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Phase Morphology in Block Copolymer Systems [and Discussion]

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Phase morphology in block copolymer systems†

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Microphase separation in block copolymer systems forms well-defined, periodic structure on the sub-micron length scale. This structure arises from the system striving to satisfy the delicate balance of minimizing the area of contact between incompatible chain segments and maximizing the conformational entropy of the macromolecules. Candidate geometries satisfying these constraints possess intermaterial dividing surfaces (IMDS) of constant mean curvature. These include triply periodic, bicontinuous structures related to minimal surfaces. These structures, recently observed in microphase-separated block copolymer systems, also arise in phase-separated surfactant–water systems, indicating the two phenomena may be driven by similar physical mechanisms. A complete description of block copolymer phase morphology requires characterization of the long-range ordered single grain microdomain structure, the defect structures within grains, and the microstructure of the boundary region between grains. The type of structure observed is sensitive to the architecture, chemical composition, and molecular mass of the copolymers. Thermodynamic treatments using a geometrical description of the IMDS provide a means for probing the physics of phase morphology in block copolymers.

1. Introduction

Upon microphase separation, a rich variety of microstructure develops in systems of block copolymers (Molau 1970; Aggarwal 1976). The evolution of microstructure is a result of two competing effects. Dissimilar blocks in the copolymer prefer to segregate due to their inherent chemical incompatibility. However, the spatial extent of phase separation is limited due to the connectivity of the blocks imposed by the architecture of the molecule. Therefore, as a compromise, periodic microstructures arise which strive to minimize the area of contact between the unlike chemical species. An interesting feature of these structures is that their length scale is comparable to the size of the block copolymer molecules – typically on the order of tens of nanometres. Therefore, the appearance of a particular microdomain geometry is quite sensitive to the volume fraction, chemical species, and architecture of the copolymers. In other words, the microstructure is highly *coupled* to the physical and chemical characteristics of the molecules and serves

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as a molecular probe. This observation has fuelled continual research – both experimental and theoretical in nature – attempting to understand the physical processes governing microphase separation. Contrast this behaviour with that observed in phase-separated polymer blends, in which the domains are typically several microns in size. In these systems, the size of the phase-separated structure is nearly independent of the detailed features of the molecules. Rather, the morphology is more a consequence of the kinetic mechanisms driving its growth (Hashimoto 1987).

The morphology present in ordered block copolymer materials in the bulk consists of the periodic long-range microstructures with local disorder arising from defects. As in atomic crystals, both point and line defects occur within 'grains' of the periodic microstructures, and two-dimensional 'grain boundary' structures arise from grain–grain misorientation. Nearly all of the investigations to date have focused on the periodic microstructure present within single grains of the material. Initially, three 'classical' microdomain geometries were found to exist at equilibrium: spheres on a body-centred-cubic lattice, hexagonally packed cylinders, and lamellae (Molau 1970). Lamellae were typically observed for systems nearly symmetric in composition with cylinders and then spheres occurring as the composition became increasingly asymmetric.

As the synthetic techniques yielding polymers improved, 'model' monodisperse materials provided means, for example, to quantitatively test theories relating microdomain size to molecular mass (Hadziioannou & Skoulios 1982). Further advances allowed chemists to synthesize block copolymers of a variety of architectures. Triblock, starblock (Fetters 1969; Bi & Fetters 1975) and more recently, cyclic (Yin & Hogen-Esch 1993) and miktoarm (mixed-arm star) (Iatrou & Hadjichristidis 1993) block copolymers were synthesized in sufficient quantity to permit characterization of their morphology. The availability of molecules having different architectures is enabling physicists to acquire a deeper understanding of the molecular parameters which rule block copolymer microstructure. One advance, directly resulting from the ability to modify block copolymer architecture, occurred in the mid 1980s the characterization of a new microdomain geometry. The ordered bicontinuous double diamond (OBDD) joined the 'classical' morphologies as an *equilibrium* microphase (Thomas *et al.* 1986, 1988; Hasegawa *et al.* 1987).

Bicontinuous structures based on triply periodic minimal surfaces were first proposed as candidate morphologies for describing phase separated microemulsions and cubic phases observed in lyotropic liquid crystals (Scriven 1976, 1977). In these proposed structures, space is partitioned into two continuous subvolumes by a triply periodic minimal surface. In a glycerol mono-oleate–water (lipid–water) system, a double-diamond structure (similar to the OBDD) was proposed to explain observed X-ray scattering patterns (Longley & McIntosh 1983). The formation of the OBDD by microphase-separated block copolymers indicated that phase separation in the two types of systems may be driven by similar physical mechanisms. In the OBDD, the intermaterial dividing surface (IMDS) separating the dissimilar chemical species is one of a family of constant mean curvature surfaces derived from the Schwarz D minimal surface (Anderson & Thomas 1988; Anderson *et al.* 1990). The observation of the OBDD in block copolymer systems signaled that the block copolymer phase diagram is more complex than originally thought, and triggered a proliferation of research to discover new microphases.

Further, the realization that microphase-separated block copolymers can form bicontinuous structures allowed investigators to target families of triply periodic minimal surfaces as candidates for block copolymer microstructure.

Two-dimensional surface defects play an important role in determining the physical properties of bulk systems. This *grain boundary* structure arises due to the impingement of grains during the growth of microphase-separated structure from the disordered state or from grain re-formation at order–order transitions, and comprises the *interphase* region between grains. By disrupting phase continuity (Newnham 1975), the presence of grain boundaries can have a deleterious effect on the transport (Kinning 1987) and mechanical properties (Albalak & Thomas 1993) of microphase-separated materials. In a continuing effort to improve these properties, processing techniques are being used to produce single crystal block copolymer microstructure (Keller *et al.* 1970; Hadziioannou *et al.* 1979; Albalak & Thomas 1993). By extending the degree of long-range order through the removal of grain boundaries, processing produces block copolymer materials with global structural anisotropy showing great promise as optical and barrier media. Although a great deal of research has concentrated on eliminating grain boundary defects, little is known about their nature in block copolymer systems. Recently, the first detailed study on grain boundary microstructure was performed on lamellae-forming block copolymer systems (Gido *et al.* 1993; Gido & Thomas 1993). Differential geometry again played a crucial role in describing this structure. As with the single grain morphologies, the IMDS of certain grain boundary structures can be related to families of minimal surfaces.

Having outlined the scope of this paper, the remaining sections are organised as follows. We first discuss the features of microphase separation in block copolymer systems and present a typical phase diagram for the 'single grain' microdomain morphologies. Following a discussion of the techniques used to characterise block copolymer microstructure, we will present protocols used to develop the phase diagram. We discuss criteria that signal equilibrium behaviour in block copolymer systems, and their application to current experimental procedures. Bicontinuous structures observed in block copolymer systems are then addressed. In this discussion, the intermaterial dividing surface (IMDS) is presented as a general construct to describe the interface in microphase-separated structures. The key geometrical parameters characterizing the IMDS are then outlined. We will show that analyses of the bicontinuous structures in terms of their IMDS is a convenient means for assessing their thermodynamic stability. Finally, we conclude with a discussion of the recent discovery of another new equilibrium morphology. The G^* *phase* is a bicontinuous cubic structure based on Schoen's G (*gyroid*) minimal surface and can be related to the the associate D minimal surface upon which the OBDD structure is based.

2. The block copolymer phase diagram

The block copolymer phase diagram depicts the nature of transitions from the homogeneous, disordered state to an ordered microphase (commonly known as the order–disorder transition or ODT) and transitions between one ordered microphase and another (order–order transitions). Typically, the phase diagram characterizes the dependence of the morphological behaviour on the tempera-

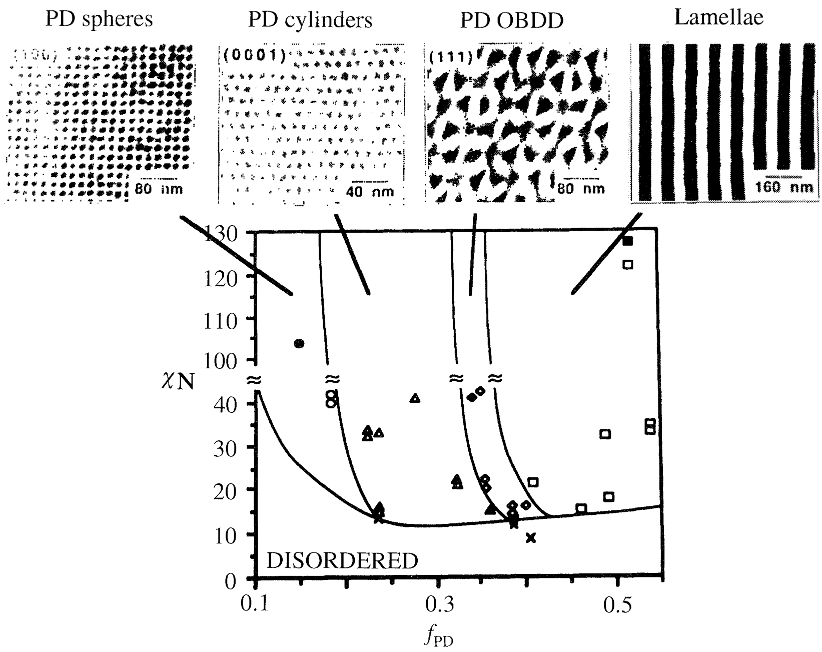

Figure 1. Experimental phase diagram depicting the periodic microphases observed in PS–PD diblock copolymer systems for $f_{\mathrm{PD}} < \frac{1}{2}$: disordered (×), BCC spheres (○), HP cylinders (△), OBDD (◇), and lamellae (☐). The filled symbols depict the characteristics of the diblock systems (χN and f_{PD}) corresponding to the micrographs. The PS phase appears light, and the PD phase appears dark due to staining with $\mathrm{OsO_4}$.

ture of the specimen and the chemical composition of the diblock copolymer. However, guided by theoretical treatments (Leibler 1980; Helfand & Wasserman 1982; Fredrickson & Helfand 1987), the lumped quench parameter, χN, is used rather than temperature. Theories predict that by using χN, the phase diagram for a specified block copolymer architecture will be *universal*; independent of the detailed block copolymer chemistry. χ is the Flory–Huggins parameter used to capture the enthalpic effect of the bonded and non-bonded interactions present in the system (Flory 1953). N is the number of statistical segments in the block copolymer and is proportional to its molecular mass (de Gennes 1979). The temperature dependence of χ is usually expressed as $\chi(T) = a/T + b$, where T is the absolute temperature and a and b are constants depending on the chemical species forming the blocks. However, recent research suggests that $\chi(T)$ may be an oversimplification of the complex array of interactions present within a particular system. In isotopic polymer blends χ exhibits a weak, but non-negligible dependence on composition and molecular mass due to a combination of statistical segment asymmetry and composition fluctuations present in the disordered phase (Bates 1991).

In figure 1 we show a portion of the phase diagram for poly(styrene)–poly(diene) (PS–PD) diblock copolymers (Winey *et al.* 1994; Winey *et al.* 1992; Kinning *et al.* 1987). Plotted as χN versus f, the phase diagram displays the equilibrium microphases currently observed to exist in this system for $f_{\mathrm{PD}} < \frac{1}{2}$. The diene component is either isoprene or butadiene with f_{PD} denoting the volume fraction of diene (assuming incompressibility, $f_{\mathrm{PS}} = 1 - f_{\mathrm{PD}}$). Although the boundaries delineating the phase transitions observed for this system are asymmetric about $f = \frac{1}{2}$, a similar sequence of morphologies is observed for $f_{\mathrm{PD}} > \frac{1}{2}$ for large values of χN with the roles of each component in the microphases transposed. This asymmetry is attributed to differences in the statistical segment lengths and the specific volumes of the styrene and diene components.

For very large values of χN, the block copolymers are *strongly segregated* (Helfand & Wasserman 1982). The interface between the microdomains is quite narrow, with the monomer composition profile resembling a sharp step. In this régime, thermotropic order–order transitions are not expected. The boundaries delineating the different microphases are expected to be vertical and denote the *strong segregation limits* for the observed microstructures (Helfand & Wasserman 1982). At a fixed composition, when χN is decreased (T is increased), the interface between the domains broadens and the system becomes *weakly segregated* near the order–disorder transition (ODT) (Leibler 1980; Fredrickson & Helfand 1987). Weakly segregated systems display a weakly varying, nearly sinusoidal composition profile across the interface which is accurately described by a single Fourier component (Leibler 1980). This prediction has been observed experimentally in a variety of block copolymer systems (Bates & Fredrickson 1990). Thermotropic order–order transitions are predicted approaching the weak segregation régime (Leibler 1980; Fredrickson & Helfand 1987). As shown in figure 1, a disorder–order transition to any microphase can occur by quenching a system of the appropriate composition.

3. Development of the phase diagram

(*a*) *Characterization of the microstructure*

The most effective way to characterize block copolymer morphology is through a combination of experimental techniques. Ideally, this combination should provide information on all relevant length scales. Transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) are just such a combination. Bright-field TEM imaging provides direct visualization of the often complex morphological features (particularly so in the bicontinuous structures). This technique yields *local* detail that is otherwise inaccessible, and facilitates a preliminary selection of candidate microstructures. However, deducing the three-dimensional structure from a systematic tilt series of two-dimensional projections obtained in the TEM is a challenging morphological problem. In addition, selected area low angle electron diffraction performed *in situ* on well-ordered structure allows a preliminary characterization of the microlattice. However, due chiefly to the small sections of material examined, the possible effects of staining, and sample deformation during microtoming, quantitative information available on the characteristics of the microlattice is limited. SAXS performed on bulk samples of unstained material on the other hand, provides information on a *global* scale; allowing quantitative determination of the symmetries and parameters describing the microlattice. This technique enables ‘averages’ to be taken over large statistical samples by probing millions of unit cells. Unfortunately this ‘averaging’ process, coupled with grain misorientation and the presence of defects, tends to obscure high order reflections needed to precise the fine features of the microstructure for a unique assignment of a microdomain geometry to a particular system.

However, in combination, these techniques are quite powerful and provide a nearly complete description of the ordered microphases on all length scales. Due to the complementary nature of TEM and SAXS, they may be used self-consistently. Low angle electron diffraction patterns and digitally Fourier transformed TEM micrographs can be compared with the observed X-ray scattering patterns, allowing quantitative assignment of the projection direction and symmetries present in an image. Moreover, candidate structure models can be critically assessed by comparison of the calculated scattering profile and simulated images with experimental SAXS and TEM data. Relying solely on either a local or global technique quite often leads to a misinterpretation of block copolymer microstructure.

Investigators have also been successful by using other combinations of techniques such as small-angle neutron scattering and rheological measurements to characterize systems where there is insufficient contrast for TEM studies (Bates & Fredrickson 1990). Although this combination suffers from the problems associated with global techniques, a wealth of information about block copolymer microstructure can be obtained; particularly for single crystal systems (which overcome global averaging). These techniques were successful in characterizing the ODT in symmetric, lamellae-forming block copolymer systems and detecting order–order transitions (Hamley *et al.* 1993).

(*b*) *Experimental protocols and equilibrium conditions*

To develop a phase diagram for a given block copolymer architecture, ideally one would perform the following set of experiments. First, synthesize a system of block copolymers having a well-defined molecular mass and composition. Then, having N and f specified, quench the system from the high temperature (low χN) disordered state into the microphase-separated state by decreasing temperature (increasing χN) and observe the morphological behaviour at selected temperatures. A suitable range of temperatures would be chosen to permit characterization of the system in states ranging from disordered, through the weak segregation régime, and ending in the strongly segregated state. Temperature could then again be increased and the morphological behaviour followed as the system approaches the disordered phase by the reverse pathway. This critical additional protocol would be used to ensure an important criterion for the establishment of equilibrium behaviour; the *reversibility* of each transition.

There are practical problems inherent in this approach. One is thermodynamic in nature and concerns the behaviour of χ. In addition to being weakly temperature dependent, χ can be quite large, especially for the usual systems suitable for analysis by TEM. Therefore a temperature range of several hundred degrees may be necessary to span all the régimes of segregation. Unfortunately, the temperature range may involve quenching the system below its glass transition (a concern when trying to explore strong segregation behaviour in systems having low N) or heating the system above its thermal decomposition temperature (problematic when trying to place high N systems in the weak segregation régime). To avoid this difficulty, one could synthesize a series of systems at a fixed composition, but varying in molecular mass. However, another problem still exists, which originates from the 'polymeric' nature of the systems and its impact on kinetics. The relaxation processes necessary to equilibrate the systems exhibit a strong molecular mass dependence. Consider a melt of amorphous bulk homopolymer chains above their glass transition temperature. For unentangled systems Rouse dynamics prevail, with the chain relaxation time in the bulk, τ_B, proportional to N^2 (Doi & Edwards 1986). For highly entangled, reptating chains the relaxation process slows dramatically, with $\tau_B \sim N^3$ (Doi & Edwards 1986). The situation for block copolymers only worsens. Imposing an interface between the blocks restricts centre-of-mass motion, further retarding chain relaxation; particularly for the high molecular mass, strongly segregated systems. In this case, systems may have to anneal at a large quench depth for extremely long periods of time to form equilibrium structures.

To circumvent these difficulties alternative experimental protocols have been developed. Historically the first, and still the most widely used procedure is to slowly cast films of block copolymers from a solution, followed by an annealing treatment. An ideal solvent for the system would be non-preferential, having no affinity toward any of the chemical species present in the copolymer. The advantages of this approach are two-fold. The first is that with solvent added, the thermodynamics, specifically the degree of quench can be controlled. By dilution of the block copolymer molecules, the solvent effectively mediates interactions between the dissimilar blocks. The quench parameter becomes $\phi\chi N$, with ϕ the concentration of block copolymer in the solution (Fredrickson & Leibler 1989)†. Therefore, any block copolymer system may be placed in the disordered state with the proper choice of ϕ. This is particularly advantageous for high molecular mass block copolymers, which would otherwise require extreme heating to become disordered.

The second advantage is the reduction in the chain relaxation time. Typically at the outset of solution casting, the block copolymer chains are in the semidilute régime. The added solvent decreases the molecular relaxation time appreciably. For example, in the semidilute régime entangled homopolymers in a good solvent display $\tau_{SD} \sim \phi^{3/2}N^3$ (Doi & Edwards 1986), a substantial decrease from τ_B when ϕ is small. (In solution casting, initial concentrations are typically $\phi \sim 0.05$, then $\tau_B \sim 100\tau_{SD}$.) Therefore, when a system is slowly cast from solution, the chain relaxation process occurs more rapidly than in the bulk state. This effect is important during the critical stages of the organization process; typically near the ODT and in the weak segregation régime where order–order transitions are expected. After solvent removal, a subsequent annealing treatment is expected to facilitate further chain relaxation allowing the microphase-separated structure to approach equilibrium.

Complications, however, may result from this approach and perturb the system away from equilibrium. In addition to the solvent acting as another component in the system, obtaining a non-preferential solvent over a range of temperatures can be difficult, if not impossible. (No solvent is absolutely non-preferential, even the best choice of solvent for a particular system will exhibit some block-affinity.) Thermotropic order–order transitions can occur from a metastable microphase-separated 'state' induced by casting the system from a strongly preferential solvent, to the typically observed equilibrium structure (Thomas *et al.* 1986; Saku-

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† The use of $\phi\chi N$ to represent the degree of quench is a *mean-field* approximation, strictly valid for *concentrated* solutions. All effects of composition fluctuations and excluded volume interactions in dilute and semidilute solutions are ignored (Fredrickson & Leibler 1989).

rai *et al.* 1993). Another concern is the unknown effect of the weak convective flow fields, caused by solvent evaporation, on the evolving microstructure. These potential non-equilibrium effects can be minimized by ensuring slow solvent evaporation followed by an annealing treatment.

A different experimental protocol uses the direct application of a flow field on the bulk block copolymer system to drive the system toward equilibrium (Hamley *et al.* 1993). In general, this technique tends to eliminate surface (grain boundary) defects and promote single crystal orientation. As an inherent part of a morphological characterization technique mentioned above, rheometry, the imposed flow field has an additional feature, it can act as a *symmetry breaking* element (Amit 1978). The current rationale behind the use of external fields to probe block copolymer microstructure is that the application of a symmetry breaking operation on the system facilitates a phase transition. Typically, a shear field is applied to the system, strongly perturbing the microstructure. To investigate thermotropic transitions, temperature is varied at a fixed rate of shear and the storage and loss moduli of the material are measured. A discontinuous change in the storage modulus versus temperature curve is considered to signal an order–disorder or an order–order transition. In the case of an order–order transition, the shear field may assist the molecular re-organization process and reduce any kinetic barriers that could impede the transition. This appears to be particularly attractive for studying high molecular mass systems where microstructures can become essentially locked-in due to the inherently slow molecular relaxation processes.

Although this technique benefits by not introducing additional chemical components into the system, the applied shear field may affect equilibrium properties. Care must be taken to determine that the imposed flow field does not induce a phase transition that otherwise would not occur. One must also ensure that a newly discovered ‘equilibrium phase’ is not a ‘metastable state’ precipitated by the flow field. When studying order–order transitions in the presence of a strong flow field, one should keep in mind the Curie principle: The ordered microstructure under flow will retain only those symmetries of its crystallographic point group which are common with those of the applied flow field (Newnham 1975). Moreover, should the pre-transitional microstructure possess point group symmetries incompatible with the symmetries associated with the flow field, defects may form, strongly affecting the mechanical behaviour of the system. If a large number of defects arise in the system, trends in the modulus versus temperature curve are highly dependent on relative dynamics of the mechanism of defect formation (through shearing) and that of defect annihilation (promoted by annealing). Therefore, an extremum in the modulus versus temperature curve may result from a transition in the dominant mechanism (defect creation versus annihilation) rather than from an order–order transition. Therefore, to ensure that an observed order–order transition corresponds to phase behaviour under quiescent conditions, *weak* flow fields with varying symmetry elements should be used. As with solvent casting, ensuring the reversibility of observed order–order transitions is critical. However, if strong flow fields are used, this may be impossible since the accumulation of defects and their subsequent annihilation is not a thermodynamically reversible process.

To determine that an ordered system is in a state of thermodynamic equilibrium, one should use the following criteria. First, determine that the observed

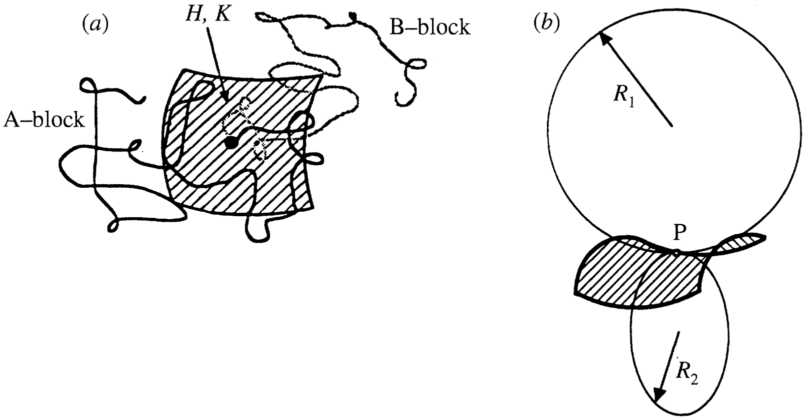

Figure 2. (*a*) A patch of an intermaterial dividing surface (IMDS) containing a single A–B diblock copolymer junction. (*b*) A schematic illustrating the two principal radii of curvature (R_1 and R_2) at a point P on the IMDS.

microstructure displays a high degree of *long-range order* and second, verify that any observed transition is *reversible*. These criteria were used in recent studies to establish that observed thermotropic transitions between spheres and cylinders (Sakurai *et al.* 1993) and cylinders to lamellae (Hajduk *et al.* 1994*a*) were equilibrium processes.

4. Bicontinuous structure in block copolymers

(*a*) *The intermaterial dividing surface*

In strongly segregated block copolymers the composition profile across the interface is quite narrow. The interfacial region between the components can therefore be well-represented as an *intermaterial dividing surface* (IMDS). A schematic of a saddle-shaped patch of an IMDS containing the junction point of a single A–B diblock copolymer chain is shown in figure 2*a*. The surface is conveniently described in terms of its local *mean* and *gaussian* curvatures, which are functions of the principal radii of curvature at each point on the surface (Struik 1988). As shown in figure 2*b*, the *principal curvatures* are the reciprocals of the two radii of curvature, $c_1 = 1/R_1$ and $c_2 = 1/R_2$. The *mean curvature*, H, of a surface at any given point is the arithmetic average of the two principal curvatures, $\frac{1}{2}(c_1 + c_2)$, and is a measure of the rate of change in area to first order under a normal deformation. The *gaussian curvature*, K, is the product of the principal curvatures, $c_1 c_2$.

Knowledge of the behaviour of H and K for the IMDS of a candidate microdomain geometry also allows one to address its thermodynamic properties. Based on a formulation of the free energy for surfactant systems (de Gennes & Taupin 1982) a phenomenological description of the thermodynamics of microphase-separated block copolymer systems has been developed in terms of these parameters (Wang & Safran 1991). Formulated as a curvature expansion, the free energy of the system is related to H and K through the calculated bending and saddle-splay moduli, respectively (Helfrich 1973). This approach appears to be a viable method for addressing the thermodynamics of microphase separation, particularly for bicontinuous structures derived from minimal and constant mean curvature surfaces.

(*b*) *Periodic minimal surfaces and the stability of the OBDD*

In the strong segregation régime, the interfacial energy (the enthalpic contribution to the thermodynamic free energy) is the predominant thermodynamic driving force and is at a minimum for microdomain geometries possessing interfaces of *constant mean curvature* (CMC). The connectivity constraint (the entropic contribution) characteristic of the long-chain nature of polymers, however, requires that the resulting structure must be periodic in space. As a result, *triply periodic minimal surfaces* arise as suitable candidates for block copolymer microstructures. These surfaces are special classes of triply periodic CMC surfaces ($H = C$) having zero mean curvature ($H = 0$) and, in general, partition space into two equal three-dimensional continuous subvolumes†. For certain minimal surfaces, constant mean curvature and *constant thickness* (CT) families may be derived which partition space unequally. Triply periodic CMC and CT surface families, then, may serve as candidate interfaces to describe microphase-separated block copolymers that are asymmetric in composition.

The OBDD observed in PS–PI starblock and and diblock copolymers occurs at $f_{\mathrm{PS}} = 0.27 - 0.32$ and $f_{\mathrm{PS}} = 0.62 - 0.66$, and is described by members of the CMC family of the triply periodic Schwarz D (diamond) minimal surface. Inscribed on a lattice having the symmetries of the $Pn3m$ space group, the CMC D-surface exhibits a pronounced minimum in surface area per unit volume, when $f_{\mathrm{M}} = 0.262$, where f_{M} is the volume fraction of the minority component (Anderson & Thomas 1988; Anderson *et al.* 1990). Thus, the calculated interfacial free energy density for this structure is at a minimum in the vicinity of the observed region of stability of the OBDD. However, in an initial evaluation of the total free energy (including both entropic and enthalpic contributions) of the OBDD along with other candidate microdomain geometries, hexagonally packed cylinders were predicted to be stable in the range of composition that the OBDD is observed. This result was attributed to a series of approximations used to evaluate the entropic contribution to the free energy, and their impact on the small discriminations in free energy performed when assessing the stability of candidate microstructures.

However, a recent development using a geometric model of the IMDS within polymer brush theory (Milner *et al.* 1988) to describe strongly segregated block copolymers predicts that an OBDD structure *is* stable and lies between hexagonally packed cylinders and lamellae at compositions $f_{\mathrm{M}} = 0.19 - 0.27$ (Olmsted & Milner 1993). Further, similar calculations for a surface derived from the Schwarz P (cubic) surface (related to the D-surface through the *Bonnet transformation* (Anderson *et al.* 1990)) using this formalism show that it is unstable relative to the D-surface present in the OBDD (Olmsted & Milner 1993). This method of addressing the shape of the IMDS in this formalism was previously used to model the doubly periodic CMC surfaces in grain boundary structures (Gido & Thomas 1994). Although the predicted composition range for OBDD is at a lower minority component than the observed range for PS–PI block copolymers, the predicted

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† Two notable exceptions are the $I - WP$ and the $F - RD$ minimal surfaces which subdivide volume in a ratio of 53:47 volume percent (Anderson *et al.* 1990).

stability of the OBDD strongly suggests that it is an equilibrium microphase in strongly segregated block copolymer systems.

(*c*) *The G* phase: a new equilibrium microstructure*

As part of a SAXS study on the order–disorder transition of a series of PS–PI block copolymers, one system (a PS–PI diblock copolymer, $M_{\text{tot}} = 27\,400$, $f_{\text{PS}} = 0.33$) exhibited a high temperature diffraction signature inconsistent with any of the observed equilibrium microstructures: BCC spheres, HP cylinders, OBDD, and lamellae (Gobran 1990). Upon solution casting from toluene, lamellar microdomains were observed. After annealing at a temperatures above 120 °C, the lamellar diffraction pattern vanished, and a new set of peaks evolved, appearing at spacing ratios of $\sqrt{3}$ and $\sqrt{4}$. TEM investigations of quenched samples (to retain the high temperature phase) confirmed that an order–order transition occurred, from lamellae to another microphase possibly displaying a cubic symmetry. Unfortunately, due to the limited long-range order in the sample, definitive characterizations of the 'new' microdomain geometry and the nature of the order–order transition were not possible.

A recent study of this diblock system, using TEM and SAXS, further probed the questions raised in the first investigation (Hajduk *et al.* 1994*b*). By using long annealing periods to extend the degree of long-range order in the sample, improved X-ray instrumentation, in combination with TEM projections along axes of high symmetry and their Fourier transforms, a complete characterization of the morphological behaviour of this system was possible. Figure 3 shows the two types of SAXS diffraction patterns obtained for this sample. The first, lower temperature pattern (*a*) is characteristic of lamellae while the second, higher temperature pattern (*b*) is consistent with a microstructure possessing cubic symmetry and best corresponds with the $Ia3d$ space group. The $Ia3d$ symmetry is a likely candidate for block copolymer microstructures, since structures exhibiting $Ia3d$ symmetries occur in systems of liquid crystals (Charvolin & Sadoc 1987).

TEM played a key role in developing a specific model for the structure. Comparison of the TEM micrographs with computer simulated projections of possible interfacial geometries enabled a selection of suitable candidate IMDS structures. Figure 4*a* is a digitized bright-field TEM micrograph of the diblock quenched from a high temperature phase, microtomed, and stained with OsO_4. The indexed Fourier transform of this projection (figure 4*b*, *c*) indicates that it is taken along a three-fold axis of symmetry. Other views display four-fold symmetry. The observation of both three- and four-fold projections in the same sample signals that the microstructure possesses cubic symmetry. The three-fold projection is reminiscent of the [1 1 1] projection of the OBDD, typically observed in this compositional region of the phase diagram. It is also consistent with [1 1 1] projection of *constant thickness structures* (CT) families of another minimal surface – the triply periodic G (*gyroid*) surface (Schoen 1970), shown in figure 4*d* (see caption)†. Although the [1 1 1] projections are of the G* phase and the OBDD are quite similar, the structure of the OBDD is inconsistent with the X-ray data. This was shown by

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† Note, that since the G-surface is minimal, it partitions space into two equal volumes. Since $f = 0.33$ for this system, *constant thickness surfaces* derived from the G-surface were used for the computer simulated projections and scattering profiles. Although a CMC family is not yet developed for the G-surface, it is likely that one exists.

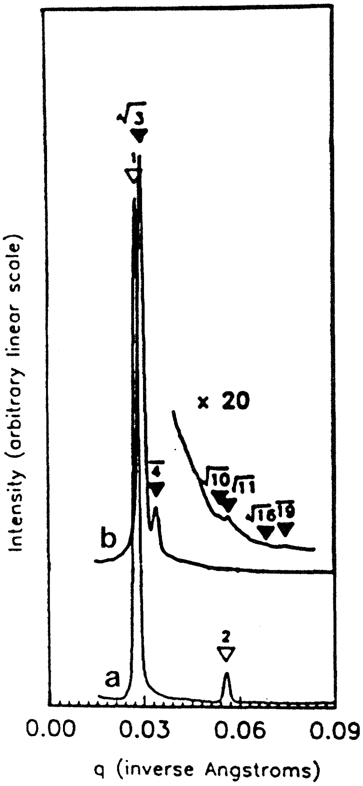

Figure 3. SAXS diffraction patterns observed for PS–PI diblock, $M_{\text{tot}} = 27\,400$, $f_{\text{PS}} = 0.33$ annealed at (*a*) 90 °C for 2 h, and (*b*) 150 °C for 4 h, then 120 °C for 4 h. (*a*) exhibits integer order reflections, consistent with a lamellar microstructure having $D = 226$ Å. (*b*) characterizes the high-temperature cubic phase, with reflections consistent with those of the $Ia3d$ space group. Reflections are observed at spacing ratios of $\sqrt{3}$, $\sqrt{4}$, $\sqrt{10}$, $\sqrt{11}$, $\sqrt{16}$, and $\sqrt{19}$.

using the CT-G and CT-OBDD models to simulate the X-ray scattering patterns. The scattering peak intensities calculated for the G* phase closely match those experimentally observed, while the calculated reflections for the OBDD structure are incompatible with the data. (This is a prime example of a situation where relying on a single TEM projection of the structure along an axis of high symmetry can lead to a misinterpretation of the three-dimensional microstructure.)

Further heating allowed an investigation of the order–disorder transition in this system. As the specimen was heated, the higher-order diffraction peaks disappeared with the $\sqrt{3}$, $\sqrt{4}$ peaks persisting up to a temperature of 175 °C, at which the sample rapidly became disordered, exhibiting one broad diffraction peak. The equilibrium nature of the lamellae–G* and G*–disorder transitions was tested by reversing the above procedure, cooling the sample from 175 °C through the range of temperatures described above. As the sample cooled from 175 °C, the $\sqrt{3}$, $\sqrt{4}$ peaks reappeared, signaling the appearance of the G* phase ($Ia3d$) morphology. With further cooling to 110 °C, the diffraction peaks corresponding to the lamellar diffraction signature became well developed as the system was annealed for long times. Therefore, the observed G* phase and the lamellar phase are *equilib-*

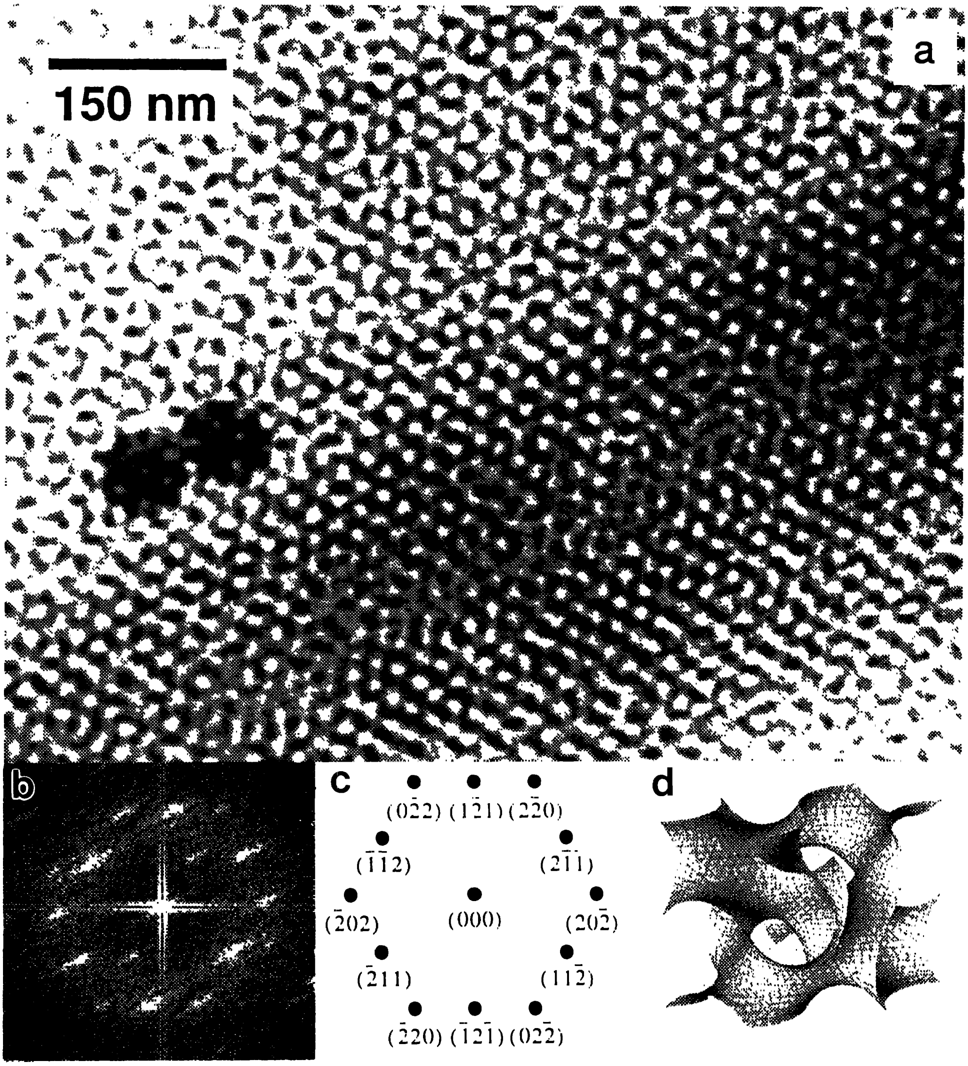

Figure 4. Bright-field TEM micrograph (a) of the sample analysed by SAXS in figure 3b. This projection shown exhibits three-fold symmetry as indicated in its indexed digital Fourier transform ((b) and (c)). A constant thickness (CT) surface structure consistent with this projection can be derived from Schoen's triply periodic minimal gyroid surface shown (d). (Anderson *et al.* 1992.)

rium phases due to their observed long-range order and the *reversibility* of the disorder–G* and the G*–lamellae transitions.

It is interesting to examine on a molecular level the physical mechanism promoting the lamellae–G* transition. The lamellar microstructure at 120 °C initially exhibits a domain spacing, $D = 212$ Å. This implies half-layer (brush) thicknesses of 36 Å for PS and 70 Å for PI. After annealing at 120 °C for 5 h, the lamellae-G* phase transition is nearly complete. Calculations using the CT-G-surface for $f = 0.33$ predict a constant half-layer thickness of 60 Å for the PI half-layers and a range of half-thicknesses of the PS channels, varying from 50 Å to 80 Å with an average of 60 Å. In the G* phase the PS chains are more relaxed in this phase than in the lamellar microstructure. Although the PI chains are slightly more compressed in the G* phase than in lamellae, the shorter PS chains are 'stiffer' entropy springs (de Gennes 1979) and play a dominant role in the total chain deformation energy. At higher temperatures, this entropic contribution is expected to be the predominant contribution to the total free energy of the system. Therefore, the lamellae–G* transition is entropically driven, and originates from the relaxation of the PS chains. Calculations of the interfacial area per chain for the CT-G-surface and the lamellar microstructure further confirm this mechanism.

5. Conclusions

Significant advances have occurred in the understanding of the physics of phase morphology in block copolymers over the past 30 years, and research in this area continues to intensify. Improvements in the synthetic routes to novel block copolymers, the use of complementary techniques to characterize microphase-separated structure, and advances in the theoretical formalisms have allowed detailed investigation of aspects of the equilibrium phase diagram. Due to the slow kinetics governing chain relaxation in polymeric systems, care must be exercised when developing the phase diagram for a particular block copolymer system. The observation of long-range order, and reversibility are useful criteria to establish equilibrium behaviour in order–order transitions. In addition to developing the phase diagram, recent research further probes the more challenging aspects of the evolution of microphase-separated structure between the ordered phases. Largely open areas include the characterization and role of defect morphology and its impact on both phase transitions and on physical properties, and the effect of confinement (e.g. thin film constraints) on block copolymer microstructure. As with the long-range ordered, periodic bulk morphology, structures derived from minimal surfaces and their CMC and CT families appear to be likely candidates for these new morphologies.

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References

Aggarwal, S. L. 1976 Structure and properties of block copolymers and multiphase polymer systems: an overview of present status and future potential. *Polymer* **17**, 938–956.

Albalak, R. J. & Thomas, E. L. 1993 Microphase separation of block copolymer solutions in a flow field. *J. Polym. Sci. (Phys.)* **31**, 37–46.

Amit, D. J. 1978 *Field theory, the renormalization group, and critical phenomena.* New York: McGraw Hill.

Anderson, D. M. & Thomas, E. L. 1988 Microdomain morphology of star copolymers in the strong-segregation limit. *Macromolecules* **21**, 3221–3230.

Anderson, D. M., Davis, H. T., Scriven, L. E. & Nitsche, J. C. C. 1990 Periodic surfaces of prescribed mean curvature. *Adv. chem. Phys.* **77**, 337–396.

Anderson, D. M., Bellare, J. B., Hoffman, J., Hoffman, D., Gunther J. & Thomas, E. L. 1992 Algorithms for the computer simulation of 2D projections from structures determined by dividing surfaces. *J. Coll. Int. Sci.* **148**, 398–414.

Bates, F. S. & Fredrickson, G. H. 1990 Block copolymer thermodynamics: theory and experiment. *A. Rev. Phys. Chem.* **41**, 525–557.

Bates, F. S. 1991 Polymer–polymer phase behavior. *Science, Wash.* **251**, 898–905.

Bi, L.-K. & Fetters, L. J. 1975 Domain morphology of star block copolymers of polystyrene and polyisoprene. *Macromolecules* **8**, 90–92.

Charvolin, J. & Sadoc, J. F. 1987 Periodic systems of frustrated fluid films and bicontinuous cubic structures in liquid crystals. *J. Phys.* **48**, 1559–1569.

de Gennes, P.-G. 1979 *Scaling concepts in polymer physics.* Ithaca: Cornell University.

de Gennes, P.-G. & Taupin, C. 1982 Microemulsions and the flexiblity of oil/water interfaces. *J. Phys. Chem.* **86**, 2294–2304.

Doi, M. & Edwards, S. F. 1986 *The theory of polymer dynamics.* Oxford: Clarendon.

Fetters, L. J. 1969 Synthesis of block polymers by homogeneous anionic polymerization. *J. Polym. Sci.* C **26**, 1–35.

Flory, P. J. 1953 *Principles of polymer chemistry.* Ithaca: Cornell University.

Fredrickson, G. H. & Helfand, E. 1987 Fluctuation effects in the theory of microphase separation in block copolymers. *J. chem. Phys.* **87**, 697–705.

Fredrickson, G. H. & Leibler, L. 1989 Theory of block copolymer solutions: nonselective good solvents. *Macromolecules* **22**, 1238–1250.

Gido, S. P., Gunther, J., Thomas, E. L. & Hoffman D. 1993 Lamellar diblock copolymer grain boundary morphology. 1. Twist boundary characterization. *Macromolecules* **26**, 4506–4520.

Gido, S. P. & Thomas, E. L. 1994 Lamellar diblock copolymer grain boundary morphology. 2. Scherk twist boundary energy calculations. *Macromolecules.* **27**, 849–861.

Gobran, D. A. 1990 Ph.D. Dissertation, University of Massachusetts, Amherst.

Hadziioannou, G. & Skoulios, A. 1982 Molecular mass dependence of lamellar structure in styrene/isoprene two- and three-block copolymers. *Macromolecules* **15**, 258–262.

Hadziioannou, G., Mathis A. & Skoulios, A. 1979 'Monocristaux' de copolymeres trisequences styrene/isoprene/styrene presentant la structure cylindrique. I. Etude de l'orientation par diffraction des rayons X aux petits angles. *Coll. Polym. Sci.* **257**, 15–22.

Hajduk, D. A. *et al.* 1994*a* Observation of a reversible thermotropic order–order transition in a diblock copolymer. *Macromolecules* **27**, 490–501.

Hajduk, D. A. *et al.* 1994*b* The gyroid: a new equilibrium morphology in weakly segregated diblock copolymers. *Macromolecules.* (In the press.)

Hamley, I. W., Koppi, K. A., Rosedale, J. H., Bates, F. S., Almdal, K. & Mortensen, K. 1993 Hexagonal mesophases between lamellae and cylinders in a diblock copolymer melt. *Macromolecules* **26**, 5959–5970.

Hasegawa, H., Tanaka, H., Yamasaki, Y. & Hashimoto, T. 1987 Bicontinuous microdomain morphology of block copolymers. 1. Tetrapod-network structure of polystyrene–polyisoprene diblock polymers. *Macromolecules* **20**, 1651–1662.

Hashimoto, T. 1987 Structure formation in polymer mixtures by spinodal composition. In *Current topics in polymer science* (ed. R. M. Ottenbrite, L. A. Utracki & S. Inoue), vol. 2, pp. 199–242. New York: Hanser.

Helfand, E. & Wasserman, Z. R. 1982 Microdomain structure and the interface in block copolymers. In *Developments in block copolymers* (ed. I. Goodman), vol. 1, pp. 99–125. New York: Applied Science.

Helfrich, W. 1973 Elastic properties of lipid bilayers: theory and possible experiments. *Z. Naturf.* C **28**, 693–703.

Iatrou, H. & Hadjichristidis, N. 1992 Synthesis of a model 3-miktoarm star terpolymer. *Macromolecules* **25**, 4649–4651.

Keller, A., Pedemonte, E. & Willmouth, F. M. 1970 Macro-lattice from segregated amorphous phases of a three block copolymer. *Nature, Lond.* **225**, 538–539.

Kinning, D. J., Thomas, E. L. & Ottino, J. M. 1987 Effect of morphology on the transport of gases in block copolymers. *Macromolecules* **20**, 1129–1133.

Leibler, L. 1980 Theory of microphase separation in block copolymers. *Macromolecules* **13**, 1602–1617.

Longley, W. & McIntosh, T. J. 1983 A bicontinuous tetrahedral structure in a liquid-crystalline lipid. *Nature, Lond.* **303**, 612–614.

Milner, S. T., Witten, T. A. & Cates, M. E. 1988 Theory of the grafted polymer brush. *Macromolecules* **21**, 2610–2619.

Molau, G. E. 1970 Colloidal and morphological behavior of block and graft copolymers. In *Block polymers* (ed. S. L. Aggarwal), pp. 79–106. New York: Plenum.

Newnham, R. E. 1975 Structure-property relations. In *Crystal chemistry of non-metallic materials* (ed. R. Roy), vol. 2. New York: Springer-Verlag.

Olmsted, P. D. & Milner, S. T. 1993 Strong-segregation theory of bicontinuous phases in block copolymers. Preprint.

Sakurai, S., Momii, T., Taie, K., Shibayama, M. & Hashimoto, T. 1993 Morphology transition from cylindrical to lamellar microdomains of block copolymers. *Macromolecules* **26**, 485–491.

Sakurai, S., Kawada, H., Hashimoto. T & Fetters, L. J. 1993 Thermoreversible morphology transition between spherical and cylindrical microdomains of block copolymers. *Macromolecules* **26**, 5796–5802.

Schoen, A. H. 1970 Infinite periodic minimal surfaces without self-intersections. *NASA Tech. Note*, TN D–5541.

Scriven, L. E. 1976 Equilibrium bicontinuous structure. *Nature, Lond.* **263**, 123–125.

Scriven, L. E. 1977 Equilibrium bicontinuous structures. In *Micellization, solubilization, and micromemulsions* (ed. Mittal, K. L.), vol. 2, pp. 877–893. New York: Plenum.

Struik, D. J. 1988 *Lectures on classical differential geometry.* New York: Dover.

Thomas, E. L., Alward, D. B., Kinning, D. J., Martin, D. C., Handlin, D. L. & Fetters, L. J. 1986 Ordered bicontinuous double-diamond structure of star block copolymers: a new equilibrium microdomain morphology. *Macromolecules* **19**, 2197–2202.

Thomas, E. L., Anderson, D. M., Henkee, C. S. & Hoffman, D. 1988 Periodic area-minimizing surfaces in block copolymers. *Nature, Lond.* **334**, 598–601.

Wang, Z.-G. & Safran, S. A. 1991 Curvature elasticity of diblock copolymer monolayers. *J. chem. Phys.* **94**, 679–687.

Winey, K. I., Gobran, D. A., Xu, Z., Fetters, L. J. & Thomas, E. L. 1994 Compositional dependence of the order–disorder transition in diblock copolymers. *Macromolecules.* **27**, 2392–2397.

Winey, K. I., Thomas, E. L. & Fetters, L. J. 1992 The ordered bicontinuous double-diamond morphology in diblock copolymer/homopolymer blends. *Macromolecules* **25**, 422–428.

Yin, R. & Hogen-Esch, T. E. 1993 Synthesis and characterization of narrow molecular weight distribution polystyrene–poly(dimethyl siloxane) macrocyclic block copolymers and their isobaric precursors. *Macromolecules* **26**, 6952–6957.

Discussion

F. C. FRANK (*University of Bristol, U.K.*). I think your method of generating a daughter surface adds a constant increment to all principal radii of curvature, and so, starting from one having total curvature $1/R_1$ and $1/R_2$, does not produce one which we might like to have with constant sum of the reciprocals of principal radii of curvature but one with constant sum of the reciprocals of principal curvatures instead.

E. L. THOMAS. If we take the principal radii of curvature of the base surface at a point u, v to be R_1 and R_2 then the mean curvature of the base surface is $H(u,v) = \frac{1}{2}[1/R_1 + 1/R_2]$. For a daughter surface displaced a distance s along the local normal to the base surface, the principal radii of curvature become as you indicate $(R_1 + s)$ and $(R_2 + S)$. In general the daugher surface has a local mean curvature H_s given by $H_s = (H + sK)/(1 + 2sH + s^2K)$, where H and K

are the mean curvature and gaussian curvature of the base surface at the point (u, v) respectively.

The gaussian curvature is equal to the product of the two principal curvatures $c_1(u, v)c_2(u, v)$. Because $c_1(u, v) = -c_2(u, v)$ for a minimal surface, $H = 0$ everywhere while the gaussian curvature varies over the base surface. Thus the constant thickness daughter surface has variable mean curvature. For certain triply periodic minimal surfaces it has been shown that the constant thickness surface is a close approximation to a constant mean curvature surface with the same space group symmetries as theminimal surface, provided the displacement of the daughter surface is not too large (D.M. Anderson *et al.*, *Proc. natn. Acad. Sci. U.S.A.* **85**, 5364 (1988)).

J. S. HIGGINS (*Imperial College, U.K.*). What would be the effect on the phase diagram and the structure if the block lengths of the copolymer were polydisperse?

E. L. THOMAS. The polydispersity of our sample (synthesized by L. Fetters of Exxon) is low, around 1.05, but I do not believe a narrow molecular mass distribution is necessarily critical for obtaining the gyroid phase. The only published work that addresses really large variation of molecular mass at constant composition is that by Hashimoto's group, where they purposely blended two lamellar forming diblocks of the same composition but various molecular masses (T. Hashimoto *et al.*, *Macromolecules* **26**, 2895 (1993)). They found that for molecular mass ratios of less than about 4, the blend formed a single lamellar structure and only for very different molecular mass diblocks $M_1/M_2 > 10$ did macrophase separation into two lamellar phases occur. Work by our group has shown that a blend of a cylindrical forming diblock with a lamellar forming diblock will form the OBDD structure if the composition is adjusted to that of the OBDD composition window for a single diblock (D.W. Schwark, Ph.D thesis, University of Massachusetts, U.S.A. (1992)).

A. KLUG (*Cambridge, U.K.*). Are the crystals or crystallites that you have shown good enough to be able to carry out a more complete three-dimensional analysis of the structure rather than simply relying on simulation of projections? If the crystals were big and well ordered enough one could cut sections at different angles and do a complete three-dimensional image reconstruction as has been done for certain biological assemblies.

E. L. THOMAS. The TEM micrographs I have shown are in fact fairly typical. The quality of the long-range order for this polystyrene–polyisoprene block copolymer is quite high due to our use of long annealing times above the T_g of the polystyrene phase and the relatively low molecular sample mass ($M_n = 27\,400$). The 2D SAXS patterns of both the lamellar and gyroid phases show Bragg spots indicative of very large grains of highly ordered material.

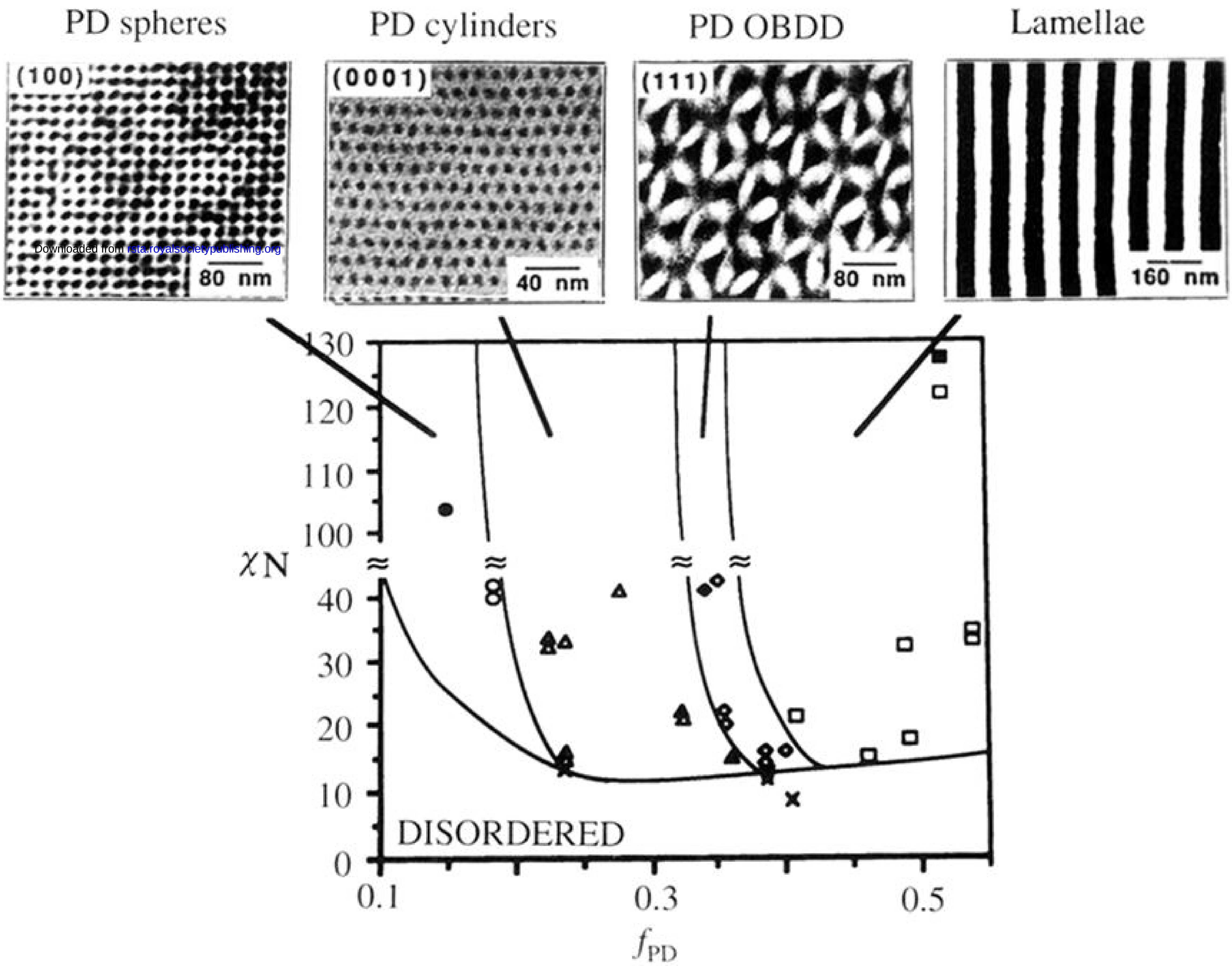
The range of tilt angle that we have explored for the gyroid phase is around 60° (this allows one to view [001] and [111] projections corresponding to 4-fold and 3-fold symmetry directions). Thus far we have not yet tried to do a 3D reconstruction from a systematic tilt series. Serial sectioning to derive the 3D structure is not possible for our sample since the unit cell size, approximately 500 Å, is comparable to the finest section thickness which we can microtome.

I. W. Hamley (*University of Durham, U.K.*). You mentioned that your samples were prepared by the solvent casting technique. As it has been shown that solvent can influence the morphology in copolymer films, could you comment on the effect of solvent on the equilibrium structures in your materials? I also note that you have used homopolymer dissolved in a diblock copolymer to explore the region of stability of the fascinating 'Schoens Gyroid' phase you have observed, varying the volume fraction of one of the components without having to sythesize several samples. But will such a blend show the same phase behaviour as the pure diblock? Related to this, Professor Bates' group in Minnesota has also observed a complex structure resembling the Gyroid in several pure polystyrene–polyisoprene diblocks, part of a series prepared to determine the phase behaviour of this system near the order–disorder transition, which proves to be remarkably rich. Indeed, when the other recent work you mentioned is considered, it appears that complex phase behaviour could be ubiquitous for low molecular mass copolymers in certain composition ranges.

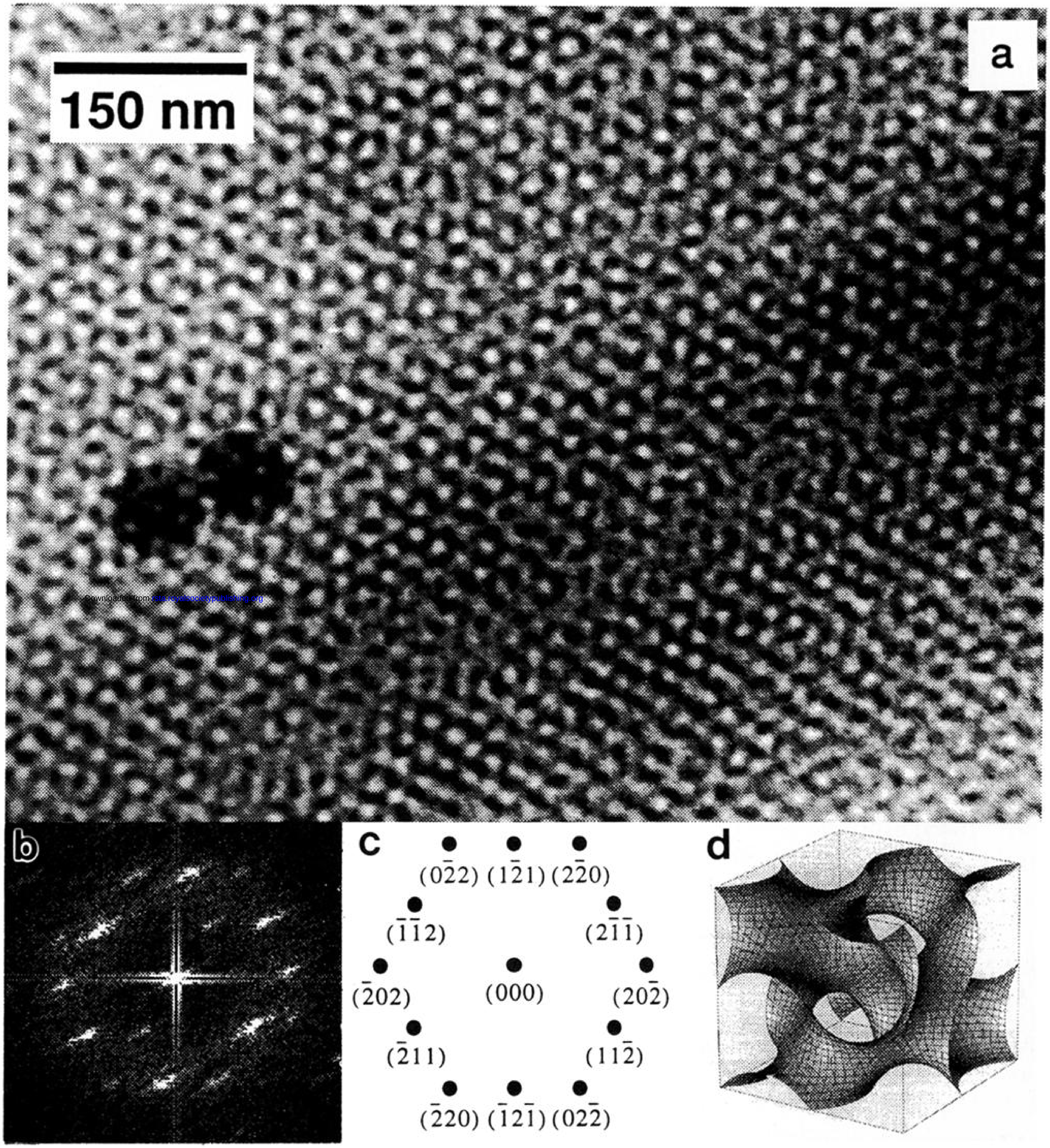
E. L. Thomas. Our sample was initially slow solution cast from toluene. The structure is lamellar after solvent evaporation and shows an improvement in long-range order upon raising the temperature to about 110 °C. Above 120 °C, the transition to the gyroid phase occurs, occurring more rapidly at higher temperatures. Importantly we can drive the sample into the homogeneous disordered state above 175 °C and then cool and nucleate the gyroid phase and then with further cooling renucleate the lamellar phase below 120 °C. Thus, we have reversibility of the order–order transition upon coming from an initial melt state so there is no question about solvent effects on the gyroid phase.

The compositional window of stability of the gyroid is unknown. Hajduk *et al.* have only explored the composition of the gyroid in blends with homopolymer. We will be examining the compositional dependence with a series of diblocks synthesized by L. Fetters. Of course the thermodynamics of a diblock/homopolymer blend is different than for a pure diblock. Still one gets some feeling for the possible extent of phase stability by doing sample blend experiments before synthesizing more diblocks. Winey *et al.* (*Macromol.* **25**, 422 (1992)) found reasonably close correspondence between the compositional window of the OBDD in a blend of lamellar forming diblock and low molecular mass homopolymer.

The work by Bates and coworkers concerning a possible gyroid structure in a PS–PI diblock is of course quite interesting to us. They have termed their new phase 'X1' and speculated that it may be a gyroid structure but the evidence so far is only rheological data and a few TEM micrographs suggesting some sort of cubic phase. There really needs to be careful small angle scattering work to assign a space group with confidence. I certainly agree that the two hexagonal phases which you discovered (Hamley *et al.*, *Macromol.* **26**, 5959 (1993)) in a polyolefin block copolymer also demonstrate that there is a lot of interesting physics in the intermediate to weak segregation régime.



igure 1. Experimental phase diagram depicting the periodic microphases observed in PS–PD iblock copolymer systems for $f_{PD} < \frac{1}{2}$: disordered (×), BCC spheres (○), HP cylinders (△), BDD (◇), and lamellae (□). The filled symbols depict the characteristics of the diblock systems (N and f_{PD}) corresponding to the micrographs. The PS phase appears light, and the PD phase ppears dark due to staining with OsO$_4$.



igure 4. Bright-field TEM micrograph (*a*) of the sample analysed by SAXS in figure 3*b*. This proection shown exhibits three-fold symmetry as indicated in its indexed digital Fourier transform (*b*) and (*c*)). A constant thickness (CT) surface structure consistent with this projection can be erived from Schoen's triply periodic minimal gyroid surface shown (*d*). (Anderson *et al.* 1992.)