

Theory of Polygonal Phases Self-Assembled from T-Shaped Liquid Crystalline Molecules

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backbone, two flexible end chains, and a flexible side chain. However, a comprehensive understanding of the stability and formation mechanisms of these intricately nanostructured phases remains incomplete. Here, we fill this gap by carrying out a theoretical study of the phase behavior of TLCMs. Specifically, we construct phase diagrams of TLCMs by computing the free energy of different ordered phases of the system. Our results reveal that the number of polygonal edges increases as the length of the side chain or interaction strength increases, consistent with exper-



imental observations. The theoretical study not only reproduces the experimentally observed phases and phase transition sequences but also systematically analyzes the stability mechanism of the polygonal phases.

INTRODUCTION

Liquid crystalline molecules (LCMs) are a class of soft materials that can self-assemble into numerous ordered structures in both crystalline states and liquid crystalline states.¹ The rich phase behavior and unique properties of LCMs make them useful advanced materials with applications in many fields such as biomedical engineering, electronics, and communications.^{2–5} Among the many types of LCMs, the T-shaped liquid crystalline molecules (TLCMs), composed of a rigid backbone with two incompatible end blocks and a flexible side chain, have been extensively studied experimentally,⁶⁻¹⁸ revealing that these LCMs can self-assemble into an amazing array of complex ordered phases. Specifically, increasing the side chain length results in an interesting phase transition sequence of onedimensional smectic phases \rightarrow simple polygons \rightarrow giant polygons \rightarrow three-dimensional lamellar phases \rightarrow threedimensional bicontinuous cubic networks. Besides providing a platform for engineering intricately nanostructured materials, the TLCMs offer an interesting model system to study the selfassembly and stability of complex ordered phases from macromolecular systems containing rigid and flexible components.

Theoretical and simulation studies can provide a good understanding of the phase behavior of self-assembling macromolecules. For the case of TLCMs, several simulation methods have been used to investigate their self-assembly. In particular, molecular dynamics of coarse-grained models has been employed to explore the phase behaviors of several TLCM systems.^{19–22} These studies observed the formation of layered phases, simple polygons, and three-dimensional bicontinuous cubic networks. Furthermore, dissipative particle dynamics simulations^{23–26} have been utilized to study the influence of side chain length, temperature, and hydrogen bonding on the phase behavior of TLCMs, and observed layered, simple polygonal, giant polygonal, and gyroid phases. Monte Carlo simulations²⁷ have been used to study the role of entropy players in self-assembled layered and hexagonal phases. These simulation studies of TLCMs mainly looked at the layered phases and simple polygons, with limited results of giant polygons. A comprehensive understanding of the stability and formation mechanisms of these intricately liquid crystalline polygons remains incomplete.

In this work, we report a theoretical study of the phase behavior of TLCMs using the self-consistent field theory (SCFT), which is a flexible and powerful theoretical framework for analyzing the equilibrium phase behaviors of inhomogeneous macromolecular systems. It has been successfully applied to flexible and semiflexible polymeric systems.^{28–36} In our SCFT study of the TLCMs, the rigid liquid crystalline segments are described as wormlike chains with liquid crystalline interactions, whereas the end- and side-chains are modeled as flexible Gaussian chains. The resulting SCFT equations represent a

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great computational challenge due to the existence of both flexible and semiflexible components. We overcome this challenge by developing an efficient and precise parallel algorithm to solve the SCFT equations, enabling us to obtain solutions corresponding to many polygonal and layered phases. The thermodynamic stability of these ordered structures is examined by comparing their free energy. Phase diagrams of the system are constructed in the plane spanned by the volume fraction of the side chain and interaction strength. Furthermore, we model the experimental process by changing the number of side chain monomers and obtain a phase transition sequence that is consistent with experimental observations.

MODEL AND METHODS

We consider an incompressible melt consisting of n TLCMs in a volume V. Each TLCM, with a degree of polymerization N, consists of five blocks constructed from three chemically distinct monomers (A, B, R), as shown schematically in Figure 1. The number of monomers for the



Figure 1. Schematic of TLCM chain containing a rigid backbone block R (blue), two ends flexible blocks A (red), and a flexible side block B (green).

five blocks is denoted by $N_i = f_i N$, where f_i is the volume fraction of the *i* block, $i = A_1, A_2, B, R_1, R_2$. It is noted that $f_{A_1} + f_{A_2} + f_B + f_{R_1} + f_{R_2} = 1$, $N_{A_1} + N_{A_2} + N_B + N_{R_1} + N_{R_2} = N$. The statistical segment lengths of monomers α are b_α ($\alpha \in \{A, B, R\}$), respectively. We employ the Gaussian chain model and the wormlike chain model to describe flexible and semiflexible blocks, respectively.³⁷ The conformation of a block is described by a space curve $\mathbf{R}^i_\alpha(s)$ ($s \in I_\alpha$), where $I_A = I_{A_1} \cup I_{A_2} = [0, f_{A_1}] \cup [0, f_{A_2}]$, $I_B = [0, f_B]$, and $I_R = I_{R_1} \cup I_{R_2} = [f_{A_1}, f_{A_1} + f_{R_1}] \cup [f_{A_2}, f_{A_2} + f_{R_2}]$, which specifies the position of the *s*-th monomer in the α -block of the *i*-th chain. According to this definition, the normalized concentrations of monomers A, B, and R at a spatial position r are

$$\hat{\rho}_{\mathbf{A}}(\mathbf{r}) = \frac{N}{\rho_0} \sum_{i=1}^n \int_{I_A} \delta[\mathbf{r} - \mathbf{R}_A^i(s)] ds$$

$$\hat{\rho}_{\mathbf{B}}(\mathbf{r}) = \frac{N}{\rho_0} \sum_{i=1}^n \int_{I_B} \delta[\mathbf{r} - \mathbf{R}_B^i(s)] ds$$

$$\hat{\rho}_{\mathbf{R}}(\mathbf{r}) = \frac{N}{\rho_0} \sum_{i=1}^n \int_{I_R} \delta[\mathbf{r} - \mathbf{R}_R^i(s)] ds$$
(1)

where ρ_0 is the per unit volume of density. The incompressibility condition requires $\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}) + \hat{\rho}_R(\mathbf{r}) = 1$.

There are various order parameters to describe the orientational order of rigid segments.³⁸ Here, we choose the two-dimensional order parameter

$$\hat{\mathbf{S}}(\mathbf{r}) = \frac{N}{\rho_0} \sum_{i=1}^n \int_{I_R} \delta[\mathbf{r} - \mathbf{R}_R^i(s)] \left(\mathbf{u}^i(s) \mathbf{u}^i(s) - \frac{\mathbf{I}}{2} \right) \mathrm{d}s$$
(2)

where $\mathbf{u}^i(s) = \mathbf{d}\mathbf{R}_R^{\ i}(s)/ds$ is the unit tangent vector to the semiflexible block at contour location *s*. The stretching conformational energy of noninteracting flexible chains is

$$H_{0} = \frac{3}{2b_{A}^{2}} \sum_{i=1}^{n} \int_{I_{A}} \left| \frac{\mathrm{d}\mathbf{R}_{A}^{i}(s)}{\mathrm{d}s} \right|^{2} \mathrm{d}s + \frac{3}{2b_{B}^{2}} \sum_{i=1}^{n} \int_{I_{B}} \left| \frac{\mathrm{d}\mathbf{R}_{B}^{i}(s)}{\mathrm{d}s} \right|^{2} \mathrm{d}s$$
(3)

The bending conformational energy of noninteracting semiflexible blocks is

$$H_{1} = \frac{\lambda}{2b_{R}^{2}} \sum_{i=1}^{n} \int_{I_{R}} \left| \frac{d\mathbf{u}^{i}(s)}{ds} \right|^{2} ds$$
(4)

where λ is the stiffness of the semiflexible block. The energy of the parallel alignment between semiflexible chains, described using the Maier–Saupe type of orientational interaction

$$H_{\rm S} = -\frac{\eta \rho_0}{2} \int \hat{\boldsymbol{S}}(\boldsymbol{r}) : \, \hat{\boldsymbol{S}}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \tag{5}$$

where Maier–Saupe parameter η represents the magnitude of the orientational interaction that favors parallel alignment of the semi-flexible segments. Following the standard Flory–Huggins approach, the interaction potential $H_{\rm F}$ of the system is given by

$$H_{F} = \rho_{0} \int [\overline{\chi}_{AA} \hat{\rho}_{A}(\mathbf{r}) \hat{\rho}_{A}(\mathbf{r}) + 2\overline{\chi}_{AB} \hat{\rho}_{A}(\mathbf{r}) \hat{\rho}_{B}(\mathbf{r}) + \overline{\chi}_{BB} \hat{\rho}_{B}(\mathbf{r}) \hat{\rho}_{B}(\mathbf{r}) + 2\overline{\chi}_{AR} \hat{\rho}_{A}(\mathbf{r}) \hat{\rho}_{R}(\mathbf{r}) + 2\overline{\chi}_{BR} \hat{\rho}_{B}(\mathbf{r}) \hat{\rho}_{R}(\mathbf{r}) + \overline{\chi}_{RR} \hat{\rho}_{R}(\mathbf{r}) \hat{\rho}_{R}(\mathbf{r})] d\mathbf{r}$$

$$(6)$$

where the Flory–Huggins interaction parameter $\overline{\chi}_{ij}$ ($i, j \in \{A, B, R\}$) represents the interaction between monomers i and j. It is assumed that these interaction parameters $\overline{\chi}_{ij}$ can be positive or negative, representing repulsive and attractive interactions, respectively. Hydrogen bonding is commonly modeled by attractive interaction,³⁹ i.e., $\overline{\chi}_{ij} < 0$. Considering the incompressible condition and ignoring the contributions from terms linear in the monomer density, the interaction potential $H_{\rm F}$ becomes

$$H_{F} = \rho_{0} \int [\chi_{AB} \hat{\rho}_{A}(\mathbf{r}) \hat{\rho}_{B}(\mathbf{r}) + \chi_{AR} \hat{\rho}_{A}(\mathbf{r}) \hat{\rho}_{R}(\mathbf{r}) + \chi_{BR} \hat{\rho}_{B}(\mathbf{r}) \hat{\rho}_{R}(\mathbf{r})] d\mathbf{r}$$
(7)

where the effective Flory-Huggins parameters are given by $\chi_{ij} = 2\overline{\chi}_{ij} - (\overline{\chi}_{ii} + \overline{\chi}_{jj}).$

The particle-based partition functional is

$$\mathcal{Z} = \frac{z_T^n}{n!} \iint \delta[\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}) + \hat{\rho}_R(\mathbf{r}) - 1]$$
$$\exp[-H_0 - H_1 - H_F - H_S] d\mathbf{u}(s) \mathcal{D} \mathbf{R}^i_\alpha(s)$$
(8)

where z_T is the partition function of the TLCM chain, which is influenced by kinetic energy. The delta function constrains the local incompressibility condition. Taking the Hubbard–Stratonovich transformation and the saddle-point approximation,³⁷ the particle form of the partition function can be transformed into the mean field form of the partition function as

$$\mathcal{Z} \propto \int \int \int \int \exp(-H[\mu_{+}, \mu_{1}, \mu_{2}, \mathbf{M}]) \mathcal{D}\mu_{+} \mathcal{D}\mu_{1} \mathcal{D}\mu_{2} \mathcal{D}\mathbf{M}$$
(9)

The free energy per chain in the unit of thermal energy $k_{\rm B}T$ at temperature *T*, where $k_{\rm B}$ is the Boltzmann constant, can be expressed as

$$\frac{H}{\eta k_{\rm B}T} = \frac{1}{V} \int_{\mathcal{B}} \left(\frac{1}{4N\zeta_1} \mu_1^2(\mathbf{r}) + \frac{1}{4N\zeta_2} \mu_2^2(\mathbf{r}) - \mu_{\rm +}(\mathbf{r}) \right) d\mathbf{r} + \frac{1}{2\eta NV} \int_{\mathcal{B}} \mathbf{M}(\mathbf{r}) \colon \mathbf{M}(\mathbf{r}) d\mathbf{r} - \log Q$$
(10)

The single-chain free energy, $H/nk_{\rm B}T$, of the system can be divided into three parts: interfacial energy $H_{\rm inter}/nk_{\rm B}T$, orientation interaction energy $H_{\rm orien}/nk_{\rm B}T$, and entropic energy $-TS/nk_{\rm B}T$. .

$$\frac{H_{\text{inter}}}{nk_{\text{B}}T} = \frac{1}{V} \int_{\mathcal{B}} \frac{1}{4N\zeta_1} \mu_1^2(\mathbf{r}) + \frac{1}{4N\zeta_2} \mu_2^2(\mathbf{r}) - \mu_+(\mathbf{r}) d\mathbf{r},$$

$$\frac{H_{\text{orien}}}{nk_{\text{B}}T} = \frac{1}{2\eta NV} \int_{\mathcal{B}} \mathbf{M}(\mathbf{r}) \colon \mathbf{M}(\mathbf{r}) d\mathbf{r},$$

$$\frac{-TS}{nk_{\text{B}}T} = -\log Q$$
(11)

where $\mu_1(r)$ and $\mu_2(r)$ are general "exchange" chemical potentials of the system, $\mu_+(r)$ is the "pressure" chemical potential to ensure the local incompressibility of the system, $\mathbf{M}(r)$ is the orientation tension field of semiflexible segments, and Q is the single chain partition function. The parameters in eqn 10 are defined by

$$\begin{aligned} \zeta_1 &= \frac{-\Delta}{4\chi_{AB}}, \qquad \zeta_2 &= \chi_{AB}, \\ \Delta &= \chi_{AB}^2 + \chi_{AR}^2 + \chi_{BR}^2 - 2\chi_{AB}\chi_{AR} \\ &- 2\chi_{AB}\chi_{BR} - 2\chi_{AR}\chi_{BR} \end{aligned}$$

The mean fields $\omega_{\alpha}(r)$ ($\alpha \in \{A, B, R\}$) are the function of $\mu_{+}(r)$, $\mu_{1}(r)$, $\mu_{2}(r)$

$$\omega_a(\mathbf{r}) = \mu_+(\mathbf{r}) - \sigma_{1a}\mu_1(\mathbf{r}) - \sigma_{2a}\mu_2(\mathbf{r})$$
(12)

where

$$\sigma_{1A} = \frac{1}{3}, \quad \sigma_{1R} = -\frac{2}{3}, \quad \sigma_{1B} = \frac{1}{3},$$

$$\sigma_{2A} = \frac{1+\alpha}{3}, \quad \sigma_{2R} = \frac{1-2\alpha}{3}, \quad \sigma_{2B} = \frac{\alpha-2}{3},$$

$$\alpha = \frac{\chi_{AB} + \chi_{AR} - \chi_{BR}}{2\chi_{AB}}$$

The partition function of single chain Q is determined by

$$Q = \frac{1}{V} \int q_{B}(\boldsymbol{r}, s) q_{B}^{\dagger}(\boldsymbol{r}, s) d\boldsymbol{r}, s \in I_{B}$$
(13)

where flexible forward propagator $q_B(\mathbf{r}, s)$ describes the probability of finding the *s*-th segment at a spatial position \mathbf{r} ranging from s = 0 to $s = f_B$ under the mean field $\omega_B(\mathbf{r})$. Similarly, the flexible backward propagator $q_B^{\dagger}(\mathbf{r}, s)$ represents the probability from $s = f_B$ to s = 0. Both the $q_B(\mathbf{r}, s)$ and $q_B^{\dagger}(\mathbf{r}, s)$ satisfy the modified diffusion equations (MDEs)

$$\frac{\partial}{\partial s}q_{\mathbf{B}}(\mathbf{r},s) = \nabla_{\mathbf{r}}^{2}q_{\mathbf{B}}(\mathbf{r},s) - \omega_{\mathbf{B}}(\mathbf{r})q_{\mathbf{B}}(\mathbf{r},s),$$

$$q_{\mathbf{B}}(\mathbf{r},0) = 1, s \in I_{\mathbf{B}}$$
(14)

$$\frac{\partial}{\partial s} q_{\mathbf{B}}^{\dagger}(\mathbf{r}, s) = \nabla_{\mathbf{r}}^{2} q_{B}^{\dagger}(\mathbf{r}, s) - \omega_{B}(\mathbf{r}) q_{B}^{\dagger}(\mathbf{r}, s),$$

$$q_{\mathbf{B}}^{\dagger}(\mathbf{r}, 0) = \int q_{R_{1}}(\mathbf{r}, \mathbf{u}, f_{R_{1}}) q_{R_{2}}(\mathbf{r}, \mathbf{u}, f_{R_{2}}) d\mathbf{u}, s \in I_{B}$$
(15)

The propagators $q_{A_1}(\mathbf{r}, s)$, $q_{A_2}(\mathbf{r}, s)$, $q_{A_1}^{\dagger}(\mathbf{r}, s)$, and $q_{A_2}^{\dagger}(\mathbf{r}, s)$ of flexible A_1 and A_2 blocks satisfy similar MDEs

$$\frac{\partial}{\partial s} q_{A_1}(\boldsymbol{r}, s) = \varepsilon^2 \nabla_{\mathbf{r}}^2 q_{A_1}(\boldsymbol{r}, s) - \omega_A(\boldsymbol{r}) q_{A_1}(\boldsymbol{r}, s),$$

$$q_{A_1}(\boldsymbol{r}, 0) = 1, s \in I_{A_1}$$
(16)

$$\frac{\partial}{\partial s} q_{A_1}^{\dagger}(\boldsymbol{r}, s) = \varepsilon^2 \nabla_{\boldsymbol{r}}^2 q_{A_1}^{\dagger}(\boldsymbol{r}, s) - \omega_{A}(\boldsymbol{r}) q_{A_1}^{\dagger}(\boldsymbol{r}, s),$$

$$q_{A_1}^{\dagger}(\boldsymbol{r}, 0) = \int q_{R_1}^{\dagger}(\boldsymbol{r}, \mathbf{u}, f_{R_1}) \, \mathrm{d}\mathbf{u}, \, s \in I_{A_1}$$
(17)

$$\frac{\partial}{\partial s}q_{A_2}(\mathbf{r},s) = \varepsilon^2 \nabla_{\mathbf{r}}^2 q_{A_2}(\mathbf{r},s) - \omega_{A}(\mathbf{r})q_{A_2}(\mathbf{r},s),$$

$$q_{A_2}(\mathbf{r},0) = 1, s \in I_{A_2}$$
(18)

$$\frac{\partial}{\partial s} q_{A_2}^{\dagger}(\mathbf{r}, s) = \varepsilon^2 \nabla_{\mathbf{r}}^2 q_{A_2}^{\dagger}(\mathbf{r}, s) - \omega_A(\mathbf{r}) q_{A_2}^{\dagger}(\mathbf{r}, s),$$

$$q_{A_2}^{\dagger}(\mathbf{r}, 0) = \int q_{R_2}^{\dagger}(\mathbf{r}, \mathbf{u}, f_{R_2}) d\mathbf{u}, s \in I_{A_2}$$
(19)

where $\varepsilon = b_A/b_B$ measures the conformational asymmetric ratio of components *A* and *B* statistical segment lengths.

The forward propagator $q_{R_j}(\mathbf{r}, \mathbf{u}, s)$ (j = 1, 2) of the semiflexible block, physically represents the probability of finding the *s*-th segment, from the end point $s = f_{A_j}$ to $s = f_{A_j} + f_{R_j}$ at spatial position \mathbf{r} with orientation \mathbf{u} under the mean field ω_{R} . These propagators satisfy the "convection diffusion" equations

$$\begin{aligned} \frac{\partial}{\partial s} q_{R_1}(\boldsymbol{r}, \, \mathbf{u}, \, s) &= -\beta \mathbf{u} \cdot \nabla_{\!\!\boldsymbol{r}} q_{R_1}(\boldsymbol{r}, \, \mathbf{u}, \, s) \\ &- \Gamma(\boldsymbol{r}, \, \mathbf{u}) q_{R_1}(\boldsymbol{r}, \, \mathbf{u}, \, s) + \frac{1}{2\lambda} \nabla_{\!\!\mathbf{u}}^2 q_{R_1}(\boldsymbol{r}, \, \mathbf{u}, \, s), \\ q_{R_1}(\boldsymbol{r}, \, \mathbf{u}, \, 0) &= \frac{q_{A_1}(\boldsymbol{r}, f_{A_1})}{2\pi}, \, s \in I_{R_1} \end{aligned}$$
(20)

$$\frac{\partial}{\partial s}q_{R_2}(\mathbf{r}, \mathbf{u}, s) = \beta \mathbf{u} \cdot \nabla_{\mathbf{r}} q_{R_2}(\mathbf{r}, \mathbf{u}, s)
- \Gamma(\mathbf{r}, \mathbf{u}) q_{R_2}(\mathbf{r}, \mathbf{u}, s) + \frac{1}{2\lambda} \nabla_{\mathbf{u}}^2 q_{R_2}(\mathbf{r}, \mathbf{u}, s),
q_{R_2}(\mathbf{r}, \mathbf{u}, 0) = \frac{q_{A_2}(\mathbf{r}, f_{A_2})}{2\pi}, s \in I_{R_2}$$
(21)

where $\Gamma(\mathbf{r}, \mathbf{u}) = \omega_{R}(\mathbf{r}) - \mathbf{M}(\mathbf{r})$: $\left(\mathbf{uu} - \frac{1}{2}\mathbf{I}\right)$ is \mathbf{r}, \mathbf{u} dependent field, $\beta = (b_{R}/b_{B})(6N)^{1/2}$ is the aspect ratio of the rods. Similarly, backward propagators of the semiflexible blocks R_{1} and R_{2} can be written as

$$\frac{\partial}{\partial s}q_{R_{1}}^{\dagger}(\boldsymbol{r}, \mathbf{u}, s) = \beta \mathbf{u} \cdot \nabla_{\mathbf{r}} q_{R_{1}}^{\dagger}(\boldsymbol{r}, \mathbf{u}, s)
- \Gamma(\boldsymbol{r}, \mathbf{u}) q_{R_{1}}^{\dagger}(\boldsymbol{r}, \mathbf{u}, s) + \frac{1}{2\lambda} \nabla_{\mathbf{u}}^{2} q_{R_{1}}^{\dagger}(\boldsymbol{r}, \mathbf{u}, s),
q_{R_{1}}^{\dagger}(\boldsymbol{r}, \mathbf{u}, 0) = \frac{q_{B}(\boldsymbol{r}, f_{B}) q_{R_{2}}(\boldsymbol{r}, \mathbf{u}, f_{R_{2}})}{2\pi}, s \in I_{R_{1}}$$
(22)

$$\frac{\partial}{\partial s}q_{R_2}^{\dagger}(\boldsymbol{r}, \mathbf{u}, s) = -\beta \mathbf{u} \cdot \nabla_{\boldsymbol{r}} q_{R_2}^{\dagger}(\boldsymbol{r}, \mathbf{u}, s)$$
$$-\Gamma(\boldsymbol{r}, \mathbf{u})q_{R_2}^{\dagger}(\boldsymbol{r}, \mathbf{u}, s) + \frac{1}{2\lambda} \nabla_{\mathbf{u}}^2 q_{R_2}^{\dagger}(\boldsymbol{r}, \mathbf{u}, s),$$
$$q_{R_2}^{\dagger}(\boldsymbol{r}, \mathbf{u}, 0) = \frac{q_B(\boldsymbol{r}, f_B)q_{R_1}(\boldsymbol{r}, \mathbf{u}, f_{R_1})}{2\pi}, s \in I_{R_2}$$
(23)

The SCFT equations obtained from the first-order variational derivative of the free energy with respect to the field function are

	Morphology	Density of component A	Density of component B	Density of component R	Local orientation distribution	Diffraction patterns of components A and B
(a1) SmA-AR		1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0		
(a2) SmA-ABR	1	1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0		•
(b1) SmP-ABR	1	1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0	$\rightarrow \rightarrow $	•
(b2) SmP-BR		1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0		
(c1) Chol-AR	0	0.5	1.0 0.5 0.0	1.0 0.5 0.0		•
(c2) Chol-ABR		1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0		
(d) Zig-ABR		1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0		

Figure 2. Layered structures self-assembled from TLCMs. Smectic-A phases (a1) SmA-AR; (a2) SmA-ABR; Smectic-P phases (b1) SmP-ABR; (b2) SmP-BR; Cholesteric phases (c1) Chol-AR; (c2) Chol-ABR; and Zigzag phase (d) Zig-ABR. In the second column, red, green, and blue represent components A, B, and R with high concentrations, respectively. The third, fourth, and fifth columns present the density distributions of components A, B, and R, respectively. The sixth column exhibits the orientation distribution of the region framed by the white line in the second column. The last column shows the main diffraction peaks of components A (red) and B (green).

$$\begin{aligned} \phi_{A}(\mathbf{r}) + \phi_{B}(\mathbf{r}) + \phi_{R}(\mathbf{r}) - 1 &= 0, \\ \frac{1}{2N\zeta_{1}}\mu_{1}(\mathbf{r}) - \sigma_{1A}\phi_{A}(\mathbf{r}) - \sigma_{1R}\phi_{R}(\mathbf{r}) - \sigma_{1B}\phi_{B}(\mathbf{r}) &= 0, \\ \frac{1}{2N\zeta_{2}}\mu_{2}(\mathbf{r}) - \sigma_{2A}\phi_{A}(\mathbf{r}) - \sigma_{2R}\phi_{R}(\mathbf{r}) - \sigma_{2B}\phi_{B}(\mathbf{r}) &= 0, \\ \frac{1}{\eta N}\mathbf{M}(\mathbf{r}) - \mathbf{S}(\mathbf{r}) &= 0 \end{aligned}$$

$$\begin{aligned} & (24) \qquad \phi_{B}(\mathbf{r}) &= \frac{1}{Q}\left(\int_{I_{A_{1}}}q_{A_{1}}(\mathbf{r},s)q_{A_{1}}^{\dagger}(\mathbf{r},s)ds + \int_{I_{A_{2}}}q_{A_{2}}(\mathbf{r},s)q_{A_{2}}^{\dagger}(\mathbf{r},s)ds + \int_{I_{A_{2}}}q_{A_{2}}(\mathbf{r},s)q_{A_{2}}^{\dagger}(\mathbf{r},s)ds \end{aligned}$$

$$\begin{aligned} & (25) \\ & (24) \qquad \phi_{B}(\mathbf{r}) &= \frac{1}{Q}\int_{I_{A}}q_{B}(\mathbf{r},s)q_{B}^{\dagger}(\mathbf{r},s)ds \end{aligned}$$

 $\phi_{\rm B}(\boldsymbol{r}) = \frac{1}{Q} \int_{I_{\rm B}} q_{\rm B}(\boldsymbol{r},\,s) q_{\rm B}^{\dagger}(\boldsymbol{r},\,s) \mathrm{d}s$ (26)

	Morphology	Density of component A	Density of component B	Density of component R	Diffraction patterns of components A and B
(a) Triangle		1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0	
(b) Square		1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0	
(c) Diamond		1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0	
(d) Pentagon		1.0 0.5 0.0	1.0 0.5 0.0	1.0 0.5 0.0	
(e) Hexagon		1.0 00000000000000000000000000000000000	1.0 0.5 0.0	1.0 0.5 0.0	
(f) Dual-Pentagon		1.0 0.5 0.0	1.0 0.5 0.0 0.0	1.0 0.5 0.0	

Figure 3. Simple polygonal phases self-assembled from TLCMs. (a) Triangle; (b) Square; (c) Diamond; (d) Pentagon; (e) Hexagon; and (f) Dual-Pentagon. The second column presents the morphologies combined with schematic arrangement diagrams, in which *A*-, *B*-, and *R*-rich domains are plotted in red, green, and blue colors, respectively. The third, fourth, and fifth columns show the density distributions of components *A*, *B*, and *R*, respectively. The last column shows the main diffraction peaks of components *A* (red) and *B* (green).

$$\phi_{\mathbf{R}}(\mathbf{r}) = \frac{2\pi}{Q} \left(\int_{I_{R_{1}}} \int q_{R_{1}}(\mathbf{r}, \mathbf{u}, s) q_{R_{1}}^{\dagger}(\mathbf{r}, \mathbf{u}, s) d\mathbf{u} ds + \int_{I_{R_{2}}} \int q_{R_{2}}(\mathbf{r}, \mathbf{u}, s) q_{R_{2}}^{\dagger}(\mathbf{r}, \mathbf{u}, s) d\mathbf{u} ds \right)$$
(27)

$$\mathbf{S}(\mathbf{r}) = \frac{2\pi}{Q} \left(\int_{I_{R_1}} \int q_{R_1}(\mathbf{r}, \mathbf{u}, s) \left(\mathbf{u}\mathbf{u} - \frac{1}{2}\mathbf{I} \right) q_{R_1}^{\dagger}(\mathbf{r}, \mathbf{u}, s) \mathrm{d}\mathbf{u} \mathrm{d}s \right. \\ \left. + \int_{I_{R_2}} \int q_{R_2}(\mathbf{r}, \mathbf{u}, s) \left(\mathbf{u}\mathbf{u} - \frac{1}{2}\mathbf{I} \right) q_{R_2}^{\dagger}(\mathbf{r}, \mathbf{u}, s) \mathrm{d}\mathbf{u} \mathrm{d}s \right)$$
(28)

where $\phi_{\alpha}(r)$ ($\alpha \in \{A, B, R\}$) and S(r) are the monomer density of the α -block and the orientational order parameter, respectively.

Theoretical study of the phase behavior of complex block copolymer systems within the SCFT framework generally follows two steps.^{40,41} The first step is to construct a library of candidate structures, which should contain as many candidate phases as possible. The construction of the candidate phases is inspired by relevant experimental and simulated findings, as well as theoretical considerations.^{40,41} The

second step uses an accurate and efficient algorithm to calculate the free energies of these candidate phases and then analyzes their relative stability. The phase diagram is then constructed by comparing the free energies of all candidate phases.

In the current study, we are interested in the stability of polygonal phases and their transition sequences. These two-dimensional polygonal phases can be regarded as columnar structures because of their homogeneity perpendicular to the polygonal plane. For these twodimensional phases, the computations can be confined to twodimensional space. The orientational calculation can be realized on the unit circle. The most time-consuming step of solving the SCFT equations is computing these propagators, which are solutions of the partial different equations. We employed the fourth-order backward differentiation⁴² and fourth-order Runge–Kutta methods⁴³ to solve the flexible and semiflexible propagators equation, respectively. The pseudospectral method is used to treat both spatial and orientational variables due to periodic boundary conditions.44-46 An accelerated hybrid scheme that combines alternate iteration and conjugate gradient methods is utilized to search for the equilibrium states⁴⁷ and optimize the computational box. We carry out a parallel implementation in C++ language, utilizing the FFTW-MPI package,⁴⁸ to accelerate the SCFT



Figure 4. Giant polygonal phases: (g) $Diamond_{8j}$ (h) $Square_{8j}$ (i) $Hexagon_{8j}$ (j) $Pentagon_{9j}$ and (k) $Square_{10}$. The meanings represented by subfigures are similar to Figure 3.

computation. Section S2 in the Supporting Information presents a detailed description of these algorithms.

RESULTS AND DISCUSSION

Equilibrium Phases. Based on extensive simulations, we obtained ten-layered and sixteen-polygonal phases as candidate phases for the TLCMs. The layered phases include smectic-A (SmA-AR, SmA-ABR, SmA-AB), smectic-P (SmP-ABR, SmP-BR, SmP-AB), cholesteric (Chol-AR, Chol-ABR, Chol-AB), and zigzag (Zig-ABR) phases. More detail of smectic phases can refer to Section S3. The density distributions of components A, B, R, and the local orientation distribution of component R in these layered phases are presented in Figures 2 and S2. The diffraction patterns obtained by Fourier transformation (see Section S2.1 for details) of the density distributions are also presented in these figures. The primary diffraction patterns of components A and B are marked with red and green dots, respectively. The sizes of these dots are proportional to the intensities of diffraction peaks. We scale the size of the diffraction peak dots of component A to be smaller than those of *B* to ensure that the main green dots will not be obscured by the red dots.

The polygonal phases are classified into simple polygons (Figure 3) and giant polygons (Figures 4 and 5), based on the number of R-rich domains on the polygonal edges. In simple polygons, the number of polygonal edges is equal to the number

of R-rich domains, whereas in giant polygons, the number of polygonal edges is smaller than the number of R-rich domains. The naming rules for these polygons are determined by both their polygonal shape (PS) and the number of R-rich domains (NR) on the polygonal edges, denoted as PS_{NR} . For the simple polygons, the subscript is omitted. Figures 3-5 display the polygonal structures combined with molecular arrangement diagrams, the density distributions of components A, B, and R, and the diffraction patterns of components A and B. In simple polygons, the edges, vertices, and interiors of the Triangle, Diamond, Square, Pentagon, and Hexagon are composed of R-, A-, and B-rich domains. The density distribution of A- and B-rich domains in the Dual-Pentagon⁹ exhibits a reciprocal relationship to that of the Pentagon, as illustrated in Figure 3f. The phases in Figure 5m,n are named as Hexagon₁₀ having a hexagonal shape containing ten R-rich domains. The phase depicted in Figure 5m has more pronounced stretching on the B-rich domains, causing deformation of the hexagonal shape. This phase is named S-Hexagon₁₀, with the 'S' prefix indicating more stretching on the B-rich domains.

We focus on studying the influence of the side chain length and the block–block interactions on the stability of polygonal phases. To ensure the stability of polygonal phases, a specific set of parameters, $\varepsilon = 1$, $\lambda = 300$, $\beta = 6$, $\eta = 0.35$, $f_{R_1} = f_{R_2} = 0.10$, $f_{A_1} = (1 - f_B - f_{R_1} - f_{R_2})/2$ and $f_{A_2} = f_{A_2}$, are selected, while the rest of



Figure 5. Giant polygonal phases: (1) Pentagon₁₀; (m) S-Hexagon₁₀; (n) Hexagon₁₀; (o) Square₁₂; and (p) Hexagon₁₂. The meanings of each subfigure are similar to Figure 3.

parameters could vary. To guarantee sufficient precision of the SCFT calculations, we scan the phase space by primarily using discrete grids according to ordered phases and interaction strengths (see Table S1). The termination criterion of self-consistent field iteration is the free energy difference between two consecutive iterations less than 10^{-8} . For convenience, we designate χ_{AB} as χ and use it as a reference, and express χ_{BR} and χ_{AR} as functions of χ . **Stability of Polygonal Phases.** In the experiments, the end

A blocks can form hydrogen bonds.^{11,16} We can use attractive A-A interactions $\overline{\chi}_{AA}$ with negative value to model the hydrogen-bond interaction, arising the variation of effective Flory–Huggins parameters χ_{ij} .³⁹ Consequently, we investigate the influence of the attractive A-A interactions of stabilizing polygonal phases. We simulate the phase behavior for distinct χ_{ii} with $\chi \in [0.36, 0.44]$. Seven phase diagrams in the (χ, f_B) -plane have been constructed with combinations of the parameters χ_{ii} as presented in Figure S3. The free energy difference in determining the phase boundaries is about 10^{-4} . It is evident that seven phase diagrams exhibit similar phase behaviors. As $f_{\rm B}$ increases, phase transitions occur, from layered structures, to simple polygons, to giant polygons, and then to layered structures again. These results demonstrate that a slight perturbation of χ_{ij} has negligible influence on the relative stability of candidate structures, and only leads to a slight change in phase boundaries. These phase diagrams also allow us to

systematically investigate the impact of interaction strength by considering only one of the seven cases. Specially, we expand χ to [0.20, 0.46], with $\chi_{AR} = \chi + 0.04$, $\chi_{BR} = \chi - 0.02$, and vary f_B . A detailed phase diagram, as shown in Figure 6, can be constructed with respect to f_B and χ . This phase diagram presents much rich phase behaviors by varying χ and f_B . In the following, we will carefully analyze the impact of parameters χ and f_B on the phase transitions.



Figure 6. Phase diagram of TLCMs in the χ - f_B plane with $\chi_{AR} = \chi + 0.04$, $\chi_{BR} = \chi - 0.02$, N = 100, $f_{R_1} = f_{R_2} = 0.10$. The red and blue dashed lines mark the phase sequence of $\chi = 0.44$ and $f_B = 0.58$, respectively.

https://doi.org/10.1021/acs.macromol.3c02295 Macromolecules 2024, 57, 2154-2164 **Influence of Interaction Parameter** χ . We examine the phase transition path from layers to simple polygons, and to giant polygons by varying χ and fixing f_B . When $f_B = 0.58$, a phase sequence emerges, taking the system from the SmP-ABR (0.25 $\leq \chi < 0.27$) to the simple Hexagon polygon ($0.27 \leq \chi < 0.293$), and to the giant Hexagon₈ polygon ($\chi \geq 0.293$), as shown by the blue dash line in Figure 6. The energy curves, taking the SmP-ABR phase as the baseline, are plotted in Figure 7a. To better analyze the factors influencing the stability, we split



Figure 7. (a) Free energy, (b) interfacial energy, (c) orientation interaction energy and (d) entropic energy of the Hexagon (blue line) and Hexagon₈ (green line) relative to the SmP-ABR (red line) along increasing χ values for fixed $\chi_{AB} = \chi$, $\chi_{AR} = \chi + 0.04$, $\chi_{BR} = \chi - 0.02$, $f_B = 0.58$, $f_{R_1} = f_{R_2} = 0.10$, and N = 100.

the free energy into three parts, the interfacial energy $H_{\rm inter}$ $nk_{\rm B}T$, the orientation interaction energy $H_{\rm orien}/nk_{\rm B}T$, and the entropy energy $-TS/nk_{\rm B}T$, see the definition in eqn 11. The density distribution demonstrates that polygonal structures have more A-, B-, and R-rich subdomains than the layered SmP-ABR, and Hexagon₈ has the most subdomains among the three patterns. As shown in Figure 7b, the more subdomains the structure has, the larger interfacial energy the system has. On the other hand, more subdomains provide an opportunity that molecular chains have much freedom of stretch, thus leading to a lower entropy energy, as Figure 7d illustrates. Meanwhile, the orientation distribution of polygonal phases, including the Hexagon and the Hexagon₈₁ are more disordered than that of the layered SmP-ABR (see Figure S4), arising a larger orientation interaction energy (see Figure 7c). Interestingly, for the polygonal phases, as χ increases, the orientation interaction energies of the Hexagon and the Hexagon₈ have an intersection point at $\chi = 0.324$. Below this intersection, the Hexagon has lower orientation interaction energy. Otherwise, the Hexagon₈ has a lower value. The reason can be attributed to the Flory-Huggins interaction.

As shown in Figure 8, with an increase of χ from 0.28 to 0.34, the peak of the *R*-rich domain in the Hexagon increases from 0.4 to 0.63, with an increment of 0.23. While the peak of the *R*-rich domain in the Hexagon₈ rises from 0.47 to 0.65, with an increment of 0.18. This indicates that as χ increases, the A-R and B-R repulsion interactions in the Hexagon increase faster than that of Hexagon₈, yielding a disordered orientation distribution. Consequently, the orientation interaction energy in the Hexagon phase gradually exceeds that in the Hexagon₈ phase. During the subtle competition among three parts of energies, the above-mentioned phase sequence emerges.



Figure 8. Solid and dashed lines represent the density distributions of the Hexagon₈ and Hexagon, respectively. (a) $\chi = 0.28$, (b) $\chi = 0.34$ for fixed $L_x/4$ (see Figure S5), $\chi_{AB} = \chi$, $\chi_{AR} = \chi + 0.04$, $\chi_{BR} = \chi - 0.02$, $f_B = 0.58$, $f_{R_1} = f_{R_2} = 0.10$, and N = 100.

Influence of Volume Fraction f_{B} . Here, we consider the effect of volume fraction f_B on the stability of candidate patterns. For a fixed $\chi = 0.44$, an interesting phase sequence of Chol-AR \rightarrow SmA-AR \rightarrow SmA-ABR \rightarrow Chol-ABR \rightarrow Triangle \rightarrow Dual- $Pentagon \rightarrow Square \rightarrow Pentagon \rightarrow Hexagon \rightarrow Hexagon_8 \rightarrow$ Hexagon₁₀ \rightarrow SmP-AB appears as f_B increases. The free energy curves of these structures relative to the homogeneous phase are plotted in Figure 9a. To better analyze the factors of influencing stability, we again separate the free energy into three parts, the interfacial energy, the orientational interaction energy, and the entropic energy. When the volume factor f_B is smaller than 0.14, the length of the B subchain is too small to separate from the Rrich domain, leading to the formation of the two-layered phases of Chol-AR (0.045 < $f_B \le$ 0.065) and SmA-AR (0.065 < $f_B \le$ 0.14). As f_B increases, monomer-*B* can condensate into the new B-rich layer, causing three layered patterns of SmA-ABR (0.14 < $f_B \leq 0.214$) and Chol-ABR (0.214 < $f_B \leq 0.218$). It is noted that the SCFT calculation predicts stable Chol-AR and Chol-ABR, which were not observed experimentally. This discrepancy might be attributed to the thermodynamic fluctuations, which are not accurately captured by the SCFT. When 0.218 < $f_B \leq$ 0.657, the system enters the stability region of polygonal phases. Compared to layered phases, polygonal structures possess more A-, B-, and R-rich subdomains which increase the interfacial energy (see Figure 9b). These divided subdomains also disrupt the parallel arrangement of rigid blocks resulting in a small increase of the orientation interaction energy (see Figure 9c). On the other hand, these subdomains in polygonal phases also make the chain arrangement more flexible, thus increasing the configurational entropy (see Figure 9d). The arising entropy energy is more than the unfavorable interfacial and orientation energies, driving the phase transition from layered phases to polygonal phases. In the range of polygonal phases, as the relative length of the *B* block increases, the interior of the *B*-rich domain swells. To alleviate the packing frustration of compressing the B-rich domain, the system increases the number of polygonal edges, driving a phase transition from simple polygons to giant polygons when $f_B > 0.56$. Meanwhile, several novel metastable giant polygons are also observed, including Square₈, Square₁₀, Square₁₂, Diamond₈, Pentagon₉, and Hexagon₁₂ which might be stable at more strong segregation.

Influence of the Side Chain Length. The above simulations have examined the influence of Flory-Huggins interaction χ and relative volume factor f_B on the stability of polygonal phases. Previous experiments have demonstrated that the TLCMs exhibit an interesting phase transition sequence of SmA-AR \rightarrow SmA⁺ \rightarrow Triangle \rightarrow Diamond \rightarrow Square \rightarrow Pentagon \rightarrow Hexagon \rightarrow Hexagon₁₀ \rightarrow Pentagon₁₀ \rightarrow Lamellar \rightarrow bicontinuous cubic phases when pubs.acs.org/Macromolecules



Figure 9. (a) Free energy, (b) interfacial energy, (c) orientation interaction energy, and (d) entropic energy of the candidate phases relative to the homogeneous phase by varying f_B when $\chi_{AB} = 0.44$, $\chi_{BR} = 0.42$, N = 100, and $f_{R_1} = f_{R_2} = 0.10$.



Figure 10. Phase transition as N_B increases with $\chi_{AB} = 0.36$, $\chi_{AR} = 0.40$, $\chi_{BR} = 0.34$, $N_{A_1} = N_{A_2} = 10$, and $N_{R_1} = N_{R_2} = 10$.

the side chain length of TLCMs is increased.^{7,11,16} In what follows we theoretically investigate this phase transition sequence by varying the side chain length. To model the experimental systems, we use the monomer number N_i ($i \in \{A_1, i\}$ A_2 , B_1 , R_1 , R_2) to describe the block length. Varying N_i is equivalent to changing the length of the different blocks. Based on the aforementioned calculations, we fix a set of parameters $\chi_{AB} = 0.36, \chi_{AR} = 0.40, \chi_{BR} = 0.34, N_{A_1} = N_{A_2} = 10, N_{R_1} = N_{R_2} = 20,$ and change $N_{\rm B}$. With an increase in the side chain length $N_{\rm B}$, the SCFT calculations obtain a phase transition sequence of SmA- $AR \rightarrow SmA-ABR \rightarrow Triangle \rightarrow Square \rightarrow Pentagon \rightarrow$ $Hexagon \rightarrow Hexagon_8 \rightarrow Hexagon_{10} \rightarrow SmP-ABR \rightarrow SmP-BR$ \rightarrow Nematic phase, as shown in Figure 10. The reason for forming the nematic phase when $351 \le N_B \le 370$ may be ascribed to the microphase separation of different chemical components. As a result, the concentration of a rigid backbone in the R-rich domain is high and can lead to the long-range orientation order. The theoretical phase transition sequence is consistent with existing experimental observations.^{7,11,16} There are slight differences between the experimental observations and our theoretical predictions. For example, our theoretical results indicate that the Pentagon₁₀ and Diamond phases are metastable (see Figure S6), while these phases were reported as stable ones in experiments. This discrepancy might be ascribed to the fact that our simulation parameters could be not entirely identical to the experimental conditions, or due to the use of the Gaussian chain model to describe short flexible chains.

CONCLUSIONS

In summary, we have established a SCFT model of TLCMs to investigate the formation and stability of polygonal phases. The development of an accurate and efficient numerical method for SCFT equations enables us to construct a set of phase diagrams by precisely computing the free energy of different selfassembled ordered structures. We examined the influence of the side chain length and the interaction strength on the stability of polygonal phases and their transitions. We systematically analyzed the stability mechanism by examining the free energy. The resulting phase transition sequences are in good agreement with experimental observation. Several new metastable polygonal structures and several smectic, cholesteric, and zigzag layers are also predicted in our study. These theoretical findings fill the gap between theoretical understanding and experimental observation of the phases and phase transitions of TLCMs. In the future, we will investigate complicated phases and phase transitions in more liquid crystalline molecular systems based on the SCFT and advanced numerical methods developed in the current study.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.3c02295.

Free energy of homogeneous phase, Numerical methods, Figures S1–S6, and Table S1 PDF

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Notes

The authors declare no competing financial interest.

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