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THEORY AND SIMULATION

Concentrated Dispersions and Melts from Block-Copolymer Micelles: Computer Simulation

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Abstract—A technique for simulation of concentrated solutions and melts of spherical micelles composed of diblock copolymers is presented; the degrees of polymerization of blocks are 20 and 80, respectively. The concentration of solutions is varied in a wide range up to 67 vol %, which corresponds to the dense packing of spheres in the volume-centered lattice. It is shown that, at all the values of the Flory–Huggins parameter, such inverted phases are instable and fairly rapidly transformed into more equilibrated phases without any long-range order.

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INTRODUCTION

It is well known that diblock copolymers in an equilibrated melt may experience microphase separation; in many cases this process is accompanied by the formation of structures with long-range order. Depending on the ratio of block lengths and the degrees of incompatibility of monomer units of various kinds, structures of a certain symmetry-including lamellas, cylinders, and spheres—appear [1]. The experimental data are usually in satisfactory agreement with theoretical estimates and computer-simulation results; however, unlike in the analytical treatment, in real experiments, structures with good longrange order are far from always being obtained. Relatively simply ordered structures are formed in thin films by casting from a good solvent when the layer thickness is commensurable with the characteristic size of microphase separation (5-50 nm). After passage to thicker films and self-supporting membranes (with a thickness of 10 um or more), no self-assembled structures with long-range order, as a rule, appear: A multidomain material with a large amount of defects is formed [2]. In this case, it is frequently impossible to distinguish any characteristic motif in the system. There are several causes of this behavior, including polydispersity of block copolymers, but, most frequently, the cause is the kinetic "freezing" of the structure in a random local minimum of the phase space. In part, this problem may be solved with the help of a specially selected procedure of annealing, but for each structure, solvent, and film thickness, the annealing procedure should be selected separately. Moreover, this circumstance markedly decelerates the production of films for any practical application and makes the process more expensive.

An alternative approach to the formation of structured polymer films consists in their preparation from structural blocks preformed in solution [3]. Such blocks may be, for example, spherical or cylindrical micelles of a diblock copolymer in a selective solvent. As opposed to the above-described casting from a common "good" solvent, here, the solvent is "good" for blocks of the micelle shell and "poor" for blocks of the micelle core. After formation, films will preserve the structure and the shape of individual "structural" elements in their depth. This structure already occurs at the local minimum and is observed without annealing throughout the depth of the material. Moreover, if this minimum is sufficiently stable (i.e., the degree of incompatibility of blocks is high and the solvent is removed rapidly), it may be expected that unusual phases will be formed, i.e., "inverted" micelles and cylinders, in which the component with the minor volume forms the percolating matrix, while the major component forms regularly packed spheres and cylinders. Experimental examples of such phases may be found in [4, 5]. The authors of [5] described the controlled synthesis of a block copolymer by the radical heterophase polymerization in the form of dispersions of latex particles based on poly(acrylic acid) and poly(*n*-butyl acrylate) with length ratios of hydrophilic and hydrophobic blocks from 1:10 to 1:2. When dispersions were precipitated on a substrate, sometimes the "inverted" phase composed of hexagonally packed spherical aggregates with thin layers of the minor phase between them was observed.

Although the described method of forming structured films from micelles preformed in solution is simple and may be easily implemented experimentally, it has not found use in labs. Until now, it has been impossible to ascertain tendencies and features of the stable preparation of structured films from a micellar dispersion of a block copolymer. Moreover, the range of parameters varied during the synthesis is very wide, and the study of all variants and dependences is a very laborious task. Thus, it makes sense to apply a computer simulation that makes it possible to determine the boundaries of stability for films formed from micelles.

At present, no data are available on the technique of formation of metastable phases in melts and concentrated solutions by computer-simulation methods. At the same time, plenty of studies have been devoted to the simulation of equilibrium properties of block copolymer melts and their comparison with the experimental data. It is of interest both to develop a special simulation methodology for studying melts derived from micelles preformed in solution and to analyze the main factors affecting the stability of the resulting phases. This study, which is predominantly methodological, concerns approaches and first data on the simulation of block copolymer melts from preformed micelles.

SIMULATION TECHNIQUE

Dissipative particle dynamics (DPD) is a computer simulation method that makes it possible to investigate the dynamic and rheological properties of liquids and polymer melts. The objects of simulation are point particles moving in a continuous space. Such particles are whole molecules or groups of molecules, whose internal degrees of freedom are ignored. With the use of DPD, the behavior of a system can be effectively treated within much wider time intervals than those used in the molecular-dynamics method. A significant increase in the step of integration is allowed by the use of special "soft" interaction potentials between particles. In addition, the choice of random forces in the DPD technique provides conservation of the amount of motion for each pair of interacting particles and, therefore, correctly allows for hydrodynamic effects. The method was first proposed in 1992 for modeling a simple liquid [6, 7]. In 1995, a new version of this algorithm in which particles linked to a chain were simulated was developed [8].

A system of interacting point particles whose motion obeys Newton's second law is considered:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i, \quad m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i \tag{1}$$

where \mathbf{r}_i is the coordinate of the *i*th particle, \mathbf{v}_i is its velocity, m_i is its mass, and f_i is the action force. As a rule, to simplify calculations, the mass of each particle is assumed to be unity. The force acting on each particle is represented as

$$\mathbf{f}_i = \sum_{i \neq j} (\mathbf{F}_{ij}^{c} + \mathbf{F}_{ij}^{d} + \mathbf{F}_{ij}^{r}), \qquad (2)$$

where the summation is over all particles that occur within potential-cutoff radius r_c . For a system with reduced coordinates, this radius is generally assumed

to be unity. In addition, \mathbf{F}_{ij}^{c} is the conservative force of soft repulsion directed along the line connecting the centers of particles *i* and *j*:

$$\mathbf{F}_{ij}^{c} = \begin{cases} a_{ij}(1 - r_{ij})\hat{\mathbf{r}}_{ij}, & r_{ij} < 1\\ 0, & r_{ij} > 1 \end{cases}$$

$$\mathbf{r}_{ij} = \mathbf{r}_{i} - \mathbf{r}_{j}, \quad r_{ij} = |r_{ij}|, \quad \hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}, \qquad (3)$$

where a_{ii} is the maximum repulsive force between particles i and j. This "soft" potential was first proposed in [9]. It was obtained by averaging of molecular potentials (e.g., the Lennard-Jones potential) over small time intervals for rapidly moving particles. The "soft" potential does not exhibit a singularity at r = 0, as the Lennard-Jones potential does, or the characteristic energy minimum; therefore, it permits the use of larger integration steps than those for the classical potentials. The other two forces are dissipative force F^d and random force F^r .

For the system of connected units, the conservative repulsive force is supplemented by a force that describes interaction between units in a freely-jointed chain:

$$\mathbf{F}_{ii}^{b} = -k(\mathbf{r}_{ii} - \mathbf{r}_{0})\hat{\mathbf{r}}_{ii}, \qquad (4)$$

where k is the bond stiffness and r_0 is the equilibrium distance between connected units.

It was shown that the DPD method is consistent with the scaling theory of polymers (e.g., it gives the correct relationship between the average radius of gyration of a coil and the amount of units in the coil) and agrees with the Rouse dynamics in a melt and the Kirkwood theory in a good solvent [10, 11]. In [11], a direct relationship was found between the friction coefficient in the Rouse model and the friction coefficient in the DPD method at various values of potential-cutoff radius r_c . This circumstance indicates that the DPD method can be used to simulate polymer systems with high concentrations (melts). Previously [12], this method was used to describe the phase behavior of melts of random and regular copolymers. It was the first time that the simulation resulted in microphase separation for random copolymers. This result could not be obtained earlier, because of large characteristic relaxation times for these systems.

In [13], the method of rendering chains nonphantom in the DPD without the introduction of any additional conditions was described. This method is based on geometrical considerations (Fig. 1a): If any two units in the system cannot approach each other at a distance smaller than r_{\min} , the excluded radius of the unit is $r_{\min}/2$. If it is assumed that each bond has maximum length l_{max} , the condition of self-avoiding chains is as follows: $\sqrt{2}r_{\min} > l_{\max}$. Although particles in the DPD are formally pointlike, they have an excluded volume owing to the repulsive potential at all nonzero parameters a_{ii} . Similarly, the existence of a bond potential causes the bond to have the maximum possi-

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Fig. 1. Illustration of the conditions of the nonphantom state: (a) graphical presentation of the condition for the absence of selfavoiding chains [13] and (b) normalized distributions of distances between neighbors (I) along the chain and (2) in space.

ble length. Hence, the values of parameters of these potentials should be chosen so that the condition $\sqrt{2r_{\min}} > l_{\max}$ is fulfilled. In practice, it turns out that this requirement is excessive; it is sufficient that $2r_{\min} > l_{\max}$. In our studies, the nonphantom nature is ensured by the following values: $a_{ii} = 150$, $r_0 = 0.5$, and k = 150. The distributions of distance between particles in space and neighbors along the chain are shown in Fig. 1b. In this case, $r_{\rm min} = 0.5$ and $l_{\rm max} = 0.85$, and this condition is fulfilled. Periodic boundary conditions were used in all directions. On the whole, this model is equivalent to the model of the nonphantom polymer network [14]. The only difference is that the system contains various kinds of particles simulating the composition of dispersions of micelles formed from the block copolymer based on acrylic acid (hydrophilic monomer units A) and *n*-butyl acrylate (hydrophobic monomer units B) in a solvent (particles S). Hence, in our model, parameter of interaction Δa for various kinds of particles will be the only varied parameter. The step of integration at most of the simulation stages was taken to be $\Delta t = 0.04$; the exception was the initial stage, where a much smaller step of integration of $\Delta t = 0.001$ was used over 100–1000 steps.

The described model was implemented in the original parallel program code that was run on the Lomonosov Cluster of the Supercomputer Complex at Moscow State University [15].

DIBLOCK COPOLYMERS and the RELATED INDIVIDUAL MICELLES

Above all, the length and parameters of an individual chain of the block copolymer nAmB were chosen. On the one hand, such chains should not be too short, so that the dynamics of their melts and concentrated solutions is sufficiently slow and may be described by the Rouse model. On the other hand, in the vicinity of equilibrium, the characteristic size of heterogeneity in the melt in the first approximation may be described by the Gaussian model (i.e., the square root of chain length), and our simulation cell should accommodate at least several heterogeneities of this kind in each direction. On the basis of this reasoning and taking the ratio of blocks A : B to be 1 : 4, which is close to the experimental data, we chose n = 20 and m = 80, that is, chain 20A80B, as the initial model of the individual diblock copolymer.



Then, the initial micelle should be formed from such block copolymers. The method of self-assembly from solution, which is frequently used in simulation studies, is inapplicable in this case because attainment

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Fig. 2. (Color online) Stages of individual micelle formation: (a) uniform arrangement of the individual conformation of the block copolymer over the sphere of the future micelle; (b) primary equilibration of the micelle in excess solvent, 1×10^6 steps; and (c) compaction of hydrophilic blocks for subsequent packing into the concentrated dispersion, 1000 steps.

of high aggregation numbers presents a difficulty. Note that, in miniemulsion polymerization, which is treated here as an example of the analogous experimental system, and the result that is mimicked by our study, no self-assembly occurs. In this case, the block copolymer is formed immediately in the form of a micellar aggregate. Moreover, in experiments, the average aggregation number of macromolecules in micelles is frequently known exactly. Therefore, in this study, we used our own original technique to form micelles with the specified aggregation number. The main ideas of this technique are as follows.

(i) Any one conformation of the block copolymer is formed in a good solvent with the center of mass not occurring in the direct proximity of a chain (see the conformation of block copolymer 20A80B).

(ii) This conformation is arranged in space via rotation by various spherical angles, the quantity of which corresponds to the desired aggregation number in the future micelle (Fig. 2a).

(iii) Simulation with phantom chains and a large incompatibility of A and B units is activated; the micelle with the loose edge is formed (Fig. 2b).

(iv) As potential changes, units A become hydrophobic and thus are attracted to the core consisting of B blocks to produce a practically even spherical micelle with the core—shell structure and the specified aggregation number (Fig. 2c). In this study, an aggregation number of 400 was chosen because several attempts showed that, at such a number of molecules, the micelle has a dense edge and preserves the spherical shape. In addition, on the whole, this value corresponds to aggregation numbers estimated for the experimental micelles [5].

CREATION OF CONCENTRATED SOLUTIONS AND MELTS

Let us turn to the design and study of concentrated dispersions from the formed micelles. All the studied systems of concentrated dispersions and melts were simulated not in a cubic simulation cell but in a cell with axial sizes that are multiples of the period for hexagonally packed micelles:

$$box_{x} = S_{m}*k,$$

$$box_{y} = S_{m}*k*\sqrt{3}/2,$$

$$box_{z} = S_{m}*k*\sqrt{2}/\sqrt{3};$$

where $S_{\rm m}$ is the size (diameter) of the individual micelle and *k* is the number of unit cells in the simulation cell. The starting conformation of the cell was always taken in the form of an ideally packed face-centered crystal from micelles. The arrangement of micelles in the form of the face-centered crystal and the structure of crystallographic indices for the corresponding lattice are schematically shown below.







Fig. 3. (Color online) General view of the simulation cell at a polymer concentration of 30%: (a) the cell in the starting conformation and (b) after a relaxation of 1×10^6 steps. The solvent is omitted.

As a rule, cells with four micelles along each axes (k = 4) were studied and only the distance between them was varied to mimic various degrees of dilution. All the remaining free volume was uniformly filled with solvent particles. Hence, 64 micelles occurred in each simulated space, and the sizes of the cell in terms of maximum size was varied from 120 to 160 units for solvent fractions from 67 to 30%, respectively. Note that the maximum packing density of spheres in the BCC crystal (atomic packing factor) is about 68%. The theoretical maximum attainable density of packing of spheres into a more complex face-centered structure is 74%.

The above-described technique of preparing melts from spherical monodisperse micelles is applicable only for a fraction of the residual solvent of no less than 30%. No reliable data are available on the real fraction of the residual solvent in typical samples produced from the dispersion of micelles. In any case, it is practically impossible to fully remove the solvent by simple drying, because some amount of solvent bound to hydrophilic blocks always remains. However, an analysis of microscopic images of the experimental samples [4, 5] indicates that the packed micelles have not a spherical shape but a somewhat distorted shape in the places where the contact with other micelles is the densest. Hence, density may be increased further owing to distortion of the spherical shape of micelles. In addition, note that the micelles in experimental samples feature a certain polydispersity that is favorable for denser packing of even ideally spherical objects.

After the formation of the starting conformation, all the remaining free volume was filled with solvent particles S until an even density was attained; then, the simulation with parameters corresponding to nonphantom chains and specified incompatibility between various kinds of particles was activated. Specifically, the used parameters were as follows: k = 150; $a_{AA} = a_{BB} = a_{SS} = a_{AS} = 150$, $a_{AB} = a_{BS} = 150 + \Delta a$; and $\Delta a = 3.3$, 6.7, 10, or 30. The formula relating Flory–

Huggins lattice parameter χ and simulation parameter Δa was deduced under the assumption that $a_{ii} = 25$: $\chi k_{\rm B}T = (0.286 \pm 0.002)\Delta a$ [16]. This formula is not applicable to the value $a_{ii} = 150$ used in this study, because the presence of such an additional repulsion increases the Kuhn segment and, hence, the spatial density of conformations in the volume. As follows from our roughest estimates, the above formula vields values of Flory–Huggins parameter χ overestimated by a factor of ~ 2 for the used set of parameters. Therefore, the used parameters approximately correspond to the values of incompatibility of $\chi = 0.5, 1.0, 1.5, and$ 4.5. Note that the value of $\chi = 0.5$ corresponds to θ conditions, while $\chi = 4.5$ corresponds to the incompatibility of typical fluorinated and sulfonated blocks in the aqueous surroundings.

The general view of the starting simulation cell is shown in Fig. 3a; the same system after equilibration during 10^6 steps is depicted in Fig. 3b. Our studies showed that, at moderate polymer concentrations up to 50%, micelles remain stable and do not aggregate. Moreover, their hydrophobic cores preserve the spherical shape with a good accuracy, as is clear from Fig. 3 and the structural-factor plots constructed for various concentrations of the minor hydrophobic phase and presented in Fig. 4.

For more concentrated dispersions up to a maximum attainable concentration of 67%, micelles are instable and aggregate at various rates and degrees of heterogeneity. Because our initial aim was to investigate properties of systems close to melts (mimicking membranes based on such dispersions), in what follows, we consider only the maximally concentrated system of the micelles densely packed into a crystal with a total polymer concentration of 67%. Because the entire remaining volume (33%) is occupied by the solvent and the fraction of hydrophilic units A makes up 20% of the total fraction of the polymer, the general ratio of hydrophilic particles A+S to the hydrophobic B particles is approximately 0.45. As is known, at this



Fig. 4. (Color online) Structural factor of dispersion (the minor hydrophobic phase) at polymer concentrations of (1) 30, (2) 40, and (3) 50% when aggregation is absent from the system. The count time is 1×10^6 steps.

ratio of blocks, the melt of the diblock copolymer should segregate to give rise to the lamellar phase. In addition, the presence of a considerable fraction of the solvent leads to an increased translational entropy and, consequently, the formation of the equilibrium lamellar phase may be expected only at fairly high values of the incompatibility parameter; at its medium values, the system is disordered. Hence, even though, in the starting conformation, the hydrophobic cores of micelles are packed densely and do not contact each other, the long-term stability of the dense face-centered crystal formed from micelles cannot be expected. Only a more or less rapid destruction of such micelles and the transition from the local minimum of free energy to a more equilibrated state may be observed.

STUDY OF PHASE STABILITY

In fact, the crystal formed from micelles is gradually destroyed at all the used incompatibility values; typical images of the system with various parameters χ and at various time periods are shown in Fig. 5. The most incompatible system, that with $\chi = 4.5$, is destroyed most rapidly; as is seen even after 20000 steps, the micelles began to aggregate. After 2 × 10⁵ steps, the micelles are destroyed, and after 2 × 10⁶ steps, a practically defect-free lamellar structure is formed. At $\chi = 0.5$, the micelles are destroyed slower. In this case, as expected for θ conditions, the homogeneous phase is formed without any marked density fluctuations. The systems with the intermediate values of $\chi = 1.0$ and 1.5 are destroyed most slowly. Some residues of the micellar structure may be observed even after 2 × 10⁶ steps. No further calculations were performed for these systems, because of considerable resource requirements. It may be proposed that the system with $\chi = 1.0$ will gradually become homogeneous and that the system with $\chi = 1.5$ will transform into metastable perfluorinated lamellas.

The same is true of the structural factor for the mentioned systems; this parameter was calculated for solvent particles and is shown in Fig. 8. Although the long-range order had already disappeared after 1×10^6 steps (no satellite peaks were observed), the characteristic size of heterogeneities in the system may still be assessed; it corresponds to the initial system of densely packed micelles.

The question about the time of the real experiment that corresponds to our simulation time is ambiguous, and no consideration has been given to this problem. In any case, in our model system, chains are fairly short and do not correspond to real experimental systems, where molecular masses are higher than those of the studied 100-unit chains by several times or more. The relaxation time of the polymer melt depends on the degree of polymerization at least as N^3 ; therefore, it may be supposed that time scales on the order of several seconds are simulated.

CONCLUSIONS

In this study, an original technique of designing micelles from block copolymers has been presented. This simulation technique may be used in cases when the process of self-assembly of micelles from solution is of no importance. For example, this may be the case

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CONCENTRATED DISPERSIONS AND MELTS



Fig. 5. (Color online) Images of the process of aggregation of micelles in the concentrated system (67%) for several incompatibility parameters and logarithmic times $t = 0, 20000, 200000, \text{ and } 2 \times 10^6 \text{ DPD}$ steps. The starting conformation is shown on the left.



Fig. 6. (Color online) Structural factors of the minor phase (solvent) at a polymer concentration of 67%: (1) starting conformation equilibrated over 1×10^6 steps, (2) at medium incompatibility values ($\chi = 1.0$), and (3) during strong incompatibility ($\chi = 4.5$). The curves are shifted along the vertical for the sake of clarity and convenience of analysis. The vertical dotted line indicates the vector of maximum scattering for ideally packed micelles.

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simulating the results of miniemulsion polymerization. The proposed technique of designing concentrated dispersions of micelles by arrangement of the starting conformation on a face-centered crystal lattice makes it possible to conveniently investigate the dispersions of spherical micelles up to a volume concentration of nearly 70%. In order to further increase the concentration of the polymer, the volume of the simulated space should be changed or the spherical shape of the micelles should be distorted. Another promising trick consists in gradual removal of the solvent from the system and, consequently, reduction in the volume of the concentrated phase, similarly to what was recently done in [17].

From the viewpoint of the phase behavior of the studied systems, the following general conclusion can be made: Namely, in all the examined systems at a high concentration, no stable "inverted" phase is observed for any of the used incompatibility values. A somewhat higher stability and prospective interest than those of other systems are demonstrated by melts with average χ values of nearly 1.5. There is no need to investigate higher concentrations in this case, because, during drying, the film formed from micelles will pass through all the concentrations of the residual solvent and the stability of these micelles at all intermediate concentrations is of importance. Thus, we have shown that the micelles built of relatively short chains cannot preserve their structures in a melt only owing to hydrophobic-hydrophilic interactions.

The additional stability of these systems (including that in the thermodynamic sense) may be imparted by electrostatic interactions. Recently [18], it was shown that, at a certain ratio of blocks and in the case of their charged state, thermodynamically stable phases with a minor percolating phase may exist.

Note also that additional kinetic stability may be provided by additional entanglements resulting from a higher degree of polymerization. In our system, the average distance between entanglements is $N_{\rm e} \sim 50$ [19]. This value is commensurable with the length of the hydrophobic block 80B; hence, the contribution of entanglements to the total dynamics of the system is insignificant. If the degree of polymerization is increased by at least an order of magnitude, this situation will better correspond to the experimental data reported in [5]; then, the contribution of entanglements will be decisive for dynamics and the kinetic freezing of the "inverted" phase may be expected. Unfortunately, the length of the block copolymer cannot be increased to such an extent in the computer model, because of limitations imposed on the sizes of the simulation cell and the processor time required for calculations.

With consideration of the system obtained as a result of miniemulsion polymerization, analogous to the system described in [5], the above-said may be interpreted as follows:

(i) It is impossible to obtain stable micelles in films by hydrophobic—hydrophilic interactions only; additional mechanisms and interactions are needed.

(ii) There is no need to tend to very small micelles in an emulsion: The larger the micelle, the longer the hydrophobic blocks contained in it and, hence, the more complex the disentanglement of hydrophobic blocks and the inversion of phases.

(iii) During film formation from micelles, it is desirable to have charged groups on hydrophilic blocks either because of dissociation or by the introduction of additional ionogenic groups. As a result, additional binding of the residual solvent and the formation of ion pairs and multiplets in the minor percolating phase may occur.

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