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PAPER

Preparation and self-assembly of two-length-scale A-*b*-(B-*b*-A)_{*n*}-*b*-B multiblock copolymers†

Martin Faber, Vincent S. D. Voet, Gerrit ten Brinke* and Katja Loos*

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A-*b*-(B-*b*-A)_{*n*}-*b*-B multiblock copolymers composed of short middle diblock units (B-*b*-A)_{*n*} and two long A- and B-outer blocks were successfully prepared. The multiblock copolymers consist of polystyrene (S) and poly(*p*-hydroxystyrene) (*p*HS) and were prepared through sequential anionic polymerization of styrene and 4-*tert*-butoxystyrene, followed by hydrolysis of the *tert*-butoxy group. A hexablock and an octablock copolymer with a low overall polydispersity were synthesized. The self-assembled structures were investigated using Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM). Due to the smaller number of inner blocks and their relatively small molar mass, a single periodic lamellar morphology was observed for the hexablock copolymer while a lamellar-*in*-lamellar morphology with two thin layers within successive thick layers was observed for the octablock copolymer with larger middle diblock units. These observations are in excellent agreement with existing theories.

Introduction

Driven by the prospects to develop nanotechnology applications, the ability of block copolymer systems to form highly ordered complex nanostructures has been in the focus of scientific attention for many years.^{1–12} The self-assembly of diblock copolymers is well understood by now,^{5,6} although new developments still occur.^{7,8} Gradually, the research shifts to the study of self-assembly in copolymers with a more complex molecular architecture, such as triblock copolymers and star copolymers.^{13–16} In comparison to diblock copolymers, the addition of a third block, in the case of ABC triblock copolymers, gives rise to many more morphologies. In particular, the order in which the linkage occurs is an additional parameter leading to different levels of frustration and thus strongly influencing the phase morphology.^{13,14} For ABC star terpolymers the spring of three different polymers from a single junction point is the determining factor that may result in typical two dimensional Archimedean tiling patterns, where these junction points are located on straight lines.¹⁶ Another development in complexity involves binary multiblock copolymers with two different intrinsic length scales.^{17–21} A number of theoretical studies appeared dealing with the intricacies of the self-assembly in specific representatives of such systems, *e.g.* AB multiblock copolymers involving end blocks that differ in length from the blocks of the middle multiblock.^{22–30} Despite the fact that only two chemically

different species are involved, the presence of two different intrinsic length scales may result in hierarchical structure formation. Such a “structure-in-structure” morphology was first reported for supramolecules consisting of poly(styrene-*b*-4-vinylpyridine) diblock copolymers with relatively short side chains (pentadecyl phenol) hydrogen bonded to the pyridine blocks.^{31,32} The molecular architecture of these supramolecules resembles that of A-*b*-(B-*graft*-C) block copolymers. It is characterized by two intrinsic length scales, that of the whole molecule and that of the repeat unit of the graft block. In the case of lamellar-*in*-lamellar structures, the graftlike architecture is also responsible for both lamellar structures being oriented perpendicularly with respect to each other. An alternative way to obtain a similar two-length-scale molecular architecture consists of linear multiblock copolymers, such as C-*b*-(A-*b*-B)_{*n*}-*b*-C, where the middle multiblock consists of several diblocks that are much shorter than the two end blocks. Matsushita and co-workers showed the presence of a lamellar-*in*-lamellar morphology in P(IS)₄IP undecablock copolymers (P = poly(2-vinylpyridine), I = polyisoprene, S = polystyrene).^{17,18}

The presence of structures at two different length scales for ternary multiblock copolymers with two intrinsic length scales does not come as a surprise. For binary multiblock copolymers this is less obvious. A Random Phase Approximation (RPA) analysis of different representatives of this class of systems revealed a very interesting double maxima behavior of the scattering function.²² The theoretically best studied system involves the fully symmetric A_{*mN*/2}-(B_{*N*/2}-A_{*N*/2})_{*n*}-B_{*mN*/2} multiblock copolymer. Here *m* denotes the relative length of both outer blocks with respect to the length *N*/2 of the blocks of the symmetric diblocks that make up the middle multiblock and *n* denotes the number of

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diblocks of middle multiblock. In the weak segregation limit the behavior of the symmetric $A_{mN/2}-(B_{N/2}-A_{N/2})_n-B_{mN/2}$ multiblock copolymers resembles that of symmetric ABC triblock copolymers with a non-selective middle B-block. For the multiblock, the middle $(B_{N/2}-A_{N/2})_n$ multiblock plays the role of the nonselective B-block in the case of the ABC triblock copolymer. There are obviously subtle differences due to the difference in molecular architecture. In particular for systems near the equimaximum of the two scattering peaks, two-length-scale body-centered tetragonal mesophases become stable.^{25,26} If for a given n the end blocks are sufficiently long (m sufficiently large) first a lamellar structure will be formed due to the segregation between the two end blocks. If the segregation is further increased the relatively short diblocks of the middle multiblock will also segregate and may form “thin” lamellae inside the thicker lamellae formed by the end blocks. The presence and the number of “thin” internal layers depend on the segregation and on the number and relative length of the internal diblocks n .²⁹ Furthermore, on the formation of the internal layers the overall long period will increase or decrease depending on the number of diblocks n and the commensurability of the two length scales involved (*i.e.* m).³⁰

So far the only experimental realization of this class of polymers, albeit a not fully symmetric system, was presented by Matsushita and co-workers,¹⁸ who showed a S-ISISISIS-S undecablock copolymer with two long polystyrene (S) end blocks and a middle multiblock consisting of short polystyrene and isoprene (I) blocks self-assembled in a lamellar-*in*-lamellar morphology with three successive thin I, S and I layers inside two thick S layers.

To verify the intriguing phase behavior predicted, it is of great interest to develop additional experimental model systems. To be useful, the design has to satisfy two important requirements. First of all, the value of the Flory–Huggins parameter between the two different monomers has to be large enough to preferably already induce microphase separation for diblocks of a relatively small molar mass in the order of 10 000 g mol⁻¹ or less. This will allow us to use for the middle multiblock relatively short diblocks. For the above mentioned S-ISISISIS-S multiblock copolymer of styrene and isoprene the interaction parameter value is actually somewhat smaller, $\chi_{IS} \cong 0.05$ ³³ (of course it is temperature dependent) and the IS diblocks used had a considerably larger molar mass of *ca.* 28 000 g mol⁻¹. Additionally, the multiblock copolymer should preferably be as narrow in polydispersity as possible to avoid polydispersity effects.

A combination of monomers that satisfies these requirements is styrene and *p*-hydroxystyrene. Poly(*p*-hydroxystyrene) (*p*HS) and its derivatives are of interest for, *e.g.*, applications in photoresist materials,^{34–37} removal of organic material from aqueous waste *via* adsorption,³⁸ and as light-emitting devices.^{39,40} In order to effectively polymerize *p*-hydroxystyrene, the acidic proton needs to be protected. Different kinds of protecting groups like *tert*-butyl,^{41,42} various alkylsilyl,^{43–45} and *tert*-butoxycarbonyl⁴³ are used. The protecting groups can be easily removed *via* acidic cleavage. Subsequently, post-polymerization modifications of the polymer *via* a reaction with the phenolic group are possible.⁴⁴ Protected *p*-hydroxystyrene has been polymerized *via* different polymerization methods like free radical polymerization,^{42,43} nitroxide mediated polymerization,⁴⁶ cationic polymerization,⁴² and anionic polymerization^{41,42,44,45}

and combined with different comonomers like styrene,^{41,45,47} 4-vinylpyridine,^{47,48} 4-*tert*-butylstyrene,^{49,50} and ethylene oxide⁵¹ in both random copolymers as well as block copolymers. In order to obtain (multi)block copolymers with a narrow polydispersity, anionic polymerization is indicated.^{18,52–54} Anionic polymerization of diblock copolymers of styrene and 4-*tert*-butoxystyrene has been synthesized starting both from styrene⁵⁵ and from 4-*tert*-butoxystyrene.⁵⁶ This indicates that the stability of the anion is relatively the same and sequential anionic polymerization is possible. Finally, the interaction parameter between both species is expected to be quite large. The only value available in the literature is $\chi_{S, pHS} \cong 0.68$.⁵⁶ However, this value is based on a solubility parameter estimation and should merely be considered as an order of magnitude.

In this publication we will present the preparation of two-length-scale symmetric multiblock copolymers of *p*HS and S and discuss the self-assembly of the hexablock and octablock copolymers. The latter $A-b-(B-b-A)_6-b-B$ consists of six short inner blocks and two long outer blocks. Due to the symmetry its self-assembled structure will be lamellar with possibly 0, 2, 4 or 6 “thin” internal layers (Fig. 1a–d). The lamellar state of the corresponding $A-b-(B-b-A)_6-b-B-A$, with two chemically identical long A end blocks studied experimentally by Matsushita and co-workers¹⁸ and theoretically in our group,²⁹ will have 1, 3, 5 or 7 “thin” internal layers (see ESI†).

Experimental

Materials

Styrene (S, Acros, 99%) was dried overnight under nitrogen atmosphere over finely ground CaH₂ and condensed at room temperature (10⁻⁶ mbar) into a flask containing dibutyl magnesium. After stirring overnight, a second condensation into a storage ampule was performed. The purified styrene was stored at -18 °C under nitrogen atmosphere. 4-*tert*-Butoxystyrene (*t*BOS, Aldrich, 99%) was distilled twice under reduced pressure from finely ground CaH₂ and stored under nitrogen at -18 °C. *sec*-Butyllithium (*s*-BuLi, Acros, 1.3 M solution in cyclohexane/hexane (92/8)) was used without further purification. Tetrahydrofuran (THF, Acros, 99.9%) was reacted with *tert*-butyllithium for 1 hour at -78 °C under nitrogen atmosphere during which a yellow color indicated that the solvent was suitable for anionic polymerization. It was condensed at room temperature

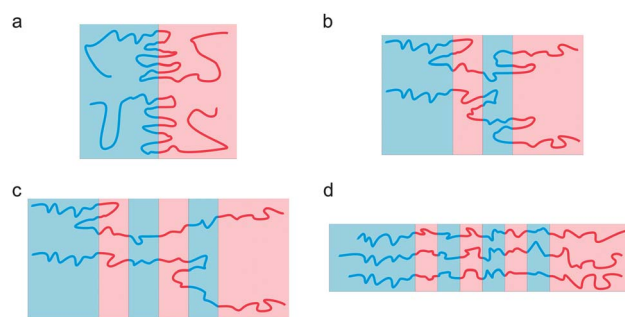


Fig. 1 Possible lamellar self-assembled structures with 0, 2, 4 and 6 thin internal layers respectively for a symmetric $A-b-(B-b-A)_3-b-B$ octablock copolymer consisting of six short inner blocks and two long outer blocks.

into the polymerization flask and subjected to three freeze–pump–thaw cycles. Methanol (MeOH, Lab-Scan, 99.8%) was degassed by nitrogen gas flow for 1 h at room temperature. 1,4-Dioxane (Acros, 99+%), hydrochloric acid (HCl, Merck, 37%) and osmium(VII)-tetroxide (OsO₄, Acros, 99.9+%) were used as received.

Sequential anionic polymerization of *S-b-(tBOS-b-S)_n-b-tBOS*

S-b-(tBOS-b-S)_n-b-tBOS multiblock copolymers composed of multiple short inner diblocks and two long end blocks were synthesized through a multi-step sequential anionic polymerization in THF at $-78\text{ }^{\circ}\text{C}$ using *s*-BuLi as an initiator; the synthesis is presented in Scheme 1. All anionic polymerizations were performed under nitrogen atmosphere in a round-bottomed flask attached to a high vacuum line. Solvent was condensed into the reaction vessel. Initiator and monomers were transferred to the reaction vessel *via* a degassed stainless steel needle and syringe.

At room temperature 500 mL THF was condensed into a 1000 mL flask and after three freeze–pump–thaw cycles the THF was titrated with *s*-BuLi until the solution turned slightly yellow. The solution was cooled down to $-78\text{ }^{\circ}\text{C}$ and the calculated amount of styrene was added, followed by the calculated amount of *sec*-BuLi to initiate the polymerization; a bright yellow-orange color appeared. After 30 minutes of reaction time an aliquot of the polystyrene was isolated for analysis by dispersing the sample in degassed methanol. Subsequently, the calculated amount of 4-*tert*-butoxystyrene was added and the reaction mixture was reacted for another 30 minutes. Upon the addition of 4-*tert*-butoxystyrene the color changed immediately to bright yellow. Alternating, calculated amounts of styrene and 4-*tert*-butoxystyrene were added to obtain the desired multiblock copolymer; each block was reacted for 30 minutes while the temperature of the reaction mixture was kept at $-78\text{ }^{\circ}\text{C}$. The addition of each block was accompanied by the corresponding color change. The color changes happened immediately upon addition of the respective other monomers

proving that the rate of reinitiation is very fast as it is required for a living anionic polymerization. The polymerization was terminated by the addition of 1 mL degassed methanol. The reaction mixture was concentrated to *ca.* 100 mL and precipitated in tenfold excess of water. After filtration, the crude product was dried overnight under vacuum at $40\text{ }^{\circ}\text{C}$. The crude product was dissolved in 80 mL CHCl₃ and reprecipitated in a tenfold excess of methanol, followed by filtration. The obtained white powder was dried under vacuum overnight at $40\text{ }^{\circ}\text{C}$.

Hydrolysis of *S-b-(tBOS-b-S)_n-b-tBOS*

The *tBOS* blocks in the resulting *S-b-(tBOS-b-S)_n-b-tBOS* multiblock copolymer were hydrolyzed to obtain a *S-b-(pHS-b-S)_n-b-pHS* multiblock copolymer, as depicted in Scheme 1.

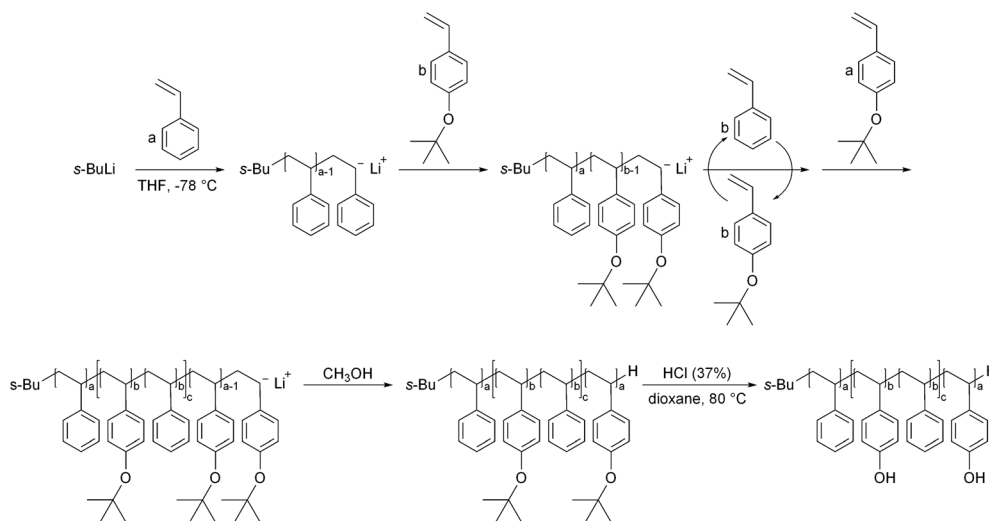
The *S-b-(tBOS-b-S)_n-b-tBOS* multiblock copolymer was dissolved in dioxane and a five-fold excess of concentrated HCl was added. Hydrolysis was carried out overnight at $80\text{ }^{\circ}\text{C}$ under nitrogen atmosphere. The reaction mixture was concentrated and precipitated in a tenfold excess of water. After neutralization with 5 wt% NaOH solution to a pH value of 6–7, the crude product was filtered and dried overnight under vacuum at $40\text{ }^{\circ}\text{C}$. The crude product was dissolved in THF and reprecipitated in a tenfold excess of hexanes, filtered and dried under vacuum overnight at $40\text{ }^{\circ}\text{C}$ to obtain a white solid.

Sample preparation

S-b-(pHS-b-S)_n-b-pHS multiblock copolymer films were cast from either THF or dioxane. The solvent was slowly evaporated and the sample was annealed in a saturated vapor for at least one week. Subsequently the film was placed in an oven for 30 minutes at $140\text{ }^{\circ}\text{C}$.

Characterization

Gel permeation chromatography (GPC) measurements were performed in THF at $25\text{ }^{\circ}\text{C}$ (1 mL min^{-1}) on a Spectra-Physics AS 1000, equipped with PLGel 5 μ 30 cm mixed-C columns.



Scheme 1 Synthesis of a *S-b-(pHS-b-S)_n-b-pHS* multiblock copolymer *via* sequential anionic polymerization of styrene and *tert*-butoxystyrene and subsequent hydrolysis of the *tert*-butoxy group.

Universal calibration was applied using a Viscotek H502 viscometer and a Shodex RI-71 refractive index detector. The GPC was calibrated using narrow disperse polystyrene standards (Polymer Laboratories).

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a 300 MHz Varian VXR at room temperature, using $(\text{CD}_3)_2\text{CO}$ as a solvent unless noted differently.

Attenuated total reflection infrared (ATR-IR) spectrometry was performed at room temperature on a Bruker IFS 88.

Bright-field transmission electron microscopy (TEM) was performed on a JEOL-1200EX transmission electron microscope operating at an accelerating voltage of 120 kV. To prepare TEM samples, ultrathin sections (*ca.* 80 nm) of a solvent-cast block copolymer film embedded in epoxy resin (Epofix, Electron Microscopy Sciences) were microtomed using a Leica Ultracut UCT-ultramicrotome and a Diatome diamond knife at room temperature, placed on copper grids and vapor stained with OsO_4 to obtain contrast during TEM measurements.

Small-angle X-ray scattering (SAXS) measurements were performed at the Dutch–Belgian Beamline (DUBBLE) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.^{57,58,59} The sample–detector distance was about 8 m, while the X-ray wavelength was 1.24 Å ($E = 10$ keV). The scattering vector q is defined as $q = (4\pi/\lambda) \sin \theta$, where θ is half of the scattering angle. The samples were heated shortly to 200 °C before collecting the data at room temperature.

Results and discussion

Synthesis of S - b -($p\text{HS}$ - b - S) $_n$ - b - $p\text{HS}$ multiblock copolymers

S - b -($p\text{HS}$ - b - S) $_n$ - b - $p\text{HS}$ multiblock copolymers with a two-length-scale molecular architecture were prepared through a multistep sequential living anionic polymerization of S - b -($t\text{BOS}$ - b - S) $_n$ - b - $t\text{BOS}$ multiblock copolymers followed by hydrolysis of the *tert*-butoxy group (Scheme 1).

A lot of research has been conducted on the synthesis of block copolymers of styrene and protected hydroxystyrene *via* living anionic polymerization.^{41,42,44,45} In order to obtain $p\text{HS}$ blocks with a narrow polydispersity, protection of the phenol groups prior to anionic polymerization is required, to avoid termination of the living chain ends. Therefore, *tert*-butoxystyrene was used since it is commercially available and the *tert*-butyl ether can be hydrolyzed under relative mild conditions. Furthermore, styrene and *tert*-butoxystyrene can be polymerized sequentially.

A hexablock copolymer and an octablock copolymer were successfully synthesized. The corresponding molecular parameters, together with the results from GPC analysis, are presented in Table 1.

Fig. 2 compares the GPC chromatograms of the two multiblock copolymers synthesized, both indicating a narrow molecular weight distribution. The polydispersity index (PDI) values for the hexablock and the octablock copolymers, determined by universal calibration, are 1.09 and 1.25 respectively.

The corresponding FTIR spectra of the S - b -($p\text{HS}$ - b - S) $_n$ - b - $p\text{HS}$ multiblock copolymers after hydrolysis (Fig. 3b for $n = 6$) display a broad peak at 3340 cm^{-1} that is initially absent. This indicates the successful conversion from *tert*-butoxy to hydroxyl groups.

Table 1 Molecular characteristics of S - b -($t\text{BOS}$ - b - S) $_n$ - b - $t\text{BOS}$ multiblock copolymers

# of blocks	\overline{M}_n inner blocks ^{a/} kg mol ⁻¹		\overline{M}_n outer blocks ^{a/} kg mol ⁻¹		\overline{M}_n total ^{a/} kg mol ⁻¹	PDI ^b
	S	<i>t</i> BOS	S	<i>t</i> BOS		
6	2.9	4.3	29.7	42.6	86.7	1.09
8	8.7	12.7	26.0	38.1	128.3	1.25

^a On the basis of the initiator/monomer ratio and the molecular weight of the polystyrene precursor. ^b Determined by GPC (THF).

Hydrolysis was also studied by ^1H -NMR spectroscopy. Fig. 4 displays for the multiblock copolymers typical ^1H -NMR spectra before (a) and after hydrolysis (b). The large chemical shift around 1.31 ppm, corresponding to the *tert*-butyl protons in the initial S - b -($t\text{BOS}$ - b - S) $_n$ - b - $t\text{BOS}$ multiblock copolymer, completely disappears in the spectrum of the deprotected S - b -($p\text{HS}$ - b - S) $_n$ - b - $p\text{HS}$ multiblock copolymer indicating that the hydrolysis was completed. A broad peak located around 8.0 ppm, corresponding to phenol protons, appears after the acidic cleavage thus proving the successful hydrolysis of the ester groups.

In addition, ^{13}C -NMR spectra of the multiblock copolymers were recorded before and after deprotection (Fig. S1†). The signal located around 77 ppm, corresponding to the quaternary carbon atoms of *tert*-butyl groups in *t*BOS, entirely disappears in the spectrum of the hydrolyzed copolymer, again proving the successful conversion.

The compositions of the S - b -($p\text{HS}$ - b - S) $_n$ - b - $p\text{HS}$ multiblock copolymers were determined using the relative intensities of the aromatic protons of styrene and *p*-hydroxystyrene (6.1–7.4 ppm), and the results are presented in Table 2.

Morphology

To study the microphase separation, solvent-cast films of the multiblock copolymers were prepared and the structure was

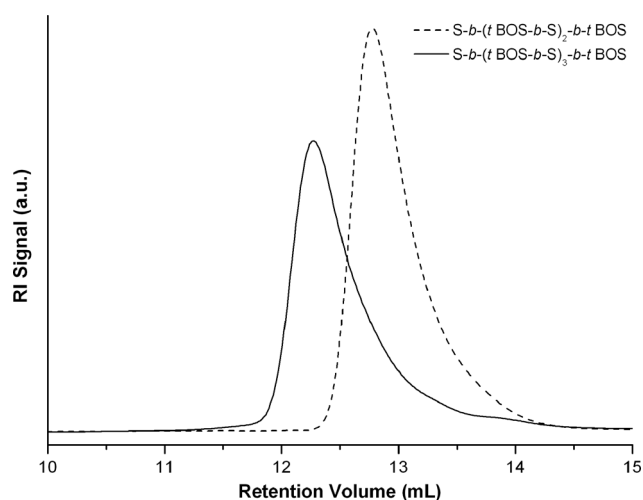


Fig. 2 GPC chromatograms of the hexablock (dashed line) and the octablock (solid line) copolymers.

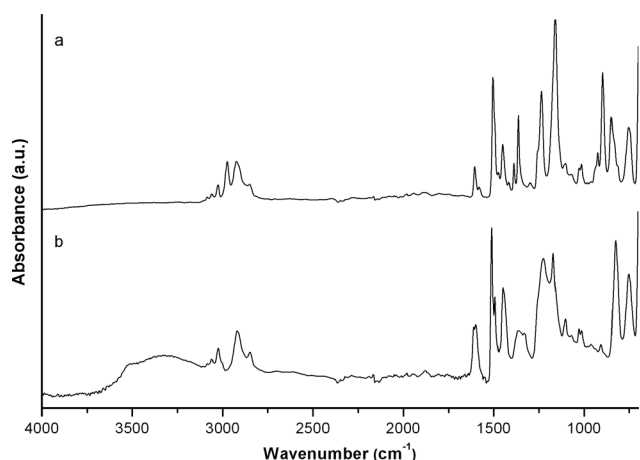


Fig. 3 FTIR spectra of the octablock copolymer (a) before and (b) after hydrolysis.

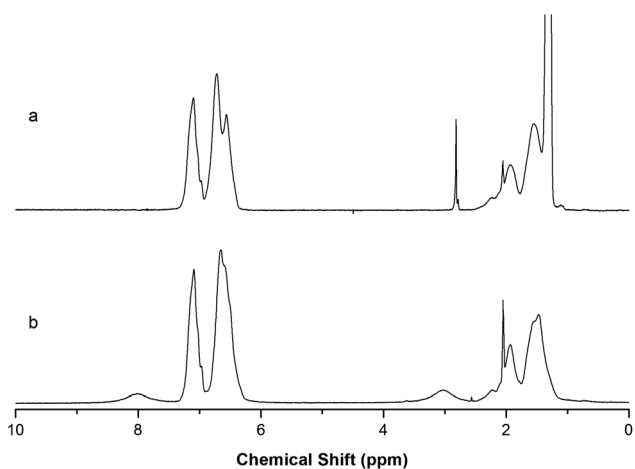


Fig. 4 ¹H-NMR spectra of a multiblock copolymer in acetone-d₆ (a) before and (b) after hydrolysis.

Table 2 Molecular characteristics of the *S-b-(pHS-b-S)_n-b-pHS* multiblock copolymers

# of blocks	\overline{M}_n inner blocks ^{a/} kg mol ⁻¹		\overline{M}_n outer blocks ^{a/} kg mol ⁻¹		\overline{M}_n total ^{a/} kg mol ⁻¹	Weight fraction <i>pHS</i> ^b
	S	<i>pHS</i>	S	<i>pHS</i>		
6	2.9	2.9	29.7	29.0	70.3	0.48
8	8.7	8.7	26.0	26.0	104.2	0.47

^a On the basis of the molecular weight of the *tBOS* precursor.

^b Determined by ¹H-NMR.

investigated by Small-Angle X-ray Scattering and Transmission Electron Microscopy.

Hexablock copolymer. Fig. 5 shows the SAXS intensity profile for the *S-b-(pHS-b-S)₂-b-pHS* hexablock copolymer. The

scattering peaks are in the ratio 1 : 2 : 3 indicating a lamellar ordered structure. From the value of the first order peak $q = 0.171 \text{ nm}^{-1}$, the characteristic domain spacing D is calculated to be 37 nm.

Fig. 6 shows TEM images of thin film sections of the *S-b-(pHS-b-S)₂-b-pHS* hexablock copolymer stained with OsO₄. After staining the *pHS* phase appears dark and the lamellar structure can clearly be seen. The distance between the lamellar planes is 36 to 39 nm. Furthermore, it is clear from Fig. 6 that there are no separate thin layers present originating from the short inner blocks. This implies that the short blocks of the middle multiblock either organize at the interface as schematically illustrated in Fig. 1a for the octablock copolymer system, or, alternatively, are too short to microphase separate and are simply distributed throughout the layers formed by the long outer blocks. Since $\chi_{S, pHS} \cong 0.68$, implying $N > 30$ for N being the length of the middle diblock, the last possibility can be dismissed. Lamellar-*in*-lamellar self-assembly of *A-b-(B-b-A)_n-b-B* two-length-scale multiblock copolymers has not yet been analyzed theoretically in the strong segregation limit. The first experimental realization of two-length-scale multiblock copolymers, due to Matsushita and

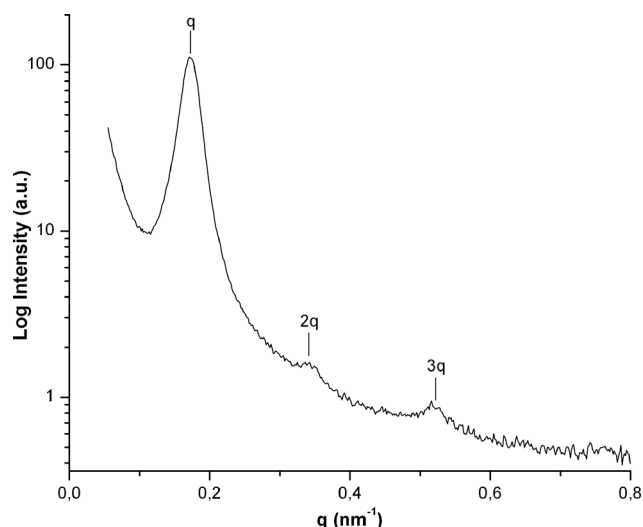


Fig. 5 SAXS intensity profile for a *S-b-(pHS-b-S)₂-b-pHS* hexablock copolymer, where \overline{M}_n (outer blocks) = 29 000 g mol⁻¹ and \overline{M}_n (inner blocks) = 2900 g mol⁻¹.

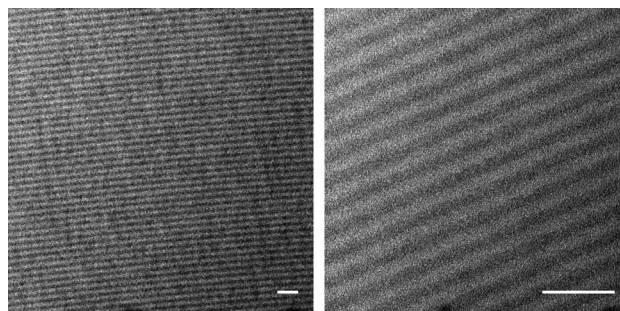


Fig. 6 Bright-field TEM images of a *S-b-(pHS-b-S)₂-b-pHS* hexablock copolymer, where \overline{M}_n (outer blocks) = 29 000 g mol⁻¹ and \overline{M}_n (inner blocks) = 2900 g mol⁻¹, stained with OsO₄. Scale bar represents 100 nm.

co-workers, concerned a S-ISISISIS-S undecablock copolymer system,¹⁶ which prompted a theoretical strong segregation analysis of the corresponding $A-b-(B-b-A)_n-b-B-b-A$ system.²⁹ It was demonstrated that the extra entropy due to different ways of organizing loops and bridges in the case of internal structures alone is not sufficient to make the hierarchical structure formation favorable. The presence of strongly anisotropic stretching of the long end blocks in the outer thick A-layers due to the presence of many loops of the short middle A-blocks, which necessarily accompanies structure formation without thin layers (*cf.* Fig. 1a), gives an additional unfavorable free energy contribution that is essential for internal domain formation. Although the theoretical predictions reported in the literature²⁹ were restricted to $n \geq 3$, it was shown that for certain values of the characteristic parameters (relative length of internal blocks, value of the interaction parameter) no additional internal structure formation should take place for the smallest values of $n = 3$ and 4 considered. As already mentioned in the Introduction and illustrated in Fig. S2†, for $A-b-(B-b-A)_3-b-B-b-A$ the number of thin layers is 1, 3, 5 or 7 compared to 0, 2, 4 or 6 for our octablock copolymer. According to the analysis presented in ref. 29, for molar masses of the outer and inner blocks as for our hexablock copolymer and a Flory–Huggins interaction parameter equal to 0.68,⁵⁴ the number of internal layers for $A-b-(B-b-A)_3-b-B-b-A$ would have been the minimal number 1. Hence, even though the reported theoretical analysis addresses a slightly different system, the fact that for our hexablock copolymer no internal layers are observed, which is the minimum in this case, is in excellent agreement with these findings.

Octablock copolymer. Fig. 7 shows the SAXS intensity profile for the $S-b-(pHS-b-S)_3-b-pHS$ octablock copolymer. The scattering peaks are in a ratio of 1 : 2 : 3 : 4 : 5 : 6 indicating a lamellar ordered structure. From the value of the first order peak the domain spacing is calculated to be 80 nm, which is much larger than would be expected on the basis of microphase separation between the outer blocks alone. It indicates that the inner blocks of the octablock copolymer, which are considerably longer than those of the hexablock copolymer considered above, are now microphase separated as well. Of course, if both types of layers are parallel only the overall periodicity will show up in SAXS. The lamellar-*in*-lamellar morphology is confirmed by the TEM images presented in Fig. 8 (for TEM of a larger area we refer to Fig. S3†). It shows that the self-assembled state consists of two large layers separated by two thin inner layers, which corresponds to the situation schematically presented in Fig. 1b.

The two $A-b-(B-b-A)_n-b-B$ multiblock copolymers considered differ in two aspects. The octablock contains an additional short diblock and these middle diblocks have a considerable larger molar mass than those of the hexablock. According to the reported theoretical predictions,²⁹ both aspects favor internal structure formation for the octablock in comparison to the hexablock copolymer. The former because of the entropic contribution associated with the many different conformations (loops and bridges, see Fig. 1b) and the latter because of the larger block incompatibility. Larger block lengths lead to additional chain stretching (*cf.* simple diblocks) and additional chain stretching is at some point relieved by additional layer formation. For the block lengths involved and a χ -parameter value of 0.68,

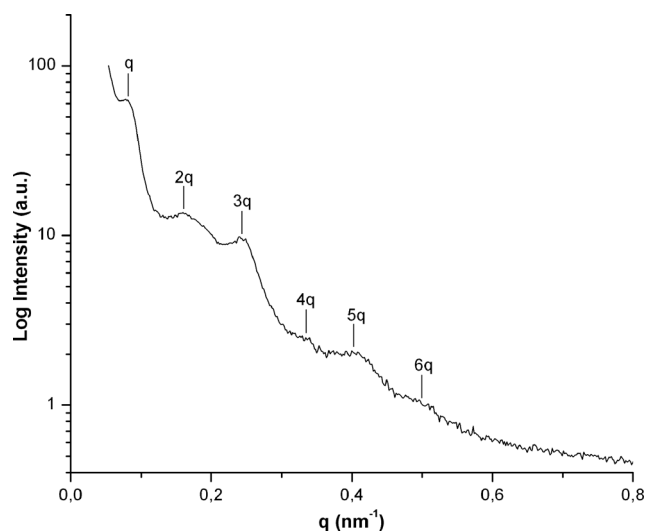


Fig. 7 SAXS intensity profile for a $S-b-(pHS-b-S)_3-b-pHS$ octablock copolymer, where \overline{M}_n (outer blocks) = 26 000 g mol⁻¹ and \overline{M}_n (inner blocks) = 8700 g mol⁻¹.

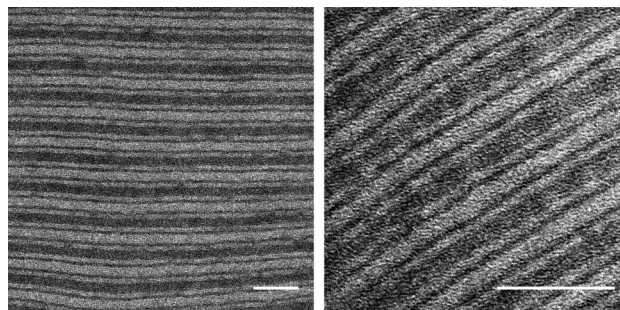


Fig. 8 Bright-field TEM image of a $S-b-(pHS-b-S)_3-b-pHS$ octablock copolymer, where \overline{M}_n (outer blocks) = 26 000 g mol⁻¹ and \overline{M}_n (inner blocks) = 8700 g mol⁻¹, stained with OsO₄. Scale bar represents 100 nm. This morphology is found over a large area of the film. A TEM image of a larger field is shown in the ESI (Fig. S3†).

the corresponding $A-b-(B-b-A)_3-b-B-b-A$ multiblock copolymer system considered theoretically is predicted to have 3 internal layers, which again nicely corresponds to the 2 internal layers observed in the $S-b-(pHS-b-S)_3-b-pHS$ octablock.

Conclusion

A hexablock copolymer and an octablock copolymer, both with a large polystyrene and a large poly-*p*-hydroxystyrene end block, and 2 resp. 3 short inner $S-b-pHS$ diblocks, have been successfully synthesized. Using TEM and SAXS the morphology of both polymers was investigated. For the hexablock a single periodic lamellar morphology was observed. The absence of additional “thin” layers is due to the small number of inner blocks and the relatively small molar mass of the inner blocks. The octablock showed a lamellar-*in*-lamellar morphology where two thin layers formed by the inner blocks are present inside the two thick layers formed by the end blocks. Both results are in excellent agreement with the theoretical predictions for

a comparable A-b-(B-b-A)_n-b-B-b-A two-length-scale binary multiblock copolymer system.²⁶

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