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Phase Contrast Matching in Lamellar Structures Composed of Mixtures of Labeled and Unlabeled Block Copolymer for Small-Angle Neutron Scattering

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ABSTRACT: To extract the single-chain scattering function of polystyrene block chain in lamellar structures of styrene–2-vinylpyridine diblock copolymers, the method of "phase contrast matching" was studied for small-angle neutron scattering from blends of the deuterium-labeled and unlabeled block copolymers. The phase contrast matching is successfully applied for the samples with the lowest molecular weights (3.4×10^4 for the labeled portions) but not for the samples with the higher molecular weights (9.2 and 16.2×10^4). It is concluded that the mismatching may be caused by concentration fluctuation in the mixture of hydrogenated and deuteriated polystyrenes in domains, as well as by nonuniform distribution of deuteriated species along the direction perpendicular to the lamellae due to the difference in lengths of the labeled and unlabeled blocks.

Introduction

The conformation of a single polymer chain in bulk can be determined by measuring small-angle neutron scattering (SANS) from a random mixture of deuterium-labeled and unlabeled polymers with the same chain length at any mixing ratio. The same method is applicable for determining the conformation of a block chain of diblock copolymer even in a microdomain structure, if strong diffraction intensities from the microdomain structure could be eliminated. Three methods were employed to eliminate the diffraction. In the first method a single-chain scattering function is obtained as the difference between the coherent scatterings from a blend of labeled and unlabeled block copolymers and its corresponding unlabeled block copolymer. This method is straightforward, but it is difficult to obtain reliable data for a single-chain conformation since the diffraction intensity due to the domain structure is much higher than the single-chain scattering and also identical domain structures are required for the both specimens in order to eliminate the scattering due to the domain structure. Richards and Thomason[2] employed this method to study styrene block dimensions in the spherical domain of styrene–isoprene block copolymer. Unfortunately, the chain lengths of the parent and deuteriated samples were not the same and the measurements were carried out at a low content of deuteriated sample.

The second method involves the utilization of anisotropy of a microdomain structure. If the plane of lamellar surface could be aligned perpendicular to the incident neutron beam, the diffraction due to the lamellar structure would not be observed and only a single-chain scattering from labeled and unlabeled blocks could be obtained. Hadziioannou et al.[3] and Hasegawa et al.[4] investigated conformations of polystyrene block in a lamellar structure of styrene–isoprene copolymers by this method. Since the orientation of lamellae was not perfect in their experiments, Hadziioannou et al.[3] obtained a single-chain scattering at a particular azimuthal angle where the diffraction was not observed, while Hasegawa et al.[4] subtracted the contribution of diffraction with the use of the scattering data from the parent block copolymer.

In the third method, the diffraction is eliminated by matching the average scattering lengths between the two phases ("phase contrast matching") due to random mixing of labeled and unlabeled block chains. This method was first proposed for polymer blends by Jahshan and Summerfield[5] and subsequently extended to block copolymers by Koberstein.[6] According to their theory the coherent scattering intensity from a single chain in a microdomain structure of blend of labeled and unlabeled A–B diblock copolymers with the same chain length can be written as

$$I(q) = [(I_{\mathrm{L}} - I_{\mathrm{B,L}}) - R(I_{\mathrm{U}} - I_{\mathrm{B,U}})] \qquad (1)$$

where I_{L} and I_{U} are the total scattering intensities from the labeled and unlabeled polymers, respectively, and the subscript B refers to the background mainly composed of incoherent scattering. In eq 1 the first term of the right-hand side is the total coherent scattering from the microdomain structure containing labeled block chains, and the second term is the contribution from the microdomain structure itself. R in the second term is the magnitude of contrast between two phases such as

$$R = [\beta_{\mathrm{B}} - x\beta_{\mathrm{AD}} - (1 - x)\beta_{\mathrm{AH}}]^2/(\beta_{\mathrm{B}} - \beta_{\mathrm{AH}})^2 \qquad (2)$$

where β_{B}, β_{AH}, and β_{AD} are the coherent scattering length densities of block B and hydrogenated and deuteriated

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Table I
Molecular Characteristics of Samples

	sample code	$M_n \times 10^{-5\,a}$	M_w/M_n (GPC)	C_s,[b] wt %
I	DP-33	**0.34**–0.32	1.04	49
	SP-33	0.37–0.26	1.03	50
II	DP-77	**0.92**–0.75	1.09	48
	SP-77	0.77–0.72	1.02	51
III	DP-15	**1.62**–1.31	1.10	47
	SP-15	1.19–1.24	1.06	48

[a] Numbers written in boldface denote the molecular weights of deuteriated blocks. [b] C_s is the total polystyrene content in the sample. Values for DP-33 and SP-33 are determined by pyrolysis–gas chromatography, while others are determined by elemental analysis.

block A, respectively, and x is the volume fraction of deuteriated block chain within the A phase. Therefore, one should observe the single-chain scattering in a microdomain structure only when $R = 0$. However, this requires that $\beta_{AH} < \beta_B < \beta_{AD}$ and also a uniform distribution of deuteriated block chain in the A phase.

Bates et al.[7] applied this method for determining the single-chain conformation of polybutadiene block in the spherical domain of styrene–butadiene diblock copolymer with low butadiene content. Miller et al.[8-10] also studied the conformation of the soft segment in polyether–polyurethane block copolymer and the conformations of both soft and hard segments and also the entire chain in polyether–polyester block copolymer by the same method. They have successfully extracted the single-chain scattering and evaluated chain conformations in microdomain structures.

Since the conformation of a block chain is considered to be very much distorted in a microdomain structure as expected from the molecular weight dependence of the dimension of the microdomain,[11] it is essential to determine not only the overall dimension but also the anisotropy of the chain conformation in order to understand the domain structure from a molecular point of view. If we prepare a film sample with a lamellar structure which is highly oriented along the film surface, we should be able to determine the block chain dimensions projected onto the plane perpendicular to each of the orthogonal coordinate axes by measuring scattering from the film sample with an incident neutron beam either perpendicular or parallel to the lamellar structure. In the perpendicular case (that is, the incident beam is perpendicular to the film surface) the second method is applicable and only a single-chain scattering is observed, while in the parallel case, we have to apply the third method for extracting the single-chain scattering. The requirement of phase contrast matching is more strict in a highly oriented lamellar structure than in a spherical domain structure of randomly oriented lamellar structure because the small difference of contrast due to nonuniform distribution of labeled species in a microdomain structure may be averaged out in the latter case but not in the former case. In this paper, therefore, we report our study on the applicability of phase contrast matching techniques to highly oriented lamellar structures.

Experimental Section

The samples used here were styrene and 2-vinylpyridine diblock copolymers with narrow molecular weight distributions, prepared by an anionic polymerization technique reported previously.[12] They satisfy the first requirement of phase contrast matching; that is, the scattering length of poly(2-vinylpyridine) β_P lies between those of poly(styrene-h_8) β_{SH} and poly(styrene-d_8) β_{SD}, i.e., $\beta_{SH} < \beta_P < \beta_{SD}$. Characteristics of three pairs of labeled and unlabeled samples are listed in Table I, where the symbols D, S, and P stand for the blocks of poly(styrene-d_8), poly(styrene-h_8), and poly(2-vinylpyridine), respectively, and the block chains are connected in the order of the symbols. Three out of six samples, DP-77, SP-77, and DP-15, were newly prepared and characterized in almost the same way as reported previously.[12] The compositions were determined by elemental analysis and pyrolysis–gas chromatography.[13] The films of unlabeled parent copolymers and blends of labeled and unlabeled copolymers with various compositions of deuteriated species were prepared by solvent-casting from ca. 3–5 wt % solutions of THF, which is a common good solvent, on a glass petri dish in a desiccator. THF was slowly evaporated under the vapor atmosphere at room temperature for 4–5 days and then the cast films were dried in vacuo at room temperature for 3–4 days. We confirmed that the residual amounts of solvent in the film were less than 0.5% by comparing the weights of the dried film and the polymer sample dissolved before casting. The thickness of the film was about 0.15 mm. It has been confirmed by electron micrographs that films of parent copolymers as well as blends are composed of alternating lamellae predominantly oriented parallel to the film surface.

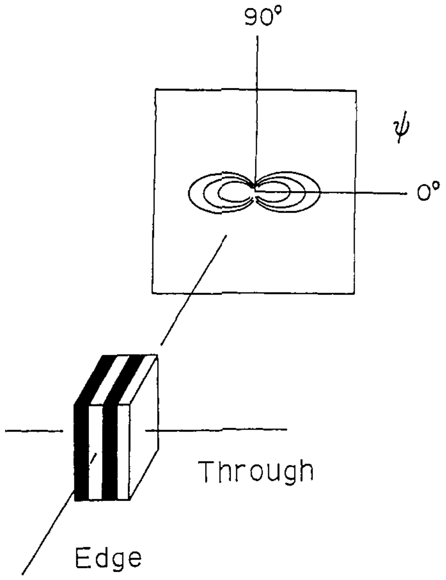

Figure 1. Schematic diagram of the geometric relationship between sample and the two-dimensional detector.

A SANS spectrometer at the National Bureau of Standards with a two-dimensional position sensitive detector was used in this study. Details of the apparatus were described previously.[14] SANS measurements were carried out at room temperature (~23 °C) for every film sample with the two geometries we defined, i.e., the edge and through views, in which the lamellae are set parallel and perpendicular to incident neutron beam, respectively. The specimens for SANS measurements at the through view were prepared by stamping out 22-mm diameter disks from the cast films and piling up 5–7 disks to make about 1 mm total thickness, while the specimens for the edge view were prepared by cutting the cast films into 13 mm by 1.5 mm rectangles and by stacking about 50 pieces together. The specimens were then sandwiched between two quartz plates and the effective thickness of the specimens was 0.7–1 mm for both views. The irradiated size on the specimen was 12-mm diameter. The wavelength λ used here was 6.0 Å and the width of its distribution $\Delta\lambda/\lambda$ is 0.25. The range of magnitude of the scattering vector q [$=(4\pi/\lambda)\sin(\theta/2)$] covered in this study was $0.007 < q$ (1/Å) < 0.13, where θ is the scattering angle. The geometric relationship between sample and detector is illustrated schematically in Figure 1, where the azimuthal angle is defined as ψ on the detector.

Results

In the evaluation of coherent scattering from neutron scattering data, incoherent scattering must be properly subtracted from the total scattering, particularly for samples containing fairly large amount of hydrogen atoms. Since there is no routine method correcting incoherent scattering, we employed the following method, which may

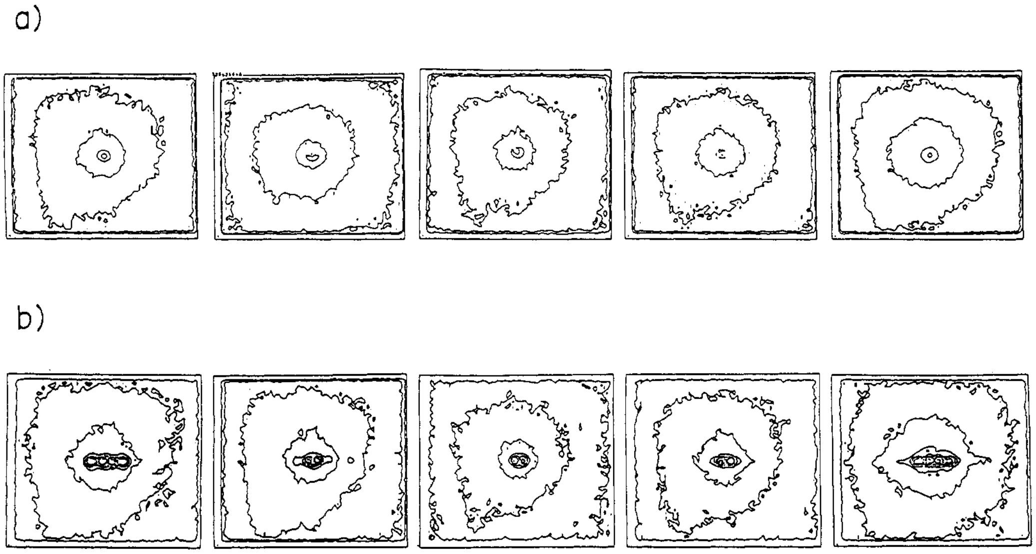

Figure 2. Whole images of contour maps of a two-dimensional detector for blends DP-33/SP-33: (a) through view; (b) edge view. Compositions are 8.3/91.7, 9.8/90.2, 10.5/89.5, 10.7/89.3, and 14.0/86.0 by weight from left to right.

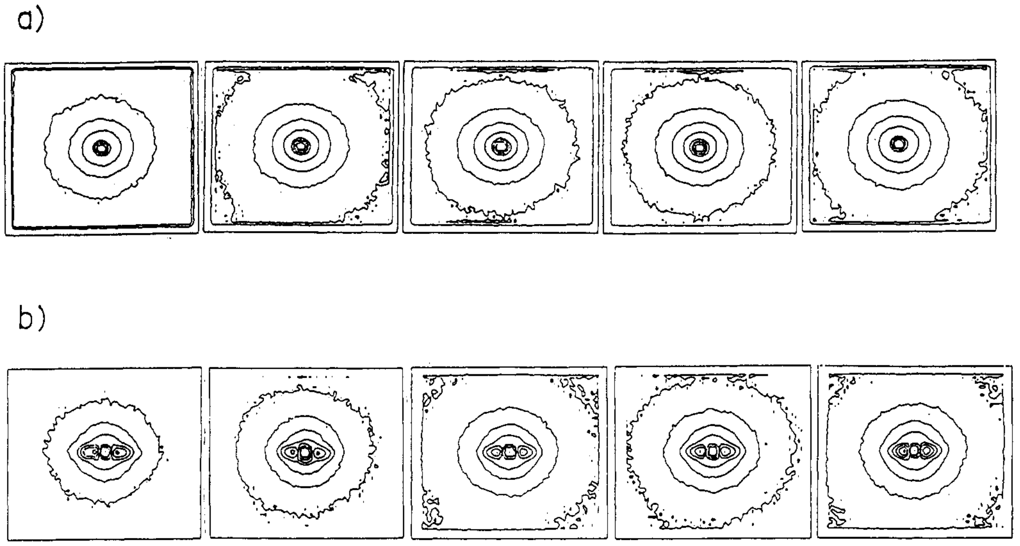

Figure 3. Whole images of contour maps for DP-15/SP-15: (a) through view; (b) edge view. Compositions are 7.0/93.0, 9.1/90.9, 10.0/89.9, 11.0/89.0, and 13.1/86.9 from left to right. The scales are the same as those in Figure 2.

be considered as a possible standard way of estimating incoherent levels of scattering.[15,16] The incoherent scattering intensity for the unlabeled parent polymer is determined from the scattering intensity at a large scattering angle where the diffractions from microdomain structure do not appear. Then, the incoherent scattering intensity for a blend of labeled and unlabeled polymers is evaluated from the product of the experimental values of parent polymer and the calculated ratio of $(1 - T)$ for the blend sample to that for the unlabeled parent polymer. Here T, which is the transmission of the sample film, is given by $\exp(-n\sigma_T d)$, where n is the number density of scatterers, σ_T is the total scattering cross section, and d is the thickness of the sample. For the most contrast-matched sample, DP-33/SP-33, of which the weight composition ratio is 10.5/89.5, the maximum magnitude of correction relative to total scattering intensity is about 12% at the first-order diffraction peak where the R value is evaluated as described below.

Contour maps of scattering intensities of blends of the lowest molecular weight samples, DP-33/SP-33 (I), on the two-dimensional detector are shown in order of mixing ratio in Figure 2. No anisotropic pattern due to diffraction can be observed for the through-view maps regardless of the composition, while strong diffraction patterns are observed and the intensity changes systematically with the composition for the edge-view maps. The second peak in the edge-view maps is regarded as the third-order diffraction maximum, since the even-order diffraction maxima do not appear for samples having equivolume adjacent lamellar phases.[4] The results confirm the fact that the lamellae predominantly align parallel to the film surface and also suggest that the phase contrast matching may be achieved in these systems. In Figure 3, contour maps for blends of the highest molecular weight samples, DP-15/SP-15 (III), are shown. In every edge-view map only one distinct peak is observed and it can be assigned as the third-order diffraction maximum, since the first-order peak cannot be observed in the present q range owing to high molecular weight of the sample. Moreover, it is to be noted that the diffraction intensities for edge views are almost independent of the composition for DP-15/SP-15 (III) blends.

For a more quantitative discussion of phase contrast matching, calculated and experimental values of log R are plotted against the volume fraction of deuteriated chain x in Figure 4. The calculated curve was obtained by introducing 6.47, 1.41, and 1.95 × 10^{10} cm^{-2} for β_{SD}, β_{SH},

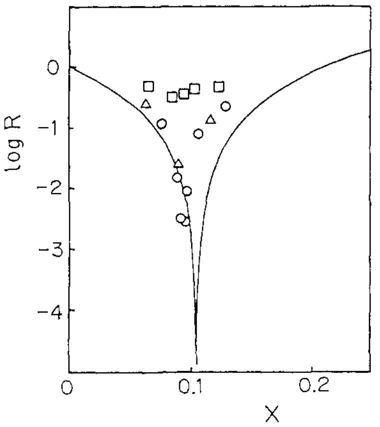

Figure 4. Variation of contrast factor R as a function of x on semilogarithmic scale. Solid line is obtained from eq 2. (○) DP-33/SP-33; (△)DP-77/SP-77; (□) DP-15/SP-15.

and β_P,[17] respectively, into eq 2. The experimental values R_e, on the other hand, were evaluated with the use of the relation

$$R_e = [I_0(1) - I_{90}(1)]_x / [I_0(1) - I_{90}(1)]_0 \qquad (3)$$

where $I_0(1)$ and $I_{90}(1)$ are the intensities of the first- or third-order[4] diffraction at the angle $\psi = 0°$ and 90° on the detector. The subscripts x and 0 refer to the blend sample with volume fraction x of deuteriated chain in polystyrene phase and the unlabeled sample, respectively. Here, x is calculated from weight fraction of labeled and unlabeled copolymers, the polystyrene contents of the copolymers and the bulk densities of poly(styrene-h_8) (1.05) and poly(styrene-d_8) (1.13). It is to be noted that eq 3 is derived under the assumption that lamellae are perfectly oriented so that there is no diffractions at 90°; that is, the diffraction intensity equals the difference between scattering intensities at 0° and 90°. Experimentally, the intensities at 0° and 90° were evaluated by averaging data within the sector of ±5° around 0° and 90°, respectively.

Discussion

As shown in Figure 4, experimental data for the blends with the lowest molecular weights, DP-33/SP-33 (I), are in good agreement with the calculated curve (note that this is a semilogarithmic plot), at least for the lower concentration side of the curve, though there is a difference between the experimental and calculated concentrations at the minimum contrast points. However, the agreement becomes worse with increasing molecular weights and no distinct minimum can be observed for the blend with the highest molecular weight, DP-15/SP-15 (III). Although the orientation of lamellar structures to film surfaces are not perfect in the present samples, the imperfect orientation, on the contrary, makes the discrepancy between the calculated curve and data points smaller, because the diffraction is strongest at the perfect orientation. The results, therefore, indicate that a uniform distribution of a deuteriated block chain can be achieved for the lowest molecular weight blend but not for the higher molecular weight blends.

One possible reason for the nonuniform distribution may be the thermodynamic interactions, since the compatibility becomes less favorable with increasing molecular weight. Yang et al.[18,19] reported that the interaction parameter between hydrogenated and deuterated polystyrene, χ_{HD}, has a value of less than 10^{-4}, while Bates et al.[20] reported the larger value of 1.7×10^{-4} for χ_{HD}. Even if we use the larger value, we have $\chi_{HD}Z \sim 0.2$ for DP-15 which has the highest molecular weight in all our samples, where Z is the degree of polymerization. These values are much lower than the critical value 2, which is the highest value for compatibility of two polymers. The criterion for critical point of unconstrained homopolymers is not necessarily applicable to mixed block chains in a domain structure but the higher critical value may be expected for constrained polymers since the critical value is about 10 block copolymers in a homogeneous phase.[21] As reported in an following paper,[22] moreover, the molecular weights of the deuteriated blocks determined by the single-chain scattering from the through view are comparable with the number-average molecular weights. This result implies that there is no association of deuteriated blocks, at least in the plane parallel to the lamellae. These results, therefore, suggest that the main reason for mismatching is not due to the segregation.

Even if there are no distinct segregations in polystyrene domains, however, we cannot rule out a possibility of excess scattering due to concentration fluctuation[23] in homogeneous mixtures of hydrogenated and deuteriated polystyrenes in the domains, unless χ_{HD} is equal to zero, as suggested by the scattering theory of de Gennes.[24] If this is the case, an assumption that intermolecular correlation of hydrogenated and deuteriated chains is equivalent (eq 29 in ref 6) fails so that eq 1 is not strictly valid. According to de Gennes[24] the scattering intensity increases with increasing molecular weight and concentration up to 50% volume fraction. Since the experimental results in Figure 4 are consistent with this theoretical prediction, the concentration fluctuation in the polystyrene domains may be one possible reason for mismatching.

The difference in chain lengths of labeled and unlabeled blocks also may cause the nonuniform distribution of scattering length density, since segment distributions of block chains may be different for different chain lengths. This may be another reason for the failure of phase contrast matching for DP-15/SP-15 (III) described before since the chain length of DP-15 is larger than that of SP-15.

We conclude, therefore, that the mismatching may be caused by concentration fluctuation in mixtures of hydrogenated and deuteriated polystyrenes in the domains, as well as by a nonuniform distribution of deuteriated species along the direction perpendicular to the lamellae owing to the difference in lengths of the labeled and unlabeled blocks.

In a following paper[22] we will report on the conformations of block chains in the lamellae of the present samples.

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Structural Studies of Semifluorinated n-Alkanes. 3. Synthesis and Characterization of $F(CF_2)_n(CH_2)_m(CF_2)_nF$

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ABSTRACT: A series of semifluorinated triblock oligomers of the form $F(CF_2)_n(CH_2)_m(CF_2)_nF$ (FnHmFn in our notation) have been synthesized and characterized by thermal analysis and low-frequency Raman measurements. Only a single endotherm is observed for the series of F12HmF12 ($6 \le m \le 22$) molecules corresponding to the crystalline melting point. In the limit of vanishing m, the melting point of $F(CF_2)_{24}F$ has been predicted by extrapolation and compared with that which recently appeared in the literature. Low-frequency (30–330 cm^{-1}) Raman measurements revealed the presence of two bands attributable to the longitudinal acoustical mode oscillations (LAM) of the extended molecule.

Introduction

The use of the Raman-active longitudinal acoustical mode (LAM) to characterize ordered chain extension in long-chain oligomers[1] and polymer crystalline lamellae[2] has been well established.[3] The relationship between vibrational frequency and inverse chain length has been found to hold in most cases and allows the determination of the length of an ordered chain sequence once a calibration curve has been determined. In particular, the Raman-active LAM has been useful[4-7] in the study of semiflexible diblock oligomers of the form $F(CF_2)_n(CH_2)_mH$ (referred to as FnHm in our notation). These molecules have been of particular interest because they are precursors of semiflexible polymers and, in addition, exhibit solid–solid phase transitions[7] that have been shown to be analogous to the "rotator" phase in n-paraffins. Previous studies[4] of these materials above their melting points using the Raman-active LAM indicated that only the n-alkyl part of the molecule became disordered, while the stiffer fluorocarbon portion remained rigid (provided that the number of CF_2 units was equal to or less than 12). This unique behavior of the FnHm molecules prompted the synthesis of a series of triblock materials of the form F12HmF12 (with $6 \le m \le 22$).

The preparation of linear diblock materials FnHm is generally accomplished in two steps by the addition of perfluoroalkyl iodide $F(CF_2)_nI$ to a 1-alkene C_mH_{2m} that produces an iodine-containing intermediate (FnHmI), which is subsequently dehalogenated to the final diblock compound (FnHm). The first step generally involves heating the perfluoroalkyl iodide neat with the olefin in the presence of an initiator. Many initiators and catalysts for this process have been described, but simple free radical initiators such as azobis(isobutyronitrile) (AIBN) at an elevated temperature (typically >70 °C for AIBN reactions) are very effective. The second step most often involves the reduction of the iodide intermediate with zinc in ethanolic HCl. We have found that these reaction conditions suffice for most FnHm where n = 6–12 and m = 6–20. Reactions involving perfluoroalkyl or olefin components with boiling points significantly less than 70 °C require the use of pressure vessels or flow systems.

Brace has reported the successful preparation of the triblock halogenated (FnHmFnI2) compounds F4H6F4I2 and F4H8F4I2 (from iodoperfluorobutane and 1,5-hexadiene and 1,7-heptadiene, respectively) under conditions essentially identical with those used for the diblock FnHmI materials.[8] The dehalogenation of these iodine-containing materials to F4H6F4 and F4H8F4 apparently has not been described. In these low molecular weight cases it was possible to fractionate and purify the diiodo intermediates by simple distillation. Brace also describes reactions between 1,3-butadiene and 1,6-heptadiene with iodoperfluorobutane; the butadiene reaction leads to an unstable product, and the heptadiene reaction is unusual in that cyclic reaction products predominate.[9]

In the case at hand, the overall synthetic approach as in Figure 1 is the same. However, with the larger perfluoroalkyl iodides (n = 12) and diolefins (particularly m = 22), the preparation of the triblock FnHmFnI2 intermediates and FnHmFn materials required some modifications in the methods that had previously been successfully used for the preparation of the diblock materials and the smaller triblock systems. It was impossible to distill any of the intermediates or products, and their general lack of solubility or unusual solubility made their overall preparation, purification, and subsequent characterization more difficult. The initial reaction between the per-

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