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Microphase separation in rod–coil copolymers

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Abstract

We investigate the morphology and kinetics of microphase separation in rod–coil diblock copolymers where each chain consists of a stiff rod block and a flexible coil block. A simplified phenomenological model system is introduced, which is coarse grained in terms of the local concentration difference between the two blocks and the local director field of the rod part. Computer simulations of this set of time-evolution equations in two dimensions reveal that the elastic energy in the rod-block-rich domains affects drastically the domain structures formed in the course of microphase separation. The effects of the external electric field are investigated to examine the domain stability and control the domain morphology. Our recent study of morphological transitions in three dimensions for coil–coil copolymers is also briefly described.

1. Introduction

Block copolymers are one of the typical soft matters which cause mesoscopic structures in thermal equilibrium. The variety of morphologies displayed by the coil–coil diblock copolymers has been studied both theoretically and experimentally for many years [1].

Recently, rod–coil diblock copolymers as illustrated in figure 1 have attracted attention because of their fascinating ability to form regular nanoscale aggregates as attempted in experiments [2–10] and become candidates for self-assembled materials and nanometre scale devices.

There are several theoretical studies of microphase separation in rod–coil copolymers [11–15]. In contrast to coil–coil diblock copolymers, the driving force of self-assembly of rod–coil block copolymers originates not only from the incompatibility between stiff and flexible components but also from the tendency of rod-like segments to form ordered domains. However, to our knowledge, no theoretical investigation has been available for dynamics or kinetics of phase separation in rod–coil copolymers.

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In the present paper, we shall describe some of our recent studies of microphase separation in rod–coil copolymers [16, 17]. Numerical simulations of domain morphology and kinetics in two dimensions will be shown, which are based on the model equations in terms of the local volume fraction and the director field. One of the characteristic features of the rod–coil copolymers is that the molecular anisotropy due to rod blocks causes a mesoscopic anisotropy of phase separated domains.

The effects of external electric field are also investigated, which might be useful for removing the grains and achieving more perfect ordered domain structures. There are several theoretical [18–21] and experimental [22] studies of domain alignment due to the dielectric asymmetry of coil–coil diblock copolymers. However, no theoretical investigation has been performed for rod–coil copolymers.

The organization of the paper is as follows. In section 2, we describe the kinetic equations together with the model free energy. An example of our recent study of morphological transitions in coil–coil copolymers [23, 24] is shown in section 3. Although this part is not directly related to those of rod–coil copolymers described in other parts of the present paper, we mention it because (we believe) this is one of the most significant theoretical results for kinetics of microphase separation and it indicates that the coarse-grained approach employed here is indeed powerful. In section 4, we show the effects of the elastic asymmetry on the domain morphology in rod–coil copolymers. The effects of the external electric field are also presented compared with the case of coil–coil copolymers. A summary and discussion are given in section 5.

2. Kinetic equations

In order to investigate the kinetics and final equilibrium structures of microphase separation of rod–coil copolymers, we employ here the coarse-grained approach. The basic variables are the local volume fractions of monomers for rod blocks ϕ_R and coil blocks ϕ_C and the tensor order parameter Q_{ij} for rod parts defined by [25]

$$Q_{ij} = \frac{d}{d-1} S \left(n_i n_j - \frac{1}{d} \delta_{ij} \right), \quad (1)$$

where S is the magnitude of the nematic order parameter, d is the spatial dimensionality and n_i is the i th component of the director vector \vec{n} ($|\vec{n}| = 1$). Assuming the incompressibility $\phi_R + \phi_C = \text{const}$, we may choose the difference $\phi = \phi_R - \phi_C$ as the independent variable.

The model free energy for rod–coil copolymer melts is written in terms of ϕ and Q_{ij} as

$$F\{\phi, Q_{ij}\} = F_C\{\phi\} + F_R\{\phi, Q_{ij}\}. \quad (2)$$

The first part $F_C\{\phi\}$ is the same as that of flexible diblock copolymers [26],

$$F_C\{\phi\} = \int d\vec{r} \left[\frac{K}{2} (\nabla\phi)^2 + W(\phi) \right] + \frac{\alpha}{2} \int d\vec{r} \int d\vec{r}' G(\vec{r}, \vec{r}') (\phi(\vec{r}) - \bar{\phi})(\phi(\vec{r}') - \bar{\phi}) \quad (3)$$

with

$$W(\phi) = -\frac{\tau}{2}\phi^2 + \frac{g}{4}\phi^4 \quad (4)$$

$$-\nabla^2 G = \delta(\vec{r} - \vec{r}'), \quad (5)$$

where K , α , τ and g are positive constants and $\bar{\phi}$ stands for the spatial average of ϕ .

It is emphasized that the long-range interaction in equation (3) originates from the osmotic incompressibility of diblock copolymers [26] and that it is independent of chemical details of the molecules.

The second part of the free energy F_R contains the tensor order parameter and is given by

$$F_R\{\phi, Q_{ij}\} = \int d\vec{r} \left[\frac{c_2}{2} (\partial_i Q_{kl})(\partial_i Q_{kl}) + \frac{c_0}{2} Q_{ij}(\partial_i \phi)(\partial_j \phi) - \frac{A(\phi)}{2} (\text{Tr } Q^2) + \frac{D}{4} (\text{Tr } Q^2)^2 \right], \quad (6)$$

where $c_0, c_2 (>0)$ and $D (>0)$ are constants. The repeated indices imply summation. The coefficient A depends on ϕ as

$$A(\phi) = a_0(\tau - \tau_0) + a_1\phi \quad (7)$$

such that the rod-rich domains tend to undergo nematic ordering. Equation (7) implies that the system in the pure rod-block limit $\phi = 1$ exhibits an isotropic–nematic transition at $\tau = \tau^* = \tau_0 - a_1/a_0$ with τ_0, a_0 and a_1 being constants.

There are several simplifications in the free energy (6). In the present paper, we consider only the term $Q_{ij}(\partial_i \phi)(\partial_j \phi)$ as the nonlocal coupling between Q_{ij} and $\partial_i \phi$. This is essentially equivalent to $(n_i \partial_i \phi)^2$ and controls the director orientation at the interface separating rod-rich and coil-rich domains. Effects of other nonlocal coupling terms having higher order gradients such as $\partial_i \partial_j \phi$ have been studied in [17]. Another simplification is that we have ignored a term $\text{Tr } Q^3$ in equation (6), which exists generally when the transition from isotropic to nematic phases is first order. We expect that this does not cause any serious change in domain evolution except for the case of an extremely large volume fraction of rod blocks.

By using the free energy functional (2) and taking account of the facts that the local volume fraction ϕ is a conserved quantity whereas Q_{ij} is a nonconserved variable, the kinetic equations are given as follows.

$$\frac{\partial \phi}{\partial t} = \nabla^2 \left[-K \nabla^2 \phi + \frac{dW}{d\phi} - c_0 \partial_i (Q_{ij} \partial_j \phi) - \frac{dA}{d\phi} \frac{\text{Tr } Q^2}{2} \right] - \alpha(\phi - \bar{\phi}) \quad (8)$$

$$\frac{\partial Q_{ij}}{\partial t} = c_2 \nabla^2 Q_{ij} - \frac{c_0}{2} \left[(\partial_i \phi)(\partial_j \phi) - \frac{1}{d} (\nabla \phi)^2 \delta_{ij} \right] - [-A(\phi) + D(\text{Tr } Q^2)] Q_{ij}. \quad (9)$$

The term with δ_{ij} arises from the requirement that the tensor Q_{ij} is traceless. A similar set of equations without the α term has been introduced in the study of phase separation in polymer-dispersed liquid crystals [27].

When one of the blocks is rigid, the Onsager coefficients are generally anisotropic as in liquid crystal–polymer mixtures [28]. However, we shall not consider this dynamical effect in the present paper since our main concern is the equilibrium morphology and the morphological change on applying the electric field.

3. Morphological transitions in coil–coil copolymers

Equation (8) can be applied to coil–coil diblock copolymers when the tensor order parameter Q_{ij} is absent. In this section, we briefly describe our recent study of the morphological transitions in flexible diblock copolymers [24] to show that the present coarse-grained approach is a powerful method for the kinetics of microphase separation.

It has been established both theoretically and experimentally that there are four equilibrium structures, lamellar, gyroid, hexagonal and BCC structures, in coil–coil copolymers [1]. We focus our attention on the transitions involving the gyroid structure. However, there is a technical difficulty in solving numerically equation (8) to investigate the structural transitions between gyroid and the other three structures. That is, the equilibrium period of gyroid is slightly different from that of lamellar, hexagonal and BCC structures. Therefore, one needs



Figure 1. Schematic illustration of a rod-coil copolymer chain. The full (broken) line indicates the rod (coil) block.

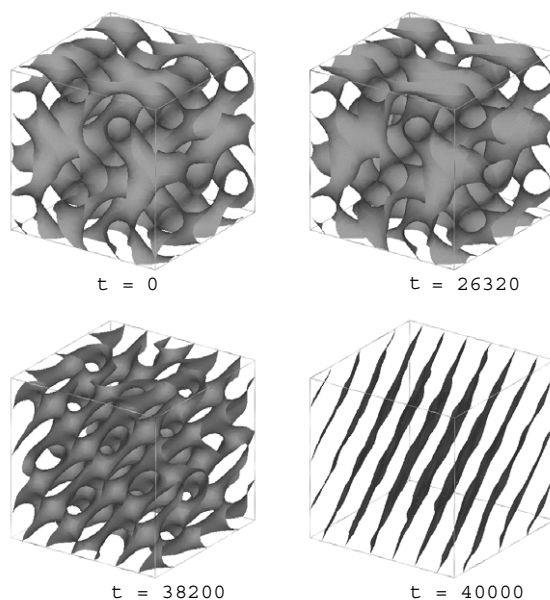


Figure 2. Structural evolution from a double gyroid to a lamellar structure for $\bar{\phi} = -0.1$ and $\tau = 2.5$.

to provide a sufficiently large system to diminish the incompatibility of the system size with the spatial period. However, this is not easy in three dimensions where gyroid structure exists.

In order to overcome the above problem, we apply a mode expansion method such that the concentration field ϕ is expanded in terms of the fundamental modes of the gyroid. Note that the other three structures are included as a special case of the mode expansion. Since the gyroid appears in the weak and intermediate segregation regimes, the higher harmonics in the mode expansion can be ignored as long as we are concerned with the weak segregation regime.

Figure 2 shows the domain evolution from gyroid structure to lamellar structure. This was obtained by solving numerically the coupled set of equations of the amplitudes for 30 modes. In order to guarantee the change of the spatial period, we need to introduce a time-evolution equation for the magnitude of the fundamental reciprocal vectors [24]. The initial gyroid structure is provided for $\tau = 2.2$ and $\bar{\phi} = -0.1$. Changing the parameter τ to $\tau = 2.5$, the morphological transition starts. Other parameters are chosen as $\alpha = g = K = 1$. As shown in figure 2, the final lamellar structure is not formed directly but a metastable structure appears in the intermediate stage at around $t = 38\,200$ and then it is followed by the lamellar structure.

We identify the intermediate structure with *Fddd* structure. The gyroid structure has a cubic symmetry. In the process of the structural transition, the cubic symmetry is first broken so that *Fddd* structure appears transiently and then the final uniaxial lamellar structure is formed. In this sense, the appearance of *Fddd* structure is not surprising. Actually, *Fddd* structure

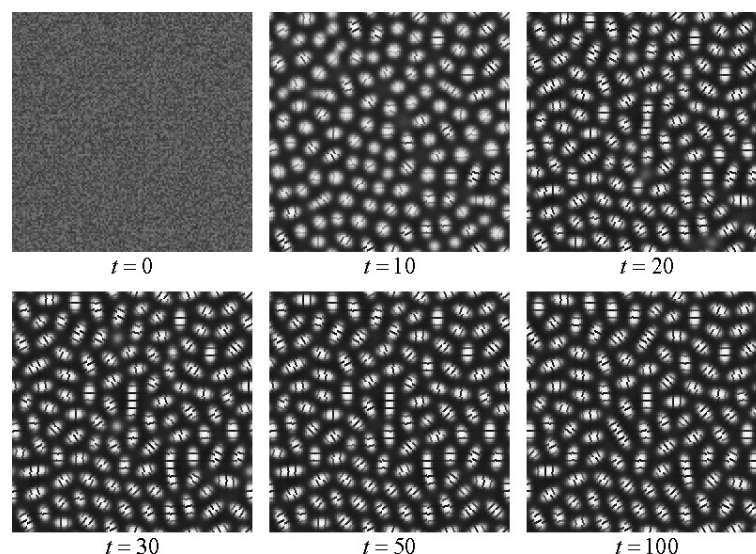


Figure 3. Time evolution of domains for $\bar{\phi} = -0.2$. In this figure and figures shown below for domain morphology, the black region is a coil-rich domain whereas the white region is a rod-rich domain with the director field indicated by bars.

emerges not only in the gyroid–lamellar transition but also in the gyroid–hexagonal transition where a similar symmetry breaking occurs.

4. Morphological transitions in rod–coil copolymers

In this section, we show the results of numerical simulations of the kinetic equations (8) and (9) in two dimensions. The space is divided into 128×128 square cells having the cell size 0.5 and periodic boundary condition is imposed at the system boundaries. When we quench the system from the high temperature disordered state to the microphase separation region at low temperature, the initial values of ϕ and Q_{ij} are chosen such that small random values are superposed around $\phi = \bar{\phi}$ and $S \approx 0$. The initial director fields have a random orientation. The parameters are fixed as $c_0 = -1.0$, $K = c_2 = 0.5$, $\tau = \tau_0 = 2.0$, $g = 4.5$, $D = 4.0$, $\alpha = 0.5$ and $a_1 = 2.0$. The time increment is set to be $2^{-10} \approx 0.00098$.

Figure 3 displays the domain evolution for $\bar{\phi} = -0.2$ after quenching from the uniform state at high temperature. The coil-rich phase is drawn in black whereas the rod-rich phase is indicated by white. The boundary between black and white regions is defined by $\phi = 0$. The rod-rich phase constitutes ellipsoidal domains inside which the director field indicated by bars exhibits an ordering perpendicularly to the interface. The elongation of domains is a consequence of the fact that the interfacial energy is lower where the interface perpendicular to rods is increased. If there were no coupling between the director field and the local concentration, i.e., $c_0 = 0$, circular domains would have taken a hexagonal structure. Note that the domain configuration and the elongated direction of each domain are almost random. This random configuration does not change appreciably for longer simulations. This is probably due to the weakness of the rod interaction between different domains since the magnitude of the nematic ordering is negligibly small in the coil-rich matrix.

Figure 4 shows the domain morphology for $\bar{\phi} = 0.2$ where the rod blocks are the majority. At the early stage of microphase separation $t \approx 10$, disconnected circular domains of the coil-

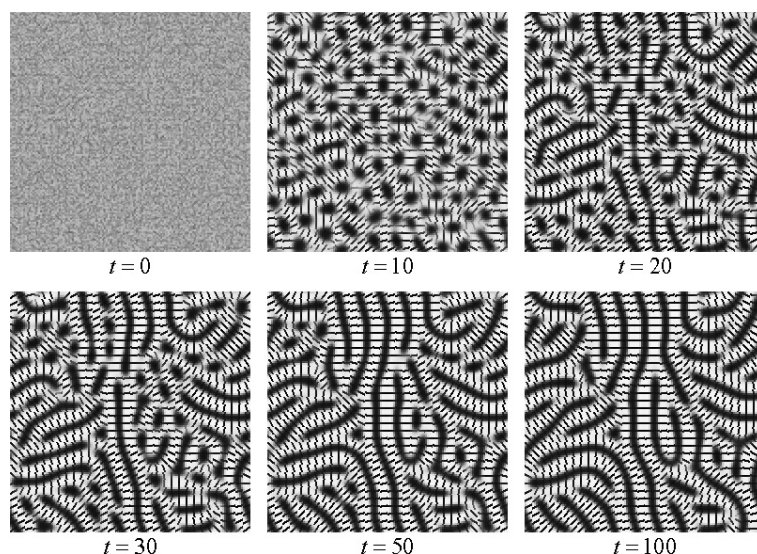


Figure 4. Time evolution of domains for $\bar{\phi} = 0.2$.

rich phase appear as in the ordinary coil–coil copolymers. However, as phase separation proceeds, these domains merge with each other to form thin stripes. This is due to the fact that the elastic energy of the rod blocks is large when the coil-rich domains are circular since the rods tend to be normal to the interfaces.

It is an interesting subject both theoretically and from the viewpoint of application to investigate the morphological change by applying the external field. In fact, there are several theoretical studies of the effect of the electric field in the microphase-separated structures [18–20]. Recently it has been pointed out that free charges enhance the effect substantially [21]. Experimental study has also been available [22]. However, these previous studies are only for coil–coil diblock copolymers. As shown in figures 3 and 4, the elastic asymmetry produces a unique domain morphology in rod–coil copolymers. Therefore, one may expect some new features by applying an external field.

We assume that the rod block has a dielectric anisotropy and add the following term in the free energy functional:

$$F_E\{Q_{ij}, \vec{E}\} = - \int d\vec{r} [Q_{ij} E_i E_j], \quad (10)$$

where the minus sign is introduced so that the rods tend to be parallel to the electric field.

We provide microphase-separated structures without external field starting from the disordered state up to $t = 300$ and then turn on the field in the range $300 < t < 600$ and see the relaxation of domains after turning off the field at $t = 600$. Figure 6 displays the time evolution of domains for $\bar{\phi} = -0.15$ and $c_0 = -0.7$ and the magnitude of the electric field $E = 0.5$. The electric field is applied to the parallel direction to the x -axis (the horizontal direction in figure 5). Initially, the rod-rich phase takes isolated ellipsoidal domains as at $t = 300$ in figure 5. After switching on the field, each rod-rich domain rotates and some adjacent domains merge with each other so that the domains are elongated parallel to the y -axis as at $t = 600$ in figure 5. After switching off the field, the domains keep their shape and no appreciable relaxation of domains is observed. This is a distinct feature of rod–coil copolymers where the elastic energy in the rod-rich domains makes the break-up of these domains unfavourable.

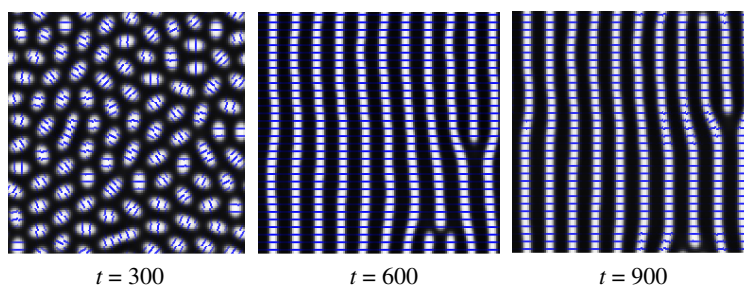


Figure 5. Morphological change induced by the electric field at $t = 300$, $t = 600$ and $t = 900$ for $\bar{\phi} = -0.15$, $c_0 = -0.7$ and $E = 0.5$. The electric field is applied in the interval $300 < t < 600$. (This figure is in colour only in the electronic version)

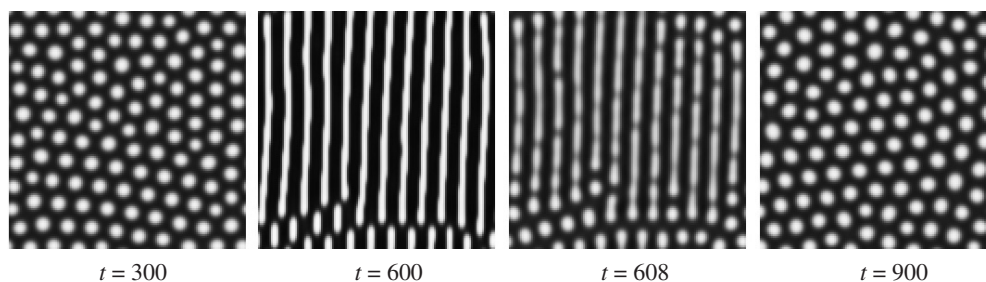


Figure 6. Morphological change for $\bar{\phi} = -0.2$ induced by the electric field $E = 0.4$ and the relaxation of the structure after removing the field. The electric field is applied in the interval $300 < t < 600$.

In fact, we have verified numerically that thin string-like domains caused by the electric field are unstable in coil–coil copolymers and break into isolated domains after removing the field as shown in figure 6. This was obtained by adding the following term in the free energy [18]:

$$F_E = - \int d\vec{r} (\vec{E} \cdot \vec{\nabla} \phi)^2, \quad (11)$$

and the numerical simulations of equation (8) without Q_{ij} were carried out for $\bar{\phi} = -0.2$ and $E = 0.4$.

5. Summary and discussion

In this paper, we have introduced a set of kinetic equations for microphase separation in rod–coil diblock copolymer melts and have carried out numerical simulations in the weak segregation regime in two dimensions. We are concerned with the elastic effect in the smectic ordering of rods and the domain ordering by applying the electric field. The morphological transitions in three dimensions have also been presented for coil–coil copolymers as a special case of the time-evolution equations (8) and (9).

The elastic asymmetry between the flexible coil-rich domains and the rod-rich domains provides us with quite unusual microphase-separated structures, especially when the average volume fraction is not close to $\bar{\phi} = 0$. That is, when the rod part is a minority the rod-rich phase takes an ellipsoidal shape of domains, whereas when it is a majority the coil-rich phase does not form isolated domains but constitutes almost interconnected thin domains.

If the external electric field is applied in the situation where the rod part is a minority, these domains merge with each other to form a stripe structure. This is not much different from those in coil–coil copolymers. However, what is remarkable in rod–coil copolymers is the fact that these string-like domains are quite stable after removing the external field. This is because the rods undergo a global ordering by the electric field, and once the ordering is achieved the domain pattern is not destroyed in the absence of the field since it would increase the elastic energy.

The present study of rod–coil copolymers is restricted to two dimensions. However, the set of time-evolution equations (8) and (9) can also be applied to three dimensions as shown in section 3. In the case of coil–coil copolymers, highly nontrivial interconnected structures such as gyroid and *Fddd* structures have been identified. It is an interesting future problem to extend the present investigation to a three-dimensional system and to explore the stability of the interconnected structures when copolymers contain the rod part.

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