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Morphology and ordering behavior of a poly(styrene)-*b*-poly(ferrocenyldimethylsilane) diblock copolymer

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Abstract

The thermal behavior and morphology of a diblock copolymer of polystyrene and poly(ferrocenyldimethylsilane) (PFS) ($M_n = 36\,000$, $\phi_{PS} = 0.308$) have been surveyed using small angle X-ray scattering and transmission electron microscopy. As cast films are partly crystalline. The crystal structure is seriously perturbed by the propensity of the molecules to microphase segregation. After annealing above the glass transition temperature of polystyrene both crystallization and definition of the microphase separated domains are improved. The system forms an ordered microphase segregated structure once annealed above the melting temperature of the PFS block. Even then both cylindrical and spherical morphologies are observed and annealing times of a few days do not force the system to develop the long range order generally associated with carefully annealed polystyrene-*b*-polydiene polymers of comparable molecular weight. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ferrocenyldimethylsilane); Polystyrene; Order to disorder transition

1. Introduction

Metal containing solid-state materials are known to exhibit an interesting and useful array of redox, magnetic, optical and electrical properties. Polymers in general, and block copolymers in particular, offer processing advantages over ceramics and metals. Thus the development of metal containing block copolymers is of great interest and the characterization of such materials present an important area of research as the behavior of these materials can be quite different from those of conventional organic polymers [1,2].

The focus of the current study is a novel diblock copolymer containing poly(ferrocenyldimethylsilane) (PFS) and polystyrene (PS) blocks. While a few properties of this and related block copolymers of PS and PFS have been surveyed, [3,4] no extensive studies dedicated to the elucidation of the block copolymer morphology and ordering behavior of these materials have yet appeared in the literature, especially for the region of the phase diagram where the PFS block is the majority component.

It is of interest to study the PFS containing block copolymers from two perspectives. Firstly, PFS has interesting properties. Secondly, the PFS block crystallizes, and the study of the interplay between crystallization and block copolymer ordering is of interest in general. In this material there is a competition between microphase separation and crystallization to derive the ordering behavior of the material and determine its final morphology. A key question is precisely what morphology results from this competition in the case of this block copolymer. This competition in semicrystalline block copolymers has been the object of study over many years, but recently it has become the focus of renewed interest and the ordering behaviors of several block copolymer systems have been investigated [5–9]. Crystallization and block copolymer microphase separation work cooperatively and against each other at the same time.

Crystallization promotes separation of the blocks by excluding the amorphous block from the forming crystal, and also prevents the system from rearranging freely by effectively locking random portions of the chain of the crystallizable block in the same crystal. However, microphase separation frustrates the system, preventing the formation of large “equilibrium” crystals. The final morphology is

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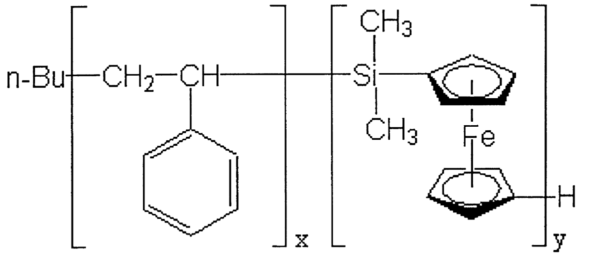

Fig. 1. Schematic representation of the PFS-*b*-PS block copolymer structure.

strongly influenced by the relative energies of the two processes as well as by the thermal history of the sample.

2. Materials and methods

Synthesis of the poly(styrene-*b*-ferrocenyldimethylsilane) block copolymer was achieved via the generation of a living lithium polystyrene in tetrahydrofuran (THF), followed by sequential addition of the methylated silicon-bridged ferrocenophane $Fe(\eta\text{-}C_5H_4)_2Si(CH_3)_2$ via living anionic ring-opening polymerization. A detailed description [3] of the synthesis has been presented elsewhere. The block copolymer had an overall molecular weight M_n of 36 000 and polydispersity index (PDI) of 1.16 relative to polystyrene (PS) standards. The composition as determined from NMR measurements corresponded to a mole ratio PS:PFS of 0.74:1.00, which corresponds to a PS weight fraction of 0.245 and PS volume fraction of 0.308 assuming a density of 1.44 g/cm^3 for PFS. The chemical structure of the block copolymer is presented in Fig. 1.

Samples were solution cast over 6 days at room temperature from tetrahydrofuran solutions of concentrations of about 2.0% (w/v). The resulting films were then dried in roughing vacuum at room temperature for one week to yield samples of about 0.2 mm thickness. Some of the samples for morphological studies were then sealed in glass ampoules at high vacuum and annealed further at different temperatures.

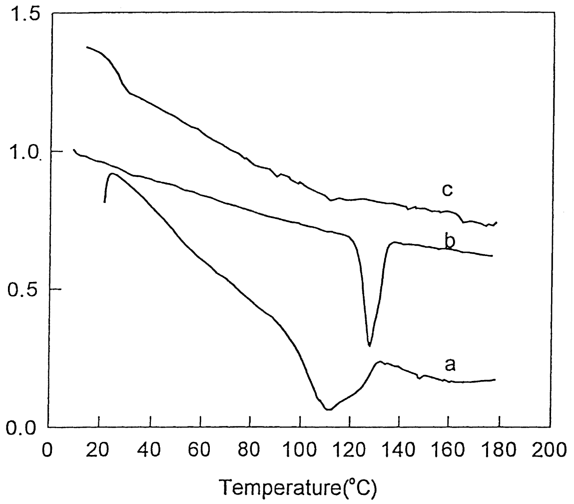

Fig. 2. DSC traces for a sample: (a) as-cast; (b) after annealing at 115°C for 30 min; and (c) after annealing at 140°C for 30 min.

Differential scanning calorimetry (DSC) experiments were run using a DuPont 900 DSC. Crystallization behavior was investigated by annealing an approximately 1.5 mg sample at a selected temperature for 30 min and then quenching in liquid nitrogen before the DSC measurement. Thermograms were recorded from room temperature to 180°C at a heating rate of 10°C/min under N_2.

Small angle X-ray scattering (SAXS). The morphologies of the PS-*b*-PFS copolymers were characterized using small angle X-ray scattering in the Department of Polymer Science at The University of Akron (UA) and at Oak Ridge National Laboratory (ORNL). The pinhole collimated small angle X-ray scattering (SAXS) apparatus at UA is attached to a 12 kW (Rigaku) rotating anode source with a copper target operated at 50 kV and 200 mA. CuK_α radiation ($\lambda = 0.154$ nm) is selected with a nickel filter and energy discriminating electronics connected to the Braun one-dimensional position sensitive proportional counter. Details of the apparatus may be found elsewhere [10]. SAXS measurements at Oak Ridge National Laboratory (ORNL) were performed on the 10 m small angle X-ray scattering instrument [11,12] with a pinhole geometry camera and two-dimensional position sensitive detector using CuK_α radiation.

All data were corrected for background scattering and absorption of the sample. The angular calibration of the SAXS system at UA was accomplished using a silver behenate sample having a repeat distance of 5.837 nm for which five orders of reflection could be measured. Characteristic spacings in the microphase separated structures were found from the positions, q^*, of a single peak observed in each pattern using $d = 2\pi/q^*$.

Wide angle X-ray diffraction (WAXD) experiments were conducted with a Rigaku 12 kW rotating anode generator ($\lambda = 0.154$ nm) coupled with a Geigerflex D/max-RB diffractometer (with a radius of 185 mm) and operated at an excitation voltage of 50 kV and current of 100 mA. The X-ray beam was Ni filtered, line focused and monochromatized using a graphite crystal. The beam size was controlled by the slit system (a divergence slit of 0.5°, a receiving slit of 0.5 mm, and a scattering slit of 0.5°). The diffraction peak positions and widths were calibrated with silver behenate and the angular deviation measured in WAXD found to be $\pm 0.05°$.

The *d*-spacings of the crystalline portion of the PS-*b*-PFS copolymer were determined by using Bragg's law, $2d \sin\theta = n\lambda$, where d was the crystal lattice spacing and θ the half diffraction angle corresponding to a peak position. Crystallite size was estimated from the peak broadening using the Scherrer equation: $\beta_s \approx (\lambda)/(\epsilon \cos\theta)$, where β_s is the full width, in radians, of the peak at scattering angle 2θ and ϵ the mean apparent crystallite size.

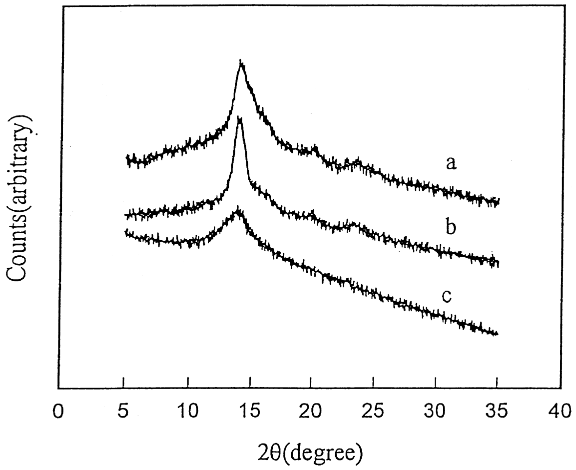

Fig. 3. WAXS data for the block copolymer: (a) as-cast; (b) after annealing at 112°C for 3 days and quenching in liquid nitrogen; and (c) after annealing at 180°C for 3 days and quenching.

Transmission Electron Microscopy (TEM) studies were done with a JEOL JEM-1200EXII electron microscope operated at 120 keV. The sections for TEM observation of bulk morphology were obtained by cryoultramicrotomy of cast samples using a Reichert Ultracut S microtome. The high electron density of PFS, as compared with that of PS, led to sufficient contrast without the need for staining.

3. Results and discussion

3.1. Crystallization behavior

The overall thermal behavior of the block copolymer was surveyed using DSC and simple flow observations. Three DSC curves are shown in Fig. 2. The as cast film shows a broad melting peak centered about 111°C with an enthalpy of 5.76 J/g. In fact, this broad peak may contain two peaks. When the sample is annealed at 115°C for 30 min, the melting peak is better defined although it still has a slight shoulder on the high temperature side, moving to a temperature of 128°C and an enthalpy of 10.5 J/g. The DSC trace for a sample annealed at 140°C shows no melting peak, as expected. These results may be compared with those published for homopolymers [13] of PFS as well with those for a similar diblock copolymer with slightly lower PFS content [3]. The melting temperature of 128°C for the diblock annealed at 115°C was in good agreement with a value of 127°C published for a PFS-*b*-PS diblock with a slightly lower molecular weight and an approximate composition of $\vartheta_{PS} = 0.38$ [3]. By way of comparison we note that the two melting peaks were observed in DSC data [13] from a 24k homopolymer annealed at 95°C. The multiple melting transitions were associated with the melting of crystallites formed in the film initially, followed by the melting at a higher temperature (as high as 133°C), of crystallites formed during heating. The melting peaks were observed to move closer together with the increasing crystallization temperature, T_c. For T_c of 110°C, a first T_m of 127°C was reported.

Any DSC evidence for glass transitions in this data is quite subtle. For the as-cast film the T_g of the PS block cannot be distinguished from the melting transition of the PFS block. Again for the sample annealed at 115°C no T_g for PS is seen, but there is a subtle feature near 30°C where one would expect the T_g for the PFS block. The sample annealed at 140°C still fails to display T_g for the PS block, although once again the presence of a glass transition for PFS may be rationalized with a feature at about 27°C. For PFS homopolymers the variation of T_g with M_n has been measured [13] and T_g for a homopolymer of $M_n = 24\ 200$ g/mol was found to be 22.4°C. The T_g of a PS homopolymer of molecular weight comparable to that of the PS block here (8800 g/mol) would be expected at about 82°C [14].

The crystallization of the PFS block was further studied by wide angle X-ray diffraction. X-ray diffraction patterns for a film as cast, after annealing for 3 days at 112°C, and after annealing for 3 days at 180°C are shown in Fig. 3. Three peaks may be seen in the data from the as-cast film, corresponding to spacings of 6.3, 4.4 and 3.9 Å. The peak at about $\theta = 14°$ is very broad and one could argue that, in fact, it might contain two peaks. Indeed two peaks at 13.3 and 14.7° were reported in the literature for the 24k homopolymer [13]. The broadness (FWHM = 1°) of the peak suggests a very small crystallite size. Using the Scherrer equation to estimate the crystallite size from the peak broadening yields a value of about 90 Å. This size is consistent with the existence of a crystalline structure that is frustrated by the tendency of the system to microphase separate even though it does not order into well-defined microdomains. No SAXS peak associated with a long spacing, such as the one seen in isothermally crystallized PFS homopolymers [13], is seen in the as-cast diblock copolymer sample.

3.2. Block copolymer ordering

The block copolymer order to disorder transition (ODT) was sufficiently subtle that it was not evidenced in the DSC measurements. An estimate of the ODT was obtained using a simple flow test, as suggested by Bates et al. [15], which requires only a very small amount of sample. The amount of material available was insufficient to determine the ODT by conventional rheology measurements. A solution cast film was sealed under high vacuum in a glass ampoule and placed in a vacuum oven; the temperature raised slowly in steps while observing the rigidity of the sample. (This amounts to observing the variation in the magnitude of storage modulus with temperature at a very low frequency.) The sample flowed at a temperature of about 220°C (±20°C). Thus, it is in a disordered structure for temperatures above 220°C. Using this value of the order–disorder

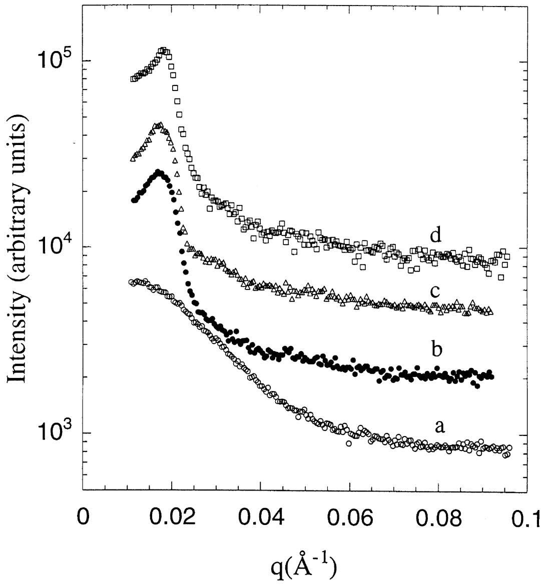

Fig. 4. SAXS data obtained at UA for the block copolymer: (a) as-cast; (b) annealed for 1 day at 150°C; (c) 180°C; (d) 200°C.

transition temperature one may crudely estimate the value of the segment–segment interaction parameter assuming that the transition temperature should be given approximately by the fluctuation corrected theory of Fredrickson and Helfand [16]. In our case, the interaction parameter is approximately 0.06 ($\chi N_{\mathrm{ODT}} = 17.5$, $N = 275$) for a segment volume of 99 cm^3/mol.

The ordering behavior was surveyed using SAXS and TEM measurements on several samples annealed at various temperatures. SAXS data taken for an as-cast sample shown in Fig. 4 give no indication of an ordered structure, in contrast to the well-known behavior of amorphous block copolymers [17] for which at least a single SAXS peak is generally observed after casting. TEM images of as-cast samples, as in Fig. 5(a), show a morphology that is phase segregated on a microscopic level, but in an irregular way. An ordered morphology could not be formed because the PFS molecules start to crystallize while still in solution. This crystallization strongly hindered the diffusion of chains and disrupted the formation of an ordered structure. The structure we observed in the as-cast sample was, thus, a result of a microphase separation under constrained conditions. Annealing at 112°C for 3 days is enough for the microphase segregation to become sufficiently defined such that a modest peak indicative of a characteristic spacing appears in the SAXS data, as shown in Fig. 6, which presents absolute intensity data measured at ORNL. Comparing the definition of the peak (width, height) with that observed after annealing for 3 days at 180°C (Fig. 6(b)) makes it clear that the spacing which appears is characteristic of the microphase separation, and not crystallization. Also, at 112°C the structure remains less well segregated than at 180°C despite the fact that at 180°C the system is near the disordering transition.

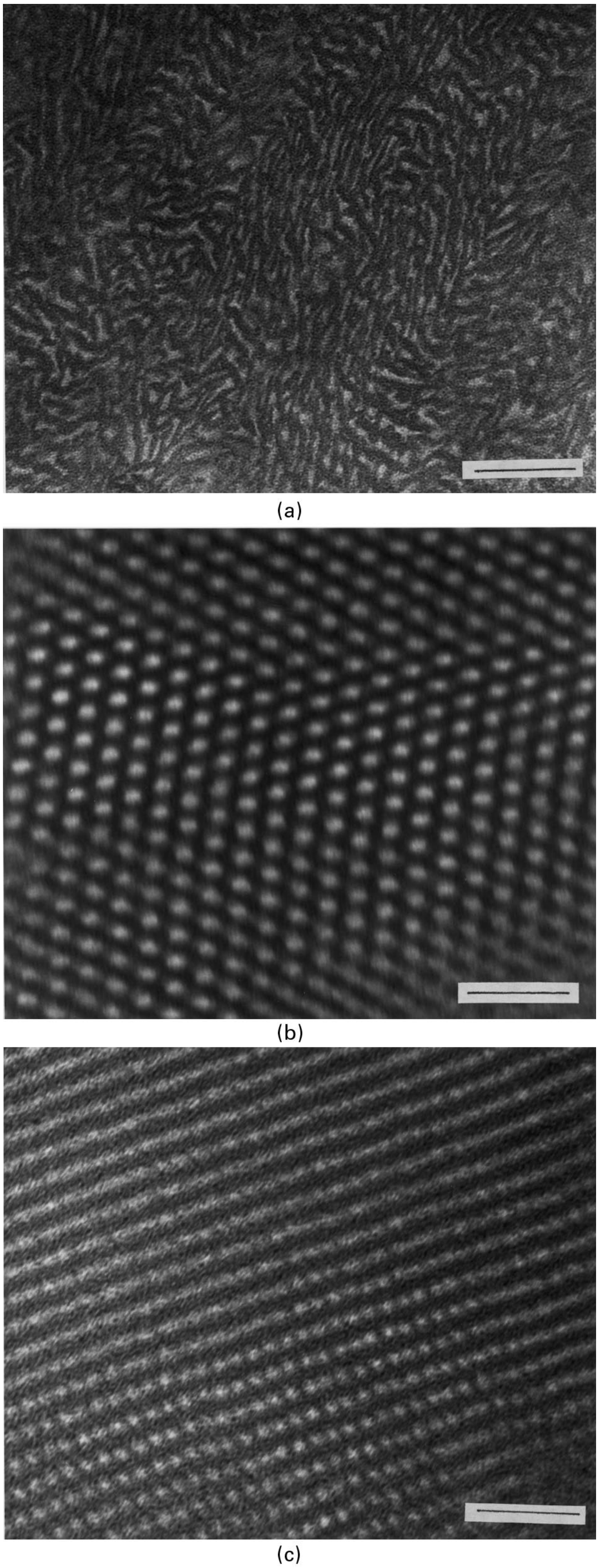
(a)
(b)
(c)

Fig. 5. TEM images of the PS-*b*-PFS bulk block copolymer morphology. (a) The morphology of a film slow cast from toluene solution is segregated on a microscopic scale, but is not regular. After annealing in vacuum for 1 h at 150°C images of both ordered cylinders “end on” (b), and ordered spheres (c), may be found. Size bars correspond to 100 nm.

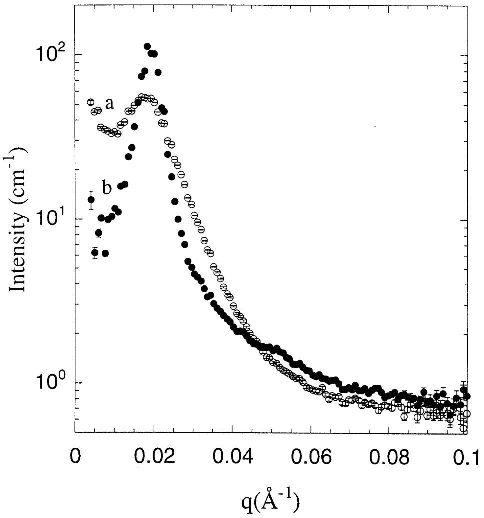

Fig. 6. Higher resolution SAXS data obtained at ORNL for separate block copolymer sample: (a) annealed for 3 days at 112°C; and (b) annealed for 3 days at 180°C.

SAXS data from samples annealed in vacuum for 1 day at 150, 180 and 200°C displayed a single clear peak (Fig. 4), with the peak position suggesting a domain spacing of ca. 330 Å for the sample quenched at 150°C. A shoulder at *q* of approximately 0.03 Å^{-1} is also seen in data for the sample quenched at 180°C (Fig. 4(c)). In this respect, the data differs from the higher resolution data taken at ORNL for the sample annealed for 3 days at 180°C, making it difficult to precisely assess its significance. It is evident, however, that the peak height diminishes somewhat, and the characteristic spacing drops as the annealing temperature increases from 180 to 200°C as expected, as the disordering temperature is approached. All in all it is seen that the ordering improves with annealing on a 1 day time scale at temperatures of 150 and 180°C, but this ordering is still imperfect. The lack of further distinct features in the SAXS curves indicates the presence of multiple morphologies or the absence of any single clearly defined morphology. TEM images of bulk morphology from samples annealed at different temperatures show directly that after annealing above the crystalline melting temperature all samples exhibit ordered morphologies, predominantly a spherical morphology coexisting with a cylindrical morphology. The average size of grains is quite small and does not increase with annealing over several days. Examples of the cylindrical morphology (seen "end on") and spherical morphology seen at different points in the same sample quenched at 150°C after annealing for 1 day are shown in Fig. 5(b) and (c).

Coexistence of two morphologies may be attributed to at least two different reasons. One possible reason is that this particular composition of PFS-*b*-PS copolymer falls on a boundary between spherical and cylindrical morphologies in the phase diagram. Thermo-reversible transitions between spherical and cylindrical morphologies were first observed for poly(styrene)-*b*-poly(isoprene) systems [18] and then observed in a number of other systems [19–21]. For block copolymer systems containing styrene and isoprene blocks (weight fraction of PS was 0.183) these studies reported the coexistence of spherical and cylindrical morphologies in the intermediate stages of the thermoreversible transition. Also poor ordering of cylindrical and spherical domains was observed for cases where these morphologies coexisted. While these copolymers exhibited the coexistence of morphologies only in a narrow temperature range, in the another system, polystyrene-*b*-polyethylene-alt-propylene [20], coexistent morphologies were observed at room temperature for two low PS content diblocks (PS volume fractions of 0.074 and 0.155, respectively, and molecular weights of 54 900 and 26 900, respectively). Another possible reason for the coexistence of morphologies could be the polydispersity in the block copolymer. In our case it seems unlikely that the coexistence is due to polydispersity in the composition of individual chains, as the molecular weight distribution was reasonably narrow. At a PDI of 1.16 this effect would only play a small role.

The general lack of good long range order seen here might also be connected with the conformational asymmetry of the PS—PFS copolymer. Gido and coworkers [22] suggest from a series of observations that the quality of long range ordering is asymmetric in composition for block copolymers which are conformationally asymmetric, i.e. for which the statistical segment lengths of the two blocks differ. When the more flexible block is in the minority, the system forms very well-defined and long range ordered domains. On the other side of the phase diagram, where the minority domains are composed of the stiffer block, the long-range order is not as good. While we have no detailed data on the conformational statistics of the PFS block, the T_g of the PFS block is considerably lower than that of the PS and both the Si backbone bonds and ferrocene moieties provide flexibility in the PFS. Thus, one may estimate that the PFS block is substantially more flexible, leading one to expect poorer ordering at the composition studied here.

In classical poly(styrene)-*b*-poly(diene) systems long annealing times have been used to drive bulk samples to well-ordered long range morphologies [23]. Here it was found that an increase in the annealing time could lead to sample degradation (annealing time of 10 days at 180°C resulted in depolymerization of the PFS block) and therefore long annealing times were not used.

4. Conclusions

The thermal behavior and morphology of a diblock copolymer of polystyrene and poly(ferrocenyldimethylsilane) have been surveyed. As cast films are partly crystalline; the crystal structure is seriously perturbed by the propensity of the molecules to microphase segregate. At the same time the system does not form a regular microphase segregated structure until annealed above the melting temperature of the PFS block. When annealed above T_m a typical block copolymer structure could be observed, but the degree of ordering is still limited and even long annealing times do not force the system to develop the long scale order generally associated with carefully annealed polystyrene-*b*-polydiene polymers of comparable molecular weight.

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