

Fluctuation scattering in a multi-arm styrene–isoprene star diblock copolymer

Lewis J. Fetters

*Exxon Research and Engineering Co., Corporate Research Science Laboratories,
Annandale, NJ 08801, USA*

and Randal W. Richards*

*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL,
UK*

and Edwin L. Thomas

*Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003,
USA*

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A summary of the microphase separation thermodynamics of star diblock copolymers is presented and special attention drawn to recent predictions regarding the small-angle scattering from the homogeneous disordered state. The results of small-angle X-ray scattering from concentrated (66% w/v) solutions of 18-arm styrene–isoprene star block copolymers are presented. A broad maximum is evident in the scattering. The dimensionless quantity $(Q_{\max}R)^2$, where Q_{\max} is the scattering vector of the maximum and R the radius of gyration of the linear diblock arm, goes through a minimum as the composition of the copolymer changes. A systematic dependence of $(Q_{\max}R_c)$, where R_c is the radius of gyration of the core, with copolymer composition is also observed. Both of these observations are in qualitative agreement with the theoretical predictions.

(Keywords: star copolymers; small angle scattering)

INTRODUCTION

The thermodynamics and kinetics of phase separation processes in homopolymer mixtures and block copolymers have attracted considerable interest in recent years^{1,2}. For homopolymer mixtures much of the thermodynamics has been adaptations of Flory–Huggins or equation-of-state theories originally developed for polymers dissolved in low-molar-mass solvents^{3–5}. Phase separation kinetics have been analysed using spinodal decomposition theory^{6–8} or a nucleation and growth⁹ description dependent on the location of the mixture on the phase diagram.

In block copolymers the covalent bond between the different components prevents macroscopic phase separation and contributes to the development of a highly organized microphase separated solid state. Leibler¹⁰ was the first to analyse block copolymer phase separation thermodynamics. Subsequently, Noolandi and others^{11–14} discussed the thermodynamics of block copolymers and their mixtures with homopolymers. All of these theories pertain to *linear* block copolymers.

In recent years, Bi and Fetters¹⁵ developed the synthesis of a new class of block copolymers, the star diblock copolymer. These materials are formed by the linking of a defined^{16,17} number of linear diblock molecules (the arms) to a common nucleus, thus forming a copolymer molecule with a core of one component and an outer region of the second component. At particular compositions for the styrene–diene star diblocks it has

been shown that a new morphological arrangement exists^{18,19}. A theory of the microphase separation thermodynamics for graft and star copolymers has been developed by de la Cruz and Sanchez²⁰. The theory predicts striking differences between the behaviour of linear diblock copolymers and graft and star copolymers. Moreover, predictions concerning the form of the radiation scattering law for star diblock copolymers and its variation with copolymer composition were made.

A précis of the theoretical background prefaces a discussion of our small-angle X-ray scattering (SAXS) measurements on a series of 18-arm styrene–isoprene star diblock copolymers.

THEORY

The transition from a microphase separated solid state to a homogeneous disordered melt in linear diblock copolymers has been described by Leibler¹⁰. As in mixtures of homopolymers, this transition takes place at a defined value of χN , where χ is the thermodynamic interaction parameter between the two components of the copolymer and N the overall degree of polymerization. At the critical point the value of χN ($(\chi N)_c$) for linear block copolymers differs greatly from that for homopolymer mixtures. When the components are labelled A and B then

$$\begin{array}{lll} (\chi N)_c = 10.5 & N = N_A + N_B & \text{block copolymers} \\ (\chi N)_c = 2 & N = N_A = N_B & \text{homopolymer mixture} \end{array}$$

Since χ varies inversely with temperature then block

* To whom correspondence should be addressed

copolymers form a homogeneous mixture at a lower temperature than an equivalent mixture of homopolymers.

In the microphase separated state the small-angle scattering from block copolymers is characterized by one or more peaks arising from the paracrystalline arrangement of the phase separated domains²¹. A broad maximum of much reduced amplitude (in comparison to the microphase separated state) persists in the disordered, homogeneous state. The scattering maximum from the disordered melt is due to thermally stimulated density fluctuations which have a spectrum of wavelengths. The most probable fluctuation wavelength is approximately equal to the radius of gyration (R) of the block copolymer; since the scattering law of the system is the Fourier transform of the density fluctuations, this leads to a maximum in the scattering pattern at a reciprocal space dimension commensurate with the most probable fluctuation wavelength. In terms of the scattering vector Q ($Q = |\mathbf{Q}| = 4\pi\lambda^{-1} \sin \theta$; λ = radiation wavelength, 2θ = scattering angle) and the copolymer radius of gyration R , this maximum will be at $QR \approx 1$.

Using the random-phase approximation of de Gennes²², Leibler obtained the scattering law for the homogeneous disordered state in linear diblock copolymers as:

$$S(Q) = N/[F(Q^2 R^2) - 2\chi N] \quad (1)$$

where $F(Q^2 R^2)$ involves a composition-weighted sum of Debye functions²³ for each component block in the copolymer. As long as the composition of the copolymer remains fixed, the maximum in $S(Q)$ is constant at the same value of Q as the temperature is altered. However, the form of $S(Q)$ is very dependent on χ , especially near the spinodal temperature, since $S(Q)$ is divergent here. Experimental confirmation of these predictions have been provided by the results of Hashimoto *et al.*²⁴ on low-molecular-weight block copolymers.

Recently de la Cruz and Sanchez²⁰ used a functional integral method to rederive all the equations obtained by Leibler¹⁰, and additionally extended the theory to copolymers of different architecture. The results reinforce the view that linear di- or triblock copolymers are special cases of graft copolymers. The microphase separation thermodynamics of star block copolymers ($A_n B_n$) and star diblock copolymers ($(AB)_n$) (see Figure 1) were also presented. For star block copolymers $(\chi N)_c = 10.5$ as for linear diblocks, whereas graft copolymers and star diblock copolymers have no critical point in the order-disorder thermodynamics but do have a spinodal curve. At a copolymer fractional composition of 0.5 the value of χN at the spinodal is 13.5 for the graft copolymer whilst for the $(AB)_n$ star diblock copolymer the value of χN decreases as the number of arms, n , increases.

It is the $(AB)_n$ diblock star copolymers we are concerned with here, in particular the behaviour of the maximum in $S(Q)$ with composition. In the homogeneous melt state, the maximum in $S(Q)$ for a linear diblock occurs at a length scale inversely proportional to the radius of gyration of the molecule. For star diblocks, the radius of gyration increases with the number of arms, at first, then rapidly levels off at approximately three times the linear arm radius of gyration as the number of arms becomes very large. Hence Q^* should decrease with n .



Figure 1 Schematic structures of star block ($A_n B_n$) and star diblock ($(AB)_n$) copolymers

However, at large n , the star diblock copolymer resembles a core-shell particle so that the dominant length scale decreases towards the core block radius of gyration proportional to the distance from the core centre to the core-shell interface, causing Q^* to increase. Figure 2a taken from de la Cruz and Sanchez²⁰ shows how the dimensionless quantity $(Q_{\max} R)^2$ goes through a minimum with copolymer composition for various fixed arm numbers. The variation of the quantity $(Q_{\max} R_c)^2$ with composition is very systematic as shown in Figure 2b. It is these two aspects which we examine here, utilizing SAXS measurements on a series of 18-arm styrene-isoprene star diblock copolymers.

EXPERIMENTAL

Materials

A series of 18-arm star diblock copolymers were prepared by the anionic polymerization methods detailed earlier^{16,17}. The specimens are designated according to their styrene content and styrene block molecular weight

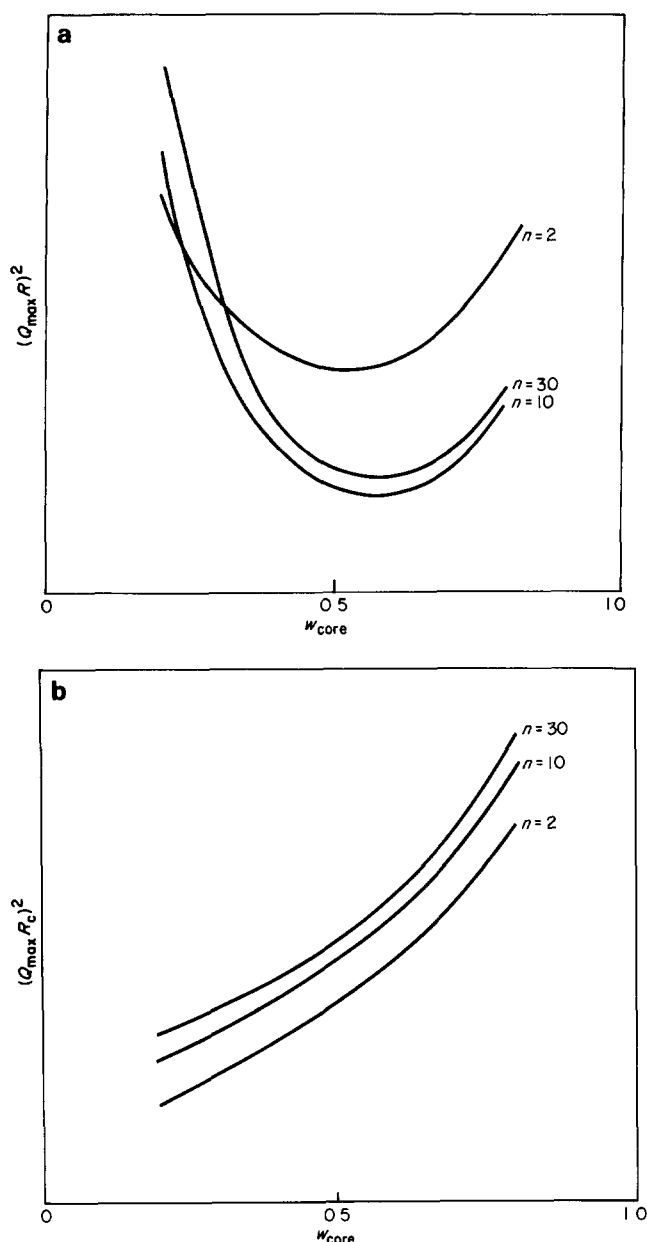


Figure 2 (a) $(Q_{\max} R)^2$ as a function of weight fraction of core block for star diblock copolymers with different numbers of arms, n . (From Figure 8 of de la Cruz and Sanchez²⁰). (b) $(Q_{\max} R_c)^2$ as a function of weight fraction of core block for different arm numbers, n , of star diblock copolymers. (From Figure 9 of de la Cruz and Sanchez²⁰)

in each arm. Thus SI-18:36:10 is an 18-arm star diblock copolymer with a styrene weight percentage of 36 and the molecular weight of each styrene block being 10 000. After removal of contaminating homopolymers and linear diblock copolymer by fractionation the compositions were determined by ^1H n.m.r. The molecular weight of the homopolystyrene precursor was obtained by size exclusion chromatography. The characteristics of the samples used here are given in Table 1.

Small-angle X-ray scattering

To determine the position of the fluctuation peak, specimens are required to be in a homogeneous melt. Initial calculations based on data for linear diblock copolymers²⁵ indicated that the 'homogenization' temperature was ~ 180 – 200°C . This temperature is far too high for the polyisoprene blocks since experience has

shown that unless oxygen is rigorously excluded oxidative crosslinking takes place at temperatures greater than 100°C . Consequently, SAXS experiments were made on concentrated solutions of the copolymers in dioctyl phthalate (DOP), a non-preferential solvent for either component of the copolymer. Solutions ($\approx 5\%$ w/v) of the copolymers were made in mixtures of dioctyl phthalate and methylene chloride. The methylene chloride was then allowed to evaporate under atmospheric conditions over a period of two weeks. In their final form the solutions had a concentration of $\sim 66\%$ (w/v) and were very viscous clear gels at room temperature.

SAXS data were obtained using a slit collimated Kratky camera with Ni-filtered $\text{Cu K}\alpha$ radiation. Scattered X-rays were detected by a one-dimensional Braun linear position-sensitive detector placed at the end of an extended, evacuated flight path. The samples were enclosed between polyimide films and a path length of 2 mm was used throughout. Intensity data were subsequently processed using a DEC PDP 11/34 minicomputer and were not desmeared.

RESULTS AND DISCUSSION

Semilogarithmic plots of the smeared scattered intensity as a function of the scattering vector Q are shown in Figure 3a for two star diblock copolymer solutions in DOP at 27°C . These are to be compared with the data for the bulk star diblock copolymer SI-18:35:10 shown in Figure 3b. Evidently, the scattering from the DOP gels differs greatly from that of bulk specimens in having only one broad maximum and no evidence for a high degree of long-range organization in the form of multiple Bragg peaks. This finding is somewhat surprising since Hashimoto *et al.*²⁶ observed multiple Bragg peaks from $\sim 40\%$ solutions of linear diblock styrene-isoprene copolymers. It appears that these star diblock copolymers are already in a homogeneously disordered state at room temperature. This was confirmed by SAXS measurements (not shown here) on the DOP solution of SI-18:23:12 at temperatures up to 110°C , where it was found that the maximum is unobservable for temperatures $\geq 60^\circ\text{C}$, the scattering continuously decreasing as Q increases. Hence, the spinodal temperature for this concentration of linear diblock copolymer is below 27°C .

A second difference from linear diblock copolymers is the continuing increase in intensity as Q approaches zero. Linear diblocks have no very large-scale density fluctuations and hence as Q approaches zero there is no scattered intensity. The source of this additional low-angle scattering in star diblocks is not apparent to us yet; however, we note that similar scattering has been observed in SAXS from mixtures of copolymers and homopolymers²⁷.

Table 2 shows the value of Q_{\max} obtained for each

Table 1 Characteristics of 18-arm star diblock copolymers

Copolymer	Wt fraction styrene	$M_w^{\text{PS}} (10^3)$	$M_w^{\text{PI}} (10^3)$	$M_w^{\text{arm}} (10^3)$
SI-18:23:12	0.226	12	41.1	53.1
SI-18:35:10	0.350	10	18.6	28.6
SI-18:66:30	0.660	30	15.4	45.4
SI-18:81:30	0.810	30	7.0	37.0
SI-18:92:30	0.92	30	3.3	33.3

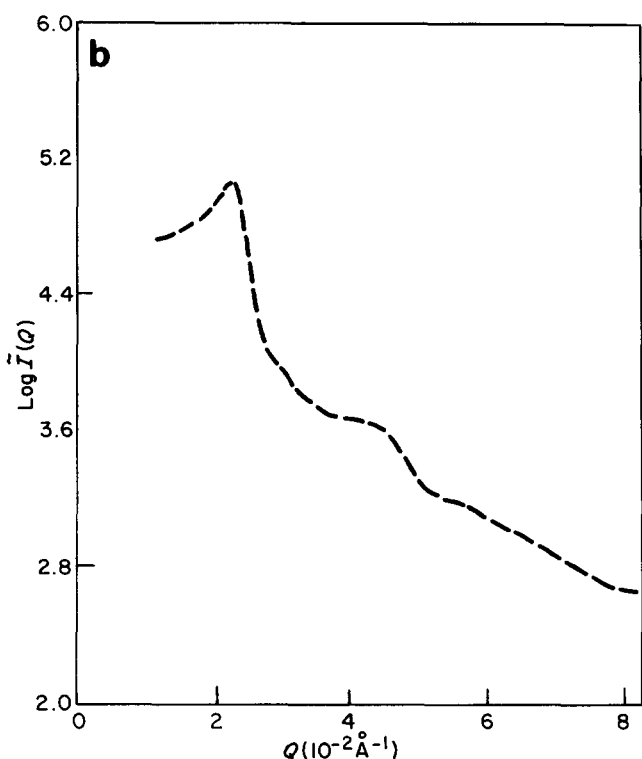
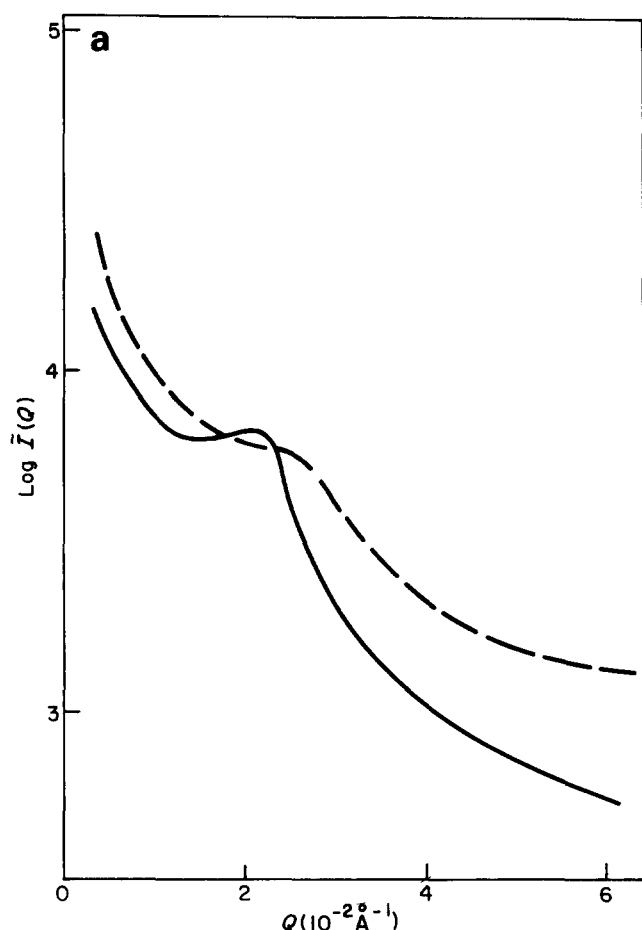


Figure 3 (a) Semilogarithmic plots of smeared intensity as a function of Q for two 18-arm star diblock copolymers in dioctyl phthalate solution at 27°C: ----, SI-18:35:10; —, SI-18:66:30. (b) Semilogarithmic plot of smeared intensity for SI-18:35:10 as a 1 mm thick solid film cast from toluene

copolymer in DOP solution. Also included in Table 2 are the radii of gyration of the polyisoprene core block and the radii of gyration of the linear diblock arm. These radii of gyration are calculated from relationships quoted in the literature for the unperturbed radius of gyration of the homopolymers^{28,29}. It is assumed that the two blocks occupy distinct spatial regions (i.e. a segregated model as employed by de la Cruz and Sanchez²⁰) and hence the linear diblock arm radius of gyration is approximated as the sum of the radius of gyration of each block.

Values of $(Q_{\max}R)^2$ (where R is the radius of gyration of the linear diblock arm) are plotted as a function of weight fraction of polyisoprene (core polymer) in Figure 4. A parabolic curve with a minimum is clearly indicated by the data. However, the absence of data for $0.4 \leq w_{PI} \leq 0.6$ precludes experimental determination of the precise minimum. A theoretical value of w_{PI} can be obtained from the variation of w_{PI} with n extracted from Figure 8 of the paper of de la Cruz and Sanchez²⁰. This is shown in Figure 5 and suggests that the minimum should be at $w_{PI} = 0.572$; however, the best smooth curve (drawn by eye) through the data points has a minimum at $w_{PI} \approx 0.5$. When the data are plotted as in Figure 6, i.e. using the radius of gyration of the core polyisoprene block, the qualitative agreement with the theoretical prediction is excellent, in that a systematic increase in $(Q_{\max}R_c)^2$ is observed with increasing weight fraction of core block.

Quantitative agreement with the predictions of de la

Table 2 Values of Q_{\max} for 18-arm star diblock copolymers in DOP at 27°C

Copolymer	Q_{\max} (10^{-2} \AA^{-1})	R_g^{PI} (\AA)	R_g^0 (\AA)
SI-18:23:12	2.055	73.6	103.8
SI-18:35:10	2.538	48.7	76.3
SI-18:66:30	2.105	41.4	89.2
SI-18:81:30	2.664	32.5	80.3
SI-18:92:30	3.242	19.9	67.7

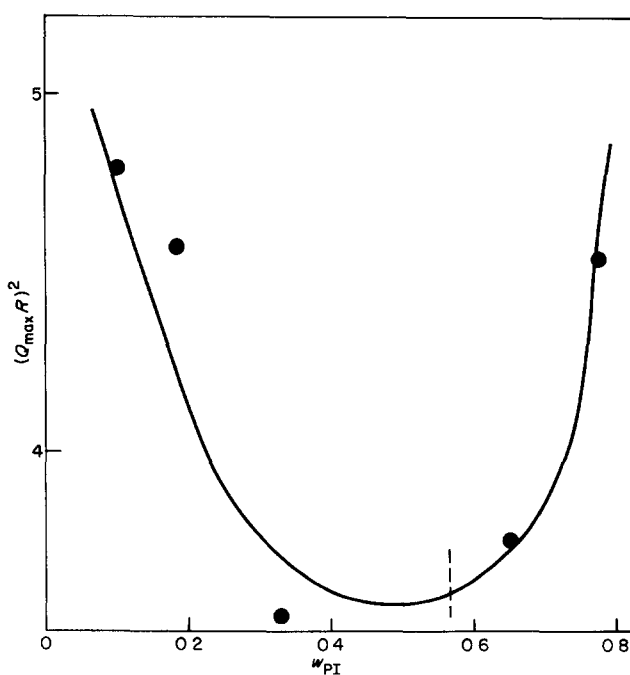


Figure 4 $(Q_{\max}R)^2$ as a function of weight fraction of polyisoprene in the copolymer: ----, position of minimum expected from data of Figure 5

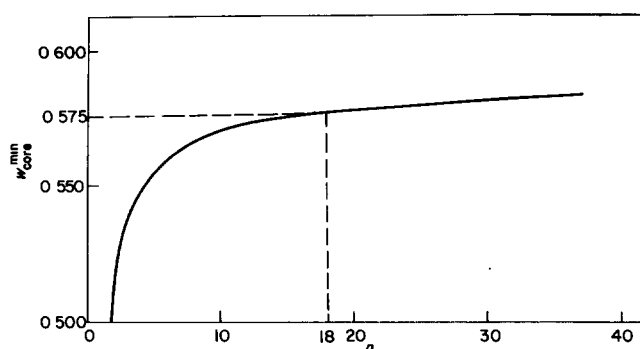


Figure 5 Dependence of the star diblock composition at the minimum (taken from plots of $(Q_{\max}R_c)^2$ as a function of weight fraction of the core block) on number of arms. (Data obtained from Figure 8 of de la Cruz and Sanchez²⁰)

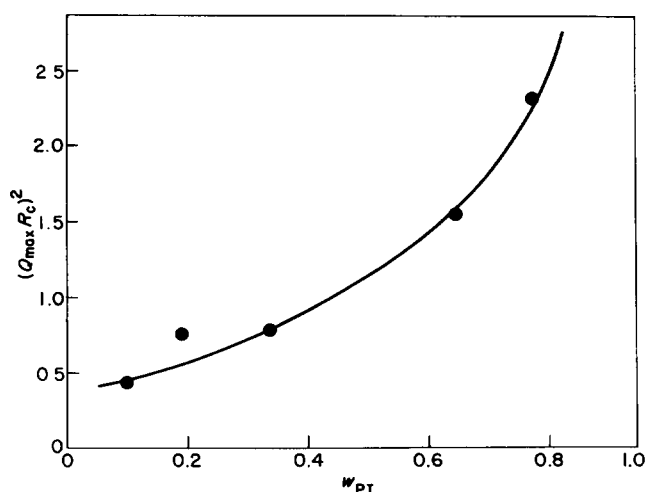


Figure 6 $(Q_{\max}R_c)^2$ as a function of weight fraction of isoprene in the copolymer

Cruz and Sanchez is not obtained. It is known that component blocks in block copolymers are extended in the microphase separated state. This extension most probably increases in the homogeneous state since the blocks will adopt less probable conformations to reduce unfavourable interblock contacts. Furthermore, for star diblock copolymers when the arm number n approaches $N_{\text{arm}}^{1/2}$ (where N_{arm} is the degree of polymerization of a linear arm), the statistics become non-Gaussian²⁰. For all the specimens studied here, n is of the same order of magnitude as $N_{\text{arm}}^{1/2}$, and for SI-18:92:30 $n \approx N_{\text{arm}}^{1/2}$. However, this will only result in a scaling of the data points along the ordinate axis and it will not alter the shapes of Figures 4 and 6. Ideally direct evaluation of the core block and total copolymer molecule dimensions are required. In principle these can be obtained by small-angle neutron scattering but this is not a trivial exercise in view of the complications in making suitably deuterium-labelled star diblock copolymer and the variety of scattering contrasts which would exist in an essentially four-component system (hydrogenous isoprene block, hydrogenous styrene block, labelled isoprene block and DOP).

CONCLUSIONS

For a fixed number of arms (18) we have experimentally confirmed the predictions of the microphase separation

theory of de la Cruz and Sanchez for star diblock copolymers: namely, the observation of a maximum in the scattered intensity from these copolymers in the homogeneously disordered state; that the squared product of the diblock arm radius of gyration and the scattering vector of this maximum goes through a minimum as the content of core block polymer increases; and lastly that the squared product of the core block polymer radius of gyration and the scattering vector of the maximum shows a systematic increase as the content of core polymer increases. The absence of quantitative agreement with theory is attributable to uncertainty in the absolute values of the radius of gyration of the linear diblock arm.

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