

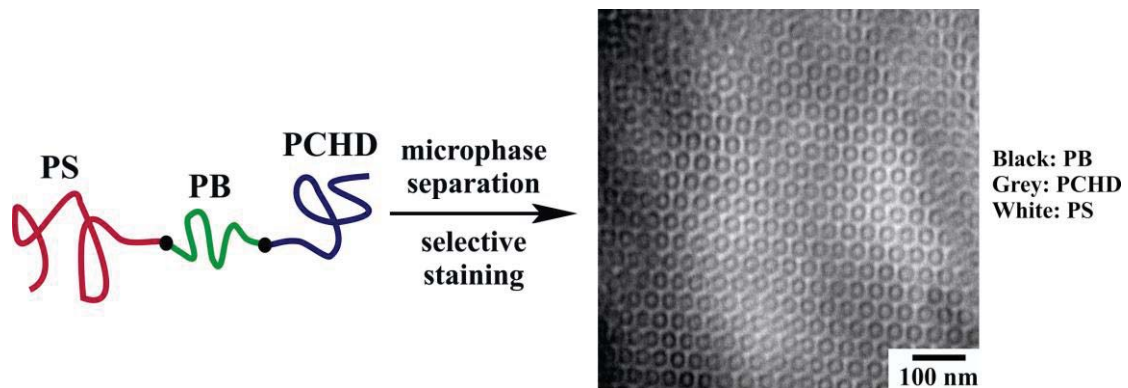
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## Synthesis, Characterization (Molecular-Morphological) and Theoretical Morphology Predictions of Linear Triblock Terpolymers Containing Poly(cyclohexadiene)

Misichronis K.<sup>1</sup>, Rangou S.<sup>1</sup>, Ashcraft E.<sup>2</sup>, Kumar R.<sup>3</sup>, Dadmun, M.<sup>2</sup>, Sumpter, B.G.<sup>4</sup>, Zafeiropoulos N.E.<sup>1</sup>, Mays J. W.<sup>2</sup>, Avgeropoulos A.<sup>1,\*</sup>

<sup>1</sup>Polymers Laboratory, Department of Materials Science Engineering, University of Ioannina, University Campus, 45110 Ioannina, Greece

<sup>2</sup>Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

<sup>3</sup>National Center for Computational Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

<sup>4</sup>Computer Science and Mathematics Division and Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

**Abstract:** The synthesis via anionic polymerization of six linear triblock terpolymers with various sequences of blocks such as PS (polystyrene), PB [poly(butadiene)], PI [(poly(isoprene))] and PCHD [poly(1,3-cyclohexadiene)] is reported. The synthesis of the terpolymers was carried out by the use of anionic polymerization with high vacuum techniques and sequential monomer addition. Molecular characterization of the samples was performed via size exclusion chromatography (SEC) and membrane osmometry (MO) to measure the polydispersity indices and the number-average molecular weights, respectively. Proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR) was employed to verify the microstructure type for the polydienes, as well as, to calculate the molar composition. Structural characterization of the terpolymers was performed via transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS), and several morphologies were observed including one which has not been reported previously. Real-space self-consistent field theory (SCFT) without *a priori* knowledge about the symmetry of the periodic structures was used to elucidate the thermodynamics of the synthesized triblock copolymers.

**Keywords:** Triblock terpolymer synthesis; molecular/structural characterization; self-consistent field theory

Corresponding Author: A. Avgeropoulos; Tel: +30 26510 09001; Fax: +30 26510 07030; E-mail address: aavger@cc.uoi.gr

## Introduction

Anionic polymerization constitutes a powerful method for synthesizing novel polymers and copolymers. Linear diblock copolymers of the AB type are the simplest case of a copolymer comprised of two blocks having different chemical structures. Microphase separation of such chains depends almost exclusively on the interaction parameter  $\chi$  and the total degree of polymerization  $N$ . By the addition of a third block with a different chemical structure (triblock terpolymers<sup>1</sup>) the morphological behavior becomes much more complicated. There are now three segmental interaction parameters  $\chi_{AB}$ ,  $\chi_{BC}$ ,  $\chi_{AC}$ , and three volume fractions ( $\phi_A$ ,  $\phi_B$  and  $\phi_C$ ) to consider. Another important difference between diblock copolymers and triblock terpolymers is the increase of the number of the junction points from one to two, respectively. As a result, the observed structures for the latter depend on the sequence and the type of the blocks, as well as on the difference between the interaction parameters. Triblock terpolymers may form core shell analogs to the well-known diblock morphologies, such as the 3-phase 4-layer lamellae where the middle block forms an additional layer between the two outer blocks. Alternatively, the middle block can form spheres or cylinders between the two outer blocks depending on the volume fraction ratios. In addition, many structures have been reported where the middle block forms a matrix around spheres or cylinders of the two outer blocks. A helical morphology has also been reported where one end block forms a cylinder which is helically surrounded by the midblock domains, both embedded in a matrix of the other end block. This morphology is reported in the case where the middle block exhibits the lowest volume fraction. Moreover, a core-shell double gyroid structure has been observed, where one end block forms the two networks which are surrounded by shells of the midblock and the remaining end block is the matrix<sup>2</sup>. All these morphologies observed in various linear triblock copolymer systems have been very well described in review articles<sup>3,4</sup>.

Most of the triblock terpolymers synthesized so far have consisted of polystyrene (PS), polydienes [e.g. polyisoprene (PI) or polybutadiene (PB)], and various polar segments as the third block, such as poly(methyl methacrylate), poly(2-vinylpyridine),

poly(4-vinylpyridine) and poly(ethylene oxide). Poly(1,3-cyclohexadiene) (PCHD) is another polydiene that has been used<sup>5-7</sup> so far in several cases, being a very interesting polymer due to its improved thermal, chemical and mechanical properties<sup>8,9</sup>. It can be dehydrogenated to poly(phenylene) (PPP), a highly conducting polymer and also it can be converted to poly(cyclohexylene) (PCHE) by homogeneous<sup>10</sup> or heterogeneous<sup>8</sup> hydrogenation. PCHE has very high glass transition temperatures ( $T_g \sim 200^\circ\text{C}$  for 95% 1,4-PCHE and  $T_g \sim 231^\circ\text{C}$  for 50% 1,2-PCHE<sup>8</sup>) as compared to the other hydrocarbon polymers, low specific gravity, high heat resistance, high flexural modulus and other desirable properties<sup>11</sup>.

Natori was the first to report the controlled anionic polymerization of 1,3-CHD with the n-BuLi/N,N,N',N'-tetramethylenediamine (TMEDA) initiating system in a 4/5 molar ratio<sup>12</sup>. The microstructure of the obtained PCHD was almost equivalent in the two isomeric microstructures obtained, being 1,2- and 1,4- respectively<sup>13</sup>. By using the above initiating system, random copolymers of CHD with butadiene, styrene and isoprene as well as diblock and triblock copolymers of CHD with butadiene or styrene were synthesized<sup>14</sup>. 1,4-Diazabicyclo-[2.2.2]octane (DABCO) with sec-BuLi was used as another initiating system by Hong and Mays<sup>5</sup> leading to PCHD with ~95% 1,4 microstructure. With the DABCO initiating system, block copolymers<sup>6</sup>, three-arm star homopolymers, and starblock copolymers of styrene and CHD were prepared<sup>15</sup>. Miktoarm stars with one PCHD arm and two or three poly(butadiene) (PB) arms were also prepared using the same system and were transformed to the corresponding miktoarm stars of PCHE and polyethylene (PE) by homogeneous hydrogenation<sup>16</sup>. Also a miktoarm star terpolymer consisting of poly(cyclohexadiene) (PCHD), polystyrene (PS) and poly(2-vinylpyridine) (P2VP) was prepared using DABCO and an initiator based on 1,3-bis(1-phenylethylene)benzene (1,3-PEB)<sup>17</sup>.

Due to the increased interest in working with such materials, in the present study we report the synthesis, molecular and structural characterization of linear triblock terpolymers of 1,3-CHD with all possible combinations of styrene, isoprene and butadiene [SIC, SBC, BSC and BIC where S is polystyrene, I is poly(isoprene) with increased 3,4-microstructure (approximately 55%), B is poly(butadiene) with ~90% 1,4-microstructure and C is poly(1,3-cyclohexadiene) with ~95% 1,4-microstructure] by

using the sequential addition of monomers, high vacuum techniques and DABCO as the polar additive. Molecular and morphological characterization confirms the formation of well-defined, narrow polydispersity, and morphologically well-organized materials with potential applications. Furthermore, we use the real-space self-consistent field theory<sup>18,19</sup> (SCFT) to study the order-order transitions in the ABC tri-blocks such as those synthesized and characterized here.

## Experimental Section

**Materials.** All triblock terpolymers were prepared by anionic polymerization via sequential addition of monomers using high-vacuum techniques in evacuated, n-BuLi washed, and benzene-rinsed glass vessels. Thorough information and detailed description of the high-vacuum technique as well as the purification procedures for the monomers (styrene, butadiene, isoprene), solvent (benzene), and initiator (sec-BuLi) to the standards required for anionic polymerization are already reported in the literature<sup>20</sup>. 1,3-Cyclohexadiene (1,3-CHD, Aldrich, 97%) was stirred overnight under CaH<sub>2</sub> and distilled three times over sodium mirrors in a high-vacuum line. Furthermore, it was distilled in a flask containing n-BuLi and was allowed to react for 30 min at 0<sup>0</sup>C. The purified 1,3-CHD was finally distilled into calibrated ampoules and was used immediately or was stored at -20<sup>0</sup>C for a short period of time (less than 2 weeks). 1,4-Diazabicyclo-[2.2.2]octane (DABCO, Aldrich, 98%) was purified by sublimation of the appropriate amount three times under high vacuum in a specifically constructed glass apparatus. Finally, the necessary amount of benzene was distilled until proper concentration of the solution was reached.

**Instrumentation Details.** The number-average molecular weights ( $\overline{M}_n$ ) of the precursors and the final products higher than 15,000 g/mol were measured with a Gonotec membrane osmometer (MO) Osmomat 090 at 35<sup>0</sup>C. Toluene, dried with CaH<sub>2</sub>, was used as the solvent for the measurements. Square-root plots were used in order to minimize the curvature due to the third virial coefficient<sup>21</sup>. In all cases, the correlation coefficient was better than 0.99. Number-average molecular weights ( $\overline{M}_n$ ) of the precursors lower than 15,000 g/mol were measured with a Gonotec vapor pressure osmometer (VPO) Osmomat 070 at 50<sup>0</sup>C using toluene vapors (purified accordingly as

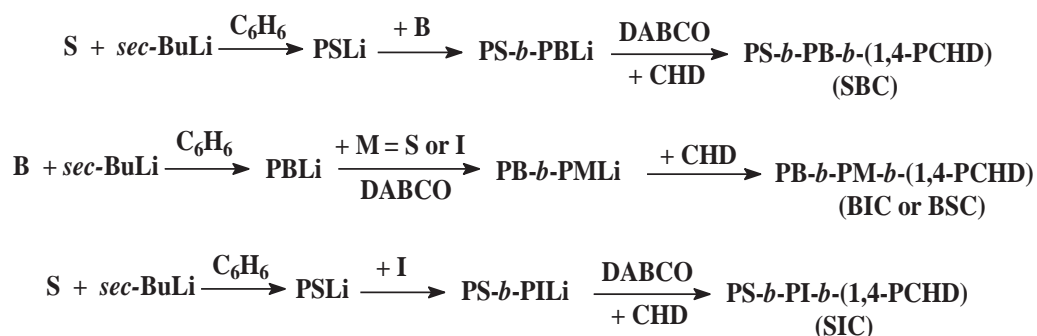
described above). The instrument was calibrated using benzyl (?) solutions as calibration standards. A size exclusion chromatograph (SEC), equipped with an isocratic pump (SpectraSystem P1000), column oven (LabAlliance) heated to 30<sup>0</sup>C, three columns in series (PLGel 5 mm Mixed-C, 300×7.5 mm), refractive index (RI, Shodex RI-101) and ultraviolet absorbance (UV, SpectraSystem UV1000) detectors, and tetrahydrofuran (THF) as the eluent, was calibrated with eight PS standards ( $M_p$ : 4,300 to 3,000,000 g/mol). In every case, prior to calculating the polydispersity indices (PDI) of the unknown materials as well as prior to making an estimation on the average molecular weights ( $\overline{M}_n$  and  $\overline{M}_w$ ), a series of standard PS solutions were always tested in order to examine the accuracy of the measurements. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy was used for determining the composition and the isomeric microstructures of the materials and was carried out in CDCl<sub>3</sub> at 30<sup>0</sup>C using a Bruker AVANCE II spectrometer. Data were processed using the UXNMR (Bruker) software.

SAXS measurements were carried out in transmission geometry on a three pinhole collimated system equipped with a Rigaku rotating anode (CuK $\alpha$  radiation  $\lambda = 1.542 \text{ \AA}$ , operating at 4.2 kW), an Osmic multilayer mirror for higher photon flux, and a MARCCD 2D detector (average pixel size  $78.7 \times 78.7 \text{ }\mu\text{m}$ ). The sample to detector distance was 1.72 m and the calibration was carried out using Ag–Behenate as the standard. All patterns were background corrected and normalized with respect to thickness, and subsequently were radially averaged yielding 1D SAXS patterns of  $I(q)$  vs  $q$ . The software package Fit2D [<http://www0.esrf.fr/computing/scientific/FIT2D/>] was used to perform background subtractions, spatially correct the scattering patterns and calculate integrations of scattered intensity. The setup of the apparatus enabled a resolvable range of  $0.07 \text{ nm}^{-1} \leq q \leq 2 \text{ nm}^{-1}$ . All peaks appearing in the 1D patterns were subsequently fitted with Lorentzian functions using Origin.

The casting protocol for film preparation was designed to prepare reproducible films from bulk at thermodynamic equilibrium by solvent casting and annealing. Approximately 1 mm thick films of the samples were cast from a dilute solution (~5 wt %) in a nearly non-selective solvent (toluene) over a period of one week at ambient conditions. To obtain near-equilibrium morphologies the films were dried under vacuum for three days at room temperature and finally annealed at 120 <sup>0</sup>C also under vacuum for

one week. For transmission electron microscopy (TEM) investigations, 50 nm thick sections of the triblock terpolymer films were ultracryomicrotomed at -110 °C using a Reichert-Jung FC 4E cryo-ultramicrotome equipped with a diamond knife to avoid mechanical deformation of the resulting thin sections during their collection in 600-mesh copper grids. To increase the mass-thickness contrast, the thin sections were exposed to OsO<sub>4</sub> vapors for 30-35 min. The stained sections were examined in a JEOL JEM 200CX electron microscope operated at 200 kV in the bright field mode.

**Triblock Terpolymers Synthesis.** The synthesis of the ABC terpolymers, where A and B were polystyrene, poly(isoprene) or poly(butadiene) and C was always 1,4-poly(cyclohexadiene), was accomplished via sequential addition of monomers. Three samples were of the PS-*b*-PI-*b*-PCHD type (SIC), one of the PS-*b*-PB-*b*-PCHD type (SBC), one of the PB-*b*-PS-*b*-PCHD type (BSC) and one of the PB-*b*-PI-*b*-PCHD type (BIC). The synthesis reactions for all six samples are demonstrated in Scheme 1.



**Scheme 1.** Synthetic routes to the linear triblock terpolymers.

In the case of BIC and BSC linear triblock terpolymers the polar additive DABCO was added just after the completion of the polymerization of the first block. This is necessary in order to increase the initiation rate of styrene or isoprene towards the PB<sup>-</sup>Li<sup>+</sup> macroinitiator. Therefore, the polymerization of styrene or isoprene has a fast initiation step and the narrow distribution of the intermediate diblock is ensured. In all other terpolymers, DABCO was introduced prior the addition of 1,3-CHD and stirred for 10 min. The polymerization of CHD was allowed to proceed for 6 h at 5<sup>0</sup>C.



**Synthesis of SIC terpolymer.** In a typical experiment to prepare the SIC triblock terpolymer, 150 mL of purified benzene was distilled into an evacuated reactor with attached ampules containing all the necessary purified reagents. The reactor was removed from the vacuum line by heat sealing after degassing and 2 g of styrene (19.2 mmol) were added to the solution followed by a 0.84 mL aliquot of sec-BuLi (0.14 mmol/mL in benzene). The polymerization started immediately (deep orange color) and was allowed to continue for 24 hours. An aliquot was taken for characterization via size exclusion chromatography, and the results indicated that the molecular weight for the first block was 17.0 Kg/mol with a PDI of 1.03. After the complete polymerization of styrene, 4.1 g of isoprene (60.29 mmol) were added and allowed to react for another 24 hours. Again an aliquot was taken from the solution for molecular characterization via SEC and the results indicated that the molecular weight for PI was 35.2 Kg/mol with a PDI of 1.04 for the copolymer. Then 0.43 mL of DABCO (0.54 mmol/mL in benzene) were introduced into the reactor and the solution remained under stirring for about 10 min followed by the addition of 2g of 1,3-CHD (25 mmol). The solution turned into yellow immediately and allowed to polymerize for six (6) hours under stirring at 5<sup>0</sup>C before terminating the reaction with degassed methanol. The final triblock terpolymer indicated a total molecular weight of 62.2 Kg/mol and PDI=1.08, verified by SEC and MO studies.

**Synthesis of SBC, BSC and BIC terpolymers.** For the synthesis of the SBC triblock terpolymer, the same procedure as described above was followed. The synthetic route for the BSC and BIC triblock terpolymers was different due to the addition of the polar reagent DABCO just after the complete polymerization of the first block in order to change the polarity of the solution and increase the initiation rate of the polymerization for the second monomer (styrene or isoprene).

For the synthesis of the BSC triblock terpolymer 3g of butadiene (55.5 mmol) were introduced into the reactor with the benzene solution (~150 mL) under vacuum, followed by the addition of 1.1 mL of sec-BuLi (0.14 mmoles/mL) and allowed to polymerize for 24 hours. An aliquot was taken for molecular characterization via SEC and the results indicated the molecular weight for PB was 19.0 Kg/mol with PDI of 1.03. After the complete polymerization of the first block 0.5 mL of DABCO (0.54 mmol/mL) were added, followed by the addition of 3 g of styrene (28.8 mmol) to the solution. The

polymerization was allowed to proceed for 24 hours. A small aliquot was taken again for molecular characterization via SEC and the results indicated that the molecular weight of the PS block was 25.2 Kg/mol with a PDI of 1.04 for the diblock. Finally 4.1g of 1,3-CHD (51.25 mmol) were introduced in the reactor and the system was left for completion of polymerization for 6 hours under stirring at 5<sup>0</sup>C. The reaction was terminated with degassed methanol. The final total molecular weight of the triblock terpolymer was 53.1 Kg/mol (from MO studies) and the PDI equal to 1.06 (from SEC characterization). All triblock terpolymer solutions were precipitated in a large excess of stabilized methanol. The final triblock terpolymers were isolated and dried under vacuum.

## Results and Discussion

**Synthesis.** The main purpose of this work was the synthesis of linear triblock terpolymers of the ABC type with very low PDIs, predictable molecular weights, controlled microstructure for the PCHD segments (~90% -1,4 and ~10% -1,2) and the ability to self-assemble into well-organized morphologies. These terpolymers were synthesized by sequential monomer addition, where 1,3-CHD was always added as the third and final monomer. For all polymerizations, sec-BuLi was used as initiator and benzene as the solvent. To minimize termination and chain transfer reactions during polymerization of 1,3-CHD, DABCO was used as the polar additive, in appropriate ratios [sec-BuLi] : [DABCO] = 1 : 2 and the polymerization of 1,3-CHD was performed at low temperatures (~5<sup>0</sup>C) for successful completion of the CHD polymerization<sup>5,6</sup>.

**Molecular Characterization.** The molecular characterization results for all terpolymers are given in Table 1. SEC chromatograms and <sup>1</sup>H-NMR spectra monitoring the synthesis of two terpolymers are exhibited in Figures 1 and 2, respectively. Fractionation was not necessary for these two materials, even though where necessary this separation technique was applied for purifying the final terpolymer from unwanted diblock and homopolymer by using as solvent / non-solvent mixture toluene and methanol, respectively. In all cases where fractionation was needed the unwanted diblock or homopolymer was lower than 10% in volume.

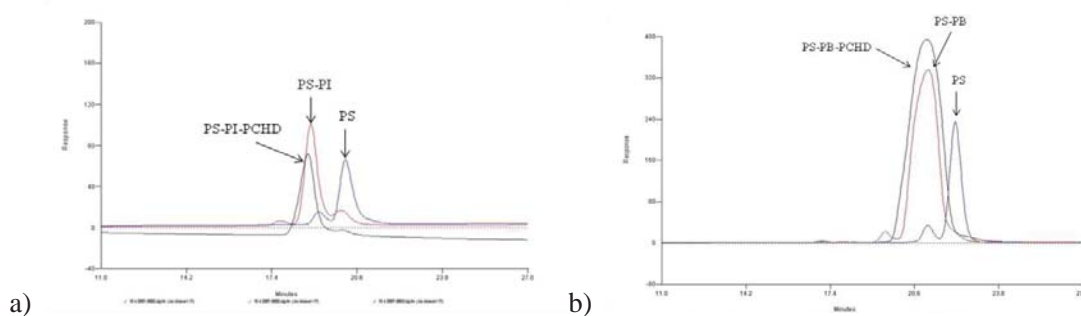
**Table 1:** Molecular Characterization Results For Linear Terpolymers Containing 1,4-PCHD.

Samples	$\overline{M}_n^{a,b}$ 1 <sup>st</sup> block (Kg/mol)	$\overline{M}_n^{a,b}$ 2 <sup>nd</sup> block (Kg/mol)	$\overline{M}_n^{a,b}$ 3 <sup>rd</sup> block (Kg/mol)	$\overline{M}_n^{a,b}$ triblock (Kg/mol)	$\overline{M}_w^c$ triblock (Kg/mol)	$\frac{\overline{M}_w^d}{\overline{M}_n}$ triblock
SIC-1	17,0	35,2	10,0	62,2	67,2	1,08
SIC-2	30,0	26,1	14,3	70,4	74,7	1,06
SIC-3	43,2	45,0	15,2	103,4	110,8	1,07
SBC	15,0	9,8	7,2	32,0	34,5	1,08
BSC	19,0	25,2	8,9	53,1	57,0	1,07
BIC	23,0	7,2	5,9	36,1	38,3	1,06

Samples	1 <sup>st</sup> block (wt%) <sup>e</sup>	2 <sup>nd</sup> block (wt%) <sup>e</sup>	1,4-PCHD block (wt%) <sup>e</sup>	$\Phi$ (% 1 <sup>st</sup> block)	$\Phi$ (% 2 <sup>nd</sup> block)	$\Phi$ (% PCHD)
SIC-1	30,0	53,9	16,1	27,3	56,6	16,1
SIC-2	43,5	41,5	15,0	42,6	37,1	20,3
SIC-3	42,2	40,6	17,2	41,8	43,5	14,7
SBC	48,9	34,6	16,5	46,9	30,6	22,5
BSC	33,0	44,3	22,7	35,8	47,4	16,8
BIC	62,3	20,4	17,3	63,7	20,0	16,3

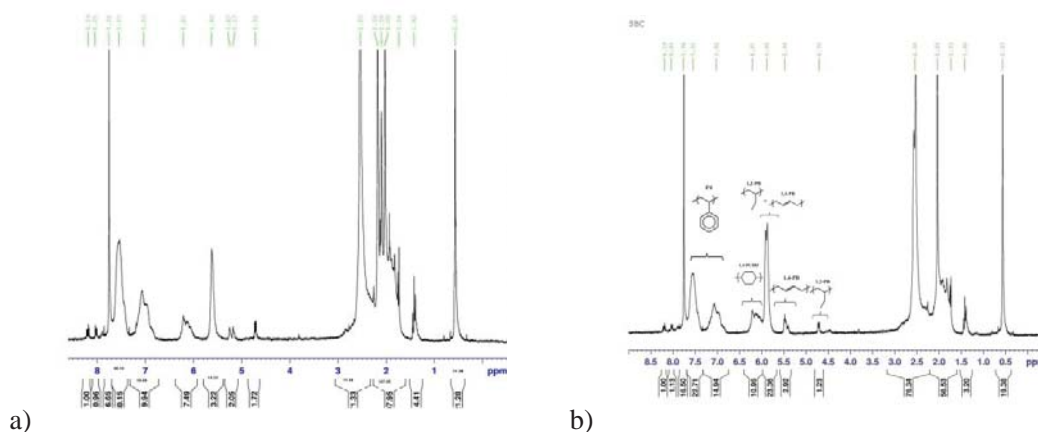
<sup>a</sup>MO in toluene at 30°C. <sup>b</sup>VPO in toluene at 30°C. <sup>c</sup>Calculated from the combination of VPO/MO and SEC results. <sup>d</sup>SEC in THF at 30°C calibrated with polystyrene standards. <sup>e</sup><sup>1</sup>H-NMR spectra.



**Figure 1:** a) SEC chromatograph of the synthetic route of the SIC-1 (17/35/10) sample. b) SEC chromatograph of the synthetic route of the SBC (15/10/7) sample.

The molecular characterization results for all samples indicate that the use of anionic polymerization and high vacuum techniques led to the synthesis of six linear triblock

terpolymers, with different volume fractions, that are well-defined and they can be considered as novel polymers since they exhibit low molecular weight distribution with low levels of molecular and compositional heterogeneity.



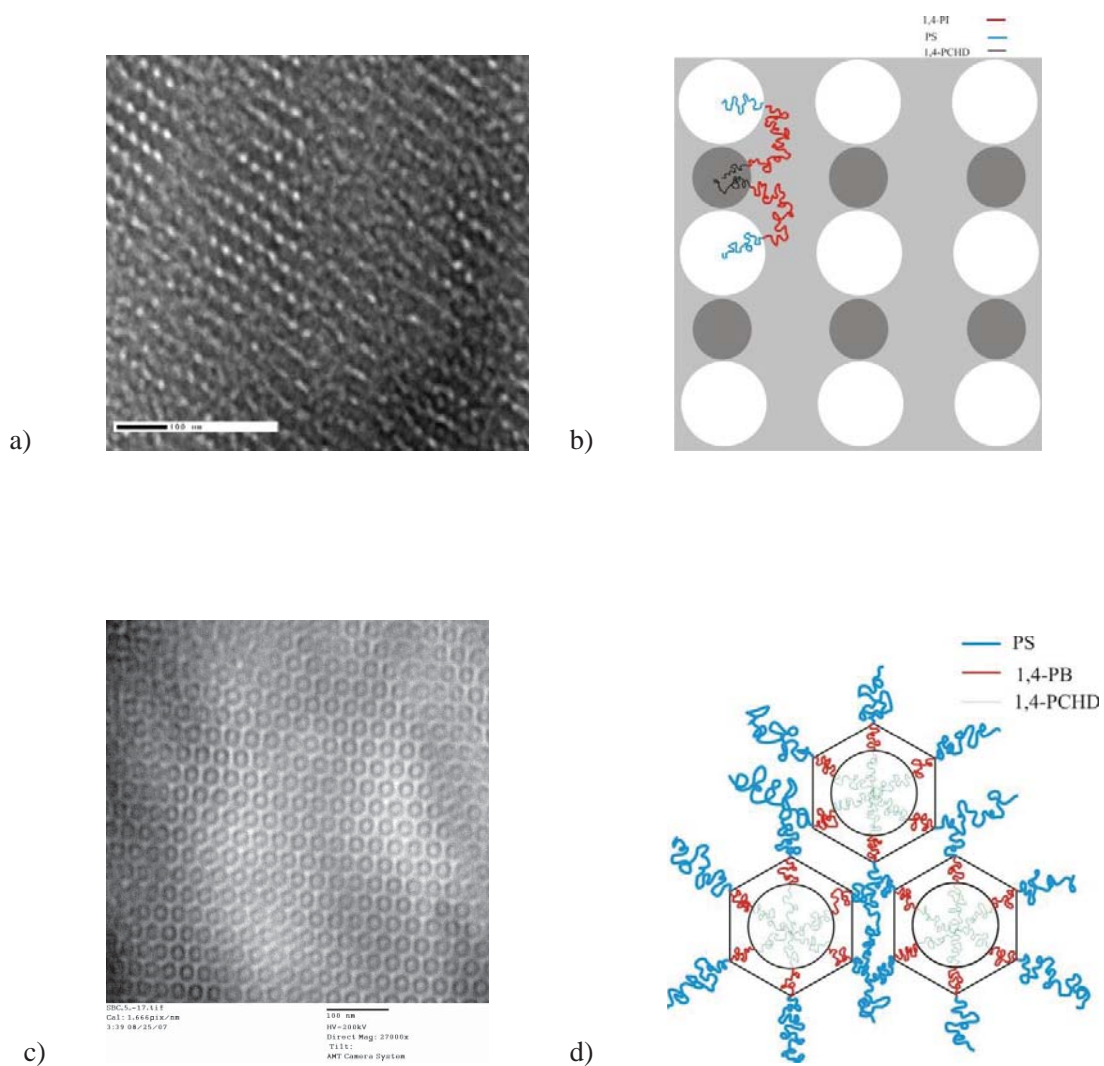
**Figure 2:** a)  $^1\text{H-NMR}$  spectra of the SIC-1 (17/35/10) sample. b)  $^1\text{H-NMR}$  spectra of the SBC (15/10/7) sample.

The polymerization of 1,3 cyclohexadiene as the last monomer and the use of DABCO as a polar additive in order to minimize any side reactions were parameters that led to the successful synthesis of well-defined terpolymers. In the case of the SIC-1 sample a small peak is observed at lower molecular weight in Figure 1a. This peak can be attributed to PCHD homopolymer, since the experimental value for the  $\overline{M}_n$  of the PCHD block is lower than expected. Despite the presence of the polar additive and the low temperature, side reactions occurred (chain transfer or termination) leading to PCHD homopolymer and resulting in lower  $\overline{M}_n$  values for the third block. In the case of the SBC sample, such side reactions also occurred but at a lower degree, as it can be verified from the SEC chromatograph (Figure 1b). Neither the molecular weight distribution of each terpolymer nor the microstructure has been effected significantly by the side reactions and the presence of PCHD homopolymer. The PCHD block in all terpolymers exhibited high (88-90%) -1,4 microstructure due to the existence of DABCO. This is verified from the  $^1\text{H-NMR}$  spectra which exhibit chemical shifts at 1,25-1,85 ppm, typical of the b-protons for the 1,4-poly(cyclohexadiene) (Figure 2a-b).

**Morphological Characterization.** The morphological characterization was performed via transmission electron microscopy (TEM) as seen in Figure 3 for two of the

six synthesized triblocks. Staining with OsO<sub>4</sub> was required for all TEM samples in order to achieve the necessary contrast between the blocks. This chemical reagent is appropriate to increase the mass contrast of polydienes during their observation via transmission electron microscopy. The polydiene phases appear gray or dark while the unstained polystyrene phase appears brighter. The morphological characterization for the SIC-1 triblock showed that the PI block constitutes the matrix and appears gray. A sequence of closed packed cylinders of PS block appears white forming an almost perfect square, while among them and adjacently, 1,4-PCHD black cylinders are exhibiting the same structure as well (Figure 3a-b). Such behavior has never been predicted before or reported in the literature. The morphology obtained approaches the one reported by Thomas et al.<sup>22</sup> with major discrepancies. The terpolymer reported in the literature was of the PS-b-PB-b-PMMA type with the middle block in a larger proportion and volume fraction ratio equal to 1:3:1. In our case, the SIC-1 triblock terpolymer shows almost the same behavior with the middle block (PI) in a larger proportion and volume fraction ratio equal to 1,7:3,6:1 which is different from the aforementioned reported sample. Nevertheless, the difference of the two end blocks (PCHD and PMMA) of each triblock terpolymer creates a significant change of the observed morphology due to the different interaction parameter  $\chi$  among them. Unfortunately, long range order of well-organized areas could not be obtained in order to definitely conclude for the type of the morphology adopted. This can be countered by increasing the casting time (slower solvent evaporation) and annealing temperature (higher than 120<sup>0</sup>C) in order to adopt equilibrium and better organized structures for SIC-1.

The morphological characterization for the SBC triblock (volume fraction 2:1,5:1) showed that the morphology of the synthesized sample was concentric hexagonally closed 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 with one that has been observed in a PS-b-PI-b-P2VP sample<sup>23</sup> (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).



**Figure 3:** a) TEM micrograph image of the SIC-1 (17/35/10) triblock. The black regions correspond to the 1,4-PCHD block, the gray regions to the PI block and the white regions to the PS block. b) Schematic simulation of the observed morphology for the SIC-1 triblock. c) TEM micrograph image of the SBC triblock. The black regions correspond to the PB block, the gray regions to the 1,4-PCHD block and the white regions to the PS block. d) Schematic simulation of the observed morphology of the SBC triblock.

The different values of the volume fractions of these two samples seem to be of no significance for the formation of the observed morphologies in addition of course to the interaction parameter  $\chi$ . Therefore, in our case it is evident that the  $\chi$  values contribute

more to the structure adopted leading to a morphology which is supposed, until now, to be observed only in relatively symmetric linear triblock terpolymers.

The results for both samples were also verified via small angle X-ray scattering (SAXS) experiments (Figure 4) in parts of the bulk films prepared and already used for the TEM studies. Cylindrical morphology for both the SIC-1 and SBC samples is confirmed as shown from the  $\log I$  vs.  $q$  plots in Figure 4a and 4b respectively. The characteristic ratios  $q_n/q_1$  equal to  $1 : \sqrt{3} : \sqrt{4} : \sqrt{7} : \sqrt{9} : \sqrt{12}$  are observed in both samples (Figure 4a and b).

For the SIC-1 triblock terpolymer, reflections can be identified up to the 4<sup>th</sup> order corresponding to the medium order exhibited in TEM (Figure 3a). For the SBC triblock terpolymer, reflections can be identified up to the 6<sup>th</sup> order corresponding to the high order observed also in the TEM image (Figure 3c). Scattering data are represented in the form of intensity measurements as a function of the scattering vector  $q$  defined by

$$q = 4\pi \sin\theta/\lambda \quad (1)$$

where  $\lambda$  is the wavelength of the X-ray and  $\theta$  is half of the scattering angle defined as  $2\theta$ . Using Bragg's equation:

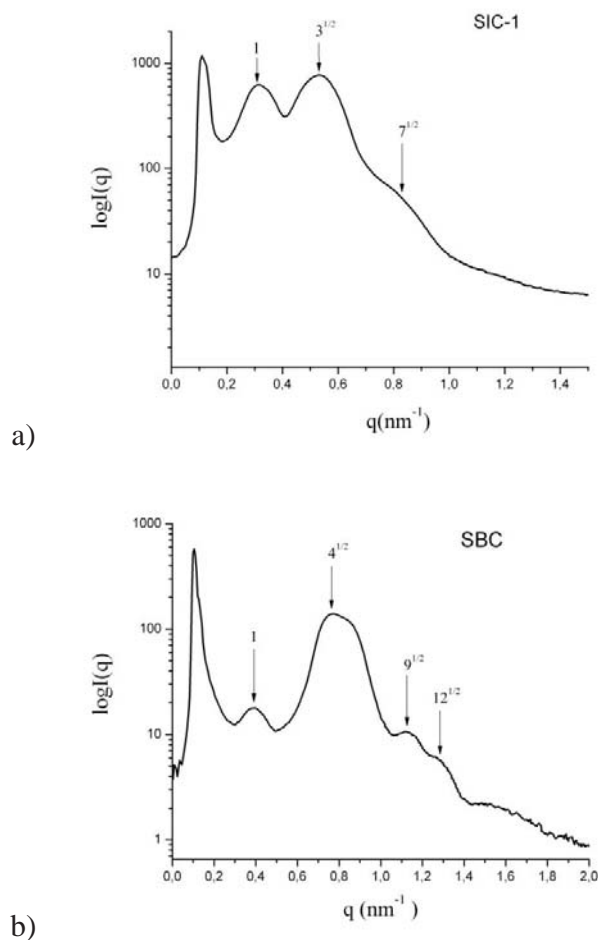
$$\lambda = 2d_{hkl} \sin\theta \quad (2)$$

in compilation with (1) the d-spacing of the reflection  $hkl$  is given by:

$$d_{hkl} = 2\pi/q_{hkl} \quad (3)$$

Considering the 1<sup>st</sup> reflection for each sample as shown in Figure 4a and 4b and using equation (3) we are able to conclude that both samples exhibit rather increased order since more than four reflections are observed in both SAXS plots.

Furthermore, it is indicated from the SAXS plots that some of the peaks are broadened leading to the possibility of overlapping of consecutive peaks. However, it is more plausible that the peak broadening might be attributed to the discrepancies in the form factor between the polydiene blocks when compared to that of the polystyrene, since the electron densities of the polydienes are quite similar, and hence, the SAXS plots are similar to the ones that would be observed from a binary system (polydienes vs. PS), rather than a tertiary system. This is not the case when the system is studied via TEM, since the staining time can be changed depending on the molecular formula of the polydiene.



**Figure 4:** a) SAXS plot for the SIC-1 triblock terpolymer which verifies the observed cylindrical morphology from TEM studies. b) SAXS plot for the SBC triblock terpolymer which also verifies the observed cylindrical morphology from TEM studies.

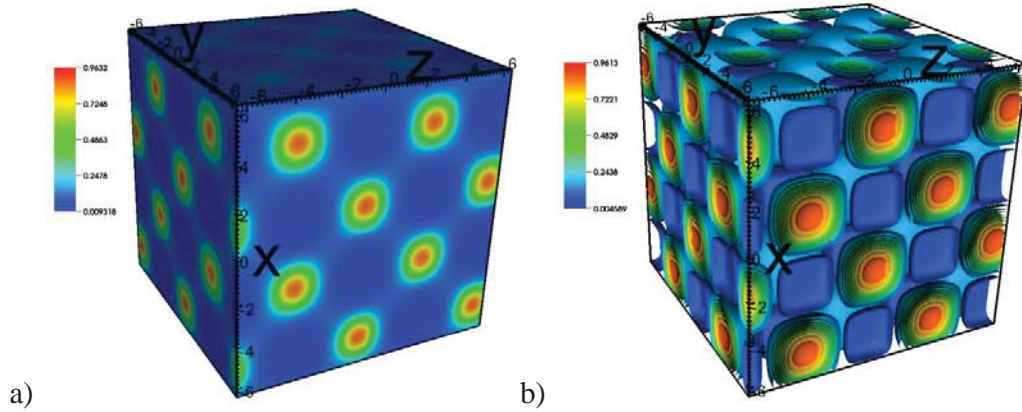
We conclude to the fact from the TEM images that the PCHD stains less than the other polydienes (PB and/or PI) due to the larger number of carbons (6 vs. 4 and/or 5 respectively), since we were able to observe a three-phase contrast from the TEM studies for both samples.

In order to understand whether the observed morphologies are in accord with thermodynamic equilibrium ones, we have carried out numerical calculations using the self-consistent field theory<sup>18,19</sup> (SCFT). Such an approach has recently reported in the literature for PCHD related materials but in diblock systems with polystyrene<sup>24</sup>. For the two samples SIC-1 and SBC, we estimate the interaction parameters to follow the orders:  $\chi_{SI} < \chi_{IC} < \chi_{SC}$ , and  $\chi_{SB} < \chi_{BC} < \chi_{SC}$ , respectively. This order of precedence of  $\chi$  is based



on the fact that an increase in the Kuhn segment lengths lead to an increase<sup>25,26</sup> in the  $\chi$  parameters. In this regard, for estimating the relative order of the  $\chi$  parameters, we have taken the Kuhn segment lengths of poly(butadiene), poly(isoprene), polystyrene, and poly(cyclohexadiene) from the literature<sup>27,28</sup> as 0.53, 0.59, 0.70 and 0.89 nm, respectively.

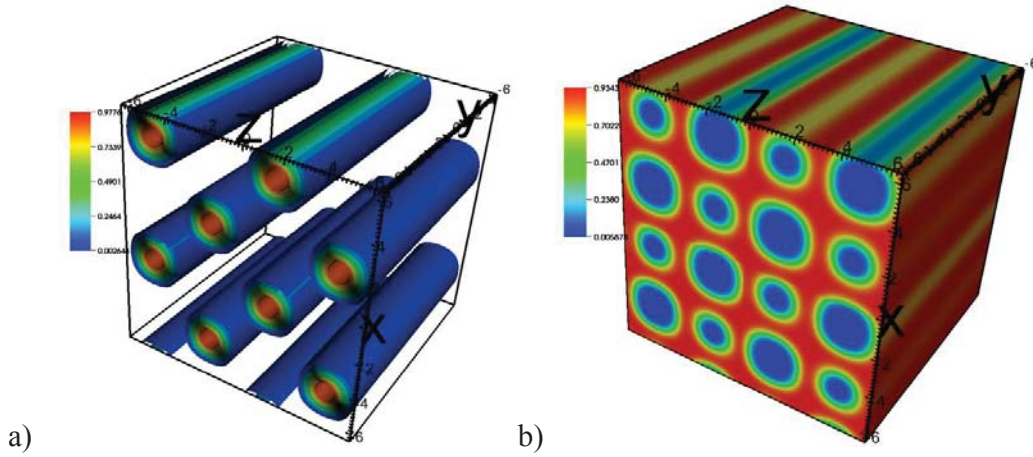
Using the SCFT calculations for ABC triblocks in real-space<sup>18</sup> without assuming any morphologies and starting from different random estimates, we have studied the possibility of the existence of different periodic structures. For comparison with the experiments, C refers to the poly(cyclohexadiene) and A,B represent the other two blocks. For the SIC-1 sample, we have carried out the SCFT calculations using 27%, 57% and 16% as the fractions of A, B and C monomers, respectively. We observed a transition from the disordered  $\rightarrow$  sphere-sphere  $\rightarrow$  cylinder-cylinder when the three  $\chi N$  parameters (N being the total number of Kuhn segments) are changed from  $[\chi_{SI}N, \chi_{IC}N, \chi_{SC}N] = [10, 15, 20]$  to  $[30,35,40]$  in increments of 5. The sphere-sphere morphology is first observed at  $[\chi_{SI}N, \chi_{IC}N, \chi_{SC}N] = [20,25,30]$ . Figure 5 shows the density distributions of the monomers in the end blocks for the sphere-sphere morphology. From the figure, it is clear that the shorter block poly(cyclohexadiene) form the spheres with a smaller diameter, as expected.



**Figure 5.** a) Volume fraction of C monomers and b) iso-surface plots for the A monomers (which represents styrene) for the sphere-sphere morphology. The plots are obtained for  $\chi_{SI}N = 20$ ,  $\chi_{IC}N = 30$ ,  $\chi_{SC}N = 35$  in the case of SIC-1.

Similarly, the monomer distributions in the cylinder-cylinder morphology are shown in Figure 6, with the PCHD block forming cylinders of shorter diameter. Furthermore, the cylinders exhibit square packing. This structure is the closest to the morphology observed in the experiment (cf. Fig. 3a) but it has a different cylinder packing symmetry (alternating small and large diameter cylinders of PS and PI respectively versus rows as depicted in Fig. 3b). We point out that the real-space SCFT calculations can not explicitly rule out the possibility of its existence and that further SCFT calculations using spectral<sup>29</sup> methods with a known symmetry of the periodic structure might better elucidate the equilibrium nature of the new morphology. In that regard, more experiments and theoretical calculations are needed.

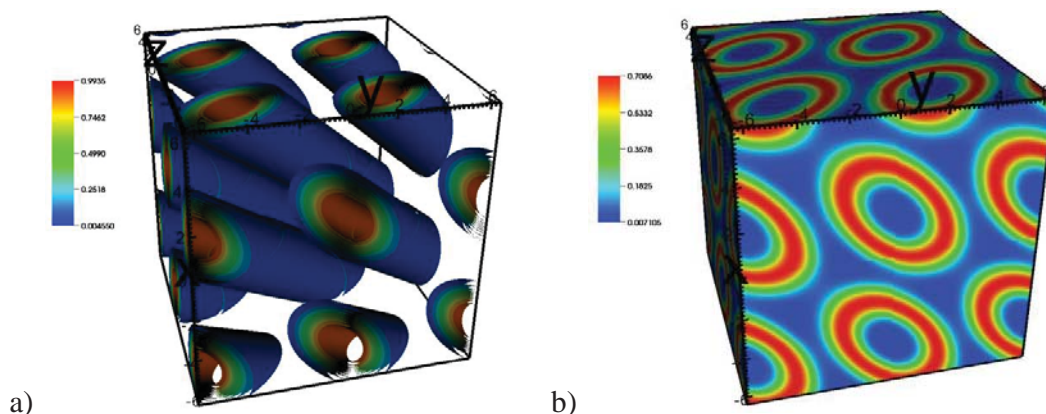
For the SBC sample, we have carried out the SCFT calculations with 47%, 31% and 22% as the fractions of A, B and C, respectively. Using the SCFT, we have observed order-order transitions from the disordered  $\rightarrow$  body centered cubic (with PCHD forming the core)  $\rightarrow$  double continuous network  $\rightarrow$  core-shell cylinders when the three  $\chi N$  parameters are changed from  $[\chi_{SB}N, \chi_{BC}N, \chi_{SC}N] = [10, 15, 20] \rightarrow [10, 20, 25] \rightarrow [15, 20, 25] \rightarrow [15, 25, 30] \rightarrow [20, 25, 30] \rightarrow [20, 30, 35]$ . The body centered cubic morphology is observed for  $[10, 20, 25]$ .



**Figure 6.** a) Iso-surface plot of the volume fraction of C monomers and b) the density plots of the B monomers (representing isoprene) for the cylinder-cylinder morphology. These plots are obtained for  $\chi_{SI}N = 30$ ,  $\chi_{IC}N = 35$ ,  $\chi_{SC}N = 40$  representing SIC tri-blocks.

The core-shell cylindrical morphology sustains for the last three set of  $\chi N$  parameters and is shown in Figure 7. In agreement with the experiments, the block with the highest Kuhn

segment length (i.e., PCHD) forms the core of these cylinders with the shell formed by the middle block. Also, the core-shell cylinders are packed hexagonally, again in agreement with the experiments.



**Figure 7.** 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 core-shell cylindrical morphology. These plots correspond to  $\chi_{SB}N = 20$ ,  $\chi_{BC}N = 30$ ,  $\chi_{SC}N = 35$  representing SBC tri-block.

Comparing the three  $\chi N$  parameters at which an ordered morphology is first observed for the two cases studied here using the SCFT, it is clear that the SIC triblock copolymers have a less tendency to micro-phase separate compared to the SBC triblocks. This is in qualitative agreement with the experiments, where relatively poor long-range order is observed for the SIC-1 sample.

## Conclusions

Linear triblock terpolymers of 1,3-cyclohexadiene with styrene, isoprene and butadiene can be successfully synthesized by sequential anionic polymerization using *sec*-BuLi as initiator, benzene as solvent and DABCO as polar reagent. The molecular characterization results obtained using size exclusion chromatography (SEC), MO / VPO and  $^1\text{H-NMR}$  spectroscopy indicate a high degree of molecular and compositional homogeneity. The obtained microstructure of the PCHD using DABCO was mainly 1,4 (~90%) while the obtained microstructure of PI was altered in 3,4 (~50%) when its polymerization initiated in the presence of DABCO. The morphological characterization results obtained by transmission electron microscopy (TEM) and small angle X-ray

scattering (SAXS) indicated a high degree of self-assembly with very interesting structures for two of the synthesized samples. It can be concluded that there is a significant dependence of the self-assembly from the  $\chi$  interaction parameter and the polymerization degree for the majority of the synthesized samples, as expected.

The real-space SCFT calculations employing conformational asymmetry predicted core-shell cylindrical morphology for the SBC tri-blocks, thus indicating it as an equilibrium structure. The structural features such as the hexagonal packing and formation of the core by the PCHD block are in good agreement with the experiments. While we were not able to identify the parameter space where the new morphology for the SIC triblocks is obtained, we believe that SCFT calculations using spectral methods and known symmetry of the periodic structures should be able to elucidate the new morphology and further clarify that it is an equilibrium one.

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