# Ordered Bicontinuous Double-Diamond Structure of Star Block Copolymers: A New Equilibrium Microdomain Morphology

**Edwin L. Thomas,* David B. Alward,† David J. Kinning, and David C. Martin**

*Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003*

**Dale L. Handlin, Jr.**

*Shell Development Company, Houston, Texas 77001*

**Lewis J. Fetters**

*Corporate Research—Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801.* *Received March 27, 1986*

ABSTRACT: Experimental evidence is provided for a new equilibrium domain morphology for styrene–isoprene star block copolymers having 30 wt % polystyrene outer blocks. The basic unit of this structure is a tetrahedral arrangement of short polystyrene rods. Such units are interconnected on a cubic lattice having the symmetry of the *Pn*3*m* space group. The resultant structure consists of two translationally displaced, mutually interwoven, but unconnected three-dimensional networks of polystyrene rods embedded in a polyisoprene matrix. Each of these separate polystyrene networks exhibits the symmetry of a diamond cubic lattice.

## Introduction

Recent studies[1-4] of the morphology of star block copolymers of polystyrene and polyisoprene indicated that changes in equilibrium domain morphology can occur as the topological constraints of the core are varied while maintaining the same relative volume fractions of the components. In particular, as the functionality (number of diblock arms) of the star molecule increased, a transition from hexagonally packed polystyrene cylinders to an ordered bicontinuous (OB) morphology occurred. The functionality at which this transition occurred was also found to be dependent on the molecular weight of the diblock arms. Whereas the aim of our previous papers[1,3] was to investigate the transition and provide evidence of the existence of a new equilibrium morphology in block copolymers, this paper provides an explicit structural description of the new ordered bicontinuous morphology.

## Experimental Methods

Because the experimental methods used in this work are identical with those described in detail previously,[1-6] only a brief outline of the procedures will be given.

Star block copolymers were synthesized by the reaction of anionically prepared diblock arms and chlorosilane linking agents. Number-average and weight-average molecular weights of the linear arm precursors and fractionated star molecules, determined by a combination of high-speed membrane osmometry, light scattering, and size exclusion chromatography, showed that the linear arm precursor polydispersities were approximately 1.05 or less. For the 30% by weight polystyrene series of total arm molecular weight $3.3 \times 10^4$, functionalities of 3.9, 4.9, 6.0, 7.8, 11.7, and 17.6 were achieved for the fractionated 4-, 5-, 6-, 8-, 12-, and 18-armed materials, respectively. The nomenclature used to describe the samples is as follows: SI 18/30/10 is an 18-armed styrene–isoprene star block copolymer containing 30 wt % polystyrene outer blocks with polystyrene arm molecular weight $1.0 \times 10^4$ and inner blocks of polyisoprene with arm molecular weight $2.3 \times 10^4$.

Solid films (1 mm thick) were prepared by slowly casting from ca. 3% (w/v) solutions in toluene, a nonpreferential solvent for polystyrene and polyisoprene, and, in certain cases, from cyclohexane, a preferential solvent for polyisoprene. The systems were driven toward thermodynamic equilibrium by annealing at 120 °C for 7 days under high vacuum. Transmission electron microscopy (TEM) was performed on osmium tetraoxide stained, cryoultramicrotomed specimens. Small-angle X-ray scattering (SAXS) data were obtained by using Kratky collimation and a Braun one-dimensional position-sensitive detector.

## Results and Discussion

The delineation of the OB structure can be first made on a rudimentary level by determining the phase connectivity within the sample. The gas sorption measurements, discussed previously,[1] indicated that the polyisoprene phase was continuous, not unexpected in this high polyisoprene ($\phi_{\mathrm{PI}} = 0.73$) content material. An approximate 10-fold increase in the room-temperature storage modulus in the case of the OB structure over that of the cylindrical morphology indicated the continuity of the polystyrene phase.

Electron microscopic examinations on relatively thick (~600 Å) sections revealed a complicated, yet highly ordered, two-phase morphology. Micrographs A and B of Figure 1 show two symmetric projections of the OB structure (sample 8/30/10). It is significant that projections possessing both 4-fold (Figure 1A) and 3-fold (Figure 1B) symmetry are present. This fact narrows the search to systems having cubic symmetry, as only the cubic system possesses both 4- and 3-fold axes of symmetry.

In sections this thick, the projections have significant overlap of the basic building blocks of the structure. By prehardening the sample with osmium tetraoxide, coupled with careful cryoultramicrotomy techniques, one can cut sections approximately 300 Å thick. A micrograph from such a section (sample 8/30/10) is shown in Figure 2. There is a variation in thickness within the field of view, the section being thinner in the left-hand region where the sample is more transparent to electrons. Note that the thinner the section, the less connected the respective domains should appear, assuming discrete domains. The highly connected appearance of the morphology in the thinnest region of the section is strong evidence for phase bicontinuity. In this region of the section there are essentially three contrast levels; the brightest areas arise from projections through the polystyrene phase only, the gray areas arise from projections through both polystyrene and polyisoprene, and the darkest areas arise from projections through the polyisoprene phase only. This thin-section

---

* To whom correspondence should be addressed.

† Present address: Monsanto Polymer Products Co., Springfield, MA 01151.

0024-9297/86/2219-2197$01.50/0

**Table I**
**First Four Allowed Reflections and Their Relative Spacings for Various Structures**

| SC | | BCC | | FCC | | OBDD | | HEX CYL | | LAM | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (*hkl*) | $d_n/d_1$ | (*hkl*) | $d_n/d_1$ | (*hkl*) | $d_n/d_1$ | (*hkl*) | $d_n/d_1$ | (*hk*) | (*hk*) | (00*l*) | $d_n/d_1$ |
| 100 | 1.0 | 110 | 1.0 | 111 | 1.0 | 110 | 1.0 | 10 | 1.0 | 001 | 1.0 |
| 110 | 0.71 | 200 | 0.71 | 200 | 0.87 | 111 | 0.82 | 11 | 0.58 | 002 | 0.50 |
| 111 | 0.58 | 211 | 0.58 | 220 | 0.61 | 200 | 0.71 | 20 | 0.50 | 003 | 0.33 |
| 200 | 0.50 | 220 | 0.50 | 311 | 0.52 | 211 | 0.58 | 21 | 0.38 | 004 | 0.25 |

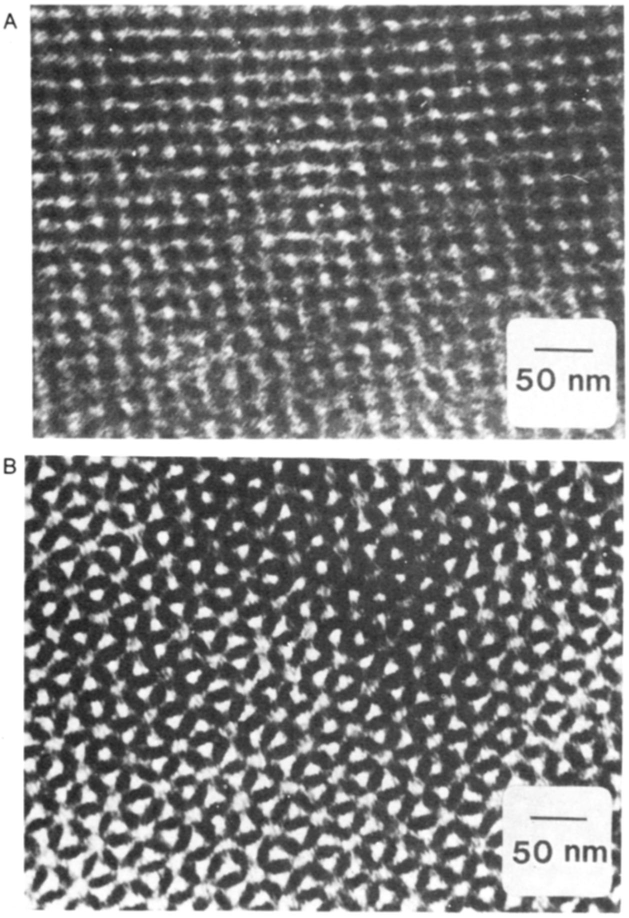

**Figure 1.** Bright-field transmission electron micrographs of sample SI 8/30/10 showing (A) 4-fold symmetry and (B) 3-fold symmetry.

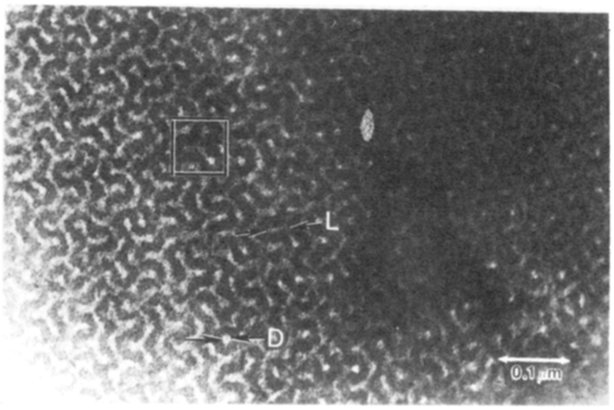

**Figure 2.** Micrograph of an ultrathin section of sample SI 8/30/10. The basic polystyrene tetrahedral unit is outlined in the box. *L* and *D* characterize the cylinders constituting the diamond networks.

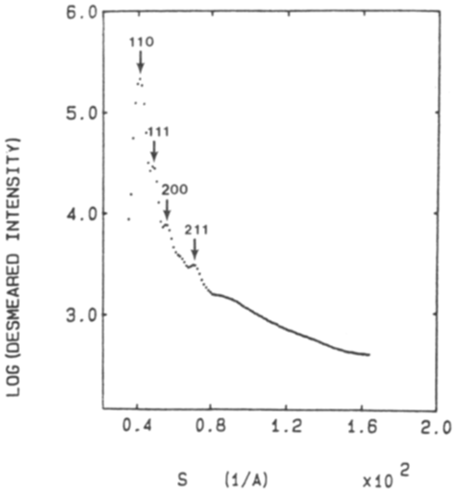

**Figure 3.** Small-angle X-ray scattering pattern for the OBDD structure (SI 18/30/10). The lattice peaks of the *Pn*3*m* double-diamond structure are indicated.

micrograph provides a key piece of information, namely the identification of the basic unit from which the OB structure is assembled. On the left-hand side of the figure one sees assemblies of triads of short polystyrene rods, the angular separation between rods within the plane being 120° (see enclosed area). Also evident are the lightest circular regions, which are locations of polystyrene rods which lie perpendicular to the plane of the figure. The building block of the OB structure is thus deduced to be an assembly of short polystyrene rods whose individual elements lie in the direction of the corners of a regular tetrahedron (this assembly of polystyrene rods will henceforth be referred to simply as a tetrahedron).

In Figure 2, then, one is viewing the structure along the axis of one of the rods, the observed 120° angle between the other three rods being the inplane projection of the actual 109° angle between rods. One can also observe that in the thicker portion of the section projection through more than one layer of these tetrahedra results in the previously described[1] "wagon wheel" image (e.g., figure in ref 7 and Figure 1B).

It now remains to assemble the polystyrene tetrahedra on a cubic lattice such that both the polystyrene and polyisoprene phases are continuous. Small-angle X-ray scattering proved invaluable in performing this assembly. An example of a SAXS pattern from the OB morphology (sample 18/30/10; data corrected for sample absorption, parasitic scattering, wire sensitivity, and slit-length smearing) is given in Figure 3. The pattern has four clearly distinguishable lattice peaks, evidence of an extremely high degree of order for a block copolymer system. The weak shoulder between the (200) and (211) peaks and the very broad higher angle peak ($S \simeq 0.9$ Å$^{-1}$) are likely due to the form factor scattering of the tetrahedral units. The ratios of the *d* spacings for these peaks relative to the *d* spacing of the main interference peak are 1.0:0.84:0.73:0.57. The ratios of the *d* spacings of the first four allowed reflections for structures commonly found in block copolymer systems are given in Table I. The observed ratios are clearly a poor match to the predicted ratios for the familiar simple cubic (SC), body-centered cubic (BCC), face-centered cubic (FCC), hexagonally

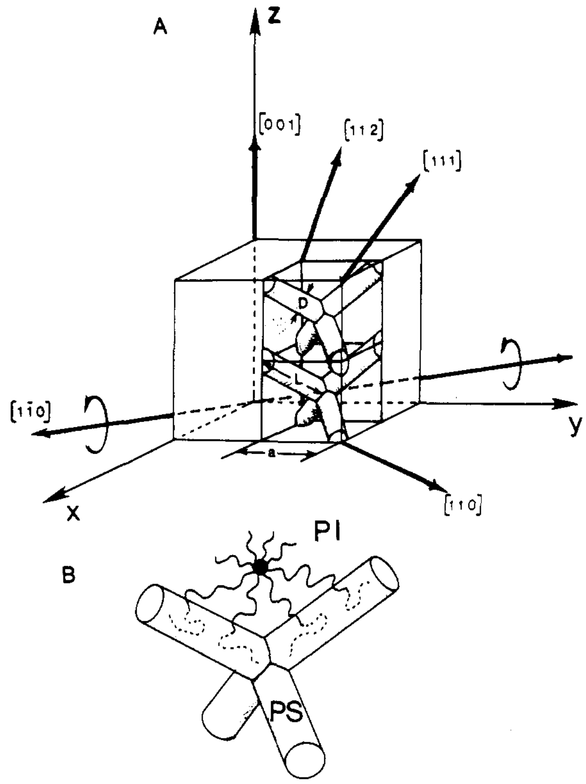

**Figure 4.** (A) *Schematic of the* OBDD *structure showing the* arrangement of the basic tetrahedral units. These interconnect to form two interwoven, but independent diamond networks of polystyrene rods. (B) Schematic of the arrangement of the polystyrene and polyisoprene chains in the OBDD domain space.

packed cylinders (HEX CYL), or lamellar (LAM) structures.

As mentioned previously, the occurrence of 3-fold and 4-fold axes of symmetry signals the presence of a cubic lattice. Of the seventeen sets of cubic space groups listed in the International Tables for X-Ray Crystallography,[8] only one set contains reflections whose relative spacings match up with those observed for the OB structure. This set contains the two tetrahedral space groups *Pn*3 and *Pn*3*m* (which differ only in the presence of mirror planes in *Pn*3*m*). For these space groups the first four allowed reflections are the 110, 111, 200, and 211 whose relative spacings are listed in Table I. These spacings are in excellent agreement with those observed for the OB structure.

It is now possible to propose a three-dimensional model for the OB morphology. As shown schematically in Figure 4, a unit cell can be constructed in which eight polystyrene tetrahedral elements are arranged on a cubic lattice having the symmetry of the *Pn*3*m* space group. The resulting structure consists of two distinct, mutually interwoven, but unconnected three-dimensional networks of polystyrene, each of which exhibits the symmetry of a diamond lattice, surrounded by a continuous polyisoprene phase. One of the networks is displaced by half of the unit cell body diagonal with respect to the other network. Consequently, the overall symmetry of the structure may be thought of as being double diamond. The OB structure will henceforth be referred to as the ordered bicontinuous double-diamond (OBDD) structure.

Further confirmation of the OBDD structure can be obtained by comparing computer-generated images based on the model structure to experimental images acquired via electron microscopy. In particular, a critical comparison is the detailed agreement of the EM images to the corresponding computed images as a function of tilt about a certain crystallographic axis. Computer-generated images were obtained with the MULTISLICE program developed by the Arizona group[9] for high-resolution microscopy of crystals. This program has the capability to generate the image of a crystal structure as viewed along any chosen direction. While the MULTISLICE program is capable of incorporating the detailed microscope optical parameters into the image simulations, in the present case of mass-thickness contrast dominated bright-field images, it is sufficient for the level of detail available in the experimental images to calculate the projected atomic potential from the model structure. The basic unit in the OBDD model structure was taken as a tetrahedral unit in which each continuous cylindrical strut of polystyrene was approximated by a set of five discrete spherical scattering objects (carbon atoms) equidistantly spaced along its axis embedded in a matrix (polyisoprene) of zero scattering power. Thus the darkest areas in the projected potential image represent regions with the highest concentration of polystyrene. The section thickness was fixed at $3^{1/2}/2$ times the unit cell size (i.e., images correspond approximately to projections from a 600-Å-thick section).

The type of tilting experiment which was performed in the electron microscope and simulated with the computer is illustrated in Figure 4. By tilting the unit cell about the [1$\bar{1}$0] axis, it is possible to sample several high-symmetry projections. The micrographs in Figure 5 show the results of such an experiment. The micrographs in Figure 5 (and Figure 6) have been printed with reversed contrast so that the polystyrene phase appears dark. This was done so as to facilitate comparison to the computer-calculated projections. Initially, a section was tilted −24° from normal incidence and a grain exhibiting a [001] (square) projection was located. The boundaries of the grain have been outlined in Figure 5A. The sample was then tilted about the indicated [1$\bar{1}$0] axis to produce symmetric projections B and C in Figure 5, which correspond to the [112] and [111] projections, respectively. Note that the predicted tilt angles between the [001] and [112] and the [001] and [111] projections are 35.3 and 54.7°, respectively, compared to the experimental values of 34 and 52° measured from the microscope goniometer stage.

Figure 6 shows highly magnified views of the micrographs in Figure 5 along with the corresponding projections of the OBDD model structure calculated with the MULTISLICE program. The excellent agreement between each of the computed and observed projections is further compelling evidence for the validity of the OBDD model. For example, in the [111] projection as shown in Figure 6C, regions of 3- and 6-fold rotational symmetry are evident. The darker 3-fold nodes represent regions of the section where the projection is along a full polystyrene rod axis. The 6-fold nodes correspond to regions in the section where triplets of polystyrene rods emanating from neighboring tetrahedra overlap in projection.

The arrangement of the polystyrene and polyisoprene chains in the OBDD domain space is shown schematically in Figure 4B. The core of the star molecule must be located within the continuous polyisoprene phase while the junctions between the polyisoprene and polystyrene chains *are restricted to lie on the periodic surface defining the* boundary between the two phases. The polystyrene volume fraction, $\phi_{PS}$, in the OBDD structure is approximately 4 times the volume of one of the cylindrical struts divided by the total volume of a subcell; i.e.

$$\phi_{PS} = \pi L D^2 / a^3 \qquad (1)$$

where $L$ is the length of a polystyrene strut, $D$ is the strut

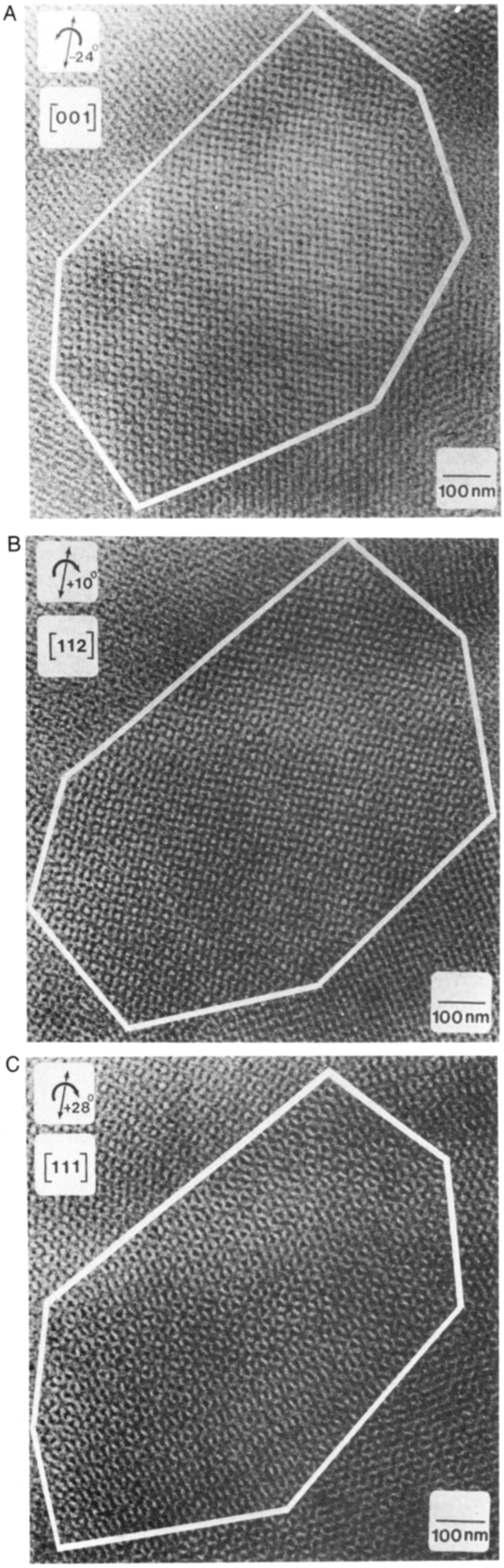

**Figure 5.** Micrographs from a tilt series of sample SI 8/30/10 showing (A) the [001] projection, (B) the [112] projection, and (C) the [111] projection. The contrast has been reversed for easy comparison to computer-calculated projections.

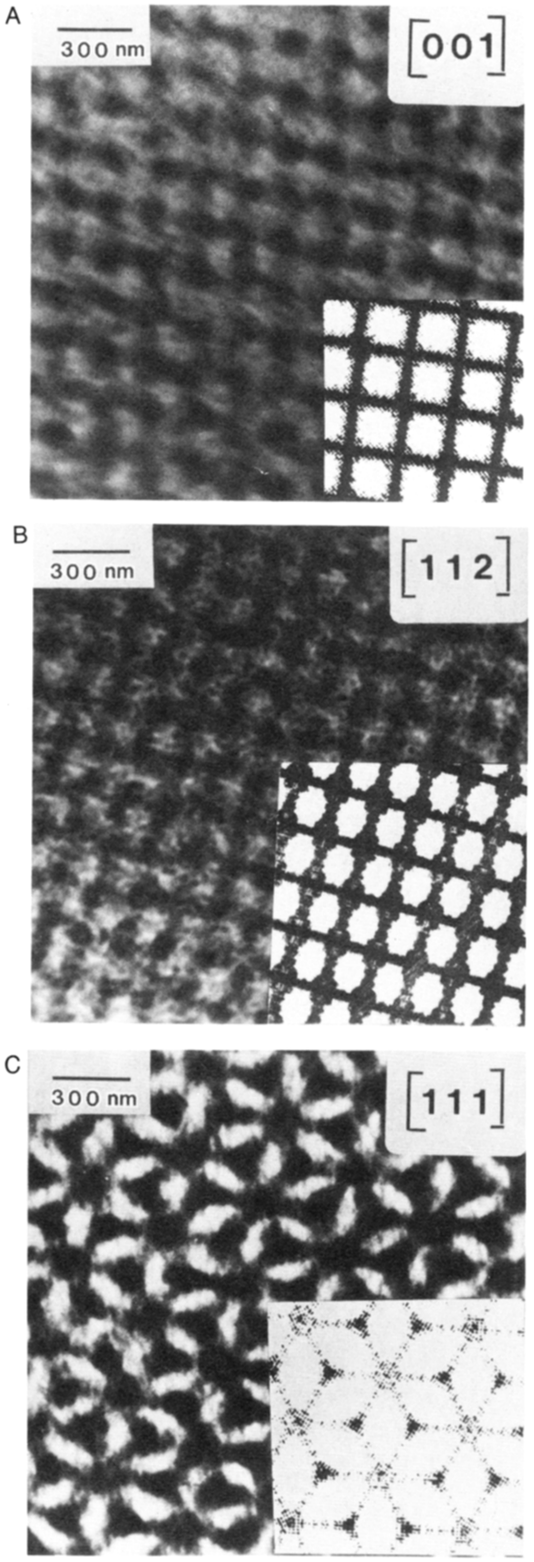

**Figure 6.** Enlarged portions from Figure 5 showing the (A) [001], (B) [112], and (C) [111] projections and the corresponding computer-generated images.

diameter, and $a$ is the size of the subcell (see Figure 4). Using the relationship $a = 2L/3^{1/2}$, one can rewrite eq 1 as

$$\phi_{\mathrm{PS}} = 2.04(D/L)^2 \quad (2)$$

Measurements from the electron micrographs (e.g., see Figure 2) yield values for $D$ and $L$ of approximately 100 and 290 Å, respectively, which gives a calculated polystyrene volume fraction of 0.24, in good agreement with

Table II
Star Annealing Study ($10^4$ PS/$2.3 \times 10^4$ PI)

| | morphology | | |
|---|---|---|---|
| sample | toluene cast | cyclohexane cast | annealed |
| 5 arm | cylinder | cylinder | cylinder |
| 6 arm | double diamond | cylinder | double diamond |
| 8 arm | double diamond | cylinder | double diamond |

the actual polystyrene volume fraction of 0.27.

Of central concern is the assertion that the OBDD is a new *equilibrium* morphology general to block copolymer systems. A simple experiment involving different casting solvents was performed to address the question of equilibrium. The experiment consisted of casting films from both a polyisoprene-preferential solvent and a nonpreferential solvent. The morphologies of the films were examined before and after the annealing treatment. As one would expect, samples cast from a PI-preferential solvent (cyclohexane) promoted the formation of discrete polystyrene domains, cylinders in this case, for the 5-, 6-, and 8-armed samples used for this experiment. After an annealing treatment, the 5-armed samples remained as hexagonally packed cylinders but the 6- and 8-armed samples transformed into the OBDD structure. The arm number dependence of the equilibrium microdomain morphology is discussed in our ref 3. Casting from a nonpreferential solvent (toluene) resulted in a cylindrical morphology for the 5-armed star and the OBDD morphology for the 6- and 8-armed stars. Annealing these samples caused no structural transformation (the results are summarized in Table II). It is clear from this experiment that the annealing treatment used was capable of erasing any nonequilibrium casting effects and that the OBDD structure is indeed a thermodynamic equilibrium morphology.

In addition to being observed in styrene–isoprene star block copolymers having between 30 and 36 wt % polystyrene outer blocks as well as in inverted stars (styrene cores, 30 wt % isoprene outer blocks),[10,11] the OBDD structure has also been recently identified in *linear* polystyrene–polydiene diblock copolymers containing 62–66 vol % polystyrene.[12] All observations indicate that the OBDD structure exists for linear diblocks in a narrow composition window between that of the hexagonal cylindrical and lamellar structures. A double-diamond structure has been proposed previously by Longley and McIntosh[13] to explain the X-ray patterns of the viscous isotropic (cubic) phase of glycerol monooleate (a lipid) in water. This lyotropic liquid crystal phase contains approximately 40% water, which is thought to be located in the diamond network channels.

Scriven[14] was the first to suggest equilibrium bicontinuous structures as morphological candidates for microstructured fluid systems such as microemulsions and lyotropic liquid crystals. Scriven further asserted that the partitioning of space into each continuous subvolume may be accomplished by three-dimensional periodic minimal surfaces. A minimal surface is one for which the local mean curvature, defined as the average of the principal curvatures, is zero. (The principal curvatures of a surface at a point are the reciprocals of the principal radii of curvature.) This is the local condition produced by the variational problem of minimizing area. More generally, a surface has constant mean curvature if this average is constant. Constant nonzero mean curvature is the local condition arising from minimization of the area of a surface interface subject to fixed volume constraints on the bounded regions. Examples of surfaces of nonzero constant mean curvature are spheres, cylinders, and the rotationally symmetric surfaces of Delauney.[15]

Recently, Anderson and Scriven[16] studied the problem of triply periodic surfaces of constant nonzero mean curvature. They explored the connection between volume fraction, constant mean curvature, and the problem of finding a structure which has the correct phase connectivity and symmetry. It is well-known for fluids that the minimization of surface contact area subject to fixed phase volume fraction leads directly to structures having surfaces of constant mean curvature (spheres). If molecular structure and topology present further requirements of structural symmetry and phase continuity, periodic surfaces of zero or constant mean curvature may appear which have the least surface area for a given phase volume fraction under these constraints.

Interface curvature in A–B block copolymer systems arises from the asymmetry of the respective species molar subvolumes $v_A$ and $v_B$, which depend on the respective density and block molecular weight. For $v_A \simeq v_B$ flat interfaces (lamellar morphology) result but as $v_A$ and $v_B$ become disparate, interface curvature arises, with the smaller molar volume species lying on the concave side of the interface (cylindrical and ultimately spherical morphologies).

The location of the OBDD structure between that of the cylindrical and lamellar would suggest a decreased mean interfacial curvature over that of the hexagonally packed cylinders. As Longley and McIntosh[13] point out, the matrix space in the double-diamond structure is bounded by a single, continuous surface quite like Schwarz's periodic tetrahedral minimal surface[17] (a model of this surface appears in Figure 4 of ref 13).

There are several interesting possible applications for structures having an ordered bicontinuous microdomain morphology. For example, an A-conducting/B-insulating diblock arm would provide good electrical transport with a relatively minor amount of the conducting block. Leaching out of one of the networks (say of the rubber by ozonolysis) could produce microporous separation membranes with the diameter of the channels and the interchannel spacing readily controllable by selection of arm molecular weight of the star copolymer.[1]

## Conclusions

The ordered bicontinuous double-diamond (OBDD) structure is a new equilibrium morphology for star and linear diblock copolymers. The basic unit is a tetrahedral arrangement of short rods. Such units are interconnected on a cubic lattice having the symmetry of the *Pn*3*m* space group. The resultant structure consists of two translationally displaced, mutually interwoven, but unconnected three-dimensional networks of rods (polystyrene) embedded in a matrix (polyisoprene). Each network exhibits the symmetry of a diamond lattice. The OBDD morphology lies between the hexagonal-packed cylindrical structure and the lamellar structure. Since both polymer phases are continuous and interwoven, the OBDD structure is thus a true interpenetrating polymer network.

This study presents the first examples of real-space observations of an ordered bicontinuous structure resembling Schwarz's periodic tetrahedral minimal surface. The occurrence of a new equilibrium morphology for block copolymers due to the special topological constraints of the star architecture is significant since undoubtedly further molecular variants of block copolymers (star with multiblock arms, heteroarm stars, etc.) will produce further polymorphism with the likely possibility of unique properties from nature's solutions to energy minimization in variously constrained phase-separating macromolecules.[18]

**Acknowledgment.** The financial support of the Polymers Division of the NSF through Grant DMR 84-06079 is greatly appreciated. We thank Professors L. E. Scriven (University of Minnesota) and D. A. Hoffman (University of Massachusetts) and Dr. D. B. Anderson (University of Minnesota) for helpful discussions concerning periodic minimal surfaces and Drs. H. Hasegawa and T. Hashimoto (Kyoto University) for discussions concerning the OBDD structure in linear diblock systems. E.L.T. and L.J.F. thank the organizers of the China–U.S. Bilateral Symposium on Polymer Chemistry and Physics held in Beijing, October 1979. It was at that meeting that this work had its inception.

**Registry No.** (Styrene)·(isoprene) (block copolymer), 25038-32-8.

## References and Notes

(1) Alward, D. B.; Kinning, D. J.; Thomas, E. L.; Fetters, L. J. *Macromolecules* 1986, *19*, 215.
(2) Alward, D. B. Ph.D. Dissertation, University of Massachusetts, 1985.
(3) Kinning, D. J.; Alward, D. B.; Thomas, E. L.; Fetters, L. J.; Handlin, D. L., Jr. *Macromolecules* 1986, *19*, 1288.
(4) Kinning, D. J. Ph.D. Dissertation, University of Massachusetts, 1986.
(5) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* 1978, *11*, 668.
(6) Hadjichristidis, N.; Fetters, L. J. *Macromolecules* 1980, *13*, 191.
(7) Aggarwal, S. L. *Polymer* 1976, *17*, 938.
(8) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England; Vol. II, p 147.
(9) Arizona State University, MULTISLICE Program. See, for example: Cowley, J. M.; Moodie, A. F. *Acta Crystallogr.* 1957, *10*, 609.
(10) Herman, D.; Kinning, D. J.; Fetters, L. J.; Thomas, E. L., to be published.
(11) Kinning, D. J., unpublished results.
(12) Hasegawa, H.; Hashimoto, T.; Kinning, D. J.; Thomas, E. L.; Fetters, L. J., to be published.
(13) Longley, W.; McIntosh, T. J. *Nature (London)* 1983, *303*, 612.
(14) Scriven, L. E. *Nature (London)* 1976, *263*, 123.
(15) Delauney, C. *J. Math. Pures. Appl., Ser. 1* 1841, *6*, 425.
(16) Anderson, D.; Davis, H. T.; Nitsche, J. C.; Scriven, L. E., to be published.
(17) Schwarz, H. A. *Gesammelte Mathematische Abhandlung*; Springer: Berlin, 1890; Vol. 1. Also see: Schoen, A. H. *NASA Tech. Note* 1970, D-5541.
(18) Matsushita, Y.; Yamada, K.; Hattori, T.; Fujimoto, T.; Sawada, Y.; Nagasawa, M.; Matsui, C. *Macromolecules* 1983, *16*, 10. A wagon wheel type of arrangement (Figures 2b and 3b) was observed by these authors in unannealed benzene-cast films of a styrene–(4-vinylbenzyl)dimethylamine–isoprene terpolymer.

---

# Dynamics of a Face-Centered Cubic Lattice Model for Polymer Chains

**James Patton Downey, Charles C. Crabb,[†] and Jeffrey Kovac***

*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600.*
*Received January 29, 1986*

ABSTRACT: The dynamic behavior of a face-centered cubic lattice model for a polymer chain was simulated with and without excluded volume using a Monte Carlo technique. The chain relaxation was analyzed with both the end-to-end vector autocorrelation function and the autocorrelation functions of the Rouse normal coordinates. In the absence of excluded volume we find almost exact agreement with the predictions of the Rouse theory. In the presence of excluded volume the $N$ dependence of the relaxation times of the first three modes conforms quite well to scaling theory predictions. The $k$ dependence of the relaxation times deviates from the Rouse value in the presence of excluded volume and the deviation is consistent with that seen for the cubic lattice model. The problem of the proper definition of the time scale in Monte Carlo simulations is discussed.

## I. Introduction

The study of the dynamics of lattice models for polymer chains using Monte Carlo techniques was initiated long ago by Verdier and Stockmayer.[1] Probably the most interesting and important aspect of these conceptually and computationally simple simulations is their ability to explore the effects of excluded volume on the chain dynamics. Recently, there has been a lot of interest in lattice model simulations because they offer an opportunity to simulate entangled polymer systems without the expenditure of immense amounts of computer time.[2] Much of the recent effort has been focused on the study of the reptation model introduced by de Gennes.[3]

Most of the studies of the dynamic lattice models have used either a cubic[2,4,5] or a tetrahedral lattice.[6,7] Dynamic models based on these two lattices have one important feature in common. In order to create a dynamic model that is ergodic it is necessary to have a set of elementary motions involving different numbers of bonds. In the tetrahedral lattice model both a three- and a four-bond motion are required. In the cubic lattice model both the two-bond "normal bead" motion and the three-bond 90° crankshaft motion are needed to obtain reasonable dynamic behavior in the presence of excluded volume. The need for two different types of motions raises a problem with the definition of the time scale in the simulation model.

In the dynamic Monte Carlo method time is defined in terms of a "bead cycle", (although this particular term is not universally employed). A bead cycle consists of the choice of a random position on the chain, examination of the local conformation surrounding that point, identification of a particular elementary motion to be attempted, and acceptance or rejection of the proposed movement as

---

[†] Present address: Rohm and Haas Research Laboratories, Rohm and Haas Co., Bristol, PA 19007.

0024-9297/86/2219-2202$01.50/0