Polymer Bulletin 39, 361–368 (1997)

Polymer Bulletin

Transition metal complex induced morphology change in an ABC-triblock copolymer

L. Bronstein[1], M. Seregina[1], P. Valetsky[1], U. Breiner[2,3], V. Abetz[2,4,*], R. Stadler[2,4]

[1] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 Vavilov St., 117813 Moscow, Russia
[2] Institut für Organische Chemie, Johannes-Gutenberg-Universität Mainz,
D-55099 Mainz, Germany
[3] *Present address:* BASF AG, D-67056 Ludwigshafen, Germany
[4] *Present address:* Makromolekulare Chemie II, Universität Bayreuth,
D-95440 Bayreuth, Germany

Received: 20 June 1997/Accepted: 11 July 1997

Summary

The short 1,2-polybutadiene center block of the ternary polystyrene-block-polybutadiene-block-poly(methyl methacrylate) $S_{45}B_6M_{49}{}^{225}$ -triblock copolymer (subscripts indicating the weight fractions and the superscript indicating the total molecular weight in kg/mol) has been selectively modified by complexation with metal complexes of two different transition metals, namely Pd and Fe. These modifications cause significant variations in the microphase morphology. The original *ls*-morphology (spheres at lamellar interphase) belonging to the lamellar class changes via a cocontinuous morphology in the case of the Pd-complex to a morphology belonging to the cylindrical class for the Fe-complex.

Introduction

There is a growing interest in homopolymers and block copolymers containing metal compounds [1-8]. Selective interaction of the transition metal compounds with functional groups of one block of a block copolymer is of especial interest. Cohen & Schrock and coworkers have elaborated the synthesis of Pt and Pd nanoclusters within microphase-separated diblock copolymers by ring-opening metathesis polymerization of organometallic complexes derived from norbornene and η^3-1-phenylallyl followed by casting of films and subsequent reduction of the organometallic complexes using molecular hydrogen [8]. Au and Ag nanoclusters were prepared by the same authors through chemical modification of a precursor diblock copolymer by gold and silver compounds [6]. In these cases the metal nanocluster formation did not change the morphologies in the microphase-separated blocks. Other authors studied the metal colloid formation in the cores of block copolymer micelles in selective solvents [9-15]. Depending on the system and conditions micellar morphologies remained unaltered [9-11] or changed [12-13]. The present paper deals with the complexation of transition metal complexes with the olefinic double bonds of a PS-b-PB-b-PMMA triblock copolymer based on polystyrene (PS), polybutadiene (PB) and poly(methyl methacrylate) (PMMA). As has been shown recently, this ternary ABC-triblock copolymer system shows a large variety of morphologies as a result of the balance of three binary interaction parameters. The various morphologies may be assigned to various morphological classes (lamellar, cylindrical...). It also has been shown that the polymer analogous hydrogenation of the PB-block may cause changes of the morphology and even of the morphology class. $S_{45}B_6M_{49}{}^{225}$ [16] is one example of such a block copolymer in which hydrogenation

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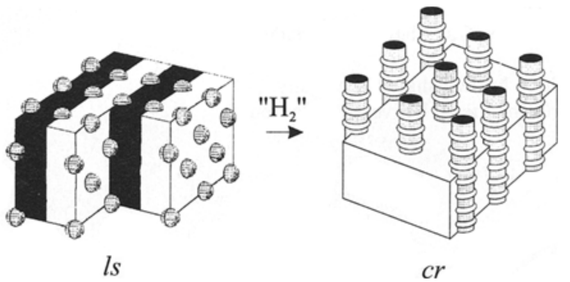
* Corresponding author

caused a morphological change from the *ls*- to the *cr*-structure [17] (Scheme 1). *ls* denotes a lamellar morphology of the outer blocks with spheres containing the center block at the lamellar interphase. *cr* denotes rings containing the center block surrounding cylinders containing one of the outer blocks. The other outer block forms the matrix in the *cr*-morphology. In this paper it will be shown that the modification with transition metal complexes also may lead to significant changes in the morphology.



Scheme 1: Morphological transition of the „spheres at lamella" (ls) morphology to the „rings around cylinder"-mophology (cr) upon hydrogenation (according to reference 17).

Experimental part

$S_{45}B_6M_{49}{}^{225}$ was synthesized by anionic polymerization [18,19], M_n= 225000, M_w/M_n = 1.11, weight fractions w_{PS}=0.45, w_{PB}=0.06, w_{PMMA}=0.49. The polybutadiene block contains mainly 1,2-units, since the polymerization was carried out in a polar solvent (tetrahydrofurane). The reactions of this triblock copolymer with iron dodecacarbonyl $Fe_3(CO)_{12}$ and bis(acetonitrile) palladium chloride $(CH_3CN)_2PdCl_2$ were studied. $Fe_3(CO)_{12}$ was synthesized from $Fe(CO)_5$ as described in [20]. Bis(acetonitrile)palladium chloride (BAPd) was synthesized according to ref. [21]. Neither polystyrene nor poly(methyl methacrylate) react with these transition metal complexes under these conditions. Reaction only occurs with the polybutadiene block. Polybutadiene-1,2 (PB-1,2) was prepared by anionic polymerization and contained 86% of 1,2-units, M_n=130000. Polybutadiene-1,4 (PB-1,4) was prepared at the Institute of Synthetic Rubber, Voronezh, Russia and contained 34.1% of 1,4-trans units, 56.8% of 1,4-cis units and 9.1% of 1,2 units; M_n= 150000.

For the reaction with $Fe_3(CO)_{12}$, 0.34 g of $S_{45}B_6M_{49}{}^{225}$ (which corresponds to $3.8 \cdot 10^{-4}$ mol of PB-repeating units) were charged into a flask equipped with argon inlet and reflux condenser. 31 ml of toluene and 4 ml of ethanol were added and the mixture was stirred under Argon atmosphere. After polymer dissolution 0.213 g (4.2×10^{-4} mol) of $Fe_3(CO)_{12}$ were added. The reaction mixture was heated to 80°C and stirred at this temperature for 1 hour under argon. After cooling and precipitation of the polymer in isopropanol containing 10 vol. % HCl (to remove excess of iron), the polymer was isolated, washed with isopropanol and dried *in vacuo*. The overall iron content was 2.27 wt % (elemental analysis). This corresponds to 80% of 1,2-PB-block double bonds taking part in complexation (2 double bonds per one Fe atom). PB-1,2•$Fe(CO)_3$ with iron content 3.3 wt.% and PB-1,4•$Fe(CO)_3$ containing 3.9 wt.% of iron were synthesized according to ref. [3].

Pd-containing $S_{45}B_6M_{49}{}^{225}$ ($S_{45}B_6M_{49}{}^{225}$•$PdCl_x$) was prepared by ligand exchange reaction of bis(acetonitrile) palladium chloride with the butadiene double bonds of $S_{45}B_6M_{49}{}^{225}$. Because the block copolymer is not soluble in common solvents of the Pd-complex, a solid film of $S_{45}B_6M_{49}{}^{225}$ was put into a solvent mixture consisting of 1.4 ml of methanol and 0.6 ml of acetone which contained 0.1 g of bis(acetonitrile) palladium chloride. This mixture does not dissolve the polymer, but permits bis(acetonitrile) palladium chloride to penetrate into the film. After one day of exposure of the film in this Pd complex solution the block copolymer turned brown which is evidence of palladium complex formation. After removing excess of the complex with the mixture of methanol and acetone, the modified film was dried *in vacuo*. The piece of the film was dissolved in chloroform and precipitated with isopropanol. The isolated polymer was dried *in vacuo* and examined by elemental analysis. Pd content was 0.4 wt.% which corresponds to a degree of complexation of 3.3 mol% of the double bonds.

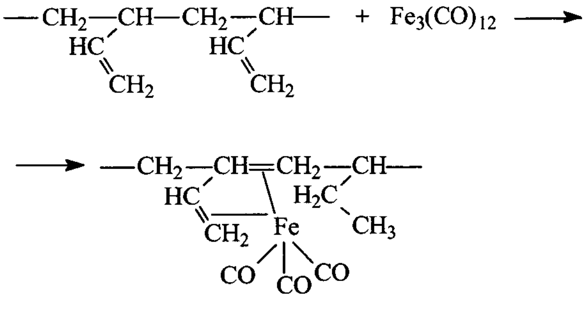
For transmission electron microscopy the samples were cast from $CHCl_3$ solution and dried slowly over several weeks, finally under vacuum at high temperatures (ca. 160°C). Transmission electron microscopy (TEM) was performed on ultra thin sections obtained by a Reichert ultramicrotome equipped with a diamond knife and stained with OsO_4 and RuO_4 to give sufficient contrast of the polybutadiene block or the polystyrene block, respectively. TEM was performed in the bright field mode on a JOEL 100 CX transmission electron microscope operating at 100 kV.

Results and discussion

Characterization of the samples

The FTIR spectrum of $S_{45}B_6M_{49}{}^{225}\bullet Fe(CO)_3$ contains two strong absorption bands at 1964 and 2032 cm^{-1} and a shoulder at 1956 cm^{-1} which are characteristic of the $Fe(CO)_3$ species [22]. In the ^1H NMR spectrum of $S_{45}B_6M_{49}{}^{225}\bullet Fe(CO)_3$ the signals at 4.94 and 5.32 ppm which can be assigned to the vinyl protons of the butadiene units almost disappeared. Because of π-complexation with iron carbonyl species, we should observe upperfield shifts of the double bond resonances, however, the complicated spectrum of SBM does not permit to detect the exact location of these resonances. In control experiments we have synthesized similar complexes using pure PB-1,2. The ^1H NMR spectrum of PB-1,2•$Fe(CO)_3$ sample exhibits a decay of the signals characteristic of double bond protons and the appearance of a new resonance signal with a chemical shift of 1.46 ppm which can be attributed to protons of double bonds participating in complex formation. Such a noticable shift of an NMR signal is an evidence of strong π-complexation.

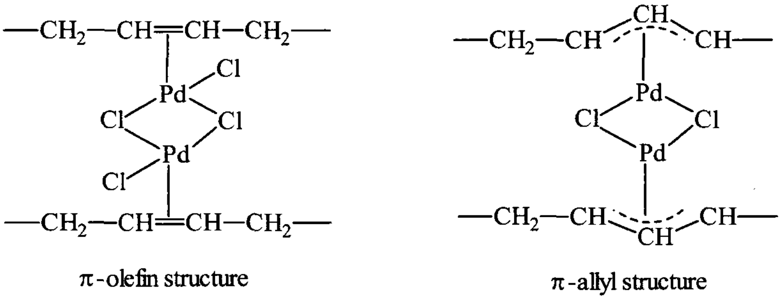
Scheme 2



In our previous work [3] on the interaction of $Fe_3(CO)_{12}$ with a polystyrene-polybutadiene-polystyrene block copolymer containing mainly 1,4-units in PB block we have shown that such a complexation results in the formation of π-complexes of $Fe(CO)_3$ species with conjugated double bonds which form due to double bond migration [23]. However, double bonds located in side groups of PB-1,2 might behave differently. To clarify this question we have compared FTIR and NMR spectra of Fe-containing polymers derived from PB-1,2 and PB-1,4. Because FTIR- and NMR spectra of these polymers seemed to be qualitatively the same, we can conclude that for PB-1,2 complexation with iron carbonyls is also accompanied by double bond migration. Thus, a formation of iron tricarbonyl complexes with conjugated diene fragments occurs as shown in Scheme 2.

As follows from previous work [4], the interaction of double bonds with $(CH_3CN)_2PdCl_2$ results in the formation of both π-olefin and π-allyl μ-halogenide complexes which form both intramolecular and intermolecular bonds (Scheme 3). Because the Pd-containing polymer derived from a similar SBM-triblock copolymer, but containing a longer polybutadiene block (25% of PB) becomes insoluble after precipitation and drying (a result which also was obtained earlier for Pd-containing polystyrene-polybutadiene-polystyrene triblock copolymers like Kraton [4]), intermolecular complex formation definitely takes place. However, in the case of SBM with low content of PB (3 and 6 wt. %), the Pd-containing polymers remain soluble. Due to the intermolecular complexation the short PB blocks may form something similar to micelle cores as they were observed for solutions of PS-b-PB-Pd diblock copolymer with 15.5 wt.% of PB block [24].

Scheme 3



The FTIR spectrum of the $S_{45}B_6M_{49}^{225}$-$PdCl_x$ shows a significant weakening of the bands at 994 and 910 cm^{-1} and also at 1638 cm^{-1} . This is due to a complex formation with vinyl groups. The band at 1638 cm^{-1} (C=C) as a result of complexation should be shifted to longer wavelengths. However, this was not observed because of the presence of other bands in the 1500-1400 cm^{-1} region. Another reason could be a decrease of the absorption coefficient of this vibration due to a change in the dipole moment of the complex.

Transmission Electron Microscopy

The TEM micrograph of $S_{45}B_6M_{49}^{225}$ (Figure 1) stained with OsO_4 shows the *ls* - morphology: Small polybutadiene spheres (dark due to OsO_4-staining) are located at the lamellar interphase of polystyrene (gray) and poly(methyl methacrylate) (white). The TEM micrograph of the iron-complex modified sample $S_{45}B_6M_{49}^{225}$•$Fe(CO)_3$ (stained with OsO_4) is shown in Figure 2. Obviously the polystyrene block no longer forms lamellae, but takes a cylindrical structure which is covered by small spherical objects which can be recognized as the modified polybutadiene block due to the staining with OsO_4. This morphology is very similar to the *cr*-morphology of the corresponding hydrogenated block copolymer $S_{45}EB_6M_{49}^{225}$ [17], where rings of the center block surround the cylinders formed by the polystyrene block.

In the case of the $S_{45}B_6M_{49}^{225}$•$PdCl_x$ a completely different, highly ordered morphology is obtained, as is shown in Figure 3a and 3b. The morphology seems to be cocontinuous with respect to both PS and PMMA with PB-microdomains again located at the common interphase. The TEM-image obtained from this material by sytining with RuO_4 (Figure 3b) is identical to those reported from cocontinuous cubic structures in simple asymmetric AB diblock copolymers [25]. Based on the two dimensional projections available so far we assign a gyroid structure to this morphology.

Fig. 1: $S_{45}B_6M_{49}^{225}$ (stained with OsO_4)

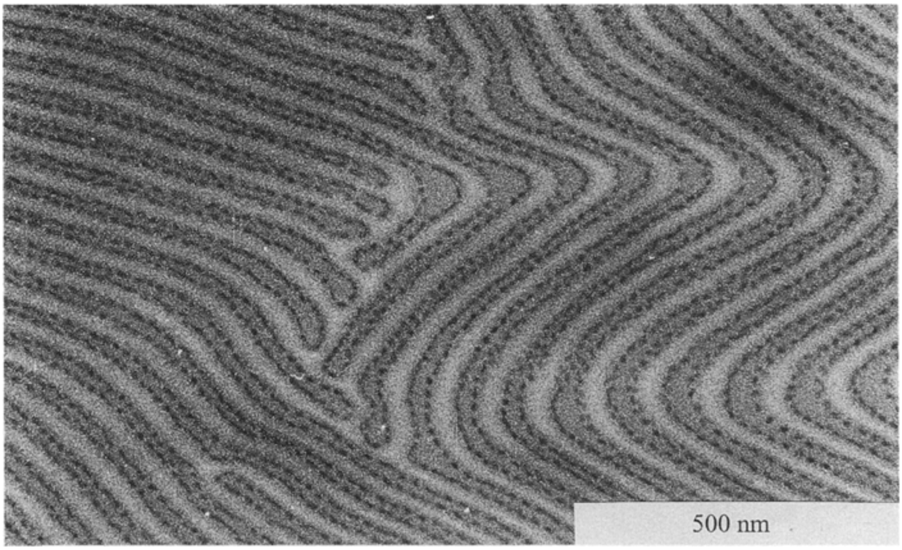


Fig. 2: $S_{45}B_6M_{49}^{225}$ •$Fe(CO)_3$ (stained with OsO_4)

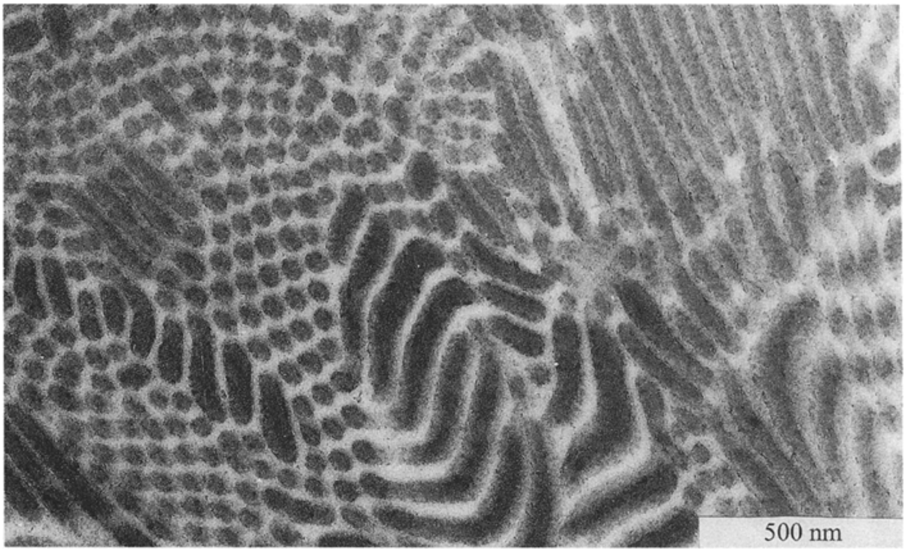


Fig. 3a: $S_{45}B_6M_{49}^{225}$ *•*$PdCl_x$ *(stained with* OsO_4*)*

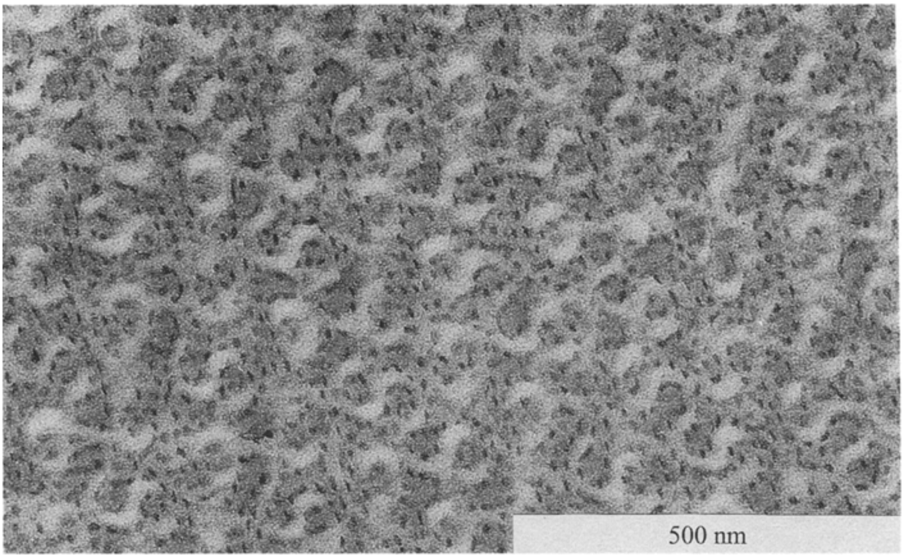
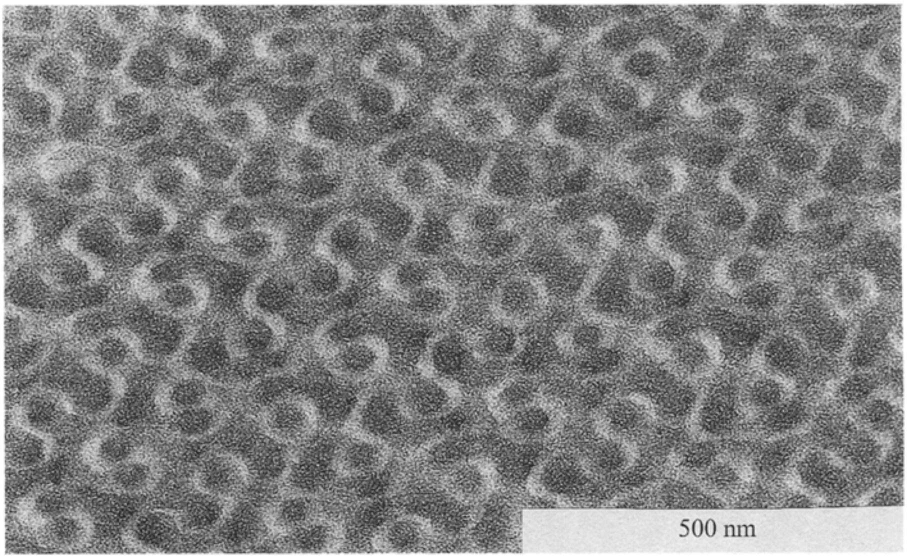
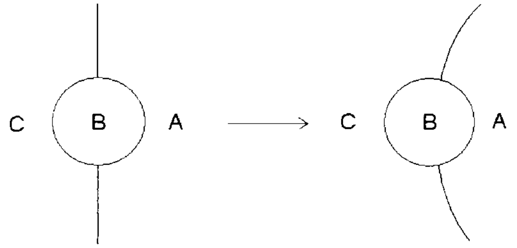


Fig. 3b: $S_{45}B_6M_{49}^{225}$ *•*$PdCl_x$ *(stained with* RuO_4*)*



Thus we focus a situation where a lamellar, a cylindrical and a cubic morphology result from relatively minor chemical modifications of a single ternary triblock copolymer. In the following we want to give some qualitative arguments which might explain the observation of these morphologies respectively the morphological transitions.

In the case of $S_{45}B_6M_{49}^{225}$ PB-spheres are located almost symmetrically at the lamellar interface between PS and PMMA. If the thermodynamic properties of the PB-sphere are changed, a stronger asymmetry in the interactions towards PS on one side and PMMA on the other side may result. This would lead to a displacement of the PB-sphere out of its centered position and thus cause a curvature of the interface between PS and PMMA (Scheme 4). The stronger this asymmetry, the larger will be the curvature of the interface between the outer blocks. As is known from diblock copolymers the curvature increases from lamellae via a cocontinuous cubic to a cylindrical morphology [for further arguments using curvature to analyze the stability limits of binary block copolymers see: EL Thomas et al [26] and FS Bates et al [27].].



Scheme 4: Change of curvature of the interface between the A- and C-domains by displacement of the B-domain at the AC-interface

Such a morphological sequence is also predicted for diblock copolymers within the weak segregation limit upon lowering the repulsive interactions between the blocks [28-30]. Further lowering of the repulsive interactions in a diblock copolymer would finally lead to the homogeneous phase. This indicates that a short strongly interacting center block between two immisible end blocks may force the two long blocks to behave like a diblock copolymer close to the order-disorder transition. This possibility to enhance the compatibility of the end blocks of an ABC-triblock copolymer by a strongly interacting center block has been shown also by theory [31, 32].

At present we can only speculate why $S_{45}B_6M_{49}{}^{225}\bullet PdCl_x$ and $S_{45}B_6M_{49}{}^{225}\bullet Fe(CO)_3$ display different morphologies. Two main contributions may be important. First the complexation may change the interaction parameter. In addition complexation might alter the segment length of the PB-units. This latter effect has been found to greatly influence the stability region of different morphologies for both diblock and triblock copolymers [33,34]. In the present experiments only a very small part of the vinyl double bonds has been complexed with Pd, while most of the double bonds are reacted with the Fe complex. Thus the Pd-complexation only will correspond to a small perturbation of the system in comparison to the neat block copolymer. This would be in agreement with the transition from the lamellar to the gyroid morphology. Only a weak perturbation is necessary because the interaction parameters $\chi_{S/B}$ and $\chi_{B/M}$ are not identical. Thus already in the SBM block copolymer the B-spheres may not be located strictly symmetrical at the interface. The strong complexation with $Fe(CO)_3$ would correspond to a complete hydrogenation. Future work will have to address the question at which degree of chemical manipulation of the double bond the morphological changes may happen.

Acknowledgment

The authors are grateful to E. L. Thomas (MIT, Boston) for giving access to the electron microscopy facilities during the visit of U.B. at MIT. V.A. and R.S. would like to express their thanks to I. Ya. Erukhimovich (MSU, Moscow) for very fruitful discussions. Financial support was provided by INTAS (grant No. 93-2694) and BMBF grant 03M40861 (jointly funded with BASF AG). L.B. and M.S. are also grateful to the financial support of the Russian Science Foundation (grant No. 96-03-32335).

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