PHYSICAL REVIEW B VOLUME 47, NUMBER 21 1 JUNE 1993-I

Microdomain contraction in microphase-separated multiblock copolymers

S. D. Smith*
Corporate Research Division, The Procter & Gamble Company, Cincinnati, Ohio 45239

R. J. Spontak*
Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695

M. M. Satkowski and A. Ashraf
Corporate Research Division, The Procter & Gamble Company, Cincinnati, Ohio 45239

J. S. Lin
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

(Received 21 December 1992)

Linear multiblock copolymers, like their diblock analogs, undergo microphase separation and order into periodic morphologies when the blocks are sufficiently incompatible. To explore the conformations of such materials, four symmetric poly(styrene-*b*-isoprene)$_n$ copolymers with $2n$ ($1 \leq n \leq 4$) perfectly alternating blocks of nearly equal mass have been synthesized. Small-angle x-ray scattering reveals that the microdomain periodicity decreases with n along the lamellar normal, thereby confirming theoretical predictions and providing direct evidence for bridging among the $2(n-1)$ middle blocks.

When the chemically dissimilar contiguous sequences (blocks) of an AB diblock copolymer are sufficiently incompatible, the copolymer undergoes microphase separation and self-organizes into periodic microdomains which measure on the order of the gyration radius (R_g) of the domain-forming block. For a symmetric (50/50 vol %) copolymer, the transition from a disordered state to one possessing long-range order occurs[1] when $\chi N = (\chi N)_c \approx 10.5$ (χ is the Flory-Huggins interaction parameter and N is the number of monomers along the copolymer backbone) in the absence of critical fluctuations.[2] When $\chi N \gg (\chi N)_c$, a strongly segregated symmetric copolymer orders into a lamellar morphology of alternating A and B blocks.

Experimental studies of lamellar copolymers in the melt state have shown[3-5] that the microdomain periodicity (D) scales as M^v, where M denotes the total molecular weight and $v \approx 2/3$. Since $v > 1/2$, the copolymer molecules adopt a stretched conformation along the lamellar normal, to minimize the number of repulsive A-B interactions. Theoretical formalisms[6-9] designed to elucidate the thermodynamic properties of strongly segregated diblock copolymers in the melt state predict the same scaling relationship when χN is safely removed from $(\chi N)_c$.[10]

The principles governing microphase separation of diblock copolymers also apply to copolymers possessing more complex molecular architectures, such as the ABA and ABC triblock and starblock designs.[11] If the chemical composition (i.e., volume fraction) of each monomer species present is approximately equal, the lamellar morphology is prone to develop, even in ternary[12] and quaternary[13] copolymers. All of these architectures, including the AB diblock, share a common characteristic: each monomer species is responsible for comprising either the terminal block(s) or the middle block(s), but not both. A terminal block is covalently bonded at only one end (the junction), whereas a middle block is more highly constrained since it is anchored at both ends. Depending on the molecular architecture, a middle block may either loop back upon itself (both junctions reside within the same interphase region) or extend across a microdomain core (each junction resides within a different interphase). In this work, we refer to these two cases as the *looping* and *bridging* conformations, respectively.

Past efforts designed to ascertain the conformational behavior of middle blocks in microphase-separated block copolymers have concentrated on ABA copolymers. These materials, however, possess a single middle block, which renders systematic studies difficult, if at all possible. In linear $(AB)_n$ multiblock copolymers, where n is the number of AB block pairs, each monomer species comprises a terminal block *and* $n-1$ middle blocks. An increase in n therefore yields a corresponding increase in (i) the fraction of middle blocks, $(n-1)/n$, and (ii) the number of possible molecular conformations, $2^{2(n-1)}$. This paper addresses the microstructural and conformational properties of a series of symmetric $(AB)_n$ copolymers in which $1 \leq n \leq 4$.

Four poly(styrene-*b*-isoprene)$_n$ copolymers with blocks of nearly equal mass (M_0) were synthesized via living anionic polymerization in cyclohexane at 60 °C. Details regarding the polymerization of these[14] and related[15] perfectly alternating multiblock copolymers have been provided earlier. In previous efforts[16] $(AB)_n$ copolymers of constant block mass were referred to as variable length copolymers, since M_0 remains constant while M increases as $2nM_0$. The molecular characteristics of these materi-

0163-1829/93/47(21)/14555(4)/$06.00

als (i.e., composition and molecular weight/molecular weight distribution) were analyzed at 25 °C with proton nuclear magnetic resonance (^{1}H NMR) and gel permeation chromatography (GPC) and are tabulated in Table I. Each of these materials is relatively monodisperse, with $\overline{M}_w/\overline{M}_n < 1.09$. Note from Table I that the tetrablock ($n=2$) and hexablock ($n=3$) copolymers possess nominally longer blocks (by $\approx 20\%$) than those of the corresponding diblock ($n=1$) and octablock ($n=4$) copolymers.

Films measuring ~3 mm thick were prepared from 5% toluene solutions according to the protocol described elsewhere[17] for neat copolymers and copolymer/homopolymer blends. The films were dried slowly over the course of three weeks and were subjected to extensive annealing to generate morphologies believed to be representative of near equilibrium. To determine the microdomain periodicity of each copolymer, small-angle x-ray scattering (SAXS) was conducted on the 10 m instrument at the National Center for Small-Angle Research at Oak Ridge National Laboratory. Copolymer films were cut into thin (~2–3 mm) strips, mounted side by side, and subjected to edge-on radiation (with the main beam passing normal to the cut surface). SAXS patterns were recorded for 1–4 h at 40 kV and 100 mA using a two-dimensional detector. Due to the collimation characteristics of the instrument and the large sample to detector distance (5.18 m), smearing effects were virtually eliminated. Scattering patterns were corrected for background scattering, absorption, detector sensitivity, and dark current.

Resulting SAXS profiles obtained from each of the four copolymers are presented in Fig. 1. (The curves corresponding to $n<4$ have been shifted along the ordinate for clarity.) The scattering intensity is provided in arbitrary units as a function of the magnitude of the scattering vector h, which is defined as

$$h \equiv (4\pi/\lambda)\sin\theta \;, \tag{1}$$

where λ is the wavelength of the incident beam (0.154 nm for CuK_α radiation) and 2θ is the scattering angle. The profile from the diblock copolymer, shown at the top of Fig. 1, exhibits two orders of scattering reflections over the range of h shown, indicating that the material possesses long-range correlation and is, by inference, microphase separated. Based on earlier calculations,[17] χN evaluated at the glass transition temperature (T_g) of 15 kDa homopolystyrene is safely removed from $(\chi N)_c$ even when critical fluctuations[2] are considered. Profiles from the tetrablock ($n=2$) and hexablock ($n=3$) copolymers display an intermediate peak in the vicinity of 0.45 nm^{-1}, which suggests that these two copolymers are not quite symmetric. Transmission electron microscopy reveals that each of the four copolymers studied here possesses the lamellar morphology, and that both D and the grain size of oriented lamellae (G) decrease with n. When $n=4$, $G \sim O(D)$.

TABLE I. Average molecular and microstructural characteristics.

n	M_0 (kDa)	M (kDa)	D (nm)	D_c (nm)
1	15	30	27.5	27.5
2	18	72	27.0	24.6
3	18	108	26.0	23.7
4	15	120	19.6	19.6

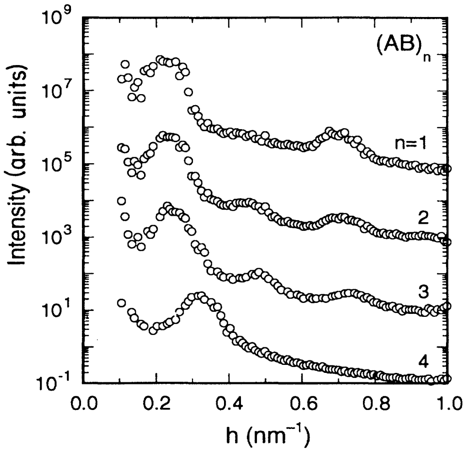

FIG. 1. SAXS profiles of four perfectly alternating $(AB)_n$ multiblock copolymers possessing blocks of nearly equal mass and (from top to bottom) $n=1,2,3$, and 4. The profiles for $n<4$ have been shifted vertically to facilitate discrimination of the scattering peaks.

While the intensity of the higher-order scattering maximum decreases with n, the position of the principal scattering reflection (denoted here by h^*) is observed to increase with n (see Fig. 1). Since $h^*=2\pi/D$ by Bragg's law, this trend indicates that D decreases with n. Average values of D, measured to within ±1 nm, are provided in Table I. To ascertain the systematic effect of n on D in this series of $(AB)_n$ copolymers, the periodicity is corrected with respect to the block gyration radii to account for the minor difference in block lengths among the four copolymers. Rescaling each $R_g(n)$ with respect to that of the diblock copolymer ($n=1$) and recalling that $R_g \sim M_0^{1/2}$, this corrected periodicity (D_c) is given by

$$D_c(n) = D(n)[M_0(1)/M_0(n)]^{1/2} \;. \tag{2}$$

Values of D_c obtained from Eq. (2) are also tabulated for comparison with D in Table I. Normalization with respect to the mean periodicity of the diblock copolymer more clearly demonstrates the extent to which D decreases with n. These reduced periodicities (D_r), defined by $D_c(n)/D_c(1)$, are provided as a function of n for each of the copolymers in Fig. 2.

The noticeable decrease in D_r with n seen in Fig. 2 ($\approx 30\%$ when $n=4$) indicates that the microdomain cores contract as n increases. This feature is attributed to the bridging conformation adopted by a significant fraction of the $2(n-1)$ middle blocks, a fraction which increases with n. A double-anchored middle block which bridges a microdomain core along the lamellar normal must stretch further than a terminal block that is anchored at only one end or a middle block that loops back

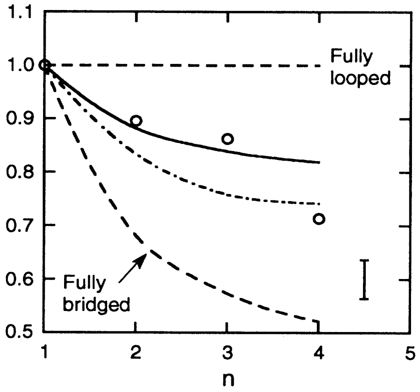

FIG. 2. Reduced periodicity D_r as a function of n for linear $(AB)_n$ copolymers. Data obtained here with SAXS (○) compare well with theoretical predictions from Refs. 19 and 20 (solid line). Predictions corresponding to the two limiting molecular conformations (dashed lines) and the most probable conformation (dotted-dashed line) addressed in Ref. 23 are also shown for comparison. The vertical bar reflects the experimental uncertainty associated with the D values derived from Fig. 1 (±1 nm).

upon itself, and is faced with a considerable entropic penalty. Bridged middle blocks can lessen such a penalty by contracting the microdomain cores in which they reside. The extent of contraction depends principally on the population of bridged middle blocks relative to the population of looped middle blocks and terminal blocks. If the microdomains contract, then so will the periodicity D. To gain more insight into this behavior, we turn our attention to theoretical treatments which address linear $(AB)_n$ multiblock copolymers and compare, on a quantitative basis, predictions with the SAXS results obtained here.

Krause[18] first developed a thermodynamic treatment to explain the phase behavior of linear multiblock copolymers and predicted that the driving force for microphase separation in such materials decreased with n. The first theoretical formalism to address not only the phase behavior but also the microstructural characteristics of a variety of molecular architectures was proposed by Benoit and Hadziioannou.[19] They extended the mean-field theory of Liebler[1] for microphase-separated diblock copolymers to symmetric $(AB)_n$ copolymers. Within the context of their theory, they predict that both $(\chi N)_c$ and h^* initially increase with n, but reach a limiting value as $n\rightarrow\infty$. In this limit, for a 50/50 copolymer, the scattering intensity per monomer (i_0) is given by

$$i_0=\frac{1}{2\mu}-\frac{2(1-e^{-\mu/2})^2}{\mu^2(1-e^{-\mu})}\ , \tag{3}$$

where $\mu=[hR_g^{(AB)}]^2$ and $R_g^{(AB)}$ is the gyration radius of the AB block pair, equal to $\sqrt{2}R_g$ for the copolymers studied here. Equation (3) reveals that i_0 reaches a maximum at $h=h^*$ when $\mu=6.43$.

A more recent approach taken by Kavassalis and Whitmore[20] extends the functional integral formalism developed by Hong and Noolandi[21] to address both $(AB)_n$ and $(AB)_nA$ copolymers. When $n\rightarrow\infty$, their treatment yields an explicit value for $h^{*2}\langle r^2\rangle$ of 19.3, where $\langle r^2\rangle=6R_g^2$. Upon simple substitution, $h^{*2}\langle r^2\rangle$ can be shown to equal $3[h^*R_g^{(AB)}]^2$, in which case $h^{*2}\langle r^2\rangle=19.3$ corresponds to $\mu=6.43$, in excellent agreement with the Benoit and Hadziioannou[19] formalism in the many-block limit. When $n=1$, each theory also predicts that $h^*R_g^{(AB)}=1.96$. According to these predictions, D_r is bounded between 1.0 and 0.77. Since both approaches render identical predictions for h^* (and hence D), we restrict further discussion to the work of Kavassalis and Whitmore,[20] since they have provided an explicit graphical relationship for $h^*(n)$ over the range $1\le n\le 500$. Their predictions, in terms of $h^{*2}\langle r^2\rangle$, can be accurately correlated with n to yield

$$h^{*2}\langle r^2\rangle(n)\approx a-bn^{-c}\ , \tag{4}$$

where $a=19.3$ is the value of $h^{*2}\langle r^2\rangle$ evaluated as $n\rightarrow\infty$, $b=7.9$ is the difference in $h^{*2}\langle r^2\rangle$ between $n\rightarrow\infty$ and $n=1$, and $c=0.86$ is an empirical constant obtained from a nonlinear least-squares regression. The functional relationship of $D_r(n)$ predicted from the theory of Kavassalis and Whitmore[20] is consequently given by

$$D_r\approx\left[\frac{a-b}{a-bn^{-c}}\right]^{1/2} \tag{5}$$

and is observed from Fig. 2 to agree well with our experimental data. It is of interest to note here that extension of the Benoit and Hadziioannou[19] formalism to include the $(AB)_nA$ architecture has yielded[22] predictions which accurately reflect the small-angle scattering behavior of disordered copolymers composed of alternating protonated and deuterated polystyrene blocks.

An approach[16,23] taken to model the microstructural dimensions of symmetric $(AB)_n$ copolymers, in the strong segregation regime only, relies on confined single chain statistics.[6,8] In this treatment, all of the possible looping and bridging conformations available to the $2(n-1)$ middle blocks of an $(AB)_n$ molecule must be considered. Looped middle blocks are treated in the formalism in an equivalent fashion as terminal blocks, implying that (i) a fully looped molecule with equal block masses effectively behaves as a diblock copolymer and (ii) the number of different interphases traversed by the molecule (σ) is 1. If the copolymer is fully extended, all of the middle blocks bridge their respective microdomains and $\sigma=2n-1$. Within these two limits lies the most probable conformation, in which the mean number of loops per molecule is $n-1$ and $\sigma\approx2(n-1)^{1/2}$ when $n>1$. Predictions obtained from this formalism are provided in Fig. 2. For the copolymers studied here, the *fully looped* conformation corresponds to $D_r=1$ for all n and does not reflect the decreasing $D_r(n)$ relationship observed experimentally. While the *fully bridged* conformation sorely underpredicts the SAXS data, predicted D_r

assuming the most probable conformation are in reasonably good agreement with both the data and the predictions made by Kavassalis and Whitmore.[20]

The results presented here are obtained from a systematic study of strongly segregated $(AB)_n$ copolymers possessing nearly equal block masses. Small-angle x-ray scattering reveals that the microdomain periodicity decreases noticeably with n, indicating that the microdomains contract as the number of middle blocks increases. This observation provides insight into the role of middle block conformation on quiescent microstructural development in microphase-separated multiblock copolymers. Predictions obtained from theories[19,20,23] developed to elucidate the phase behavior and microstructural characteristics of $(AB)_n$ materials are found to be in good agreement with the data obtained here.

---

*To whom correspondence should be addressed.

[1] L. Leibler, Macromolecules **13**, 1602 (1980).

[2] G. H. Fredrickson and E. Helfand, J. Chem. Phys. **87**, 697 (1987).

[3] T. Hashimoto, M. Shibayama, and H. Kawai, Macromolecules **13**, 1237 (1980); T. Hashimoto, M. Fujimura, and H. Kawai, *ibid.* **13**, 1660 (1980).

[4] G. Hadziioannou and A. Skoulios, Macromolecules **15**, 267 (1982).

[5] Y. Matsushita *et al.*, Macromolecules **23**, 4313 (1990).

[6] D. J. Meier, in *Thermoplastic Elastomers: A Comprehensive Review,* edited by N. R. Legge, G. Holden, and H. E. Schroeder (Hanser, New York, 1987), pp. 269–301.

[7] E. Helfand and Z. R. Wassermann, Macromolecules **9**, 879 (1976); **11**, 960 (1978); **13**, 994 (1980).

[8] C. P. Henderson and M. C. Williams, J. Polym. Sci., Polym. Phys. Ed. **23**, 1001 (1985).

[9] A. V. Semenov, Zh. Eksp. Teor. Fiz. **88**, 1292 (1985) [Sov. Phys. JETP **61**, 733 (1985)].

[10] K. R. Shull, Macromolecules **25**, 2122 (1992).

[11] A. A. Mayes and M. Olvera de la Cruz, J. Chem. Phys. **91**, 7228 (1989).

[12] Y. Matsushita *et al.*, Macromolecules **16**, 10 (1983).

[13] S.-I. Takahashi *et al.*, Polym. J. **18**, 41 (1986).

[14] R. J. Spontak *et al.*, in *Polymer Solutions Blends, and Interfaces,* edited by I. Noda and D. N. Rubingh (Elsevier, Amsterdam, 1992), pp. 65–88.

[15] D. W. Dwight *et al.*, J. Electron Spectrosc. Relat. Phenom. **52**, 457 (1990).

[16] J. M. Zielinski and R. J. Spontak, Macromolecules **25**, 653 (1992).

[17] R. J. Spontak, S. D. Smith, and A. Ashraf, Macromolecules **26**, 956 (1993).

[18] S. Krause, J. Polym. Sci. Part A-2 **7**, 249 (1969); Macromolecules **3**, 85 (1970).

[19] H. Benoit and G. Hadziioannou, Macromolecules **21**, 1449 (1988).

[20] T. Kavassalis and M. D. Whitmore, Macromolecules **24**, 5340 (1991).

[21] K. M. Hong and J. Noolandi, Macromolecules **14**, 727 (1981); **16**, 1083 (1983).

[22] G. Hadziioannou *et al.*, Polymer **33**, 4677 (1992).

[23] R. J. Spontak, J. M. Zielinski, and G. G. Lipscomb, Macromolecules **25**, 6270 (1992).