Morphology of block copolymers in a selective environment

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The morphology of poly(styrene-*block*-butyl methacrylate) (SBMA) copolymer with 42 wt% S was studied by transmission electron microscopy in a selective environment. Micelles with S cores were observed in dilute solutions in 2-propanol, a non-solvent for S and a theta solvent for the BMA blocks. The solvent influence on the final morphology of SBMA films was investigated. Films obtained from solution in tetrahydrofuran had ordered cylindrical structures. When 10% poly(phenylene oxide) (PPO), which has a preferential interaction with the S blocks, was added to the copolymer, the cylinders turned into spheres with PPO cores separated by the swollen S blocks from a BMA matrix. In PPO/SBMA 50/50 blends multilayer vesicles and lamellar structures coexist. For blends with SBMA content lower than 5%, micelles with BMA cores were observed in a PPO matrix.

(Keywords: block copolymers; morphology; selective solvents)

INTRODUCTION

Block copolymers in a selective solvent form micelles even at a very low concentration[1,2]. This induces a very characteristic thermodynamic and rheological behaviour, which makes them suitable for many interesting applications, such as motor-oil viscosity control[3]. Recently[4] the rheological behaviour of poly(styrene-*block*-butyl methacrylate) (SBMA) copolymers in 2-propanol was investigated. Propanol is a theta solvent for BMA blocks[5,6] and a non-solvent for the S blocks. Micelles are formed[7] at concentrations even below 0.004 wt%. Above 4 wt% the micelles entangle and a change to non-Newtonian behaviour is verified. Owing to micelle formation, the rheological behaviour differs considerably from that of the PBMA homopolymer in the same solvent. One interesting point is that the viscosity increases with the temperature.

In this work the morphology of SBMA block copolymers in selective environments was investigated by transmission electron microscopy. Micelles were observed in 2-propanol at low concentrations. Similar structures have been reported in the literature for other block copolymers in selective solvents[1,2]. The morphological investigation of block copolymers in solution by electron microscopy has, however, been limited in the literature to very dilute solutions or to pure polymers[8–10]. It was shown that the morphology of block-copolymer films depends on the solvent used in the casting solution. Here further information on the morphology of block copolymers in a selective environment was obtained by electron microscopy in the whole range of concentration using a homopolymer as the 'solvent'. The selective 'solvent' for SBMA was poly(phenylene oxide) (PPO). It has a very favourable interaction with styrene blocks, while it is a bad solvent for BMA. Previous investigations reported in the literature on binary mixtures of a block copolymer and a homopolymer have been focused on A–B/A systems[9–16]. They are athermal systems. The situation should resemble that expected for an A–B block copolymer in a theta solvent for A and non-solvent for B. Few reports[13,17] describe the morphology of A–B block copolymers in a selective C homopolymer. The phase behaviour in this case may, however, be considerably different owing to the favourable A–C enthalpy of mixing.

MATERIALS

Poly(styrene-*block*-butyl methacrylate) (SBMA) was purchased from Polymer Standard Service, Mainz, Germany, fractionated[4] and characterized by gel permeation chromatography with $M_w = 280\,000\ \mathrm{g\,mol^{-1}}$ and $M_w/M_n = 1.15$. The styrene and methyl methacrylate contents are respectively 42 and 58 wt%. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was kindly supplied by Coplen-General Electric, Campinas, Brazil, and characterized by g.p.c. with $M_w = 48\,800\ \mathrm{g\,mol^{-1}}$ and $M_w/M_n = 2.67$.

EXPERIMENTAL

Micelles of SBMA copolymers in 2-propanol

SBMA micelles in 2-propanol were observed by two different methods.

Method I. Very dilute solutions (ca. 0.008 wt% copolymers) were dropped on a copper grid covered with a thin carbon and palladium film. The solvent was carefully evaporated. The samples were stained with RuO_4 vapour for 30 min, as described by Trent[18,19]. RuO_4 stains only the S blocks. The samples were observed in a Zeiss CEM-902 transmission electron microscope.

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Method II. A 1 wt% copolymer solution in 2-propanol (2-POH) was dropped on a copper grid covered with a thin formvar film with small holes prepared as described in the literature[20]. The sample was immediately frozen in liquid propane and kept in liquid nitrogen in the cryo system of the transmission electron microscope. The advantage of this method is that the micelles can be observed still in solution.

Influence of solvent on the morphology of copolymer films

SBMA films were prepared by two different methods.

Method III. First, 1 wt% SBMA solutions were prepared in tetrahydrofuran (THF) and in 2-propanol. THF is a good solvent for both S and BMA blocks, while 2-propanol is a theta solvent for BMA blocks and a non-solvent for S blocks. In both cases, the solutions were dropped on glass plates and the solvent evaporated at room temperature. Some samples were annealed at 120°C in vacuum for 5 days. The plates containing the SBMA films were immersed in a dilute solution of hydrofluoric acid (HF) and collected on 300 mesh copper grids.

Method IV. First, 2 wt% SBMA solutions in 2-POH and in THF were prepared and the solvent evaporated slowly for 5 days. The samples were then annealed at 120°C in vacuum for 5 days. After this period, thin cuts (ca. 80 nm thick) were obtained by means of a Reichert Jung F4 cryo ultramicrotome.

All samples were stained with RuO_4 for 30 min and observed in a Zeiss EM 902 transmission electron microscope.

Blends of SBMA and PPO

The 1 wt% PPO/SBMA solutions in chloroform were prepared with the following polymer proportions: 99/1, 95/5, 50/50 and 10/90. Chloroform is a good solvent for both S and MBA blocks. The solutions were dropped on glass plates, following the procedure described in method III.

The 50/50 and 10/90 PPO/SBMA solutions were also prepared in THF, using the procedure described in method IV.

The samples were stained with RuO_4 and observed by TEM.

RESULTS AND DISCUSSION

Micelles in 2-propanol

Dilute solutions of block copolymers will be considered first. *Figures 1* and *2* show that SBMA micelles are formed in 2-propanol. The micrograph in *Figure 1* was obtained by method II, while in *Figure 2* the sample was prepared by method I. It was confirmed by light scattering that the critical micellar concentration (c.m.c.) for this system is below 0.004 wt%. In *Figure 2*, dark styrene cores stained by RuO_4 with average radius ca. 25 nm are clearly differentiated from brighter BMA coronas also ca. 25 nm thick. The spherical structures in *Figure 1* are actually S cores. For non-stained copolymers in propanol, the electron-density differences are only suitable for the identification of S cores in an apparently homogeneous matrix of solvent and swollen BMA shells. The coronas cannot in this case be differentiated from the solvent. The micelles are monodisperse, which indicates that micellization occurs in only one stage. There is only a single equilibrium between free molecules and the micelles. Block-copolymer micelles have been well investigated by Price and coworkers[1,2,21]. In these macromolecular systems, a large negative enthalpy change on association gives micelle stability, in contrast to surfactant association in aqueous media. A very

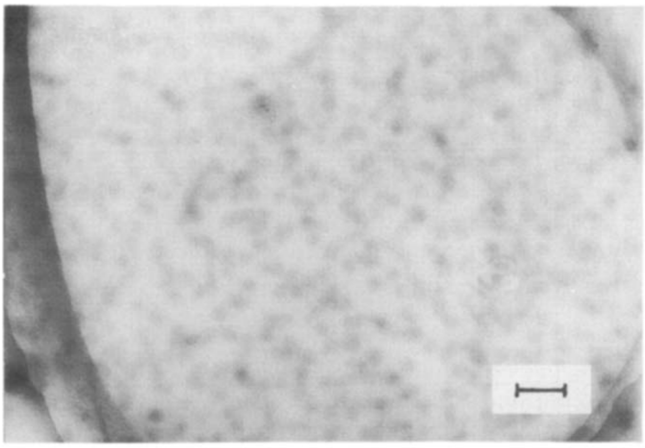

Figure 1 Micelles of a 1 wt% SBMA solution in 2-propanol, observed in the cryo system of a CEM 902 transmission microscope (method II). Non-stained samples. Scale bar 0.1 μm

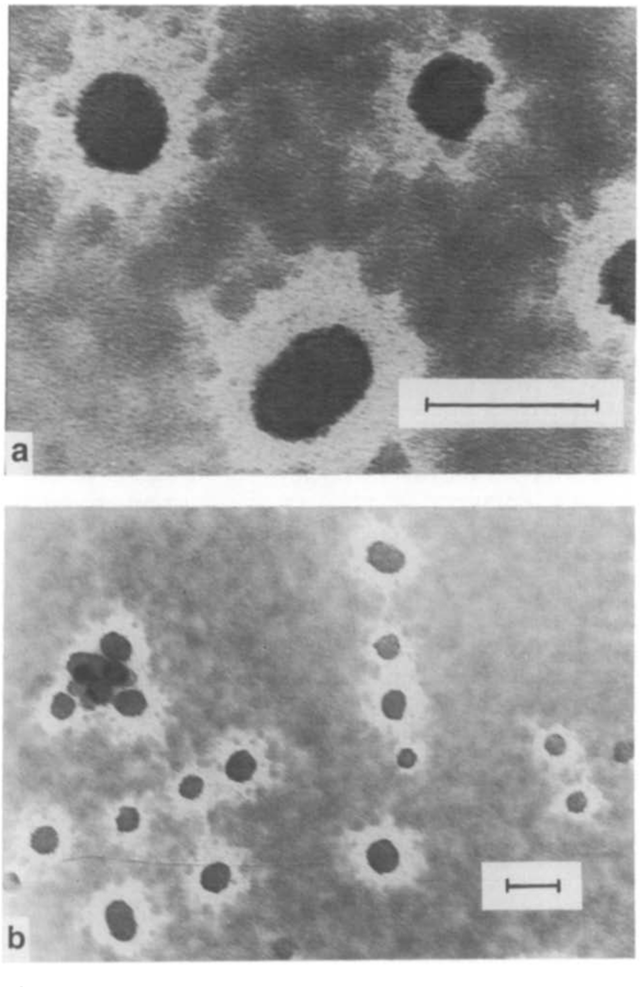

Figure 2 Micelles obtained from a 0.008 wt% SBMA solution in 2-propanol, by method I. The sample was stained by RuO_4. The dark cores correspond to styrene blocks. Scale bars 0.1 μm

unfavourable interaction between S segments and 2-propanol leads them to be protected from contact with each other by a BMA shell even at very low concentrations. The c.m.c. is approximately proportional to e^{-N_A} and $e^{-\gamma_{AS}}$, N_A being the polymerization index of the core blocks[22]. Spherical structures were detected by small-angle X-ray scattering in 2-propanol/SBMA solutions with concentrations at least up to 15 wt%[7]. A number of theoretical treatments have been proposed in order to account for the micellization of block copolymers in selective solvents[21–23].

Block-copolymer films: solvent influence

Taking into account the other extreme range of concentration, the microphase separation in films of pure block copolymers has been well reported in the literature[24–28], and the observed morphology is highly dependent on the block molecular weights. For copolymers with immiscible blocks of the same size, a lamellar structure is expected. As soon as the block sizes diverge, cylindrical structures predominate, as shown by Meier[29]. The microphase separation in block copolymers has been the object of continued theoretical work[29–33]. As shown in *Figure 3a* for films obtained from solutions in THF, cylinders with S blocks inside were observed for SBMA with 42 wt% styrene blocks. The average cylinder radius is 20–25 nm, which is the same size as the S core in the micelles of 2-propanol/SBMA. As detected by SAXS[7] for 8–15 wt% SBMA solutions in 2-propanol and confirmed by electron microscopy in dilute solutions, the core size does not change with concentration. Only the distance between cores decreases when the SBMA content is increased. A quite different structure can be observed in a block-copolymer film cast from solution in 2-propanol, even after five days annealing above the glass transition temperature of both blocks. Both *Figures 3a* and *3b* are thin cuts of thick samples (method IV). In dilute solutions micelles are expected only in 2-propanol, the selective solvent. The micelle cores contain almost no solvent, although in many cases its presence has been shown[21]. The glass transition temperature of the hard S domains is about 100°C and the mobility of the blocks inside these S cores does not allow a total change in morphology as the solvent evaporates. Furthermore the rather unfavourable interaction between S and BMA blocks does not stimulate chain rearrangement and change of morphology. In the case of samples prepared from THF solutions, since the solvent is a good one for both blocks, during a slow solvent evaporation the system can easily pass through an intermediate disordered state for which the repulsion between blocks is minimized by the presence of a common solvent and can achieve the final pure block-copolymer equilibrium state.

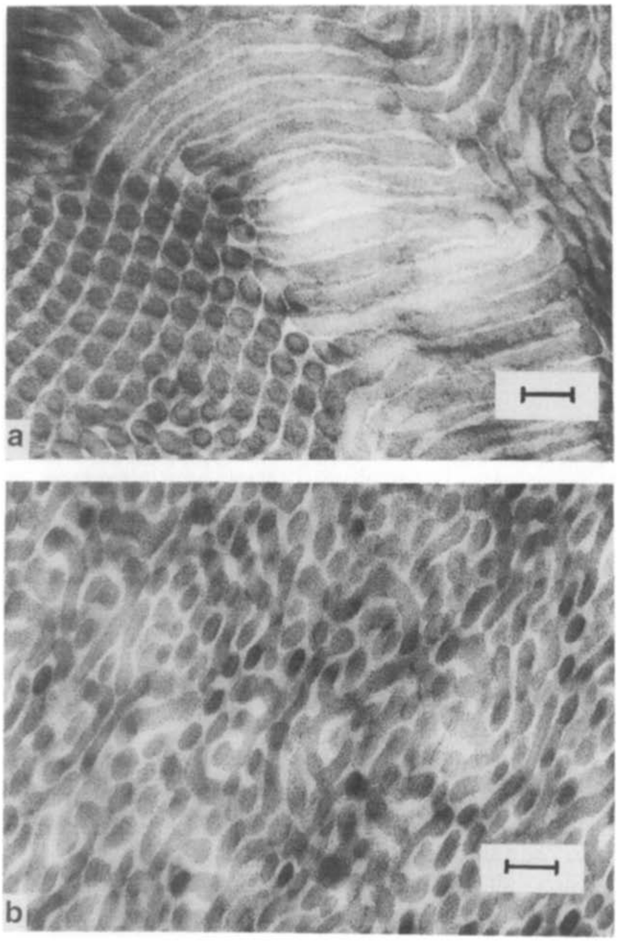

Figure 3 Thin cuts of annealed SBMA samples obtained by method IV from solutions in (a) THF and (b) 2-propanol, stained with RuO_4. Scale bars 0.1 μm

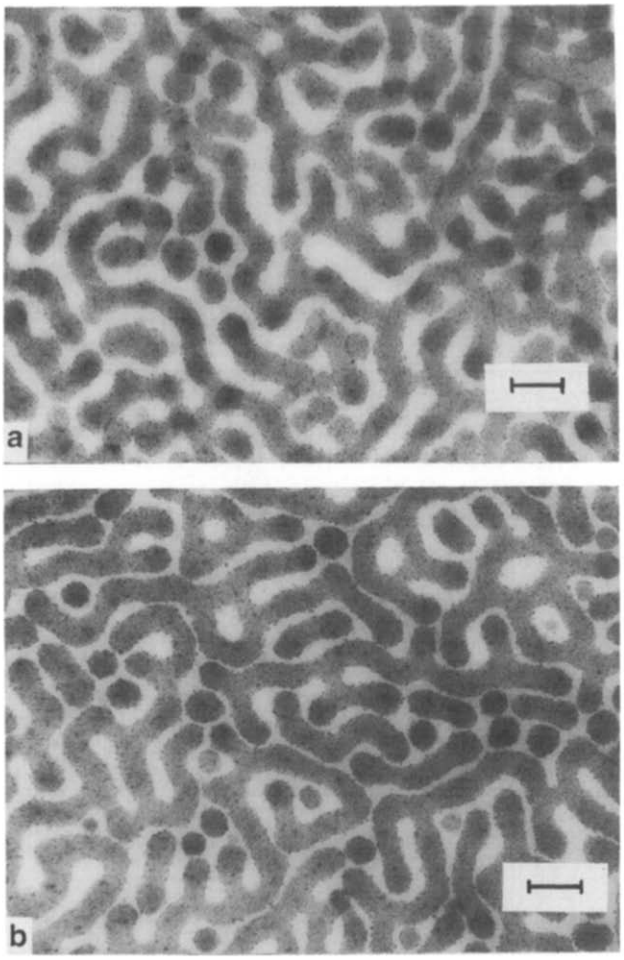

Figure 4 Thin films of SBMA cast from solutions in (a) THF and (b) 2-propanol, according to method III, annealed for 5 days at 120°C and stained with RuO_4. Scale bars 0.1 μm

When the morphology of thin films cast according to method III and annealed for 5 days at 120°C is analysed, both films, obtained from either THF (*Figure 4a*) or 2-propanol solutions (*Figure 4b*), have the same pattern.

The periodic distance between non-stained regions is ca. 40 nm and the film thickness is ca. 100 nm. Therefore the structures in these thin films are ordered in just one dimension. The ordered cylindrical structures of films cast from THF solutions (see *Figure 3a*) are only favoured in the bulk, where the structures are allowed to be ordered in three dimensions. Thin films cast by rapid solvent evaporation without annealing show a more disordered structure.

PPO/SBMA blends

The morphology of block copolymers in a selective environment was investigated in intermediate concentration ranges using PPO as the selective 'solvent'. It is well known that PPO and PS form a miscible blend[34]. If the SBMA content is low, micelles are observed as in 2-propanol solutions. Since the unfavourable interaction is now between the BMA blocks and the matrix, the micelle cores contain BMA blocks, which are not stained by RuO_4. The swollen S corona is the dark part of the micelles shown in *Figure 5* for PPO/SBMA with 5 wt% block copolymer. The core radius is around 20 nm, with a total micelle radius of ca. 40 nm. The interface BMA–PPO matrix is diffuse. RuO_4 also stains PPO, although with much lower intensity than S. The micelle sizes are the same order of magnitude as those observed for SBMA in 2-propanol.

Going to the other extreme of concentration range, cylinders of pure block copolymer are observed (*Figure 3a*). In blends with 10 wt% PPO, the cylindrical morphology of the block copolymer changes to spheres with PPO cores separated by styrene blocks from the BMA matrix (*Figure 6a*). The S–BMA interface is again better defined than the S–PPO. The S blocks are swollen by PPO, which is also stained but with lower intensity. When very small amounts of PPO were added to the SBMA sample, the homopolymer was dissolved inside the S-cylinder cores owing to the very favourable PS–PPO interaction. However when 10 wt% PPO was added to the copolymer sample, cylinders were not observed any more. The spherical structure optimizes the PPO–S block contact, allowing the favourable enthalpic interaction between them. The low homopolymer molecular weight also supports a successful interaction. BMA blocks are expelled from the S–PPO domains forming the matrix.

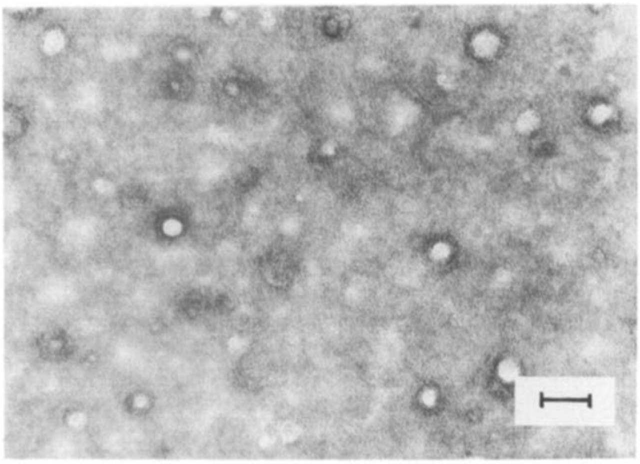

Figure 5 PPO/SBMA blend with 5 wt% SBMA obtained by method III and stained with RuO_4. Scale bar 0.1 μm

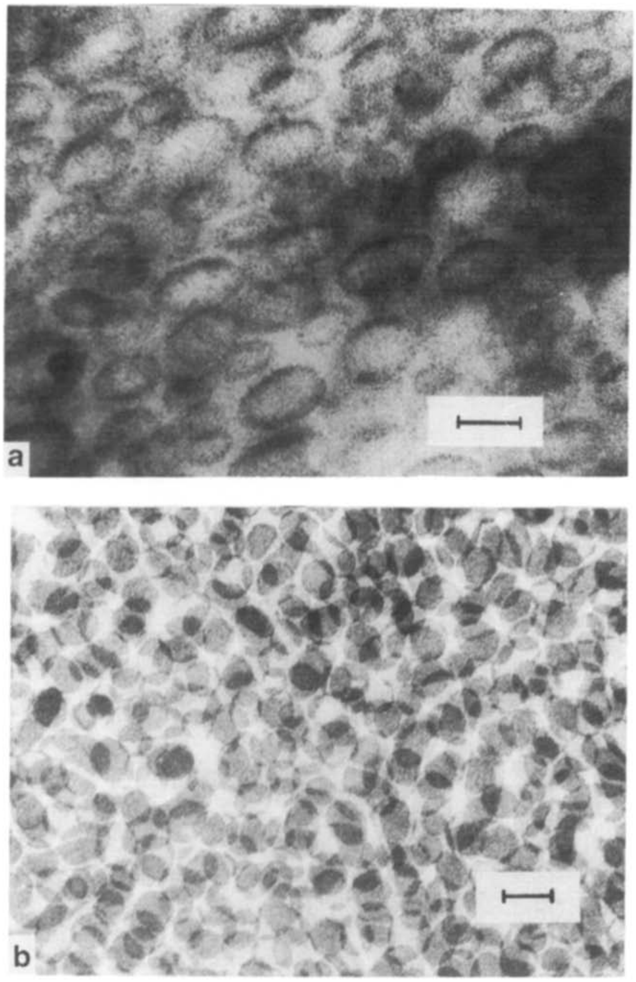

Figure 6 PPO/SBMA blends with 90 wt% SBMA obtained by (a) method IV (cut) and (b) method III (thin film), stained by RuO_4. Scale bars 0.1 μm

Thin films of PPO/SBMA 10/90 obtained by rapid solvent evaporation (*Figure 6b*) have spherical structures of ca. 30 nm radius, larger than that of pure block-copolymer films, but smaller than in thin cuts from a bulky sample. For thicker samples annealed for 5 days (*Figure 6a*), the spherical domains have radius up to 60 nm. The samples that are not annealed reflect more closely the influence of the casting solvent, a good one for both S and BMA blocks. The solvent minimizes the repulsion between blocks, and smaller microdomains are formed. After annealing, the radius of the spheres increases, decreasing the interfacial area between S and BMA microphases, whose interaction is not favoured in the absence of solvent. Inside the S–PPO cores there is probably a concentration gradient with pure PPO in the middle. As the PPO content increases, the (PPO+S block)/BMA block volume ratio becomes too high to allow the morphology shown in *Figure 6*, with a BMA matrix. If the PPO spherical domain is now surrounded by a block-copolymer bilayer, PPO may also occupy the space between the spherical domains.

A higher PPO content leads to a macroscopic phase separation as shown for the PPO/SBMA 50/50 system in *Figure 7*, a thin film cast by method III. Periodic structures of ca. 400 nm of alternate PPO- and SBMA-rich phases probably reflect a spinodal decomposition taking place during solvent evaporation. A higher

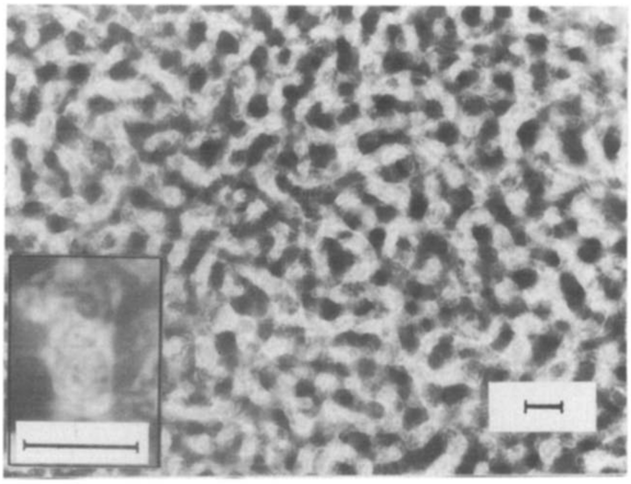

Figure 7 PPO/SBMA blends with 50 wt% SBMA obtained by method III and stained with RuO_4. Scale bars 0.1 μm

magnification (*Figure 7*) shows details of the morphology of the SBMA-rich phase. The ordered structure can be better observed in *Figure 8* in a sample prepared by method IV. Lamellar structures and multilayer vesicles coexist. The vesicles have a total diameter around 600 nm with 20 nm between layers. Vesicles have also been reported in the literature[16] with ca. 500 nm diameter and 20 nm interlayer distance for PS/poly(styrene-*block*-butadiene) blends with 4–18% PS. Wang[35] predicted the stability of curved surfaces upon flat layers for block copolymers in solution. According to their calculations, the curved geometry decreases the free energy of the outer block layer. In solution, such vesicles are considered metastable states in many cases. Wang[35] showed, however, that they may have lower energy than a flat bilayer. Although the energy of the inner monolayer increases in a curved geometry, if there are more molecules in the outer monolayer, a total decrease in

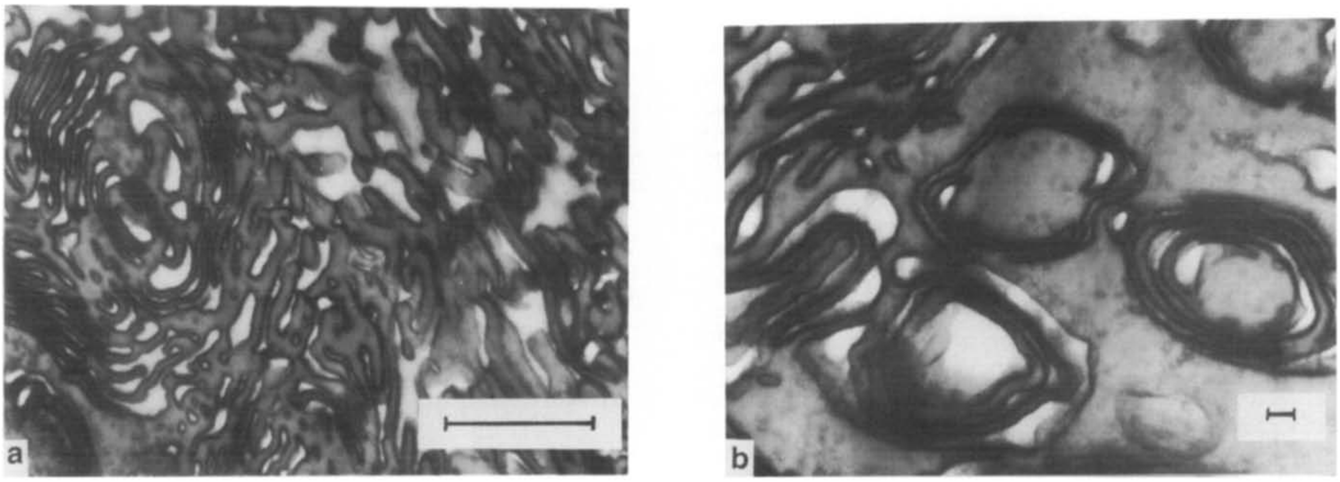

Figure 8 PPO/SBMA blends with 50 wt% SBMA obtained by method IV and stained with RuO_4. Scale bars 0.1 μm

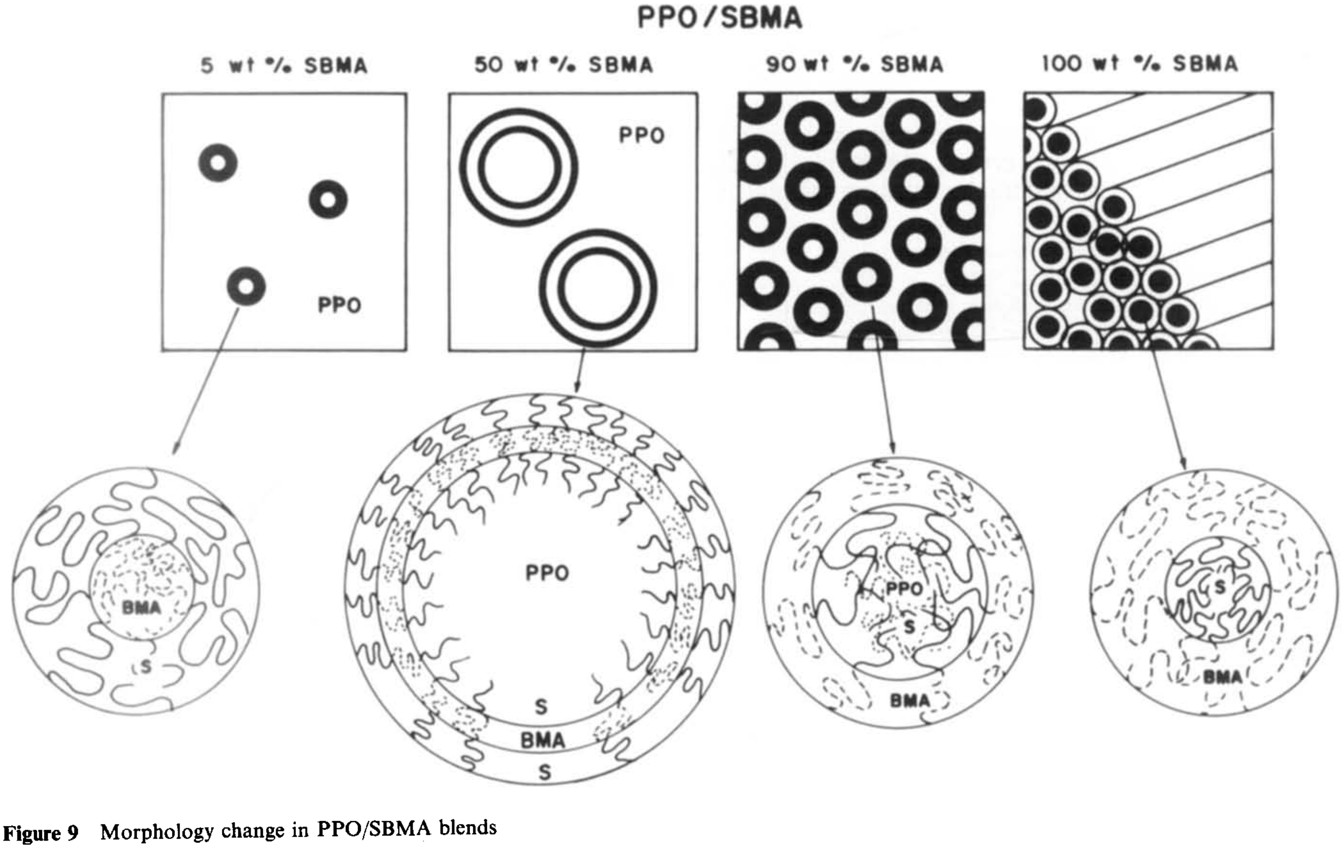

Figure 9 Morphology change in PPO/SBMA blends

free energy is expected. Other second-order curvature effects must also be considered, however. If the PPO content is increased further, the isolated micelles shown in *Figure 5* are again the predominant structure.

CONCLUSIONS

Dilute solutions of SBMA block copolymers with 42 wt% S form micelles in a selective environment. S cores are observed in solutions in 2-propanol and BMA cores are detected in a PPO/SBMA blend, in both cases with a core size of ca. 20–25 nm. Films of pure block copolymer have cylindrical structures also with 20–25 nm radius when cast from THF solutions and annealed, but the film morphology is highly dependent on the casting conditions. The cylinders turn into spheres with radius up to 30 nm if 10% of PPO is added to the copolymer. The PPO dissolves into the S-block domains with a very favourable interaction and the BMA blocks are expelled from the spheres forming the matrix. If the PPO content in the blend is increased, a macrophase separation takes place. For PPO/SBMA 50/50 blends, lamellar structures and multilayer vesicles coexist with segregated PPO-rich regions. Even higher PPO content leads again to SBMA micelles in a PPO matrix.

Vesicles and other self-assemblies may also occur in solution with low-molecular-weight solvents[35]. Although the morphology may be similar in many aspects, comparison between different selective environments should be carefully conducted. Concentrated SBMA solutions as well as homopolymer PBMA solutions in 2-propanol gels[6] and gelation may also interfere in the morphology. The morphology change for the PPO/SBMA system is represented in *Figure 9*.

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