Macromolecules **1999,** *32,* 5165−5167

Core−Shell Cylinders and Core−Shell Gyroid Morphologies via Blending of Lamellar ABC Triblock and BC Diblock Copolymers[†]

Thorsten Goldacker and Volker Abetz*

Makromolekulare Chemie II, Universität Bayreuth,
D-95440 Bayreuth, Germany

Received February 24, 1999
Revised Manuscript Received May 21, 1999

There has been some activity in blending different microphase-separated diblock copolymers with various compositions or different overall molecular weight and the same composition in order to study their morphological behavior.[1−3] Part of that research was motivated by the observation of cocontinuous morphologies in a relatively small composition range of the phase diagrams of pure diblock copolymers.[3] Rather than synthesizing block copolymers with a variety of compositions, it is easier to blend block copolymers with different compositions in different ratios with each other and by doing that, systems with various overall compositions with respect to one of the two kinds of repeating units are obtained. In addition, blends of AB diblock copolymers with A homopolymers have shown morphological transitions depending on the relative amount of the components.[4] Thereby, it was also found that the molecular weight of the free chain should not be larger than the corresponding block of the block copolymer. If the free chain is too large, it will not wet the interface with the corresponding block, and the system stays macroscopically phase-separated.

The morphology of blends of polystyrene-*b*-polyisoprene-*b*-poly(2-vinyl pyridine) (SIVP) with polystyrenes of different molecular weights has been reported recently.[5] It was shown that SIVP with similar amounts of all three components forms a core−shell cylindrical morphology with a VP core, an I shell and an S matrix.[6] In this system, the curvature is induced by the very dissimilar interfacial tensions leading to different interfacial areas per chain at the I−VP and S−I interfaces. Due to the volume fraction of S, it cannot fill the matrix space without inhomogeneous stretching in different directions of the hexagonal unit cell, which leads to a nonconstant mean curvature of the interfaces. Adding polystyrene homopolymer with sufficiently low molecular weight to this triblock copolymer leads to a swelling of the matrix, and the morphology of the blend has cylinders with circular-shaped cross sections and thus achieves a constant mean curvature of the interfaces. The core−shell cylindrical morphology for pure ABC triblock copolymers was first suggested by Riess et al.[7] In polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) triblock copolymers, core−shell cylindrical morphologies were only found when the system has an asymmetric composition.[8] A core-shell cylindrical morphology has also been reported for asymmetric polystyrene-*block*-polycyclohexadiene diblock copolymers, but there it is most likely only metastable.[9]

Recently, the possibility of superstructure formation in a blend of diblock and triblock copolymers was shown.[10] In that particular case, a lamellar polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (SBT) was combined with a lamellar ST diblock copolymer giving rise to flat parallel interfaces in the noncentrosymmetric lamellar sequence SBT TS SBT TS. The driving force for the formation of this superlattice is a net reduction of the elastic energy contributions of the endblocks of SBT and the two blocks of the diblock copolymer, when their chemically similar blocks interpenetrate each other.

Here, we present morphological investigations by transmission electron microscopy (TEM) on blends of lamellar SBM and BM block copolymers. Their molecular characteristics are given in Table 1. The synthesis and the TEM investigations of these materials followed procedures detailed elsewhere.[10,11]

When blending lamellar ABC with lamellar BC block copolymers, many different superstructures can be formed. Besides a macrophase separation between the two block copolymers, various lamellar blends with flat interfaces are also possible. For example, a lamellar blend with a sequence of (ABC CB BC CBA) can occur, which is a centrosymmetric structure of double layers of both diblock and triblock copolymers. Another possibility is a kind of random sequence between BC and ABC block copolymers, which will occur when the C blocks of both the diblock and the triblock copolymers do not show any preferential mixing with either a C block of the same species or the other one. In this case, an aperiodic superstructure will be obtained. In addition, a possible superstructure is the incorporation of the BC diblock chains with the same direction into the ABC structure. This last way of mixing between the blocks of diblock and triblock copolymer can be envisioned as an increase of the volume fractions of both B and C blocks with respect to the A block. Due to this, a lamellar superstructure may be only expected for small volume fractions of diblock copolymer when incorporated in this fashion. For larger amounts of diblock copolymer, chains should no longer form a lamellar superstructure but a superstructure with curved intermaterial dividing surfaces, such as cocontinuous or cylindrical morphologies may occur with the A block forming the inner core structure.

Due to the nearly similar block lengths in the tri- and diblock copolymers and the comparable interfacial tensions at the S−B and the B−M interfaces in the triblock copolymer, both the di- and triblock copolymers form lamellar structures in the pure state with the sequences SBM MBS and BM MB, respectively.

Table 2 summarizes the morphologies found for blends with different amounts of these block copolymers. The blends containing 79% and 61% of BM show a core−shell cylindrical morphology with an M matrix besides lamellae of the excess diblock copolymer. This structure is also present in the blend with 52% of SM. A domain of long-range hexagonally packed core−shell cylinders is shown in Figure 1. In this nonlamellar superstructure, the B domains are strongly curved. The S side has a negative curvature according to its reduced volume fraction in the blend. The B shell appears black due to the staining with OsO_4. It separates the inner S cylinders from the matrix of M. Due to the similar amount of both B and M, the cylinders have a noncircular hexagonal-like cross section, as was observed by Gido et al.[6]

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

10.1021/ma990277n CCC: $18.00 © 1999 American Chemical Society
Published on Web 07/08/1999

Table 1. Block Copolymer Molecular Characteristics

name	$M_n{}^a$/kg mol^{-1}	$M_w/M_n{}^b$	$w_S{}^c$	$w_B{}^c$	$w_M{}^c$	$\phi_S{}^d$	$\phi_B{}^d$	$\phi_M{}^d$
SBM	173	1.038	0.33	0.34	0.33	0.33	0.37	0.30
BM	94	1.031		0.53	0.47		0.58	0.42

[a] Determined by membrane osmometry. [b] SEC (calibrated for PS). [c] w = weight fractions as determined from ^{1}H NMR. [d] ϕ = volume fractions using the following densities:[24] $\rho_S = 1.05$ g/cm^3, $\rho_B = 0.96$ g/cm^3, and $\rho_M = 1.15$ g/cm^3.

Table 2. Block Copolymer Morphologies[a]

L-BM	++	++	+	+	−	−	−	−
CYL	−	+	++	+	+	−	−	−
GYR	−	−	−	+	+	++	+	−
L-SBM	−	−	−	−	−	−	++	++
ϕ_S	0.00	0.07	0.13	0.16	0.20	0.26	0.30	0.33
ϕ_{BM}	1.00	0.79	0.61	0.52	0.40	0.22	0.10	0.00

[a] Key: L-BM, lamellae of BM; CYL, core−shell cylinder with S core; GYR, core−shell double gyroid; L-SBM, lamellae of SBM; ϕ_S, overall volume fraction of polystyrene; ϕ_{BM}, volume fraction of BM diblock copolymer; ++, dominant structure; +, structure occurs less often; −, structure absent.

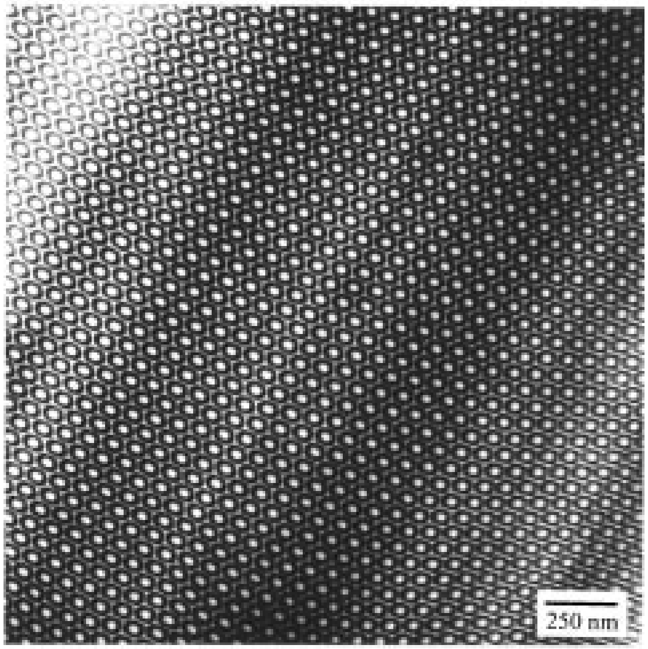

Figure 1. TEM micrograph of a blend of 48% SBM and 52% BM showing the core−shell cylindrical superlattice.

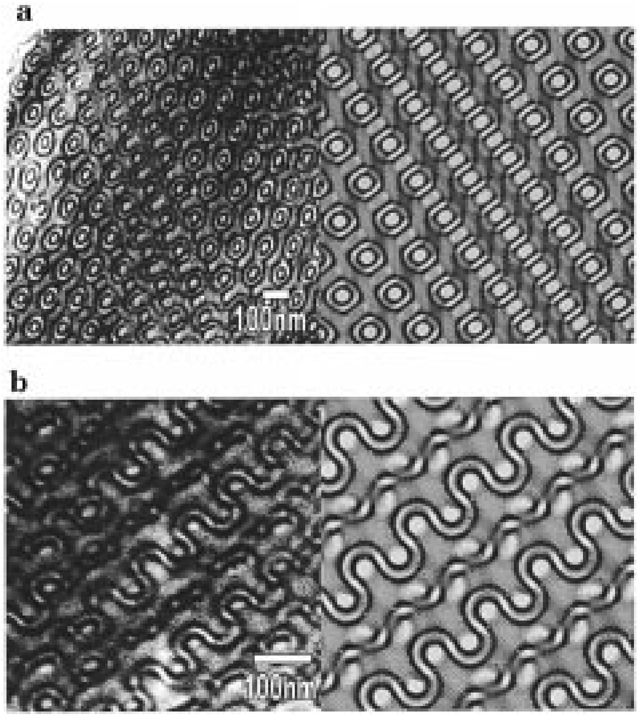

Figure 2. Blend of 79% SBM and 21% BM. (a) Left: TEM micrograph along the [110] projection. Right: simulation of TEM, [1.02 0.99 0.05] projection; translation, 50% of unit cell; and thickness, 67% of unit cell. (b) Left: TEM micrograph along the [112] projection. Right, simulation [112] projection; translation, 50% of unit cell; and thickness, 72% of unit cell.

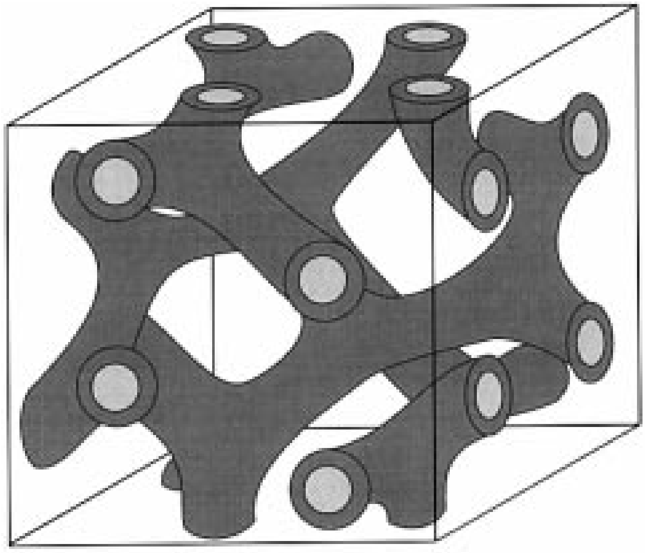

Figure 3. Scheme of the core−shell double-gyroid morphology.

This blend containing 52% of BM diblock copolymer also shows regions of lamellae of the diblock copolymer, as well as other regions with a core−shell double-gyroid morphology. The coexistence of three different morphologies may be attributed to kinetic reasons. We believe the two core−shell morphologies to be stable mixed morphologies and the lamellae of pure diblock copolymer to be metastable, because at a blend composition of 40% diblock copolymer only the two different core−shell morphologies are observed and no pure phases of either diblock or triblock copolymer occur. This indicates the mixed morphologies to be stable with respect to macrophase separation between the two block copolymers. In a blend with 20% diblock copolymer, the core−shell double-gyroid morphology becomes dominant (Figure 2). The left sides of parts a and b of Figure 2 show TEM images, and the right sides show computer simulations obtained by TEMsim.[12] The core−shell double-gyroid morphology schematically shown in Figure 3 corresponds to the well-known double gyroid found for binary block copolymers [13] with $Ia\bar{3}d$ symmetry, where the minor phase builds up two interpenetrating trifunctional cylinder networks. Here, S forms these networks and is covered by a shell of B, which separates it from the matrix of M. The view shown in Figure 2a corresponds approximately to the [110] projection of a double-gyroid structure, and the TEM micrographs more likely represent cross sections rather than projections. Due to the relatively large periodicity of this block copolymer blend, the TEM images can visualize fractions of the thickness of a unit cell. Thus, a small deviation of the [110] projection leads to a continuous change of the appearance of the domains from the bottom left to the

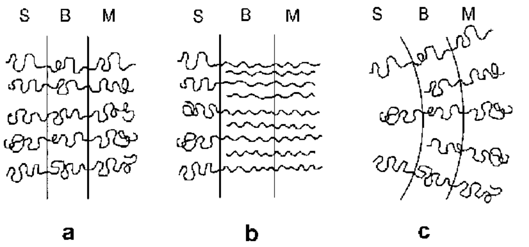

Figure 4. Schemes of chains in various structures. (a) Lamellae of an SBM triblock copolymer. (b) Lamellae of an SBM triblock copolymer containing BM diblock copolymer. B and M blocks have to be stretched. (c) Curved morphology of a blend of SBM and BM block copolymers where the chains are less stretched than those in part b.

top right corner of Figure 2a. The section crosses different heights corresponding to the (110) plane. Therefore, different typical [110] views are obtained. Also specific for the double-gyroid structure is the [112] projection as shown in Figure 2b. A core−shell double gyroid has been recently observed in a polyisoprene-*block*-polystyrene-*block*-poly(dimethylsiloxane) triblock copolymer, too.[14] A blend of 90% SBM and 10% SM block copolymer shows macrophase separation between the double-gyroid morphology and lamellae of the pure triblock copolymer.

For ISVP triblock copolymers, cocontinuous morphologies have been reported, where both I and VP each form a gyroid network with S as the matrix.[15] It was shown theoretically that in these materials a double-gyroid structure should be more stable than a double-diamond structure in both the weak and intermediate segregation regime[16] and in the strong segregation regime,[17] although in the latter case other morphologies are more stable than the cocontinuous ones.

The formation of the two superlattices formed by blends of SBM and BM presented here cannot only be understood as a consequence of the overall change of the volume fractions of the different components. Curvature of the interfaces between the SBM triblock lamellae upon addition of BM diblock copolymer is induced also by an increase in the number of block junction points between the B and M domains, while the number of block junction points between S and B stays constant. In the pure SBM structure, the same number of block junctions are located at both interfaces of the B lamella (Figure 4a). When the BM diblock copolymer is located at the B−M interface, its number of junctions increases. One possibility is the stretching of the chains in order to reduce the interfacial area per chain, which reduces the conformational entropy (Figure 4b). To avoid this crowded situation, the interfacial area B−M enlarges compared to the B−S interface. This leads to a curvature (Figure 4c) that is larger for the core−shell cylindrical structure (more BM diblock copolymer in the blend) than for the core−shell double-gyroid structure (less BM diblock copolymer in the blend) and is finally zero in the pure SBM lamellae. A similar argument is used to explain the increasing curvature in AB_n ($n = 2$ or 3) miktoarm star polymers compared to a linear AB diblock copolymer with the same overall composition.[18−21]

In this study, we showed that blends of lamellar ABC and BC triblock copolymers can be used to obtain nonlamellar morphologies known from pure triblock copolymers. This concept also works for blends of asymmetrically composed block copolymers.[22,23]

Acknowledgment. The authors are deeply indebted to R. Stadler for many stimulating discussions. V.A. acknowledges fruitful discussions with T. M. Birshtein (Sankt Petersburg) on the blends of ABC with BC block copolymers. T.G. is grateful to J. Hofman (Berkeley) for helpful comments related to the TEM simulations. We also thank E.L. Thomas (M.I.T.) for valuable comments on the manuscript. Financial support was given by Deutsche Forschungsgemeinschaft (SFB 481, Project A1), INTAS-RFBR 95-82 and the Bayreuther Institut für Makromolekülforschung (BIMF).

References and Notes

(1) Vilesov, A. D.; Floudas, G.; Pakula, T.; Melenevskaya, E. Yu.; Birshtein, T. M.; Lyatskaya, Yu. V. *Macromol. Chem. Phys.* **1994**, *195*, 2132.

(2) Schulz, M. F.; Bates, F. S.; Almdal, K.; Mortensen, K. *Phys. Rev. Lett.* **1994**, *73*, 86.

(3) Spontak, R. J.; Fung, J. C.; Braunfeld, M. B.; Sedat, J. W.; Agard, D. A.; Kane, L.; Smith, S. D.; Satkowski, M. M.; Ashraf, A.; Hajduk, D. A.; Gruner, S. M. *Macromolecules* **1996**, *29*, 4494.

(4) Winey, K. I.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1992**, *25*, 422.

(5) Lescanec, R. L.; Fetters, F. J.; Thomas, E. L. *Macromolecules* **1998**, *31*, 1680.

(6) Gido, S. P.; Schwark, D. W.; Thomas, E. L. *Macromolecules* **1993**, *26*, 2636.

(7) Riess, G.; Schlienger, M.; Marti, G. *J. Macromol. Sci., Phys.* **1980**, *B17*, 355.

(8) Breiner, U.; Krappe, U.; Abetz, V.; Stadler, R. *Macromol. Chem. Phys.* **1997**, *198*, 1051.

(9) David, J. L.; Gido, S. P.; Hong, K.; Zhou, J.; Mays, J. W.; Tan, N. B. *Macromolecules*, in press.

(10) Goldacker, T.; Abetz, V.; Stadler, R.; Erukhimovich, I. Ya.; Leibler, L. *Nature* **1999**, *398*, 137.

(11) Auschra, C.; Stadler, R. *Polym. Bull. (Berlin)* **1993**, *30*, 257.

(12) Website for TEMsim 1.6: http://lefty.msri.org/Computing/jim/images/stills/index.html.

(13) Bates, F. S.; Fredrickson, G. H. *Physics Today* **1999**, *52*, 32.

(14) Shefelbine, T. A.; Vigild, M. E.; Bates, F. S.; Hillmyer, M. A.; Matsen, M. W.; Hajduk, D. A. Identification of a Core-in-Shell Gyroid Morphology in an ABC Triblock Copolymer. Centennial Meeting of the American Physical Society, Atlanta, Georgia, 1999, http://www.aps.org/meet/CENT99/BAPS/abs/S9170014.html.

(15) Mogi, Y.; Nomura, M.; Kotsuji, H.; Ohnishi, K.; Matsushita, Y.; Noda, I. *Macromolecules* **1994**, *27*, 6755.

(16) Matsen, M. W. *J. Chem. Phys.* **1998**, *108*, 785.

(17) Phan, S.; Fredrickson, G. H. *Macromolecules* **1998**, *31*, 59.

(18) Hadjichristidis, N.; Tselikas, Y.; Iatrou, H.; Efstratiadis, V.; Avgeropoylos, A. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 1447.

(19) Tselikas, Y.; Hadjichristidis, N.; Lescanec, R. L.; Honeker, C. C.; Wohlgemuth, M.; Thomas, E. L. *Macromolecules* **1996**, *29*, 3390.

(20) Milner, S. T. *Macromolecules* **1994**, *27*, 2333.

(21) Gido, S. P.; Wang, Z.-G. *Macromolecules* **1997**, *30*, 6771.

(22) Goldacker, T.; Abetz, V. *Macromol. Rapid Commun.* **1999**, *8*, 415.

(23) Abetz, V.; Goldacker, T. *Macromol. Chem. Phys.*, submitted.

(24) Bandrup, J.; Immergut, G. H. *Polymer Handbook*; John Wiley & Sons: New York, 1989.

MA990277N