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Morphologies of ABC Triblock Terpolymer Melts Containing Poly(Cyclohexadiene): Effects of Conformational Asymmetry

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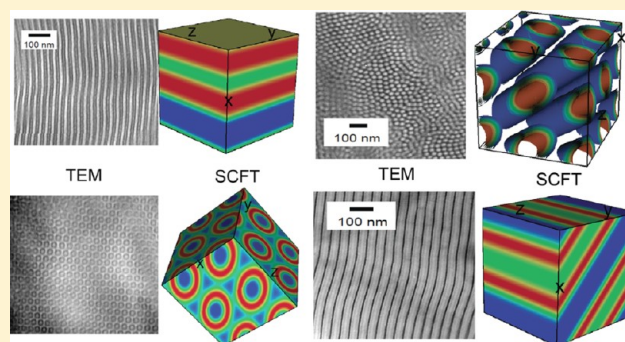
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ABSTRACT: We have synthesized linear ABC triblock terpolymers containing poly(1,3-cyclohexadiene), PCHD, as an end block and characterized their morphologies in the melt. Specifically, we have studied terpolymers containing polystyrene (PS), polybutadiene (PB), and polyisoprene (PI) as the other blocks. Systematically varying the ratio of 1,2- /1,4-microstructures of poly(1,3-cyclohexadiene), we have studied the effects of conformational asymmetry among the three blocks on the morphologies using transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and self-consistent field theory (SCFT) performed with PolySwift++. Our work reveals that the triblock terpolymer melts containing a high percentage of 1,2-microstructures in the PCHD block are disordered at 110 °C

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for all the samples, independent of sequence and volume fraction of the blocks. In contrast, the triblock terpolymer melts containing a high percentage of 1,4-microstructure form regular morphologies known from the literature. The accuracy of the SCFT calculations depends on calculating the χ parameters that quantify the repulsive interactions between different monomers. Simulations using χ values obtained from solubility parameters and group contribution methods are unable to reproduce the morphologies as seen in the experiments. However, SCFT calculations accounting for the enhancement of the χ parameter with an increase in the conformational asymmetry lead to an excellent agreement between theory and experiments. These results highlight the importance of conformational asymmetry in tuning the χ parameter and, in turn, morphologies in block copolymers.

1. INTRODUCTION

Microphase separation in linear ABC triblock^{1–33} terpolymer melts has been studied extensively using experiments^{1–22} and theory.^{23–33} In contrast to five^{1,2,34–40} stable morphologies for diblock melts (lamellar, cylinders, spheres, gyroid, and *Fddd*), around fifteen morphologies have been found for the triblock melts and studied using theoretical methods such as the self-consistent field theory^{26,28–33} (SCFT). Numerous stable morphologies are a direct outcome of a complex interplay among seven independent parameters: $\chi_{AB}N$, $\chi_{BC}N$, $\chi_{AC}N$ (characterizing repulsive interactions between the monomeric units of kind A and B, B and C, and A and C, respectively, in a triblock containing N Kuhn segments), f_A , f_B (the volume fraction of A and B, respectively, so that $f_C = 1 - f_A - f_B$), β_B^2/β_A^2 , and β_C^2/β_A^2 (where $\beta_i^2 = b_i^2/6v_i$, $i = A, B, C$ and v_i , b_i are the molar volume and the Kuhn segment length of block i , respectively). The last two parameters characterize the effects of conformational asymmetry^{41–53} on the morphologies. The laborious task of constructing the morphology diagrams for a given set of volume fractions of the three blocks has been done using the SCFT for selective cases,^{26,28–33} and in principle, a vast set of morphologies can be mapped out in the parameter space.

Despite a large body of work^{1–33} on ABC triblock copolymer melts, the effect of conformational asymmetry^{41–53} on their morphology diagrams is a relatively less studied problem. We believe the reason behind this is twofold. First, the parameter space for conformationally asymmetric triblock terpolymer is larger compared to that for conformationally symmetric triblocks, and it makes the construction of morphology diagrams using the SCFT considerably more time-consuming. Second, a direct comparison between the theoretically predicted morphology diagrams and experimental morphologies requires overcoming a serious problem in how to estimate the χ parameter for conformationally asymmetric copolymers. A number of theoretical^{42,43,54–57} and experimental^{47,48,58} studies have been devoted to addressing the second problem in the context of *diblock* copolymers and *polymer blends*. These studies reveal that χ increases with an increase in the conformational asymmetry. However, the thermodynamic origin of this enhancement (entropic or enthalpic) is not clear,⁴⁷ and a quantitative description for the enhancement is still lacking. In general, the χ parameter is considered to be independent of chain architecture,⁵⁷ and one may expect the same effect of the conformational asymmetry in the case of triblock copolymers. However, we are not aware of any explicit experimental proof of this conjecture. Furthermore, it is well-known that the nature of the morphology for given volume fractions of blocks in a triblock terpolymer depends on a delicate balance^{1–3} of interfacial energy and chain conformational entropy. In light of the fact that the interfacial energy depends^{1–3,31,54–40} on the χ parameter and the absence of a quantitative description of the χ parameter, estimating even the relative order of the three χ parameters remains challenging. This, in turn, hinders even a qualitative comparison between experiments and the theory.

terpolymer melts containing poly(1,3-cyclohexadiene) (PCHD) as an end block. Two sets of triblock terpolymers have been synthesized by tuning the relative amount of two microstructures (1,2- vs 1,4-) of a PCHD chain, as shown in Figure 1. Effects of

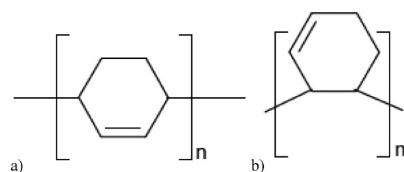


Figure 1. Chemical structures of the PCHD chain containing 1,4-microstructure and 1,2-microstructure are shown in (a) and (b), respectively.

changing the microstructure of PCHD and incorporating it as a block in the copolymers is similar to the ones observed in our previous study⁵⁹ focusing on diblock copolymer melts. In particular, triblock melts containing high percentage (~90–95%) of 1,4 microstructure form ordered structures after annealing at 110 °C. In contrast, triblock copolymers of similar molecular weight containing higher 1,2 microstructures remain disordered.

The ordered morphologies observed in our experiments belong to the known set from the literature.^{1–33} These morphological characterizations are supplemented with the SCFT calculations, and morphology diagrams are constructed for the volume fractions corresponding to the experiments. Our concerted experimental and theoretical study reveals that modeling predictions based on estimation of the relative order of the three Flory's χ parameters using the so-called^{47,48} “z-effect” are in excellent agreement with experiments. We believe that this strategy will be of great utility in the prediction of morphologies obtained in block copolymers, especially in cases where experimental data on the Flory's χ parameter are not readily available.

This paper is organized as follows: a brief description of the synthesis and morphological characterizations is presented in section 2. Details of the SCFT and estimations of the relative order of the three χ parameters are presented in section 3. Results on the morphological characterizations and numerical SCFT simulations are compared in section 4, and the conclusions are presented in the last section.

2. EXPERIMENTAL SECTION

2.1. Synthesis. Details on the synthesis and chemical characterizations of the PCHD-based ABC triblock terpolymers have been presented elsewhere.^{60–63} Here, we only provide a brief description. Triblock terpolymers were synthesized using anionic polymerization with two different initiating systems to polymerize PCHD. Use of *n*-BuLi/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) in a 4/5 molar ratio produced ~50% 1,2-PCHD microstructure, and the use of *sec*-BuLi/1,4-diazabicyclo[2.2.2]octane (DABCO) gave ~95% 1,4-microstructure.⁶² In all instances, the PCHD block was the last block grown. In the following, we use the nomenclature C1,4 for PCHD blocks with mainly 1,4-microstructures (~95%) and C1,2 for PCHD blocks with higher

1,2-microstructures (~50%). Molecular characteristics and other relevant details of all the synthesized samples are presented in Table 1.

Table 1. Summary of Morphologies Observed for the Copolymer Melts Studied in This Work and Their Molecular Characteristics

sample ^a	%v/v ^b A/B/C	$M_n \times 10^{-3c}$ (g/mol)	PDI ^c	morphology	D_1^d (nm)
1-SBC1,4 ^e	16/48/36	29.0	1.05	(ABCCBA) _n Lamellar	32.0
2-SBC1,4	47/31/22	32.0	1.08	Coaxial cylinders of PCHD (inner) and PB (outer) with hexagonal lattice in PS matrix	41.0
BSC1,4	20/33/47	39.0	1.12	(ABCCBA) _n Lamellar	41.3
BIC1,4	27/32/41	38.0	1.10	PCHD cylinders in mixed PB/ PI-matrix	38.0
1-SBC1,2	16/46/38	28.0	1.06	No microphase separation	----
2-SBC1,2	30/31/39	33.7	1.07	No microphase separation	----
BIC1,2	33/41/26	35.7	1.09	No microphase separation	----

^aS, C, I, and B stand for polystyrene, poly(1,3-cyclohexadiene), polyisoprene, and polybutadiene, respectively. ^bThe volume fractions were calculated using the respective densities and the composition results from ¹H NMR results. The densities for PS (1.05 g/mL), PI (0.91 g/mL), and PB (0.92 g/mL) are from *Polymer Handbook* (4th ed., Vol. 1); PCHD1,4 (1.07 g/mL) and PCHD1,2 (1.02 g/mL) were measured using the buoyancy method. ^c M_n are number-average molecular weights by membrane osmometry in toluene at 40 °C and the PDI were obtained from SEC in THF at 30 °C calibrated with polystyrene standards. ^dMeasured directly from TEM patterns. ^eAll PB and PI blocks had ~90% 1,4-content.

2.2. Morphological Characterization. The morphological behavior of PCHD containing triblock copolymers has been previously studied by Natori et al.^{64,65} Their investigations were focused on symmetric triblock copolymers (PS-PCHD-PS, PCHD-PS-PCHD, and PCHD-PB-PCHD, i.e., ABA triblocks) containing high 1,2-microstructures (~50%). They found that polystyrene (PS) containing triblocks micro-phase-separated into lamellar structures. However, polybutadiene (PB) containing triblocks formed weakly ordered morphologies for the chemical compositions studied.

In the present work, the procedure for morphological characterizations is the same as in our previous work on PCHD containing diblock copolymer melts.⁵⁹ Solid sample films were obtained by casting the block copolymers from ~5 w/w % solution of toluene (for high 1,4-PCHD copolymers) or chloroform (CHCl₃, for high 1,2-PCHD block copolymers) for about a week. Residual solvents were removed by placing the samples in vacuum at room temperature for three days. Annealing at 110 °C under vacuum for an extra week followed the solvent removal. A Leica Ultracut UCT microtome equipped with a diamond knife and a Leica EM FCS cryogenic sample chamber operated at -110 °C were used to cut sections of approximately ~40 nm thickness for TEM. The sections were collected on TEM grids and stained with osmium tetroxide (OsO₄) vapor. TEM was performed on a JEOL 100CX transmission electron microscope, operating at 100 kV accelerating voltage. Polystyrene latex sphere standards were used as an internal calibration for the microscope magnification.

Small-angle X-ray scattering (SAXS) was obtained using Rigaku-Molecular Metrology SAXS equipment operated at 40 kV, 200 mA with Ni-filtered Cu K α radiation (0.1542 nm) and an incident beam of 0.4 mm diameter. Scattered X-rays were collected onto a 2-D wire array detector located at a distance of 875.2 mm corresponding to the measured q -range, $0.06 \text{ nm}^{-1} < q < 1.6 \text{ nm}^{-1}$ in which $q = (4\pi/\lambda) \sin \theta$,

where 2θ is the scattering angle. Circular averaging of the raw scattering data was done to obtain plots of intensity as a function of q , where intensity was given in relative units.

3. SELF-CONSISTENT FIELD THEORY (SCFT)

The SCFT for block copolymer melts has been very well documented in the literature.^{38–41,49,66,67} For the purpose of this paper, we only describe the mesoscopic model, estimation of the relative order of the three χ parameters, and the numerical procedure for solving nonlinear equations in the SCFT.

Triblock terpolymer chains are modeled as continuous curves of length $N_A b_A + N_B b_B + N_C b_C$, where N_A , N_B , and N_C are the numbers of Kuhn segments of lengths b_A , b_B , and b_C , respectively. The number of Kuhn segment lengths are related to the volume fractions of different blocks by $f_{i=A,B,C} = N_i v_i / N v$ so that $\sum_{i=A,B,C} f_i = 1$ where v_i is the molar volume of component i , $N v = N_A v_A + N_B v_B + N_C v_C$ is the volume per chain and $N = N_A + N_B + N_C$ is the total number of Kuhn segments along the chain. In order to compare the theoretical results with the experimental investigations, A represents the styrene or butadiene block, B represents the styrene or butadiene or isoprene block, and C represents the PCHD block. Within the SCFT, the chemical nature of different monomers appears through the Flory's parameter, χ_{ij} , characterizing short-range interactions between the two kinds of monomers, i and j , so that $i \neq j = A, B, C$.

The field theory is constructed using mathematical transformations⁶⁷ for the Hamiltonian of the system describing the short-range interactions and Gaussian chain elasticity. The Hamiltonian based on the Gaussian chain elasticity limits the applicability of the SCFT to flexible copolymers, and the effects of finite persistence length cannot be described adequately using such a model. By invoking the saddle-point approximation,^{38–41,49,66,67} a set of nonlinear equations are obtained, which are solved using the iterative scheme presented by Sides and Fredrickson.⁶⁶ Starting from an initial guess generated by random numbers, the nonlinear equations are solved and the free energy of the final structure is calculated. A zone-annealing algorithm is implemented to achieve the lowest free-energy state, where the three Flory's parameters are varied in a moving zone before reaching the desired values. A brief description of the zone-annealing algorithm has already been published⁵⁹ in our previous work. More details of the algorithm will be presented in a future publication. The simulation results presented in this paper are obtained by using the parallel SCFT code PolySwift++ developed⁶⁸ at Tech-X Research in collaboration with the Oak Ridge National Laboratory (ORNL).

In this work, we have studied morphologies for the terpolymers containing fractions of different blocks as given in Table 1. We have established the equilibrium nature of the morphologies as a function of $\chi_{AB}N$, $\chi_{BC}N$, and $\chi_{AC}N$ by comparing the free energies of ordered structures obtained from different initial guesses. It is well-known that the morphology diagram for ABC terpolymers is very sensitive to the relative order of the three Flory's χ_{ij} parameters.^{1–3} In addition, it is also known from studies on diblock copolymer melts that conformational asymmetry of the blocks can shift the order–order transition boundaries.^{41–53,59} However, there is no experimental data on the quantitative values of Flory's χ_{ij} parameters for $i = \text{PCHD}$. In order to understand the origin of ordered morphologies as seen in experiments on PCHD containing terpolymers, we have used the SCFT to study morphologies with estimates of the three Flory's χ_{ij} parameters obtained from different approaches as described below.

For the estimation of the three χ parameters in the triblocks, we have used the group contribution method of Hoy⁶⁹ and computed the solubility parameters (δ_i) (Table 2) along with the

Table 2. Structural Parameters for the Different Polymers Studied in This Work

	b_i^a (nm)	δ_i^b (J/cm ³) ^{1/2} /mol	v_i^b (cm ³ /mol)	v_i^c (cm ³ /mol)	β_i^{2b} (nm ⁻¹)	β_i^{2c} (nm ⁻¹)
PS	0.70	19.75	98.19	99.05	0.50	0.50
PI	0.59	18.02	73.01	74.73	0.48	0.47
PB	0.53	18.77	57.46	58.70	0.49	0.48
1,4-PCHD	0.92	18.87	76.58	74.77	1.11	1.14
1,2-PCHD	---	18.87	76.58	78.43	1.11	1.08

^aData taken from refs 41 and 72. ^bUsing the method of Hoy as described in ref 69. ^cUsing experimental data on the polymer densities given in Table 1. Experimental data on the Kuhn segment length of 1,2-PCHD is not available, and the Kuhn segment length of 1,2-PCHD is assumed equal to that of 1,4-PCHD for the computation of the conformational asymmetry parameters.

molar volumes (v_i) of different components ($i = S, B, I, C$). Also, we have used experimentally known polymer densities (cf. Table 1) to estimate the molar volumes. These solubility parameters along with the molar volumes are used to estimate the χ_{ij} parameters for different pairs, using the relation^{3,47,48,69} $\chi_{ij} = (v_i v_j)^{1/2} (\delta_i - \delta_j)^2 / RT$, where R and T are the universal gas constant and temperature (in Kelvin), respectively. These values of the χ_{ij} parameters for different pairs are tabulated in Table 3. For comparison purposes, the χ_{ij} parameters from the literature^{70,71} are also listed for some of the pairs. Also, the conformational asymmetry parameters $\beta_i^2 = b_i^2 / 6v_i$ estimated using the experimental values of the Kuhn segment lengths and the two estimates for the molar volumes are listed in Table 2. From the table, it is clear that agreement between the estimated values for the molar volumes of different polymers using the group contribution method and experimental data is reasonable. However, the group contribution method does not distinguish between 1,2-PCHD and 1,4-PCHD due to the same number of functional groups in the two polymers. Furthermore, estimated values of the χ_{ij} parameters using the group contribution method as presented in Table 3 are not reasonable, with the exception of the styrene–isoprene pair. For example, $\chi_{BC} = 0.00021$ at 383.15 K will mean that poly(butadiene)-*b*-poly(cyclohexadiene) will be disordered³⁴ for $N = 10,000$. In contrast, we have found these diblocks to microphase separate into ordered morphologies for such high values of N .⁵⁹

This failure of the group contribution method to describe the χ_{ij} parameters has motivated us to use other techniques for the

estimation of the relative order of the three χ_{ij} parameters. It is fairly well-known that the group contribution methods fail to take into account the entropic^{3,42,43,47,48,58} effects in the calculation of χ parameters. This can be seen from Table 3 for the styrene–butadiene pair, for instance. Recently, it has been argued⁴⁷ that an increase in the conformational asymmetry parameter leads to an increase in the coordination number (z) (known as “ z -effect”), which, in turn, leads to an increase in χ_{ij} parameter (where $\chi_{ij} = z[\epsilon_{ij} - 0.5(\epsilon_{ii} + \epsilon_{jj})]/k_B T$; ϵ_{ij} is the interaction energy between i and j and k_B is the Boltzmann constant). As per the z -effect, pairs for which the sum of the conformational asymmetry parameters is maximized tend to have a higher coordination number. Using the conformational asymmetry parameters from Table 2, the “ z -effect” leads to (i) $\chi_{SI} < \chi_{IC} < \chi_{SC}$, (ii) $\chi_{SB} < \chi_{BC} < \chi_{SC}$ and (iii) $\chi_{BI} < \chi_{BC} < \chi_{IC}$. In estimating the relative order for the last trio, we have taken into account the fact that $[\epsilon_{ij} - 0.5(\epsilon_{ii} + \epsilon_{jj})]/k_B T$ for butadiene–cyclohexadiene pair is 2 orders of magnitude smaller than isoprene–cyclohexadiene pair, as seen from solubility parameter calculations (cf. Table 3), while the sum of conformational asymmetry parameters for the two pairs is almost the same. Furthermore, calculations^{42,43,56,57} based on the random phase approximation (RPA) have shown that an increase in the relative conformational asymmetry parameter (defined as $\beta_{ij} = \beta_i^2 / \beta_j^2 \geq 1$) leads to an increase in χ_{ij} . However, the RPA estimates^{42,43,56,57} need the specification of a somewhat arbitrary cutoff length and lack quantitative accuracy. Qualitatively, using the parameters listed in Tables 2 and 3, the RPA estimates for the relative order of the χ_{ij} parameters should be (i) $\chi_{SI} < \chi_{SC} < \chi_{IC}$, (ii) $\chi_{SB} < \chi_{SC} < \chi_{BC}$, and (iii) $\chi_{BI} < \chi_{BC} < \chi_{IC}$. Note that the two estimates of the relative orders are independent of PCHD microstructure, i.e., 1,2 or 1,4 even in the absence of data on the Kuhn segment length of 1,2-PCHD (assuming the Kuhn segment length of 1,2-PCHD does not differ much from 1,4-PCHD). However, the two estimates clearly point out enhanced segregation strength between pairs involving the PCHD block. Also, with the exception of the BIC trio, the two estimates for the relative order differ from each other. We have used the SCFT to study morphologies using these two sets of sequences for the three χ_{ij} parameters. The results indicate that the calculations for the SIC and SBC trios based on the RPA estimates were unable to reproduce morphologies for all of the volume fractions studied in the experiments.

In this paper, we only present the sequence of ordered morphologies obtained using the estimates based on the “ z -effect” and the parameters for different blocks tabulated in Table 2. However, a detailed theoretical results on the effects of the conformational asymmetry parameters on the transition boundaries are beyond the scope of the present work. It should be noted that our SCFT study based on the z -effect overcomes

Table 3. Estimated χ_{ij} for Different Pairs Using the Method of Hoy (cf. Table 2) along with the Published Results from the Literature^a

parameter	$i = S, j = I$	$i = I, j = C$	$i = S, j = C$	$i = S, j = B$	$i = B, j = C$	$i = B, j = I$
χ_{ij}^b	30.4794/ T (0.07955)	6.4980/ T (0.01696)	8.0769/ T (0.02108)	8.6768/ T (0.02265)	0.0798/ T (0.00021)	4.3821/ T (0.01144)
χ_{ij}	25/ T + 0.009 ^d (0.07425)			25/ T – 0.021 ^e (0.04425)		
	66/ T – 0.0937 ^d (0.07855)			28/ T – 0.027 ^e (0.04608)		
	71.4/ T – 0.0857 ^e (0.10065)					
β_{ij}^b	1.04	2.31 (2.31)	2.22 (2.22)	1.02	2.26 (2.26)	1.02
β_{ij}^c	1.06	2.42 (2.30)	2.28 (2.16)	1.04	2.37 (2.25)	1.02

^aValues in the parentheses are the values at $T = 383.15$ K, relevant for this study. Also, the estimated values for the relative conformational asymmetry parameters β_{ij} are presented and the values in parentheses correspond to 1,2-PCHD. ^bUsing the method of Hoy as described in ref 69.

^cUsing experimental data on the polymer densities given in Table 1. ^dRef 70. ^eRef 71.

the limitation of the Gaussian chain models to take into account conformational asymmetry effects in a realistic manner. Our analysis for the estimation of χ parameters clearly points out the effect of conformational asymmetry on the χ parameters. For our SCFT study, we have estimated the length fractions (N_i/N) for the triblock terpolymers using the molar volumes estimated by the group contribution method as presented in Table 2. These parameters are presented in Table 4. For the results presented

Table 4. Length Fractions of Different Components for the SCFT Study in This Work

sample	1-SBC1,4	2-SBC1,4	BSC1,4	BIC1,4
%v/v A/B/C	16/48/36	47/31/22	20/33/47	27/32/41
% N_i/N A/B/C	13/53/34	37/41/22	27/26/47	32/30/38

here, the SCFT equations are solved on a cubic grid containing 64 points in each direction with a grid spacing of $\Delta x = \Delta y = \Delta z = 0.1$ (in units of $R_g = (N_i b_i^2/6)^{1/2}$, i being the block with the smallest conformational asymmetry parameter). For some of the cases where a gyroid morphology is one of the competing candidates, a cubic grid containing 128 points in each direction and spacing of $\Delta x = \Delta y = \Delta z = 0.1$ is used. Chain contour step of $\Delta s = 0.01$ is used for the solution of modified diffusion equations using the pseudospectral method.^{66,67}

4. RESULTS AND DISCUSSION

As mentioned earlier, the PCHD chains can have different microstructures depending on the polymerization conditions, and such structural differences could significantly affect their microphase separation characteristics. We have systematically studied the morphologies at room temperature for a series of PCHD triblock copolymers, after thermal annealing at 383.15 K. Results of our experimental investigations are summarized in Table 1 along with other relevant details. A ternary diagram of the observed morphologies is shown in Figure 2.

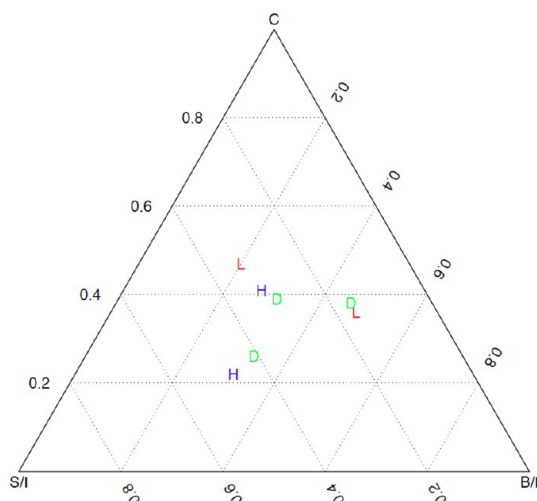


Figure 2. Morphologies observed for all the triblock terpolymer samples enlisted in Table 1. D, L, and H stand for disordered, lamellar (three phase, four layer structure), and hexagonally packed cylindrical morphology, respectively.

4.1. Experimental Results and Discussion. Table 1 indicates that all the triblock terpolymers containing $\sim 50\%$ 1,2-PCHD microstructures do not show any ordered morphology. These findings are consistent with prior observations^{59,64,65} for the diblock copolymer melts, particularly when variations in

molecular weight and microstructure are taken into account. In contrast, triblock terpolymers containing high 1,4-PCHD microstructure and similar molecular weight show well-ordered morphologies. Therefore, one can infer that the disorder–order transition temperature (DOT) is shifted with a change in the microstructure and $\chi_{1,2\text{-PCHD-other blocks}} < \chi_{1,4\text{-PCHD-other blocks}}$. An increase in the χ parameters or a shift in the DOT with an increase in 1,4 content in the PCHD block is consistent with earlier studies^{41–46,59} indicating shift^{41,59} of DOT boundaries and an increase in χ with an increase in the conformational asymmetry parameters^{41–46} (cf. Table 2). From our analysis presented in the previous section, it is clear that polymers containing higher 1,4-PCHD tend to have higher conformational asymmetry parameter in comparison with polymers containing $\sim 50\%$ 1,2-PCHD (assuming the Kuhn segment lengths of the 1,2 and 1,4-PCHD are almost the same). In the absence of experimental data on the Kuhn segment length of $\sim 50\%$ 1,2-PCHD, estimates based on the conformational asymmetry parameter provide a qualitative explanation for the enhancement of segregation strength with an increase in 1,4 content in PCHD block.

The ABC triblock terpolymer sample, 1-SBC1,4 forms the (ABCCBA)_n lamellar morphology as shown in the TEM image (Figure 3). The sample was stained with OsO₄ for 1 h, and the preferential staining sequence is as follows: PB > PCHD > PS; therefore, the contrast is black for PB, gray for PCHD, and brightest for PS in Figure 3a. The 2D SAXS pattern shown in Figure 3b indicates some partial orientation during the annealing process. The scattering pattern taken from other orthogonal directions also confirmed this observation. Circular averaged, I vs q is plotted in Figure 3c. The integral q_n/q^* ratios of 1, 2, and 3 indicate a lamellar morphology for this samples; the first three peaks in the plot are very strong, but higher orders are completely absent.

In order to estimate the interfacial widths in the (ABCCBA)_n lamellar morphology, we have used the mathematical procedure explained in ref 73. In particular, we have used the result that amplitude of X-ray scattering is proportional to the Fourier transform of the autoconvolution of the electron density profile,⁷³ $\rho(r)$, by the relation $I_{\text{obs}}(q) = F\{\Delta\rho_{\text{obs}}^{*2}\}$, where F is a three-dimensional Fourier transform, $\Delta\rho_{\text{obs}}$ is the difference between local electron density and its average, and $*2$ stands for self-convolution. Introducing a smoothing function, $h(r)$, the electron density profile for the system with diffuse boundaries is represented by a convolution between an ideal electron density profile with sharp boundaries, $\rho(r)$, and a smoothing function, $h(r)$, so that $\Delta\rho_{\text{obs}}(r) = \Delta\rho_{\text{obs}}(r) * h(r)$ where r is the distance along an arbitrary vector inside the scattering volume. Using the measured dimensions of PS, PB, and PCHD layers from the TEM data, we have constructed a model for the PS-*b*-PB-*b*-PCHD triblock terpolymer morphology (i.e., 1-SBC1,4) as shown in Figure 3d.

The simulated electron density profile of the triblock terpolymer along with the scattering amplitude is shown in Figure 4. The best scattering results are obtained when interfacial width between PB and PCHD equals 3.2 nm and that of between PS and PB equals 1.9 nm. The simulated scattering amplitude (Figure 4b) is in qualitative agreement with the SAXS data, showing the presence of only the first three peaks with higher scattering peaks significantly suppressed.

Sample, BSC1,4 also was found to form a (ABCCBA)_n lamellar morphology as shown in the TEM image (Figure 5a). Here again, the contrast is black for PB, gray for PCHD and

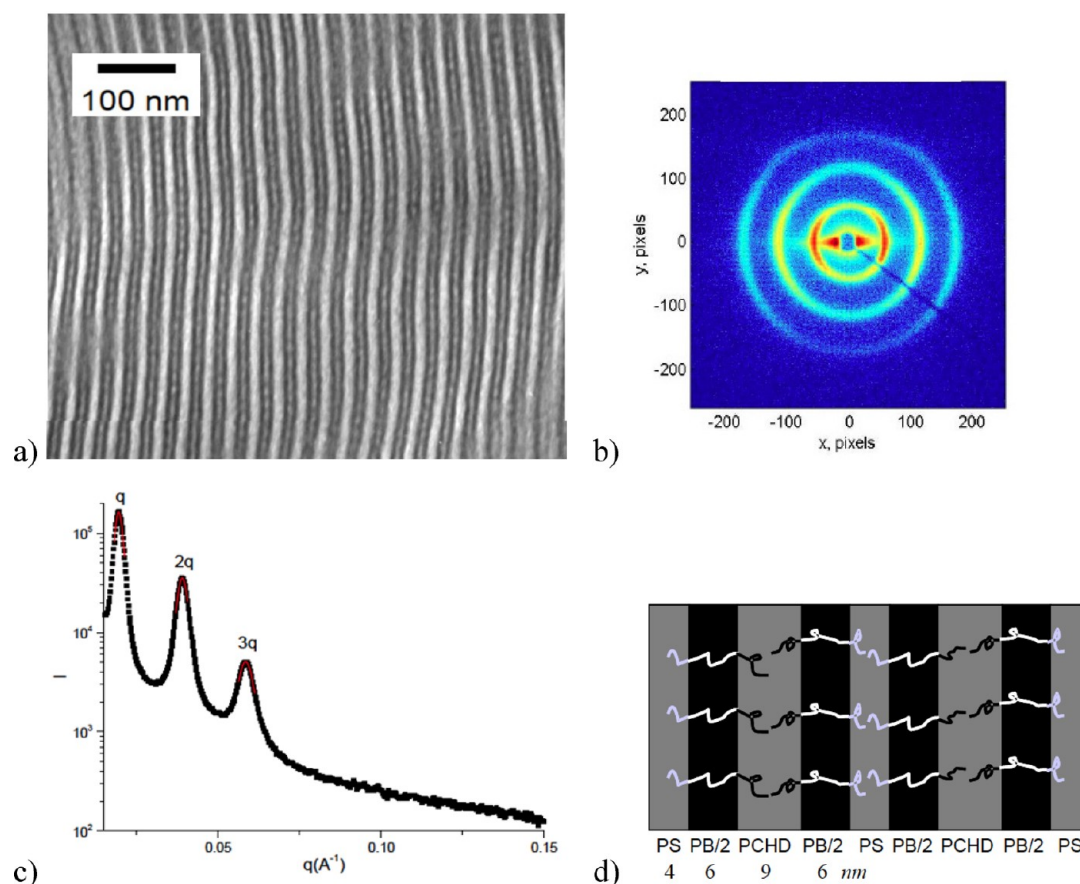


Figure 3. Morphology for 1-SBC1,4 with ~95% 1,4-microstructures for the PCHD block: (a) TEM image; (b) 2D-SAXS pattern; (c) SAXS intensity versus q profile; and (d) model based on the analysis of SAXS and TEM data as explained in the main text.

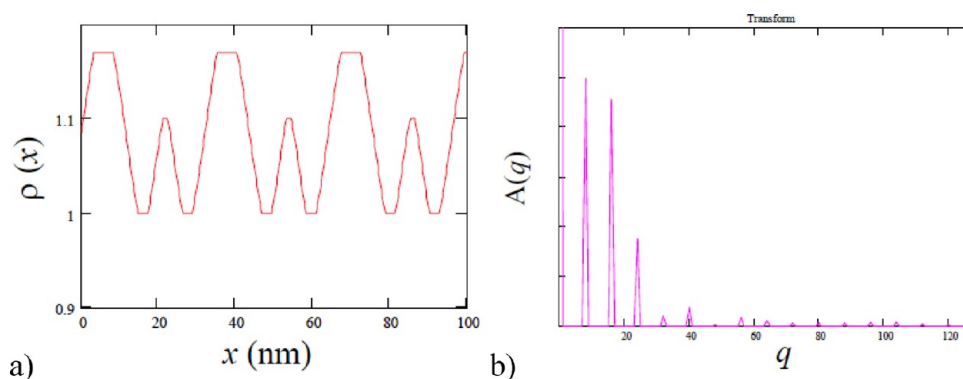


Figure 4. Electron density profile (a) for 1-SBC1,4 sample along with the scattering amplitude, $A(q)$ (b).

brightest for PS. The 2D SAXS pattern is shown in Figure 5b, and circularly averaged I vs q is plotted in Figure 5c. The integral q_n/q^* ratios of 1, 2, 3, 4, 5, and 7 indicate a lamellar morphology at strong microphase segregation strength and substantial long-range order.

The morphological characterization for the 2-SBC1,4 triblock showed (Figure 6) that the morphology of the synthesized sample was concentric hexagonally close-packed cylinders, where the inner 1,4-PCHD cylinders (gray) are surrounded from the hexagonally shaped PB cylinders (black), in a PS matrix (white). This morphology is similar to one that has been observed⁷ in a PS-*b*-PI-*b*-P2VP sample (volume fraction 1:1:1) with the major difference being only in the last two segments (PI instead of PB and P2VP instead of 1,4-PCHD, respectively). Cylindrical morphology

is confirmed from the $\log I$ vs q plots in Figure 6b. The characteristic ratios q_n/q^* equal to $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}:\sqrt{12}$ are observed.

BIC1,4 forms a cylindrical morphology as illustrated in Figure 7. PB and PI are hardly discernible from the staining using OsO₄. However, it is certain that the PCHD block forms the inner cylindrical cores in the morphology. The outer shell or matrix is composed of the diblock PI-*b*-PB; it is not possible to discern from either TEM or SAXS whether or not there is any microphase segregation between PI and PB. Upon the basis of the TEM image, the diameter of PCHD cylinders is 29 nm and the lattice spacing is 38 nm, quite consistent with the SAXS results. The calculated volume fraction of PCHD is 0.40. This value is very close to the volume fraction of PCHD 0.41 found by ¹H NMR.

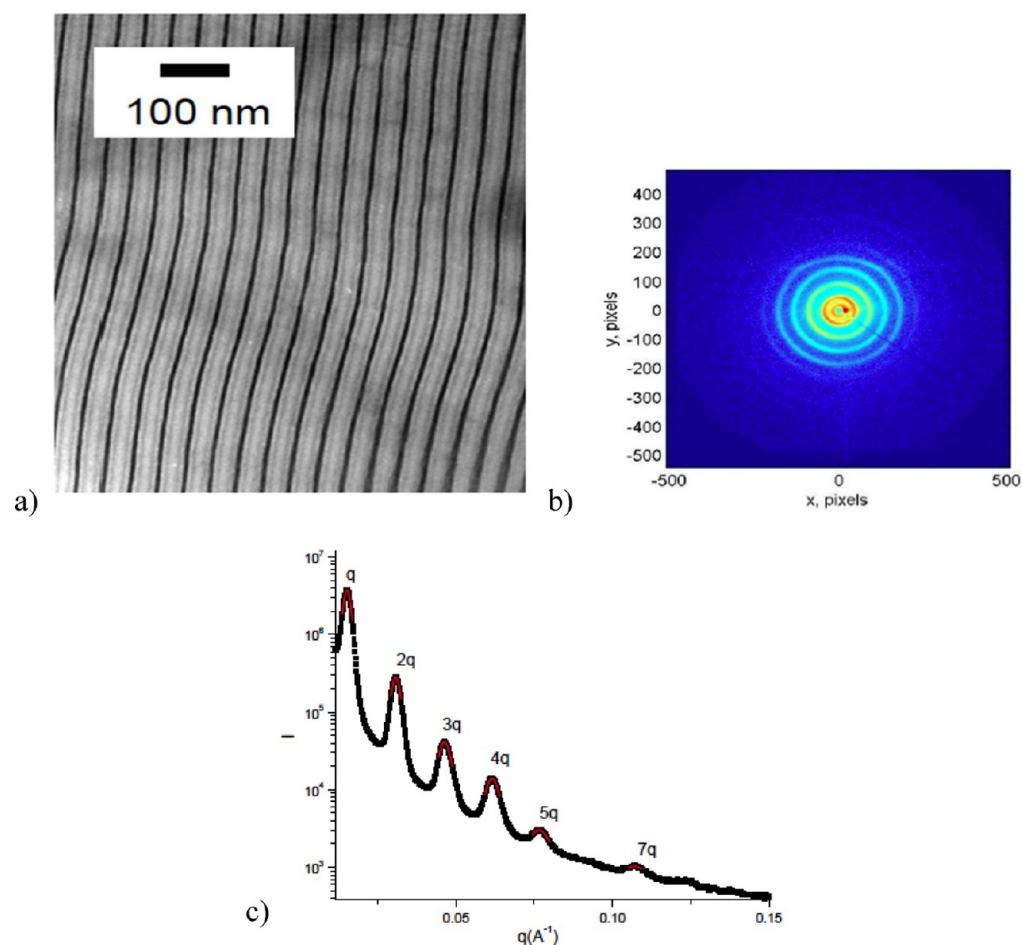


Figure 5. Morphology for BSC1,4 with ~95% 1,4-microstructures for the PCHD block: (a) TEM image; (b) 2D-SAXS pattern; and (c) SAXS intensity versus q profile.

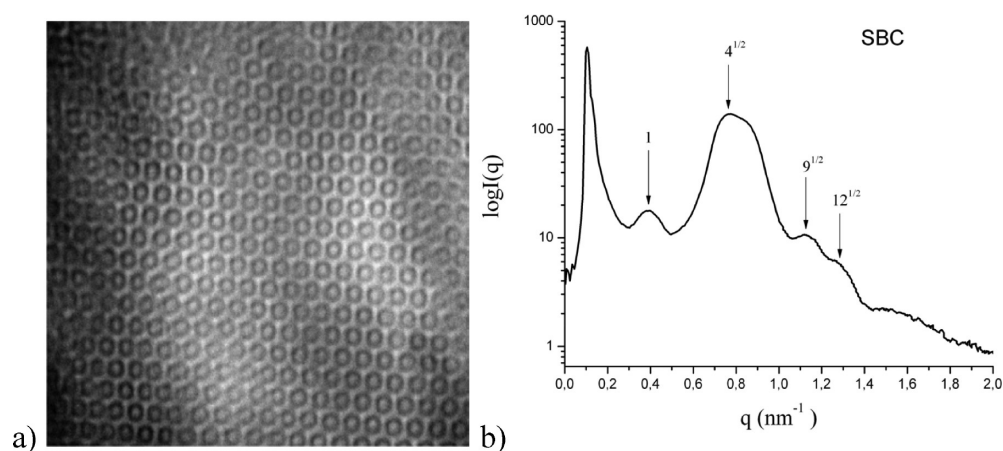


Figure 6. (a) TEM image for the 2-SBC1,4 triblock terpolymer; (b) SAXS plot for the SBC triblock terpolymer which verifies the cylindrical nature of the morphology.

We have already mentioned in the introduction that there are around fifteen morphologies that are known for ABC terpolymers. The morphologies observed in our experiments belong to the known set of morphologies. In the absence of experimental data on the χ parameters, reproducing and confirming the thermodynamic stability of all the morphologies using the SCFT for given volume fractions and conformational characteristics seems like a daunting task. However, in the following, we demonstrate that agreement between the SCFT and experiments is

excellent when the relative order of the three Flory's χ parameters is estimated on the basis of the z -effect.

4.2. Morphology Diagrams using the SCFT. We have studied morphologies for the ABC triblock terpolymers using the real-space self-consistent field theory,^{66,67} which allows us to explore the whole morphology diagram. All of these calculations (see Table 5) correspond to weak and intermediate segregation limit, depending on the volume fractions of different blocks. The results are presented in Table 5.

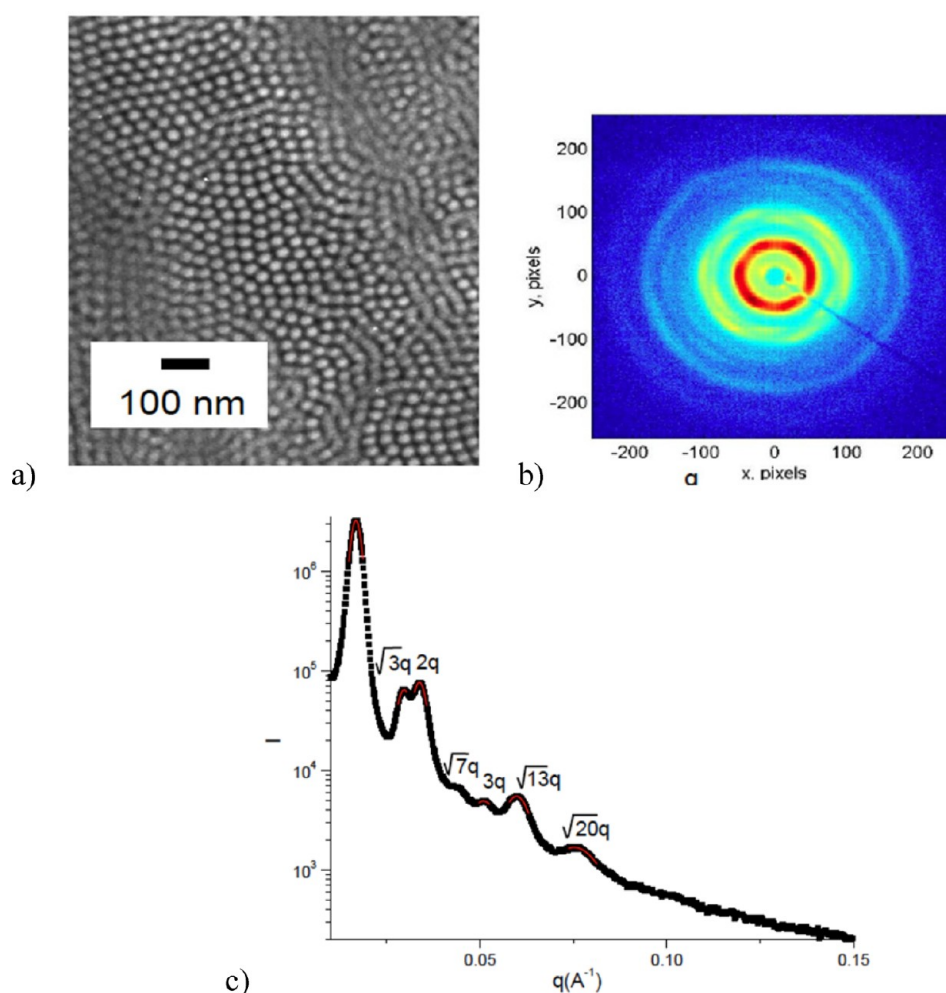


Figure 7. Morphology for BIC1,4 with ~95% 1,4-microstructures for the PCHD block: (a) TEM image; (b) 2D-SAXS pattern; and (c) SAXS intensity versus q profile.

Table 5. Morphologies for the ABC Triblock Terpolymers Using the SCFT^a

$\{\chi_{ij} N\}$	$[10,15,20] \rightarrow [10,20,25] \rightarrow [15,20,25] \rightarrow [15,25,30] \rightarrow [20,25,30] \rightarrow [20,30,35] \rightarrow [30,35,40] \rightarrow [35,40,45] \rightarrow [40,45,50]$
1-SBC1,4	B \rightarrow H \rightarrow H \rightarrow H \rightarrow H \rightarrow L \rightarrow L \rightarrow L
2-SBC1,4	D \rightarrow B \rightarrow H \rightarrow H \rightarrow G \rightarrow G \rightarrow G \rightarrow G \rightarrow G
BSC1,4	L \rightarrow L \rightarrow L \rightarrow L \rightarrow L \rightarrow L \rightarrow L \rightarrow L
BIC1,4	H \rightarrow H \rightarrow H \rightarrow H \rightarrow H \rightarrow L \rightarrow L \rightarrow L \rightarrow L

^aThe relative order of χ_{ij} parameters is given in the main text for the triblock terpolymers. Here, D, B, H, G, and L refer to disordered, body centered cubic spheres, hexagonally packed cylinders, gyroid, and lamellar (three-phase four-layer structure), respectively. Experimentally observed morphologies are highlighted in bold.

By comparison of Figure 2 with Table 5, it is clear that all of the morphologies observed in the experiments correspond to the equilibrium values in the weak and intermediate segregation limits. However, a more detailed comparison between the theory and the experiments is not possible at this stage due to the unavailability of the temperature dependence of χ_{ij} parameters for different pairs. In the following, we show the density plots for the morphologies obtained from the SCFT and restrict ourselves to a qualitative comparison between the theory and experiments.

Figure 8 shows plots for the volume fractions of the B and C components (which represent butadiene and cyclohexadiene, respectively) in the lamellar morphology (L) obtained using

the set of parameters corresponding to 1-SBC1,4. The volume fraction of the second end-block monomer (A) can be inferred using the incompressibility condition, i.e., the sum of the volume fractions of the three kinds of monomers must be unity.

Similarly, Figure 9 shows plots for the volume fractions of the two kinds of monomers (C and B) in the hexagonally packed cylindrical morphology (H) for the set of χ_{ij} parameters corresponding to 2-SBC1,4. In agreement with our experiments and theoretical calculations taking into account conformational asymmetry,^{41,44,45,59} the block with the higher conformational asymmetry parameter forms the core in this morphology.

Furthermore, in agreement with the experiments, the ABC triblock simulated using the parameters mimicking the BSC1,4 sample forms a lamellar morphology for all the segregation strengths studied in this work. Density plots similar to Figure 8 are obtained. Also, density plots for the H morphology in the case of the BIC1,4 are also similar to the ones presented in Figure 9. For the sake of completeness, we present density plots for the midblock in the case of BSC1,4 and end block for BIC1,4 in Figure 10.

One may expect morphologies occupying a large parameter space to be observed in experiments unless experimental conditions are chosen carefully. Indeed, this is the case for all the samples except the 2-SBC1,4 sample, where the cylindrical (H) morphology is observed in a narrow parameter space. Note that we have found the lamellar morphology to be stable for 1-SBC1,4

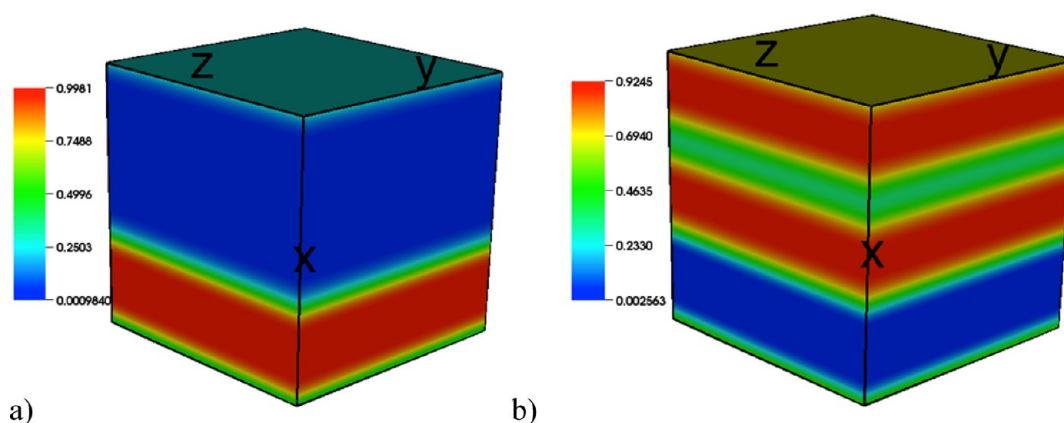


Figure 8. (a) Density profiles of C component and (b) B component in the lamellar (L) morphology obtained for $\{\chi_{ij} N\} = [30, 35, 40]$ in the case of ABC triblock terpolymer representing the 1-SBC1,4 sample.

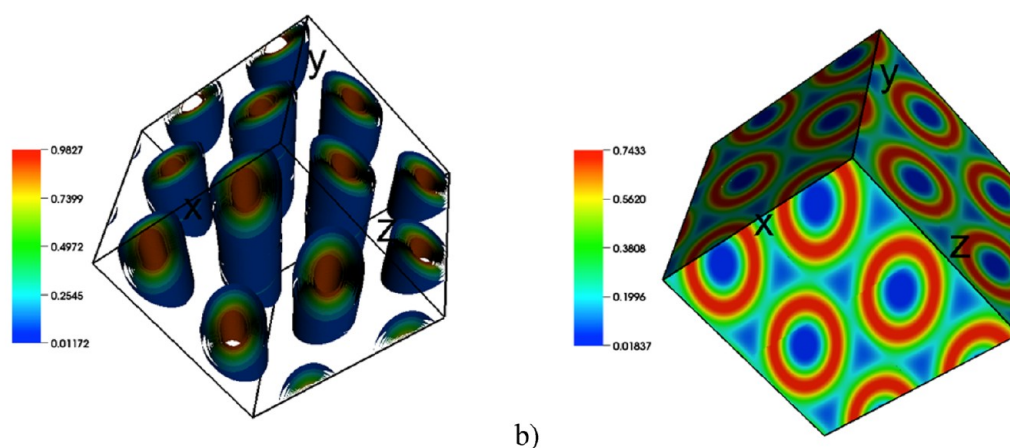


Figure 9. (a) Iso-surface plot of the density profile of C monomers and (b) the density plot for the B monomers in the case of the hexagonally packed core-shell cylindrical morphology (H). These plots correspond to $\{\chi_{ij} N\} = [15, 25, 30]$ in the case of the ABC triblock terpolymer representing the 2-SBC1,4 sample. In agreement with the experiments, the block representing the PCHD forms the core of the cylinders. In order to highlight the hexagonal packing, the simulation box is repeated in each of the x, y, z directions.

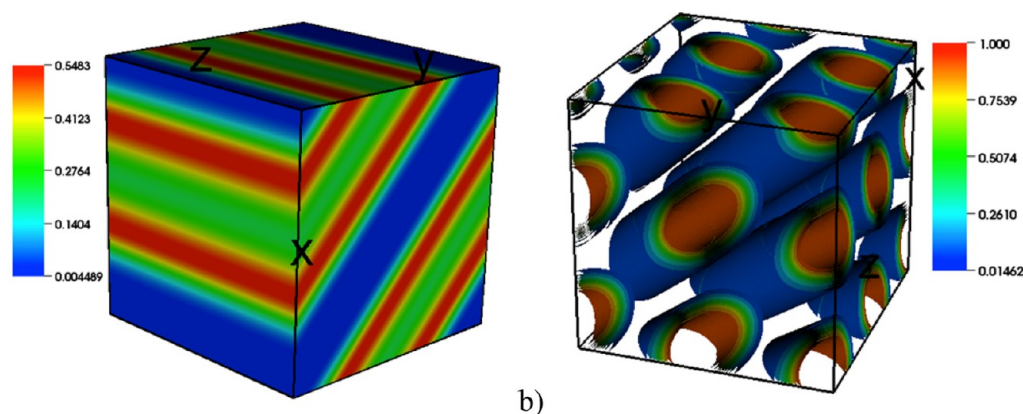


Figure 10. (a) Density profile of the midblock component, B (representing styrene), in the lamellar (L) morphology for the ABC triblock representing BSC1,4 sample. (b) Density profile of the end-block component, C, in the cylindrical (H) morphology for the ABC triblock representing BIC1,4 sample. These plots correspond to $\{\chi_{ij} N\} = [15, 25, 30]$.

sample for higher values of $\{\chi_{ij} N\}$ than those presented in Table 5. In addition to reproducing and confirming the thermodynamic stability of the experimentally observed morphologies, the SCFT predicts the stability of other morphologies not observed in the experiments. This is one of the motivations behind the use of real-space SCFT, since it is a numerical algorithm that does not

make any presumptions about the symmetry. Note that the spectral method for the prediction of symmetries has also been developed recently.⁷⁴ For example, a body-centered cubic (BCC) morphology (B) is observed (cf. Table 5) for 1-SBC1,4 and 2-SBC1,4 near the disorder–order transition. Like the H morphology, the block having highest conformational asymmetry

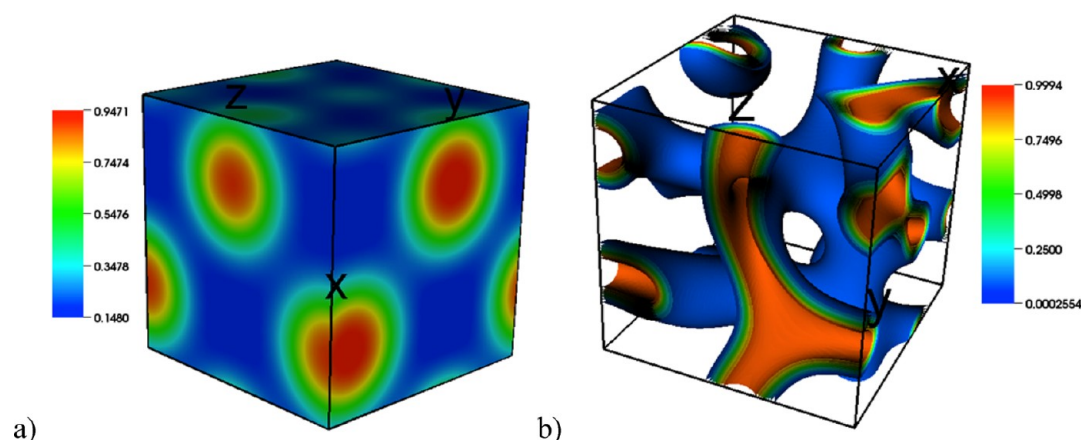


Figure 11. (a) Density profiles of C monomers in the B morphology (BCC spheres) obtained for $\{\chi_{ij} N\} = [10, 15, 20]$ in the case of 1-SBC1,4. (b) Iso-surface plots of C monomers in the G morphology (gyroid) obtained for $\{\chi_{ij} N\} = [30, 35, 40]$ in the case of 2-SBC1,4.

parameter forms the core of the spheres in the BCC (see Figure 11a). Also, we have found a window where the gyroid (G) morphology is stable, e.g., in the case of triblock representing the 2-SBC1,4 sample (see Figure 11b). Gyroid and other network phases have already been observed^{18–21} in ABC triblock terpolymer melts.

5. CONCLUSIONS

We have synthesized and studied the self-assembly of PCHD-containing triblock terpolymers using TEM, SAXS, and the SCFT. In agreement with our previous study⁵⁹ on PCHD containing diblock copolymer melts, the ratio of the 1,4 to 1,2-microstructure plays an important role in dictating the morphologies in triblock terpolymers. In particular, samples containing substantial amounts of 1,2-microstructure ($\sim 50\%$) in the PCHD block are disordered. In contrast, the triblock terpolymers containing $\sim 95\%$ 1,4-microstructures in the PCHD block produced ordered morphologies known from the literature on ABC copolymers. The observed difference in the behavior of PCHD containing triblock terpolymers highlights the dependence of the disorder–order transition temperature (DOT) and, in turn, χ_{DOT} parameters on the content of 1,2 and 1,4-microstructures of the PCHD blocks. The changes in the DOT or the χ_{DOT} parameters can be qualitatively explained on the basis of their dependence^{41–46,59} on the conformational asymmetry parameters, which changes with a change in the PCHD microstructure. However, it is not clear how different microstructures affect the conformational asymmetry parameters a priori.

Our SCFT calculations based on the relative orders of three χ 's estimated using a qualitative argument like the z-effect (i.e., χ_{ij} is higher for pairs with higher conformational asymmetry parameters) have been able to reproduce all the morphologies observed in the experiments. Furthermore, in agreement with the experiments, the block with the highest conformational asymmetry parameter (i.e., PCHD) forms the core of the curved morphologies such as the core–shell cylinders and BCC spheres. Also, we have found gyroid morphology to be stable in the weak and intermediate segregation regimes studied here. In contrast, estimation of the χ 's using solubility parameters and the RPA fails to reproduce the observed morphologies.

Our concerted experimental and theoretical analysis reveals that the z-effect provides a reasonable dependence of the Flory's χ parameters on the conformational characteristics. This conclusion for the triblock terpolymer is in agreement with our previous study⁵⁹ on the diblock copolymers and other studies^{47,48} on blends

and diblocks. These investigations highlight the importance of the conformational characteristics in tuning the χ parameters and, in turn, morphologies in block copolymers.

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The authors declare no competing financial interest.

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