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Length Control and Block-Type Architectures in Worm-like Micelles with Polyethylene Cores

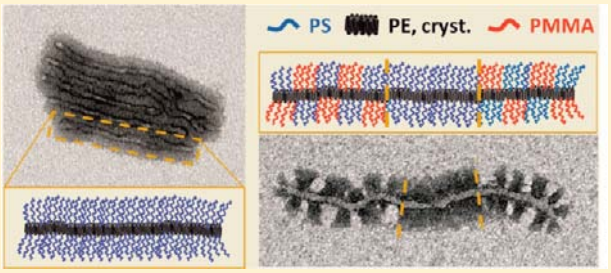
Joachim Schmelz,[§] Andreas E. Schedl,[§] Christoph Steinlein,[§] Ian Manners,[‡] and Holger Schmalz*[,§]

[§] Makromolekulare Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany

[‡] School of Chemistry, University of Bristol, Bristol BS8 1TS, U. K.

Supporting Information

ABSTRACT: We present evidence for "living"-like behavior in the crystallization-driven self-assembly of triblock copolymers with crystallizable polyethylene middle blocks into worm-like crystalline-core micelles (CCMs). A new method of seed production is introduced utilizing the selective self-assembly of the triblock copolymers into spherical CCMs in appropriate solvents. Seeded growth of triblock copolymer unimers from these spherical CCMs results in worm-like CCMs with narrow length distributions and mean lengths that depend linearly on the applied unimer-to-seed ratio. Depending on the applied triblock copolymer, polystyrene-*block*-polyethylene-*block*-polystyrene (SES) or polystyrene-*block*-polyethylene-*block*-poly(methyl methacrylate) (SEM), well-defined worm-like CCMs with a homogeneous or patch-like corona, respectively, can be produced. In a subsequent step, these worm-like CCMs can be used as seeds for the epitaxial growth of a different polyethylene containing triblock copolymer. In this manner, ABA-type triblock *co*-micelles containing blocks with a homogeneous polystyrene corona and those with a patch-like polystyrene/poly(methyl methacrylate) corona were prepared. While the epitaxial growth of SEM unimers from worm-like SES CCMs with a homogeneous corona yields triblock *co*-micelles almost quantitatively, the addition of SES unimers to patchy SEM wCCMs results in a mixture of ABA- and AB-type block *co*-micelles together with residual patchy wCCMs. Following reports on self-assembled block-type architectures from polymers containing core-forming polyferrocenylsilane blocks, these structures represent the first extension of the concept to block *co*-micelles from purely organic block copolymers.



INTRODUCTION

The development of living and/or controlled polymerization techniques revolutionized the field of polymer science.[1] Living anionic polymerization was discovered in 1956[2] and enabled the synthesis of polymers with narrow molecular weight distributions and complex architectures for the first time.[3] Due to the high requirements on purity and the limited range of applicable monomers, efforts to achieve a similar degree of control by the use of different polymerization methods were undertaken and resulted in living cationic polymerization,[4] living ring-opening metathesis polymerization,[5] and controlled radical polymerization methods like atom-transfer radical polymerization, nitroxide-mediated polymerization and reversible addition−fragmentation chain transfer.[6−11] In particular, the synthesis of well-defined block copolymers[12,13] as well as cylindrical block copolymer brushes[14] has become a cornerstone of modern soft matter research. Over the years, a myriad of different solution structures has been produced using the self-assembly of block copolymers triggered by changes in pH, temperature, or solvent environment.[15−24] The ability to manufacture defined nanostructures in bulk as well as in solution opened up a variety of possible applications, such as nanostructured polymer blends or intelligent drug delivery vehicles.[25−29]

Recently, the principle of controlled living growth was transferred to the next level. Instead of polymerizing angstrom-sized monomers, block copolymers with crystallizable poly(ferrocenyl dimethylsilane) (PFDMS) blocks were shown to crystallize in a living fashion resulting in cylindrical micelles with lengths from the nanometer to the micrometer range and polydispersities down to 1.01.[30,31] In analogy to controlled/living polymerization techniques, a different PFDMS-containing block copolymer can be added to the "living" cylindrical micelles producing ABA triblock *co*-micelles.[30] Here, the second block copolymer was added as unimers in a small amount of common solvent and subsequently grows epitaxially from the ends of the precursor cylinders. If the crystal lattice mismatch of another core-forming block is small enough, even heteroepitaxial growth is possible, as shown for a poly(ferrocenyl dimethylgermane)-containing block copolymer.[32] Additionally, this technique provides access to even more complex structures like "brush layers" of cylindrical micelles on homopolymer surfaces or scarf-like micelles, that is, cylindrical micelles grown from platelet-like aggregates, too.[32] Recently, among the block copolymer systems that are known to form one-dimensional structures via crystallization-induced self-

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assembly[33] "living"-like self-assembly was also reported for cylindrical micelles produced from block copolymers containing poly(ferrocenyl diethylsilane),[34] poly(3-hexylthiophene),[35] and enantiopure polylactide.[36] However, the length distributions of the micelles produced by these block copolymers were not as narrow as for PFDMS-based cylinders. One-dimensional block *co*-micelles were up to now only reported for diblock copolymers containing PFDMS or poly(ferrocenyl dimethylgermane). With regard to two-dimensional structures, a similar "living" behavior was observed for crystallizable poly(ethylene oxide) (PEO) blocks.[37] Here, the sequential addition of a PEO homopolymer and a PEO-*b*-PS diblock copolymer resulted in platelets with an alternating "channel-wire" array of "wires" with a PS corona and "channels" without a corona.

In general, recent efforts concerning the "living" growth to block-type architectures focused on diblock copolymers that form micellar blocks with homogeneous coronas. By using triblock terpolymers instead, the incorporation of surface-compartmentalized blocks into block *co*-micelles should be possible, too. The solution self-assembly of triblock terpolymers to one-dimensional structures results in a patch-like ("patchy") surface compartmentalization if it is induced by the collapse of the middle block—irrespective of the core state (crystalline or amorphous)—and the two outer blocks are sufficiently incompatible toward each other.[38,39] These structures are candidates for the directed incorporation of functional inorganic nanoparticles and/or dyes in spatially separated corona compartments and have the potential for further self-assembly into supramicellar mesostructures, e.g., helices.[40]

Previously, we reported the crystallization-induced self-assembly of triblock co- and terpolymers with semicrystalline PE middle blocks to form worm-like crystalline-core micelles (wCCMs).[39,41] If self-assembled using polystyrene-*block*-polyethylene-*block*-polystyrene (SES) triblock copolymers (equal outer blocks) these micelles bear a homogeneous corona, whereas the use of polystyrene-*block*-polyethylene-*block*-poly(methyl methacrylate) (SEM) triblock terpolymers (different incompatible outer blocks) results in patchy coronas. The average length of the wCCMs decreases with decreasing crystallization temperature.[41] Here, the increased nucleation density at lower crystallization temperatures results in an increased number of wCCMs and thus in fewer unimers available per growing micelle. However, using this method a precise length control is not possible. As nucleation occurs statistically, the resulting length distributions were rather broad for all crystallization temperatures ($L_w/L_n \approx 1.3$).

In this work, we address the question whether seeded growth techniques can also be applied to polyethylene containing triblock copolymers to produce wCCMs with defined lengths and narrow length distributions. For this purpose preformed spherical crystalline-core micelles (sCCMs) based on SES or SEM triblock copolymers are explored as seeds for the controlled growth of the corresponding triblock copolymer unimers into worm-like micelles with a homogeneous or patchy corona, respectively. Furthermore, in the second part the grown wCCMs are used to investigate their propensity to add unimers of a different triblock copolymer to produce ABA type triblock *co*-micelles via epitaxial growth. Similarities and differences with respect to the living self-assembly observed for PFDMS-containing block copolymers will be discussed.

RESULTS AND DISCUSSION

Seeded Growth. The use of seeded growth for the crystallization-driven self-assembly of cylindrical micelles is known to enable the production of micelles with defined lengths and narrow length distributions (low L_w/L_n values).[31,34,35] These seeds are usually produced by ultrasonication of preformed cylindrical micelles under cryogenic conditions resulting in short "stub-like" micelles with $L_w/L_n \approx 1.05$. Alternatively, cylindrical micelles can be heated to a temperature, where due to partial dissolution only small fragments are left over, a technique known as self-seeding.[42]

Here, we use an alternative method for producing well-defined seeds which is based on our previous observation that the morphology of CCMs formed by triblock copolymers with polyethylene middle blocks can be easily adjusted by the solvent environment.[41] Self-assembly in bad solvents for the polyethylene block in the molten state (dioxane, dimethylacetamide) results in well-defined sCCMs, whereas in good solvents for the polyethylene block (toluene, THF) wCCMs are formed. The exclusively one-dimensional growth in good solvents for the PE middle block was observed for different triblock copolymers with varying composition and overall molecular weight and, thus, was attributed to the middle position of the PE block in the triblock copolymers. Consequently, sCCMs as seeds were produced from a SES triblock copolymer ($S_{380}E_{880}S_{390}$, subscripts denote the number-average degree of polymerization) in a 10 g/L dioxane solution to reduce the amount of dioxane that is present in the final solvent mixture during the subsequent seeded growth process (molecular characteristics and thermal properties of the SES triblock copolymer can be found in Table 1). Therefore, the polymer was dissolved above the melting temperature of PE in dioxane (T_m = 74 °C) and subsequently cooled to room temperature. As dioxane is a bad solvent for PE, monodisperse spherical micelles are formed already before crystallization occurs at T_c = 43 °C and subsequent crystallization upon further cooling takes place in each micellar core individually.

Table 1. Molecular Characteristics and Thermal Properties of the Used Triblock Copolymers

polymer[a]	M_n [kg/mol][b]	PDI[c]	Et/100C[d]	T_c [°C][e]	T_m [°C][e]	α [%][e]
$S_{380}E_{880}S_{390}$	105	1.04	2.7	21.8	51.8	50
$S_{340}E_{700}M_{360}$	91	1.04	2.6	18.3	52.0	51

[a]Subscripts denote the number-average degree of polymerization. [b]Number-average molecular weight determined by a combination of THF-SEC and ^{1}H NMR. [c]Polydispersity index of the respective poly(1,4-butadiene) (PB)-containing precursor triblock copolymer (before hydrogenation) as obtained by THF-SEC using a polystyrene calibration. [d]Average amount of ethyl branches per 100 main-chain carbon atoms resulting from 1,2-addition in the polymerization of PB, determined by ^{1}H NMR of the precursor triblock copolymer. [e]Peak melting (T_m) and crystallization (T_c) temperatures as well as degree of crystallinity (α) of the PE middle block determined from μDSC measurements (10 g/L in THF, scanning rate 0.5 K/min).[41]

For transmission electron microscopy (TEM) investigation all samples presented in this publication were stained by RuO_4, which is known to selectively stain PS. In the micrograph sCCMs with a light, slightly rectangular PE core and a dark PS corona are observed (Figure 1). The number-average core length and the total micelle radius have been determined to L_n = 11 ± 1 nm with L_w/L_n = 1.01 and R_{total} = 21 ± 2 nm,

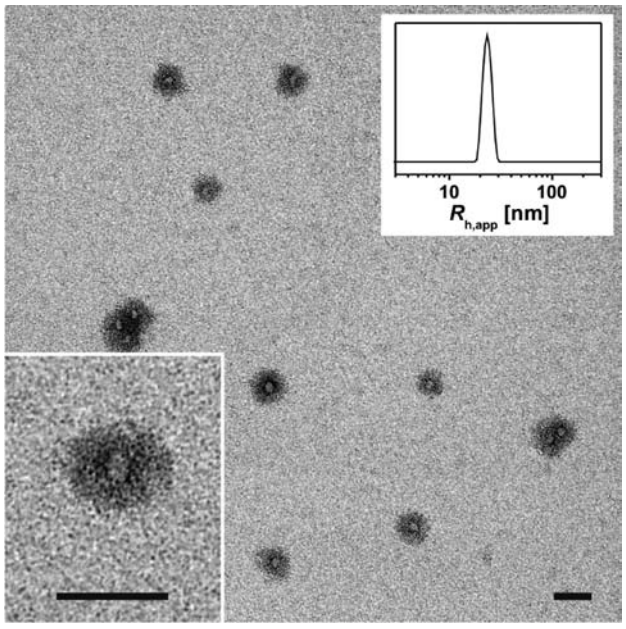


Figure 1. TEM micrographs of sCCMs self-assembled from SES in dioxane; scale bars = 50 nm. Inset: DLS CONTIN plot of a 1 g/L solution of SES sCCMs in dioxane (θ = 90°).

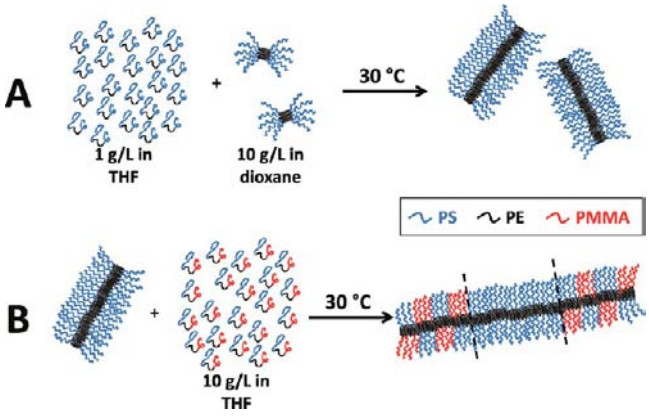
respectively. This is in good agreement with dynamic light scattering (DLS) from which a hydrodynamic radius of R_h = 23 nm is obtained (Inset in Figure 1). This direct self-assembly approach allows the production of uniform seeds on a large scale and thus represents a versatile alternative to the established methods.

As one-dimensional growth in our system was shown to only occur in good solvents for the PE middle block, that is, solvents that dissolve PE above its melting temperature like THF and toluene, seeded growth was performed in THF. In order to provide unimers that are able to grow to preformed seeds usually the same block copolymer is dissolved in a small amount of common solvent. However, as there is no solvent that dissolves crystalline PE at room temperature, SES unimers had to be produced thermally by heating a THF solution above the melting temperature of the PE block (T_m = 52 °C).[41] Consequently, the subsequent seeded growth should be conducted at a temperature between T_m and the crystallization temperature T_c = 21.8 °C,[41] to ensure that unimers are still able to crystallize onto the provided seeds while on the other hand no significant homogeneous nucleation of the unimers occurs (Scheme 1A).

Thus, a 1 g/L THF solution of SES was heated to 65 °C for 30 min and subsequently quenched to 30 °C. This procedure was directly followed by the addition of small amounts of the seed solution (10 g/L in dioxane), so that unimer-to-seed (U/S) weight ratios of 3, 6, 9, ..., 18 were obtained. Noteworthy, even for the highest seed content (U/S = 3) the dioxane content in the resulting solution is only about 3 vol %. These solutions were kept at 30 °C for 2 weeks. After the solutions were allowed to cool down to room temperature TEM samples were prepared for each U/S ratio. This procedure is denoted as the "one-step growth process" in the following text.

In all micrographs of the formed wCCMs a light PE core is detected together with a stained, dark PS corona that can be traced (Figure 2). Although these wCCMs tend to aggregate

Scheme 1. Preparation of wCCMs with Controlled Lengths via Seeded Growth (A) and Subsequent Epitaxial Growth to Triblock *co*-Micelles (B)



upon drying during TEM sample preparation, their PE cores can be clearly distinguished from the PS corona as the high energy amorphous fold interface between core and corona is also preferentially stained by RuO_4.[39] It is relevant to note that the observed aggregation only arises from TEM sample preparation as in the corresponding apparent hydrodynamic radii distribution obtained from DLS larger aggregates are clearly absent (Figure S1). A plot of the number-average wCCM core length, L_n, evaluated from the micrographs vs the U/S ratio shows a linear relationship (Figure 3, black squares; corresponding length histograms for the wCCMs prepared at different U/S ratios can be found in Figure S2). This indicates that the growth of the unimers onto the sCCM seeds proceeds in a "living"-like fashion. The intercept of the linear fit (14 ± 2 nm) is comparable to the core size of the sCCM seeds (11 ± 1 nm), which is also suggestive of selective unimer growth from the seeds.

Notably, the length polydispersities L_w/L_n show an increase up to U/S = 9 and decrease again for higher ratios (Figure 3). A similar increase of L_w/L_n for low U/S ratios with respect to the length polydispersity of the seeds was also observed for the seeded growth of poly(ferrocenyl diethylsilane)-*block*-polydimethylsiloxane (PFDES-*b*-PDMS) diblock copolymers.[34] A possible explanation for this phenomenon might be that in comparison to the addition of unimers to already grown wCCMs unimer addition to sCCMs could be more difficult, that is, "initiation" might be slow with respect to the subsequent growth. Additionally, we are not dealing with perfectly linear PE chains as crystallizable middle blocks. Due to the synthesis of the triblock copolymers via sequential anionic polymerization and subsequent hydrogenation of the poly(1,4-butadiene) middle blocks to PE,[39] these blocks contain a certain amount of ethyl side branches (Table 1) that influence crystallization. As these branches most likely are distributed randomly along the PE blocks and their number may also vary for different triblock copolymer chains, the nucleation efficiency of the pre-assembled sCCMs may vary as well. Consequently, the few observable micelles that still almost look like sCCMs in the micrographs of samples prepared at low U/S ratios (arrows in Figure 2A,B) and, thus, were not able to add unimers in the given time span, might represent sCCMs with PE cores having an above-average amount of ethyl branches.

For higher U/S ratios L_w/L_n decreases again down to 1.11 for U/S = 18. However, for high U/S values a small fraction of

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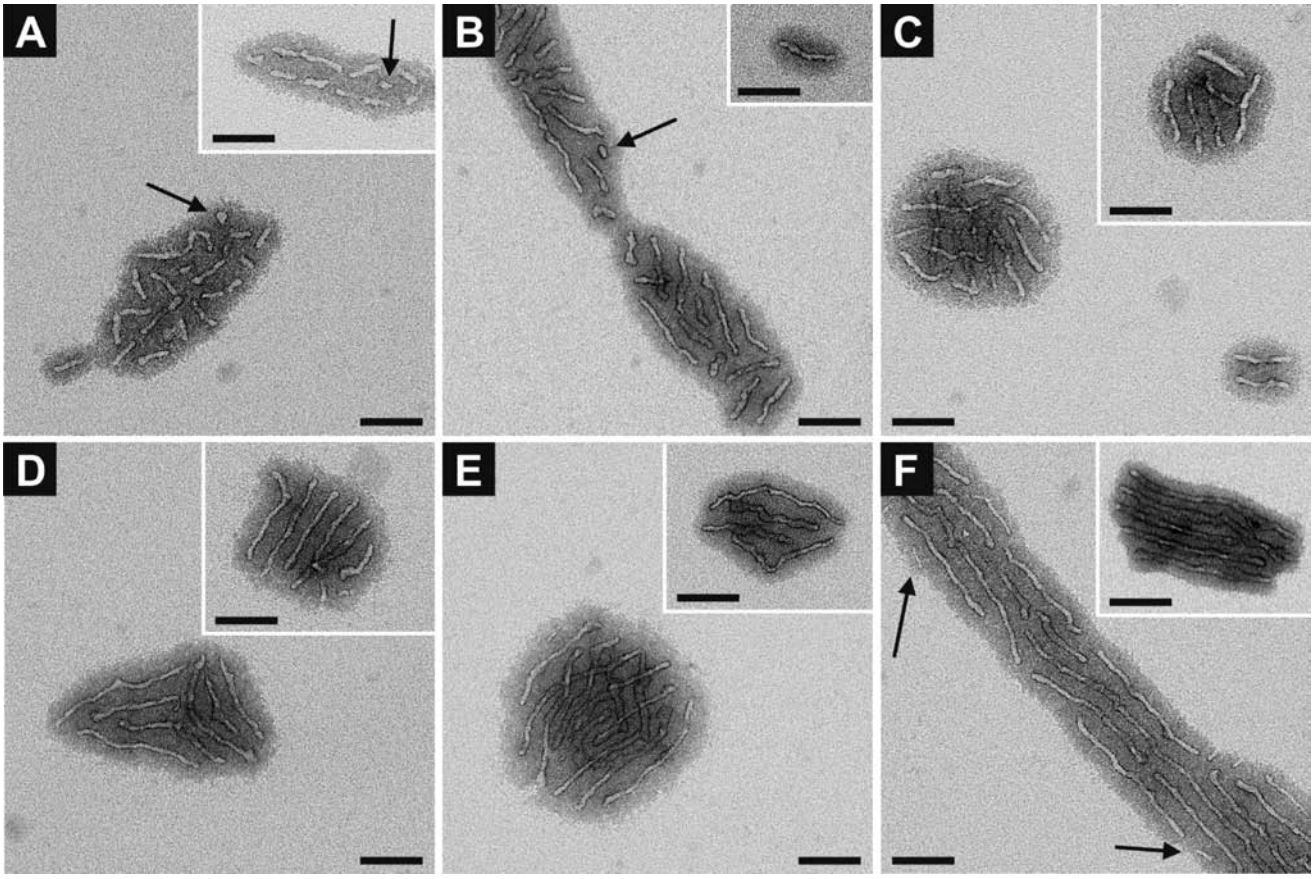

Figure 2. TEM micrographs of SES wCCMs formed by seeded growth at 30 °C in 1 g/L THF solutions applying U/S ratios (wt/wt of polymer) of 3 (A), 6 (B), 9 (C), 12 (D), 15 (E), and 18 (F). Arrows depict still remaining sCCMs at low U/S ratios (A,B) and short wCCMs with thinner PE cores at high U/S ratio (F), respectively. Scale bars = 100 nm.

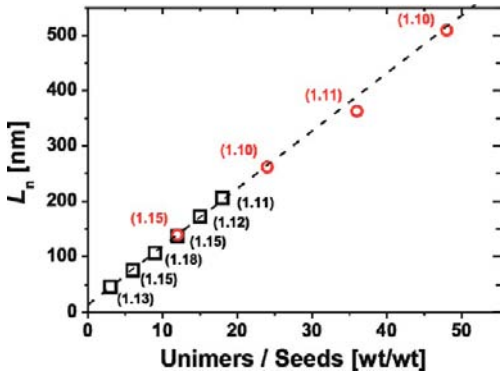

Figure 3. L_n vs applied unimer-to-seed ratio for wCCMs prepared in the one-step growth process (black squares) and via repetitive unimer addition (red circles). The values given in brackets correspond to the length polydispersities (L_w/L_n) and the dashed line represents a linear fit to the length vs U/S ratio data for the wCCMs produced by one-step growth (black squares).

significantly shorter wCCMs with thinner PE cores can be traced (arrows in Figure 2F) that most probably have formed during cooling to room temperature after 2 weeks at 30 °C or even later during sample preparation. Consequently, these micelles were not considered for the length evaluation presented in Figure 3. No significant influence of the crystallization temperature on the core diameter was observed in our previous work.[41] Thus, the thinner cores of the wCCMs that form from the remaining unimers in this case might be explained by a fractionation of unimers taking place during the growth to wCCMs. Unimers with a more perfect PE block, i.e., fewer ethyl branches, crystallize onto the micelles preferably while those with less perfect PE blocks remain in solution until they form wCCMs at lower temperatures or during sample preparation. Due to the higher amount of chain imperfections, the PE blocks of these unimers are forced to form more folds upon crystallization, resulting in a lower crystallite thickness.[43] Another reason for incomplete unimer consumption might be the low seed concentration at high U/S ratios. As the unimer concentration was kept constant in this experiment, the seed concentration and, hence, the concentration of "living" wCCMs in solution decreases for increasing U/S, presumably resulting in slower unimer consumption. As a result, even after growth for 2 weeks not all unimers are converted to wCCMs and crystallize later at lower temperatures.

It is relevant to note that the unimers forming the small micelles are not available for the seeded growth of regular micelles at 30 °C, which should result in lower values for L_n at high U/S ratios. However, the highest observed fraction of small micelles is about 14% (for U/S = 18). As these micelles exhibit an L_n of about 20 nm, which is by a factor of 10 lower than that of the regularly grown wCCMs at U/S = 18 (L_n = 206 nm), only about 1.4% of the unimers appear to form the smaller micelles. In addition, due to the thinner cores of these micelles, that is, a higher number of folds, even fewer unimers will be needed to obtain a given core length. Consequently, the fraction of unimers that is not available for regular micellar growth is too low to result in a significant deviation from the

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linear trend in the evaluation of the regularly grown micelles. If the significantly shorter micelles with thinner PE cores are included in the length statistics, L_n is shifted to lower values and the length distribution broadens for U/S = 15 and 18 (Figure S3). However, the formation of these wCCMs with thinner cores can be avoided by applying a slightly different preparation method, as will now be described.

Even though micelles with controlled lengths of up to 200 nm could be produced, the obviously slower monomer addition at low seed concentrations is an obstacle to the production of even longer wCCMs by the given method. A possible alternative growth method would be to increase the unimer concentration while keeping the seed concentration constant. However, as the crystallization temperature rises with increasing concentration,[41] this leads to a higher probability of homogeneous nucleation and thus might disturb the controlled seeded growth. In order to form longer micelles and still prevent significant dilution of the growing wCCMs, further elongation was conducted via repetitive addition of more concentrated unimer solutions (10 g/L in THF) to the wCCMs instead of the one-step growth process described above. Thus, to wCCMs that were grown in a 1 g/L THF solution employing a U/S ratio of 6 for 2 days the same amount of unimers was added again as a 10 g/L THF solution and allowed to grow for at least another 2 days. This unimer addition was repeated several times so that total U/S ratios of 12, 24, 36, and 48 were obtained. Here, we assume that in 2 days the vast majority of the unimers is able to grow from the seeds (or from the already grown wCCMs in the later stages) so that upon addition of a further batch the unimer concentration does not exceed 1 g/L significantly. In order to induce the eventual growth of the remaining unimers from the wCCMs, 2 days after the last unimer addition these solutions were cooled down stepwise from 30 to 20 °C at a rate of 1 K per 12 h. TEM micrographs of the wCCMs formed in this manner, which also aggregated during solvent removal, can be found in Figure 4. DLS again reveals the absence of aggregates in solution (Figure S1).

Length evaluation shows that the repetitive addition of unimers also results in a good length control (Figure 3, red circles; length histograms for the wCCMs prepared via repetitive growth can be found in Figure S4). The samples prepared for U/S = 12 show comparable values of L_n and L_w/L_n for both preparation methods and also at higher U/S ratios the repetitive growth procedure results in L_n values that still show the linear relationship established for the one-step growth method (Figure 3, black squares) and narrow length distributions ($L_w/L_n \approx 1.1$). Significantly, no small micelles with thinner cores were traced this time, as was the case for wCCMs produced by the one-step growth method at high U/S ratio (Figure 2F). By this "repetitive growth method", the production of wCCMs with lengths of 500 nm and beyond becomes feasible. Thus, in analogy to the "living" growth of PFDMS-containing block copolymers, in the seeded growth of the SES triblock copolymer the length of the formed wCCMs can be controlled by the U/S ratio, too.

A closer inspection of the SES wCCMs formed by the "repetitive growth method" reveals that the PE cores occasionally show some small knobby protrusions (Figure 4). Two possible reasons could account for the formation of these protrusions. Due to the inherent ethyl branches in the PE middle blocks these protrusions might arise from defects in the crystal structure of the PE core. In our previous work, small

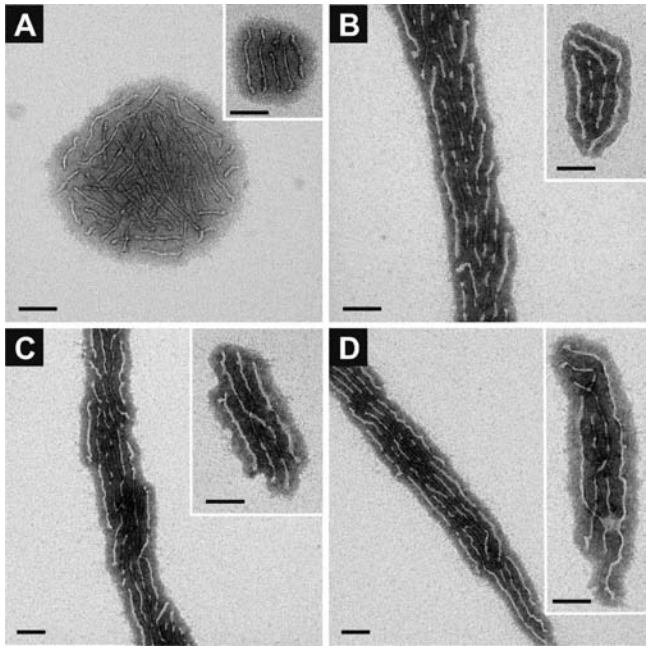


Figure 4. TEM micrographs of wCCMs formed from SES at U/S ratios (wt/wt of polymer) of 12 (A), 24 (B), 36 (C), and 48 (D) in THF solutions via repetitive unimer addition. Scale bars = 100 nm. It should be noted that the PE cores are partially covered by PS chains and can therefore only be distinguished on careful inspection due to the intensive RuO_4 staining of the amorphous fold interface between core and corona.

protrusions could also be traced for non-annealed wCCMs formed by a SEM triblock terpolymer upon isothermal crystallization.[41] These protrusions almost vanished after annealing, that is, perfection of the PE crystallites in the core, which resulted in fewer folds and hence an increased crystallite thickness accompanied by a more uniform crystallite thickness distribution. Here, the SES-based wCCMs prepared via seeded growth were not subsequently annealed which supports this assumption. In addition, in the "repetitive growth method" the wCCMs grow stepwise and for each step nucleation of unimer growth on the preformed wCCMs has to take place. This in turn might be a reasonable explanation for the observation that for the "one-step growth process" the formation of protrusions seems to be much less pronounced (Figure 2).

Block *co*-Micelles. Besides the ability to grow polymer chains of controlled length, the production of block copolymers by the sequential addition of different monomers is the key advancement of living and controlled polymerization techniques. Hence, an additional test for the living behavior of the crystallization-driven self-assembly is the epitaxial growth of unimers of a different triblock copolymer onto preformed SES wCCMs (Scheme 1B). Thus, wCCM solutions of SES were prepared via the one-step seeded growth procedure described earlier in this article applying a U/S ratio of 6. After 2 days a 10 g/L solution of a SEM triblock terpolymer ($S_{340}E_{700}M_{360}$, molecular characteristics and thermal properties of the SEM triblock terpolymer can be found in Table 1) in THF was added at 30 °C. This solution also was preheated to 65 °C so that exclusively unimers are present. In order to obtain SEM outer blocks with the same length as the SES middle block, double the amount of SEM unimers with respect to SES was added. After 2 more days at 30 °C the solution was cooled down stepwise from 30 to 20 °C at a rate of 1 K per 12 h in the

same manner as for the production of the SES wCCMs via repetitive unimer addition.

TEM investigations of the formed structures show that indeed SEM-*b*-SES-*b*-SEM triblock *co*-micelles are formed (Figure 5). Here, middle blocks with a homogeneous PS corona are surrounded by two outer blocks bearing a patch-like corona that consists of alternating PS and PMMA compartments. The PMMA patches are not stained by RuO_4 and therefore appear light, which allows them to be clearly distinguished from the intensively stained, dark PS patches. Figure S5 shows a collection of different TEM micrographs revealing the almost exclusive formation of SEM-*b*-SES-*b*-SEM triblock *co*-micelles. The triblock *co*-micelles also show a certain tendency for aggregation upon drying during TEM sample preparation as is the case for SES wCCMs. The homogeneity of the prepared triblock *co*-micelles is further supported by DLS showing a unimodal radii distribution and the absence of aggregates in solution (Figure S6). SEM-*b*-SES-*b*-SEM triblock *co*-micelles could be obtained with a yield of 96%. The remaining structures consist of about 3% SES-*b*-SEM diblock *co*-micelles and <1% pure SEM wCCMs as determined from TEM image analysis. As almost no pure SEM wCCMs are formed, the addition of SEM unimers onto the provided SES wCCM seeds is highly favored over homogeneous nucleation highlighting the suitability of the experimental conditions, i.e., 30 °C at unimer concentrations around 1 g/L, for controlled epitaxial growth. The number-average core length, L_n, of the middle blocks with a homogeneous PS corona is 79 nm, comparable to that of the pure SES wCCMs produced at U/S = 6 (75 nm, Figure 2B), that of the patchy SEM outer blocks 77 nm. While the length distribution of the middle blocks is again rather narrow (L_w/L_n = 1.13), the length polydispersity of the outer blocks is significantly higher (L_w/L_n = 1.28). This, together with the fact that a small fraction of the SES wCCM ends were not able to add SEM unimers, leads to the assumption that not all wCCM ends show exactly the same nucleation efficiency. As already proposed in the first part of this publication for seeded growth of SES unimers onto sCCMs, this might be explained by the statistical distribution of ethyl side branches in the main chain of the crystallizable PE middle blocks. Consequently, the free lateral crystal surfaces at the ends of the wCCMs might exhibit slightly different structures and, thus, different nucleation properties. Here, this phenomenon could be more pronounced as is the case for growth from sCCMs, because during the growth of the SES middle blocks the probability of SES unimers with fewer ethyl side branches, that is, a more ideal PE middle block, to crystallize onto the growing micelles will be higher. This again results in a fractionation as discussed earlier. Hence, unimers with a higher amount of ethyl branches are more likely situated at the wCCM ends and may cause a slower nucleation of SEM unimers. However, despite the fact that we are dealing with a crystallizable block that bears significant imperfections (ethyl branches), the preparation of SEM-*b*-SES-*b*-SEM triblock *co*-micelles is possible in a controlled way with almost quantitative yield.

Applying the same procedure, we also attempted to produce SES-*b*-SEM-*b*-SES triblock *co*-micelles. For this purpose,

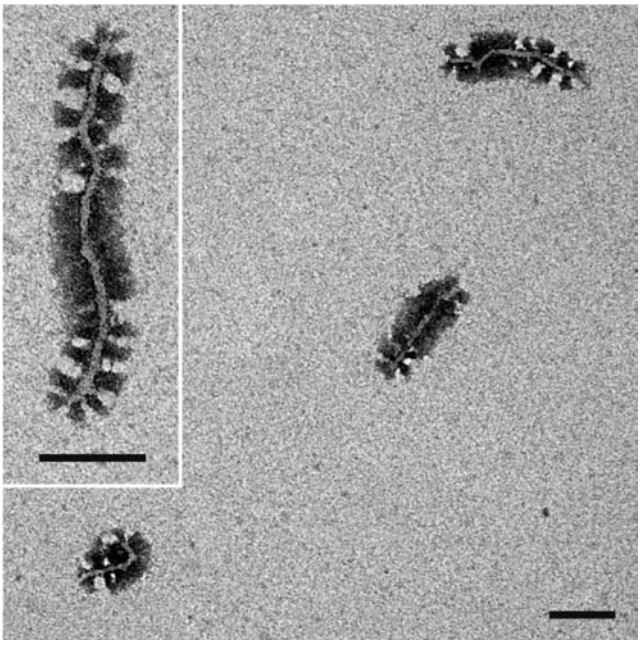


Figure 5. TEM micrographs of SEM-*b*-SES-*b*-SEM triblock *co*-micelles prepared via epitaxial growth of SEM unimers onto SES wCCM seeds in a 1 g/L THF solution. Scale bars = 100 nm.

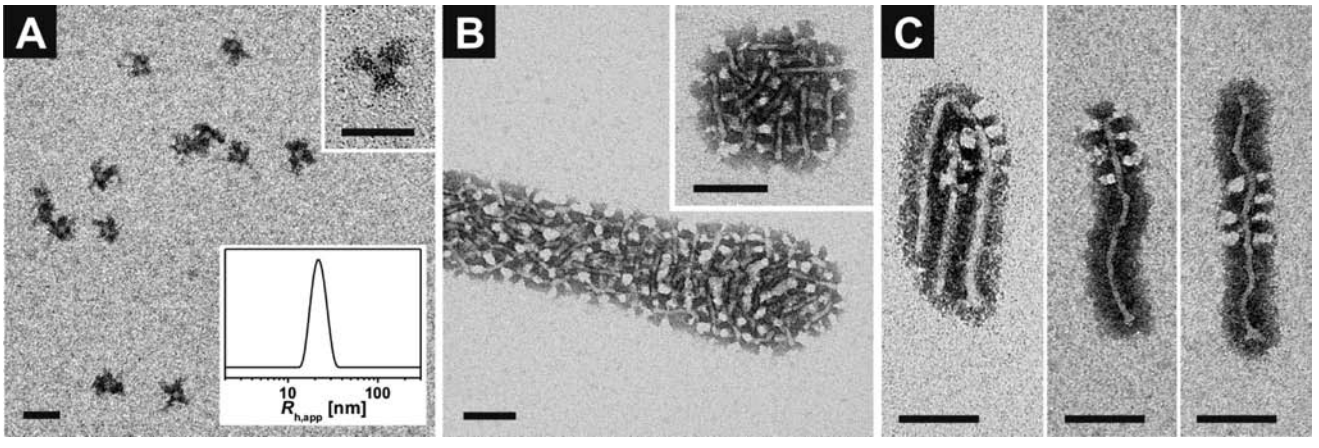


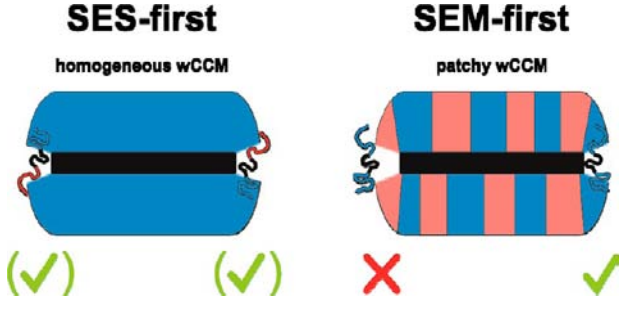
Figure 6. TEM micrographs of (A) SEM sCCMs prepared in a 10 g/L dioxane solution (inset: DLS CONTIN plot of a 1 g/L solution of SEM sCCMs in dioxane), (B) SEM wCCMs prepared by seeded growth at U/S = 6, and (C) selected SES-*b*-SEM-*b*-SES triblock *co*-micelles and SES-*b*-SEM diblock *co*-micelles prepared in 1 g/L THF solutions. Scale bars = 50 nm (A) and 100 nm (B,C).

sCCMs were prepared from SEM in dioxane followed by the seeded growth of SEM unimers from these seeds at 30 °C in THF (U/S = 6). After 2 days, double the amount of SES unimers was added to the preformed SEM wCCMs. The dimensions of the self-assembled SEM sCCMs (Figure 6A, L_n = 11 nm with L_w/L_n = 1.01) match those prepared by SES. A precise determination of the total radius of the micelles from TEM micrographs is difficult due to the patch-like surface compartmentalization of the corona, but it can be assumed to be similar to that of the SES sCCMs due to the similar hydrodynamic radius derived from DLS data (inset in Figure 6A, R_h = 22 nm). In addition, the results for the seeded growth yielding SEM wCCMs (L_n = 75 nm, L_w/L_n = 1.07; the corresponding length histogram can be found in Figure S7) are comparable to those consisting of SES, clearly showing that this seeded growth approach can be used as well to produce one-dimensional patchy micelles of controlled length and length distribution (Figure 6B). However, the epitaxial growth of SES unimers to these SEM micelles did not proceed as successfully as in the reverse case. Here, half of the structures formed are SES-*b*-SEM diblock *co*-micelles (46%) with only 45% of SES-*b*-SEM-*b*-SES triblock *co*-micelles and 9% of remaining pure SEM wCCMs (Figure 6C, additional micrographs can be found in Figure S8). The absence of aggregates in solution is again confirmed by DLS (Figure S6). In the case where SES outer blocks were able to grow they are longer on average (L_n = 90 nm) than the SEM middle blocks, as now significantly more SES unimers are available per growing chain end. Furthermore, the length polydispersity of the SES outer blocks (L_w/L_n = 1.39) is even higher than that for the SEM outer blocks of the reverse triblock *co*-micelles. Again, no pure SES wCCMs have been observed showing that homogeneous nucleation of unimers is highly improbable under the applied conditions.

Unexpectedly, we observe an asymmetric behavior, that is, unimers of SEM grow significantly better from wCCMs made of SES than the other way round. As the degrees of polymerization of the three blocks as well as the amount of ethyl side branches are comparable for both triblock copolymers (Table 1), these variables presumably are not responsible for this behavior. Thus, the hypothesis arises that the different propensity of epitaxial growth might be influenced by the corona structures in the preformed wCCM seeds. In the "SES-first" approach a triblock terpolymer grows onto wCCMs with a homogeneous corona, whereas in the "SEM-first" approach a triblock copolymer grows onto wCCMs with a patchy corona (Scheme 2).

If SEM unimers are added to SES wCCMs ("SES-first") all "living" micellar ends are surrounded by PS chains. Even though PE and PMMA are incompatible with PS, the SEM unimers obviously are able to reach the core allowing the PE block to crystallize onto it. However, as the corona purely consists of PS, each end of a SES wCCM has the same corona structure and, hence, an equal probability to add SEM chains to the crystalline core. For the reverse situation, that is, addition of SES unimers to preformed SEM wCCMs ("SEM-first"), we face a completely different situation. These wCCMs exhibit a patchy corona with alternating compartments of PS and PMMA resulting in potentially different environments of the free lateral crystal surfaces. If a micellar end is encompassed mainly by PS chains, a SES unimer can easily migrate into the corona and deposit onto the PE core of the micelle. A wCCM end that is surrounded by PMMA chains on the other hand is incompatible with all three blocks of the SES unimers. Thus, wCCM ends with a PMMA-rich corona simply might not be able to add SES unimers within the time span in which they grow to those ends that are surrounded mainly by PS. As a result, the inherently different ability of wCCM ends to nucleate the growth of SES unimers vastly increases the fractions of formed SES-*b*-SEM diblock *co*-micelles and remaining SEM wCCMs.

Scheme 2. Proposed Influence of the Corona Structure of the wCCM Seeds on the Formation of Triblock *co*-Micelles



CONCLUSION

In the first part of the manuscript, we presented the production of worm-like crystalline-core micelles (wCCMs) with controlled lengths and narrow length distributions down to L_w/L_n = 1.1 using a PS-*b*-PE-*b*-PS triblock terpolymer (SES). Here, self-assembled spherical crystalline-core micelles (sCCMs) were used as nuclei for the growth of triblock copolymer unimers. With this new method of seed formation for "living"-like crystallization-driven self-assembly, the preceding production of sacrificial cylindrical micelles that are commonly applied in the seeded growth of block copolymers containing poly(ferrocenyl dimethylsilane) or poly(3-hexylthiophene) blocks is not necessary. The average length of the produced wCCMs can be tuned by the applied unimer-to-seed ratio up to at least 500 nm. Furthermore, the possibility to extend the controlled crystallization-driven growth to a PS-*b*-PE-*b*-PMMA triblock terpolymer (SEM) for the first time allows the production of one-dimensional patchy micelles with narrow length distributions.

Upon addition of a different triblock copolymer to already grown wCCMs epitaxial growth to block *co*-micelles could be achieved. The addition of SEM unimers to preformed SES wCCMs with homogeneous corona results in ABA-type (SEM-*b*-SES-*b*-SEM) triblock *co*-micelles with a homogeneous inner block and patchy outer blocks in high yields. In the reversed case, however, a mixture of AB-type (SES-*b*-SEM) diblock *co*-micelles and ABA-type (SES-*b*-SEM-*b*-SES) triblock *co*-micelles is formed by the addition of unimers of a SES triblock copolymer to patchy SEM wCCMs. This asymmetric behavior is explained by the different incompatibility of the corona blocks in alternating compartments of patchy wCCMs toward the growing unimers, that is, wCCM ends surrounded predominantly by PS chains are easily accessible for SES unimers, while for those with a PMMA-rich corona epitaxial growth is hindered significantly.

Due to the fact that we do not achieve a complete blocking efficiency in the block *co*-micelles and the length polydispersities are higher compared to the living self-assembly of PFDMS containing block copolymers, we refer to this process as controlled crystallization-driven self-assembly rather than

living self-assembly. Nevertheless, after the discovery of block *co*-micelle formation in 2007 for block copolymers containing crystallizable PFDMS blocks,[30] our results show that this concept can also be extended to PE containing block copolymers. By the use of triblock terpolymers even more complex block *co*-micelles including blocks with a surface-compartmentalized corona are accessible. Due to the inherent structural imperfections (ethyl branches) of the PE blocks in our system that most of the common crystallizable polymers do not share, the concept of living/controlled crystallization-driven self-assembly should be generally applicable to semicrystalline block copolymers if suitable conditions for unimer growth to already existing micelles can be found, e.g., a specific solvent environment and/or temperature.

METHODS

Synthesis of Triblock Copolymers. Polystyrene-*block*-poly(1,4-butadiene)-*block*-polystyrene (SBS) and polystyrene-*block*-poly(1,4-butadiene)-*block*-poly(methyl methacrylate) (SBM) were synthesized via sequential anionic polymerization in cyclohexane and toluene, respectively, followed by catalytic hydrogenation of the polybutadiene middle block to polyethylene. Detailed information about used materials, purification methods and the polymerization procedure can be found in previous publications.[41,44]

Seed Preparation. A 10 g/L dioxane solution of the respective triblock copolymer was produced by dissolution of the polymer at 90 °C overnight. This solution was quenched in air to room temperature resulting in sCCMs that were used as seeds.

Seeded Growth. Six-milliliter unimer solutions of the respective triblock copolymers were obtained by dissolution in THF (1 g/L) at 65 °C for at least 30 min. These solutions were quenched to 30 °C before adding different amounts of the seeds (10 g/L in dioxane) at unimer-to-seed ratios (wt/wt of polymer) from 3 to 18, corresponding to 200 μL down to 33 μL of seed solution. After 2 weeks at 30 °C in a thermostated shaker unit (Ditabis Cooling-Thermomixer MKR13) the solutions were quenched in air before TEM sample preparation ("one-step growth process").

In the second experiment ("repetitive grow method") wCCMs first were produced using the technique described above and a U/S ratio of 6. After 2−4 days of shaking at 30 °C the same amount of unimers was added again as a preheated (65 °C for 30 min) 10 g/L THF solution (600 μL) in order to restore a unimer concentration of about 1 g/L and at the same time avoid significant dilution of the wCCM concentration. This procedure was repeated several times so that solutions with final U/S ratios of 12, 24, 36, and 48 were obtained. After the final unimer addition the solutions were kept at 30 °C for at least 2 more days and subsequently cooled to 20 °C stepwise at a rate of 1 K per 12 h, in order to facilitate the controlled growth of unimers with less ideal PE blocks containing above-average amounts of ethyl side branches.

Block *co*-Micelles. For the preparation of SEM-*b*-SES-*b*-SEM triblock *co*-micelles, first, the SES wCCMs that afterward form the middle block of the block *co*-micelles were produced at a U/S ratio of 6 for 2 d at 30 °C as described above. Subsequently, the double amount of SEM unimers was added as a 10 g/L THF solution (1.2 mL) that again was preheated to 65 °C for 30 min. After another 2 days at 30 °C the solution was cooled to 20 °C stepwise at a rate of 1 K per 12 h. The preparation of SES-*b*-SEM-*b*-SES triblock *co*-micelles was conducted in the reverse way under otherwise identical conditions. Hence, SEM wCCMs were produced via the seeded growth of unimers to SEM sCCMs followed by addition of the double amount of SES unimers.

Transmission Electron Microscopy. Samples were prepared by placing a drop of the diluted solution (0.5 g/L) on a carbon-coated copper grid. After 20 s, excess solution was removed by blotting with a filter paper. Subsequently, elastic bright-field TEM was performed on a Zeiss 922 OMEGA EFTEM (Zeiss NTS GmbH, Oberkochen, Germany) operated at 200 kV. Zero-loss filtered images (ΔE = 0) were registered digitally by a bottom-mounted CCD camera system (Ultrascan 1000, Gatan) and processed with a digital imaging processing system (Gatan Digital Micrograph 3.9 for GMS 1.4). Staining was performed with RuO_4 vapor for at least 20 min. RuO_4 is known to selectively stain PS, i.e., PS domains appear dark, which enables to distinguish between PS and PMMA domains in the corona of the micelles. Average values of the SES and SEM wCCM lengths were determined from at least 100 measurements using ImageTool (University of Texas Health Science Center, San Antonio). For the characterization of the triblock *co*-micelles about 200 micelles were evaluated. Due to better visibility, these average lengths were obtained by measuring the PE core length. In case micelles with thinner cores self-assembled during sample preparation or previous cooling (see Figure 2F), these were not taken into account, as their formation did not occur at the conditions suitable for controlled growth. The number-average and weight-average micelle lengths, L_n and L_w, respectively, were calculated from the obtained lengths as follows:

$$L_n = \frac{\sum_{i=1}^{n} N_i L_i}{\sum_{i=1}^{n} N_i} \quad (1)$$

$$L_w = \frac{\sum_{i=1}^{n} N_i L_i^2}{\sum_{i=1}^{n} N_i L_i} \quad (2)$$

Dynamic Light Scattering. DLS measurements were performed on an ALV DLS/SLS-SP 5022F compact goniometer system equipped with an ALV 5000/E operated in cross-correlation mode at a scattering angle of 90° and a He−Ne laser (λ_0 = 632.8 nm) was employed as light source. The decalin bath of the instrument was thermostated to 20 °C using a LAUDA Proline RP 845 thermostat. Data evaluation of the DLS experiments was performed using the CONTIN algorithm,[45] which yields an intensity-weighted distribution of relaxation times (τ) after an inverse Laplace transformation of the intensity autocorrelation function. These relaxation times were transformed into translational diffusion coefficients and further into hydrodynamic radii using the Stokes−Einstein equation.

ASSOCIATED CONTENT

Supporting Information

DLS data for SES wCCMs prepared via seeded growth and for triblock *co*-micelles; length histograms for SES and SEM wCCMs; length evaluation of SES wCCMs including micelles with thinner cores; additional TEM micrographs of triblock *co*-micelles. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

holger.schmalz@uni-bayreuth.de

Notes

The authors declare no competing financial interest.

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