Polymer Bulletin 40, 219–226 (1998)

Polymer Bulletin

Spheres on spheres – a novel spherical multiphase morphology in polystyrene-block-polybutadiene-block-poly(methyl methacrylate) triblock copolymers

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Received: 2 December 1997/Accepted: 3 December 1997

Summary

A novel morphology for linear ABC-triblock copolymers is presented, where A forms spherical microdomains, covered by small B-spheres and C forming the matrix. This morphology is characterized by transmission electron microscopy and small angle X-ray scattering. The morphology forms both in solution cast and melt extruded samples. Qualitative arguments to understand the thermodynamic stability of this morphology are given.

Introduction

Block copolymers consisting of three chemically different constituents show a much richer phase behaviour than binary diblock or triblock copolymers. In recent work we have evaluated a number of lamellar and cylindrical morphologies/1,2,3/. In contrast to binary block copolymers, where microphase separation is controlled by the composition ϕ, the overall degree of polymerization N and the Flory-Huggins χ-interaction parameter/4/, with ϕ being the quantity with the strongest influence on the type of microphase morphology (while χN defines the location of the order - disorder transition), the morphologies of ternary block copolymer systems are governed by two independent volume fractions ϕ_A, ϕ_B, three binary interaction parameters χ_{AB}, χ_{BC}, χ_{AC} and the block sequence (ABC $\leftrightarrow$ BAC $\leftrightarrow$ ACB)/5/. Only few morphologies with spherical motifs have been reported in ternary block copolymers. In analogy to a lamellar sequence ..ABCB.. and core shell cylinders („rod in the tube“ = „cylinder in cylinder“ = *cic*), core shell spherical morphologies („ball in the box“ = „sphere in sphere“ = *sis*) /6/ have been predicted. For a symmetric triblock copolymer (ϕ_A= 0.11, ϕ_C = 0.09) Mogi and coworkers /7/ reported a morphology where A and C - spheres are arranged on a lattice of the CsCl-type. In the present communication we will report a novel spherical morphology where the B block forms small spheres on the surface of either A (or C) spheres in a C (or A) matrix („spheres on sphere“ = *sos*). This novel morphology is observed in polystyrene-block-polybutadiene-block-poly(methyl methacrylate) (SBM) and the corresponding hydrogenated polystyrene-block-poly(ethylene-co-butene)-block-poly(methyl methacrylate) (SEBM) triblock copolymers. It originates from the same thermodynamic reasons which resulted in the formation of the „cylinder at lamella“ (*lc*), the „cylinder at cylinder“ (*cac*) and - as a special case the „helix“ (*hel*) morphologies /3/. The new morphology is observed both in solution cast films as well as in melt processed samples.

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Experimental

The polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) and the corresponding hydrogenated polystyrene-*block*-poly(ethylene-co-butene)-*block*-poly(methyl methacrylate) (SEBM) triblock copolymers were prepared by sequential anionic polymerization as described previously/8/. Table 1 summarizes the molecular characteristics of the triblock copolymers used in the present study. The polymerization in tetrahydrofuran creates a polybutadiene microstructure with 90% 1,2-units and 10% 1,4-units.

Films of the triblock copolymers (≈ 1 mm thick) were cast from chloroform solution (10% w/v) into flat-bottomed petri dishes by slowly evaporating the solvent at 298 K over a period of a week. The films were further dried at reduced pressure for two days at 353 K, followed by annealing at 423 K under vacuum for 6 h. The lower molecular weight $S_{78}B_{07}M_{15}^{88}$ was also processed from the melt using a twin screw extruder manufactured by „Centre for Polymers and Composites“ (Eindhoven, The Netherlands) at a temperature of 473 K, a rotation speed of 30 r.p.m. at a residence time of 2 min.

Ultrathin sections (≈ 40 - 60 nm thickness) were cut with an ultramicrotome (Reichert) at room temperature. The ultrathin sections were exposed to RuO_4 or OsO_4 vapor for staining. Transmission electron micrographs (TEM) were either obtained using a Phillips electron microscope (80 kV) or a JEOL instrument operating at 100 kV. Small angle X-ray scattering experiments have been performed at room temperature at station X12B of the Brookhaven National Laboratory.

Table 1: Molecular characteristics of the block copolymers

Polymer^x	M_n/ g/mol	M_w/M_n	ϕ_{PS}	ϕ_{PB}	ϕ_{PMMA}
$S_{15}B_{05}M_{80}^{241}$	241000	1.08	0.17	0.06	0.77
$S_{15}EB_{06}M_{79}^{242}$	242000	1.17	0.17	0.06	0.77
$S_{78}B_{07}M_{15}^{88}$	88000	1,10	0.79	0.07	0.14
$S_{78}EB_{07}M_{15}^{90}$	90000	1.12	0.79	0.07	0.14

^{x} $S_xB_yM_z^m$:x,y,z denote the weight fractions of the monomer;
m the number average molecular weight in kg/mol.

Results and discussion

Figure 1 shows a TEM micrograph of solution cast $S_{15}B_{05}M_{80}^{241}$, stained with OsO_4. This agent preferentially stains the PB microdomains and to a minor degree also PS. PMMA is not sensitive towards OsO_4. Grey spheres (PS microdomains) are covered by little dark structures, which have to be assigned to PB. The bright matrix corresponds the PMMA.

Hydrogenation of the PB block does not change the morphology, as seen in Figure 2, where a TEM of $S_{15}EB_{06}M_{79}^{242}$ is shown, stained with RuO_4. Here little bright PEB spheres cover the RuO_4-stained PS spheres in a grey PMMA matrix.

Figure 3 shows a schematic representation of the „spheres on sphere“ (≡ „*sos*“) morphology. It is difficult to determine the number of PB spheres covering the PS sphere, but from the TEM micrographs a number around 6 may be estimated.

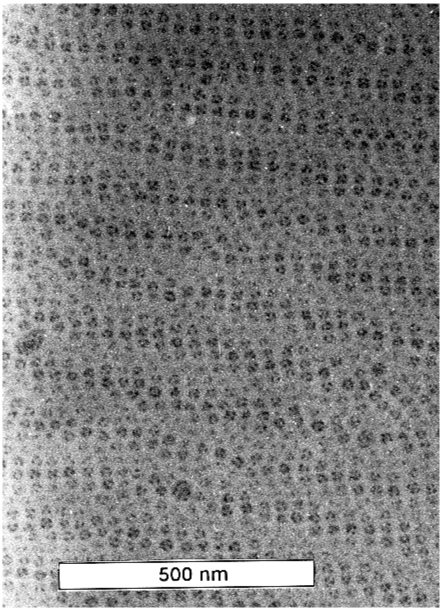

Figure 1: $S_{15}B_{05}M_{80}^{241}$ *(stained with* OsO_4*)*

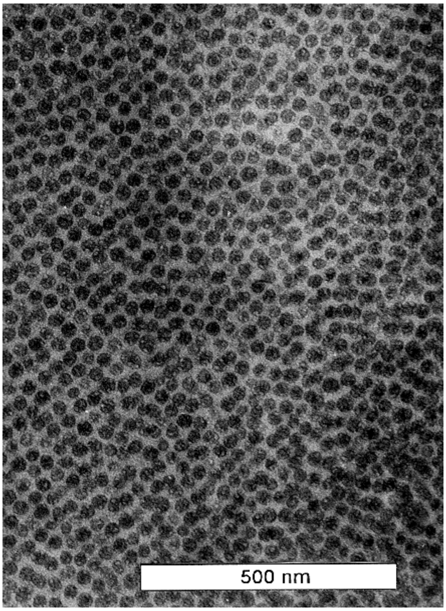

Figure 2: $S_{15}EB_{06}M_{79}^{242}$ *(stained with* RuO_4*)*

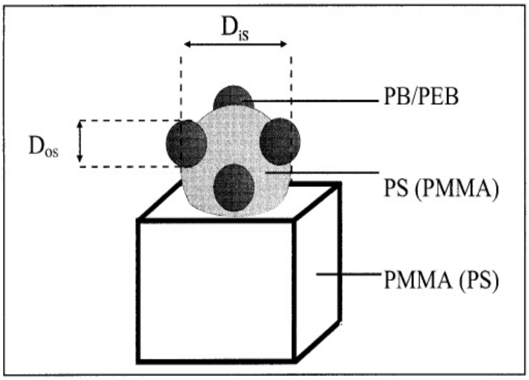

Figure 3: Scheme of the spheres on sphere (sos)-morphology

Under the assumption that half of the volume of the outer spheres is embedded in the inner sphere, the number of outer spheres per inner sphere N_{sph} can be estimated from the following relation:

$$N_{sph} = \frac{\phi_B}{\phi_A + \frac{\phi_B}{2}} \cdot \left(\frac{D_{is}}{D_{os}} \right)^3$$

ϕ_x is the volume fraction of component x. Taking the diameters of the inner D_{is} and outer spheres D_{os} from the TEM micrographs (see Table 2) a number of about 10 is obtained for N_{sph}. However, this number is subject to a relatively large error and should only be used as a first estimate of the number and arrangement of the outer spheres on the inner sphere.

Table 2: Dimensions from the sos morphology

Polymer	D_{is} [nm]	D_{as} [nm]	N_{sph}
$S_{15}B_{05}M_{80}^{241}$	26.3 ± 3	7.9 ± 1	11
$S_{15}EB_{06}M_{79}^{242}$	44.5 ± 3	10.2 ± 1	10
$S_{78}B_{07}M_{15}^{88}$	23.4 ± 3	7.8 ± 1	11
$S_{78}B_{07}M_{15}^{88}$ (extruded)	15.4 ± 3	5.4 ± 1	9

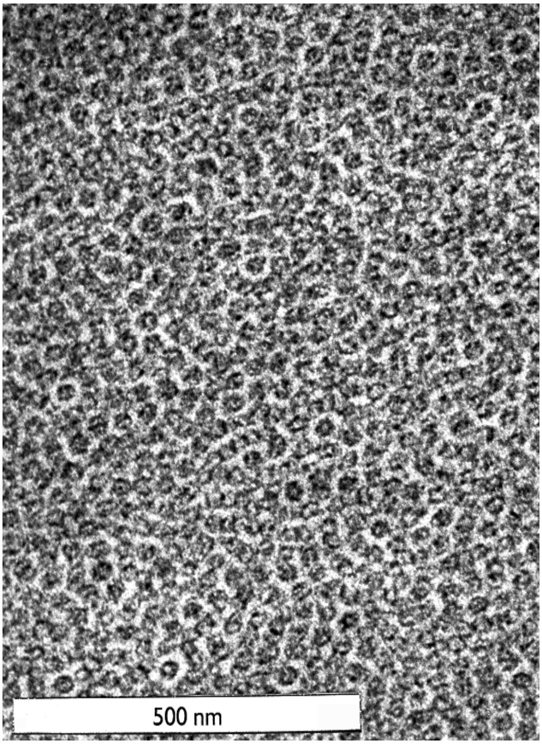

Figure 4: $S_{78}B_{07}M_{15}^{88}$ (stained with OsO_4)

Figure 4 shows the TEM micrograph of $S_{78}B_{07}M_{15}^{88}$ stained with OsO_4. In this block copolymer PS forms the matrix and PMMA spheres are covered by little PB spheres. The hydrogenated analogue, $S_{78}EB_{07}M_{15}^{90}$, forms the same morphology (not shown). Further confirmation of the spherical morphology is obtained from small angle X-ray scattering experiments (SAXS). In ternary systems the differences between the three electron densities have to be taken into account to estimate the contrast governing the scattering. From the electron densities at room temperature it turns out that the major contrast exists between PS and PMMA. Thus the scattering in the small angle region should be dominated by these two components - which in addition are the majority components.

Figure 5 shows the SAXS intensity pattern of $S_{78}B_{07}M_{15}^{88}$. Besides the primary peak which occurs at the scattering vector ($\mathbf{q}_1$= 0.188 nm^{-1}) maxima at higher q-values are located at $\mathbf{q}_2 = 0.265\ \text{nm}^{-1} \approx \sqrt{2}\ \mathbf{q}_1$ and at $\mathbf{q}_4 = 0.36\ \text{nm}^{-1} \approx \sqrt{4}\ \mathbf{q}_1$ as it would be expected for a body centered cubic lattice (*bcc*) or a simple cubic (*sc*) lattice. To distinguish between these two lattices higher order reflections would have to be resolved. However, due to the rather poor long range ordering of this morphology (see Figure 4) higher order reflections are smeared out. The expected maximum at $\mathbf{q}_1 * \sqrt{3}$ does not appear, probably due to a minimum in the form factor of the spheres. The broad maximum at $\mathbf{q} \approx 0.43\ \text{nm}^{-1}$ may relate to the structure factor of the spherical domains. Using Bragg's law, a long period (distance between two inner spheres) of 33±3 nm is obtained from the first peak. This relates well with the TEM in Figure 4. Using this long period together with the volume fraction of the inner sphere allows us to calculate the diameter of the inner sphere, D_{is}. The values obtained under the assumption of a *bcc* or an *sc* lattice are rather similar (22 and 25 nm, respectively) and very close to the value directly obtained from TEM (Table 2).

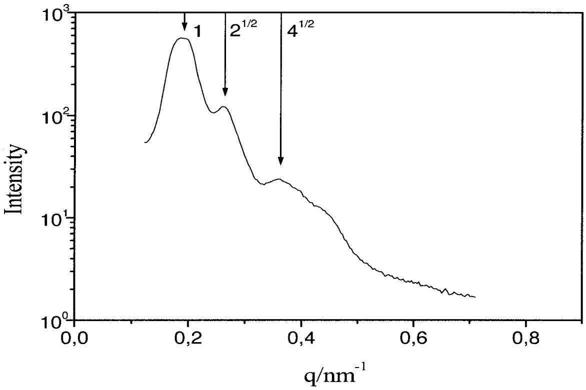

Figure 5:

SAXS-pattern of $S_{78}B_{07}M_{15}^{88}$ *(scattering vector* $q = 4\pi/\lambda \sin\theta$*; with* λ *being the wavelength of the X-ray beam and* 2θ *the scattering angle)*

It is well known that the preparation conditions might influence the morphology of a block copolymer /9,10/. Depending on the solvent, solution casting may result in the formation of nonequilibrium structures. This has been studied in some detail in binary block copolymers but may be of even more importance in ternary systems. An alternative to solution casting is processing from the melt. Melt processed materials often show a much poorer long range order. Figure 6 shows the morphology of the polymer $S_{78}B_{07}M_{15}^{88}$ after melt processing and subsequent annealing without shear. Independent of the cutting direction the same image is obtained. Again a *sos*-morphology is observed. Though the morphology has not changed via melt processing the sphere diameters are somewhat smaller as compared to the solution cast sample (see Table 2). Annealing of the sample at 170°C for ten days did not alter the sphere size. At present it is not clear if the sample processed from the melt or the sample cast from solution is closer to the thermodynamic equilibrium. To coarsen the morphology (or to reduce its size) triblock copolymer chains would need to diffuse through a highly incompatible environment (for example

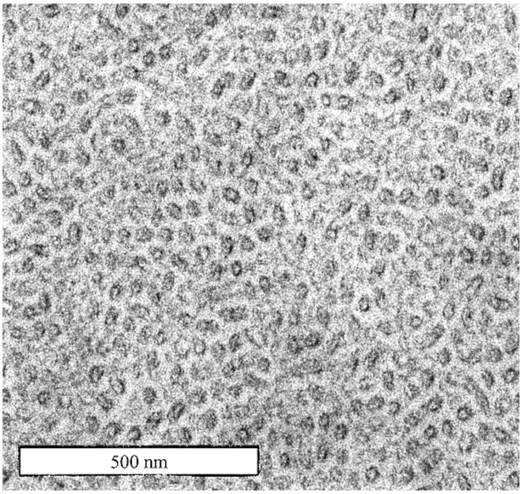

Figure 6: Transmission electron micrograph of melt processed $S_{78}B_{07}M_{15}^{88}$ *(extruded, stained with* OsO_4*))*

PB-blocks diffuse through PMMA-domains). This would require a high activation energy and in order to achieve such an equilibration of the morphology size, the system should be annealed much closer to the disordered state which has not been done in the present experiments.

Even if the size of the morphology of the samples is metastable, the morphology itself most likely is a stable one. This is further supported by the observation that hydrogenation of the PB-block did not lead to another morphology. Thus the system under investigation seems not to be close to a morphological transition region, since the change of the segmental interaction parameters (by hydrogenation) does not alter the morphology. In other SBM block copolymers morphological changes have been observed as a consequence of hydrogenation, such as the change from „sphere on lamella“ and „cylinder on lamella“ morphologies to a „ring on cylinder“ morphology for certain compositions /1,11/, or the change from the lamellar morphology to the „knitting pattern“ morphology /12/. Such transitions were only observed if the sample composition was close to a border line of the stability window of that particular morphology.

In the case of the cylindrical morphologies of ABC-triblock copolymers a series of different structures has been found. With increasing relative volume fraction of the center block with respect to the core component the B block took the following shapes: spheres, helices (curved cylinders), straight cylinders, and a closed shell around the core cylinder /2/. If one end block forms the matrix, only two types of spherical morphologies seem plausible: core shell spheres (*sis*) and the sphere on spheres (*sos*) shown in the present work.

To estimate the relative stabilities of these two morphologies and the composition range which determines the stability windows, the free energies need to be compared. The free energy of block copolymers in the strong segregation limit may be described in the most simple approach by the minimization of the elastic and interfacial contribution /1/. While an expression for the elastic energy can be easily derived for the *sis*, this is a rather nontrivial task for the *sos* morphology. In the following discussion only the different interfacial free energies will be considered to estimate the transition between these two spherical morphologies. The approximations used for the calculations are: the different domains are strongly segregated, i.e. the interfaces are sharp (i), and in the *sos* morphology the little spheres of the middle block share equal amounts of their surface with both the centre sphere and the matrix (ii).

This leads to the following ratio between the two surface energy contributions to the free energies:

$$\left(\frac{F_{sos}}{F_{sis}}\right)^{surf} = \frac{a_{sos}^2}{a_{sis}^2} \cdot \frac{\frac{N_{sph}}{2}\left(\frac{\phi_B}{N_{sph}}\right)^{2/3}\left(\gamma_{AB}+\gamma_{BC}\right)+\left(\left(\phi_A+\frac{\phi_B}{2}\right)^{2/3}-\frac{N_{sph}}{4}\left(\frac{\phi_B}{N_{sph}}\right)^{2/3}\right)\gamma_{AC}}{\phi_A^{2/3}\cdot\gamma_{AB}+\left(\phi_A+\phi_B\right)^{2/3}\cdot\gamma_{BC}}$$

The size of the unit cell is given by *a*, and γ_{xy} denotes the interfacial tension between two blocks *x* and *y*. As can be seen from this equation it is a ratio between different interfacial tensions rather than the absolute value of the individual interfacial tensions, which controles the relative stability of the two morphologies being compared. For the following discussion we define the ratio f_{AC}:

$$f_{AC} = \frac{\gamma_{AC}}{\gamma_{AB}+\gamma_{BC}}$$

and assume further $\gamma_{AB} = \gamma_{BC}$. This latter assumption is reasonable for SBM-triblock copolymers. In Figure 7 the ratio of the interface (surface) contributions to the free energy is plotted as a function of the ratio of the volume fraction of the center block B over the volume fraction of the centre sphere block A, ϕ_B/ϕ_A for different parameters f_{Ac} and N_{sph}. The unit cells are considered to be of the same size, i.e. $a_{sis} = a_{sos}$. Values for the surface free energy ratio above unity indicate the stability of the *sis* morphology, while the *sos* morphology becomes stable for values below unity. For a given value of f_{AC} an increasing number of middle block spheres on the centre sphere enlarges the stability region of the *sis* morphology towards small ratios ϕ_B/ϕ_A. The same behaviour is obtained upon increasing f_{Ac} for a constant value of N_{sph}. It turns out that these curves are independent of the volume fraction of the matrix, ϕ_C (in the calculations $\phi_C = 0.8$ was used, but any other value would have led to the same results). This is due to the neglection of the elastic energy contribution (i) and also due to the approximation of the same size of the unit cells of both morphologies (ii). Note that in principal for a given morphology an optimization of the number of block copolymer chains per elemental cell has to be carried out in the calculation, which is only possible if both competing effects (surface energy and elastic energy) are accounted for. If the elastic energy is taken into account, the transitions between the two morphologies should occur at lower ratios ϕ_B/ϕ_A. This calculation gives a qualitative picture. For SBM and SEBM-triblock copolymers f_{AC} is approximately 0.1. For the block copolymers considered in the present work we expect the formation of the „spheres on sphere“ morphology for the ratio $\phi_B/\phi_A \approx 0.5$ (ϕ_C representing the matrix component) even if the number of small spheres is 10 and the elastic contributions would be taken into account. Furthermore, it can be speculated that it will be very difficult to obtain the core shell spherical (*sis*) morphology in systems with a low value of f_{AC}, unless triblock copolymers with very large molecular weights are considered. On the other hand only core shell spherical morphologies should be observed in BSM triblock copolymers.

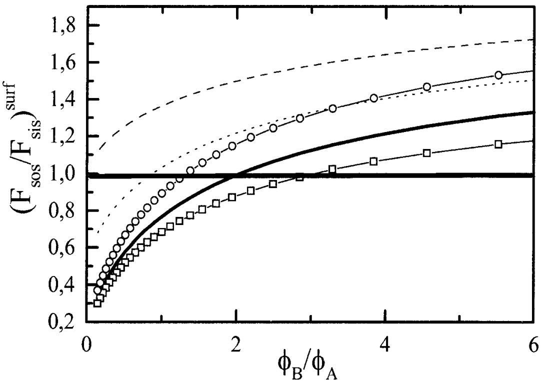

Figure 7: Calculation of the relative surface energis for the „spheres on sphere“ and the „sphere in sphere“ morphology $\phi c = 0.8$;

—— $f_{AC} = 0.1; N_{sph} = 6$

······ $f_{AC} = 0.5; N_{sph} = 6$

------ $f_{AC} = 1.0; N_{sph} = 6$

—□— $f_{AC} = 0.1; N_{sph} = 4$

—○— $f_{AC} = 0.1; N_{sph} = 10$

Acknowledgment

The authors are grateful to the group of EL Thomas (MIT, Boston) for the SAXS-measurement and giving access to their TEM facilities. Financial support from BMBF and BASF AG (project 03M40861) and the DFG (Graduiertenkolleg „Chemie und Physik supramolekularer Systeme“ and Sonderforschungsbereich 262 at the University of Mainz) is gratefully acknowledged.

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