0) = G_A(x,k|x_0)\, G_0(y,k|y_0)\, G_0(z,k|z_0), \tag{4}$$

where the Green function $G_A(x,k|x_0)$ is equal to

$$G_A(x,k|x_0) = \frac{2}{L}\sum_{n=1}\exp\left(-\frac{n^2\pi^2a^2}{6L^2}k\right)\sin\frac{n\pi x_0}{L}\sin\frac{n\pi x}{L}, \tag{5}$$

and the Green functions $G_0(y,k|y_0)$ and $G_0(z,k|z_0)$ describe completely free random walks along the axes y and z, $G_0(y,k|y_0) = \sqrt{\frac{3}{2\pi ka^2}}\exp\left(-\frac{3}{2ka^2}(y-y_0)^2\right)$.[44,45]

In a homogeneous melt, the integral $\int_{V_L} d\mathbf{r}\, G_A(\mathbf{r},k|\mathbf{r}_0)$ gives the number of chain trajectories consisting of k steps that begin at the point $\mathbf{r}_0$ and stay within the lamella, in proportion to the total number of trajectories for a free chain. The fraction of trajectories composed of from k to $k + \Delta k$ steps, $P_A(k)\cdot\Delta k$, is determined by a decrement of that integral. Therefore, the probability distribution $P_A(k)$ can be calculated directly from the Green function using the integration over the lamella or as an integral probability flux through the boundary surface,[40,46]

$$P_{\mathrm{A}}(k) = -\frac{\partial}{\partial k}\int_{V_L} d\mathbf{r}\, G_{\mathrm{A}}(\mathbf{r},k|\mathbf{r}_0) = -\frac{a^2}{6}\left(\left.\frac{\partial G_{\mathrm{A}}(x,k|x_0)}{\partial x}\right|_{x=L} - \left.\frac{\partial G_{\mathrm{A}}(x,k|x_0)}{\partial x}\right|_{x=0}\right), \quad (6)$$

where the normalization condition for the one-dimensional Green functions G_0 ($\int_{-\infty}^{\infty} dy\; G_0(y,k|y_0) = 1$) is taken into account. From expressions (5) and (6), the probability distribution $P_{\mathrm{A}}(k)$ can be written as follows:

$$P_A(k) = \frac{2\pi}{3\tilde{L}^2}\sum_{n=1,3,5,\ldots} n \exp\left(-\frac{n^2\pi^2}{6\tilde{L}^2}k\right)\sin\frac{n\pi\tilde{x}_0}{\tilde{L}}, \quad (7)$$

where $\tilde{L} = L/a$, $\tilde{x}_0 = x_0/a$ are the dimensionless layer thickness and initial coordinate, respectively. The block size distribution $P_{\mathrm{A}}(k)$ also obeys the normalization condition,

$$\int_0^\infty dk\; P_A(k) = 1. \quad (8)$$

The asymptotic forms of block size distribution (7) can be written for two different regimes,

$$P_{\mathrm{A}}(k) \cong \begin{cases} k^{-3/2}, & 1 << k << (L/a)^2 \\ \left(\dfrac{a}{L}\right)^3 \exp\left(-\dfrac{\pi^2 a^2}{6L^2}k\right), & k >> (L/a)^2 \end{cases}. \quad (9)$$

The first regime describes not very long polymer loops that begin and end at one of the boundary planes and do not touch the other plane; the corresponding dependence $P_{\mathrm{A}}(k) \sim k^{-3/2}$ is the asymptotic form of the solution of the probabilistic "first return" problem for the probability for a random walk to start at the plane and to return to it for the first time after k steps.[46] The second regime describes very long random trajectories of a polymer chain which avoids the boundary surfaces. These regimes are separated by a certain value of an A-block size k_L corresponding to the characteristic number of monomer units in a Gaussian chain of the spatial size L:$L^2 \approx k_L a^2$.

Let us study the statistical properties of these sequences in more detail. The number average size of an A-block is equal to

$$\bar{k} = \int_0^\infty dk\; kP_A(k) = \frac{24\tilde{L}^2}{\pi^3}\sum_{n=1,3,5,\ldots}\frac{1}{n^3}\sin\frac{n\pi\tilde{x}_0}{\tilde{L}}, \quad (10)$$

and the weight average size is

$$\bar{k}_w = \frac{1}{\bar{k}}\int_0^\infty dk\; k^2 P_A(k) = \frac{288\tilde{L}^4}{\pi^5\bar{k}}\sum_{n=1,3,5,\ldots}\frac{1}{n^5}\sin\frac{n\pi\tilde{x}_0}{\tilde{L}}. \quad (11)$$

For a large enough lamella thickness ($\tilde{x}_0/\tilde{L} = x_0/L << 1$), the summation over n in formulas (10) and (11) can be approximated by the integration in the limits from $n = 1$ to ∞. Then, the number average size depends linearly on the layer thickness,

$$\bar{k} \approx \frac{24}{\pi^2}\tilde{x}_0\tilde{L}, \quad \tilde{x}_0/\tilde{L} << 1, \quad (12)$$

and weight average block size (11) is approximately proportional to the square of the layer thickness,

$$\bar{k}_{\mathrm{w}} \approx \frac{96}{\bar{k}\pi^4}\tilde{x}_0\tilde{L}^3 \approx \frac{4}{\pi^2}\tilde{L}^2, \quad \tilde{x}_0/\tilde{L} << 1. \quad (13)$$

The asymptotic value of the polydispersity index (PDI) can be estimated from expressions (12) and (13),

$$\frac{\bar{k}_w}{\bar{k}} \approx \frac{1}{6\tilde{x}_0}\tilde{L} \approx \frac{\pi^2}{144\tilde{x}_0^2}\bar{k}. \quad (14)$$

Thus, our pattern-modified multiblock copolymers are characterized by a very broad block-size distribution, with the polydispersity index being comparable with the number average block size $\bar{k}$ (or the lamellar thickness $\tilde{L}$).

To analyze the scaling behavior of probability distribution (7), it is convenient to compare it to the well-known most probable distribution (the Flory distribution characterizing the step-growth polymerization in homogeneous systems) $P_{\mathrm{Fl}}(k)$ with the same number average block size $\bar{k}$,

$$P_{\mathrm{Fl}}(k) = \frac{1}{\bar{k}-1}\left(1-\frac{1}{\bar{k}}\right)^k, \quad k = 1,2,\ldots. \quad (15)$$

The dependence of $\ln P_{\mathrm{Fl}}$ on k is linear: $\ln P_{\mathrm{Fl}} = \mathrm{const} + \ln(1-1/\bar{k})k$. The coefficient characterizing the line slope at $L/a >> 1$, $\bar{k} >> 1$, $x_0 = a/2$ is approximately equal to $1/\bar{k} \approx \pi^2/(12\tilde{L})$. The "tail" of the probability distribution $P_{\mathrm{A}}(k)$ at $k \to \infty$ is described by exponential asymptotic form (9) corresponding also to the linear dependence of $\ln P_{\mathrm{A}}$ on k: $\ln P_{\mathrm{A}} \approx \mathrm{const} - \pi^2 k/(6\tilde{L}^2)$. From these dependences, one can conclude that the probability distribution $P_{\mathrm{A}}(k)$ decays slower at $k \to \infty$ than the Flory distribution $P_{\mathrm{Fl}}(k)$.

In order to compare the analytical probability distribution $P_{\mathrm{A}}(k)$ with the block-size distribution obtained in simulations, the following discrete probability distribution:

$$\tilde{P}_{\mathrm{A}}(k) = \int_{k-1}^{k} dk' P_{\mathrm{A}}(k') = \frac{4}{\pi}\sum_{n=1,3,\ldots}\frac{1}{n}\sin\frac{n\pi\tilde{x}_0}{\tilde{L}}\left(\exp\left(-\frac{n^2\pi^2}{6\tilde{L}^2}(k-1)\right) - \exp\left(-\frac{n^2\pi^2}{6\tilde{L}^2}k\right)\right), \quad (16)$$

$k = 1,2,\ldots$, was introduced; $\tilde{P}_A(k)$ is normalized to unity: $\sum_{k=1}^{\infty}\tilde{P}_{\mathrm{A}}(k) = \int_0^\infty dk\; P_A(k) = 1$. The position of the beginning of an A-block should be taken near the border surface. In numerical calculations, the value of $x_0 = a/2$ is used.

The probability distributions $\tilde{P}_A(k)$ given by Eq. (16) are plotted in Figure 2 for a set of different lamellar thicknesses $\tilde{L}$. Deviations from the asymptotic dependence $\tilde{P}_A(k) \sim 1/k^{3/2}$ arise at large enough k starting from the smallest $\tilde{L}$, as given by the characteristic value $k_L = \tilde{L}^2$ demarcating two asymptotic regimes (9).

B. The simulation technique

DPD is a version of the coarse-grained molecular dynamics adapted to polymers and mapped onto the classical

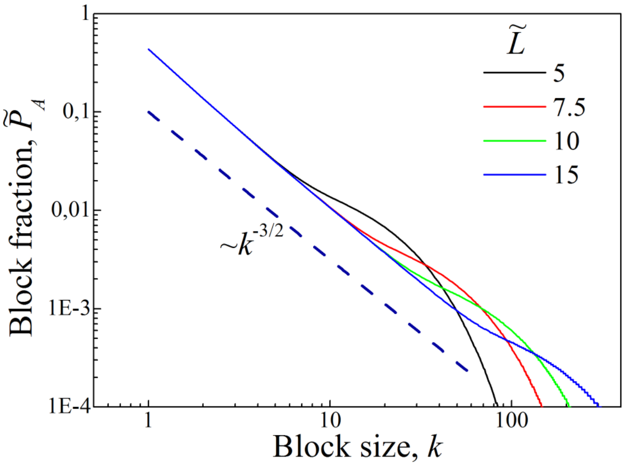

FIG. 2. The probability distributions of A-block sizes $\tilde{P}_A(k)$ given by Eq. (16) for different lamellar thicknesses are plotted (solid lines); $x_0 = a/2$. The asymptotic dependence $\tilde{P}_A(k) \sim 1/k^{3/2}$ for loops at relatively small k is shown by the dashed line.

lattice Flory–Huggins theory.[47–50] This method has been extensively used to simulate different polymer systems at a mesoscale level, especially polymer melts and other systems with high polymer concentration. Soft interaction potentials permit to take a much larger integration time step, as compared with the classical molecular dynamics, and thus to study various systems on rather long time scales. Moreover, such a potential does not prohibit self-intersections of bonds (i.e., the chains are "phantom"), which greatly decreases the simulation time necessary to reach an equilibrium.

Macromolecules are represented in terms of the bead-and-spring model, with particles (monomer units) interacting by a bond stretching force (only for connected beads) $\mathbf{f}^{\mathbf{b}}$, a conservative force (repulsion) $\mathbf{f}^{\mathbf{c}}$, a dissipative force (friction) $\mathbf{f}^{\mathbf{d}}$, and a random force (heat generator) $\mathbf{f}^{\mathbf{r}}$,

$$\mathbf{f}_i = \sum_{j \neq i} \left(\mathbf{f}_{ij}^{\mathrm{b}} + \mathbf{f}_{ij}^{\mathrm{c}} + \mathbf{f}_{ij}^{\mathrm{d}} + \mathbf{f}_{ij}^{\mathrm{r}} \right). \tag{17}$$

The summation is performed over all other particles in the sphere of the cut-off radius r_c surrounding the ith particle. We assume that all particles have the same mass $m_i = m$ and below use the dimensionless parameters setting r_c, m, and $k_{\mathrm{B}}T$ (k_{B} is the Boltzmann constant and T is the thermodynamic temperature) equal to unity.

The spring force acts on the ith monomer unit from the neighbor ones in the same macromolecule,

$$\mathbf{f}_{ij}^{\mathrm{b}} = -K\mathbf{r}_{ij}, \quad \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j, \tag{18}$$

where K is a spring constant (bond stiffness); in our simulations, we set $K = 4$. The soft core repulsion force is equal to

$$\mathbf{f}_{ij}^{\mathrm{c}} = \begin{cases} a_{\alpha\beta}\left(1 - r_{ij}\right)\mathbf{r}_{ij}/r_{ij}, & r_{ij} \leq 1 \\ 0, & r_{ij} \geq 1 \end{cases}, \tag{19}$$

where $a_{\alpha\beta}$ is the interaction parameter if the particle i has the type α and the particle j has the type β. More information regarding the DPD method can be found elsewhere.[5,50] The dissipative and random forces are used as they are proposed in Ref. 43 with the noise parameter $\sigma = 3$. A modified velocity-Verlet algorithm[51] with the time step $\Delta t = 0.04$ is used for the integration of the equations of motion.

In our simulations, we used $a_{\alpha\alpha} = 25$. In this case, the interaction parameters $a_{\alpha\beta}$ and a more common Flory-Huggins parameter χ are linearly related to each other,[51]

$$a_{\alpha\beta} = \chi/0.306 + 25, \quad \alpha \neq \beta. \tag{20}$$

The behavior of macromolecules in a melt was modeled using a box of the size $70 \times 70 \times 30$ units at the reduced mean number density $\rho = 3$ (441 000 particles). The initial conformation (for 1722 homopolymer chains consisting of $N = 256$ monomer units) was generated as random walks with the spatial step of unit length and homogeneously distributed over the box taking into account the periodic boundary conditions. The resulting system was equilibrated during 200 000 time steps to ensure that the macromolecules have equilibrium conformations. After the equilibration, a monomer type modification was performed: a periodic lamellar-like pattern was introduced so that the monomer units with the coordinate $x \in [i_l, i_l + L]$, $i_l = 0, 1, \ldots, n_l$, got the type A and other monomer units got the type B (see Fig. 1(b)). We use $L = 5$ and $n_l = 6$ in the results presented below; therefore, the period of the structure obtained this way was equal to 10. It should be noted that due to the choice of the parameters $a_{\alpha\alpha}$ and K, the statistical segment length in the equilibrated systems was very close to unity; therefore, in our simulations, $L = \tilde{L}$.

Structure formation was monitored by snapshot observations of the spatial distribution of A and B units and by calculating the static structure factor $S(q)$,

$$S(q) = \frac{1}{n_p}\left\langle \left| \sum_{i=1}^{n_p} \exp(i\mathbf{q}\mathbf{r}_i) \right|^2 \right\rangle, \tag{21}$$

where n_p is the total number of particles in the simulation box and averaging is performed over a large number of spatial directions and over a sequence of independent system conformations. By analyzing the q-dependence of the structure factor, one can detect a long-range (presence of satellite peaks) or short-range ordering and estimate the characteristic size of domains (by the main peak position) and its dispersion (by the half-height width).

The behavior of the pattern-modified system was studied starting from two completely different initial states: directly from the lamellar-like state (Fig. 1(b)) and from a completely disordered state. In order to obtain a disordered state, a long relaxation after the modification was additionally performed at $\chi = 0$. The systems were relaxed at $\chi = 2.4$ and their static structure factors were monitored in the course of the simulations. After 70 million time steps, the structure factor became time-constant thus indicating that the systems had reached some kind of equilibrium with very similar resulting structures (curved lamellae with nearly equal periods) in the both cases.

III. RESULTS AND DISCUSSIONS

The theoretically derived probability distribution $\tilde{P}_A(k)$ for $\tilde{L} = 5$ is plotted in Figure 3 in comparison with the direct computer realization of the proposed patterned modification and with the Flory block-size distribution. The theory and

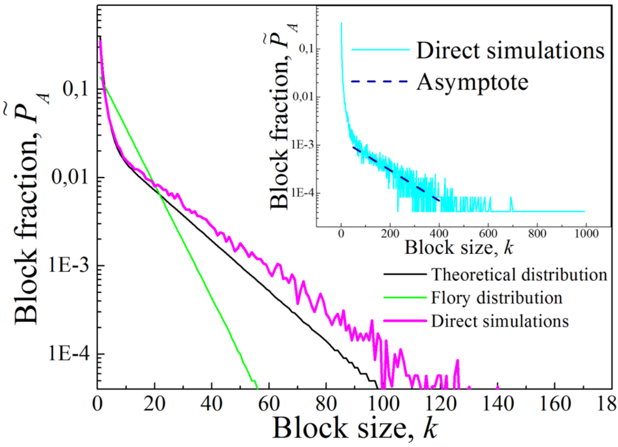

FIG. 3. Theoretically derived probability distribution of A-block sizes $\tilde{P}_A(k)$ for $\tilde{L} = 5$ (black line), most probable (Flory) distribution $P_{\mathrm{Fl}}(k)$ (green line) calculated at the same number average block size $\bar{k} \approx 7.3$, and block fraction in the direct computer simulation for $\tilde{L} = 5$, $N = 256$ (magenta line). The inset shows the simulation results for wider lamellae ($\tilde{L} = 15$ and $N = 1000$) and line with the slope $-a^2\pi^2/(6L^2)$ characterizing the asymptotic behavior of $\tilde{P}_A(k)$ at large k.

simulation results are close for short blocks, whereas the simulation curve is somewhat higher than the theoretical one at large k that can be related to a more broad theoretical distribution (with infinitely long blocks possible), whereas both distributions are normalized to unity.

It can be seen that the pattern-modified copolymer contains a considerable amount of very short and some very long blocks, while the fraction of blocks of the average size $\bar{k}$ is less than that for copolymers with the Flory distribution given by Eq. (15). The Flory block-size distribution (the green line) decreases exponentially at all k values, whereas the probability distribution for the pattern-modified copolymers decreases exponentially only at large enough k ($k >> k_L = \tilde{L}^2$ in Eq. (9)). The inset shows the simulation results for polymer chains of length 1000 for wider lamellae ($\tilde{L}$ = 15) and corresponding asymptotic line.

The dependence of the polydispersity index of the pattern-modified multiblock copolymers on the layer thickness $\tilde{L}$ is plotted in Fig. 4 (top). It is well described by linear asymptotic dependence (14) and shows that the block-size distribution of pattern-modified copolymers is very broad, especially in comparison with the most probable distribution. The weight average A-block size and polydispersity index for Flory distribution (15) are, respectively, equal to

$$\bar{k}_{\mathrm{w(Fl)}} = \bar{k}\left(2 - \frac{1}{\bar{k}}\right) \quad \text{and} \quad \frac{\bar{k}_{\mathrm{w(Fl)}}}{\bar{k}} = 2 - \frac{1}{\bar{k}}. \qquad (22)$$

Another important characteristic of the polymer chain conformations in a block copolymer melt with the proposed domain structure is the bridge/loop ratio, where bridges are the blocks connecting the neighbor domains of the same type, and loops are the blocks with the ends located at the same domain boundary (see Fig. 1(a)). Using formulas (1), (4), and (6), the contribution of bridges $P_{\mathrm{A(br)}}(k)$ and loops $P_{\mathrm{A(loop)}}(k)$ to the total probability distribution $P_{\mathrm{A}}(k) = P_{\mathrm{A(br)}}(k) + P_{\mathrm{A(loop)}}(k)$ can be written as

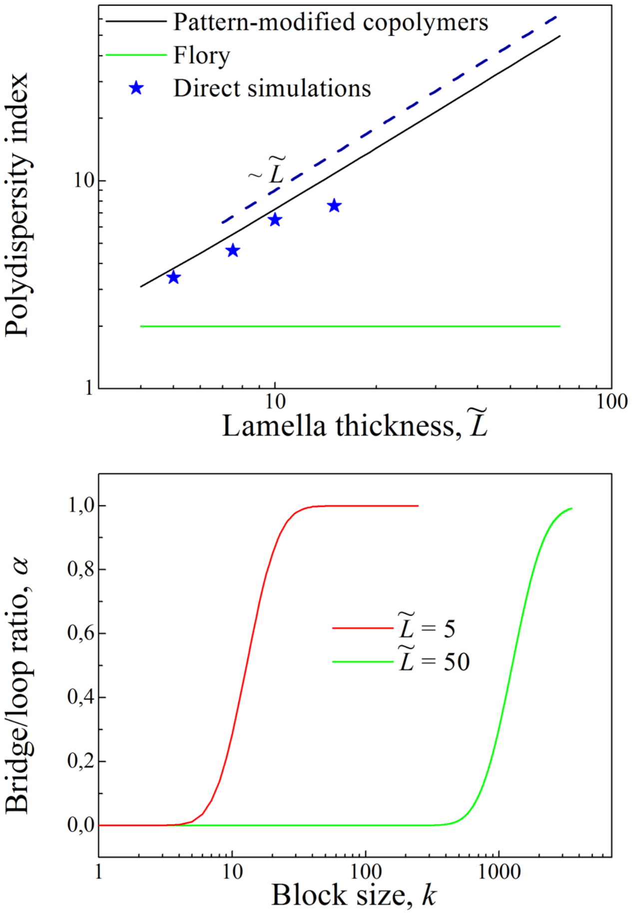

FIG. 4. The dependences of (top) the polydispersity index and (bottom) bridge/loop ratio on the lamellar thickness $\tilde{L}$. The dashed line shows asymptotic dependence (14) and green line gives the result for the most probable (Flory) distribution. The bridge/loop ratio is calculated using formulas (23) and (24).

$$\begin{aligned} P_{\mathrm{A(br)}}(k) &= -\frac{a^2}{6}\left.\frac{\partial G_{\mathrm{A}}(x,k|x_0)}{\partial x}\right|_{x=L} \\ &= -\frac{\pi^2}{3\tilde{L}^2}\sum_{n=1}^{\infty}(-1)^n n \sin\frac{n\pi\tilde{x}_0}{\tilde{L}}\exp\left(-\frac{n^2\pi^2 k}{6\tilde{L}^2}\right), \\ P_{\mathrm{A(loop)}}(k) &= \frac{a^2}{6}\left.\frac{\partial G_{\mathrm{A}}(x,k|x_0)}{\partial x}\right|_{x=0} \\ &= \frac{\pi^2}{3\tilde{L}^2}\sum_{n=1}^{\infty} n \sin\frac{n\pi\tilde{x}_0}{\tilde{L}}\exp\left(-\frac{n^2\pi^2 k}{6\tilde{L}^2}\right), \end{aligned} \qquad (23)$$

where it is assumed that the beginning of a block ($k = 0$) is located at the plane $x = 0$. The ratio of the fraction of bridges to the fraction of loops $\alpha(k)$ can be calculated as follows:

$$\alpha(k) = \tilde{P}_{\mathrm{A(br)}}(k)/\tilde{P}_{\mathrm{A(loop)}}(k), \qquad (24)$$

where $\tilde{P}_{\mathrm{A(br)}}(k) = \int_{k-1}^{k} dk' P_{\mathrm{A(br)}}(k')$ and $\tilde{P}_{\mathrm{A(loop)}}(k) = \int_{k-1}^{k} dk'\, P_{\mathrm{A(loop)}}(k')$, $k = 1, 2, \ldots$.

The dependence $\alpha(k)$ for the layer thicknesses $\tilde{L}$ = 5 and 50 is presented in Figure 4. Practically, all short blocks are loops, whereas the blocks of size exceeding the characteristic value $k_L = \tilde{L}^2$ can form a loop or a bridge with the probability 1/2. The fraction of bridges among all blocks was calculated using the formula $p_{\mathrm{br}} = \sum_{k=1}^{\infty} \tilde{P}_{\mathrm{A}}(k)\frac{\alpha(k)}{\alpha(k)+1}$. It was obtained that

$p_{\rm br} \approx 0.1$ for $\tilde{L} = 5$, $p_{\rm br} \approx 0.05$ for $\tilde{L} = 10$, and $p_{\rm br} \approx 0.01$ for $\tilde{L} = 50$.

Note that the total fraction of bridges formed by blocks of the pattern-modified copolymers is considerably smaller than that formed by middle blocks of the monodisperse triblock (or multiblock) copolymers, which was found earlier theoretically[52,53] and in computer simulations[54] to be approximately equal to 0.4 in bulk. The smaller values of that fraction for the pattern-modified copolymers can be explained by a great deal of short blocks in the probability distribution $\tilde{P}_A(k)$, all of which prefer to be loops.

Assuming that the bridge/loop ratio is the important characteristic responsible for the film mechanical durability, we can say that smaller lamellar periods correspond to a greater bridge fraction thus providing better overall material properties for polydisperse multiblocks. This conclusion is not valid for diblock copolymers which cannot form bridges. However, even the middle blocks of triblock copolymers influence the low-frequency viscoelastic response[55] and stress-strain dependences[56] due to the formation of bridges.

Finally, let us consider the applicability of the presented analytical approach to patterned polymer films with layers of different types perpendicular to the substrate. For a polymer film of constant density confined between planes $z = 0$ and $z = D$, the Green function of an A-block $G_{\rm A}(\mathbf{r}, k|\mathbf{r}_0)$ satisfies diffusion-type Eq. (1) with boundary conditions (3) and $\frac{\partial G_A}{\partial z} = 0$ at $z = 0$ and $z = D$ if the thickness of polymer film $D >> a$. In that case, same expression (7) for the probability distribution of A-block sizes can be derived using definition (6) and taking into account all boundary conditions. Therefore, all discussed features of block-size distributions are expected to be valid for pattern-modified multiblock copolymers in not very thin polymer films as well.

In order to test the theoretical findings and investigate the phase behavior of our pattern-modified copolymers, we performed dissipative particle dynamics simulations.

Figure 5 (top) presents the system which was relaxed directly after the sequence modification: it transformed to lamellae with rough boundaries and larger period than it was set initially. A special feature of the structure is the presence of a considerable amount of A-monomer units in the B-lamellae and B-monomer units in the A-lamellae. The period of the structure D can be found through the analysis of the structure factor dependence on wave vector (22): the main peak corresponds to $D = 1/0.0585 \approx 17.1$. The total interface area decreased by around 25% (we used ParaView software[57] to visualize the structures and calculate the interfacial areas) as compared with the initial value.

We can conclude that after the relaxation, the structure period increased from 10 to 17.1 demonstrating that the interaction between monomer units leads to a considerable stretching of blocks. The mean square of the end-to-end distance of blocks of pattern-modified copolymers ($\tilde{L} = 5$) for the system immediately after preparation (upper solid curve) and for the system after relaxation (lower solid curve) is plotted vs. the block size in Fig. 6. The straight dashed line represents the dependence $\langle R_{\rm A}^2 \rangle = ka^2$ for blocks of size k in a homogeneous melt. The end-to-end distance of short blocks (loops) is almost unchanged, whereas the long blocks ($k > 20$), which can be bridges, are noticeably stretched. The mean square of the end-to-end distance of long blocks after the relaxation is about 1.2 times greater than before.

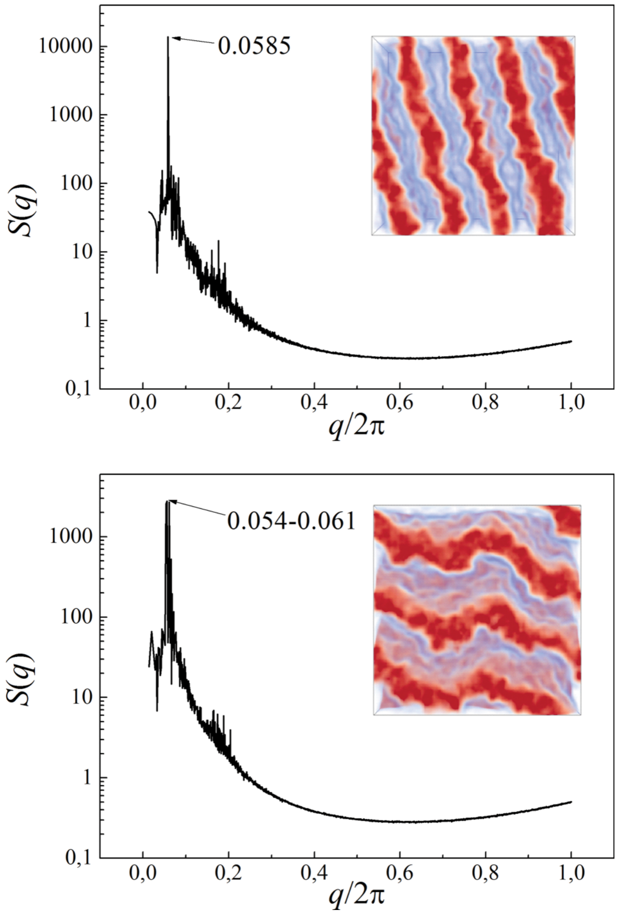

FIG. 5. The structure factor $S(q)$ for the final melt state after (top) the sequence modification and subsequent relaxation and (bottom) relaxation directly from a disordered state. The insets give the snapshots of the corresponding 3D structures.

The fractions of long loops and bridges ($k >> k_{\rm L}$) in the system immediately after preparation are equal to 0.5 that correspond to the bridge/loop ratio $\alpha = 1$ (see Fig. 4). With an increase in the structure period, the bridge fraction is expected to decrease, as confirmed, for example, by the computer simulations for monodisperse triblocks.[54] Assuming that the end-to-end distance increases mainly due to bridges rather than loops, we can estimate that for bridges, $\langle R_{\rm A}^2 \rangle_{\rm br}$ increases more than 1.4 times.

Besides, the increase of the lamella thickness is related to the penetration of short A- and B-blocks into the domains of another type that lowers the surface tension, the concentration of A or B monomer units in an “alien” phase being of 5%-7%. Therefore, both the chain stretching and penetration of A monomer units into B-domains (and vise versa) are responsible for the increase in the structure period.

Figure 5 (bottom) shows the structure factor for the final state of the system, which was relaxed from a disordered state. The structure is again lamellar with the presence of a considerable amount of short blocks in the domains of another type; however, the structure factor has a quite broad main peak

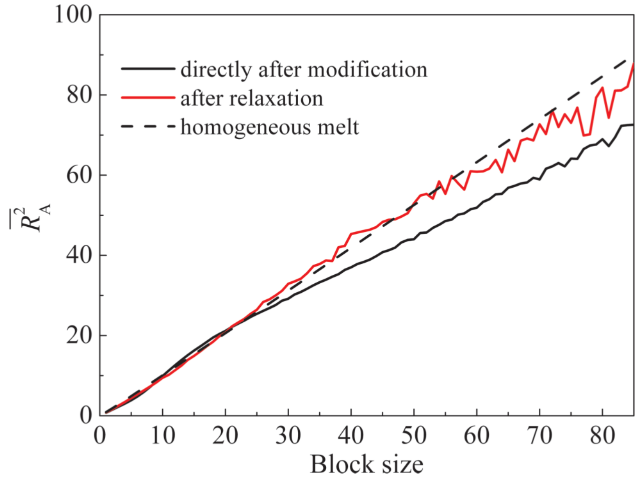

FIG. 6. The mean square of the end-to-end distance R_{A} of blocks of pattern-modified copolymers ($\tilde{L} = 5$) for the system immediately after preparation (upper solid curve) and for the system after relaxation (lower solid curve). The straight dashed line represents the dependence $\langle R^2_{\mathrm{A}} \rangle = ka^2$ for blocks of size k in a homogeneous melt.

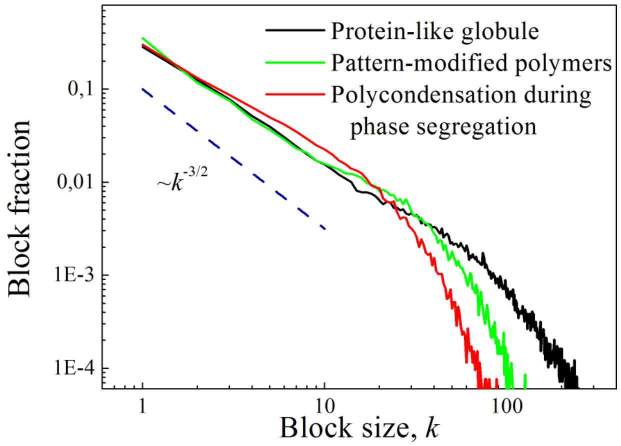

FIG. 7. Comparison of block-size distributions for sequences prepared by the patterned modification (this work) for $\tilde{L} = 5$, protein-like modification, and copolymerized during phase separation (see Refs. 40 and 59, and supplementary material[58]). The parameters of the protein-like modification and step-growth polymerization are chosen to provide the similar spatial scales as for the pattern-modified multiblock copolymers.

which can be described by the correlated large-scale bending of the lamellae, which is clearly seen from the inset. The period of the structure calculated from the position of the main peak was between 18.5 and 16.4, which is in agreement with that found for the first initial state (17.1).

Therefore, we can conclude that a stable non-ideal lamellar structure with the period sufficiently larger than that introduced by the modification is the equilibrium morphology of the melt of copolymers with sequences prepared by lamellar patterned modification.

Besides, an attempt was made to find the equilibrium morphology of the pattern-modified copolymers prepared with the modification period $\tilde{L} = 15$. As was done previously for $\tilde{L} = 5$, the evolution was studied starting from two different initial states (lamellar-like and homogeneous); an increase of the period was observed for the first system and the formation of A- and B-domains for the second one. However, the accessible simulation time was not sufficient to achieve the equilibrium state of those systems.

IV. CONCLUSION

Random multiblock AB copolymers with a broad block-size distribution and special sequence statistics are studied in this paper. The copolymers are prepared by a modification of the homopolymer chains in a melt according to a geometrical criterion: the monomer units' types are simultaneously changed so that the resulting structure is alternating equal-width layers of A and B types (pattern-modified copolymers). The statistical characteristics of the monomer sequences in such copolymers are studied including the probability distributions of block sizes, number and weight average block sizes, polydispersity index, and bridge/loop ratio. Asymptotic forms (9) of the block size distributions are similar to those of protein-like copolymers where hydrophobic units are located in the globule core and polar units in a surface spherical layer.[40] Besides, they are similar to the block-size distributions of copolymers prepared by copolymerization during phase separation (Fig. 7); an example of such a process is presented in the supplementary material[58] and Ref. 59. We claim that the described power-law scaling in the block-size distribution for sufficiently short blocks is a general feature of any multiblock copolymer system, in which the phase separation governs the formation of copolymer sequences.

The probability distribution of block sizes in the obtained pattern-modified multiblock copolymers is very broad. Comparing it with the most probable (Flory) distribution (characterizing the step-growth polymerization in a homogeneous system) with the same number average block size, we can conclude that the pattern-modified copolymer sequences contain more short blocks, less blocks of the average size, and more very long blocks. The polydispersity index of pattern-modified copolymers is proportional to the lamella width. We estimate the bridge/loop ratio and found that the total fraction of bridges decreased considerably with the lamella width. The equilibrium state of the pattern-modified multiblock copolymers with 50:50 composition was studied by direct DPD computer simulations. Lamellae with rough boundaries formed in the melt with the structure period 1.7 times larger than the initial pattern size. A noticeable amount of short blocks was located in the domains of other type. It is worth noting that despite the obtained lamellar structures are far from perfect, they are formed by multiblock copolymers with a very broad block size distribution (PDI ~ 3.5 in the presented simulation).

We suppose that such sequences may occur during interfacial polymerization and its modifications,[60] which are actively used nowadays for different applications.[61,62] However, there are not so many experimental data about the details of block-mass distributions in those cases. The copolymers with such block-size distributions could be suitable for pattern reproduction in the case when an ideal domain structure is not important. Due to the presence of very long blocks, such copolymers are somewhat similar to mixtures of homopolymers and block copolymers, which nowadays are considered as good candidates for reproducing various (even irregular) substrate patterns.[63,64] The other attractive feature of multiblock copolymers is greater toughness of the materials made on their basis compared to, for example, diblock copolymers.[3] Blocks connecting neighboring domains of the same type (bridges) provide strong mechanical connection of those domains, which is important for the mechanical durability of the material.

ACKNOWLEDGMENTS

We appreciate the financial support from the Russian Science Foundation (Project No. 14-13-00683). We thank Moscow State University Supercomputer Center for providing the computational resources.[65]

[1] H. Hu, M. Gopinadhan, and C. O. Osuji, Soft Matter **10**, 3867 (2014).
[2] S. B. Darling, Prog. Polym. Sci. **32**, 1152 (2007).
[3] I. Lee and F. S. Bates, Macromolecules **46**, 4529 (2013).
[4] S. Li, R. A. Register, J. D. Weinhold, and B. G. Landes, Macromolecules **45**, 5773 (2012).
[5] A. A. Gavrilov, Y. V. Kudryavtsev, and A. V. Chertovich, J. Chem. Phys. **139**, 224901 (2013).
[6] A. A. Gavrilov, Y. V. Kudryavtsev, P. G. Khalatur, and A. V. Chertovich, Chem. Phys. Lett. **503**, 277 (2011).
[7] A. A. Gavrilov, Y. V. Kudryavtsev, P. G. Khalatur, and A. V. Chertovich, Polym. Sci., Ser. A **53**, 827 (2011).
[8] V. Ganesan, N. A. Kumar, and V. Pryamitsyn, Macromolecules **45**, 6281 (2012).
[9] I. Erukhimovich, Y. Kriksin, and G. ten brinke, Soft Matter **8**, 2159 (2012).
[10] S. O. Ilyin, A. Ya. Malkin, V. G. Kulichikhin, Yu.I. Denisova, L. B. Krentsel, G. A. Shandryuk, A. D. Litmanovich, E. A. Litmanovich, G. N. Bondarenko, and Y. V. Kudryavtsev, Macromolecules **47**, 4790 (2014).
[11] B. Steinmüller, M. Müller, K. R. Hambrecht, G. D. Smith, and D. Bedrov, Macromolecules **45**, 1107 (2012).
[12] M. A. Hillmyer, J. Polym. Sci., Part B: Polym. Phys. **45**, 3249 (2007).
[13] N. A. Lynd, A. J. Meuler, and M. A. Hillmyer, Prog. Polym. Sci. **33**, 875 (2008).
[14] Y. Matsushita, A. Noro, M. Iinuma, J. Suzuki, H. Ohtani, and A. Takano, Macromolecules **36**, 8074 (2003).
[15] A. Noro, M. Iinuma, J. Suzuki, A. Takano, and Y. Matsushita, Macromolecules **37**, 3804 (2004).
[16] A. Noro, D. Cho, A. Takano, and Y. Matsushita, Macromolecules **38**, 4371 (2005).
[17] A. Noro, M. Okuda, F. Odamaki, D. Kawaguchi, N. Torikai, A. Takano, and Y. Matsushita, Macromolecules **39**, 7654 (2006).
[18] D. Bendejacq, V. Ponsinet, M. Joanicot, Y.-L. Loo, and R. A. Register, Macromolecules **35**, 6645 (2002).
[19] A.-V. Ruzette, S. Tencé-Girault, L. Leibler, F. Chauvin, D. Bertin, O. Guerret, and P. Gerard, Macromolecules **39**, 5804 (2006).
[20] N. A. Lynd and M. A. Hillmyer, Macromolecules **38**, 8803 (2005).
[21] N. A. Lynd and M. A. Hillmyer, Macromolecules **40**, 8050 (2007).
[22] A. J. Meuler, C. J. Ellison, C. M. Evans, M. A. Hillmyer, and F. S. Bates, Macromolecules **40**, 7072 (2007).
[23] P. G. de Gennes, Faraday Discuss. Chem. Soc. **68**, 96 (1979).
[24] G. H. Fredrickson and S. T. Milner, Phys. Rev. Lett. **67**, 835 (1991).
[25] G. H. Fredrickson, S. T. Milner, and L. Leibler, Macromolecules **25**, 6341 (1992).
[26] S. V. Panukov and S. I. Kuchanov, J. Phys. II **2**, 1973 (1992).
[27] A. V. Dobrynin and L. Leibler, Macromolecules **30**, 4756 (1997).
[28] A. M. Gutin and E. I. Shakhnovich, J. Phys. **50**, 1843 (1989).
[29] H. Angerman, G. ten Brinke, and I. Erukhimovich, Macromolecules **29**, 3255 (1996).
[30] H. Angerman, G. ten Brinke, and I. Erukhimovich, Macromolecules **31**, 1958 (1998).
[31] I. I. Potemkin and S. V. Panyukov, Phys. Rev. E **57**, 6902 (1998).
[32] A. V. Subbotin and A. N. Semenov, Eur. Phys. J. E **7**, 49 (2002).
[33] R. D. Groot and T. J. Madden, J. Chem. Phys. **108**, 8713 (1998).
[34] V. Ortiz, S. O. Nielsen, D. E. Discher, M. L. Klein, R. Lipowsky, and J. Shillcock, J. Phys. Chem. B **109**, 17708 (2005).
[35] X. Li, J. Guo, Y. Liu, and H. Liang, J. Chem. Phys. **130**, 074908 (2009).
[36] T. Klymko, V. Markov, A. Subbotin, and G. ten Brinke, Soft Matter **5**, 98 (2009).
[37] A. R. Khokhlov and P. G. Khalatur, Chem. Phys. Lett. **461**, 58 (2008).
[38] A. R. Khokhlov and P. G. Khalatur, Physica A **249**, 253 (1998).
[39] A. R. Khokhlov and P. G. Khalatur, Phys. Rev. Lett. **82**, 3456 (1999).
[40] E. N. Govorun, V. A. Ivanov, A. R. Khokhlov, P. G. Khalatur, A. L. Borovinsky, and A. Y. Grosberg, Phys. Rev. E **64**, R40903 (2001).
[41] E. N. Govorun, A. R. Khokhlov, and A. N. Semenov, Eur. Phys. J. E **12**, 255 (2003).
[42] V. I. Lozinsky, Adv. Polym. Sci. **196**, 87 (2006).
[43] V. I. Lozinsky, I. A. Simenel, V. K. Kulakova, E. A. Kurskaya, T. A. Babushkina, T. P. Klimova, T. V. Burova, A. S. Dubovik, V. Ya. Grinberg, I. Y. Galaev, B. Mattiasson, and A. R. Khokhlov, Macromolecules **36**, 7308 (2003).
[44] I. M. Lifshits, A. Y. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978).
[45] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
[46] W. Feller, in *An Introduction to Probability Theory and Its Applications*, 3rd ed. (Wiley, New York, 1971), Vol. II.
[47] P. J. Hoogerbrugge and J. M. V. A. Koelman, Europhys. Lett. **19**, 155 (1992).
[48] A. G. Schlijper, P. J. Hoogerbrugge, and C. W. Manke, J. Rheol. **39**, 567 (1995).
[49] P. Espanol and P. B. Warren, Europhys. Lett. **30**, 191 (1995).
[50] R. D. Groot and P. B. Warren, J. Chem. Phys. **107**, 4423 (1997).
[51] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987).
[52] M. W. Matsen and M. Schick, Macromolecules **27**, 187 (1994).
[53] M. W. Matsen, J. Chem. Phys. **102**, 3884 (1995).
[54] S. Ji, U. Nagpal, G. Liu, S. P. Delcambre, M. Müller, J. J. de Pablo, and P. F. Nealey, ACS Nano **6**, 5440 (2012).
[55] M. D. Gehlsen, K. Almdal, and F. S. Bates, Macromolecules **25**, 939 (1992).
[56] Y. Takahashi, Y. Song, N. Nemoto, A. Takano, Y. Akazawa, and Y. Matsushita, Macromolecules **38**, 9724 (2005).
[57] See http://www.paraview.org for information about ParaView visualization applications.
[58] See supplementary material at http://dx.doi.org/10.1063/1.4921685 for the procedures and illustrations of the protein-like copolymer preparation and step-growth polymerization during phase separation in the computer simulations.
[59] A. A. Gavrilov and A. V. Chertovich, Macromolecules **46**, 4684 (2013).
[60] E. L. Wittbecker and P. W. Morgan, J. Polym. Sci. **40**, 289 (1959).
[61] F. Gaudin and N. Sintes-Zydowicz, Colloids Surf., A **415**, 328 (2012).
[62] L. Chen and R. K. Prud'homme, Ind. Eng. Chem. Res. **53**, 8484 (2014).
[63] K. Ch. Daoulas, A. Cavallo, R. Shenhar, and M. Müller, Phys. Rev. Lett. **105**, 108301 (2010).
[64] M. P. Stoykovich, M. Müller, S. O. Kim, H. H. Solak, E. W. Edwards, J. J. de Pablo, and P. F. Nealey, Science **308**, 1442 (2005).
[65] See http://hpc.msu.ru for Lomonosov Moscow State University Supercomputing Center.