

Phase and orientational ordering of A–B–A tri-block co-polymers guest in a quenched host of low molecular weight rod molecules

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Abstract

We investigate the effects of thermodynamical variables, intermolecular interactions and block lengths on phase and orientational ordering of guest tri-block co-polymers in a host glassy matrix of short molecular rods. The A and B blocks can align to the short rod molecules. Using a field theoretic formulation we demonstrate the occurrence of a nematic–nematic (N/N) first order transition from a guest stabilized to a guest–host stabilized region, a reentrant transition from a guest stabilized nematic region to a host only stabilized regime via an isotropic phase and the possibility to selectively stabilize the orientation of the A or B blocks.

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Co-polymers and short molecular rod molecules are instrumental in the supra-molecular construction of guest–host systems. Manipulation of the guest–host interaction alignment and co-polymer composition opens new avenues for the design of technologically valuable properties [1–3]. While di-block co-polymers have been studied in the context of possible self-assembly patterns and their interactions with nanoparticles [4–6] tri-block co-polymers received less attention. When made of stiff non-adjacent blocks and a middle flexible block and incorporated in a semi-flexible polypropylene (PP) [7], tri-block co-polymers can increase significantly the host toughness and mechanical stability. The effects of additives such as salts, alkali acids, polymers and ionic surfactants on the cloud points in hydrophilic/hydrophobic

tri-block co-polymers has been studied recently [8]. In bio-medicine tri-block co-polymers made of *PLGA-PEG-PLGA* are instrumental in enhancement of gene transfection efficiency of various cationic polymeric carriers and as additives in non-viral gene transfection [9].

Manipulation of molecular alignment is important in optical materials used in dichroic polarizers and to holographic data storage. Experiments demonstrated [14–16] that manipulation of molecular features of a B trypticene block in an A–B–A tri-block co-polymer immersed in a host of short rods can have dramatic effects on guest alignment and shifting times. Effects of composition on ordering in flexible tri-block co-polymers have been addressed [10], yet, to our knowledge the effects of dissimilarity in block rigidity and the effect of a host of short rods molecules on the orientational ordering of the different tri-block segment types was not studied. Herein we investigate the phase diagram and orientational ordering of a guest

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of A–B–A tri-block co-polymers mixed with short molecular rods. A typical guest–host system is depicted in Fig. 1. The simplest microscopic Hamiltonian for the A–B–A tri-block/short rod mixture that captures these interaction alignment features is

$$\begin{aligned}
 H = & \sum_{i=1}^N \left(\int_0^{L_A} + \int_{L_A+L_B}^L \right) \frac{\beta\epsilon_{A,A}}{2} \dot{\mathbf{u}}^2(n_i) dn_i \\
 & + \int_{L_A}^{L_A+L_B} \frac{\beta\epsilon_{B,B}}{2} \dot{\mathbf{u}}^2(n_i) dn_i - \frac{w_{r,r}}{2} \sum_{k,l=1}^{M,M} \delta(\mathbf{r}_k - \mathbf{r}_l) \\
 & \times (1 - (\mathbf{u}_k \times \mathbf{u}_l)^2) - w_{r,A} \sum_{i,k=1}^{N,M} \left(\int_0^{L_A} + \int_{L_A+L_B}^L \right) \\
 & \times dn_i \delta(\mathbf{r}(n_i) - \mathbf{r}_k) (1 - (\mathbf{u}(n_i) \times \mathbf{u}_k)^2) \\
 & - w_{r,B} \sum_{i,k=1}^{N,M} \int_{L_A}^{L_A+L_B} dn_i \delta(\mathbf{r}(n_i) - \mathbf{r}_k) (1 - (\mathbf{u}(n_i) \times \mathbf{u}_k)^2) \\
 & - \frac{w_{A,A}}{2} \sum_{i,j=1}^{N,N} \left(\int_0^{L_A} + \int_{L_A+L_B}^L \right) dn_i \left(\int_0^{L_A} + \int_{L_A+L_B}^L \right) \\
 & \times dn'_j \delta(\mathbf{r}(n_i) - \mathbf{r}(n'_j)) \left(1 - (\mathbf{u}(n_i) \times \mathbf{u}(n'_j))^2 \right) - \frac{w_{A,B}}{2} \\
 & \times \sum_{i,j=1}^{N,N} \left(\int_0^{L_A} + \int_{L_A+L_B}^L \right) dn_i \int_{L_A}^{L_A+L_B} dn'_j \delta(\mathbf{r}(n_i) - \mathbf{r}(n'_j)) \\
 & \times \left(1 - (\mathbf{u}(n_i) \times \mathbf{u}(n'_j))^2 \right) - \frac{w_{B,B}}{2} \sum_{i,j=1}^{N,N} \int_{L_A}^{L_A+L_B} dn_i \\
 & \times \int_{L_A}^{L_A+L_B} dn'_j \delta(\mathbf{r}(n_i) - \mathbf{r}(n'_j)) \left(1 - (\mathbf{u}(n_i) \times \mathbf{u}(n'_j))^2 \right), \quad (1)
 \end{aligned}$$

where i, j are chain indexes, k, l are indexes for the short molecular rods, M is the number of short rods and N is the number of polymer chains. $\mathbf{r}(n_i)$ is the spatial location of the n th segment on the i th chain, $\mathbf{u}(n_i)$ is the tangent vector at n_i on the backbone of the i th polymer chain. \mathbf{r}_k is the spatial location of the k th rod, \mathbf{u}_k is the director of the k th rod, L_A , L_B and L are the A block, B block and polymer lengths, respectively. First and second terms in Eq. (1) are interaction potentials among adjacent segments which reside in the A and B semi-flexible blocks and $\beta\epsilon_{A,A}/2$, $\beta\epsilon_{B,B}/2$ are the local bending penalties. Third, fourth and fifth terms in Eq. (1) represents the rod–rod, rod–A segment and rod–B segment microscopic alignment, respectively. Last three terms are the A–A, A–B and B–B interactions, respectively. Most generally the short range anisotropic potential among molecular species o, m has the form: $\frac{w_{o,m}}{2} \sum_{o,m} \delta(\mathbf{r}_o - \mathbf{r}_m) (1 - (\mathbf{u}_o \times \mathbf{u}_m)^2)$. Positive $w_{o,m}$ indicate a reduction in the o/m inter-molecular free volume from alignment of the molecular directors.

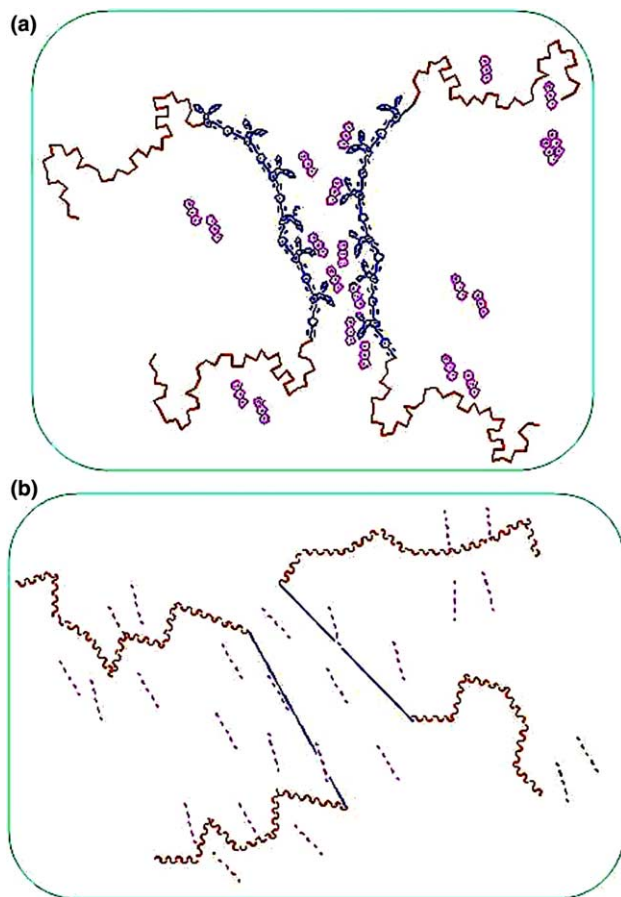


Fig. 1. Schematic representation of two symmetric tri-block copolymers in a guest–host tri-block/short rod molecular mixture: in (a) the middle block is a polystyrene polymer. The connected thin lines of the A blocks are long hydrocarbons while host matrix short rod components are the anthracene molecules. (b) is an implicit representation of (a).

First, we express Eq. (1) with microscopic densities – $\rho_m(\mathbf{r})$ and orientational tensors – $\sigma_m(\mathbf{r})$ given by:

$$\begin{aligned}
 \hat{\rho}_A(\mathbf{r}) &= \sum_i \left(\int_0^{L_A} + \int_{L_A+L_B}^L \right) dn_i \delta(\mathbf{r} - \mathbf{r}(n_i)); \\
 \hat{\rho}_B(\mathbf{r}) &= \sum_i \int_{L_A}^{L_A+L_B} dn_i \delta(\mathbf{r} - \mathbf{r}(n_i)); \\
 \rho_r(\mathbf{r}) &= \sum_k \delta(\mathbf{r} - \mathbf{r}_k); \\
 \hat{\sigma}_A^s(\mathbf{r}) &= \sum_i \left(\int_0^{L_A} + \int_{L_A+L_B}^L \right) dn_i \delta(\mathbf{r} - \mathbf{r}(n_i)) \mathbf{u}^s(n_i) \mathbf{u}^t(n_i); \\
 \hat{\sigma}_B^s(\mathbf{r}) &= \sum_i \int_{L_A}^{L_A+L_B} dn_i \delta(\mathbf{r} - \mathbf{r}(n_i)) \mathbf{u}^s(n_i) \mathbf{u}^t(n_i); \\
 \hat{\sigma}_r^s(\mathbf{r}) &= \sum_k \delta(\mathbf{r} - \mathbf{r}_{r,k}) \mathbf{u}_k^s \mathbf{u}_k^t. \quad (2)
 \end{aligned}$$

The index values of m and o , i.e., r, A and B , stand for LC rods and co-polymer A and B blocks. s, t indexes

represent the x, y, z space components. We impose now delta function constraints on the partition function of the guest–host system and exchange the discrete microscopic orientational tensors with continuous orientational tensors for LC rods and A and B segments. The LC rod endpoints are free and a local constraint is required on rod orientational fluctuations. The partition function for the guest–host system is given by

$$Z[\mathbf{u}(n_i), \mathbf{u}_k] = \left[\prod_{i=1}^N \int D\mathbf{r}(n_i) \prod_{m=A,B,r} \int D\sigma_m(\mathbf{r}) \right] \times \left[\prod_{k=1}^M \int d\mathbf{r}_k \int d\mathbf{u}_k \right] \exp(-H[\sigma_m(\mathbf{r})]) \times \prod_{i,n_i,\mathbf{r}} \delta[\sigma_A(\mathbf{r}) - \hat{\sigma}_A(\mathbf{r})] \delta[\sigma_B(\mathbf{r}) - \hat{\sigma}_B(\mathbf{r})] \times \delta[\mathbf{u}(n_i)^2 - 1] \prod_{k,r} \delta[\sigma_r(\mathbf{r}) - \hat{\sigma}_r(\mathbf{r})] \delta[\mathbf{u}_k^2 - 1]. \quad (3)$$

$\hat{\sigma}_m(\mathbf{r})$ are given in Eq. (2); the $\hat{\sigma}_m(\mathbf{r})$ delta function constraints are expressed with auxiliary fields $\psi_m(\mathbf{r})$. A global constraint set on chain director fluctuations of the A and B blocks is sufficient due to chain connectivity (viz. [17] for further details).

$$Z[\mathbf{u}(n_i), \mathbf{u}_k] = \left[\prod_{i=1}^N \int D\mathbf{r}(n_i) \prod_{m=A,B,r} \int D\psi_m(\mathbf{r}) \right] \times \left[\prod_{k=1}^M \int d\mathbf{r}_k \int d\mathbf{u}_k \right] \times \exp(-H[\hat{\sigma}_m(\mathbf{r})]) \times \prod_{i,n_i,\mathbf{r}} \exp\left(i \int d\mathbf{r} \psi_p(\mathbf{r}) : [\sigma_p(\mathbf{r}) - \hat{\sigma}_p(\mathbf{r})]\right) \times \int \prod_{p=A,B} d\lambda_p \exp(-i\lambda_p[\mathbf{u}(n_i)^2 - 1]) \times \prod_{k,r} \int d\lambda_{r,k} \exp\left(i \int d\mathbf{r} \psi_r(\mathbf{r}) : [\sigma_r(\mathbf{r}) - \hat{\sigma}_r(\mathbf{r})]\right) \times \exp\left[-i \sum_k (\lambda_{r,k}(\mathbf{u}_k^2 - 1))\right], \quad (4)$$

where k is the index of the rods. The orientational tensor matrix for the molecular species – $m = r, p$, in principal axis representation has the form:

$$\sigma_m = \begin{pmatrix} a_m - b_m & 0 & 0 \\ 0 & a_m + b_m & 0 \\ 0 & 0 & 2a_m \end{pmatrix}. \quad (5)$$

Herein, we address the orientational phase diagram and the relation among uniaxial ordering guest–host described by the average order parameter $\langle S \rangle_m$ with

$m = A, B, r$: $\langle S \rangle_m = .5 \frac{V}{N_m} \sum_{\alpha} \langle 3(\mathbf{v}_m^{\alpha} \cdot \mathbf{n}_m)^2 - 1 \rangle$. \mathbf{v}_m^{α} is the unit vector which points along the long axis of molecule α of type m located at \mathbf{r}^{α} ; N_m is the number of molecules of type m present in the system. For uniaxial ordering, the orientational order parameter, $\langle S \rangle_m$, is related to the principal axis components of the orientational tensor in the following way $\langle S \rangle_m = -3a_m/\rho_m$. $1 > \langle S \rangle_m > 0$ signals uniaxial nematic ordering while $-0.5 < \langle S \rangle_m < 0$ signals discotic ordering. In Einstein notation (alike indexes are summed over), $\sigma_m^{i,t} = \rho_m$. The tri-block entropy is calculated now exactly for finite chains by noting that:

$$S_{\text{tri-block}} = d\mathbf{u}_0 \int d\mathbf{u}_{L_A} \int d\mathbf{u}_{L_B} \int d\mathbf{u}_L G_1(\mathbf{u}_{L_A} - \mathbf{u}_0; L_A) \times G_2(\mathbf{u}_{L_B} - \mathbf{u}_{L_A}; L_B - L_A) G_1(\mathbf{u}_L - \mathbf{u}_{L_B}; L - L_B), \quad (6)$$

where G is the propagator for an harmonic oscillator in imaginary time adapted to the present polymer problem. We carry out the integrals exactly in Eq. (6) and obtain

$$S_{\text{tri-block}} = \left[\frac{A_2^{0.5}}{C_1 \sqrt{A_1(C_1 - C_1^{-1}) + A_2 C_2}} \right] \times \left[\frac{\sqrt{\pi}}{\sqrt{A_1(C_1 - C_1^{-1}) + A_2 C_2 + \frac{A_2^2 C_1}{A_1(1 - C_1^2) - A_2 C_2 C_1}}} \right], \quad (7)$$

with

$$A_1 = \frac{2e_A(\lambda_A + \psi_A)^{0.5}}{2 \sinh \left[L_A \left(\frac{2(\lambda_A + \psi_A)}{e_A} \right)^{0.5} \right]};$$

$$A_2 = \frac{2e_B(\lambda_B + \psi_B)^{0.5}}{2 \sinh \left[L_B \left(\frac{2(\lambda_B + \psi_B)}{e_B} \right)^{0.5} \right]};$$

$$C_1 = \cosh \left[L_A \left(\frac{2\lambda_A + \psi_A}{e_A} \right)^{0.5} \right];$$

$$C_2 = \cosh \left[L_B \left(\frac{2\lambda_B + \psi_B}{e_B} \right)^{0.5} \right]. \quad (8)$$

The expression above is exact for finite length blocks. Here, we consider long blocks; in fact for blocks of ≈ 15 – 20 segments, the long chain limit is very close to the exact result. With a Legendre transforms we obtain the free energy dependence on $\langle S \rangle_r$, $\langle S \rangle_A$ and $\langle S \rangle_B$. Herein, we investigate the situations where the interaction alignment among the A and B blocks is negligible. The free energy for the guest–host system, we investigate is:

$$\begin{aligned}
& F(\langle S \rangle_r, \lambda_A, \lambda_B, \langle S \rangle_A, \langle S \rangle_B) \\
&= \frac{w_{r,r}(1-\rho_p)^2}{3} \left(\langle S \rangle_r^2 + \langle S \rangle_r + 1 \right) \\
&\quad - 0.572365(1-\rho_p) - (1-\rho_p) \\
&\quad \times \log \left[\frac{\text{Erfi} \left[\sqrt{w_{r,r}(1-\rho_p)\langle S \rangle_r} \right]}{w_{r,r}(1-\rho_p)\langle S \rangle_r} \right] \\
&\quad \times \left(\frac{\rho_p qx}{1+qx} \left(-\lambda_B + \left(\left(\frac{\rho_p qx}{1+qx} (-1 + \langle S \rangle_B^2) w_{B,B} \right) / 3 \right) \right) \right) \\
&\quad + \frac{1}{\sqrt{2}} \left(\frac{1}{e_B} \right)^{0.5} \left(\left(\lambda_B - \left(2(1-\rho_p)(-1 + \langle S \rangle_r) w_{B,r} \right. \right. \right. \\
&\quad \left. \left. \left. + \left(\frac{\rho_p qx}{1+qx} (-1 + \langle S \rangle_B) w_{B,B} \right) / 3 \right)^{0.5} \right) \right) \\
&\quad + 2 \left(\lambda_B + \left((1-\rho_p)(2 + \langle S \rangle_r) w_{B,r} \right. \right. \\
&\quad \left. \left. + \left(\frac{\rho_p qx}{1+qx} (2 + \langle S \rangle_B) w_{B,B} \right) / 3 \right)^{0.5} \right) \\
&\quad + \left(\frac{\rho_p}{1+qx} \left(-\lambda_A + \left(\left(\frac{\rho_p}{1+qx} (-1 + \langle S \rangle_A^2) w_{A,A} \right) / 3 \right) \right. \right. \\
&\quad \left. \left. + \frac{1}{\sqrt{2}} \left(\frac{1}{e_A} \right)^{0.5} \left(\left(\lambda_A - \left(2(1-\rho_p)(-1 + \langle S \rangle_r) w_{A,r} \right. \right. \right. \right. \\
&\quad \left. \left. \left. + \left(\frac{\rho_p}{1+qx} (-1 + \langle S \rangle_A) w_{A,A} \right) / 3 \right)^{0.5} \right) \right) \right) \right) \\
&\quad + 2 \left(\lambda_{p,A} + \left((1-\rho_p)(2 + \langle S \rangle_r) w_{A,r} \right. \right. \\
&\quad \left. \left. + \left(\frac{\rho_p}{1+qx} (2 + \langle S \rangle_A) w_{A,A} \right) / 3 \right)^{0.5} \right). \tag{9}
\end{aligned}$$

Erfi in Eq. (9) is the imaginary error function [18]. The first four terms represent the free energy of the short rod quenched host. Other terms are free energy terms of the tri-blocks and also tri-block host interactions. $\langle S \rangle_r$, $\langle S \rangle_A$ and $\langle S \rangle_B$ are rod, A and B block orientational order parameters, respectively. qx is the block length quotient for the A and B blocks. It is given by $qx = L_B/2L_A$.

The limit $1 - \rho_p \rightarrow 0$ of Eq. (9) and $qx \rightarrow 0$ recovers the free energy of a many-chains LCPs solution obtained in Eq. (32) of reference [17], and the minimal value for uniaxial ordering $\langle S \rangle_p^c = 0.25$. The $\rho_p \rightarrow 0$ limit of Eq. (9) recovers the Mayer–Saupe [11–13] result for the magnitude of the orientational ordering at of the N–I transition of short rods, i.e., $\langle S \rangle_r^c = 0.42$. Our result $w_{r,r}^c = 6.78$ is consistent with the infinitely stiff limit of long worm like chains [19] of $w \cong 7$. The host is below the glass transition thus the free energy of the guest–host system is minimized analytically with respect to the fields $\langle S \rangle_r$, first, in the absence of the tri-block-LC rod interaction. The $\langle S \rangle_r$ obtained is used in the total free energy $-F(\langle S \rangle_r, \lambda_A, \langle S \rangle_A, \lambda_B, \langle S \rangle_B)$. Now, the free energy is optimized with respect to $\lambda_A, \langle S \rangle_A, \lambda_B, \langle S \rangle_B$ in the pres-

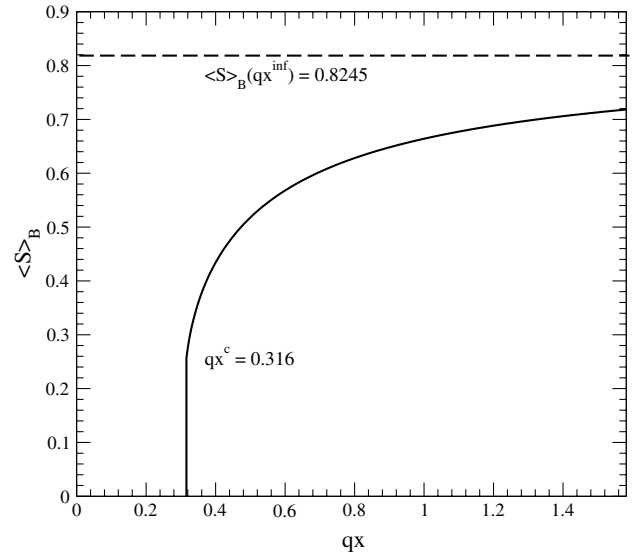


Fig. 2. Effect of the block length quotient qx on the middle block segment ordering; $\beta e_A = 0$, $\beta e_B = 7$, $w_{r,r} = 0$, $w_{B,B} = 7$, $w_{A,A} = 0$, $\rho_p = 0.9$.

ence of orientational ordering of the LC rods. The unit length chosen in all calculations, the monomer hard sphere diameter, renders chain microscopic interactions and characteristics, $L, \beta e, w, v, \rho$ dimensionless. In Fig 2, we present results for the effect of the block length quotient qx on orientational ordering of the B segment in a mixture of A–B–A tri-blocks; the A block is flexible and the B block is stiff. Fig. 2 demonstrates the existence of a lower bound for the critical block length quotient value, $qx^c = 0.316$. Below that value of qx (for the given parameters used in Fig. 2), orientational ordering of segments which reside in the stiff block B is precluded. For qx larger than qx^c , $\langle S \rangle_B$ increases fast but levels off slowly. In fact, $\langle S \rangle_B$ reaches the homo-polymer orientational ordering $\langle S \rangle$ value at very large qx . That is a direct manifestation of the nature of liquid crystallinity in polymers; the segments are connected at the endpoints with other segments and the connectivity has a significant contribution to overall polymer alignment of the blocks.

Fig. 3 displays the variation of orientational ordering with rigidity of the A and the B block, qx , and tri-block density. In the figure, the matrix of short rods orders around $\rho_r = 0.54$. For longer B blocks a transition from a guest stabilized nematic ordering to a guest + host stabilized nematic ordering occurs as a spike nematic transition. It is marked by a discontinuity in the orientational order parameter of the B segments. In Fig. 3, the transition depicted at three block length quotient values $qx = 8, 2, 1$ occurs at the density threshold $\rho_p \cong 0.455$. At larger fractions of A segments, i.e., $qx = 0.5$, a different physical picture emerges. Below $\rho_p \cong 0.6$ the presence of a short B block cannot sustain the guest stabilized orientational ordering and a

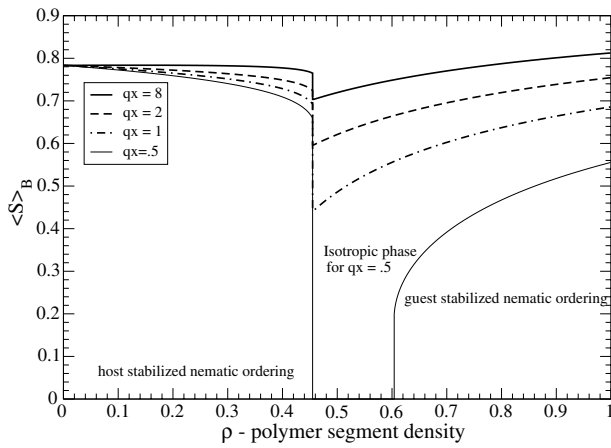


Fig. 3. Effects of block length quotient, the A and B block rigidity, and the matrix ordering on orientational ordering of the B segments; $\beta e_A = 0$, $\beta e_B = 7$, $w_{r,r} = 12.5$, $w_{A,A} = 0$, $w_{B,B} = 7$, $w_{B,r} = 3$.

transition to an isotropic phase occurs. At lower polymer densities i.e., $\rho_p = 0.54$, the glassy host orders via a typical Mayer–Saupe nematic transition. The host ordering stabilizes a non-zero average orientation of the B segments. This host stabilized nematic ordering of the B segments at low qx values occurs via a step transition from the isotropic phase. In this case the average nematic B segment director orients parallel to the host director. Thus, the reentrant transition occurs from a guest stabilized nematic phase with the average director pointed in some arbitrary direction, via an isotropic phase, to a host stabilized nematic phase with the average molecular director of the B segments aligned with the host director of the short rods. Fig. 3 suggests that the density width of the isotropic phase is controlled by the matrix ordering threshold and the tri-block copolymer quotient qx .

In Fig. 4, we present the phase diagram for A–B–A tri-blocks that reside in a LC rod glass for $qx = 1$ at dissim-

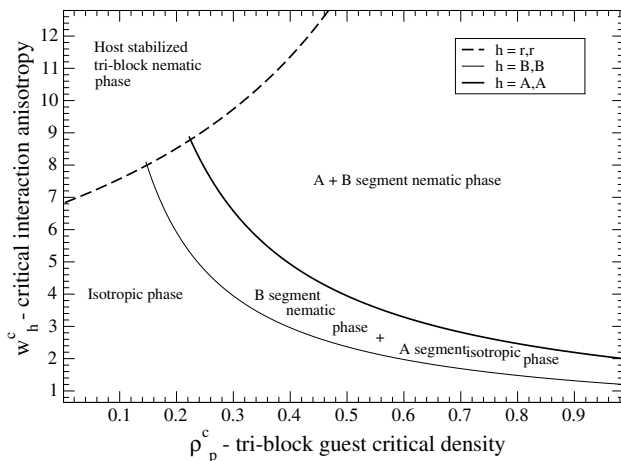


Fig. 4. Orientational phase diagram of the A and B segments – tri-block density effects; $\beta e_A = 6$, $\beta e_B = 10$, $qx = 1$, $w_{r,r} = 12.5$.

ilar bending rigidities of A and B segments, i.e., $e_A \neq e_B$. At interaction alignment values $w_{r,r}$ above the dashed line, the LC rod molecules are ordered. The A and B segments align their average director parallel to the host and an A + B nematic phase occurs. Below the thin solid line, the tri-block co-polymer resides in the isotropic phase; above the thin line a guest stabilized isotropic/nematic transition with $\langle S \rangle_B \neq 0$ occurs. In that regime of interaction alignment $w_{A,A}$, the bending rigidity of the A segment – e_A is low, and $\langle S \rangle_A = 0$. Above the thick solid line, the A segments order and a transition to an A + B guest stabilized nematic phase takes place.

Fig. 5 illustrates the orientational phase dependence on qx^c . At low values of alignment interaction parameters, $\langle S \rangle_A = 0$, $\langle S \rangle_B = 0$; $\langle S \rangle_A \neq 0$; $\langle S \rangle_B = 0$, for long A blocks and relatively low values of $w_{A,A}$. Note, the critical $w_{B,B}^c$ required for orientational ordering of the B segments is lower in $qx \rightarrow \infty$ limit than the value of $w_{A,A}^c$ value in the limit of $qx \rightarrow 0$ for the case where the A block is less rigid than the B block. Ultimately, above $w_{r,r} \approx 11.35$ the host stabilizes the A + B segment orientational ordering.

In this work we demonstrated the occurrence of a nematic–nematic (N/N) first order transition from a guest stabilized to a guest–host stabilized region and the possibility of a reentrant transition from a guest stabilized nematic region to a host only stabilized regime via an isotropic phase. Selective NMR deuteration can be used to measure $\langle S \rangle_r$ and $\langle S \rangle_A$ and $\langle S \rangle_B$ separately. The Hamiltonian parameters $w_{r,r}$, $w_{p,p}$ and $w_{r,p}$ dependence on temperature and density can be obtained from a best fit of the theoretical $\langle S \rangle_r$ and $\langle S \rangle_B$ to their derived values from NMR measurements. e_A and e_B can be obtained from a separate small angle light scattering data of the individual long blocks. The presents analysis suggests new ways to systematically manipulate and selectively stabilize the orientational ordering of the A or/ and B blocks via a judicious choice of A and B block

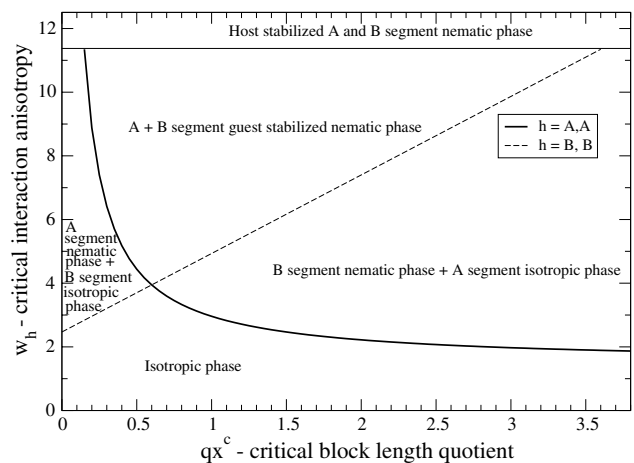


Fig. 5. Orientational phase diagram of the A and B block segments – quotient block length effects; $e_A = 6$, $e_B = 10$, $\rho_p = 0.4$.

length quotient qx , A and B segment rigidities and intersegment and guest–host interactions and to design guest–host materials with novel liquid crystalline properties.

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