Morphological Changes in ABC Triblock Copolymers by Chemical Modification

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Summary: Various SBT triblock copolymers with S being polystyrene, B being polybutadiene, and T being poly(*tert*-butyl methacrylate) and their saponified analogues, SBA with A being poly(methacrylic acid) are characterized in terms of their morphology. The chemical modification of the third block leads to a change of the overall morphology observed in solution cast films, which is interpreted as a consequence of the change of the incompatibility between the different components and the solvent.

Introduction

Block copolymers are well-known for their self-assembly into crystal-like lattices on a mesoscopic length scale. The large number of independent system variables like volume fractions and segmental interaction parameters between the different components leads to a richer morphology scheme in ternary ABC triblock copolymers as compared to linear binary block copolymers.[1,2] Quite some work has been published with the aim to understand the morphological behaviour of ABC triblock copolymers as a function of the relative composition of the different components[1,3,4,5] and also for various block sequences.[6,7] While some examples for morphological changes as a result of chemical modification of one block were given,[1,8,9] we are not aware of systematic studies on this. In the case of simultaneous modification of two blocks it was shown for example that the hydrogenation of IBS triblock copolymers (with I and B being polyisoprene and poly(1,2-butadiene), respectively) leads to EPEBS triblock copolymers (with EP and EB being poly(ethylene-alt-propylene) and poly(ethylene-co-butylene), respectively) showing other morphologies within the same morphological scheme, i.e. the increasing incompatibility between the two elastomeric blocks leads to a reduction of curvature between them and polystyrene.[10] Depending on the relative block lengths of S, the triblock copolymers exhibit a disordered state, spheres or cylinders in an IB matrix and after hydrogenation spheres, cylinders or a double gyroid of S in an EPEB matrix are formed.

The introduction of a few transition metal complexes into the middle block of a lamellar SBM triblock copolymer (with M being poly(methyl methacrylate)) with a short middle block leads to the formation of double gyroid or cylindrical morphologies.[9]

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Whereas in these systems thermodynamics seems to control the morphological changes, there are also observations on the influence of solvent effects on the film casting process of block copolymers.[11,12] Upon those the most spectacular one was the so called knitting pattern morphology, which resulted from hydrogenation of asymmetric lamellar SBM triblock copolymers.[8] In this case most likely that the significant decrease of the solubility of the middle block is responsible for the morphological change. While this morphology was found in samples cast from chloroform, the same block copolymer cast from toluene solution shows lamellar morphologies. Also, an SBM triblock copolymer with a B matrix formed different morphologies depending on the solvent.[13] For this system a new hexagonal arrangement of microphase separated S and M cylinders in a B matrix was discussed.

In this contribution we will consider ABC triblock copolymers, where only one end block is chemically modified. These are polystyrene-block-polybutadiene-block-poly(*tert*-butyl methacrylate) SBT triblock copolymers, which are converted into the corresponding SBA triblock copolymers with A being poly(methacrylic acid) via hydrolysis of the poly(*tert*-butyl methacrylate) endblock.

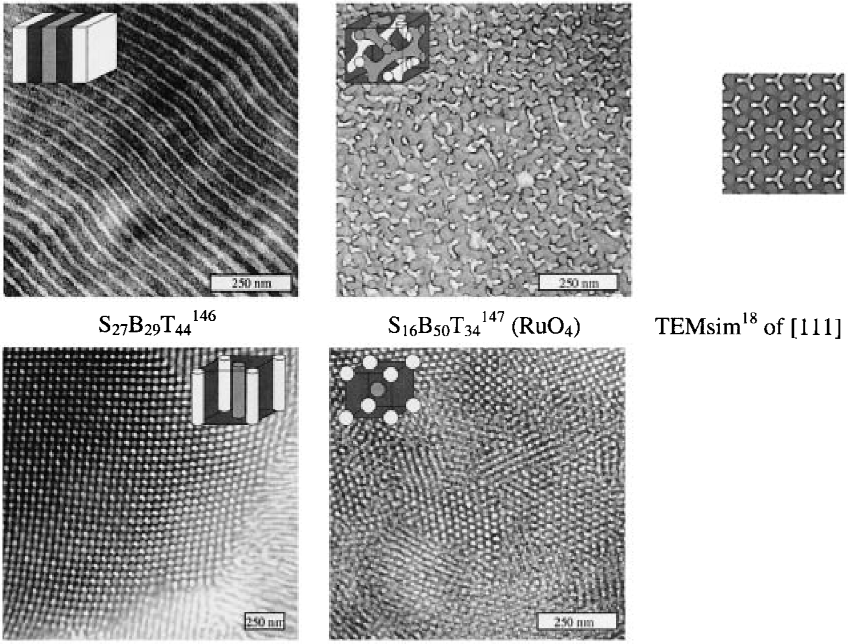
Experimental

The SBT triblock copolymers have been obtained using living sequential anionic polymerisation. The details of the synthesis have been described elsewhere.[14,15] Polymer analogous saponification of the T block was achieved by dissolution of the triblock copolymer in a mixture of dioxane and aqueous HCl.[16,17] The solution was kept under reflux conditions for 8 hours and then the polymer was precipitated, washed and isolated. The nomenclature of the block copolymers ($A_xB_yC_z^M$) is as follows: subscripts denote the weight fractions of the corresponding block and the superscript gives the number averaged molecular weight in kg/mol. Polydispersities were obtained using size exclusion chromatography calibrated with polystyrene standards and was in the range of $M_w/M_n < 1.1$.

For morphological characterisation films of the SBT triblock copolymers were cast from solution in tetrahydrofuran (THF) or chloroform ($CHCl_3$), respectively, and the SBA triblock copolymers were cast from solutions in THF over several weeks. The samples were then further dried in vacuum at 140 °C for several days. Transmission electron micrographs were obtained from a Zeiss 902 transmission electron microscope operating at 80 kV in the bright field mode. Ultrathin sections of the samples were obtained using a Reichert ultramicrotome equipped with a diamond knife. Vaporous OsO_4 and RuO_4, respectively, were used for staining the samples. In the transmission electron micrographs the B domains appear dark, the S domains appear grey and the T and A domains remain unstained.

Results and Discussion

First, the TEM micrographs of SBT and the corresponding SBA triblock copolymers having more or less similar volume fractions of the two outer blocks ($\phi_S \approx \phi_{T,A}$) are presented (Fig. 1). For increasing volume fractions of the outer blocks the morphology of the SBT triblock copolymers ranges from spheres, tetragonally packed cylinders, a cocontinuous gyroid to lamellae. The morphological sequence observed for these SBT triblock copolymers is similar to the one found for polyisoprene-block-polystyrene-block-poly(2-vinylpyridine) triblock copolymers studied by Mogi et al.[4] The two end blocks are strongly incompatible with each other and therefore do not form common mixed microdomains. The results can be understood in the following way: The different blocks microphase separate from each other when still in solution and the solubility of both endblocks are comparable, i.e. both swollen endblocks occupy volumes of comparable size. So spheres (cylinders, gyroids, lamellae) of both endblocks appear at the same time during the evaporation process and thus occupy positions with the same symmetry properties in the bulk morphology.

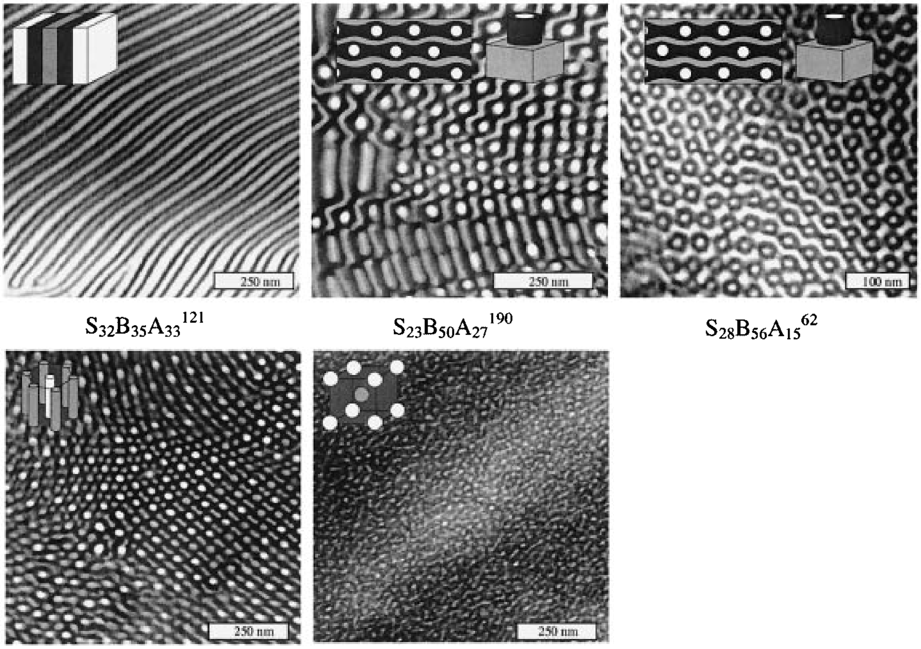


$S_{27}B_{29}T_{44}^{146}$ $S_{16}B_{50}T_{34}^{147}$ (RuO_4) TEMsim[18] of [111] plane

$S_{19}B_{57}T_{24}^{100}$ $S_{10}B_{76}T_{14}^{102}$

Fig. 1 Morphologies of SBT triblock copolymers

The SBA triblock copolymers were also cast from THF (Fig. 2). However, THF is a fairly bad solvent for poly(methacrylic acid) (e.g. water would be a good solvent, but is a nonsolvent for the other two blocks). When the A block is very short (as it is in $S_{38}B_{56}A_6^{66}$), it will be dissolved in a reasonably good way, so the morphology of the block copolymer will form at very high concentrations, where both S and A will probably separate in a highly entangled swollen state into similar microdomains of spherical shape. For SBA triblock copolymers with larger A block it will precipitate from the solution first, while S and B are still dissolved. In this case A will form cylindrical domains on a hexagonal lattice, while the swollen S and B blocks form the corona. At larger concentrations S will microphase separate from B and locate in cylindrical domains in the corners of the Wigner Seitz cell of the first hexagonal lattice defined by the A cylinders (Fig. 3). The same hexagonal motif was discussed by Brinkmann et al. for an SBM triblock copolymer.[13] At higher amounts of A all three blocks self-assemble into lamellar domains, as does the corresponding SBT triblock copolymer.



$S_{32}B_{35}A_{33}^{121}$ $S_{23}B_{50}A_{27}^{190}$ $S_{28}B_{56}A_{15}^{62}$

$S_{19}B_{57}A_{24}^{127}$ $S_{11}B_{80}A_{09}^{95}$

Fig. 2 Morphologies of SBA triblock copolymers

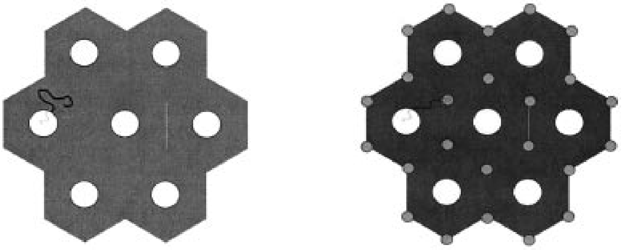
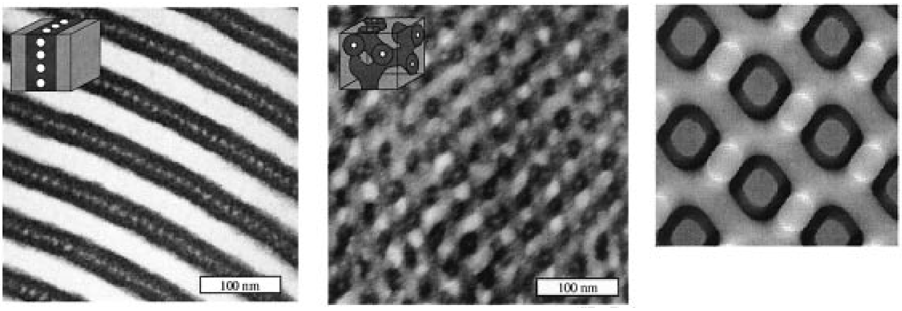


Fig. 3 Development of the hexagonal morphology by subsequent microphase separation of A (white circles) and S domains (grey circles) from the solution

For an SBT triblock copolymer with large amounts of S and B and a very short T block a lamellar structure is observed in a film cast from $CHCl_3$, where T spheres are embedded within the B lamellae (Fig. 4 left). The corresponding SBA triblock copolymer was cast from THF and forms a gyroid morphology (Fig. 4 middle). Here, the morphological change can also be attributed to the solubility of the different components. The T domain separates together with B and S and due to the fairly large amount of the latter a lamellar morphology is established with T forming small domains within the B lamellae. For the corresponding SBA triblock copolymer, the A domain microphase separates first and could possibly form either a cubic lattice of spheres (if B and S are still completely miscible at that stage) or will exhibit a gyroid network (if B and S are already weakly segregated from each other at the point, when A segregates from the solution). In the latter case S forms the other gyroid and B fills the space between the two gyroids. This interpretation is supported by TEM simulation (Fig. 4 right).



$S_{36}B_{56}T_8$[67] $S_{38}B_{56}A_6$[66] TEMsim[18] of [110] plane

Fig. 4 Morphologies of an SBT and an SBA triblock copolymer with a short third block

Since literature does not offer segmental interaction parameters for all types of binary interactions in the system "ABC triblock copolymer plus solvent", we use the solubility parameter approach following Hildebrand as a crude approximation: [19]

$$\chi \propto (\delta_i - \delta_j)^2$$

Table 1: Solubility parameters δ for estimation of interaction parameters χ

Polymer	Solubility parameter at room temperature[19,20] δ [MPa]$^{1/2}$
Polystyrene (S)	18.5
Poly(1,2-butadiene) (B)	17.4
Poly(*tert*-butyl methacrylate) (T)	18.0
Poly(methacrylic acid) (A)	21.9
Chloroform ($CHCl_3$)	19.0
Tetrahydrofuran (THF)	18.6

Comparing the solubility parameters in Table 1 it becomes obvious that the strongest incompatibility occurs between A and the other components. Thus it is likely that A microphase separates first from solution, while S and B are still soluble in it. The interactions between S, B, and T on one side and THF or $CHCl_3$ on the other are slightly different from each other and we can consider these two solvents to be much less selective for that system.
Thus there is strong evidence that solubility effects are responsible for the observation of the partly different morphological behaviour of solution cast films of SBT and SBA triblock copolymers.

Conclusions

Our results on solution cast SBT and SBA triblock copolymers demonstrate clearly the strong influence of the solvent on the final morphology. The chemical modification from T to A mainly influences the degree of selectivity of the solvent, while the increase of incompatibility towards the other two blocks (S, B) seems to be of less importance. This is probably due to the rather strong segregation of the different blocks in both SBT and SBA triblock copolymers. On the other hand, the rather different degree of swelling as a result of the selectivity of the solvent especially in the SBA system plays the key role in morphology determination.

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