A Compositional Study of the Morphology of 18-Armed Poly(styrene–isoprene) Star Block Copolymers

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ABSTRACT: The morphology of a series of 18-arm poly(styrene–isoprene) star diblock copolymers was examined as a function of composition. Samples with varying composition increments, over the range of approximately 10–90 wt % of polystyrene outer blocks, were examined by transmission electron microscopy. The ordered bicontinuous double diamond (OBDD) structure was observed at compositions of 30 and 35 wt % polystyrene (27 and 32 vol %). In addition the OBDD structure was also observed at 76 wt % (73 vol %) polystyrene when the minority component polyisoprene was the outer segment of the diblock arm. All other samples exhibited the previous common morphologies (spheres, cylinders, or lamellae) of linear block copolymers.

Introduction

Although considerable research has been reported on the morphology, mechanical properties, compatability, and general behavior of linear styrene–diene diblock and triblock copolymers, relatively little work has been done on the corresponding star-shaped materials.[1] For AB and ABA block copolymers, the commonly accepted morphologies are spheres, cylinders, or lamellae of the minority component in a matrix of the majority component. Recently a new equilibrium morphology for star diblock copolymers has been described.[1-3] For those materials having 30 wt % (~27 vol %) polystyrene outer blocks of 10^4 molecular weight and six or more diblock arms, the equilibrium structure consists of two translationally displaced mutually interwoven but unconnected three-dimensional networks of polystyrene rods embedded in the polydiene matrix. The basic unit of this structure is a tetrahedral arrangement of short polystyrene rods arranged such that each of the two separate polystyrene networks exhibits the symmetry of a diamond cubic lattice. This structure also occurs for linear diblocks in a narrow composition range between the cylindrical and lamellar morphologies.[4] The present work concerns establishing the composition range of this ordered bicontinuous double diamond (OBDD) structure for a series of star block copolymers of constant arm number (i.e. 18).

Experimental Section

The procedures used for the preparation and characterization of the star-block copolymers are available elsewhere.[1,5-7] Suffice it to note that all toluene cast films were annealed at ca. 120 °C for 1 week (under vacuum) in order to approach equilibrium conditions. Thin (400 to 10^3 Å) sections were prepared via cryoultramicrotomy (−110 °C). The films were then exposed for 3 h to osmium tetraoxide vapor. A JEOL 100 CX TEMSCAN electron microscope was utilized in the bright field mode to observe the samples. The composition analysis was carried out by ^{1}H NMR.

Table I displays the samples analyzed in this study. Each sample is designated by a two letter code and three numbers. SI indicates polystyrene outer blocks in the diblock arm, and IS refers to polyisoprene outer blocks. The first number refers to the number of diblock arms in the star molecule, the second refers to the weight percent of polystyrene in the diblock arm, and the last number refers to the number average molecular weight (kg mol^{-1}) of the polystyrene component. Within experimental error star functionality was 18 in all cases.

Table I
Characteristics of 18-Arm Star Block Copolymers

sample	$10^{-4}M_n$, g/mol: polystyrene[a]	$10^{-4}M_n$, g/mol: diblock arm[b]	ϕ_{PS}	morphology
SI-18:10:10	1.0	10.0	0.09	PS spheres
SI-18:19:10	1.0	5.3	0.17	PS cylinders
SI-18:23:12	1.2	5.0	0.20	PS cylinders
SI-18:30:10[c]	1.0	3.3	0.27	PS double diamond[c]
SI-18:35:10	1.0	2.8	0.32	PS double diamond
SI-18:40:10	1.0	2.5	0.36	lamellae
SI-18:43:10	1.0	2.3	0.39	lamellae
SI-18:56:10	2.6	4.6	0.52	lamellae
SI-18:66:30	3.0	4.3	0.63	PI cylinders
SI-18:81:30	3.0	3.7	0.79	PI cylinders
SI-18:92:30	3.0	3.3	0.91	PI spheres
IS-4:76:47[d]	4.7	6.2	0.73	PI cylinders
IS-18:76:47[d]	4.7	6.2	0.73	PI double diamond[d]
IS-18:30:10[d]	1.0	3.3	0.27	PS cylinders

[a] Via size exclusion chromatography. M_w/M_n of 1.06 or less. [b] Based on composition and polystyrene segment molecular weight. [c] Data from ref 1. [d] The outer segments of the star arms are polyisoprene.

Results and Discussion

The observed morphologies for the various star diblock copolymers are summarized in Table I. Figure 1 is a comparative collage with all micrographs at the same magnification. The dark areas represent the polyisoprene phase that has been selectively stained by osmium tetraoxide. Sample compositions were chosen to represent a wide range of styrene content (approximately 10–90 wt %) with smaller intervals around the 30 wt % sample, which was known to exhibit the OBDD structure in order to more closely define the cylinder-OBDD-lamellar transitions. Some samples showed many small areas of highly developed order interspersed between areas of poor order.

The SI-18:10:10 sample exhibits spherical domains that do not show much long-range order. The polystyrene spheres have average diameters of about 130 Å. The lack of long range order may be related to the particularly high molecular weight of the arms of this sample (1.0×10^5) which kinetically hinders the attainment of equilibrium conditions as a consequence of the high melt viscosity.

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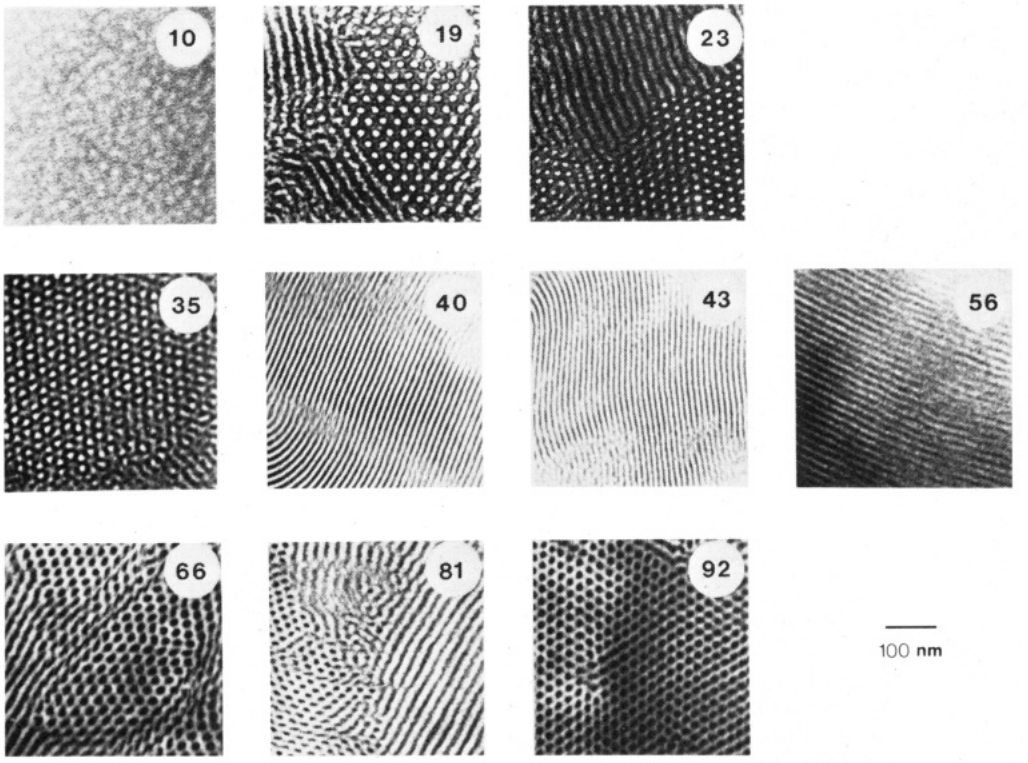

Figure 1. Bright field electron micrographs of 18-arm poly(styrene–isoprene) star diblock copolymers labeled by volume percent polystyrene of the outer block.

The SI-18:19:10 sample shows two types of well-ordered areas that appear as hexagonally close-packed circles and parallel stripes. These in fact are axial and longitudinal cross sectional views of hexagonally packed cylinders of polystyrene. In order to distinguish this structure from that of spheres or lamellae, both projections must be present. The gray, low contrast areas are projections that are not normal to or along the cylinder axis. The SI-18:23:12 sample also formed a cylindrical microstructure. In both cases, the PS cylinder diameter is approximately 100 Å.

The SI-18:30:10 sample was previously studied and found to exhibit the OBDD structure.[1-3] The double-diamond morphology shows several highly ordered projections. At least six were previously seen and confirmed through computer simulation of the OBDD structural model.[3] The SI-18:35:10 sample also clearly showed a highly ordered OBDD structure. This sample exhibits all of the projection previously seen for this morphology including the "wagon wheel" corresponding to the [111] projection (shown in Figure 2) and the "square" corresponding to the [100] projection. Previous findings[8] for a 9-armed star block copolymer demonstrate that the OBDD structure is not present when the polystyrene content is 27 wt % (24 vol %). Since the SI-18:40:10 sample is lamellar, the composition range over which the OBDD morphology is observed is ca. 28–35 wt % (25–32 vol %) of the minority outer arm component, polystyrene.[9]

Further increases in the polystyrene content induce a transition from the OBDD structure to alternating lamellae of polystyrene and polyisoprene for the SI-18:40:10, SI-18:43:10, and SI-18:56:26 samples. All images of these samples showed either lamellar structures or areas of gray indicative of a section viewed normal to the interdomain boundaries. The apparent variation in lamellar thickness is due to the angle at which the sample is viewed relative to the normal to the lamellae.

The inverse cylindrical morphology occurs in the SI-18:66:30 sample. Note that the contrast is reversed from

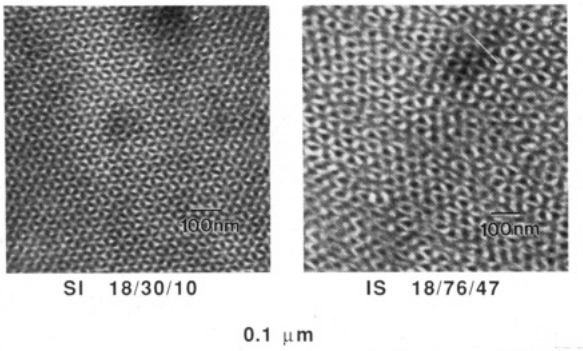

Figure 2. Bright field electron micrographs of star diblock copolymers viewed along the [111] direction of the double diamond structure; (a) sample SI-18:30:10 containing 27 vol % polystyrene outer block and (b) sample IS-18:76:47 containing 27 vol % polyisoprene outer block. Note the reversal of image contrast and the increase in lattice size for the higher molecular weight sample b.

that of the SI-18:23:10 sample indicating that a phase inversion has occurred with the isoprene now the discrete phase. Increasing the styrene content another 15% does not change the observed morphology as the SI-18:81:30 sample again shows the cylindrical morphology. The average cylinder diameter for SI-18:81:30 is 70 Å, compared to 90 Å for SI-18:66:30. This is consistent with the larger polyisoprene block molecular weight for SI-18:66:30. The SI-18:92:30 sample exhibits spheres of isoprene in a matrix of styrene. This sample shows good long-range order and regular packing of the spheres. The sphere diameter is approximately 90 Å, which is unexpectedly large for the rather low molecular weight of the polyisoprene inner block.

The three IS samples were purposefully made to check on the influence of the specific chemical nature of the inner/outer blocks of the star copolymer on the microdomain structure. The IS-18:76:47 sample matches the SI-18:30:10 sample but with the roles of polystyrene and

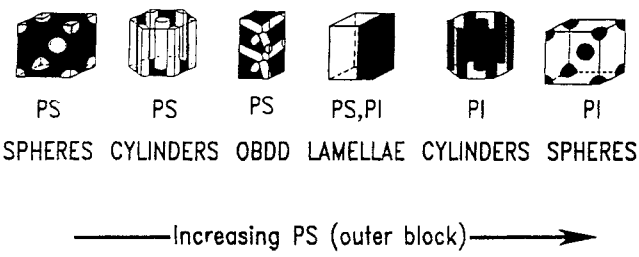

Figure 3. Schematic of the compositional dependence of microdomain structure of poly(styrene–isoprene) star diblock copolymers.

polyisoprene reversed; i.e., for the SI-18:30:10 sample, polystyrene is the outer arm component at 27 vol % while for the IS-18:76:47 sample, polyisoprene is now the outer arm component, also at 27 vol %. The observed morphology of the IS-18:76:47 sample is indeed OBDD. Figure 2 shows [111] views of both samples. Note that since now the polyisoprene phase comprises the two diamond networks in sample IS-18:76:47, the image contrast is reversed from that of SI-18:30:10 where the polystyrene phase forms the double-diamond network. The IS-18:30:10 sample with polystyrene as the inner block at 27 vol % exhibits PS cylinders. The IS-4:76:47 sample has the same composition as the IS-18:76:47 sample but a smaller number of arms. As previously observed,[1,2] for SI stars at constant composition there is a structural transition for IS stars from the hexagonally packed cylinders to the OBDD structure with increasing arm number. These data suggest that the OBDD structure is unobtainable unless the minority component is the outer segment of the star diblock arm.

As is the case for diblock copolymers, the morphological transitions can be reasoned in terms of the relative block lengths and the curvature of the interface. When the two blocks are nearly equal in molecular volume, the chain segments on either side of the interface have similar space requirements. This leads to a planar domain boundary (lamellae). As the molecular volume of the two blocks becomes more different, the interfacial surface begins to curve in order to satisfy the different space requirements of the two components. The longer block appears on the convex side of the interface while the shorter block forms the minority component phase (cylinders or spheres) on the concave side. One would anticipate that since there is an inherent molecular species asymmetry in the SI series star diblock copolymers studied here (i.e., the majority component is the inner block for $\phi_{PS} < 0.5$ whereas the majority component is the outer block when $\phi_{PS} > 0.5$), the morphological structure–composition diagram would be asymmetric. For the limited range of samples we have synthesized and examined there is a considerably enlarged cylindrical regime from 0.63 to 0.79 vol fraction outer arm polystyrene. Another indication of asymmetry is evident on comparison of the SI-18:40:10, $\phi_{PS} = 0.36$, and SI-18:66:30, $\phi_{PS} = 0.63$, pair. These samples have nearly equal compositional displacement from 0.50 yet the SI-18:40:10 sample exhibits a lamellar morphology while the SI-18:66:30 sample is cylindrical. The wings of the diagram do, however, appear symmetric: SI-18:23:12, $\phi_{PS} = 0.20$, and SI-18:81:30, $\phi_{PS} = 0.79$, are both cylindrical and sample SI-18:10:10, $\phi_{PS} = 0.09$, and SI-18:92:30, $\phi_{PS} = 0.91$, are both spherical.

The effect of the star diblock copolymer architecture is thus to increase the effective volume fraction of the outer block (polystyrene) resulting in an asymmetry in the mid range of the morphology–composition diagram (see Figure 3). These data also suggest that the OBDD structure may be unobtainable unless the minority component is the outer segment of the star diblock arm.

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Registry No. (S)(I) (block copolymer), 105729-79-1.

References and Notes

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(9) The current findings indicate that the OBDD morphology is found over a composition range in star diblock copolymers which normally exhibits for linear block copolymers the conventional cylindrical arrangement. To date, no appreciable inroad into the lamellar composition region has been observed.