ORGANIZED STRUCTURES IN BLOCK COPOLYMERS: STABILITY DOMAIN AND STRUCTURAL STUDY

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ABSTRACT

In this paper we describe a safe method for the determination of the structure of block copolymers in concentrated solution and in the dry state. This method involves the use of both low angle x-ray diffraction and electron microscopy. Using these two techniques, we have established the existence of five types of structures for block copolymers and shown that when the composition of the copolymer in the insoluble blocks increases one observes successively: a centred cubic structure, an hexagonal structure, a lamellar structure, an inverted hexagonal structure and an inverted centred cubic structure. We also describe the effect of the concentration of the solvent, the temperature and the polymerization of the solvent.

1 INTRODUCTION

It is now well known that. in the presence of suitable solvents. amorphous block copolymers exhibit liquid crystalline phases[1,2]. The structural elements of these liquid crystalline phases are in the order of some hundred Ångstroms. The study of structures on this scale obviously calls for low angle x-ray scattering and electron microscopy.

X-ray diffraction easily provides the structural type (lamellar. hexagonal or cubic) and the main lattice parameter (thickness of the sheets for a lamellar structure. distance between the axes of the cylinders for a hexagonal structure. distance of the centres of the spheres for a cubic structure). But the detailed determination of the structure and the calculation of all its parameters require an hypothesis on the respective disposition of the different blocks and the solvent.

The use of electron microscopy avoids such an hypothesis[3-5]. However. the state of viscous liquid of the mesomorphic gels presents important difficulties for electron microscopic studies. To overcome these difficulties it is necessary to solidify the copolymer–solvent system by a post polymerization of the solvent[3,4]. Another difficulty with electron microscopy is the necessity for the staining of one block.

Nevertheless, the use of both x-ray diffraction and electron microscopy is the safest method to determine the structure of block copolymers in

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solution and in the dry state. We shall justify this assertion in the present paper.

2 STRUCTURAL DETERMINATION

2.1 Principle of a safe structural determination[4, 5]

In a practical point of view, how have we to proceed to perform a safe determination of the structure of block copolymers?

At first we prepare mesomorphic gels by dissolution of the copolymer in a monomer which is a preferential solvent of one block. The principal monomers used are: styrene, MMA, BMA, VAcO, dichloropropene, acrylic acid. The principal copolymers studied are: polystyrene–polybutadiene (SB)[4, 6], polybutadiene–polystyrene–polybutadiene (BSB)[5, 7], polystyrene–polybutadiene–polystyrene (SBS)[8, 9], polystyrene–polyisoprene (SI)[1, 10, 11], polyisoprene–polyvinyl-2- or polyvinyl-4-pyridine (IVP)[12—14], polyisoprene –polymethylmethacrylate (I.MMA)[15], polybutadiene–polyvinylnaphthalene (B.VN)[16], polybutadiene–polymethylstyrene (B.MS)[17], polybutadiene–polybenzylglutamate (BG)[18].

Then, using well focussed and strictly monochromatic x-rays, we resolve the structure of the mesomorphic gel by low angle x-ray scattering. We fully polymerize the monomer by u.v. light or with a peroxide. We verify, by low angle x-ray scattering, that the periodic structure has not been destroyed by polymerization and we measure its new parameters.

After studying the solid sample by x-ray diffraction, we cut it with an ultramicrotome, stain the diene block by fixation of osmium tetroxide on the double bonds of the polydiene, and study the ultrathin sections with an electron microscope. Resulting from the method of staining used, the diene blocks appear black and the other blocks light on electron micrographs.

2.2 Determination and description of the structures

The study of x-ray diffraction patterns obtained with both mesomorphic gels (concentrated solution of the copolymer in a preferential solvent of one block) and organized copolymers (solid samples obtained by polymerization of a monomer used as solvent) prepared from block copolymers containing between 10 and 90 per cent of one block shows that:

(i) all x-ray patterns obtained can be classified in three families, each corresponding to a well determined structural type: lamellar, cylindrical or cubic;

(ii) x-ray patterns obtained before and after polymerization of the solvent belong to the same family.

Therefore, the structural type is not modified by polymerization and the results, provided by electron microscopy on solid samples, can be extrapolated to mesomorphic gels without any risk of error.

Using the results of both x-rays and electron microscopy we have established the existence of one type of lamellar structure, two of hexagonal structure and two of cubic structure. We shall describe these structures and give their characteristic features in x-ray diffraction and electron microscopy.

2.2.1 Lamellar structure

The first family of x-ray diffraction patterns is characterized by the presence

of a series of five or seven sharp lines in their central region; their Bragg spacings are in the ratio: 1, 2, 3, 4, 5, 6, 7 . . . typical of a layered structure. A typical electron micrograph provided by an ultrathin section of a solid sample giving a diffraction pattern characteristic of this layered structure is shown in *Figure 1*.

SBS.364   2000 Å
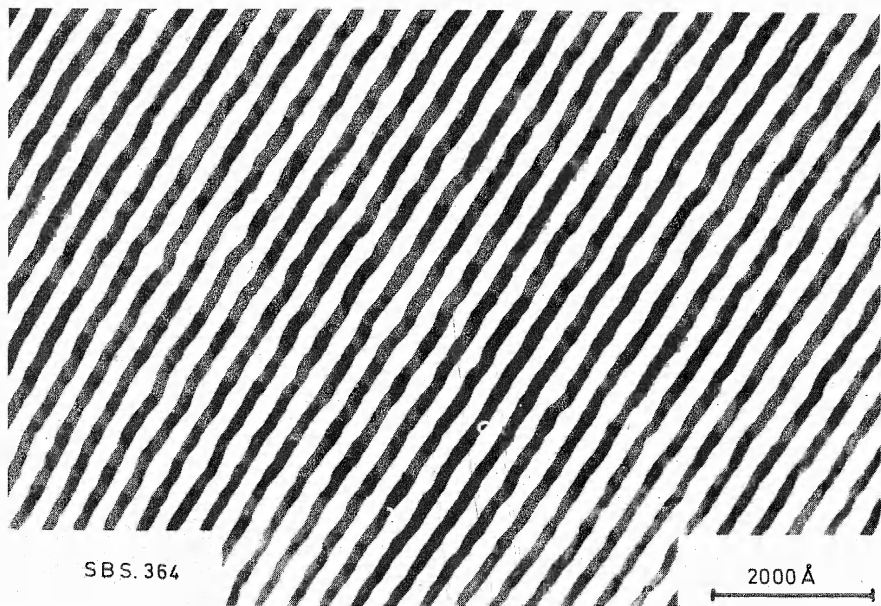
Figure 1. Electron micrograph of the copolymer SBS.364 swelled with 30% MMA

In this figure (corresponding to the copolymer SBS.364 swelled in 30 per cent MMA) one can see a striated structure formed by parallel stripes alternately black (containing the polybutadiene blocks coloured by osmium tetroxide) and white (containing the polystyrene blocks swelled by the polymerized MMA). This striated structure results from the section of the lamellar structure by a plane perpendicular to the planes of the sheets.

Therefore we can describe the lamellar structure pictured in *Figure 2* as a set of plane parallel equidistant sheets; each sheet results from the super-position of two layers, one formed by insoluble blocks B, the other by the solution in the preferential solvent S of the soluble blocks A.

The total thickness $d = d_A + d_B$ of a sheet is given directly by the Bragg spacing of the x-ray pattern, or directly measured on the electron micrographs (to have an accurate value of d by electron microscopy it is necessary to use electron micrographs provided only by sections perpendicular to the planes of the sheets[5].

The thicknesses d_A and d_B of the two layers are directly measured on the micrographs or calculated from the intersheet spacing d given by x-rays, using a formula based on simple geometry.
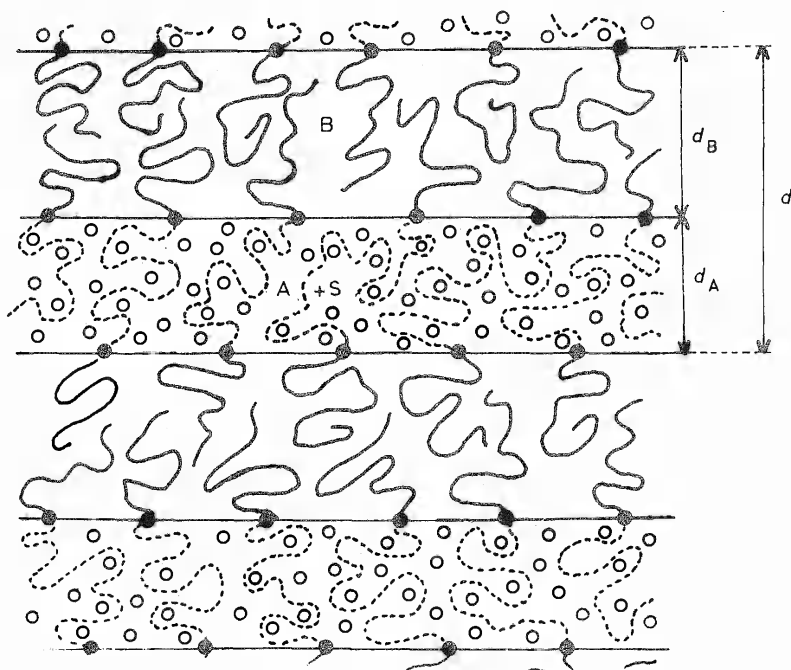
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Figure 2. Schematic representation of the lamellar structure of a BAB copolymer

$$d_A = d \left\{ 1 + \frac{C(1 - X_A)\overline{V}_B + (1 - C)\varphi_B \overline{V}_S}{C X_A \overline{V}_A + (1 - C)\varphi_A \overline{V}_S} \right\}^{-1} \tag{1}$$

where C is polymer concentration in the solution, X_A is concentration of the A block in the copolymer, $\overline{V}_A$ and $\overline{V}_B$ are specific volume of the A and B blocks, $\overline{V}_S$ is specific volume of the solvent, and φ_A and φ_B are partition coefficients of the solvent ($\varphi_A + \varphi_B = 1$).

If the solvent S dissolves only one block (A for instance), $\varphi_A = 1$ and $\varphi_B = 0$, then:

$$d_A = d \left[1 + \frac{C(1 - X_A)\overline{V}_B}{C X_A \overline{V}_A + (1 - C)\overline{V}_S} \right]^{-1} \tag{2}$$

2.2.2 *Hexagonal structures*

The second family of x-ray diffraction patterns is also characterized by the presence of five sharp lines in the central region. But their reciprocal spacings are in the ratio : 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, which is characteristic of a bidimensional hexagonal array.

Electron micrographs of solid samples providing such x-ray diagrams have allowed us to distinguish two different structures corresponding to the same family of x-ray patterns. *Figures 3* and *5* are examples of such electron micrographs. They are of two types: *Figure 3* is characterized by black spots on a

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white background, while *Figure 5* is characterized by white spots on a black background.

2.2.2.1 Hexagonal structure—In *Figure 3*, one can see electron micrographs of sections in two perpendicular directions (the insert is at a slightly higher scale than the main figure) of the copolymer BSB.374 (31.5 per cent polybutadiene).
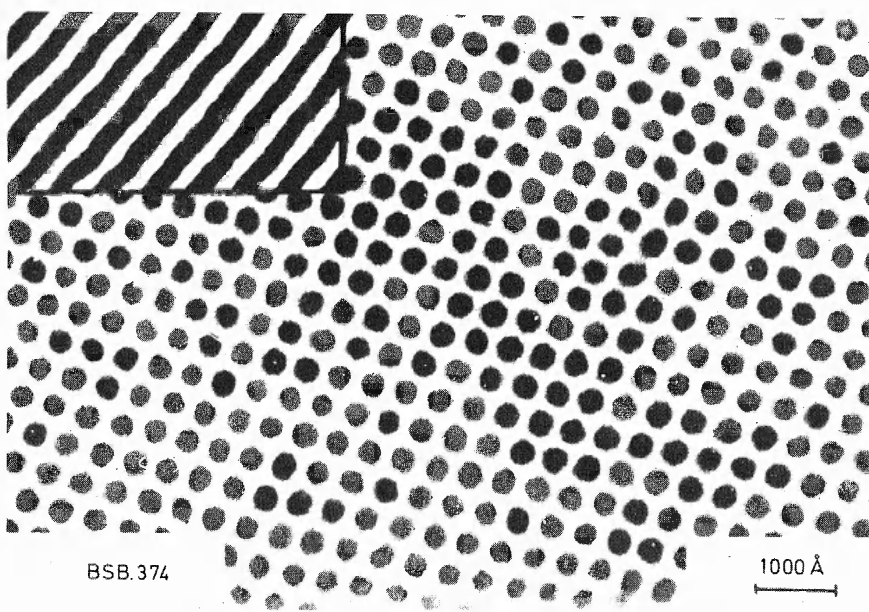
Figure 3. Electron micrograph of the copolymer BSB.274 swelled with 29% MMA. The insert is at a slightly higher scale than the main figure

For the main *Figure 3*, the plane of cutting is perpendicular to the axis of the long cylinders and one can see black spots on a white background. The spots have the shape of circles which are distinct and isolated: they are arranged in an hexagonal array in agreement with x-ray results. The insert is a section of the same copolymer by a plane perpendicular to the plane of cutting of the main figure. One can see a striated structure in which the black stripes are sections of polybutadiene cylinders by a plane nearly parallel to the direction of their axes. So we are in the presence of cylinders and not of spherical particles.

Therefore the cylindrical hexagonal structure (pictured in *Figure 4*) consists of indefinitely long cylinders arranged in a regular hexagonal two dimensional array; the long cylinders containing the insoluble blocks B are separated from one another by the solution of the soluble blocks A.
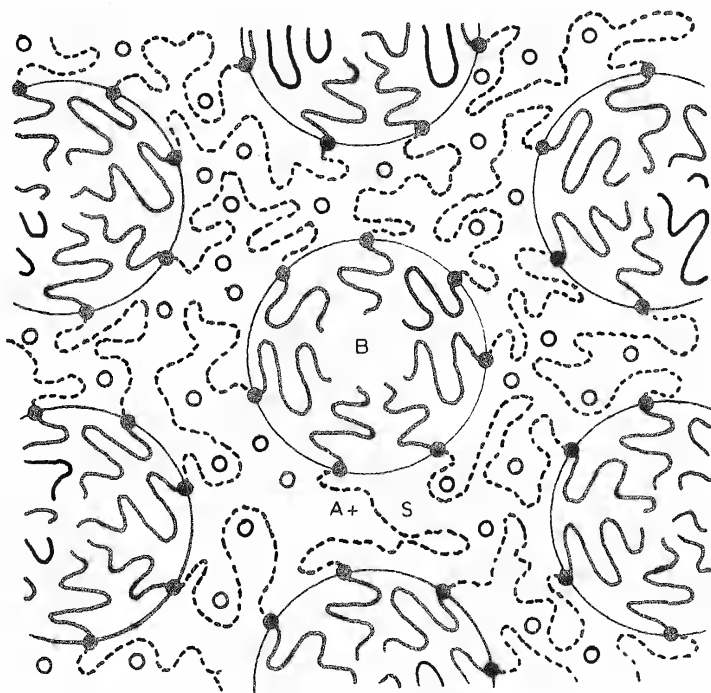
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Figure 4. Schematic representation of the hexagonal structure of a BAB copolymer

2.2.2.2 Inverted hexagonal structure—In *Figure 5*, one can see micrographs of sections in two perpendicular directions (the insert is at a slightly higher scale than the main Figure) of the copolymer BSB.421 (74.8 per cent polybutadiene).

In the main figure, one can see, on a black background, white spots arranged in an hexagonal array: they are sections of long cylinders by a plane nearly perpendicular to the direction of their axes. In the insert, one can see alternatively white and black stripes: the white stripes are sections of the cylinders by a plane nearly parallel to the direction of their axes. In the main *Figure 5*, the circles are white, therefore the cylinders are filled with the polystyrene blocks A in solution in the solvent S as pictured in *Figure 6*.

From the micrographs of *Figures 3* and *5*, one can deduce the existence of two types of cylindrical structures: one with cylinders filled by insoluble polybutadiene blocks, the other with cylinders filled by polystyrene in solution in the solvent. We call these hexagonal and inverted hexagonal structures respectively. They can be distinguished from one another only by electron microscopy.

2.2.2.3 Characteristic parameters of the two cylindrical structures—The characteristic parameters of the two types of hexagonal structures are the distance D between the axes of two neighbouring cylinders and the diameter
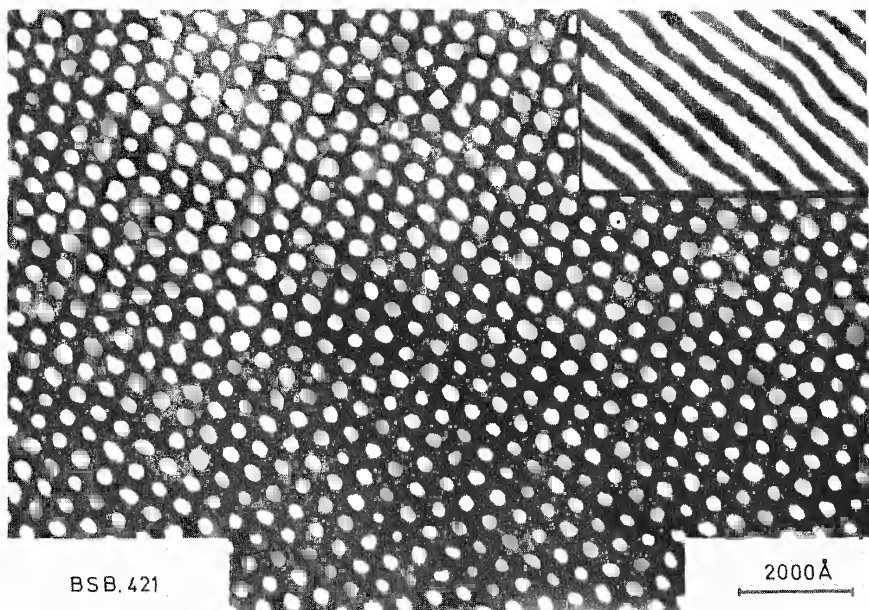
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BSB.421

2000Å

Figure 5. Electron micrographs of the copolymer BSB.421 swelled with 30% MMA. The insert is at a slightly higher scale than the main figure
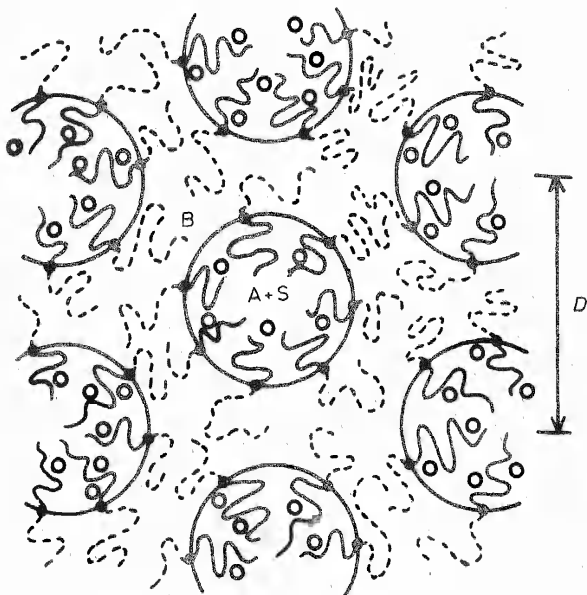

Figure 6. Schematic representation of the inverted hexagonal structure of an AB copolymer

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$2R$ of the cylinders. D is directly given by the Bragg spacings of x-ray diffraction patterns, or directly measured on electron micrographs. $2R$ is directly measured on electron micrographs[5] or calculated from the value of D given by x-rays, using formulae based on simple geometrical considerations.

For the hexagonal structure:

$$R^2 = \frac{D^2\sqrt{3}}{2\pi} \left[1 + \frac{1 - CX_B}{CX_B} \cdot \frac{\overline{V}_{AS}}{\overline{V}_B} \right]^{-1} \tag{3}$$

For the inverted hexagonal structure:

$$R^2 = \frac{D^2\sqrt{3}}{2\pi} \left[1 + \frac{CX_B}{1 - CX_B} \cdot \frac{\overline{V}_B}{\overline{V}_{AS}} \right]^{-1} \tag{4}$$

where $\overline{V}_{AS}$ is the specific volume of the solution of the block A in the solvent S.

2.2.3 Cubic structures

The third family of x-ray diffraction patterns is characterized by the presence of four sharp lines in their central region. Their reciprocal spacings are in the ratio: 1, $\sqrt{2}$, $\sqrt{3}$, $\sqrt{4}$ which is characteristic of a cubic structure; but from such patterns it is very difficult to know if the cubic lattice is simple or centred.

Electron micrographs of solid samples providing such x-ray diagrams have allowed us to distinguish two different structures corresponding to the same family of x-ray patterns[19]. One type of electron micrograph is characterized by black spots on a white background (SB copolymers < ca. 18 per cent polybutadiene) and the other type by white spots on a black background (SB copolymers > ca. 80 per cent polybutadiene)[19]. For the two types of micrograph the circular spots are arranged in an hexagonal lattice (plane 111) or in a square lattice (plane 100)[20].

Therefore we can deduce the existence of two types of cubic centred structure: the cubic centred structure and the inverted cubic centred structure,

The characteristic parameters of the two types of cubic structures are: (a) the side a of the cubic cell directly given by the Bragg spacings of x-ray patterns or directly measured on electron micrographs; (b) the diameter $2R$ of the spheres directly measured on electron micrographs or calculated from the value of a given by x-rays using formulae based on simple geometrical considerations.

For the centred cubic structure:

$$\overline{R}_{cs} = a \left(\frac{3}{4\pi} \right)^{\frac{1}{3}} \left[1 + \frac{1 - CX_B}{CX_B} \cdot \frac{\overline{V}_{AS}}{\overline{V}_B} \right]^{-\frac{1}{3}} \tag{5}$$

For the inverted centred cubic structure:

$$\overline{R}_{cs} = a \left(\frac{3}{4\pi} \right)^{\frac{1}{3}} \left[1 + \frac{CX_B}{1 - CX_B} \cdot \frac{V_B}{\overline{V}_{AS}} \right]^{-\frac{1}{3}} \tag{6}$$

2.2.4 Comparison of x-ray and electron micrograph results

The values of the structural parameters found by x-rays and electron microscopy are in good agreement as illustrated by *Tables 1. 2* and *3.* for SB, BSB and SBS copolymers.

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Table 1. Parameters of the lamellar structure

Copolymer	Gel of departure %	d, Å		d_A. Å		d_B. Å	
		XR	EM	XR	EM	XR	EM
BSB.343	29 MMA	404	425	238	225	166	200
BSB.375	29 MMA	425	405	280	245	145	160
SBS.364	30 Styr	369	380	200	205	169	175
SBS.332	37 AcV	442	420	279	250	163	170
SB.33	30 MMA	365	375	247	240	118	135

d is inter-sheet spacing, d_A is thickness of the polystyrene layer, d_B is thickness of the polybutadiene layer, XR is x-ray diffraction, and EM is electron microscopy.

Table 2. Parameters of the hexagonal structure

Copolymer	Gel of departure %	D, Å		$2R$, Å	
		XR	EM	XR	EM
BSB.372	29 MMA	348	320	155	140
BSB.373	29 MMA	403	365	200	185
BSB.374	30 Styr.	448	420	236	220
SBS.333	30 MMA	475	460	280	260
SBS.334	25 MMA	480	460	270	240
SB.32	25 Styr.	391	370	212	190

D is distance between the axes of two neighbouring cylinders. $2R$ is diameter of the cylinders, XR is x-ray diffraction, and EM is electron microscopy

Table 3. Parameters of the inverted hexagonal structure

Copolymer	Gel of departure %	D, Å		$2R$. Å	
		XR	EM	XR	EM
BSB.421	30 MMA	413	400	280	240
SBS.365	35 Styr.	545	590	415	400
SB.35	35 MMA	568	530	442	420
SB.36	30 MMA	663	710	460	450
SB.36	30 Styr.	670	655	460	440

D is distance between the axes of two neighbouring cylinders, $2R$ is diameter of the cylinders. XR is x-ray diffraction. and EM is electron microscopy.

For the intersheet spacing d of the lamellar structure and the distance D between the axis of two neighbouring cylinders of the hexagonal and the inverted hexagonal structure the agreement is very good (the measurements on electron micrographs being made on a great number of sheets or cylinders). The average difference is about 5 per cent and never exceeds 10 per cent.

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For d_A (thickness of the polystyrene layer), d_B (thickness of the polybutadiene layer), and $2R$ (diameter of the cylinders) the agreement is not so good but nevertheless it is satisfactory.

2.2.5 Localization of the solvent

Two methods can be used for studying the localization of the solvent in the mesomorphic structures.

2.2.5.1 Study of the glass transitions by differential scanning calorimetry (DSC)—For AB and ABA block copolymers of styrene and butadiene the T_g of the polybutadiene 1.2 blocks is in the vicinity of 0°C. So the use of a DSC equipped with tight cells has allowed us to evaluate the partition coefficient of the solvent between the two types of blocks by measuring the T_g of the polybutadiene 1.2 blocks in the dry copolymer and in mesomorphic gels of different concentrations in different solvents[21,22]. We have seen that, in the limits of the experimental error, the T_g of the polybutadiene 1.2 blocks is the same in the dry copolymer and in the mesomorphic gels. Therefore the solvent (MEK, MMA, styrene) does not enter the polybutadiene domains or, if it eventually enters them, it is in very small amounts (less than 10 per cent).

On the contrary, for polyisoprene–polyvinylpyridine copolymers with a microstructure of the polyisoprene block of about half-and-half 3.4 and 1.2), the T_g of the polyisoprene blocks changes with the amount of solvent in the mesomorphic gels; therefore there is an important partition coefficient for the solvent in such copolymers[23].

In the case of polystyrene–polyisoprene 1,4 *cis*, it has been impossible to use the DSC technique, because the T_g of the polyisoprene 1,4 *cis* blocks is near $-80°C$, that is to say in the vicinity of the melting point of the solvent used.

2.2.5.2 Study of the structure factor—It is well known that the respective intensities of the different diffraction orders on x-ray patterns change with the respective thicknesses of the two layers for the lamellar structure, with the diameter of the cylinders for the hexagonal structure, and with the diameter of the spheres for the cubic structure. Thus the study of the relative intensities of the reflections allows us to evaluate these structural parameters and then to calculate the partition coefficient.

To illustrate this procedure we shall take the example of the lamellar structure.

The structure factor of a lamella is given by[11]:

$$F(S) = \int_{\text{lamellar}} \rho(z) \cos 2\pi S z \, dz \tag{7}$$

where Oz is the direction perpendicular to the plane of the sheet and $\rho(z)$ is the distribution of the electron density sketched in *Figure 7*. By integration of the equation 7, taking account of the symmetry of the structure, one obtains:

$$F(d_A/d) = K(v_A - v_B)\frac{\sin \pi n d_A/d}{\pi n d_A/d} \tag{8}$$

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where n is the diffraction order and v_A and v_B are the number of electrons per Ångstrom cube for the layers of thickness d_A and d_B.
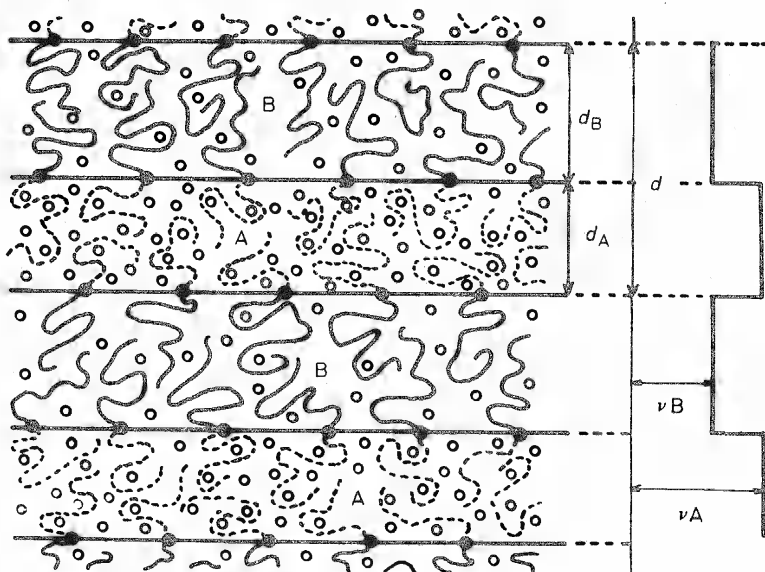

Figure 7. Schematic representation of the distribution of the electron density for a lamellar structure[11]

The intensity of the reflections is proportional to F^2 and the comparison of the relative intensities of the different diffraction orders gives the value of d_A/d. Then, by using formula 1, one can calculate the value of the partition coefficient φ_A.

We have found for toluene and SI 1,4 *cis* copolymers. $\varphi_A = \varphi_{PS} = 0.6$: for MMA and SB 1,2 copolymers. $\varphi_A = \varphi_{PS} > 0.9$. in agreement with the DSC results.

3 DOMAINS OF STABILITY OF THE DIFFERENT STRUCTURES

The principal factors governing the stability of the mesomorphic structures are the composition of the copolymer. the concentration of the solvent and the temperature.

3.1 Effect of the composition of the copolymer

For SB, BSB and SBS copolymers for instance, the type of structure adopted by the copolymer is determined by its composition. When the proportion of polybutadiene increases from 10 to 90 per cent one observes successively :

(a) a cubic centred structure formed by spheres of polybutadiene till about 18 per cent;

(b) an hexagonal structure formed by cylinders of polybutadiene till about 35 per cent;

(c) a lamellar structure formed by alternate layers of polystyrene and polybutadiene till about 65 per cent;

(d) an inverted hexagonal structure formed by cylinders of polystyrene swelled by the solvent till about 80 per cent;

(e) an inverted centred cubic structure formed by spheres of polystyrene swelled by the solvent.

3.2. Effect of the concentration of the solvent

Mesomorphic structures are observed for solvent concentrations smaller than about 45 per cent for copolymers with molecular weight between about 20 000 and 200 000.

3.3 Effect of temperature

The study, by DSC equipped with tight cells, of mesomorphic gels of SB. BSB and SBS copolymers containing less than 45 per cent of solvent. has
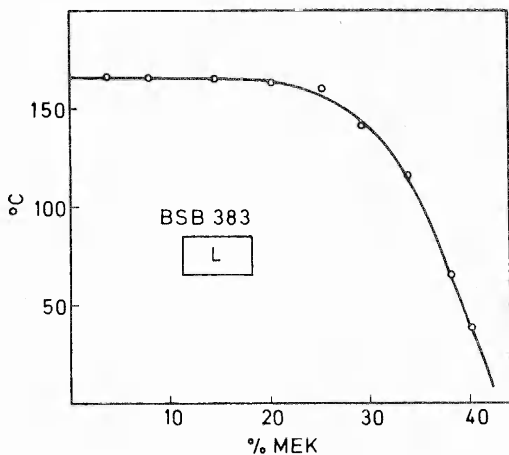
Figure 8. Phase diagram of the system BSB.383/MEK. Lamellar structure

shown that such copolymers exhibit only one mesophase as a function of temperature. The structure is lamellar (*Figure 8*), hexagonal (*Figure 9*), inverted hexagonal (*Figure 10*), centred cubic or inverted centred cubic (not represented) depending on the composition of the copolymer[5, 9].
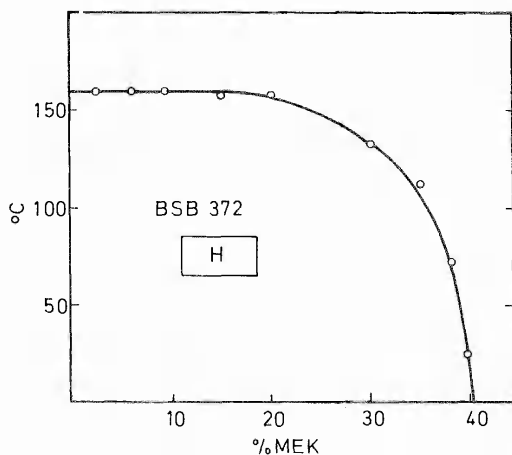
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Figure 9. Phase diagram of the system BSB.372/MEK. Hexagonal structure
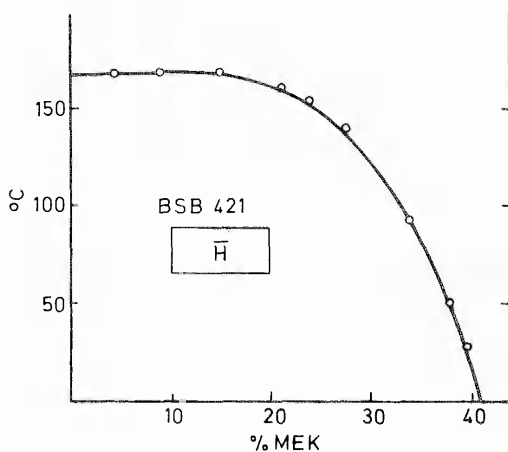

Figure 10. Phase diagram of the system BSB.421/MEK. Inverted hexagonal structure

4   FACTORS GOVERNING THE STRUCTURAL PARAMETERS

Among the factors governing the geometrical parameters of the meso-morphic structures, we shall only describe here the effect of the solvent concentration, the molecular weight of the copolymer and the polymerization of the solvent.

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4.1 Influence of the solvent concentration

We have to consider two cases. The first consists of systems copolymer–solvent with $\varphi_A \geqslant 0.9$, that is to say, the solvent practically does not enter the domains formed by the B blocks. Such systems are generally characterized by a decrease of the lattice parameter (intersheet spacing for the lamellar structure, distance between cylinders or spheres for the hexagonal or cubic structures) when the solvent concentration increases. Copolymers SB, SBS and BSB with polybutadiene 1,2 blocks, put in solution in MEK, MMA or styrene, are representative of this first class of systems. The second case is formed by systems copolymer–solvent with $0.4 < \varphi_A < 0.6$, where the solvent swells the two blocks. Such systems are generally characterized by the fact that the lattice parameter increases with solvent concentration. A typical example is polystyrene–polyisoprene 1,4 *cis* copolymers in solution in toluene or styrene.

4.1.1 AB and ABA polystyrene–polybutadiene 1,2 copolymers

We shall describe the influence of the solvent concentration upon the three following types of structure: lamellar, hexagonal and inverted hexagonal.
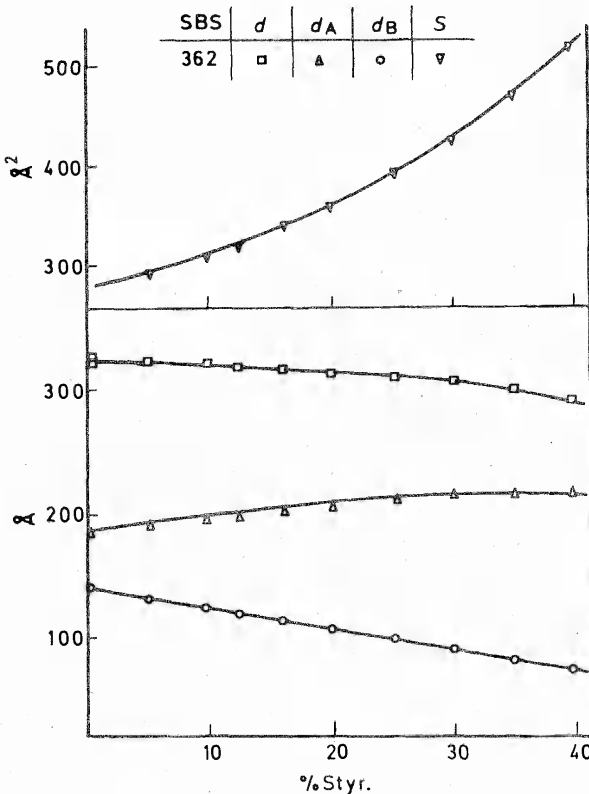

Figure 11. Variation of the parameters of the lamellar structure with solvent concentration. Copolymer SBS.362[9]

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4.1.1.1 *Lamellar structure*—The effect of the solvent concentration on the geometrical parameters of the lamellar structure is illustrated by *Figure 11* where we have plotted the structural parameters of the copolymer SBS.362 versus styrene concentration. One can see that when the solvent concentration increases: (a) the intersheet spacing d and the thickness d_B of the insoluble polybutadiene layer both decrease: (b) the thickness d_A of the soluble polystyrene layer and the average surface S available to a molecule both increase.

4.1.1.2 *Hexagonal and inverted hexagonal structures*—In order to illustrate the effect of the solvent concentration on the two types of hexagonal structures, we have plotted the variation of the structural parameters of the hexagonal and the inverted hexagonal structures versus solvent concentration in *Figure 12* and *Figure 13* respectively.
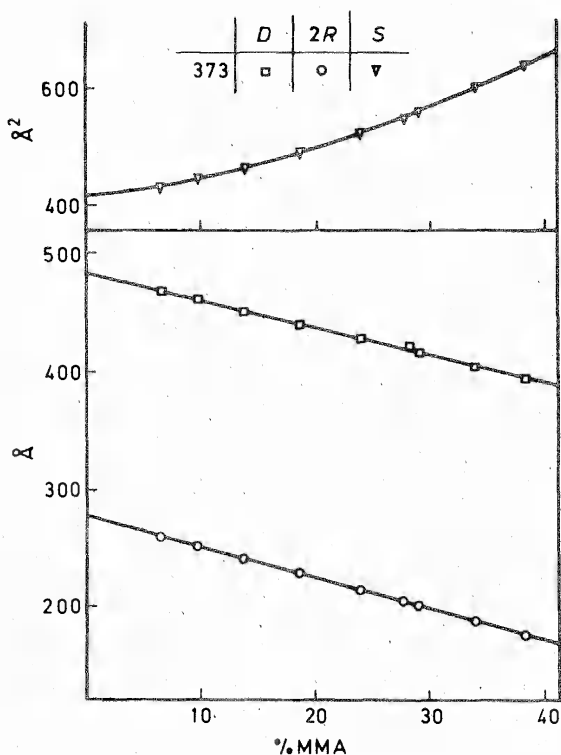

Figure 12. Variation of the parameters of the hexagonal structure with solvent concentration. Copolymer BSB.373[5]

One can see that for both the hexagonal and the inverted hexagonal structures, when the solvent concentration increases, the distance D between the axes of two neighbouring cylinders decreases and the average surface S
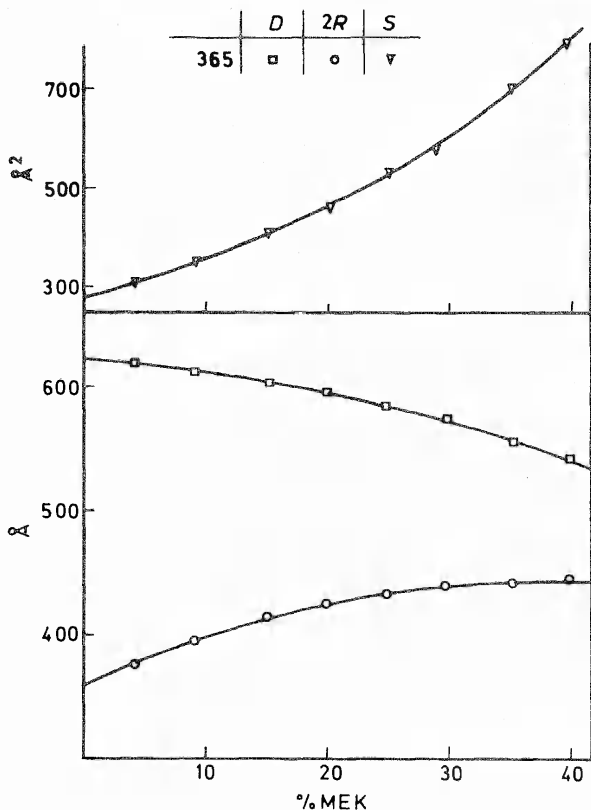
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Figure 13. Variation of the parameters of the inverted hexagonal structure with solvent concentration. Copolymer SBS.365[9]

available to a molecule increases. But the variation of the diameter of the cylinders is different for the two structures. For the hexagonal structure (copolymer BSB.373, *Figure 12*) the diameter $2R$ of the cylinders filled with the insoluble polybutadiene blocks decreases. On the contrary, for the inverted hexagonal structure (copolymer SBS.365, *Figure 13*) the diameter $2R$ of the cylinders filled with the polystyrene blocks swelled by the solvent (MEK) increases.

4.1.2 *Copolymers polystyrene–polyisoprene 1,4* cis

We shall only describe the behaviour of the lamellar structure. We shall take as example the copolymer polystyrene–polyisoprene 1,4 *cis* SI.822 in toluene solution (*Figure 14*). For this system the partition coefficient $\varphi_A = \varphi_{PS} = 0.6$[11]. One can see on the figure that the structural parameters (the intersheet spacing d, the thickness d_A of the polystyrene layer and the thickness d_B of the polyisoprene layer) all increase with toluene concentration. We

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have also plotted in dotted lines the variation of d_A and d_B calculated some years ago[10] with the hypothesis $\varphi_A = 1$, to show the influence of the partition coefficient on the values of d_A and d_B.
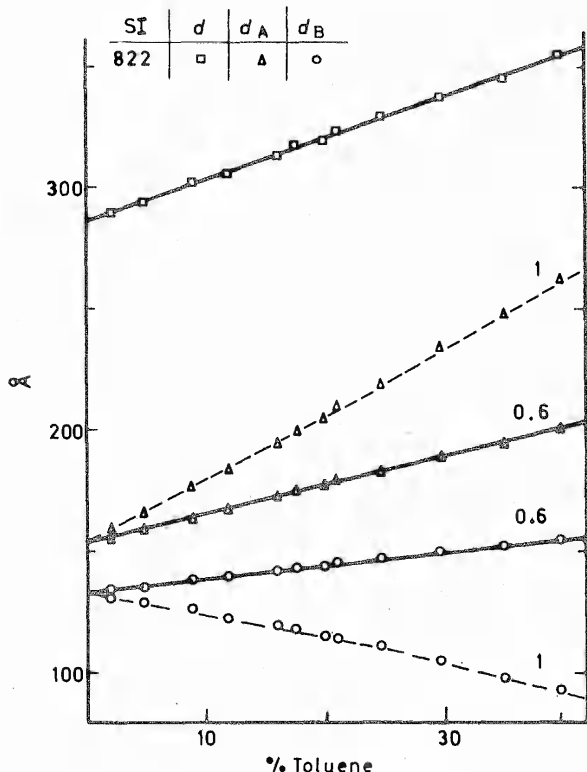

Figure 14. Variation of the parameters of the lamellar structure with solvent concentration. Copolymer SI.822. Partition coefficient $\varphi_A = 0.6$

4.2   Influence of the molecular weight of the copolymer

Among the different copolymers studied it is the lamellar structure of BSB copolymers which has the largest domain of stability. So we shall illustrate the influence of the molecular weight of the copolymer on the structural parameters with the results obtained for the lamellar structure of BSB copolymers. As shown in *Figure 15*, the intersheet spacing d increases monotonically with the molecular weight of the copolymer.
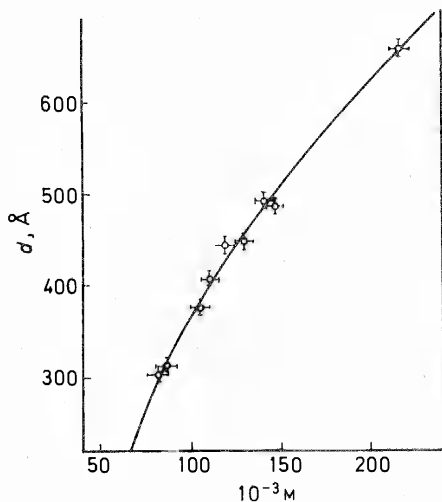
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Figure 15. Variation of the thickness (extrapolated to zero solvent concentration) of the sheets of the lamellar structure of BSB copolymers versus the molecular weight of the copolymer[5]
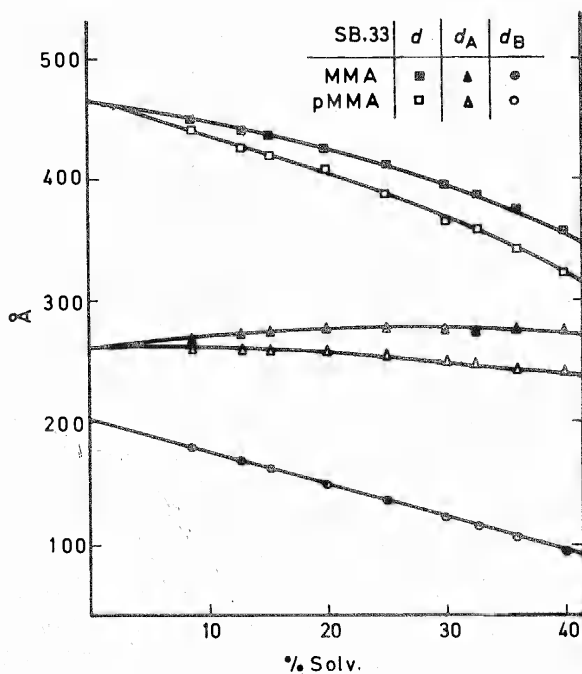

Figure 16. Variation of the parameters of the lamellar structure during the polymerization of the solvent. System SB.33/MMA[4]

4.3 Influence of the polymerization of the solvent

Mesomorphic gels prepared by swelling of the copolymer in a monomer (e.g. styrene, vinyl acetate, methyl methacrylate) have been converted to organized copolymers by polymerization of the monomer by u.v. light[4].
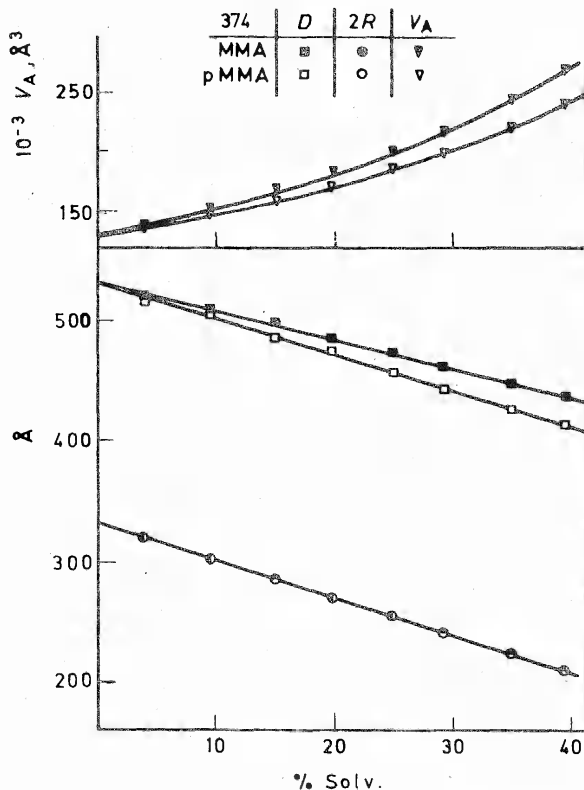

Figure 17. Variation of the parameters of the hexagonal structure during the polymerization of the solvent. System BSB.374/MMA[5]

For all systems studied x-ray diffraction gives the same structure before and after polymerization of the solvent. The *Figures 16* (SB.33), *17* (BSB.374) and *18* (SBS.365) illustrate the variation of the structural parameters of each structural type during polymerization. The examination of these figures shows that the polymerization of the monomer involves a contraction of the characteristic parameter of the soluble polystyrene blocks: d_A for the lamellar structure (*Figure 16*), D-$2R$ for the hexagonal structure (*Figure 17*) and $2R$ for the inverted hexagonal structure (*Figure 18*).
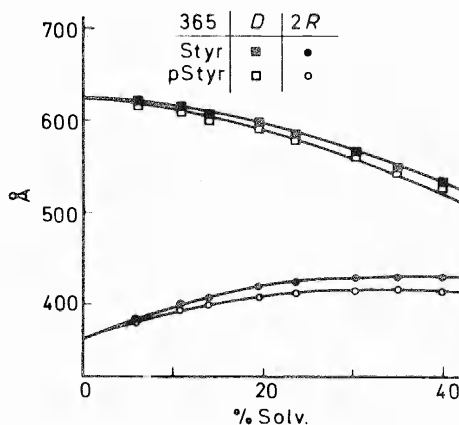
Figure 18. Variation of the parameters of the inverted hexagonal structure during the polymerization of the solvent. System SBS 365/Styrene[9]

5 STRUCTURAL STUDY OF DRY COPOLYMERS

The determination of the structure of dry copolymers has also been performed by using both low angle x-ray diffraction and electron microscopy. Nevertheless, a regular structure is obtained with dry copolymers only after submitting the copolymer to annealing, extrusion or shearing. depending upon the structural type of the polymer.

5.1. Cubic structure

Copolymers containing less than about 18 per cent of one block reveal a cubic structure after annealing at high temperature ($T > 150°C$) during more than 30 days[20].

5.2 Hexagonal structure

Copolymers with composition in the shortest blocks between about 18 and 35 per cent reveal a well ordered hexagonal structure after extrusion at high temperature in an apparatus of the type described by Keller[24-26].

5.3 Lamellar structure

Terris has obtained macrocrystals of lamellar structure with SI copolymers, by applying to the copolymer heated at high temperature a gradient of shear of about 0.07 s^{-1} (ref. 33).

A similar apparatus built in Orleans consists of an external cylinder made of two parts (perfectly adjustable) to allow an easy withdrawing of the oriented sample from the mould and a rotating inner cylinder. The diameter of the external cylinder is $R_1 = 52$ mm and the diameter of the inner cylinder is $R_2 = 50$ mm. The height of the cylinders is 50 mm. The apparatus operates under high vacuum. Eight grams of copolymer are enough to perform an experiment.

6 THEORIES OF THE MORPHOLOGY OF BLOCK COPOLYMERS

All theories are based on equilibrium considerations[27-32]. As with all problems involving the equilibrium between phases, the most favourable configuration corresponds to that which minimizes the total free energy. The problem of microphase segregation involves an evaluation of the change in the contribution to the free energy. when a certain dispersed phase is formed from some reference state, which generally corresponds to perfect mixing of the phases.

As the free energy change is:

$$\Delta G = \Delta H - T\Delta S$$

the problem will be solved if changes in the enthalpy (ΔH) and in the entropy (ΔS) can be calculated.

To simplify we shall only consider Meier's theory[29]. In Meier's theory. particular attention is given to the uniform filling of space by the chain segments to achieve a uniform density and an accurate evaluation of the configurational entropy constraints imposed by the particular domain morphology is made.

To make an analytical approach possible, he assumes that random flight statistics is applicable enabling the general diffusion equation to be used. Then he calculates the probability distribution of chains within a domain as a function of its size. The stable domain size is that corresponding to a uniform density. Thus he finds: for spheres, radius $R = 1.33\alpha\bar{K} M^{\frac{1}{2}}$; for cylinders, radius $R = 1.00\alpha\bar{K} M^{\frac{1}{2}}$; and for lamellae. thickness $d = 1.40\alpha\bar{K} M^{\frac{1}{2}}$ where $\bar{K}$ is a constant relating unperturbed end-to-end chain dimensions to molecular weight, M is the molecular weight of chains in dispersed phase, and α is the chain expansion parameter.

Thus, in order to achieve a uniform density of chain segments within a domain, the chains must have end-to-end dimensions which are different from those of a random coil.

Then he evaluates the chain density in the matrix and employs a domain separation which leads to a matrix possessing a uniform density. When such a condition is satisfied, the chain expansion parameters in the A and B phases are related by the following expressions:

$$\alpha_B \simeq \alpha_A \qquad \text{for spheres}$$

$$\alpha_B \simeq \alpha_A \left(\frac{M_B}{M_A}\right)^{\frac{1}{6}} \quad \text{for cylinders}$$

$$\alpha_B \simeq \alpha_A \left(\frac{M_B}{M_A}\right)^{\frac{1}{4}} \quad \text{for lamellae}$$

The evaluation of α_A and α_B in order to predict domain dimensions is carried out by minimizing the free energy consisting of the three following contributions:

(a) the elastic energy due to the deformation of the A and B random coils,
(b) the surface free energy due to the interface between A and B segments, and

(c) the constraint free energy due to the fact that A and B segments are confined to restricted volumes.

Thus Meier calculates the relative free energies for each domain shape and finds that morphological changes occur at determinate ratios of block lengths: expressing his results in per cent weight fraction of the shortest component, he finds 33 for the sphere–cylinder and 37.5 for the cylinder–lamellae transitions.

Experimentally we have found 18 ± 2 for the sphere–cylinder and 35 ± 5 for the cylinder–lamellae transitions.

The domain of stability predicted by Meier's theory is too large for spheres and too small for cylinders.

7 CONCLUSION

In this paper, we have shown that the safe determination of the structure of block copolymers in concentrated solution and in the dry state involves the use of both low angle x-ray diffraction and electron microscopy. Using these two techniques systematically we have established the existence of five types of structure and determined their domains of stability. The description of these five structures can be summarized as follows:

(i) The cubic structure results from the arrangement in a centred cubic lattice of spheres filled by the insoluble blocks of the copolymer.

(ii) The hexagonal structure consists of long cylinders filled with the insoluble blocks and arranged in an hexagonal array.

(iii) The lamellar structure consists of equidistant, plane and parallel sheets: each sheet is formed by the superposition of two layers: one containing the insoluble blocks the other containing the soluble block and the solvent.

(iv) The inverted hexagonal structure consists of long cylinders filled with the soluble blocks swelled by the solvent and arranged in an hexagonal array.

(v) The inverted cubic structure consists of spheres filled with the soluble blocks swelled by the solvent and arranged in a centred cubic lattice.

Studying the localization of the solvent in these structures we have shown that block copolymers can be classified in two categories. The first consists of copolymers where the solvent does not enter the microdomains formed by one type of blocks; such copolymers exhibit the five types of structures already described. The second consists of copolymers where the solvent swells the two types of blocks; for such copolymers it is not necessary to distinguish between the cubic and the inverted cubic structures, and between the hexagonal and the inverted hexagonal structures. For both categories, it is the composition of the copolymer, or more precisely the volume of the phases formed by the two types of blocks, which determines the structure adopted by the copolymer. Theoretical treatments predict such a behaviour at least qualitatively[14, 29].

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