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Core−Shell Double Gyroid Morphologies in ABC Triblock Copolymers with Different Chain Topologies[†]

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ABSTRACT: The existence of the core−shell double gyroid morphology is proven by transmission electron microscopy and computer simulation for a linear SBV triblock copolymer and a SBV heteroarm star terpolymer, where S is polystyrene, B is poly(1,2-butadiene), and V is poly(2-vinylpyridine).

Introduction

While three-dimensionally interconnected periodic structures have been known in mathematics since the work of Schwarz,[1] it took several decades before a material (soap) having this type of morphology was reported.[2] Block copolymers showing a cocontinuous morphology have been identified for the first time by Thomas' group in 1986[3] and other groups later on.[4−6] It was not until 1994 that the original assignment of two interpenetrating tetrapod networks of the minor component in the matrix of the major component (so-called "ordered bicontinuous double diamond" structure (OBDD)[3]) was found to be inconsistent with some results obtained by small-angle X-ray scattering.[7] Assuming a structure with two interpenetrating tripod networks in a matrix was consistent with the different observations and was named the gyroid morphology,[7] following the discovery of this cubic saddle-shaped morphology with triply periodic minimal surfaces with negative Gauss curvature by Schoen.[8]

While in the block copolymer systems mentioned so far two different components form three continuous domains, Mogi et al. reported on a linear ABC triblock copolymer with A and C forming interconnected networks in a B matrix.[9] They believed their system to form an "ordered tricontinuous double diamond" structure (OTDD). Matsen showed later on that also this morphology is to be considered as a gyroid rather than an OTDD morphology.[10] While this linear ABC triblock copolymer has three different continuous phases, there are other systems based on linear ABC triblock copolymers showing core−shell double gyroid morphologies with all together five continuous phases, which attract interest as potential structures for membranes or for optical applications.[11,12] So far this type of morphology has been reported for blends of block copolymers[13,14] and linear ABC triblock copolymers.[12,14] A scheme of this morphology is shown in Figure 1a.

The existence of this morphology in a heteroarm star terpolymer ($S_{14}B_{37}V_{49}{}^{145*}$, $M_W/M_N = 1.04$) and a linear ABC triblock copolymer ($S_{48}B_{31}V_{21}{}^{71}$, $M_W/M_N = 1.03$) of the same components is presented in this contribution, where S is polystyrene, B is poly(1,2-butadiene), V is poly(2-vinylpyridine), and the subscripts and superscripts denote weight fractions and the number-averaged molecular weight in kg/mol, respectively. To distinguish the linear block copolymer from the star terpolymer, the latter is labeled by an asterisk.

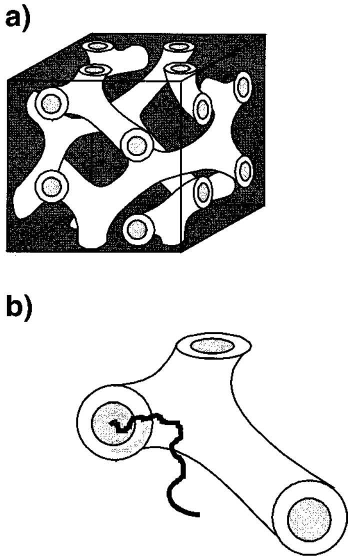

Figure 1. Scheme of the core−shell double gyroid morphology.

Experimental Section

The synthesis of the star terpolymer[15,16] and the linear triblock copolymer[17,18] followed procedures detailed elsewhere. Polymer films for transmission electron microscopy (TEM) were solution cast from THF (solubility parameter $\delta_{THF} = 9.1$ (cal/cm^3)$^{0.5}$)[19] at room temperature and then annealed for 6 h at 150 °C under vacuum. Ultrathin samples (machine setting 40 nm) were cut using a Reichert-Jung Ultracut E equipped with a diamond knife under cryogenic conditions. Staining was achieved by treating the ultrathin samples for 1 min with OsO_4 vapor[20] and/or for 12 h with CH_3I or I_2 vapor.[21,22] Electron micrographs were taken from a Zeiss 902 operating at 80 kV in the bright field mode.

Results and Discussion

Though the chain topology of heteroarm star terpolymers is incompatible with a core−shell morphology consisting of completely demixed microphases of all three components, core−shell morphologies have been reported for this type of copolymers before. This requires a certain degree of mixing between different blocks within the shell of such morphology, as shown schematically in Figure 1b. Hadjichristidis' and Thomas' groups found core−shell cylindrical morphologies for heteroarm star terpolymers of polystyrene, polyisoprene, and poly(methyl methacrylate) with certain compositions.[23] Also in a SBV heteroarm star terpolymer ($S_{21}B_{17}V_{62}{}^{188*}$) a core−shell morphology has been found,

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[†] In memoriam Prof. Dr. Reimund Stadler.

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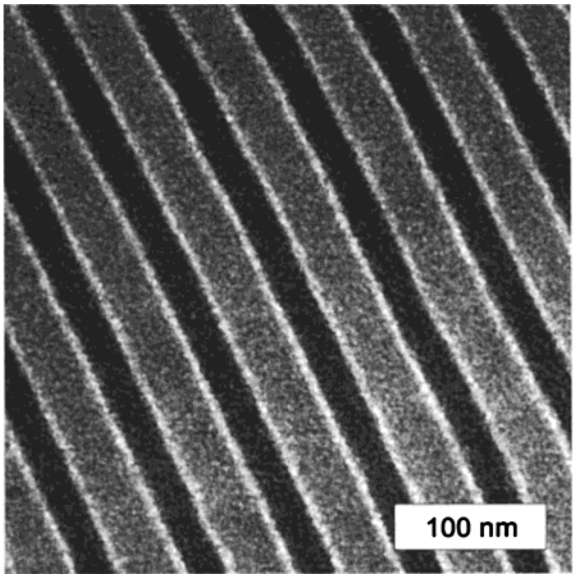

Figure 2. TEM micrograph of lamellar region of $S_{14}B_{37}V_{49}{}^{145*}$ stained with OsO_4 and CH_3I.

where B-cylinders are embedded in the S-lamella and V forms the other lamella.[16]

Investigation of $S_{14}B_{37}V_{49}{}^{145*}$ by TEM shows mainly lamellar regions of all three microphase-separated components (Figure 2). Figures 3a, 4a, and 5a show other TEM micrographs of the same sample stained with OsO_4, I_2, and $OsO_4 + CH_3I$, respectively. Since the sample thickness is on the order of 40 nm, it is below the size of a unit cell of the block copolymer morphology. Thus, it is possible to observe different patterns of a unit cell along the same projection depending on the relative height of the sample slice within the unit cell. Essential features of these micrographs could be reproduced by computer simulation using TEMsim assuming a gyroid morphology.[24] The results are shown in Figures 3b–d, 4b, and 5b. Figure 3b,c shows the view along the [112] projection at different heights within a unit cell. Since the sample was not cut exactly along the (112) plane, different features of this projection are visible in Figure 3a. A slightly inclined projection with respect to the (112) plane reproduces Figure 3a quite well, as shown in Figure 3d. In these simulations the dark stained B-domain was taken as the matrix. The white cores correspond to the V- and S-phase.

In Figure 4 a the V-domains appear dark due to the staining with iodine. They seem to be surrounded by a light corona and a gray matrix. A simulated projection onto the (112)-plane reproduces the essential features (symmetry, dark core) quite well.

Figure 5a shows the TEM micrograph of a sample stained with OsO_4 and CH_3I. As compared to Figure 3a, hardly any additional contrast is obtained. The V-domains appear light, and the dark B-domain forms the matrix. On the left side of the image there are

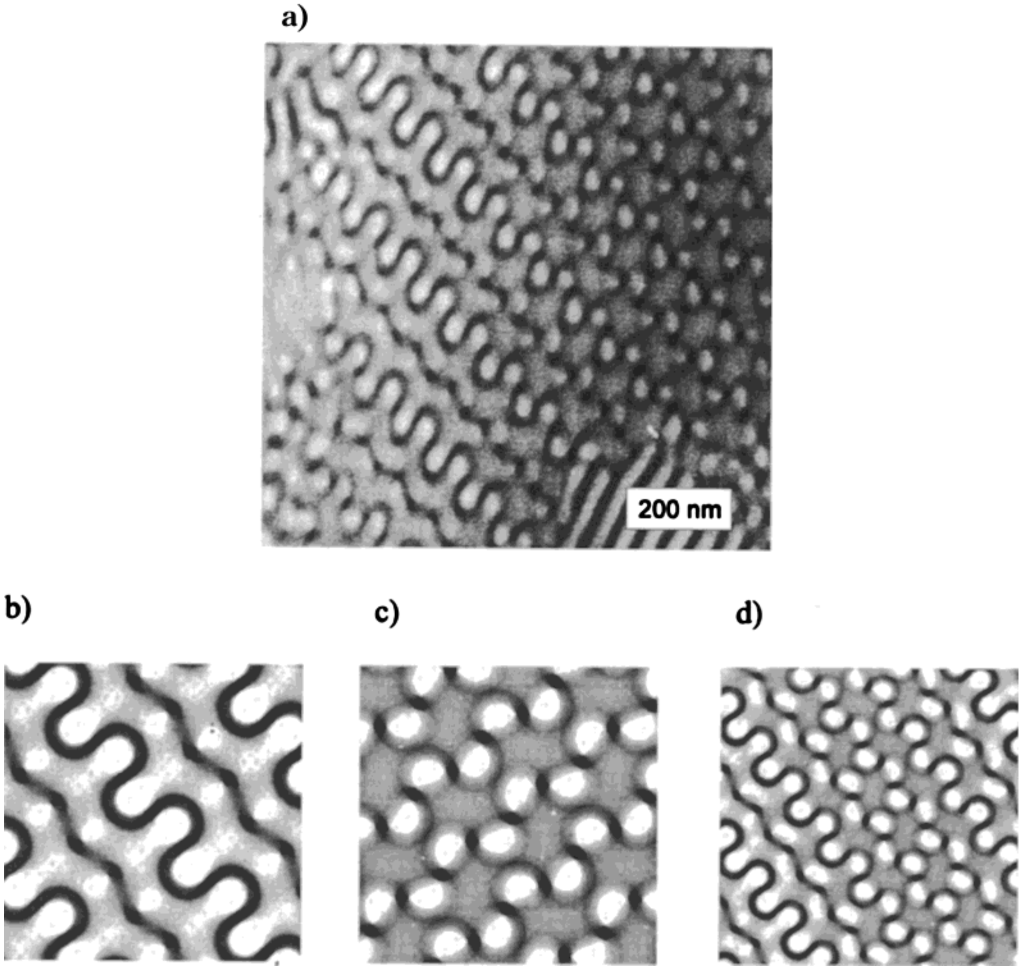

Figure 3. (a) TEM micrograph of $S_{14}B_{37}V_{49}{}^{145*}$ stained with OsO_4. (b) Simulation of [112] projection (dark matrix, translation 0, thickness 0.33). (c) Simulation of [112] projection (dark matrix, translation 0.45, thickness 0.33). (d) Simulation of "[1.08;0.84;2.04]" projection (dark matrix, translation 0.48, thickness 0.35).

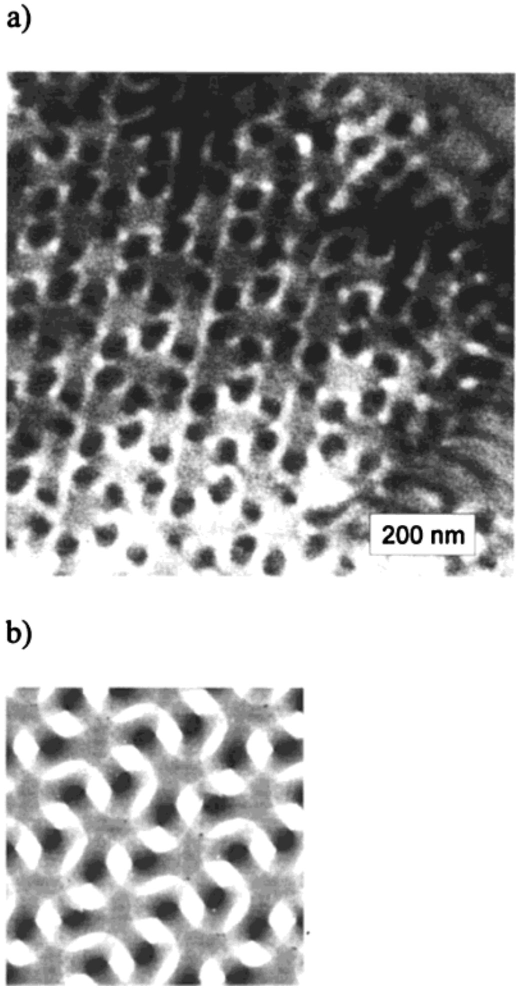

Figure 4. (a) TEM micrograph of $S_{14}B_{37}V_{49}{}^{145}$* stained with I_2. (b) Simulation of [112] projection (dark core, translation 0.45, thickness 0.33).

regions corresponding to the [112] projection, while on the right side there is the [110] projection, as shown by the simulation in Figure 5b.

From these figures it cannot be decided where the S-chains are located. Either S forms a shell around the V-gyroids and separates them from the B-matrix, or the V-domains are partly mixed with the shorter S-chains. In favor of the first assumption is the observation of Figure 2, according to which S forms lamellae between the B- and V-lamellae. Considering the χ parameters, there should be no miscibility between S and V. With the incompatibility between B and V being the strongest in this system, S tends to be enriched at the border between the gyroid cores and the B-matrix. In this sense the morphology can be considered as a core−shell double gyroid morphology. The double gyroid morphology in diblock copolymers exists in a region, where the incompatibility expressed by the product χN does not exceed approximately 60.[25] Taking the χ parameters[19,26,27] from Table 1, for all the polymer pairs S/V, S/B, and B/V the product $\chi N = 60$ is exceeded ($\chi_{SV}N_{S+V} \approx 80$, $\chi_{SB}N_{S+B} \approx 110$; $\chi_{BV}N_{B+V} \approx 530$), and thus all these blocks should be strongly segregated from each other. However, due to the strong confinements of the translational entropy of the branching point, the system might allow for a certain degree of mixing in the neighborhood of the branching point and relax by this the entropical confinements to a certain amount, but it should not involve the whole S-block.

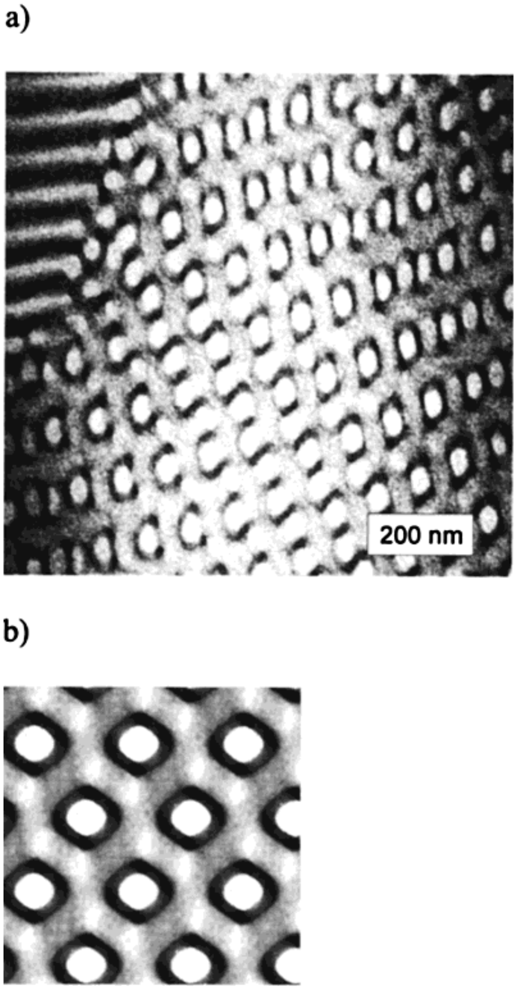

Figure 5. (a) TEM micrograph of $S_{14}B_{37}V_{49}{}^{145}$* stained with OsO_4 and CH_3I. (b) Simulation of [110] projection, (dark matrix, translation 0.45, thickness 0.33).

Table 1[a]

polymer	solubility parameter[19] δ [cal/cm^3]$^{1/2}$	density[26] [g/cm^3]	χ S	χ B	χ V
polystyrene (S)	9.10	1.05	0		
poly(1,2-butadiene) (B)	8.05	0.96	0.098	0	
poly(2-vinylpyridine) (V)	10.00[27]	1.145	0.092	0.325	0

[a] $\chi = v/(RT)(\delta_i - \delta_j)^2$; v is the geometric average of the molar segmental volume calculated from the densities at room temperature (density corrections for the real temperature are neglected), and RT is the molar thermal energy at 150 °C.

Another interesting observation is the large volume fraction of the core gyroids. Even if the cores only consist of V, they cover a volume fraction of about 45%. In comparison to the maximum value found for diblock copolymers (approximately 37%[25]), this is significantly larger. A possible reason for this behavior was given by Milner when discussing AB_2 and other star copolymers:[28] due to the branching, a larger demand for space exists for the B-phase close to the interface between the domains. This leads to an induction of interfacial curvature, and thus a gyroid morphology may become stable at an overall composition of a block copolymer, where the linear analogue of similar overall composition would still form lamellae. Hadjichristidis' and Thomas' groups presented results confirming these morphological properties for binary star copolymers.[29,30] For our system this would mean that S and B act in the same

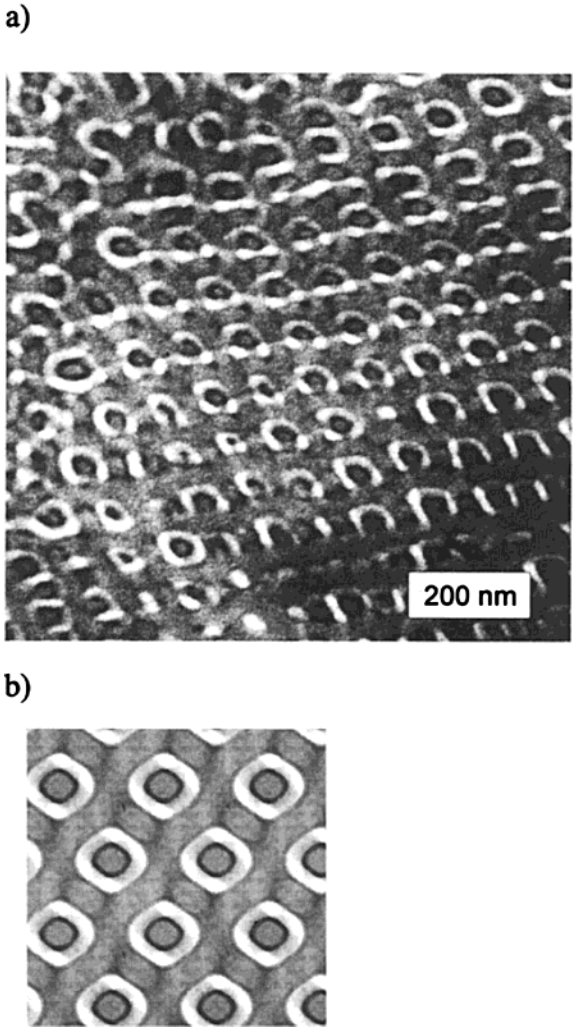

Figure 6. (a) TEM micrograph of $S_{48}B_{31}V_{21}^{71}$ stained with OsO_4 and CH_3I. (b) Simulation of [110] projection (gray core, dark shell, white matrix, translation 0.45, thickness 0.33).

way with respect to the curvature of the V-domain. However, this is in contradiction to the repulsive interactions discussed before, unless during the evaporation process the repulsive interactions between S and B are lower than the ones between S and V due to the presence of THF at the point, when the morphology forms. Also, it is questionable where the center point of the star terpolymer is located: either close to the S/V boundary or close to the S/B boundary. Another reason for B forming the matrix in $S_{14}B_{37}V_{49}^{145*}$ could be the significantly larger degree of polymerization as compared to that of the V-block. This leads to a larger contribution of the B-block to the elastic energy of the whole chain as compared to the case of the V-block, although the latter occupies a larger volume. As a consequence, there is a tendency of the B-block to form the corona around V and S leading to more conformational entropy of the system as compared to the reversed situation with V forming the matrix and B the core gyroids. However, the repulsive interactions between S/B and S/V are large and comparable but still much smaller than the repulsive interaction between B/V, so a lamellar arrangement with S separating B- and V-lamellae may represent the equilibrium morphology. In that case the coexistence of lamellae and core–shell double gyroid could indicate kinetic reasons for the formation of the latter, possibly due to the choice of the solvent. Less polar solvents could enhance the formation of core–shell morphologies in this type of heteroarm star terpolymers by swelling B and S to a larger degree than V at the point, when the structure forms during the evaporation of the solvent. An investigation of the influence of the casting solvent on the morphology of poly(2-vinylpyridine)-*block*-polyisoprene diblock copolymers (VI) showed THF to be a better solvent for the V-domains as compared to the I-domains.[31] Note that the solubility parameters of I and B are very similar.[19]

A coexistence of lamellae and a core–shell double gyroid morphology was also observed for a linear polybutadiene-*block*-polystyrene-*block*-poly(methyl methacrylate) triblock copolymer (BSM), which showed the coexistence of lamellae and core–shell double gyroid morphology with a B-core.[14]

Figure 6a shows a TEM micrograph of the linear $S_{48}B_{31}V_{21}^{71}$, which also self-assembles into a core–shell double gyroid morphology. Figure 6b shows the corresponding simulation reproducing the [110] projection of this morphology. Here V forms the cores, B forms the shells, and S is the matrix. Because of the stronger incompatibility between B and V as compared to S and B in conjunction with the smaller volume fraction of V, the system tends to form a smaller interface between B and V as compared to B and S. In addition, the larger S- and B-chains gain more conformational entropy as compared to the case of lamellar domains. The situation is similar to the one reported before for polyisoprene-*block*-polystyrene-*block*-poly(dimethylsiloxane).[12]

While the star topology allows the S-block to separate the B- and V-domains to a certain extent, this is impossible in this linear triblock copolymer. Increasing the weight fraction of the V-block by 6% leads to a distorted gyroid phase and upon further increase a lamellar morphology is obtained, while a decrease of the V-block leads to core–shell cylinders.[18]

Conclusion

Comparing the results of the present work with results from literature, we can conclude that core–shell double gyroid morphologies can be found in linear ABC triblock copolymers with two significantly different repulsive interactions between the middle and the two end blocks for various compositions. The existence of this morphology also in an ABC heteroarm star terpolymer could also be shown and strongly evidenced by computer simulation. However, since this morphology was only found as a minority structure besides lamellae, we have to assume that it may not be the equilibrium morphology for this polymer. Because of the fact that the lamellar structure clearly shows all three components forming lamellae where the two blocks with the strongest repulsive interaction are separated from each other by the third block, it is obvious that core–shell morphologies could be stable for heteroarm star terpolymers with different compositions as the one presented in this work. One example shown before was a lamellar structure of S and V where B cylinders are embedded in the S domain.[16]

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