Influence of the block sequence on the morphological behavior of ABC triblock copolymers

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In memoriam Prof. Dr Reimund Stadler

Abstract

Two series of linear SBV and BSV triblock copolymers have been prepared where S is polystyrene, B is polybutadiene and V is poly(2-vinylpyridine). While the ratio between the weight fractions of S and B was kept constant, the weight fraction of V was varied within each series. Morphological characterization was carried out by transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). While BSV triblock copolymers show lamellar morphologies independent of the V content, the SBV triblock copolymers show different core-shell morphologies and a lamellar morphology as a function of the V content. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Triblock copolymers; Transmission electron microscopy; Small angle X-ray scattering

1. Introduction

Ternary (ABC) triblock copolymers display a rich morphological behavior due to two independent composition variables and three binary segmental interaction parameters [1,2] Moreover, the chain topology can be important, i.e. the sequence of blocks in the linear chain [1,3] or their connection in a star like manner [3] Gido et al. reported on a polystyrene-*block*-polyisoprene-*block*-poly(2-vinylpyridine) triblock copolymer (SIV) with approximately similar amounts of the different components [4]. While that system self-assembled into core-shell cylinders having a non-constant mean curvature with V-cores, I-shells and S-matrix, Mogi et al. found a lamellar morphology for the same system having a sequence ISV [5]. The reason for the different morphological behavior of ISV and SIV lies in the different degrees of incompatibility between adjacent blocks in these systems, as expressed by the segmental interaction parameter χ_{ij} : χ_{IV} ⊄ $\chi_{SI} \approx \chi_{SV}$ Mogi et al. also studied other symmetric compositions keeping the volume fractions of the two endblocks equal to each other [5]. Upon reduction of the volume fractions of the endblocks, the system transformed from a lamellar via a cocontinuous and a cylindrical finally to a spherical morphology. Both strongly incompatible endblocks self-assembled into different microdomains, which lead to a tetragonal packing

of the cylinders and a CsCl-lattice in the case of the spheres. The cocontinuous morphology was identified as a gyroid morphology later on by Matsen, where both I and V form one tripod network embedded in the S-matrix [6]. Stadler et al. studied symmetric polystyrene-block-polybutadiene-block-poly(methyl methacrylate) triblock copolymers (SBM) as a function of the volume fraction of the middle block, too [1]. For increasing volume fractions of B up to approximately 50% it forms spheres, cylinders or a lamellae between lamellae of S and M. At larger values both S and M form cylinders, which are not necessarily demixed from each other due to the low incompatibility. However, in one case demixed S and M cylinders on a novel type of hexagonal lattice were found [7]. Changing the sequence into BSM also leads to a different morphological behavior. A system with 20% B and 20% M forms curved cylinders in a S-matrix [8]. No long-range order is obtained due to the different degree of incompatibility between the dispersed phases and the matrix. A BSM containing approximately similar amounts of all three components shows a core-shell double gyroid morphology [9].

It is the aim of this contribution to present a comparison between two series of linear triblock copolymers consisting of three strongly incompatible components, namely polystyrene (S), poly(1,2-butadiene) (B) and poly(2-vinylpyridine) (V). The strongest incompatibility is between B and V (solubility parameters $\delta_S = 9.1$ (cal/cm^3)$^{0.5}$ [10], $\delta_B = 8.05$ (cal/cm^3)$^{0.5}$ [10], $\delta_V = 10.0$ (cal/cm^3)$^{0.5}$ [11]).

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Table 1
Characteristics of the SBV and BSV triblock copolymers

Polymer[a]	M_n (S) (kg/mol)[b]	PDI (S) (kg/mol)[c]	M_n (B)[d]	% 1,2 (B)[e]	M_n (V) (kg/mol)[d]	PDI (SBV)[c]
$S_{55}B_{36}V_9^{62}$	34	1.02	22	92	6	1.02
$S_{48}B_{31}V_{21}^{71}$					15	1.03
$S_{44}B_{28}V_{28}^{78}$					22	1.05
$S_{25}B_{16}V_{59}^{137}$					81	1.04
	M_n (B) (kg/mol)[f]	PDI (B)[c]	% 1,2 (B)[e]	M_n (S) (kg/mol)[d]	M_n (V) (kg/mol)[d]	PDI (BSV)[c]
$B_{30}S_{58}V_{12}^{84}$	25	1.01	93	49	10	1.20
$B_{20}S_{39}V_{41}^{126}$					51	1.28
$B_{12}S_{23}V_{65}^{210}$					136	1.14

[a] Subscripts: weight fractions, superscripts: M_n in kg/mol.
[b] GPC (THF).
[c] GPC (THF with 0.25% Tetrabutyl ammoniumbromide).
[d] Calculated from overall composition and M_n(S) and M_n(B).
[e] ^{1}H-NMR (THF-d$_8$).
[f] Membrane osmometry (Toluene, 35°C).

The situation is very similar to block copolymers containing S, V and I. Within each series only the relative amount of V is varied.

2. Experimental section

2.1. Synthesis

The linear SBV triblock copolymers were synthesized via sequential living anionic polymerization in THF using *sec*-butyl lithium as initiator [12]. The BSV copolymers were prepared in the following manner: In the first step, butadiene and styrene were polymerized sequentially in benzene at 40°C with sec-butyl lithium as initiator. In order to produce a similar polybutadiene microstructure as in the SBV polymers, about 1 ml of THF was added to the solvent prior to initiation. Then the living chains were capped with 1,1-diphenyl ethylene in order to stabilize the active centers, before a large amount of dry THF was added to the

solution (THF/benzene = 3/1). Now the temperature of the solution was reduced to −80°C and the polymerization completed by incremental addition of 2-vinylpyridine. The characterization of the polymers is given in Table 1.

2.2. Polymer characterization and morphology investigations

The number averaged molecular weight M_n of the polystyrene precursor of SBV triblock copolymers as well as the molecular weight distributions of the triblock copolymers were determined by size exclusion chromatography on a Waters GPC equipped with column sets of particle size 5 μm and pore sizes of 10^5, 10^4, 10^3 and 10^2 Å with a solution of 0.25% tetrabutylammonium bromide in THF as eluent. M_n of the polybutadiene precursor of the BSV triblock copolymers was determined by membrane osmometry using a Gonotec Osmomat 090 at 35°C with toluene as solvent. ^{1}H-NMR of the triblock copolymers were recorded on a Bruker AC 250 in THF-d$_8$ with polymer concentrations being less than 3 mg/ml.

Polymer films for transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) were solution cast from THF (solubility parameter δ_{THF} = 9.1 (cal/cm^3)$^{0.5}$) [10] at room temperature and then annealed for 6 h at 150°C under vacuum. Ultrathin samples were cut using a Reichert–Jung Ultracut E equipped with a diamond knife. Staining was achieved by treating the ultrathin samples for 1 min with OsO$_4$ vapor (dark B domains) [13]. and/or for 12 h with CH$_3$I or I$_2$ vapor (gray or black V-domains) [14,15]. Electron micrographs were taken from a Zeiss 902 operating at 80 kV in the bright field mode. SAXS measurements were performed with a Bruker AXS Nanostar equipped with crossed Goebel-mirrors and a 2D Hi-star detector. The generator (sealed Cu-tube) was operated at 40 kV and 40 mA.
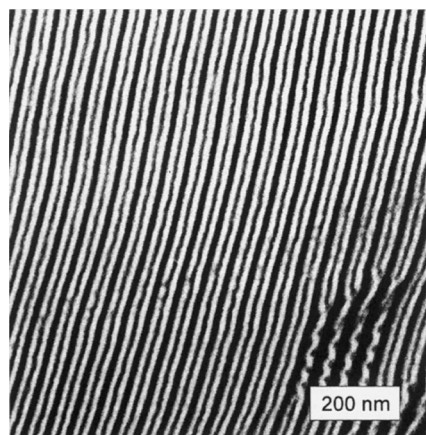

Fig. 1. TEM micrograph of $B_{30}S_{58}V_{12}^{84}$ stained with OsO$_4$ and CH$_3$I.
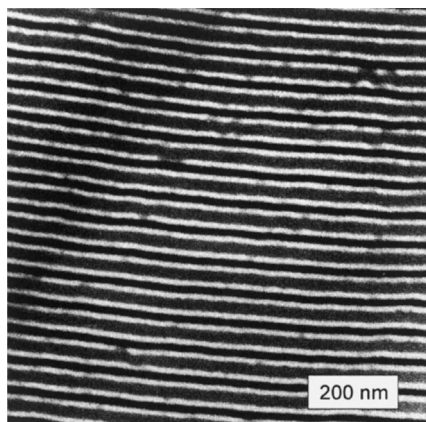
Fig. 2. TEM micrograph of $B_{20}S_{39}V_{41}^{126}$ stained with OsO_4 and CH_3I.
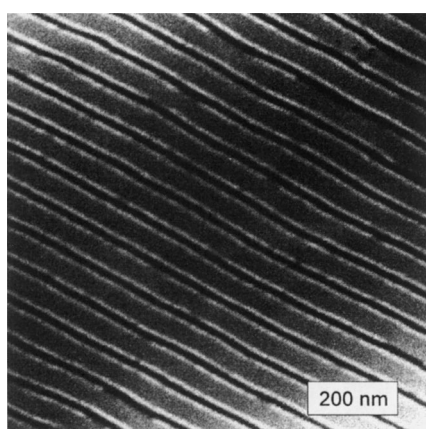

Fig. 3. TEM micrograph of $B_{12}S_{24}V_{64}^{210}$ stained with OsO_4 and CH_3I.
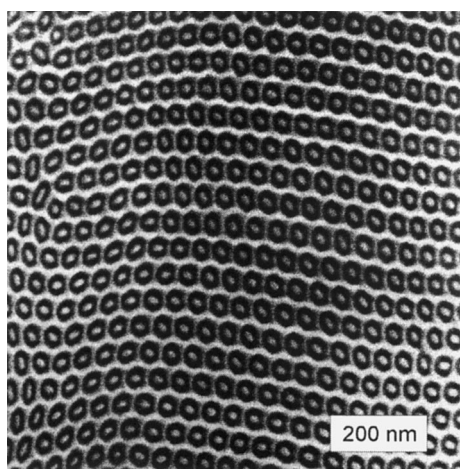

Fig. 4. TEM micrograph of $S_{55}B_{36}V_9^{62}$ stained with OsO_4.

3. Results

In Figs. 1–3 TEM micrographs of $B_{30}S_{58}V_{12}^{84}$, $B_{20}S_{39}V_{41}^{126}$ and $B_{12}S_{24}V_{64}^{210}$ are shown. All three samples show morphologies with all components being separated into

different lamellae. This is attributed to the rather strong incompatibility between all components. In the bottom right corner of Fig. 1 a different morphology is observed with V forming cylinders between B and S lamellae rather than V-lamellae between two S-lamellae. Thus in this region also direct contact areas between B and V exist, which can be related to the polydispersity of the molecular weight distribution of this series. Some of the block copolymer chains contain only very little polystyrene. Areas, where the B and V domains are in direct touch
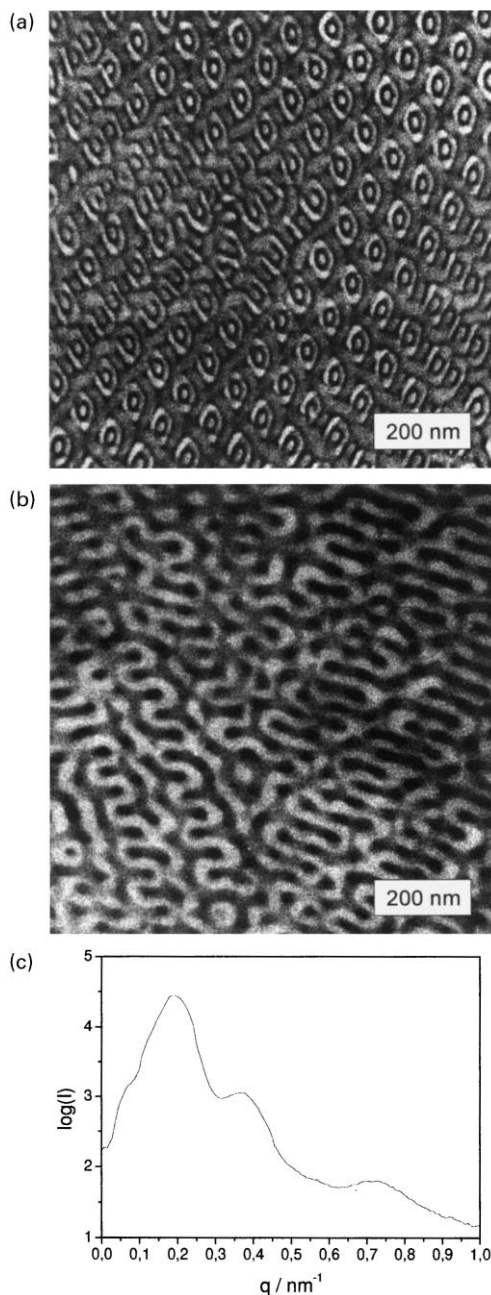

Fig. 5. TEM micrographs of $S_{45}B_{32}V_{23}^{76}$: (a) stained with OsO_4; (b) stained with I_2; (c) SAXS of $S_{45}B_{32}V_{23}^{76}$ ($q = 4\pi/\lambda \sin\theta$; $\lambda = 0.1542$ nm, 2θ is the scattering angle).
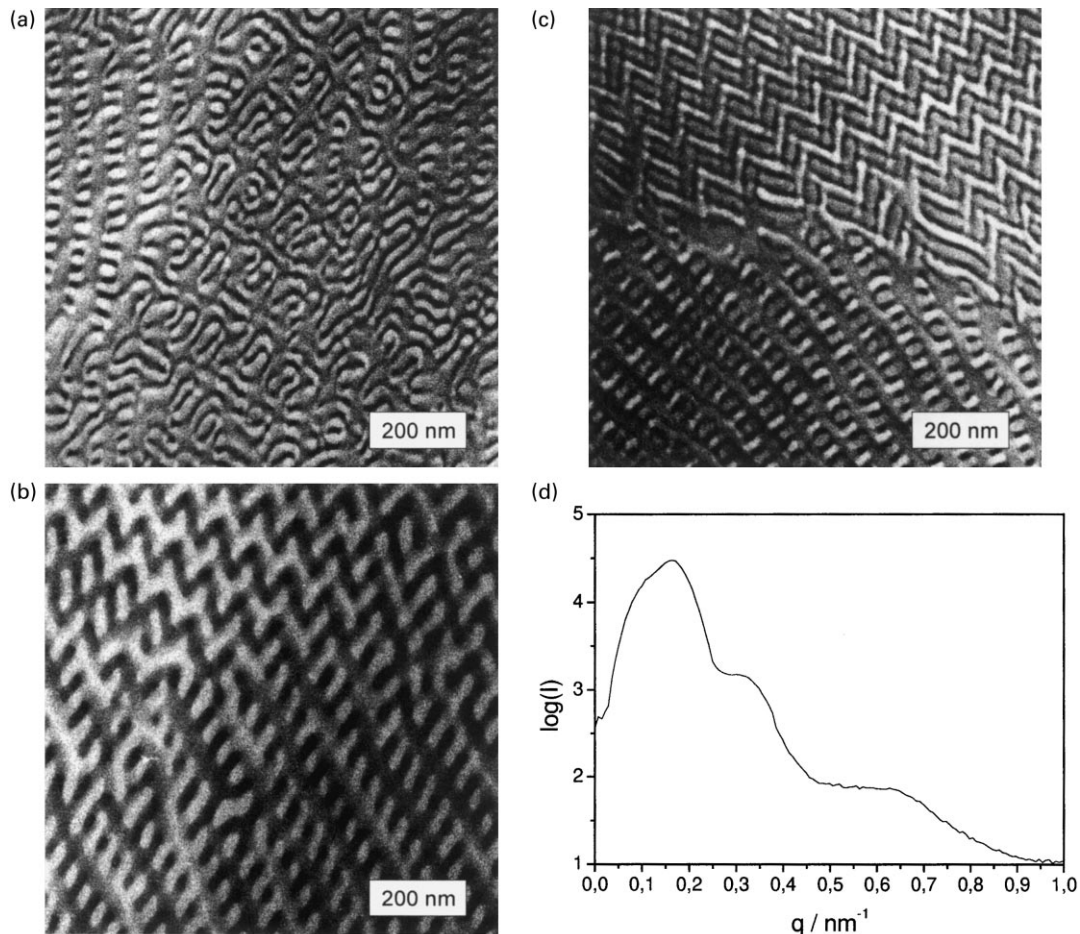
Fig. 6. TEM micrographs of $S_{44}B_{27}V_{29}^{78}$ (a) stained with OsO_4; (b) stained with I_2; (c) stained with OsO_4 and CH_3I; (d) SAXS of $S_{44}B_{27}V_{29}^{78}$ ($q = 4\pi/\lambda \sin\theta$; $\lambda = 0.1542$ nm, 2θ is the scattering angle).

with each other can also be seen in Figs. 2 and 3, although there they do not suppress the formation of V-lamellae.

Changing the sequence from BSV to SBV, the morphological behavior becomes significantly different. Fig. 4 shows the TEM micrograph of $S_{55}B_{36}V_9^{62}$. Here V forms hexagonally packed cylinders surrounded by a B-shell in the S-matrix. The shells do not have a constant mean curvature and look like honeycombs. The situation is similar to the one found and discussed by Gido et al. [4], although the composition is very different. Owing to the stronger incompatibility between B and V as compared to S and B in conjunction with the small amount 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 conformational entropy in lamellar domains.

Increasing the amount of V, the system transforms to a core-shell double gyroid morphology [16], as shown in Fig. 5a and b for $S_{45}B_{32}V_{23}^{76}$. The SAXS-pattern has been discussed before and the three maxima appear at positions in agreement to a cubic lattice under the assumption that the large peak corresponds to the $\langle 110 \rangle$ reflection [6] (Fig. 5c). Further increase of the volume fraction of V ($S_{44}B_{27}V_{29}^{78}$)

leads to a distorted core-shell gyroid morphology, as shown in Fig. 6a–c. The SAXS pattern in Fig. 6d shows two maxima at 0.162 and 0.311 nm^{-1} and a shoulder around 0.64 nm^{-1}. The relative position of the two maxima is
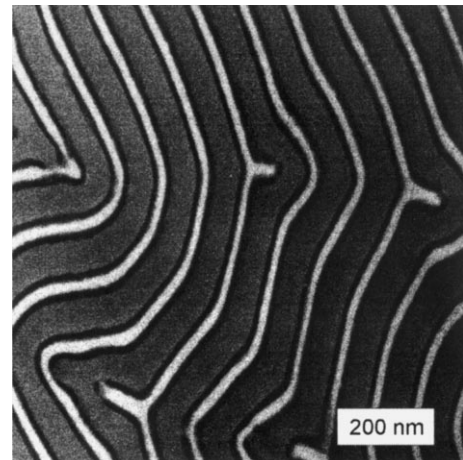

Fig. 7. TEM micrograph of $S_{25}B_{17}V_{58}^{137}$ stained with OsO_4 and CH_3I.

Table 2
χ-parameters between the different block copolymer components ($(\chi = v/(RT)\,(\delta_i - \delta_j)^2$; 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), RT is the molar thermal energy at 150°C))

Polymer	Solubility parameter δ (cal/cm^3)$^{1/2}$ [10,25]	Density (g/cm^3) [25]	χ		
			S	B	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 [11]	1.145	0.092	0.325	0
Poly(methyl methacrylate) (M)	9.48	1.118	0.016	0.168	0.026

1.92 and thus rather similar to the value 1.96 obtained for relative positions of the first two maxima in Fig. 5c.

As the last example for this series, Fig. 7 shows a TEM micrograph of $S_{25}B_{17}V_{58}^{137}$, which forms a lamellar morphology. Due to the increasing volume fraction of V in this series and thus an increasing contribution of the V-domains to the elastic energy of the system, the interface between V and B-domains becomes larger in this sequence.

4. Discussion

In this section we compare SBV and BSV with SBM and BSM triblock copolymers. As compared to poly(2-vinylpyridine), poly(methyl methacrylate) (M) shows a much lower incompatibility towards polystyrene, while the incompatibility towards polybutadiene is still large. Table 2 lists the χ-parameters between the different polymers. In Table 3 the morphological behavior of SBM and BSM triblock copolymers is listed together with the SBV and BSV triblock copolymers having the same compositions in terms of S and B, while M substitutes V.

$B_{30}S_{58}V_{12}^{84}$ shows a lamellar morphology, where all three components are microphase separated. $B_{25}S_{63}M_{12}^{195}$ forms B-cylinders in a matrix, which contains a mixed S/M-phase [17], although the molecular weight of this polymer is much larger as compared to $B_{30}S_{58}V_{12}^{84}$. This reflects the significant difference of the incompatibilities S/V and S/M. $B_{20}S_{39}V_{41}^{126}$ forms lamellae of all three components, while $B_{21}S_{36}M_{43}^{146}$ shows a core-shell double gyroid morphology with B-cores, S-shells and M-matrix [17,18]. Here the larger

interface between S/M as compared to S/B indicates the larger incompatibility of the latter. For comparison, in $B_{20}S_{39}V_{41}^{126}$ similar interfaces between the middle and endblocks are found, which shows the strong and comparable incompatibility between the middle block and the two endblocks in this system.

$S_{45}B_{32}V_{23}^{76}$ and $S_{44}B_{27}V_{29}^{78}$ both form core-shell double gyroids with V-cores. In this block sequence the much larger repulsion between B and V as compared to S and B allows the system to form a larger interface between the latter, while in $S_{37}B_{30}M_{33}^{54}$ and $S_{45}B_{29}M_{26}^{24}$ the much smaller dissimilarity of the interactions between S and B or B and M lead to no curvature of the interfaces for these relative compositions of the three blocks [19]. Also a comparison of $S_{45}B_{32}V_{23}^{76}$ with $B_{21}S_{36}M_{43}^{146}$ is interesting. Both form core-shell double gyroid morphologies with the smallest block forming the cores (V and B). The strongest incompatibility in both cases is between that core and the adjacent middle block (B and S), which again in both cases is connected to a less incompatible block forming the matrix on the other side (S and M). Note that in this comparison topologically similar blocks are having similar volume fractions.

The last example shows a lamellar $S_{25}B_{17}V_{58}^{137}$, where despite the large volume fraction of V the system does not allow for a core-shell type morphology with an S-core, due to the strong incompatibility between B and V. In comparison, $S_{25}B_{12}M_{63}^{218}$ forms such a core-shell morphology, where due to the low volume fraction of the middle block it forms helices rather than a closed shell around the S-core [20].

Table 3
Comparison of the morphologies of BSV, BSM, SBV and SBM and triblock copolymers ((ll), all components form lamellae; (c), cylinders in a matrix; (c$_i$c), core-shell cylinders; (g$_i$g), core-shell double gyroid; (lc), cylinders of middle block at lamellar interface of outer blocks; (hel), helices of middle block surrounding a core cylinder)

BSV	BSM	SBV	SBM
$B_{30}S_{58}V_{12}^{84}$ (ll)	$B_{25}S_{63}M_{12}^{195}$ (c)	$S_{55}B_{36}V_{9}^{62}$ (c$_i$c)	
		$S_{45}B_{32}V_{23}^{76}$(gig) $S_{44}B_{27}V_{29}^{78}$ (distorted g$_i$g)	
			$S_{37}B_{30}M_{33}^{54}S_{45}B_{29}M_{26}^{24}$(ll)
$B_{20}S_{39}V_{41}^{126}$ (ll)	$B_{21}S_{36}M_{43}^{146}$ (g$_i$g)		$S_{39}B_{19}M_{42}^{210}$ (lc)
$B_{12}S_{24}V_{64}^{210}$ (ll)		$S_{25}B_{17}V_{58}^{137}$ (ll)	$S_{25}B_{12}M_{63}^{218}$ (hel)

5. Conclusion

In conclusion we can state that similar repulsive interactions between middle and endblocks lead to lamellar morphologies for even rather asymmetric composed ABC triblock copolymers, when these repulsive interactions are strong. In addition, when the endblocks are strongly incompatible with each other, all components tend to form lamellae, while in the case of less incompatible endblocks (in comparison to their interaction with the middleblock) they may form a common lamellar interface with the minority middleblock forming cylinders or spheres [1] at this interface. While this latter statement holds for systems with comparable volume fractions of the end blocks, other morphologies with direct contact between the endblocks may be obtained for asymmetrically composed systems. A strong tendency to form core-shell morphologies is given in systems, where the interactions of the middle block towards the two endblocks is very dissimilar and the two endblocks are also strongly incompatible with each other, like some of the SBV block copolymer presented here or the symmetrically composed SIV triblock copolymer reported by Gido et al. [4]. Depending on the composition, core-shell analogues of the typical morphologies known from diblock copolymers (like cylinders, double gyroid and lamellae) can be obtained. A similar analogy exists also for morphologies, where due to a weaker repulsion between the two end blocks they form a common interface and a small middle block forms small spheres covering the interface of a sphere [21], a cylinder [22] or a double gyroid [23] in a matrix, or finally the lamellar interface between the two endblocks [1,24].

Acknowledgements

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