Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Study of Liquid-Crystalline Structures of Polystyrene-Polybutadiene Block Copolymers by Small Angle X-ray Scattering and Electron Microscopy

André Douy [a] & Bernard R. Gallot [a]
[a] C. B. M., 45, Orleans 02, France
Version of record first published: 28 Mar 2007.

To cite this article: André Douy & Bernard R. Gallot (1971): Study of Liquid-Crystalline Structures of Polystyrene-Polybutadiene Block Copolymers by Small Angle X-ray Scattering and Electron Microscopy, Molecular Crystals and Liquid Crystals, 14:3-4, 191-207

To link to this article: http://dx.doi.org/10.1080/15421407108084637

Molecular Crystals and Liquid Crystals. 1971. Vol. 14, pp. 191–207

Printed in Great Britain

Study of Liquid-Crystalline Structures of Polystyrene-Polybutadiene Block Copolymers by Small Angle X-ray Scattering and Electron Microscopy†

ANDRÉ DOUY and BERNARD R. GALLOT

C.B.M.
45–Orleans 02
France

Received October 12, 1970; *in revised form February* 1, 1971

Abstract—We have studied by small angle X-ray scattering and electron microscopy the liquid crystalline structures exhibited by polystyrene-polybutadiene block copolymers. For that purpose we have developed an original method of electron microscopy. The types of structure (lamellar and hexagonal) and the values of the structural parameters found by X-ray diffraction and by electron microscopy are in good agreement. Induced by this good agreement we have applied our method of electron microscopy to the study of solutions of copolymers at all concentrations and we may picture a way of formation for liquid-crystalline structures exhibited by block copolymers.

1. Introduction

Using well-focused and strictly monochromatic X-rays, we have already shown,[1,2] by small angle X-ray scattering that *AB* polystyrene-polybutadiene (PS-PB) block copolymers exhibit, in solution in preferential solvents of polystyrene, liquid-crystalline structures for solvent concentration smaller than 45%.

We have also shown, by X-ray diffraction[3] that, when the composition of the copolymer changes, the liquid-crystalline structure of the copolymer also changes. We have found that:

—if the copolymer contains less than 35% of polybutadiene the structure is hexagonal,
—if the copolymer contains between 35 and 60% of polybutadiene the structure is lamellar,

† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

—if the copolymer contains more than 60% of polybutadiene the structure is hexagonal.

We know that[1] the hexagonal structure consists of a set of indefinitely long cylinders arranged in a regular hexagonal two-dimensional array. But different questions arise about this stucture. Which block is in the cylinders, the soluble block or the insoluble one? Is the same block in the cylinders for copolymers containing less than 35% of polybutadiene and for copolymers containing more than 60% of polybutadiene?

X-ray diffraction cannot surely solve the problem. It only says: the structure is hexagonal and the distance D between the axes of two neighboring cylinders is x Å. So it is necessary to hypothesize on the position of the blocks for calculating the diameter of the cylinders. But, if we study the cylinders by electron microscopy, we surely solve the problem. Therefore we have undertaken the study of concentrated solution of polystyrene-polybutadiene block copolymers by using both small angle X-ray scattering and electron microscopy.

2. Preparation and Characterization of Block Copolymers

Polystyrene-polybutadiene (PS-PB) block copolymers were prepared by anionic polymerization under high vacuum.[1]

Molecular weight (Table 1) determinations were performed by light scattering, osmometry and Gel Permeation Chromatography.

TABLE 1 Molecular Weights and Compositions of the Copolymers

Cop.	M_w PS	% PB	$M_{w\,\text{Cop.}}$
SB. 32	49.000	30.5	70.500
SB. 33	49.000	39.8	81.400
SB. 34	49.000	50.2	98.400
SB. 36	49.000	71.7	173.000
SB. 1	71.000	39	117.000

3. Preparation of Solid Samples

As electron microscopy requires solid samples thinner than 1000 Å, we have used as preferential solvents of polystyrene different

monomers easily polymerizable by UV light (styrene, methylmethacrylate, vinyl acetate···) and applied the following method to prepare our samples.[4]

At first, by small angle X-ray scattering, we resolve the structure of the mesomorphic gels prepared with the monomer as a preferential solvent. Then we make a total polymerization of the monomer by UV light. At last, by small angle X-ray scattering, we verify that the periodic structure has not been destroyed by polymerization and we measure its new parameters.

In Fig. 1 we give an example of the variation of the structural parameters during polymerization. We have plotted the structural parameters of the lamellar structure before polymerization of the methylmethacrylate (black points) and after polymerization of the methylmethacrylate (white points) for the copolymer SB. 33.

We see that during polymerization:

—the inter-sheet spacing d decreases
—the thickness d_A of the polystyrene soluble layer decreases
—the thickness d_B of the polybutadiene insoluble layer remains constant.

After studying the solid sample by X-ray diffraction, we cut it with an ultramicrotome (Ultratome III L.K.B.). We stain the diene block by fixation of osmium tetroxide on the double bonds of polybutadiene by allowing the sections to stand in the vapour of osmium tetroxide dissolved in an aqueous solution of sodium cacodylate for about 3 hours). Then we study the ultrathin section with an electron microscope (Hitachi HU. IICS).

Some questions may arise about our sample preparative method. Is there any polymerization of the monomer induced by X-rays during the exposure of the mesomorphic gels? Is there any fixation of osmium tetroxide on some unpolymerized monomer or on polystyrene and polymethecrylate? We have verified that in our experimental conditions X-rays do not polymerize the styrene or the MMA and that there is no unpolymerized monomer remaining in our solid samples. We have also verified that there is no fixation of Osmium tetroxide on polystyrene and polymethylmethacrylate homopolymers with our staining procedure.

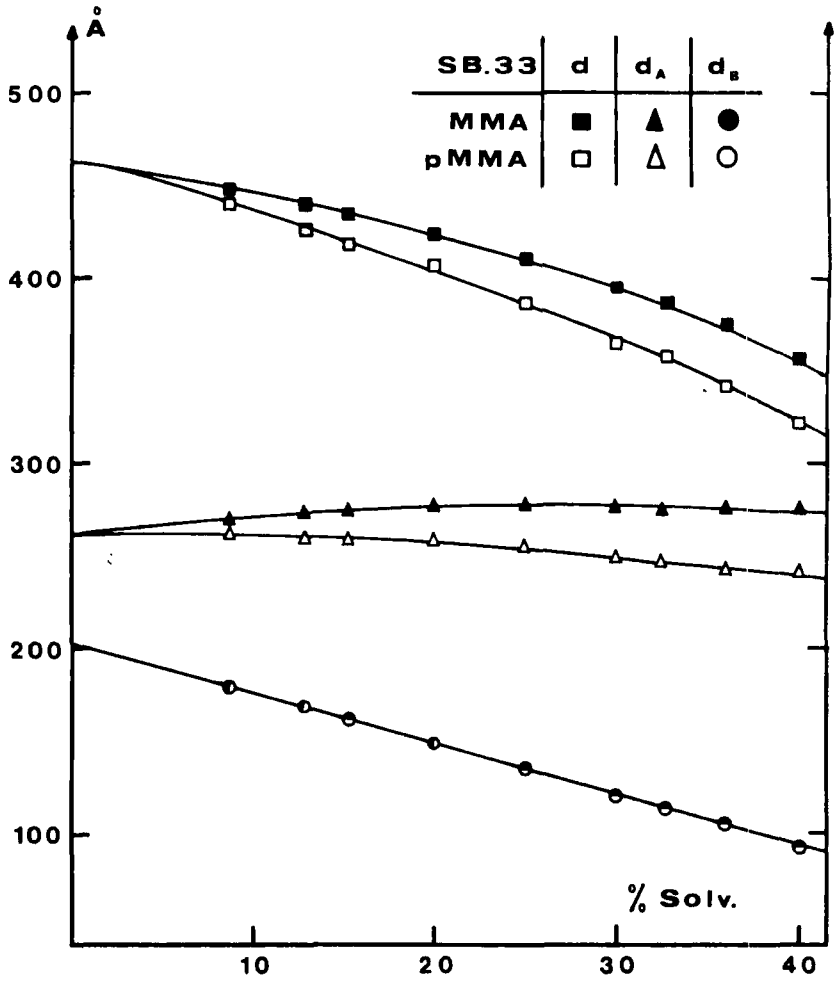

Figure 1. Variation of structural parameters during polymerization. Structural parameters of lamellar structure (a) before polymerization of methylmethacrylate (black points); (b) after polymerization of methylmethacrylate (white points) for the copolymer SB. 33.

4. Study of Liquid-Crystalline Structures

In Figs. 2 to 7 we give examples of electron micrographs provided by ultrathin sections of solid samples prepared from solutions of copolymers in methyl methacrylate (MMA).

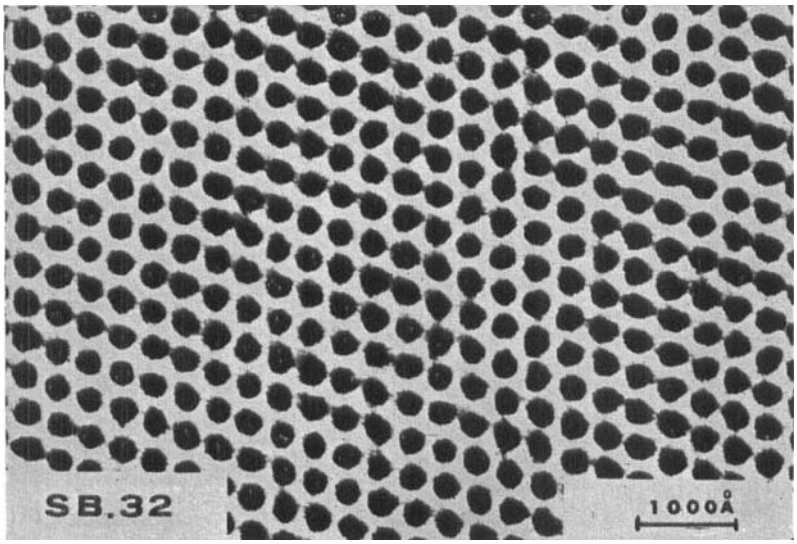

Figure 2. Electron micrograph of the copolymer SB. 32.

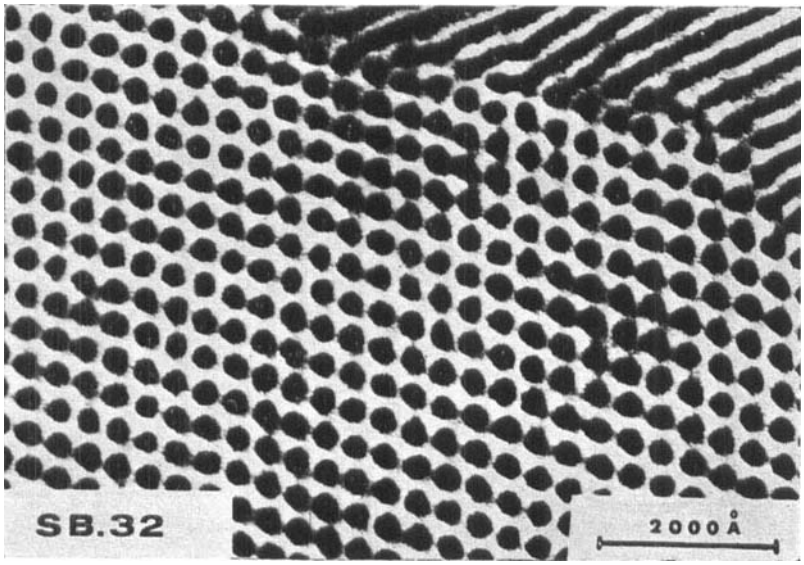

Figure 3. Electron micrograph of the copolymer SB. 32.

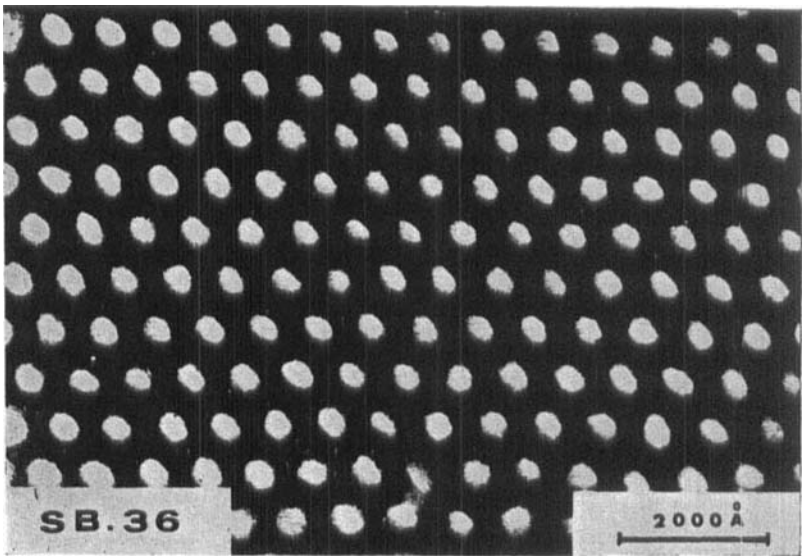

Figure 4. Electron micrograph of the copolymer SB. 36.

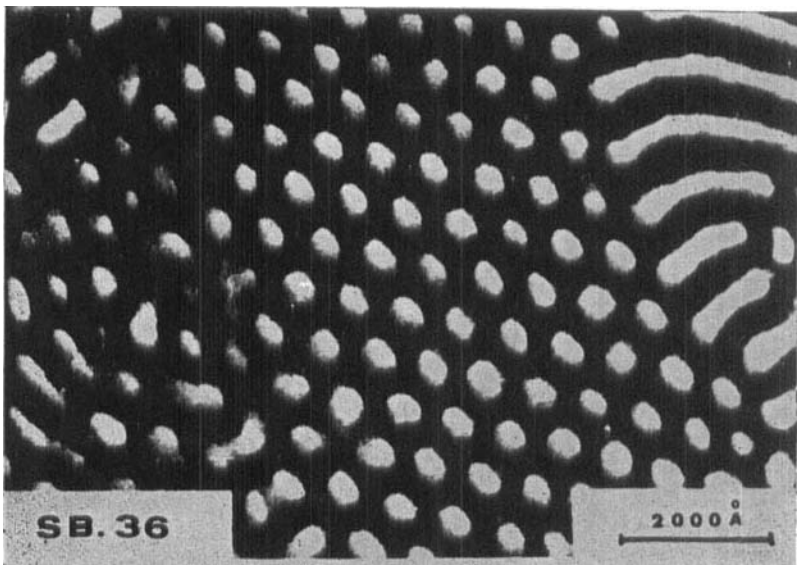

Figure 5. Electron micrograph of the copolymer SB. 36.

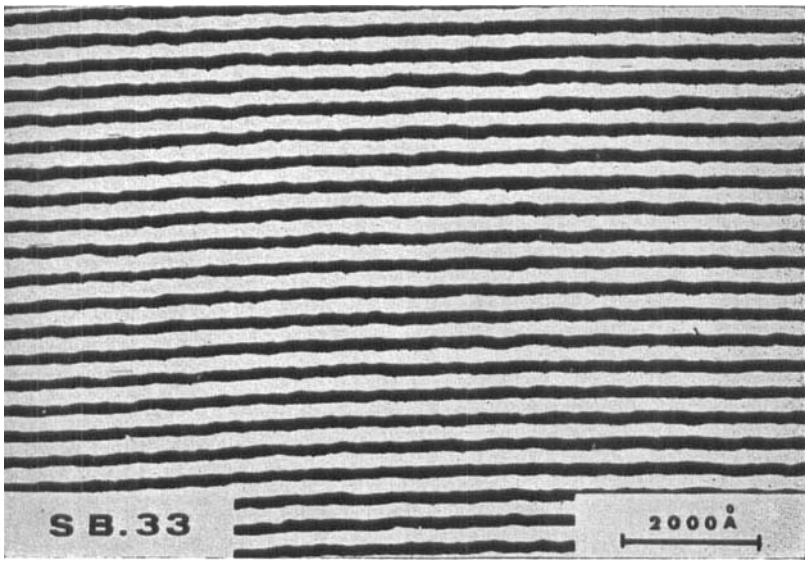

Figure 6. Electron micrograph of the copolymer SB. 33.

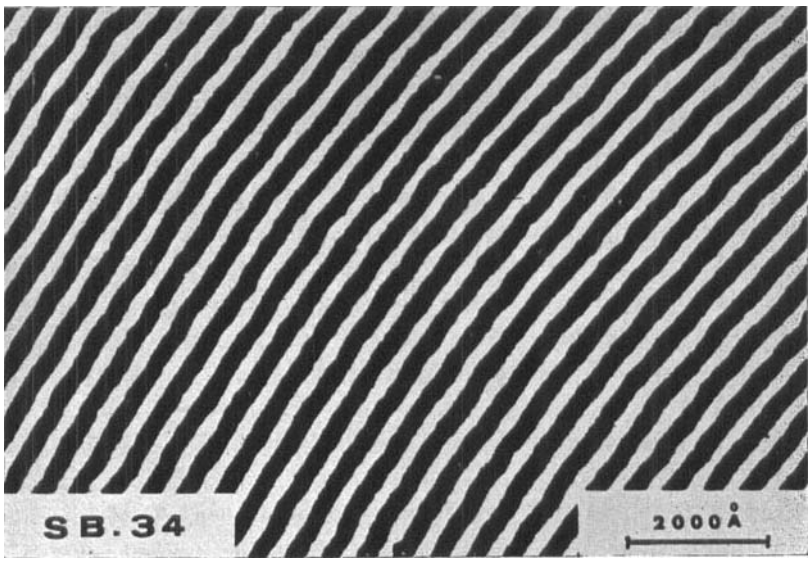

Figure 7. Electron micrograph of the copolymer SB. 34.

As we have coloured the samples by fixation of osmium tetroxide on the double bonds of polybutadiene, polystyrene appears in white and polybutadiene in black in all electron micrographs.

A. Case of the Hexagonal Structure

Figures 2 and 3 are electron micrographs of sections of the copolymer SB. 32 having a composition of 30,5% polybutadiene.

In the Fig. 2 we see black spots on a white background. The spots have the shape of circles which are distinct and isolated; they are arranged on an hexagonal array. The circles are cross-sectional views of cylinders (the plane of cutting is practically perpendicular to the axis of the long cylinders).

In the right upper corner of Fig. 3, we see some stripes, alternatively black and white; these stripes are sections of cylinders cut by a plane parallel to their axis. Therefore the structure cannot be cubic, but necessarily consists of a set of indefinitely long cylinders arranged in a regular hexagonal two-dimensional array.

In Figs. 2 and 3 the circles are black and we are sure that the cylinders are filled with polybutadiene.

Figures 4 and 5 show electron micrographs of sections of the copolymer SB. 36 having a composition of 71,7% polybutadiene.

In Fig. 4 we see a section of the long cylinders by a plane nearly perpendicular to the direction of their axes and we observe white circles arranged on an hexagonal array.

In the main part of Fig. 5 we observe white spots which have nearly the shape of ellipses (the plane of cutting makes a small angle with the plane perpendicular to the direction of the axis of the cylinders). In the right part of the Fig. 5, we observe some cylinders cut by a plane parallel to the direction of their axes. Therefore, like in the case of the copolymer SB. 32, the structure is hexagonal. But, for the copolymer SB. 36, the circles being white the cylinders are filled by the polystyrene in solution in the solvent.

From the four preceding micrographs we can conclude that if the copolymer contains less than 35% of polybutadiene the cylinders are filled with polybutadiene, but if the copolymer contains more than 60% polybutadiene the cylinders are filled with polystyrene.

B. Case of the Lamellar Structure

In Figs. 6 and 7 we give examples of electron micrographs provided by sections of the lamellar structure which covers the field of compositions in polybutadiene between 35 and 60%.

The sections have been made in a direction perpendicular to the plane of the sheets of the lamellar structure and we observe a striated structure. In this striated structure, the black stripes contain the polybutadiene and the white stripes contain the polystyrene and the polymerized solvent.

If we compare the micrograph of the copolymer SB. 33 containing 39,8% of polybutadiene (Fig. 6) with the micrograph of the copolymer SB. 34 containing 50,2% of polybutadiene (Fig. 7) we see that when the composition in polybutadiene of the copolymer increases the broadness of the black stripes of polybutadiene increases as it has been demonstrated elsewhere.[3,4]

These micrographs reveal an ordered structure which extends over several microns. The order which is seen in Figs. 6 and 7 and in similar other pictures, extend appreciably further than can be recorded on a single negative; in fact it covers the full area of a hole of the grid without any essential interruption of this order within it.

C. Comparison of the Structural Parameters Found by X-ray and Electron Microscopy

We have shown how one can distinguish the different structures by electron microscopy. Now we have to compare the values of the structural parameters found by X-ray diffraction (X.R.) and by electron microscopy (E.M.).

We have collected (as an example) in Tables 2 and 3 the values of the structural parameters of solid samples prepared from solutions of copolymers in 30 ± 1% of MMA.

For the hexagonal structure, the structural parameters have been measured on electron micrographs resulting from sections by a plane perpendicular to the axis of the cylinders and in which the circles are well isolated (see Fig. 2 for instance).

For the lamellar structure, the structural parameters have been measured on electron micrographs resulting from sections by a plane perpendicular to the plane of the sheets. If we cut the lamellar

TABLE 2 Comparison of the Values of the Structural Parameters Found by X-rays (X.R.) and Electron Microscopy (E.M.) for the Two Types of Hexagonal Structure

	S.B. 32		SB. 36	
	X.R.	E.M.	X.R.	E.M.
D(Å)	380	360	663	710
2R(Å)	205	180	460	400

TABLE 3 Comparison of the Values of the Structural Parameters Found by X-rays (X.R.) and Electron Microscopy (E.M.) for the Lamellar Structure

	S.B. 33		S.B. 34	
	X.R.	E.M.	X.R.	E.M.
d(Å)	365	375	424	440
d_A(Å)	247	240	253	240
d_B(Å)	118	135	171	200

structure by planes making different angles with the plane of the sheets, the thickness found for the sheets is a minimum when the plane of cutting is perpendicular to the plane of the sheets.

In order to facilitate the understanding of Tables 2 and 3 we recall that:

(1) for the hexagonal structure:
—D is the distance between the axis of two neighboring cylinders
—$2R$ is the diameter of the cylinders
(2) for the lamellar structure:
—d is the inter-sheet spacing
—d_A is the thickness of the polystyrene soluble layer
—d_B is the thickness of the polybutadiene insoluble layer.

Examination of Tables 2 and 3 shows that the agreement between the values of the structural parameters found by X-ray diffraction (X.R.) and by electron microscopy (E.M.) is very good:

—about 6% for D and d
—about 15% for $2R, d_A$ and d_B.

A similar agreement is found for solid samples prepared from copolymer solutions of different concentrations in styrene or MMA.

5. Study of Dilute Solutions

Induced by this good agreement, we have applied our method of study by electron microscopy to the field of higher concentrations in solvent, i.e. concentrations between 45 and 99% of solvent. In this field of concentrations there is no regular periodicity, so X-ray diffraction is very difficult to be applied and gives very poor results.

We shall take the example of the copolymer SB. 1 containing 39% of polybutadiene and giving a lamellar structure for solvent concentrations smaller than 45%. All the samples used for electron microscopic studies have been prepared by polymerization of solutions of the copolymer in styrene monometer. We have chosen styrene as solvent in order to prevent any effect of incompatibility between polymeric chains during the polymerization of the monomer.

For solvent concentrations smaller than 45% the structure is lamellar, and one can see in Fig. 8 the black stripes of polybutadiene and the white stripes of polystyrene, for a composition of 32% of solvent.

When the solvent concentration increases and exceeds 45%, the regularity of the lamellar structure decreases. The lamellae of polybutadiene edge away from one another and do not remain plane and parallel. The disorder increases with solvent concentration; it is higher for 70% (Fig. 10) than for 49% (Fig. 9).

For a solvent concentration of about 75% the lamellar structure crashes and gives raise to cylinders more or less rectilinear (Fig. 11). When the solvent concentration increases the cylinders edge away from one another and break into shorter cylinders (Figs. 12 and 13).

At last, for a concentration of 1% of copolymer (99% of solvent), the average length of the cylinders of polybutadiene is about 5 times their diameter (Fig. 14).

6. Conclusion

From this paper we can draw two important conclusions. First, we bring the material proof of the existence of liquid-crystalline

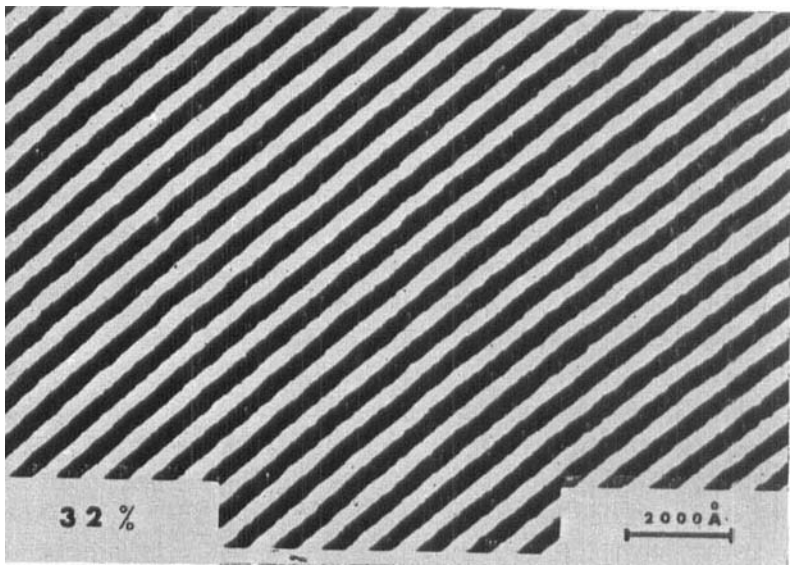

Figure 8. Electron micrograph of the copolymer SB. 1 plus 32% polystyrene.

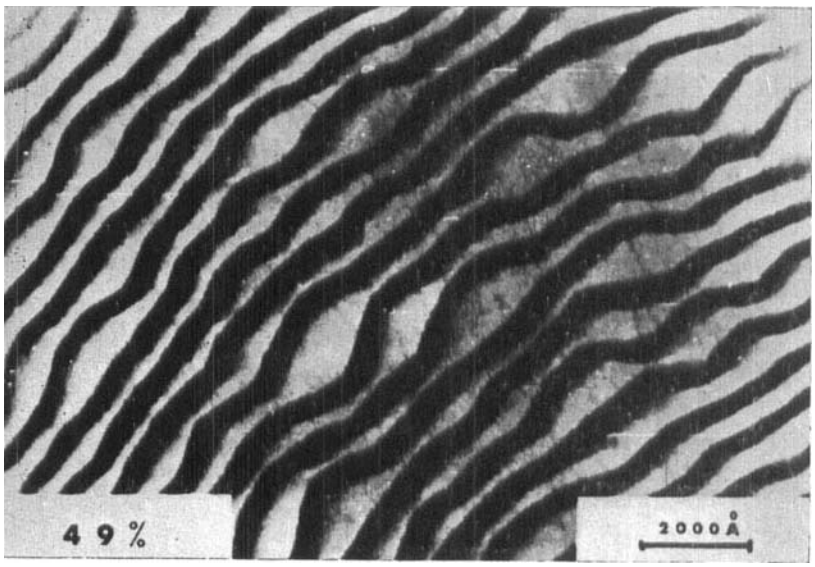

Figure 9. Electron micrograph of the copolymer SB. 1 plus 49% polystyrene.

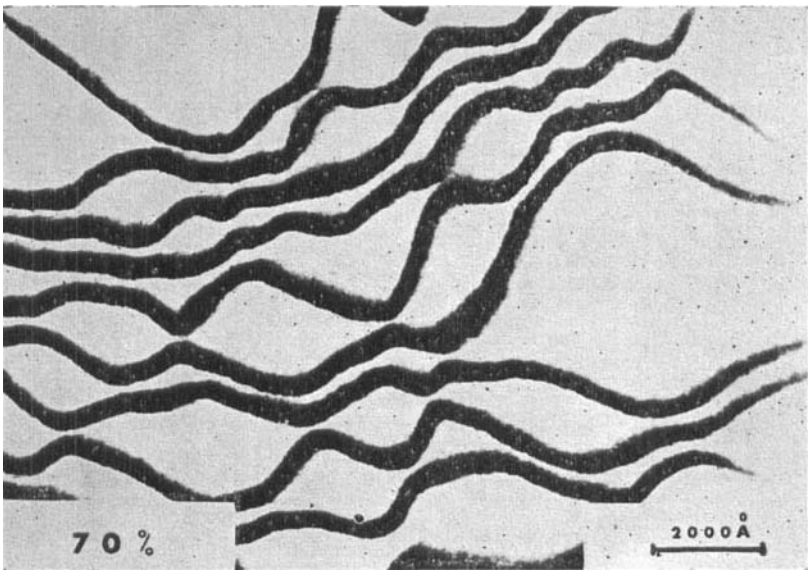

Figure 10. Electron micrograph of the copolymer SB. 1 plus 70% polystyrene.

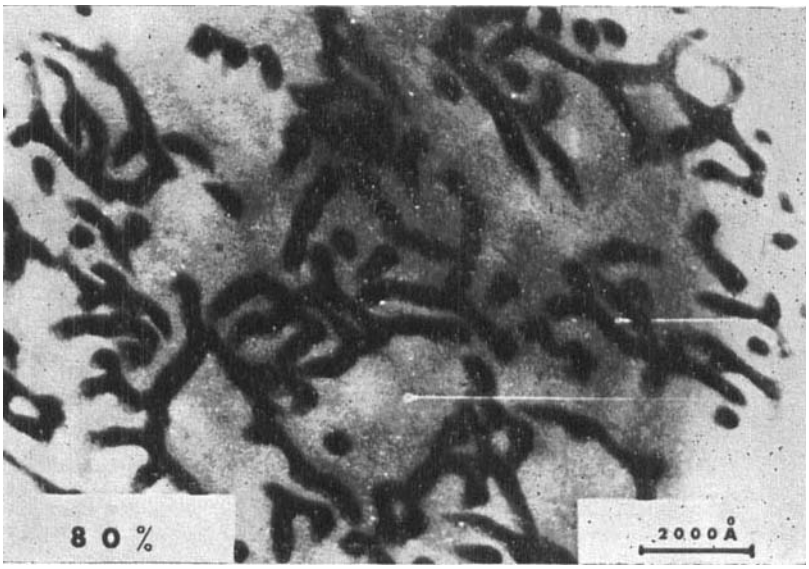

Figure 11. Electron micrograph of the copolymer SB. 1 plus 80% polystyrene.

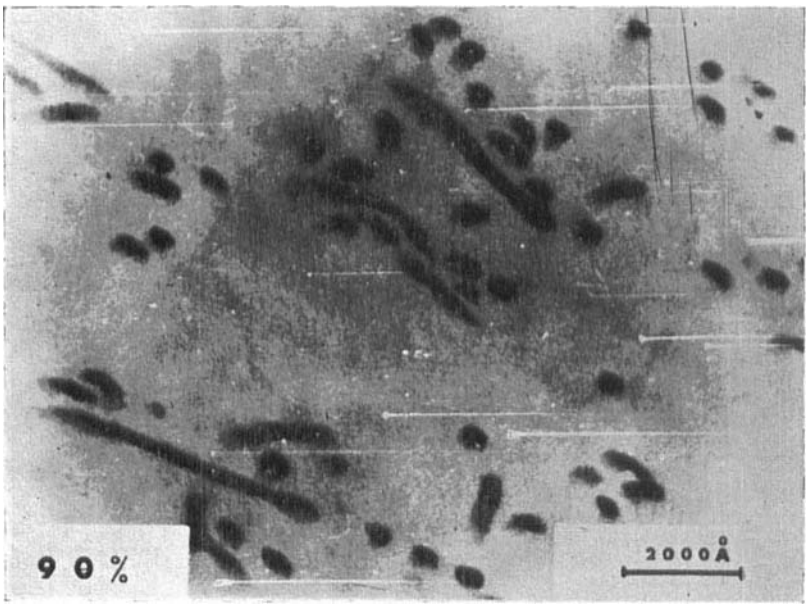

Figure 12. Electron micrograph of the copolymer SB. 1 plus 90% polystyrene.

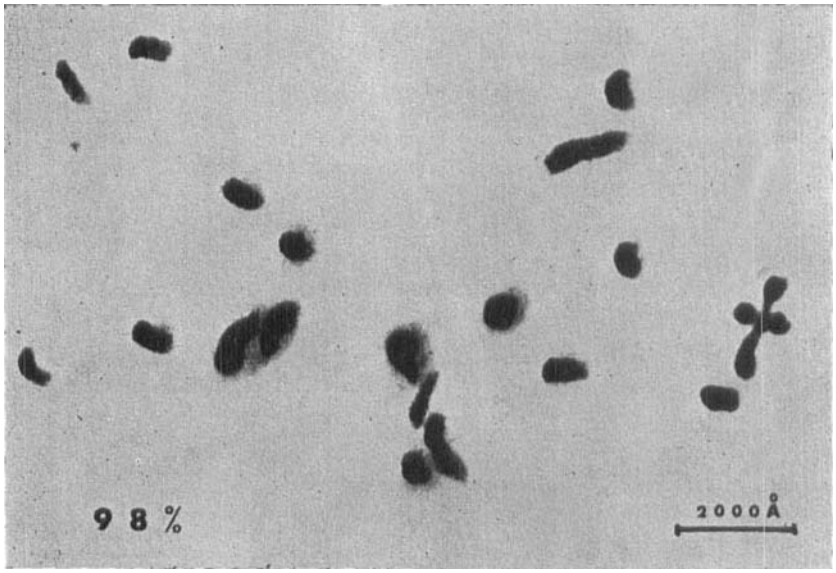

Figure 13. Electron micrograph of the copolymer SB. 1 plus 98% polystyrene.

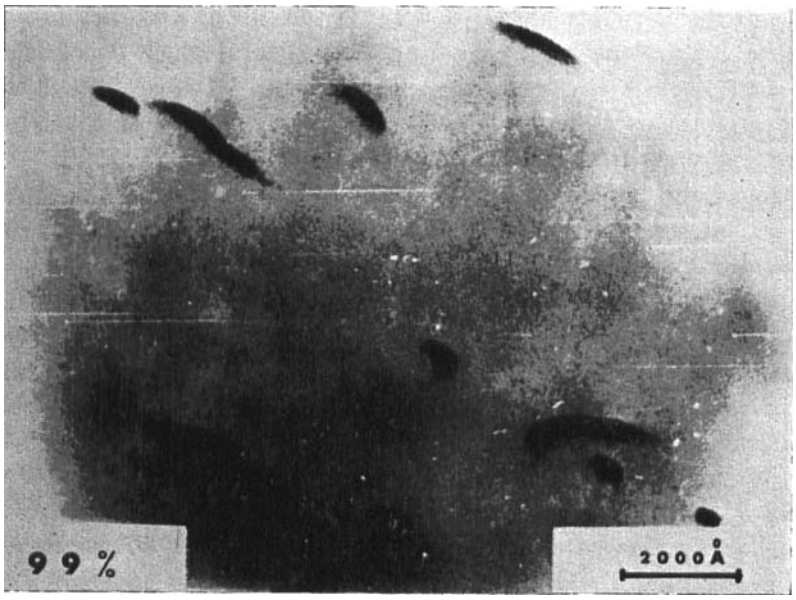

Figure 14. Electron micrograph of the copolymer SB. 1 plus 99% polystyrene.

structures for concentrated solutions of block copolymers. Secondly we show the mechanism of formation of liquid-crystalline structures.

Different authors have already studied concentrated solutions of block copolymers by X-ray diffraction[5,6,7] and proposed three models of structure (lamellar, hexagonal and cubic). They have also shown that the nature of the blocks, the composition of the copolymer, the nature and the concentration of the solvent are the principal factors governing the type of structure and the values of the structural parameters adopted by the copolymers.[1] In this paper we give electronmicrographs of liquid-crystalline structures exhibited by block copolymers and therefore we demonstrate directly the reality of their existence. We also show, by our technique of electron microscopy, the existence of two types of hexagonal structures one with cylinders filled with the insoluble block and corresponding to copolymers containing less than 35% of the insoluble block, the other with cylinders filled with the soluble block in solution in the solvent and corresponding to copolymers containing more than about

60% of the insoluble block. Lastly, we prove the accuracy of our former conclusions[1] inferred from the study of block copolymers by small angle X-ray scattering since the types of structure and the values of the structural parameters found by X-rays and electron microscopy are in good agreement (Tables 2 and 3).

The second important conclusion concerns the formation of liquid crystalline structures. Our study of copolymer solutions of all concentrations show that, starting from very dilute solutions where mono and pluri molecular micellae have been postulated,[8] we pass through aggregates of different sizes and shapes (at first cylindrical aggregates: Figs. 14 to 11; then lamellar aggregates: Figs. 10 and 9;) and we reach a lamellar liquid-crystalline structure for copolymers containing between 35 and 60% of the insoluble block (Fig. 8). A nearly similar process is found for copolymers containing less than 35% or more than 60% of the insoluble block, but it does not involve lamellar aggregates and leads to an hexagonal liquid crystalline structure (Figs. 2 and 4).

Such a formation of liquid-crystalline structures would be of some interest to explain the disagreement between the conclusions about the structure of " dry copolymers " drawn by different authors[9] from electron microscopic studies of films prepared by evaporation from dilute solutions of copolymers. Depending on the speed of evaporation they fix any structure corresponding to concentrations between 1 and 100% of polymer. On the contrary, with our solid sample preparative method (by polymerization of a monomer used as a solvent of the copolymer) we have the advantage of studying systems in equilibrium[5] and of any concentration between 1 and 100% of copolymer. Furthermore, we are able to perform (for solvent concentration smaller than 45%) our studies by X-rays and electron microscopy on the same samples.

Is it necessary to claim that our solid samples form a new class of rigid polimeric materials presenting a large interest in an industrial point of view. These materials are two or three component systems depending on the fact that the monomer used as a polymerizable solvent is or is not the monomer of one block, and their properties can be changed at will by changing the nature and the amount of the monomer.

Acknowledgements

Professor J. Bardolle, from the University of Orleans, is greatly acknowledged for allowing us to use his electron microscope.

We also acknowledge the Referee for inducing us to give more details on our solid sample preparative method.

REFERENCES

1. Douy, A., Mayer, R., Rossi, J. and Gallot, B., *Mol. Cryst. and Liq. Cryst.* **7**, 103 (1969).
2. Douy, A. and Gallot, B., *C.R. Acad. Sci. Paris* **268**, 1218 (1969).
3. Douy, A. and Gallot, B., *Makromol. Chemie*, in press.
4. Douy, A. and Gallot, B., *IUPAC International Symposium on Macromolecules*, Leiden, 1970 (Preprint 1-22, p. 99).
5. Douy, A. Gervais, M. and Gallot, B., *C.R. Acad. Sci. Paris* **270**, 1646 (1970).
6. Gallot, B., Mayer, R. and Sadron, C., *C.R. Acad. Sci. Paris* **263**, 42 (1966).
7. Skoulios, A. and Finaz, G., *J. Chim. Phys.* 473 (1962).
8. Gallot, Y., These, Strasbourg (1964).
9. Hendus, H., *Kolloid Z.* **216**, 110 (1967).
   Bradford, E. B., *J. Polymer Sci.* **A. 1–6**, 1661 (1968).
   Inoue, T., *J. Polymer Sci.* **A. 2–7**, 1283 (1969).
   Lewis, *Nature* **223**, 494 (1969).
   Matsuo, M., *Polymer* **10**, 79 (1969).