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Different Mechanisms of Translational Symmetry Breaking in Liquid-Crystal Coil–Rod–Coil Triblock Copolymers

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Abstract: A molecular-statistical theory of coil-rod-coil triblock copolymers with orientationally ordered rod-like fragments has been developed using the density functional approach. An explicit expression for the free energy has been obtained in terms of the direct correlation functions of the reference disordered phase, the Flory–Huggins parameter and the potential of anisotropic interaction between rigid rods. The theory has been used to derive several phase diagrams and to calculate numerically orientational and translational order parameter profiles for different polymer architecture as a function of the Flory–Huggins parameter, which specifies the short-range repulsion and as functions of temperature. In triblock copolymers, the nematic–lamellar transition is accompanied by the translational symmetry breaking, which can be caused by two different microscopic mechanisms. The first mechanism resembles a low dimensional crystallization and is typical for conventional smectic liquid crystals. The second mechanism is related to the repulsion between rod and coil segments and is typical for block copolymers. Both mechanisms are analyzed in detail as well as the effects of temperature, coil fraction and the triblock asymmetry on the transition into the lamellar phase.

Keywords: phase transitions; block copolymers; liquid crystals; symmetry breaking



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1. Introduction

Rod–coil block copolymers attract significant attention as they combine anisotropic properties of smectic liquid crystals and microphase-separation properties of coil–coil block copolymers. Their molecules contain both flexible chains and rod-like segments of different chemical structure [1–6] and exhibit several anisotropic phases characterized by translational and orientational ordering [7–9]. Rod–coil block copolymers are promising polymer materials and can be applied, for example, in polymer photovoltaics [1,10,11] and LEDs [12–14]. From the materials science point of view, triblock copolymers are of particular interest because they possess more flexible molecular architecture. For example, it may be possible to tune the properties of these materials by changing the parameters of the third block. The overall structure of coil–rod–coil triblock copolymers is most reminiscent of the conventional liquid crystals, which usually possess the rod-like rigid core and two flexible tails. At the same time, the triblock macromolecules are significantly larger than typical low molecular weight mesogenic molecules, and their flexible chains are substantially longer.

Coil–rod–coil triblock copolymers may exhibit several different phases, but the most common one is the orthogonal lamellar phase, which is similar to the smectic A liquid crystal phase. Although it has the same symmetry as the smectic A phase, the mechanism of the translational symmetry breaking transition is apparently very different. Indeed, the classical statistical theory of conventional smectic liquid crystals assumes that the transition

into the smectic phase is similar to the effective one-dimensional crystallization determined by anisotropic interaction between orientationally ordered molecules [15–17]. On the other hand, one may consider another mechanism of translational symmetry breaking, which is determined by the microphase separation. This is a predominant mechanism of translational ordering in lyotropic liquid crystals and block copolymers. In block copolymers, such a local separation is related to the repulsion between monomers of different kinds, and the regular layered structure appears mainly for entropic reasons. At the same time, an element of microphase separation (more exactly the nanoscale segregation) between different molecular fragments (i.e., between rigid cores and flexible tails) may also be important in thermotropic liquid crystals. The corresponding molecular theory, which takes both mechanisms into account, has been developed in Reference [18]. It is reasonable to assume that the properties of rod-coil block copolymers are mainly determined by the separation effect. On the other hand, the orientational interaction between rod-like fragments of the macromolecules may be relatively large, and hence the “crystallization” mechanism of the translational symmetry breaking may also be important in these systems. Thus, it is important to assess the relative role of these two mechanisms in coil-rod-coil triblock copolymers, which is the primary goal of this paper.

One notes that the triblock macromolecules can be in the looped and bridged configurations in the lamellar phase. In the looped configuration, the end coil chains reside in the same layer, while in the bridged one, the end chains reside in two different layers separated by the layer occupied by rods. The presence of such bridges strongly affects the mechanical rigidity of the coil-rod-coil block copolymer materials including, for example, thermoplastic elastomers.

The theory of triblock copolymers is mainly based on the Landau-de Gennes approach to the theory of phase transitions [19–21] and is mainly limited to coil-coil triblock copolymers. In this approach, the density-density correlation functions of ideal Gaussian chains are used to calculate the parameters of the theory. The advantage of this approach is in its generality, and it has been used to describe a number of non-conventional morphologies. One notes, however, that in this theory, the equilibrium inhomogeneous densities contain only one Fourier harmonic, and the amplitude of this harmonic is assumed to be small. Thus, the approach is justified mainly in the region of the phase diagram, which is close to the isotropic phase, i.e., for weak segregation.

A statistical theory of rod-coil diblock copolymers has also been developed in the framework of the SCFT theory [22–27]. In this approach, the free energy of a copolymer macromolecule in a self-consistent field is evaluated numerically by calculating the corresponding path integral or by solving numerically the generalized diffusion equations for semi-flexible chains. In the past decades, the SCFT theory based on the generalized diffusion equations has been repeatedly applied to rod-coil diblock copolymers [28–37]. One notes that in the system of long chains with rigid rod fragments characterized by both orientational and translational degrees of freedom, the SCFT theory remains computationally challenging even taking into account recently developed novel numerical algorithms [27,38]. This may explain why the existing theory of rod-coil triblock copolymers [39,40] does not account for the orientational interaction between rigid rod segments and their orientational ordering.

Recently, the authors have developed a novel molecular-statistical theory of rod-coil diblock copolymers [41–43] employing the same general density functional theory, which has been used before in the description of nematic and smectic liquid crystals [18,44–48]. This theory is based on the free energy functional, which depends on the one-particle distribution functions of rod and coil segments and is not expanded in powers of the order parameters. The equilibrium distribution functions, which are obtained by the free energy minimization, depend nonlinearly on the order parameters and are characterized by the infinite set of Fourier harmonics. As a result, the molecular theory is expected to be approximately valid also in the regions far from the isotropic phase, when the segregation is relatively strong. In the region close to the disordered phase, the theory can

be reduced to the corresponding Landau–de Gennes theory [42], as it employs the same correlation functions calculated for Gaussian chains. Such a molecular-statistical theory is computationally simpler than the full SCFT theory (being not so precise, however) and can be efficiently used to evaluate numerically all order parameter profiles.

The paper is arranged as follows. In Section 2, we derive a molecular theory of coil–rod–coil triblock copolymers and consider the corresponding free energy functional. In Section 3, density–density correlation functions between different segments of triblock copolymers are considered in detail together with the corresponding direct correlation functions. The results of numerical calculations of the order parameters and the corresponding phase diagrams are presented in Section 4 followed by the discussion. Finally, Section 5 contains our conclusions.

2. Molecular Theory of Coil–Rod–Coil Triblock Copolymers

A molecular theory of coil–rod–coil triblock copolymers can be developed using the general density functional theory, which has been applied before to nematic and smectic liquid crystals [44–49]. In such a theory, the free energy F of a multicomponent polymer system depends on one-particle number densities $\rho_v(\mathbf{r}, \omega)$, which depend both on the positional $\mathbf{r}$ and orientational ω degrees of freedom of the segments of type v and which satisfy the normalization condition $\int \rho_v(\mathbf{r}, \omega) d\mathbf{r} d\omega = f_v M$, where f_v is the relative fraction of segments of type v , while M is the number of macromolecules.

In the case of coil–rod–coil triblock copolymers, the free energy depends on the density of rod segments $\rho_r(\mathbf{r}, \mathbf{a})$, where the unit vector $\mathbf{a}$ is parallel to the rigid rod, and on the densities $\rho_{c1}(\mathbf{r}), \rho_{c2}(\mathbf{r})$ of the coil segments $c1$ and $c2$, which belong to the two different coils within one triblock copolymer chain. Triblock copolymer chains are characterized by the relative molar fractions f_r, f_{c1} and f_{c2} , which are related as $f_r + f_{c1} + f_{c2} = 1$, and the asymmetry of the triblock chain is described by the ratio f_{c1}/f_{c2} .

Using the fact that the second derivatives of the free energy functional with respect to one particle densities are proportional to the corresponding direct correlation functions for different segments, one can approximately express the free energy of a given phase by expanding it around the value in the isotropic phase.

Similarly to the statistical theory of rod–coil diblock polymers [41–43], such an expansion can be performed in the following way:

$$\begin{aligned} \beta F = \beta F_I + \sum_{v=r,c1,c2} \int \rho_v(\mathbf{x}) [\ln \rho_v(\mathbf{x}) - 1] d\mathbf{x} + \sum_{i=1,2} \int \chi(r_{12}) \delta \rho_r(\mathbf{x}_1) \delta \rho_{ci}(\mathbf{r}_2) d\mathbf{x}_1 d\mathbf{r}_2 \\ - \frac{\beta}{2} \int J(r_{12}) P_2(\mathbf{a}_1 \cdot \mathbf{a}_2) \delta \rho_r(\mathbf{x}_1) \delta \rho_r(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ - \frac{1}{2} \sum_{v,\eta=r,c1,c2} \int C_{v,\eta}(\mathbf{x}_1, \mathbf{x}_2) \delta \rho_v(\mathbf{x}_1) \delta \rho_\eta(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2, \quad (1) \end{aligned}$$

where $\beta = (k_B T)^{-1}$, and where the variable $\mathbf{x} = (\mathbf{r}, \mathbf{a})$ is assigned to the rod segments and $\mathbf{x} = \mathbf{r}$ to the coil segments. Here F_I is the free energy of the disordered reference phase, and $\delta \rho_v = \rho_v - \rho_v^0$ is the deviation of the one-particle density from the average density in the disordered phase. The functions $C_{cicj}(\mathbf{r}_{12})$, $C_{rci}(\mathbf{r}_{12}, \mathbf{a}_1)$ and $C_{rr}(\mathbf{r}_{12}, \mathbf{a}_1, \mathbf{a}_2)$ are the direct correlation functions between coil–coil, rod–coil and rod–rod segments, respectively, defined in the reference isotropic phase without interaction between different chains. In this free energy, the mean-field approximation is employed to take into account the interaction between different chains. These interactions include the rod–coil repulsion determined by the Flory–Huggins parameter χ , and the Maier–Saupe type interaction between rigid rods $J(r_{12})P_2(\mathbf{a}_1 \cdot \mathbf{a}_2)$.

General expressions for the one-particle densities $\rho_{ci}(\mathbf{r}_1)$ and $\rho_r(\mathbf{r}, \mathbf{a})$ can be obtained by minimization of the free energy functional (1):

$$\rho_{ci}(\mathbf{r}_1) = Z_{ci}^{-1} \exp \left\{ \sum_j \int C_{cij}(\mathbf{r}_{12}) \delta \rho_{cj}(\mathbf{r}_2) d\mathbf{r}_2 - \int [\chi(\mathbf{r}_{12}) - C_{rci}(\mathbf{r}_{12}, \mathbf{a})] \delta \rho_r(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2 d\mathbf{a} \right\} \quad (2)$$

$$\rho_r(\mathbf{r}_1, \mathbf{a}) = Z_r^{-1} \exp \left\{ \int C_{rr}(\mathbf{r}_{12}, \mathbf{a}) \delta \rho_r(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2 - \sum_i \int [\chi(\mathbf{r}_{12}) - C_{rci}(\mathbf{r}_{12}, \mathbf{a})] \delta \rho_{ci}(\mathbf{r}_2) d\mathbf{r}_2 + \beta \int J(\mathbf{r}_{12}) P_2(\mathbf{a} \cdot \mathbf{a}_2) \delta \rho_r(\mathbf{r}_2, \mathbf{a}_2) d\mathbf{r}_2 d\mathbf{a}_2 \right\} \quad (3)$$

where $i, j = 1, 2$, while Z_{ci} and Z_r are the normalization constants.

Densities of all segments in the lamellar phase are periodic functions of the position along the lamellae normal. Thus the effective “mean-field potentials” in Equations (2) and (3) are also periodic and can be expanded in Fourier series keeping the first harmonic:

$$\int C_{cij}(\mathbf{r}_{12}) \delta \rho_{cj}(\mathbf{r}_2) d\mathbf{r}_2 = \rho_0 f_{cj} \psi_{cj} C_{cij}(q) \cos(\mathbf{q} \cdot \mathbf{r}_1), \quad (4)$$

$$\begin{aligned} \int C_{rr}(\mathbf{r}_{12}, \mathbf{a}) \delta \rho_r(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2 \\ = \rho_0 f_r \psi_r \left[C_{rr}^{(0)}(q) + \frac{1}{2} C_{rr}^{(2)}(q) P_2(\mathbf{a} \cdot \mathbf{k}) \right] \cos(\mathbf{q} \cdot \mathbf{r}_1) \\ + \frac{1}{2} \rho_0 f_r \sigma C_{rr}^{(2)}(q) \cos(\mathbf{q} \cdot \mathbf{r}_1), \end{aligned} \quad (5)$$

$$\int C_{rci}(\mathbf{r}_{12}, \mathbf{a}) \delta \rho_{ci}(\mathbf{r}_2) d\mathbf{r}_2 = \rho_0 f_{ci} \psi_{ci} \left[C_{rci}^{(0)}(q) + C_{rci}^{(2)}(q) P_2(\mathbf{a} \cdot \mathbf{k}) \right] \cos(\mathbf{q} \cdot \mathbf{r}_1), \quad (6)$$

$$\int C_{rci}(\mathbf{r}_{12}, \mathbf{a}) \delta \rho_r(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2 d\mathbf{a} = \rho_0 f_r \cos(\mathbf{q} \cdot \mathbf{r}_1) \left[\psi_r C_{rci}^{(0)}(q) + \sigma C_{rci}^{(2)}(q) \right], \quad (7)$$

and

$$\int J(\mathbf{r}_{12}) P_2(\mathbf{a}_1 \cdot \mathbf{a}_2) \delta \rho_r(\mathbf{r}_2, \mathbf{a}_2) d\mathbf{r}_2 d\mathbf{a}_2 = \rho_0 f_r [J_0 S + J_2 \sigma \cos(\mathbf{q} \cdot \mathbf{r}_1)] P_2(\mathbf{a} \cdot \mathbf{k}). \quad (8)$$

where $\mathbf{k} = \mathbf{q}/q$ is the unit lamellae normal, and the Fourier transforms of the correlation functions between rod segments and rod and coil segments depend on the orientation of the rod with respect to $\mathbf{k}$. Therefore, while deriving Equations (4)–(7), we have used the expansion in Legendre polynomials $P_{2n}(\mathbf{k} \cdot \mathbf{a})$ [41,42] taking into account the first few terms:

$$C_{rci}(\mathbf{q}, \mathbf{a}) \approx C_{rci}^{(0)}(q) + C_{rci}^{(2)}(q) P_2(\mathbf{a} \cdot \mathbf{k}), \quad (9)$$

$$C_{rr}(\mathbf{q}, \mathbf{a}_1, \mathbf{a}_2) \approx C_{rr}^{(0)}(q) + \frac{1}{2} C_{rr}^{(2)}(q) P_2(\mathbf{a}_1 \cdot \mathbf{k}) + \frac{1}{2} C_{rr}^{(2)}(q) P_2(\mathbf{a}_2 \cdot \mathbf{k}), \quad (10)$$

where the symmetry of the correlation function is maintained. The correlation function between rod segments should be substituted into the “mean-field potentials” with $\mathbf{a}_1 = \mathbf{a}_2 = \mathbf{a}$, because all segments of the same rigid rod are parallel.

As a result of the straightforward expansions, Equations (4)–(8) depend on a finite set of order parameters:

$$S = \langle P_2(\mathbf{a} \cdot \mathbf{k}) \rangle_r = \frac{1}{Mf_r} \int \delta\rho_r(\mathbf{r}, \mathbf{a}) P_2(\mathbf{a} \cdot \mathbf{k}) d\mathbf{r} d\mathbf{a}, \quad (11)$$

$$\psi_r = \langle \cos(\mathbf{q}_i \cdot \mathbf{r}) \rangle_r = \frac{1}{Mf_r} \int \delta\rho_r(\mathbf{r}, \mathbf{a}) \cos(\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} d\mathbf{a}, \quad (12)$$

$$\psi_{ci} = \langle \cos(\mathbf{q}_i \cdot \mathbf{r}) \rangle_{ci} = \frac{1}{Mf_c} \int \delta\rho_{ci}(\mathbf{r}) \cos(\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}, \quad (13)$$

$$\sigma = \langle P_2(\mathbf{a} \cdot \mathbf{k}) \cos(\mathbf{q} \cdot \mathbf{r}) \rangle_r = \frac{1}{Mf_r} \int \delta\rho_r(\mathbf{r}, \mathbf{a}) P_2(\mathbf{a} \cdot \mathbf{k}) \cos(\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} d\mathbf{a}, \quad (14)$$

Here, S is the orientational (nematic) order parameter, ψ_r and ψ_{ci} are the translational order parameters of rod and coil segments, respectively, and the order parameter σ characterizes both translational and orientational ordering of rod segments.

Substitution of Equations (4)–(8) into Equations (2) and (3) and then into Equation (1) yields an approximate expression for the free energy of a coil–rod–coil triblock copolymer:

$$\begin{aligned} \beta F/V = & \frac{1}{2} \rho_0^2 \sigma \left[f_r^2 C_{rr}^{(2)}(q) \psi_r + 2f_{c1} f_r C_{rc1}^{(2)}(q) \psi_{c1} + 2f_{c2} f_r C_{rc2}^{(2)}(q) \psi_{c2} \right] \\ & + \frac{1}{2} \beta \rho_0^2 S^2 f_r^2 J_0 + \frac{1}{2} \beta \rho_0^2 f_r^2 J_2 \sigma^2 \\ & + \frac{1}{2} \rho_0^2 f_r^2 C_{rr}^{(0)}(q) \psi_r^2 + \frac{1}{2} \rho_0^2 f_{c1}^2 C_{c1c1}^{(0)}(q) \psi_{c1}^2 + \frac{1}{2} \rho_0^2 f_{c2}^2 C_{c2c2}^{(0)}(q) \psi_{c2}^2 + \rho_0^2 f_{c1} f_{c2} C_{c1c2}^{(0)}(q) \psi_{c1} \psi_{c2} \\ & + \rho_0^2 f_r f_{c1} C_{rc1}^{(0)}(q) \psi_r \psi_{c1} + \rho_0^2 f_r f_{c2} C_{rc2}^{(0)}(q) \psi_r \psi_{c2} - \rho_0^2 f_r f_{c2} \chi \psi_{c2} \psi_r - \rho_0^2 f_r f_{c1} \chi \psi_{c1} \psi_r \\ & - \rho_0 f_r \ln Z_r - \rho_0 f_{c1} \ln Z_{c1} - \rho_0 f_{c2} \ln Z_{c2} \end{aligned} \quad (15)$$

where V is the polymer volume and

$$\begin{aligned} Z_{c1} = & \int dz \exp \left[\rho_0 \cos(qz) \left(f_{c1} C_{c1c1}^{(0)}(q) \psi_{c1} + f_{c2} C_{c1c2}^{(0)}(q) \psi_{c2} \right. \right. \\ & \left. \left. + f_r C_{rc1}^{(2)}(q) \sigma + f_r C_{rc1}^{(0)}(q) \psi_r - f_r \chi \psi_r \right) \right], \end{aligned} \quad (16)$$

$$\begin{aligned} Z_{c2} = & \int dz \exp \left[\rho_0 \cos(qz) \left(f_{c2} C_{c2c2}^{(0)}(q) \psi_{c2} + f_{c1} C_{c1c2}^{(0)}(q) \psi_{c1} \right. \right. \\ & \left. \left. + f_r C_{rc2}^{(2)}(q) \sigma + f_r C_{rc2}^{(0)}(q) \psi_r - f_r \chi \psi_r \right) \right], \end{aligned} \quad (17)$$

$$\begin{aligned} Z_r = & \int dz d\mathbf{a} \exp[\rho_0 \cos(qz) \\ & \times (f_r C_{rr}^{(0)}(q) \psi_r + f_{c1} C_{rc1}^{(0)}(q) \psi_{c1} + f_{c2} C_{rc2}^{(0)}(q) \psi_{c2} - f_{c1} \chi \psi_{c1} - f_{c2} \chi \psi_{c2}) \\ & + \rho_0 \cos(qz) P_2(\mathbf{a} \cdot \mathbf{k}) \left(f_{c1} C_{rc1}^{(2)}(q) \psi_{c1} + f_{c2} C_{rc2}^{(2)}(q) \psi_{c2} + \frac{1}{2} f_r C_{rr}^{(2)}(q) \psi_r + f_r \beta J_2 \sigma \right) \\ & + \frac{1}{2} \cos(qz) \rho_0 f_r C_{rr}^{(2)}(q) \sigma + \rho_0 f_r \beta J_0 S P_2(\mathbf{a} \cdot \mathbf{k})], \end{aligned} \quad (18)$$

where $J_0 > 0$, $\chi > 0$ and the z -axis points along the wavevector $\mathbf{q}$.

In the general case, all orientational and translational order parameters can be calculated numerically by the free energy minimization. However, simultaneously, one has to take into consideration the polymer incompressibility, which plays the role of a constraint during the minimization process. In the first approximation, the incompressibility can be accounted for by supplementing the free energy with the following term (15):

$$\delta F = \lambda \left[\int \cos(\mathbf{q} \cdot \mathbf{r}) \rho_r(\mathbf{r}, \mathbf{a}) d\mathbf{r} d\mathbf{a} + \int \cos(\mathbf{q} \cdot \mathbf{r}) \rho_{c1}(\mathbf{r}) d\mathbf{r} + \int \cos(\mathbf{q} \cdot \mathbf{r}) \rho_{c2}(\mathbf{r}) d\mathbf{r} \right], \quad (19)$$

where λ is the Lagrange multiplier (see [42] for more detail). In practice, λ is calculated numerically using the equations for the translational order parameters before the total free energy is evaluated. After that, the free energy is minimized as a function of the order parameters.

3. Direct and Total Correlation Functions of Triblock Copolymers

The free energy of the lamellar phase depends on the Legendre polynomial expansion coefficients of the direct correlation functions of the system, which are not known explicitly. At the same time, the direct correlation function of a simple fluid is determined by the Ornstein–Zernike equation:

$$h_2(\mathbf{x}_1, \mathbf{x}_2) = C_2(\mathbf{x}_1, \mathbf{x}_2) + \int C_2(\mathbf{x}_1, \mathbf{x}_3) h_2(\mathbf{x}_3, \mathbf{x}_2) \rho(\mathbf{x}_3) d\mathbf{x}_3, \quad (20)$$

where the variable $\mathbf{x}$ denotes both the orientation and the position degrees of an anisotropic particle and $h_2(\mathbf{x}_1, \mathbf{x}_2)$ is the total pair correlation function, which can be expressed in terms of the pair distribution function $f_2(\mathbf{x}_1, \mathbf{x}_2) = f_1(\mathbf{x}_1) f_1(\mathbf{x}_2) [1 + h_2(\mathbf{x}_1, \mathbf{x}_2)]$.

Similarly to the case of rod–coil diblock copolymers [41,42], the Ornstein–Zernike equations for coil–rod–coil triblock copolymers are expressed as:

$$h_{\nu,\eta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{a}_1, \mathbf{a}_2) = C_{\nu,\eta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{a}_1, \mathbf{a}_2) + \sum_{\gamma} \int C_{\nu,\gamma}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{a}_1, \mathbf{a}_3) h_{\gamma,\eta}(\mathbf{r}_2, \mathbf{r}_3, \mathbf{a}_2, \mathbf{a}_3) \rho_{\eta}(\mathbf{r}_3, \mathbf{a}_3) d\mathbf{r}_3 d\mathbf{a}_3, \quad (21)$$

where $\nu, \eta, \gamma = (r, c1, c2)$ and where $h_{\nu,\eta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{a}_1, \mathbf{a}_2)$ are the corresponding total pair correlation functions.

Taking into account that the equilibrium densities of all segments are constants in the isotropic phase, the Fourier transforms of the direct correlation functions satisfy the equation:

$$h_{\nu,\eta}(\mathbf{q}, \mathbf{a}) = C_{\nu,\eta}(\mathbf{q}, \mathbf{a}) + \rho_{\gamma} h_{\nu,\gamma}(\mathbf{q}, \mathbf{a}) C_{\gamma,\eta}(\mathbf{q}, \mathbf{a}), \quad (22)$$

where all terms depend on the orientation of the rigid rod $\mathbf{a}$.

The solution of this equation enables one to express the direct pair correlation functions in terms of the total ones:

$$C_{\nu,\gamma}(\mathbf{q}, \mathbf{a}) = h_{\nu,\eta}(\mathbf{q}, \mathbf{a}) [\delta_{\gamma,\eta} + \rho_{\gamma} h_{\gamma,\eta}(\mathbf{q}, \mathbf{a})]^{-1} = \rho_{\nu}^{-1} \delta_{\nu,\gamma} - [\rho_{\nu} \delta_{\nu,\gamma} + \rho_{\nu} \rho_{\gamma} h_{\nu,\gamma}(\mathbf{q}, \mathbf{a})]^{-1}. \quad (23)$$

At the same time, the density–density correlation function of coil–rod–coil triblock copolymers is defined as the following ensemble average:

$$G_{\nu,\gamma}(\mathbf{x}_1, \mathbf{x}_2) = \langle \delta \rho_{\nu}(\mathbf{x}_1) \delta \rho_{\gamma}(\mathbf{x}_2) \rangle, \quad (24)$$

where $\delta \rho_{\nu}(\mathbf{x}) = \rho_{\nu}^M(\mathbf{x}) - \rho_{\nu}$ and where ρ_{ν} is the corresponding average density. The microscopic number density $\rho_{\nu}^M(\mathbf{x})$ is defined by the following general expression:

$$\rho_{\nu}^M(\mathbf{x}) = \sum_i \delta(\mathbf{x} - \mathbf{x}_i), \quad (25)$$

where $\mathbf{x}_i$ denotes the orientational and translational coordinates of the molecule i .

Taking into account that $\langle \rho_{\nu}^M(\mathbf{x}) \rangle = \rho_{\nu}$ the density correlation function between the segments of types ν and γ can be expressed as:

$$G_{\nu,\gamma}(\mathbf{r}_{12}, \mathbf{a}) = \rho_{\nu} \delta_{\nu,\gamma} \delta(\mathbf{r}_{12}) + \rho_{\nu} \rho_{\gamma} h_{\nu,\gamma}(\mathbf{r}_{12}, \mathbf{a}). \quad (26)$$

Using Equations (23) and (26) it is possible to obtain a simple relationship between the density–density correlation functions $G_{\nu,\gamma}(\mathbf{r}_{12}, \mathbf{a})$ and the corresponding direct correlation functions $C_{\nu,\gamma}(\mathbf{q}, \mathbf{a})$:

$$C_{v,\gamma}(\mathbf{q}, \mathbf{a}) = \rho_v^{-1} \delta_{v,\gamma} - G_{v,\gamma}(\mathbf{q}, \mathbf{a})^{-1}, \quad (27)$$

which allows obtaining the direct correlation functions by inverting the matrix of the density–density correlation functions.

In a particular case of symmetric triblock copolymers, $G_{v,\gamma}(\mathbf{q}, \mathbf{a})$ is a symmetric matrix:

$$\hat{G}(\mathbf{q}, \mathbf{a}) = \begin{pmatrix} G_{rr}(\mathbf{q}, \mathbf{a}) & G_{rc}(\mathbf{q}, \mathbf{a}) & G_{rc}(\mathbf{q}, \mathbf{a}) \\ G_{rc}(\mathbf{q}, \mathbf{a}) & G_{cc}(q) & G_{c1c2}(q) \\ G_{rc}(\mathbf{q}, \mathbf{a}) & G_{c1c2}(q) & G_{cc}(q) \end{pmatrix}. \quad (28)$$

The determinant of this matrix reads as:

$$\det \hat{G} = (G_{cc} - G_{c1c2})[G_{rr}(G_{cc} + G_{c1c2}) - 2G_{rc}^2], \quad (29)$$

and the inverse of (28) is expressed as:

$$[\hat{G}]_{rr}^{-1} = \frac{(G_{cc} + G_{c1c2})/2}{G_{rr}(G_{cc} + G_{c1c2})/2 - G_{rc}^2}, \quad (30)$$

$$[\hat{G}]_{rc1}^{-1} = [\hat{G}]_{rc2}^{-1} = -\frac{G_{rc}/2}{G_{rr}(G_{cc} + G_{c1c2})/2 - G_{rc}^2}, \quad (31)$$

$$[\hat{G}]_{c1c1}^{-1} = [\hat{G}]_{c2c2}^{-1} = \frac{G_{rr}G_{cc} - G_{rc}^2}{(G_{cc} - G_{c1c2})[G_{rr}(G_{cc} + G_{c1c2}) - 2G_{rc}^2]}, \quad (32)$$

$$[\hat{G}]_{c1c2}^{-1} = [\hat{G}]_{c2c1}^{-1} = -\frac{G_{rr}G_{c1c2} - G_{rc}^2}{(G_{cc} - G_{c1c2})[G_{rr}(G_{cc} + G_{c1c2}) - 2G_{rc}^2]}. \quad (33)$$

The analytical expression for the coil–coil density correlation function of long Gaussian chains has been obtained by a number of authors [50–52] including the original paper by Leibler [50]:

$$\begin{aligned} G_{cc}(q) &= \rho_0 \frac{1}{N} \int_0^{Nf_c} \int_0^s \exp[(s-s')q^2a^2/6] ds ds' \\ &= \rho_0 N \frac{2}{x^2} (f_c x + \exp(-f_c x) - 1), \end{aligned} \quad (34)$$

where N is the number of monomers in the chain, f_c is the fraction of coil monomers, a is the monomer radius, $x = q^2 Na^2/6 = q^2 R^2$ and $f_c N \gg 1$.

Density correlation functions for rod–coil diblock copolymers, averaged over all orientations, have been derived by Reenders and ten Brinke [53], and the non-averaged functions $G_{rc}(\mathbf{q}, \mathbf{a})$ and $G_{rr}(\mathbf{q}, \mathbf{a})$, which depend on the rigid rod orientation can be derived in a similar way using the general formulae presented in [53]. For example, the correlation function between rod and coil segments can be written in the form:

$$G_{rc}(\mathbf{q}, \mathbf{a}) = \rho_0 N f_r f_c K_R^{(1)}(y) K_c^{(1)}(x), \quad (35)$$

where

$$K_c^{(1)}(x) = \frac{1}{x} [1 - \exp(-x)], \quad (36)$$

and

$$K_R^{(1)}(y) = \text{Re} \frac{1}{N f_r} \int_0^{N f_r} \exp[i(\mathbf{q} \cdot \mathbf{a})s] ds = \frac{\sin(y)}{y}, \quad (37)$$

where $y = N f_r q a (\mathbf{k} \cdot \mathbf{a})$ while f_r is the fraction of rod monomers.

The density correlation function between rod monomers can be expressed as:

$$G_{rr}(\mathbf{q}, \mathbf{a}) = \rho_0 \frac{1}{N} \int_0^{Nf_r} \int_0^{Nf_r} \exp[i(s-s')qa(\mathbf{q} \cdot \mathbf{a})] ds ds' = 2\rho_0 N f_r^2 \frac{(1 - \cos y)}{y^2}. \quad (38)$$

4. Results and Discussion. Phase Diagrams of Symmetric and Asymmetric Triblock Copolymers

In the general case of asymmetric coil–rod–coil copolymers with variable lamellar periodicity, we minimize the free energy (15) with the Lagrange term (19) by varying all order parameters S , ψ_{c1} , ψ_{c2} and σ , as well as the wavenumber q . The latter cannot be simply included as another minimization variable, since the correlation functions are obtained by the matrix inversion and eventually diverge at certain values of q . Therefore, we perform the minimization in two steps: firstly the free energy is minimized for a certain fixed q and then q is varied to obtain the lamellar state with the lowest possible free energy.

In this way, one obtains the phase diagram and the order parameter profiles of a symmetric coil–rod–coil triblock copolymer shown in Figure 1 keeping $f_{c1} = f_{c2}$ and varying the dimensionless temperature $\tau = k_B T / J_0$ and the total coil fraction $f_c = f_{c1} + f_{c2}$. At the next stage, we derive in a similar manner a phase diagram for asymmetric copolymers with $f_{c1} = 2f_{c2}$, and present it together with typical order parameter profiles in Figure 2.

Comparing Figures 1 and 2 demonstrates that breaking the polymer molecule symmetry by changing the ratio of the coil fragments produces marginal effect on the polymer thermodynamics. In particular, it does not change the phase diagram, the order parameters S and σ remain unaffected, while the coil positional order parameters ψ_{c1} and ψ_{c2} experience a weak splitting. With the decreasing temperature, both symmetric and asymmetric coil–rod–coil triblock copolymers undergo a transition into the nematic phase and then a transition from the nematic phase into the lamellar one. This is similar to a typical phase sequence observed in conventional liquid crystals. Both transition temperatures also increase with the decreasing coil fraction f_c . One notes that in the lamellar phase, the order parameter S is large and weakly temperature dependent, i.e., the rods are characterized by strong orientational order.

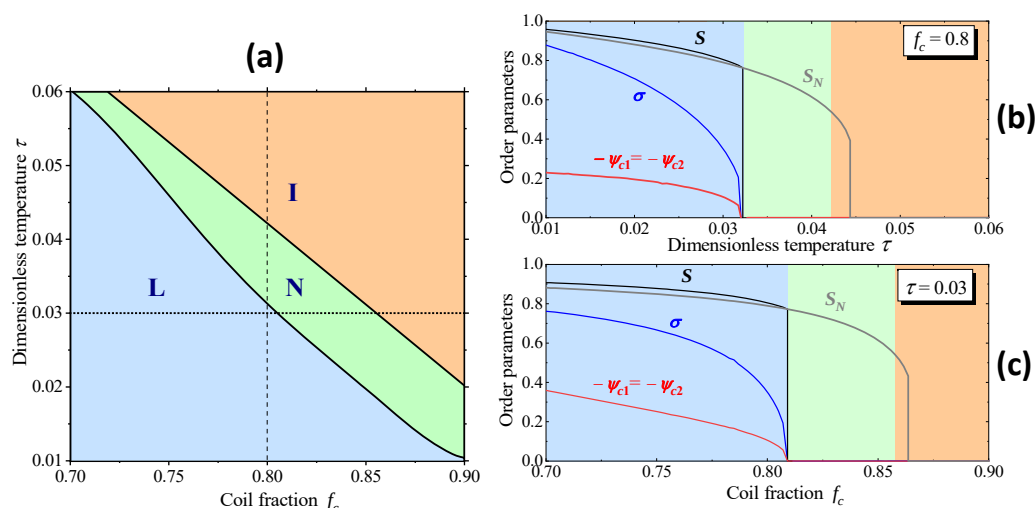


Figure 1. Phase diagram (a) and order parameters (b,c) of a symmetric triblock copolymer with $f_{c1} = f_{c2}$, $\chi = 3$ and $N = 10$ obtained by a consequent minimization of the free energy by varying the order parameters and the wavenumber. The temperature and concentration order parameter profiles are presented for two cross-sections of the diagram including the vertical dashed line ($f_c = 0.8$) and the horizontal dotted one ($\tau = 0.03$). The sign of the order parameters $\psi_{c1,2}$ is reversed for presentation convenience.

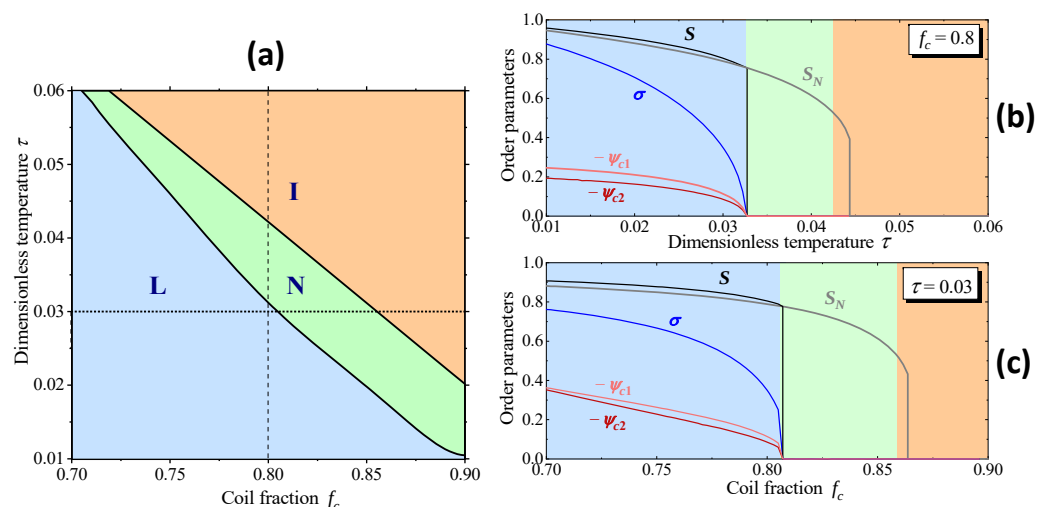


Figure 2. Phase diagram (a) and order parameters (b,c) of an asymmetric triblock copolymer with $f_{c1} = 2f_{c2}$, $\chi = 3$ and $N = 10$ obtained by a consequent minimization of the free energy by varying the order parameters and the wavenumber. The temperature and concentration order parameter profiles are presented for two cross-sections of the diagram including the vertical dashed line ($f_c = 0.8$) and the horizontal dotted one ($\tau = 0.03$). The sign of the order parameters $\psi_{c1,2}$ is reversed for presentation convenience.

For a better insight into the role of the polymer molecule asymmetry, we study the phase behavior of a coil–rod–coil triblock copolymer keeping the total fraction of coil fragments fixed and varying the ratio of the lengths of coil fragments, which is effectively expressed by the ratio of their partial fractions f_{c1}/f_{c2} . The corresponding phase diagram is shown in Figure 3 together with typical profiles of the order parameters along the indicated cross sections of the diagram. One can readily see that the molecular asymmetry has a negligible effect on the phase diagram and leaves unaffected the order parameters S and σ . At the same time, the increase in the ratio f_{c1}/f_{c2} noticeably suppresses the positional order parameter ψ_{c2} , which is related to a decrease in the coil length. The order parameter ψ_{c1} of the opposite coil is then moderately enhanced.

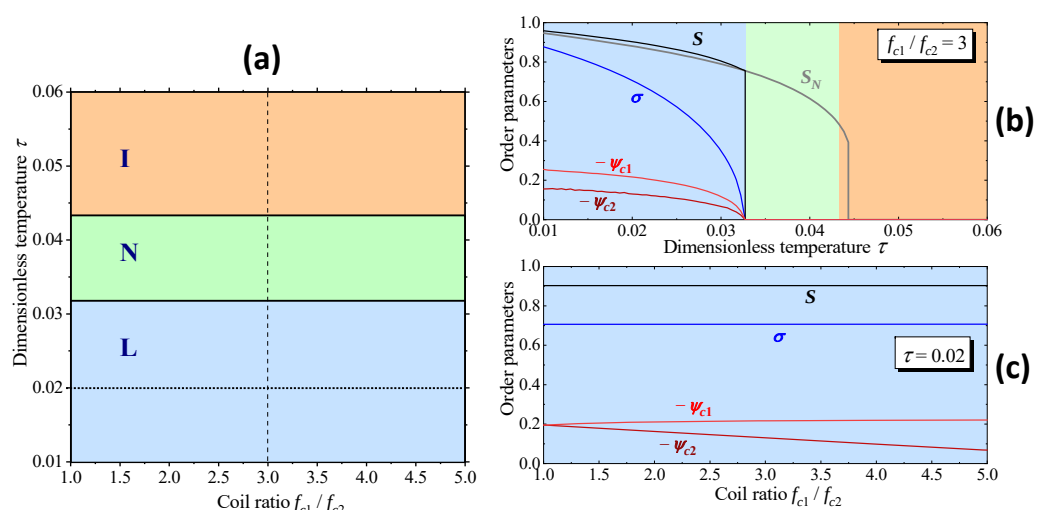


Figure 3. Phase diagram (a) and order parameters (b,c) of a triblock copolymer with variable molecular asymmetry f_{c1}/f_{c2} . The total coil fraction is kept fixed $f_{c1} + f_{c2} = 0.8$, $N = 10$, and $\chi = 3$. Temperature variation of the order parameters (b) has been calculated along the vertical dashed line ($f_{c1}/f_{c2} = 3.0$) across the phase diagram, and the dependence of the order parameters on the molecular asymmetry f_{c1}/f_{c2} (c) has been calculated along the horizontal dotted ($\tau = 0.02$) line. The sign of the order parameters $\psi_{c1,2}$ is reversed for presentation convenience.

Finally, to study the role of the Flory–Huggins parameter χ in the theory of coil–rod–coil triblock copolymers, we consider the symmetric system with fixed $f_{c1} = f_{c2} = 0.4$ and obtain the $T - \chi$ phase diagram presented in Figure 4.

One notes that all typical order parameter profiles presented in Figures 1, 2 and 4 indicate that the decrease in T and f_c or the increase in χ promote the stability of the lamellar phase in comparison to the highly ordered nematic phase. One notes also that the effect of the phase transition into the lamellar phase on the value of the nematic order parameter S is very weak.

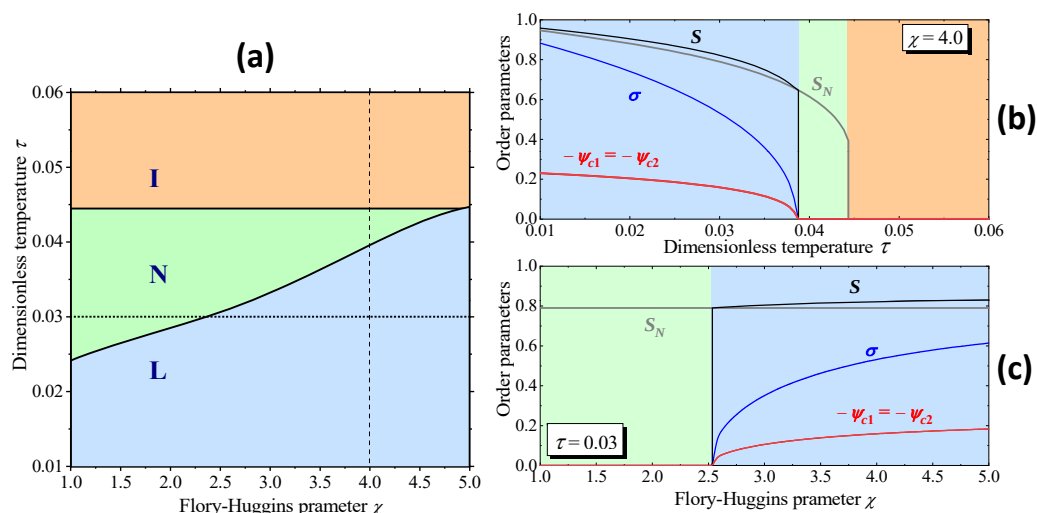


Figure 4. Phase diagram (a) and order parameters (b,c) of a symmetric triblock copolymer with $f_{c1} = f_{c2} = 0.4$ and $N = 10$ obtained by a consequent minimization of the free energy by varying the order parameters and the wavenumber. Temperature variation of the order parameters (b) has been calculated along the vertical dashed line ($\chi = 4.0$) across the phase diagram, and the dependence of the Flory–Huggins parameter χ (c) has been calculated along the horizontal dotted ($\tau = 0.03$) line. The sign of the order parameters $\psi_{c1,2}$ is reversed for presentation convenience.

To summarize, a number of phase diagrams in terms of the temperature T , the total fraction of coil segments f_c , the repulsion parameter χ and the asymmetry of the triblock macromolecule have been derived, and the orientational and translational order parameters have been numerically calculated for several cross-sections of these diagrams. The results of the theory indicate that the nematic phase–lamellar transition strongly depends both on temperature and on the Flory–Huggins parameter χ . One concludes that there are two different microscopic mechanisms of the translational symmetry breaking in coil–rod–coil triblock copolymers, which determine the transition into the orthogonal lamellar phase. The first mechanism is related to the short range repulsion between rod and coil segments, which leads to the corresponding microphase separation specific for block copolymers. The second mechanism is determined by the orientational attraction interaction potential between rigid rods, which is the predominant mechanism of smectic ordering in low molecular weight liquid crystals composed of rod-like molecules. Although certain microphase separation between rigid cores and flexible tails is also present in conventional liquid crystals, it is not a major mechanism of stabilization of smectic phases unless the molecules possess a specific structure [18,46,54–57]. One notes also that in the nematic phase, the order parameter S rapidly increases on the approach to the transition into the lamellar phase. Thus, the nematic–lamellar transition occurs in the system of nearly perfectly ordered rigid blocks and hence the effect of temperature on the transition is not related to the temperature variation of the nematic order.

It is also remarkable that the lamellar phase exhibited by coil–rod–coil triblock copolymers is accompanied by a relatively weak microphase separation. Indeed, the rigid rods are characterized by high values of the orientational and translational order parameters as

well as the sufficiently high value of the order parameter σ , which specifies simultaneous orientational-translational ordering. Thus, the rods form a well-defined layer structure. At the same time, the translational order parameter of the coil segments is relatively low, which indicates that they partially penetrate into the rigid blocks. This model is qualitatively confirmed by the temperature–concentration phase diagram, where the nematic–lamellar transition temperature strongly decreases with the increasing coil fraction f_c . On the other hand, the transition temperature practically does not depend on the triblock asymmetry specified by the ratio of the fractions of the two different coils f_{c1}/f_{c2} . Thus, the effect of triblock asymmetry on the properties of the lamellar phase deserves further experimental and theoretical research including, in particular, the study of how it affects the mechanical stability of the corresponding copolymer materials.

5. Conclusions

We have developed a molecular theory of phase transitions and liquid crystal ordering in coil–rod–coil triblock copolymers, employing the same density functional theory that has been used before in our theoretical studies of rod–coil diblock copolymers [41,42]. The expression for the free energy of the system has been obtained in terms of both orientational and translational order parameters, the Flory–Huggins parameter χ , direct correlation functions of the isotropic phase, and the potential of the orientational interaction between rod segments. The direct correlation functions between different segments of the triblock chain have been analytically related to the corresponding density correlation functions, which are calculated using the model of two Gaussian chains connected to a rigid rod. All orientational and translational order parameters of the triblock copolymer have been calculated numerically by free energy minimization also using the Lagrange multiplier technique to account for the polymer incompressibility. The results of the molecular theory indicate that there are two microscopic mechanisms of the translational symmetry breaking in coil–rod–coil copolymers, which are related to the microphase separation between rod and coil segments and to the attraction interaction between rigid rods, respectively. Both mechanisms contribute to the stability of the lamellar phase.

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References

1. Segalman, R.A.; McCulloch, B.; Kirmayer, S.; Urban, J.J. Block Copolymers for Organic Optoelectronics. *Macromolecules* **2009**, *42*, 9205–9216. [[CrossRef](#)]
2. Sivula, K.; Ball, Z.T.; Watanabe, N.; Fréchet, J.M.J. Amphiphilic Diblock Copolymer Compatibilizers and Their Effect on the Morphology and Performance of Polythiophene: Fullerene Solar Cells. *Adv. Mater.* **2006**, *18*, 206–210. [[CrossRef](#)]
3. Van Hest, J.C.M. Biosynthetic-Synthetic Polymer Conjugates. *Polym. Rev.* **2007**, *47*, 63–92. [[CrossRef](#)]
4. Klok, H.A. Biological-synthetic hybrid block copolymers: Combining the best from two worlds. *J. Polym. Sci. Part A Polym. Chem.* **2004**, *43*, 1–17. [[CrossRef](#)]
5. Loos, K.; Müller, A.H.E. New Routes to the Synthesis of Amylose-block-polystyrene Rod-Coil Block Copolymers. *Biomacromolecules* **2002**, *3*, 368–373. [[CrossRef](#)] [[PubMed](#)]

6. Haddleton, D.M.; Ohno, K. Well-Defined Oligosaccharide-Terminated Polymers from Living Radical Polymerization. *Biomacromolecules* **2000**, *1*, 152–156. [[CrossRef](#)] [[PubMed](#)]
7. Olsen, B.D.; Segalman, R.A. Self-assembly of rod-coil block copolymers. *Mater. Sci. Eng. R Rep.* **2008**, *62*, 37–66. [[CrossRef](#)]
8. Hoeben, F.J.M.; Jonkheijm, P.; Meijer, E.W.; Schenning, A.P.H.J. About Supramolecular Assemblies of π -Conjugated Systems. *Chem. Rev.* **2005**, *105*, 1491–1546. [[CrossRef](#)] [[PubMed](#)]
9. Ryu, J.H.; Lee, M. Liquid Crystalline Assembly of Rod–Coil Molecules. In *Liquid Crystalline Functional Assemblies and Their Supramolecular Structures*; Springer: Berlin/Heidelberg, Germany, 2007; pp. 63–98. [[CrossRef](#)]
10. Yu, G.; Gao, J.; Hummelen, J.C.; Wudl, F.; Heeger, A.J. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor–Acceptor Heterojunctions. *Science* **1995**, *270*, 1789–1791. [[CrossRef](#)]
11. Tao, Y.; McCulloch, B.; Kim, S.; Segalman, R.A. The relationship between morphology and performance of donor–acceptor rod–coil block copolymer solar cells. *Soft Matter* **2009**, *5*, 4219. [[CrossRef](#)]
12. Chochos, C.L.; Kallitsis, J.K.; Gregoriou, V.G. Rod-Coil Block Copolymers Incorporating Terfluorene Segments for Stable Blue Light Emission. *J. Phys. Chem. B* **2005**, *109*, 8755–8760. [[CrossRef](#)]
13. Becker, S.; Ego, C.; Grimsdale, A.C.; List, E.J.; Marsitzky, D.; Pogantsch, A.; Setayesh, S.; Leising, G.; Müllen, K. Optimisation of polyfluorenes for light emitting applications. *Synth. Met.* **2001**, *125*, 73–80. [[CrossRef](#)]
14. Tao, Y.; Ma, B.; Segalman, R.A. Self-Assembly of Rod-Coil Block Copolymers and Their Application in Electroluminescent Devices. *Macromolecules* **2008**, *41*, 7152–7159. [[CrossRef](#)]
15. McMillan, W.L. Simple Molecular Model for the Smectic A Phase of Liquid Crystals. *Phys. Rev. A* **1971**, *4*, 1238–1246. [[CrossRef](#)]
16. Kobayashi, K.K. Theory of Translational and Orientational Melting with Application to Liquid Crystals. *Mol. Cryst. Liq. Cryst.* **1971**, *13*, 137–148. [[CrossRef](#)]
17. Mederos, L.; Sullivan, D.E. Molecular theory of smectic-A liquid crystals. *Phys. Rev. A* **1989**, *39*, 854–863. [[CrossRef](#)]
18. Gorkunov, M.V.; Osipov, M.A.; Kapernaum, N.; Nonnenmacher, D.; Giesselmann, F. Molecular theory of smectic ordering in liquid crystals with nanoscale segregation of different molecular fragments. *Phys. Rev. E* **2011**, *84*, 051704. [[CrossRef](#)]
19. Erukhimovich, I.Y. Weak segregation theory and non-conventional morphologies in the ternary ABC triblock copolymers. *Eur. Phys. J. E* **2005**, *18*, 383–406. [[CrossRef](#)]
20. Mayes, A.M.; de la Cruz, M.O. Microphase separation in multiblock copolymer melts. *J. Chem. Phys.* **1989**, *91*, 7228–7235. [[CrossRef](#)]
21. Noolandi, J.; Shi, A.C.; Linse, P. Theory of Phase Behavior of Poly(oxyethylene)-Poly(oxypropylene)-Poly(oxyethylene) Triblock Copolymers in Aqueous Solutions. *Macromolecules* **1996**, *29*, 5907–5919. [[CrossRef](#)]
22. Matsen, M.W.; Barrett, C. Liquid-crystalline behavior of rod-coil diblock copolymers. *J. Chem. Phys.* **1998**, *109*, 4108–4118. [[CrossRef](#)]
23. Müller, M.; Schick, M. Ordered Phases in Rod-Coil Diblock Copolymers. *Macromolecules* **1996**, *29*, 8900–8903. [[CrossRef](#)]
24. Pryamitsyn, V.; Ganesan, V. Self-assembly of rod-coil block copolymers. *J. Chem. Phys.* **2004**, *120*, 5824–5838. [[CrossRef](#)] [[PubMed](#)]
25. Chen, J.Z.; Zhang, C.X.; Sun, Z.Y.; Zheng, Y.S.; An, L.J. A novel self-consistent-field lattice model for block copolymers. *J. Chem. Phys.* **2006**, *124*, 104907. [[CrossRef](#)]
26. Shah, M.; Pryamitsyn, V.; Ganesan, V. A Model for Self-Assembly in Side Chain Liquid Crystalline Block Copolymers. *Macromolecules* **2007**, *41*, 218–229. [[CrossRef](#)]
27. Kriksin, Y.A.; Khalatur, P.G. Parallel Algorithm for 3D SCF Simulation of Copolymers With Flexible and Rigid Blocks. *Macromol. Theory Simulations* **2012**, *21*, 382–399. [[CrossRef](#)]
28. Dücks, D.; Sullivan, D.E. Entropy-induced smectic phases in rod coil copolymers. *J. Phys. Condens. Matter* **2002**, *14*, 12189–12202. [[CrossRef](#)]
29. Hidalgo, R.C.; Sullivan, D.E.; Chen, J.Z.Y. Smectic phases in rod-coil diblock copolymers. *J. Phys. Condens. Matter* **2007**, *19*, 376107. [[CrossRef](#)]
30. Tang, J.; Jiang, Y.; Zhang, X.; Yan, D.; Chen, J.Z.Y. Phase Diagram of Rod-Coil Diblock Copolymer Melts. *Macromolecules* **2015**, *48*, 9060–9070. [[CrossRef](#)]
31. Song, W.; Tang, P.; Qiu, F.; Yang, Y.; Shi, A.C. Phase behavior of semiflexible-coil diblock copolymers: A hybrid numerical SCFT approach. *Soft Matter* **2011**, *7*, 929–938. [[CrossRef](#)]
32. Jiang, Y.; Chen, J.Z.Y. Influence of Chain Rigidity on the Phase Behavior of Wormlike Diblock Copolymers. *Phys. Rev. Lett.* **2013**, *110*, 138305. [[CrossRef](#)]
33. Li, S.; Jiang, Y.; Chen, J.Z.Y. Phase transitions in semiflexible-rod diblock copolymers: A self-consistent field theory. *Soft Matter* **2014**, *10*, 8932–8944. [[CrossRef](#)] [[PubMed](#)]
34. Li, S.; Jiang, Y.; Chen, J.Z.Y. Complex liquid-crystal nanostructures in semiflexible ABC linear triblock copolymers: A self-consistent field theory. *J. Chem. Phys.* **2016**, *145*, 184902. [[CrossRef](#)]
35. Cai, Y.; Zhang, P.; Shi, A.C. Liquid crystalline bilayers self-assembled from rod-coil diblock copolymers. *Soft Matter* **2017**, *13*, 4607–4615. [[CrossRef](#)] [[PubMed](#)]
36. Gao, J.; Song, W.; Tang, P.; Yang, Y. Self-assembly of semiflexible block copolymers: 2D numerical implementation of self-consistent field theory. *Soft Matter* **2011**, *7*, 5208. [[CrossRef](#)]
37. Gao, J.; Tang, P.; Yang, Y. Non-lamellae structures of coil-semiflexible diblock copolymers. *Soft Matter* **2013**, *9*, 69–81. [[CrossRef](#)]

-
38. Song, W.; Tang, P.; Zhang, H.; Yang, Y.; Shi, A.C. New Numerical Implementation of Self-Consistent Field Theory for Semiflexible Polymers. *Macromolecules* **2009**, *42*, 6300–6309. [[CrossRef](#)]
 39. Xia, Y.; Chen, J.; Sun, Z.; Shi, T.; An, L.; Jia, Y. Self-assembly of linear ABC coil-coil-rod triblock copolymers. *Polymer* **2010**, *51*, 3315–3319. [[CrossRef](#)]
 40. Han, X.-G.; Liang, N.; Zhang, H. Self-assembly in rod/coil block copolymers: Degenerate behavior under nonconfinement. *Condens. Matter Phys.* **2020**, *23*, 33603. [[CrossRef](#)]
 41. Osipov, M.A.; Gorkunov, M.V. Molecular theory of liquid-crystal ordering in rod-coil diblock copolymers. *Phys. Rev. E* **2019**, *100*, 042701. [[CrossRef](#)]
 42. Osipov, M.A.; Gorkunov, M.V.; Antonov, A.A. Density Functional Approach to the Molecular Theory of Rod-Coil Diblock Copolymers. *Polym. Sci. Ser. A* **2020**, *62*, 562–577. [[CrossRef](#)]
 43. Osipov, M.A.; Gorkunov, M.V.; Berezkin, A.V.; Antonov, A.A.; Kudryavtsev, Y.V. Molecular theory of the tilting transition and computer simulations of the tilted lamellar phase of rod-coil diblock copolymers. *J. Chem. Phys.* **2020**, *152*, 184906. [[CrossRef](#)] [[PubMed](#)]
 44. Singh, Y. Molecular theory of liquid crystals: Application to the nematic phase. *Phys. Rev. A* **1984**, *30*, 583–593. [[CrossRef](#)]
 45. Sluckin, T.J.; Shukla, P. Molecular field theory of nematics: density functional approach. I. Bulk effects. *J. Phys. A Math. Gen.* **1983**, *16*, 1539–1553. [[CrossRef](#)]
 46. Gorkunov, M.V.; Osipov, M.A.; Lagerwall, J.P.F.; Giesselmann, F. Order-disorder molecular model of the smectic-A–smectic-C phase transition in materials with conventional and anomalously weak layer contraction. *Phys. Rev. E* **2007**, *76*, 051706. [[CrossRef](#)] [[PubMed](#)]
 47. Longa, L.; Stelzer, J.; Dunmur, D. Density functional approach to study the elastic constants of biaxial nematic liquid crystals. *J. Chem. Phys.* **1998**, *109*, 1555–1566. [[CrossRef](#)]
 48. Osipov, M.A. Molecular Theories of Liquid Crystals. In *Handbook of Liquid Crystals*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2014; pp. 40–71. [[CrossRef](#)]
 49. Perera, A.; Patey, G.N.; Weis, J.J. Density functional theory applied to the isotropic–nematic transition in model liquid crystals. *J. Chem. Phys.* **1988**, *89*, 6941–6946. [[CrossRef](#)]
 50. Leibler, L. Theory of Microphase Separation in Block Copolymers. *Macromolecules* **1980**, *13*, 1602–1617. [[CrossRef](#)]
 51. Ohta, T.; Kawasaki, K. Equilibrium morphology of block copolymer melts. *Macromolecules* **1986**, *19*, 2621–2632. [[CrossRef](#)]
 52. Uneyama, T.; Doi, M. Density Functional Theory for Block Copolymer Melts and Blends. *Macromolecules* **2005**, *38*, 196–205. [[CrossRef](#)]
 53. Reenders, M.; ten Brinke, G. Compositional and Orientational Ordering in Rod-Coil Diblock Copolymer Melts. *Macromolecules* **2002**, *35*, 3266–3280. [[CrossRef](#)]
 54. Giesselmann, F.; Zugenmaier, P.; Dierking, I.; Lagerwall, S.T.; Stebler, B.; Kašpar, M.; Hamplová, V.; Glogarová, M. Smectic-A*–smectic-C* transition in a ferroelectric liquid crystal without smectic layer shrinkage. *Phys. Rev. E* **1999**, *60*, 598–602. [[CrossRef](#)] [[PubMed](#)]
 55. Binnemans, K. Ionic Liquid Crystals. *Chem. Rev.* **2005**, *105*, 4148–4204. [[CrossRef](#)] [[PubMed](#)]
 56. Giesselmann, F.; Germer, R.; Saipa, A. Orientational order in smectic liquid-crystalline phases of amphiphilic diols. *J. Chem. Phys.* **2005**, *123*, 034906. [[CrossRef](#)] [[PubMed](#)]
 57. Lagerwall, J.P.F.; Giesselmann, F. Current Topics in Smectic Liquid Crystal Research. *ChemPhysChem* **2006**, *7*, 20–45. [[CrossRef](#)]