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Notes

Effect of Chain Topology on Ordered Structure in Block Copolymers: Comparison of a Heteroarm A_2B_2 Star with Its Linear Diblock Analog

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The importance of block copolymer morphologies and the advantages known for homopolymers with star topologies have led several groups to study star block copolymers. Of particular interest have been the effects of arm number, arm molecular weight, and arm chemical composition on bulk morphology.[1] Most of the experimental work has been done on the morphology of star block copolymer molecules of the $(AB)_n$ type, in which the arms are identical.[2,3] Much less work has been done on the effect of molecular architecture with heteroarm (also known as “miktoarm”) stars of the A_nB_n type, in part due to the difficulty of synthesizing well-defined heteroarm stars.[4−8] Olvera de la Cruz and Sanchez[9] considered the effect of star topology theoretically using a mean field approach in the weak segregation limit. Their theory predicts that for off symmetric compositions the block domain spacing should decrease with increasing arm number. The change is predicted to be very small in going from the AB to A_2B_2 polymer, and no change at all with arm number is found for symmetric compositions. Milner[10] further described the changes in mesophase behavior expected for heteroarm stars in the strong segregation limit, accounting for the fact that the A and B blocks may differ in conformational statistics. However, the value of the conformational asymmetry parameter,[10] ϵ, for the copolymers in the present work is very close to unity (1.02).

Ishizu and Kuwahara[11] measured the domain spacings of two ordered heteroarm stars made by coupling vinylbenzyl-terminated polystyrene and polyisoprene macromonomers. They reported that the star materials' domain spacings were smaller than those reported in the literature for what they considered were linear analogues. Very recently, Gido and co-workers[12] have systematically studied morphologies in heteroarm star and model graft copolymer materials. Specifically, they have considered three silane-coupled heteroarm stars with styrene and isoprene arms of approximately an S_8I_8 structure ($\epsilon = 1.16$) that formed lamellar domains. The domain spacings of the stars are much larger than values interpolated from the literature for diblock analogues. The stars also occupy larger areas per molecule at the interface than do linear diblock analogues described in the literature. This is true even if the area is normalized by the chain's cross sectional area (R_g^2) and a correction ($N^{0.67}$) made to account for the higher stretching expected at larger molecular weights. They note that a study of a series of A_nB_n materials would be beneficial to fully characterize this behavior. The work discussed in this Note focuses specifically on a comparison within an A_nB_n series, that between a well-defined A_2B_2 star copolymer and an AB diblock copolymer of styrene and butadiene in which arm molecular weight is held constant, as depicted in Figure 1.

The heteroarm four-arm star block copolymer, S_2B_2, with styrene and butadiene arms, was prepared by *sec*-butyllithium (*sec*-BuLi) initiated anionic polymerization in cyclohexane using 1,3-bis(1-phenylethenyl)benzene as the linking agent for poly(styryl)lithium, followed by crossover to butadiene.[6,13,14] Number average molecular weight was determined by size exclusion chromatography (SEC) with a multiple angle laser light scattering (MALLS) detector using polystyrene standards, and after polymerization the polymeric material was fractionated to remove excess arm homopolymer. In addition, ^{1}H NMR spectroscopy indicated that the butadiene arms had a high content (90%) of 1,4- microstructure. The linear diblock copolymer, SB, was synthesized using sequential monomer addition with *sec*-BuLi as the initiator.[15] SEC with MALLS indicated a small amount (ca. 5%) of polystyrene homopolymer was present in the diblock. The compositions and the molecular weights for both polymers are summarized in Table 1.

Sample films were cast from the nonpreferential solvent toluene, allowing the solvent to slowly evaporate at room temperature over a period of 1 month in order to favor the formation of a well-ordered microstructure. The samples were then placed under roughing vacuum for 1 week at room temperature to further remove solvent. After the films were sealed in glass ampules evacuated under high vacuum, they were annealed at 120 °C for 24 h. After the ampules were removed from the oven, they were quenched in dry ice to freeze in the morphology characteristic of the melt state.

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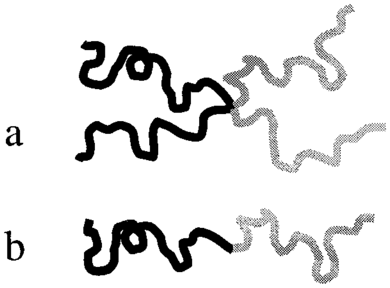

Figure 1. Schematic representations of (a) the heteroarm star copolymer A_2B_2 and (b) the diblock copolymer AB.

Table 1. Molecular Parameters and Areas Per Molecule for S_2B_2 and SB Copolymers

sample	M_n[a] (g/mol)	M_w/M_n[a]	φ_{PS}[b]	L[c] (Å)	A/R_g^2	$AN^{0.67}/R_g^2$
SB diblock	22 000	1.01	0.43	203	0.153	7.1
S_2B_2 star	47 000	1.04	0.42	228	0.216	16.6

[a] Determined by SEC−MALLS in THF at 35 °C. [b] Styrene volume fraction calculated from styrene weight fraction determined by ^{1}H NMR spectra. [c] L, the domain spacing, is given by $2\pi/q^*$, where q^* is the value of q at the first peak in the scattering curve.

The morphologies for the four-arm star and the diblock were characterized using small-angle X-ray scattering (SAXS) at Oak Ridge National Laboratory (ORNL). Measurements were performed on a 10-m spectrometer operating at 40 kV and 120 mA with Cu Kα radiation (λ = 1.54 Å). The beam was monochromatized using a graphite crystal and collimated by two slits separated by a distance of 1.6 m. In addition, there was a slit located 3 cm from the sample that served to reduce the parasitic background from the collimating slits. The slit farthest from the sample was 1.0 mm in diameter, while the other was 0.75 mm. After exiting the second slit, the beam had to travel a distance of 1.5 m to reach the sample. Data were collected with sample to detector distances of both 2.119 and 5.119 m. The data were corrected for both absorption and instrument background scattering.

Sections for transmission electron microscopy (TEM) were cut at −120 °C with a dry knife in a cryoattachment of a Reichert Ultracut S ultramicrotome. Sections were stained with OsO_4, which selectively reacted with unsaturated bonds in the butadiene and caused the butadiene-rich phases to appear dark on the TEM photographs. A JEOL JEM-1200EXII electron microscope operated at an accelerating voltage of 120 kV was used in the bright field mode to obtain images.

SAXS results for both the S_2B_2 star and the SB diblock measured with the 5 m sample-to-detector spacing are presented as plots of relative intensity versus scattering vector, q ($q = 4\pi \sin \theta/\lambda$) in Figure 2. Both samples display the scattering expected for a nearly symmetric lamellar structure[1] with relative peak position ratios of 1:2:3 and the second-order peak being considerably weaker than the third-order peak. (The third-order peak for the diblock is observed in the 2 m data not shown here.) For the star, the first peak is located at a value, q^*, of 0.0275 Å^{-1}, corresponding to a lamellar spacing ($L = 2\pi/q^*$) of 228 Å. Calibration of the angular position with a silver behenate standard indicates a maximum uncertainty in this spacing due to instrumental error of 1% or about 2 Å. That the lamellar spacing for the diblock material is smaller is clear from the plot, with the spacing being 203 Å. TEM observations are in accord with the SAXS results.

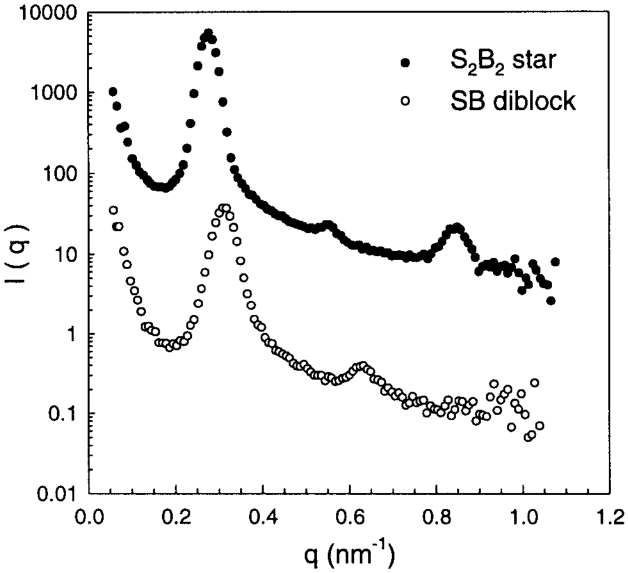

Figure 2. Small-angle X-ray scattering relative intensities for the star (●) and diblock (○). The curve for the star has been offset by 2 orders of magnitude for clarity.

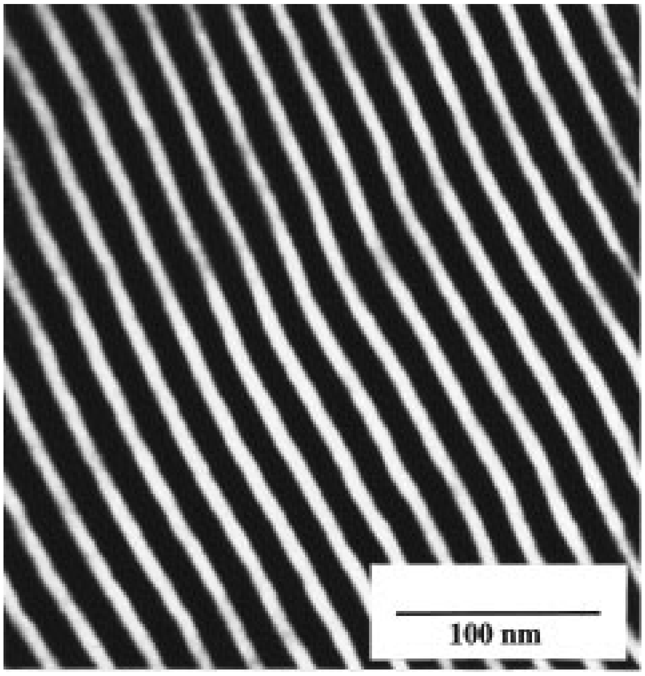

Figure 3. TEM image of the microstructure of the S_2B_2 star copolymer.

Reasonably well-ordered lamellar microstructures are observed for both materials, as shown in the images of Figure 3 and Figure 4. Domain spacings determined from TEM are approximately 220 Å for the star polymer and 190 Å for the diblock. These values are slightly smaller than those from SAXS due to observed compression of samples during the sectioning process.

Since the diblock copolymer is not a precise analogue with respect to its molecular weight, the diblock result must be slightly corrected before comparison with the result for the star. If one assumes that the SB material is strongly segregated, the spacing would be expected to scale with $N^{0.67}$, yielding a corrected diblock spacing of 212 Å. Assuming a scaling of $N^{0.8}$ for an intermediate strength of segregation as observed by some researchers[16,17] yields 214 Å. Thus, assuming either correction,

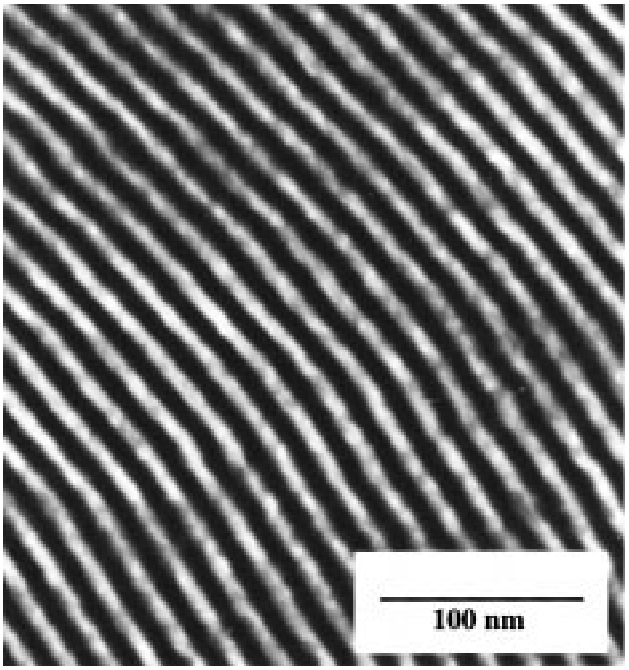

Figure 4. TEM image of the microstructure of the SB diblock copolymer.

the star is still clearly stretched with respect to the linear analogue. It should be further noted that since the diblock material contains a small amount of homopolymer, in fact the true spacing for the diblock analogue is somewhat smaller than that seen experimentally.

The variation in area per junction with junction functionality was compared with relevant results in the literature (particularly the calculations of Gido and coworkers[12]) by considering a dimensionless area per molecule, A/R_g^2, and a dimensionless area per molecule normalized for molecular weight, $AN^{0.67}/R_g^2$. Using statistical segment lengths of PS (6.7 Å) and PB (6.9 Å) from the literature[18,19] and the domain spacings from the SAXS measurements, one obtains the results summarized in Table 1. (The microstructure of the PB in ref 19 is 53% trans, 36% cis, and 11% vinyl and is thus similar to, but not identical to, the microstructure of the PB used here.) The value of A/R_g^2 for our diblock (0.153) is considerably less than the value of 0.211 found for a PI−PS diblock copolymer of very similar molecular weight (21k), but slightly higher PS composition (0.50), studied by Hashimoto et al.[20] The value of $AN^{0.67}/R_g^2$ for our diblock is likewise smaller than that for the PS−PI diblock. To calculate these two parameters for the star polymer, a value[21] of 0.625 for g, the branching factor, was used, following the calculation of Zimm and Stockmayer[22] for homopolymer four arm stars. The values of A/R_g^2 and $AN^{0.67}/R_g^2$ for the S_2B_2 star are somewhat larger than the corresponding values for the topologically asymmetric four arm star (S_1I_3) of PS and PI of much higher molecular weight (102k) and higher PS composition (0.55).[12] Differences in A/R_g^2 could be attributed to differences in molecular weight (as observed by Gido and co-workers[12] within series of polymers with the same architecture), while differences in $AN^{0.67}/R_g^2$ most probably come from architectural differences between the topologically symmetric and topologically asymmetric stars and perhaps from differences in composition. The trend in change of chain length corrected area per molecule with functionality seen here for the symmetric heteroarm S_2B_2 star of nearly symmetric composition is in good agreement with that suggested by Figure 4 in ref 12, which plots the variation in $AN^{0.67}/R_g^2$ with functionality. Regression of the values from diblock data from Hashimoto et al.,[20] our two samples, and the three S_8I_8 stars[12] (compositions φ_{PS} from 0.37 to 0.47) yields $AN^{0.67}/R_g^2 = 3.5f^{1.18}$. Overall the trend in area per molecule seen for the symmetric S_2B_2 star in this work is the same as that observed by Gido and co-workers[12] for their S_8I_8 stars but slightly different from that seen for the heteroarm A_mB_n stars of nearly symmetric composition. Further systematic study will be needed to more precisely compare the behavior of the A_nB_n and A_mB_n stars and to determine whether the variations in composition among samples considered here play a role in the apparent deviations in behavior between A_nB_n and A_mB_n stars.

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