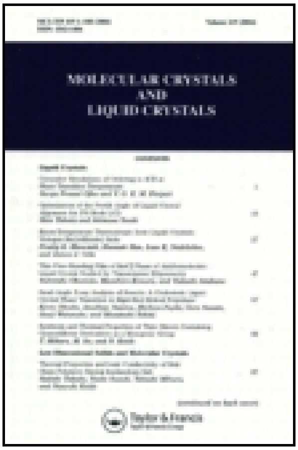

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Structure of Liquid Crystalline Phases from Amorphous Block Copolymers

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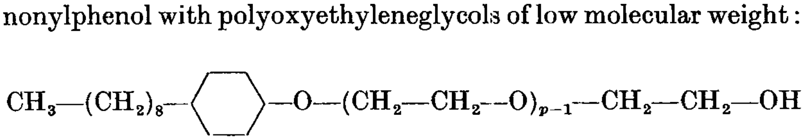
Abstract—We have studied the structure of liquid crystalline phases of *A–B* block copolymers by small-angle X-ray scattering. We have found three types of structure: lamellar, hexagonal and cubic. We have also shown the influence on the structural type and structural parameters of the following factors: concentration and nature of the solvent, molecular weight and composition of the copolymer.

Introduction

In presence of suitable solvents, amphipatic molecules exhibit, as it is well known, liquid-crystalline phases.

Systematic studies performed by X-ray diffraction method,[1,2] have allowed the determination of the structure of numerous colloidal systems, and shown that: hydrophilic groups and polar solvents on one hand, hydrophobic chains and non polar solvents on the other hand, occupy in space different fields.

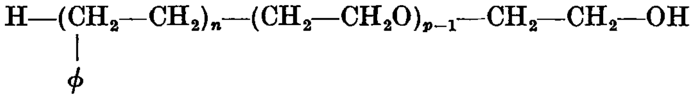
Among colloidal systems, water-Arkopals systems are of a particular interest. They result from the condensation of para-nonylphenol with polyoxyethyleneglycols of low molecular weight:



$CH_3—(CH_2)_8—C_6H_4—O—(CH_2—CH_2—O)_{p-1}—CH_2—CH_2—OH$

and exhibit two types of liquid-crystalline structures: hexagonal and lamellar.[2]

Copolymers polystyrene-polyoxyethylene have nearly the same chemical formula as Arkopals, from which they essentially differ by their molecular weight:



$$H{-}(\underset{\substack{|\\ \phi}}{C}H_2{-}CH_2)_n{-}(CH_2{-}CH_2O)_{p-1}{-}CH_2{-}CH_2{-}OH$$

so it is not surprising that they exhibit the same types of liquid-crystalline structures in the presence of a good solvent of one block.[3]

Are such structures possible with other block copolymers? We have thought that the presence in a copolymer of two blocks owning different solubilities must be sufficient to obtain liquid crystalline phases and that it is not necessary to have a crystallizable block of polyoxyethylene in the molecule.

In order to prove the truth of this assumption we have undertaken the study of concentrated solution of block copolymers by small angle X-ray scattering. We have used different amorphous *A–B* block copolymers, namely polystyrene-polyisoprene (SI), polystyrene-polybutadiene (SB) and polyisoprene-poly-2-vinylpyridine (IVP). We have found three types of liquid-crystalline structures: lamellar, hexagonal and cubic. We have also investigated the influence on the structural types and structural parameters of the following factors: concentration and nature of the solvent, molecular weight and composition of the block copolymer.

Experimental

A. PREPARATION OF BLOCK COPOLYMERS

Our block copolymers were prepared by anionic polymerization, under high vacuum, in an all glass apparatus. Monomers, solvents and initiators were rigorously purified under high vacuum. The systems used only break-seals and no greased joints or taps.

Polystyrene-polyisoprene block copolymers were prepared in toluene, at 25 °C, with secondary buthyllithium as initiator.

Polystyrene-polybutadiene and polyisoprene-poly-2-vinylpyridine block copolymers were prepared in tetrahydrofuran, at – 70 °C, with cymul potassium as initiator.

B. CHARACTERIZATION OF BLOCK COPOLYMERS

Molecular weight (Table 1) determinations by both light scattering and Gel Permeation Chromatography on all samples showed that the technique of polymerization produce polymers with ratio M_w/M_n smaller than 1,10.

TABLE 1

	Nature of sequences	M_w 1st sequence	% of weight 1st sequence	Total mass
SI.821	polystyrene-polyisoprene	23,000	74	31,000
SI.822		23,000	57	40,500
SI.823		23,000	52	44,000
SI.824		23,000	45	51,000
SI.921		30,000	63	47,500
SI.320		46,900	73	63,900
IVP.22	polyisoprene-poly-2-vinyl-pyridine	17,500	79	21,100
SB.1	polystyrene-polybutadiene	71,000	61	117,000

The microstructure of polydienes was obtained by measuring the relative amounts of I,2; I,4 and 3,4 forms by N.M.R. and Infra-red.

C. PREPARATION OF LIQUID CRYSTALLINE GELS

We have prepared liquid-crystalline gels of block copolymers by dissolution of the block copolymer in a suitable solvent, that is to say in a preferential solvent of one block.

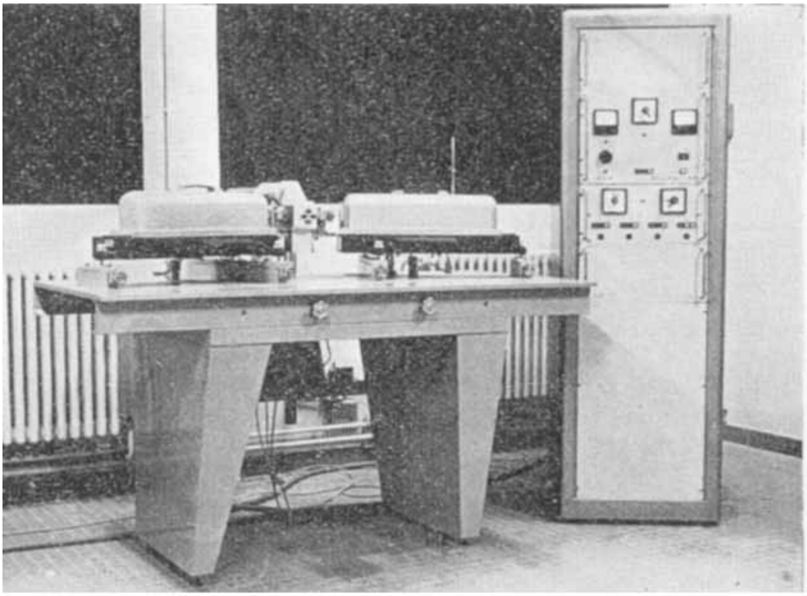


FIGURE 1

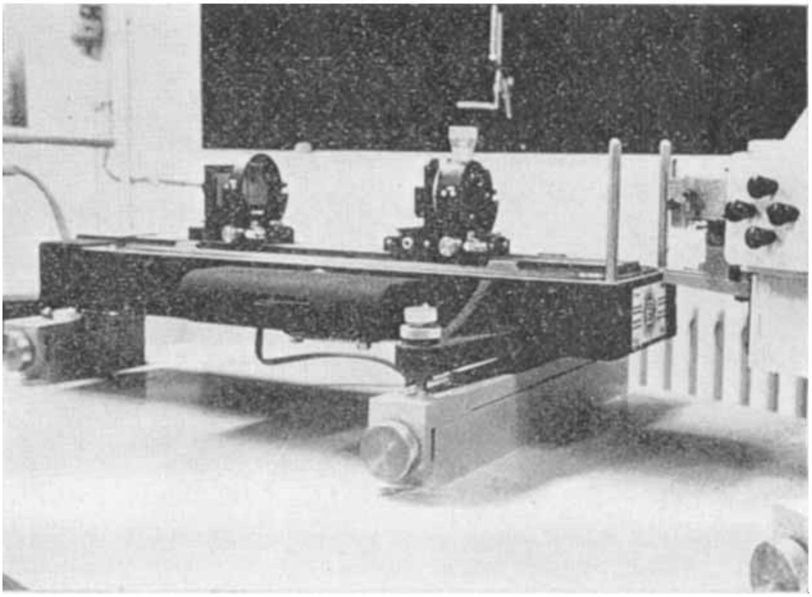


FIGURE 2

D. X-RAY DIFFRACTION

The structure of liquid-crystalline phases of block copolymers was studied by small angle X-ray scattering (Fig. 1). We performed our X-ray diffraction measurements in a focusing camera operating in vacuum (Fig. 2). Strictly monochromatic X-rays were used (Cu, $K\alpha_1$) isolated by a bent quartz monochromator and focused as a sharp line on the film.

Results

A. DESCRIPTION OF THE STRUCTURES

From X-ray diffraction patterns we have established the existence of three types of liquid-crystalline structures for our block copolymers: lamellar, hexagonal and cubic.

1. *Lamellar Structure*

The lamellar structure consists of a set of plane, parallel, equidistant sheets; each sheet results from the superposition of two layers: one formed by the insoluble block B, the other by the solution in the preferential solvent S of the soluble block A.

The characteristic parameters of the lamellar structure are:

—the inter-sheet spacing: d

—the thickness of the insoluble layer: d_B

—the thickness of the soluble layer: d_A

2. *Hexagonal Structure*

The hexagonal structure consists of a set of indefinitely long cylinders, arranged in a regular hexagonal two-dimensional array: the long cylinders containing the insoluble block B are separated from one another by the solution of the soluble block A.

The characteristic parameters of the hexagonal structure are:

—the distance between the axis of two neighbouring cylinders: d

—the diameter of the cylinders: $2R$

3. *Cubic Structure*

The cubic structure consists of spherical particles, filled by the insoluble block, packed in a centred cubic lattice and separated from one another by the solution of the soluble block.

The characteristic parameters of the centred cubic structure are:

—the side of the centred cubic cell: a

—the diameter of the spheres: $2R$

The lattice parameters: inter-sheet spacing in the lamellar structure, distance between the axis of two neighboring cylinders in the hexagonal structure, side of the centred cubic cell in the cubic structure, are given by X-ray experiments.

When, in addition, the concentration of the gel, the composition of the block copolymer and the densities of each block are known, various structural parameters can be calculated by formulae based on simple geometry; these parameters are the thickness of the soluble and insoluble layers in the lamellar structure, the diameter of the cylinders in the hexagonal structure, and the diameter of the spheres in the cubic structure.

Furthermore, it is possible to calculate, for all the structures, the average area S available to a molecule and the average volumes occupied by a whole molecule and by the soluble part and the insoluble part of a molecule.

B. INFLUENCE OF THE CONCENTRATION OF THE SOLVENT

We have studied the effect of the concentration of the solvent on structural parameters for the three types of structures previously pictured.

1. *Case of the Cubic Structure*

If we put a block copolymer polystyrene-polyisoprene in solution in isoprene monomer which is a preferential solvent of the polydiene block, we obtain a centred cubic structure for concentrations in isoprene between 10 and 40%.

In Fig. 3, where we have plotted the structural parameters of a copolymer polystyrene-polyisoprene (SI. 320) versus isoprene concentration, we see that, when the concentration of isoprene increases:

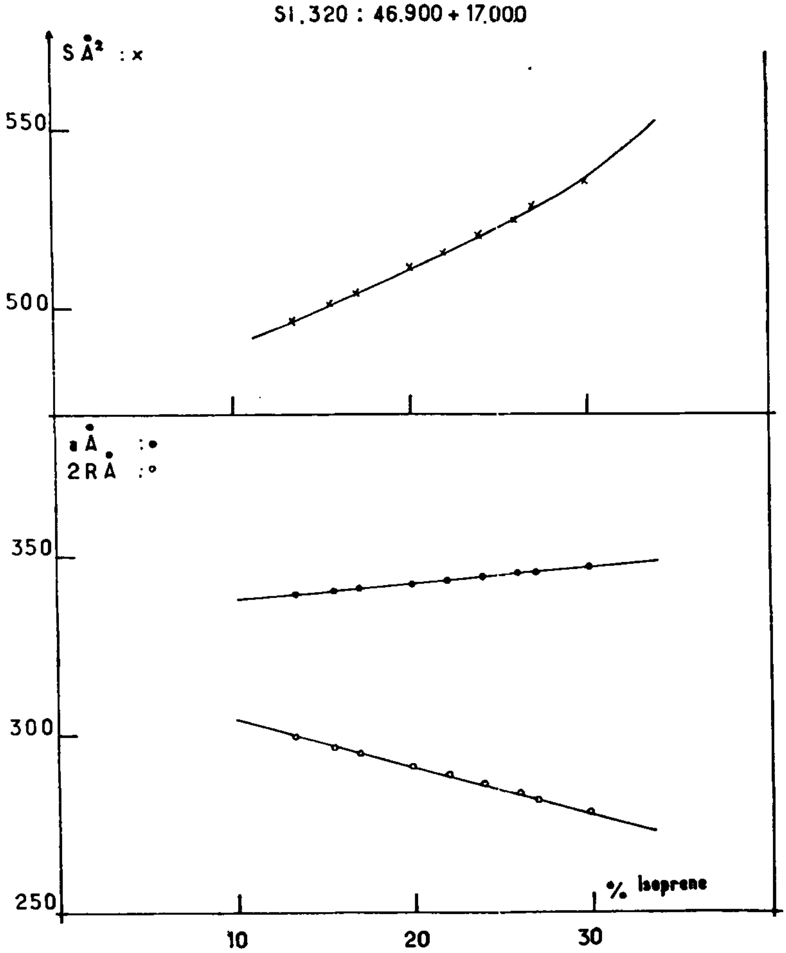


FIGURE 3

—the side *a* of the centred cubic lattice increases from 338 Å to 351 Å

—the diameter $2R$ of the spheres of polystyrene decreases

—the average surface S occupied by a molecule increases.

2. *Case of the Hexagonal Structure*

If we solubilize a polyisoprene-poly-2-vinylpyridine block copolymer in a preferential solvent of polyisoprene such as ethyl acetate, we obtain an hexagonal structure for solvent concentration between 0 and 38% (0% concentration is obtained by slow evaporation of the solvent).

In Fig. 4, where we have plotted the structural parameters of a block copolymer polyisoprene-poly-2-vinylpyridine (IVP. 22) *versus* ethyl acetate concentration, we see that when the concentration of ethyl acetate increases:

—the distance d between the axis of two neighboring cylinders decreases from 219 to 180 Å

—the diameter $2R$ of the cylinders filled with the poly-2-vinylpyridine block decreases from 95 to 63 Å

—the average surface S available to a molecule increases from 240 to 360 Å^2.

3. *Case of the Lamellar Structure*

If we made a gel with a polystyrene-polyisoprene or polystyrene-polybutadiene block copolymer in a preferential solvent of polystyrene: toluene for instance, we obtain a lamellar structure for solvent concentration between 2 and 42%.

In Fig. 5, where we have plotted the structural parameters of a block copolymer polystyrene-polyisoprene (SI. 822) *versus* toluene concentration, we see that when the concentration of toluene increases:

—the inter-sheet spacing ($d = d_A + d_B$) increases from 286 to 354 Å

—the thickness d_A of the soluble block (polystyrene) increases from 152 to 260 Å

—the thickness d_B of the insoluble block (polyisoprene) decreases from 132 to 95 Å

—the average surface S available to a molecule increases from 470 to 675 Å^2.

We have also calculated the volume occupied by each block of a molecule and by a whole molecule, and we see in Fig. 6 that when the concentration of toluene increases:

—the volume V of a whole molecule increases from 135,000 to 240,000 Å^3

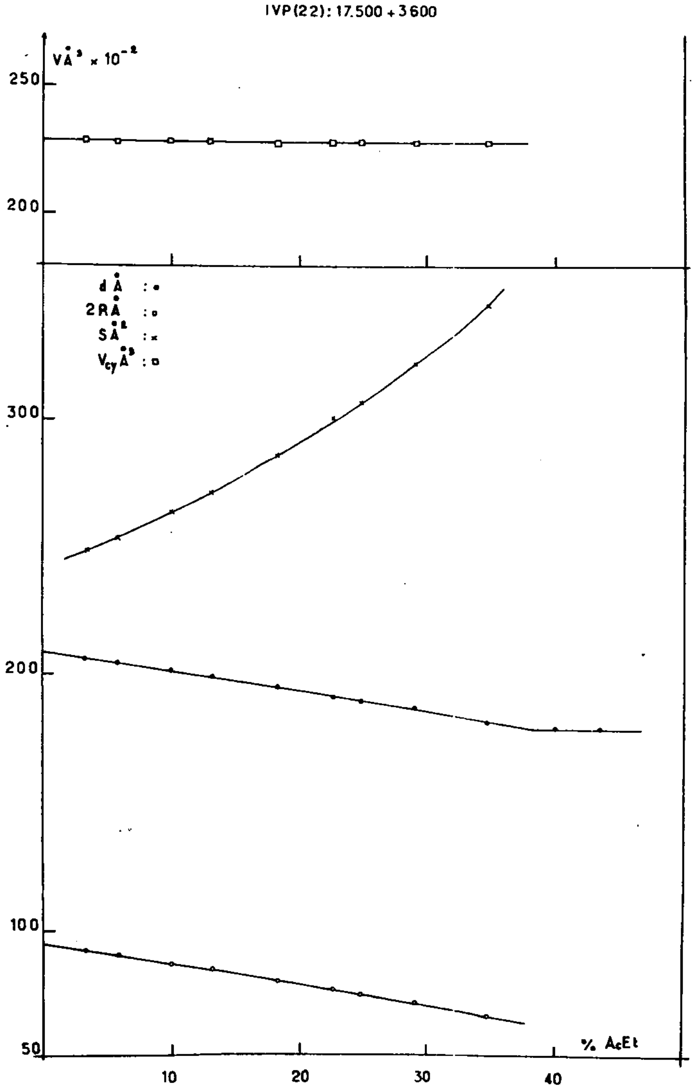

IVP(22): 17.500 + 3600
VÅ³ × 10⁻²
250
200
dÅ : ●
2RÅ : o
SÅ² : ×
V_cy Å³ : □
300
200
100
50
10
20
30
40
% AcEt

FIGURE 4

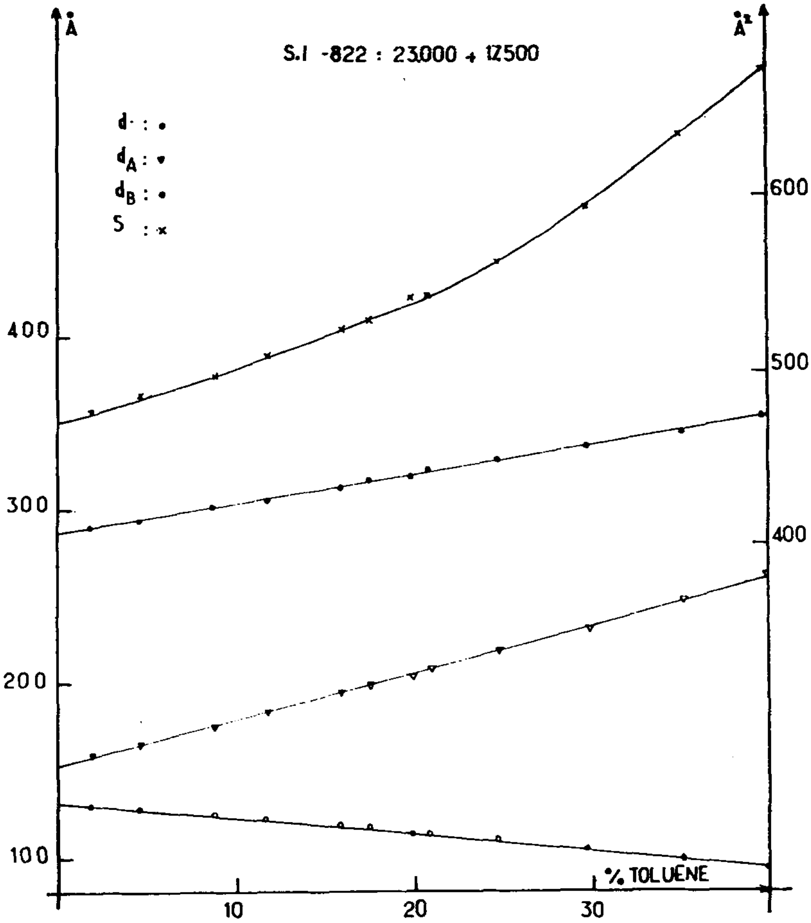


FIGURE 5

—the volume V_A of the soluble block (polystyrene) increases from 75,000 to 175,000 Å³

—the volume V_B of the insoluble block (polyisoprene) remains constant.

C. INFLUENCE OF THE COMPOSITION OF THE COPOLYMER

The study of the influence of the composition of the copolymer on the structural parameters involves two parts: the first is related to the study of a set of block copolymers with a constant soluble block and an increasing insoluble one, the second to the study of a set of block copolymers with a constant insoluble block and an increasing soluble one.

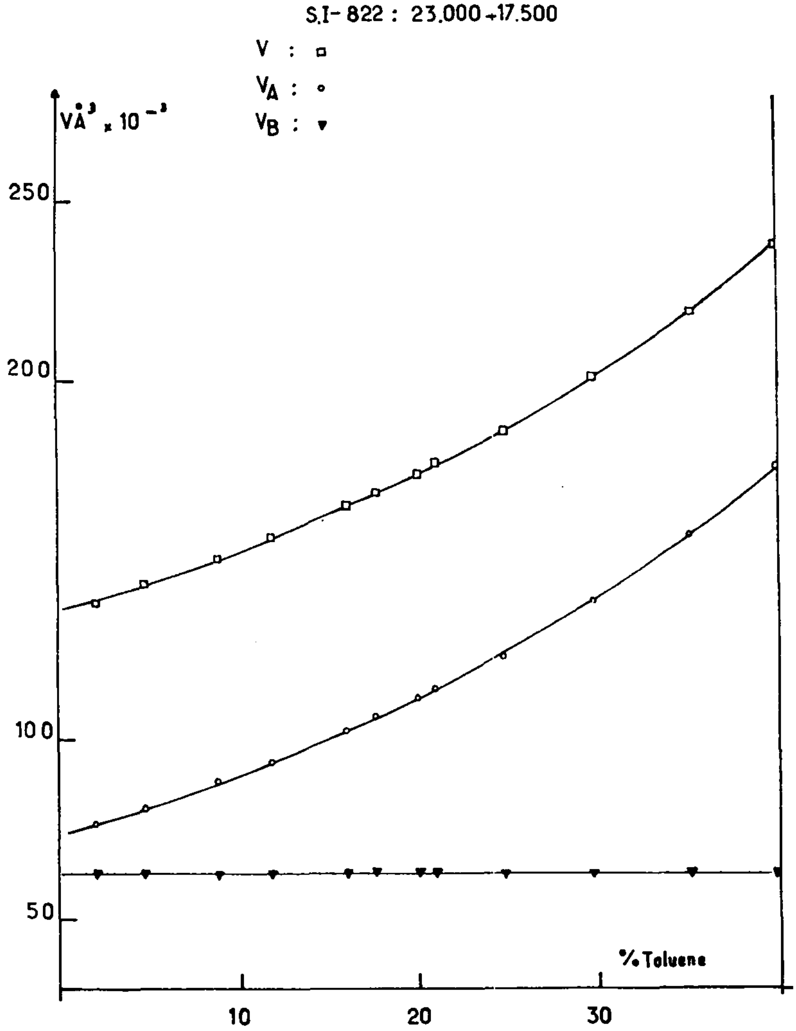


FIGURE 6

1. *Influence of the Length of the Insoluble Block*

To perform this study we have prepared four polystyrene-polyisoprene block copolymers with a constant block of poly styrene and four different blocks of polyisoprene. We have solubilized these copolymers in toluene which is a preferential solvent of the polystyrene and gives a lamellar structure, as we have previously seen.

On Fig. 7, where we have plotted the thickness d_B of the insoluble layer (polyisoprene) *versus* solvent concentration, we see that d_B increases with the molecular weight of the insoluble block.

In order to know the law of variation of d_B *versus* the molecular weight of the insoluble block, we have plotted the thickness d_B (extrapolated at zero concentration in toluene) *versus* polyisoprene molecular weight (Fig. 8). We have found that the variation is linear and the law of variation is:

$$d_B = 0.0075 M_B$$

For all other concentrations of toluene we have also obtained straight lines by plotting d_B as a function of M_B (molecular weight of the insoluble block).

2. *Influence of the Length of the Soluble Block*

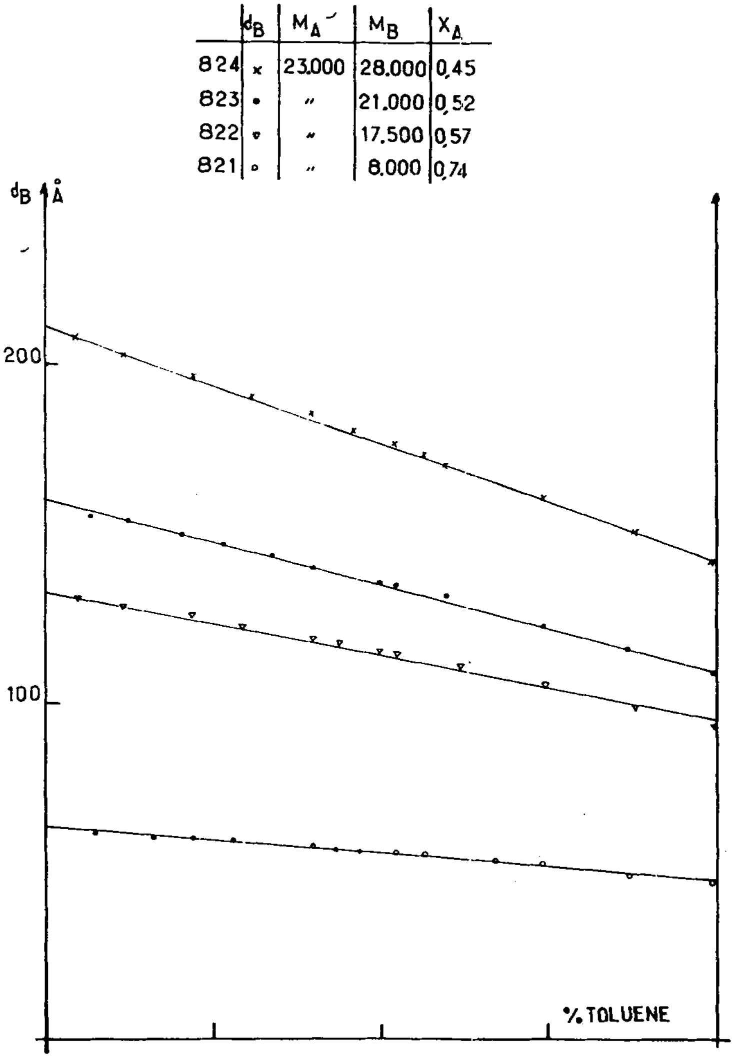
To perform this study, we have used three polystyrene-polyisoprene block copolymers with a constant block of polyisoprene and three different blocks of polystyrene. We have used toluene as a preferential solvent of polystyrene. In this case the structure is lamellar.

The thickness d_A of the soluble block (Fig. 9) and the intersheet spacing d (Fig. 10) increase with the molecular weight of the soluble block.

On the contrary the thickness d_B of the insoluble block (polyisoprene) remains constant when the molecular weight of the soluble block increases (Fig. 12).

D. INFLUENCE OF THE MOLECULAR WEIGHT OF THE COPOLYMER

To study the influence of the molecular weight of the copolymer on the structural parameters we have used the six copolymers polystyrene-polyisoprene already employed.



	d_B	M_A	M_B	X_A
824	×	23.000	28.000	0,45
823	•	"	21.000	0,52
822	▽	"	17.500	0,57
821	○	"	8.000	0,74

FIGURE 7

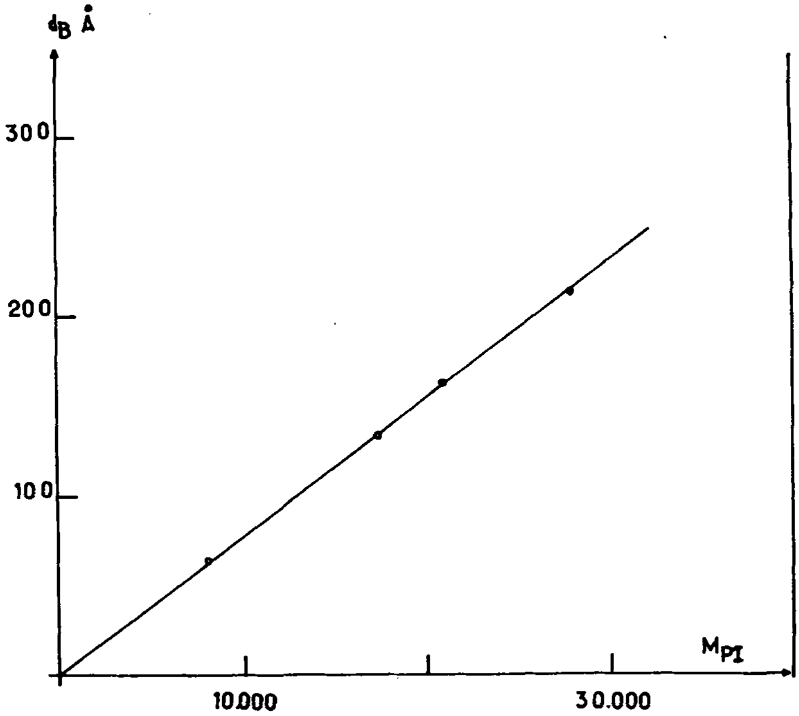


FIGURE 8

In Figs. 11 and 12, we have plotted respectively the inter-sheet spacing d and the average volume V available to a molecule *versus* solvent concentration, for the six different copolymers to show that: both the inter-sheet spacing of the lamellar structure and the average volume occupied by a molecule increase with the molecular weight of the copolymer.

E. INFLUENCE OF THE NATURE OF THE SOLVENT

We have studied the influence of the nature of the preferential solvent on the structural parameters for the two following structures: hexagonal and lamellar.

1. *Case of the Hexagonal Structure*

To perform the study of the influence of the nature of the preferential solvent on the parameters of the hexagonal structure,

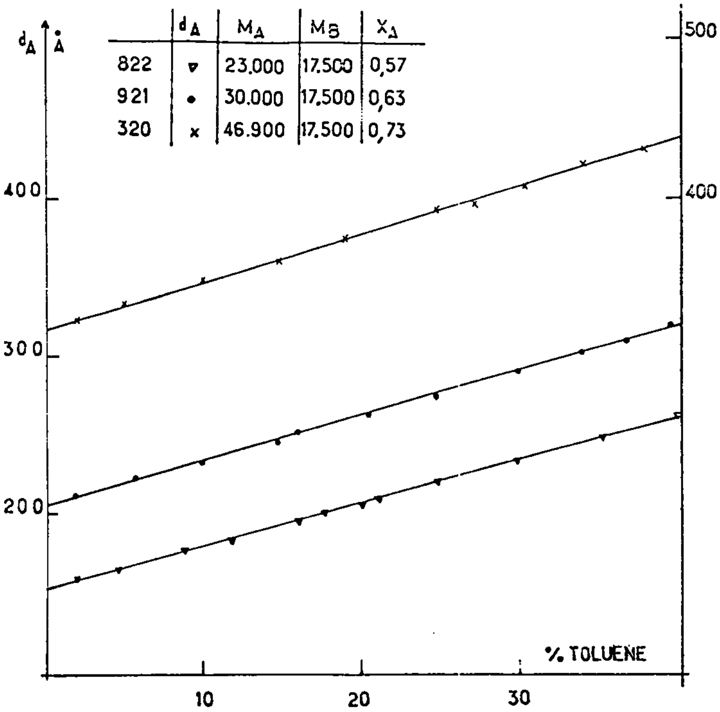
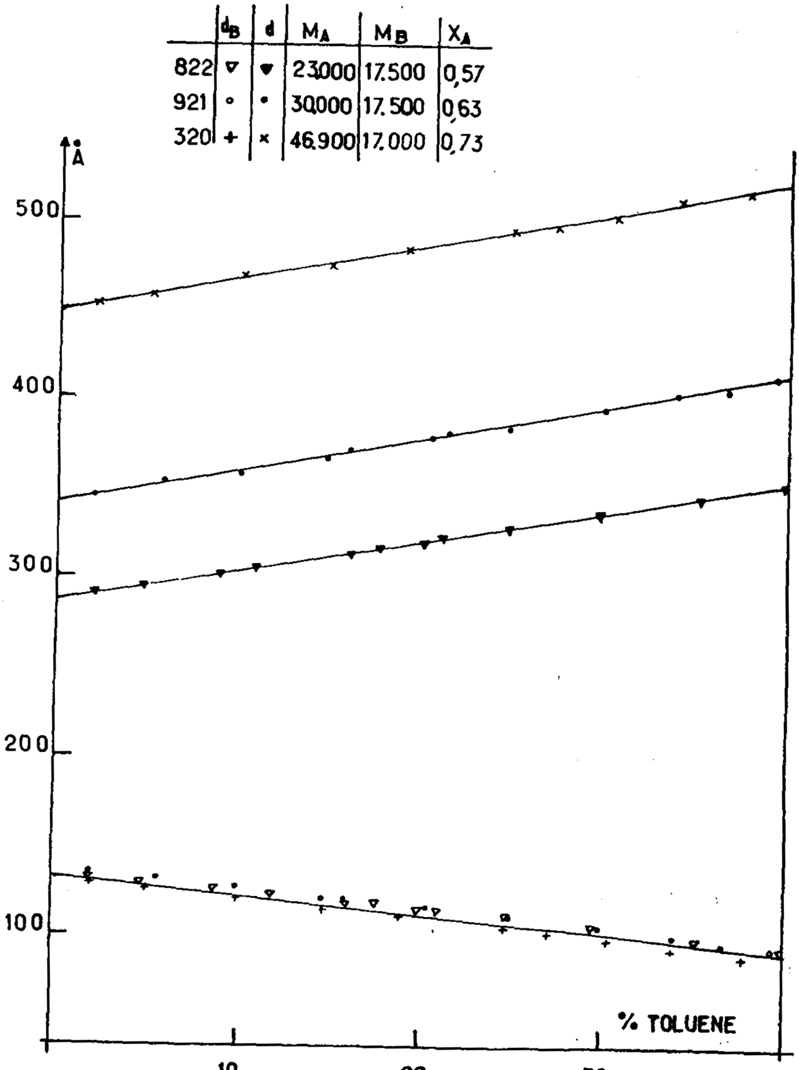


FIGURE 9

we have used a block copolymer polyisoprene-poly-2-vinylpyridine (IVP. 22) whose average molecular weights are: 17,500 for the polyisoprene block and 3600 for the poly-2-vinylpyridine block.

We have used four solvents of the polyisoprene block: ethyl acetate (AcOEt), vinyl acetate (AcOV), methyl ethyl Ketone (MEC) and styrene and a solvent of the poly-2-vinylpyridine block: dioxane.

In Fig. 13, we have plotted both the distance *d* between the axis of two neighboring cylinders and the diameter 2*R* of the cylinders to show that: all the points concerning the four preferential solvents of the polyisoprene block take place on the same line for each parameter, while the points concerning dioxane (a preferential solvent of the poly-2-vinylpyridine block) take place on another line.



	d_B	d	M_A	M_B	X_A
822	▽	▼	23.000	17.500	0,57
921	○	●	30.000	17.500	0,63
320	+	×	46.900	17.000	0,73

Å
500
400
300
200
100
10
20
30
% TOLUENE

FIGURE 10

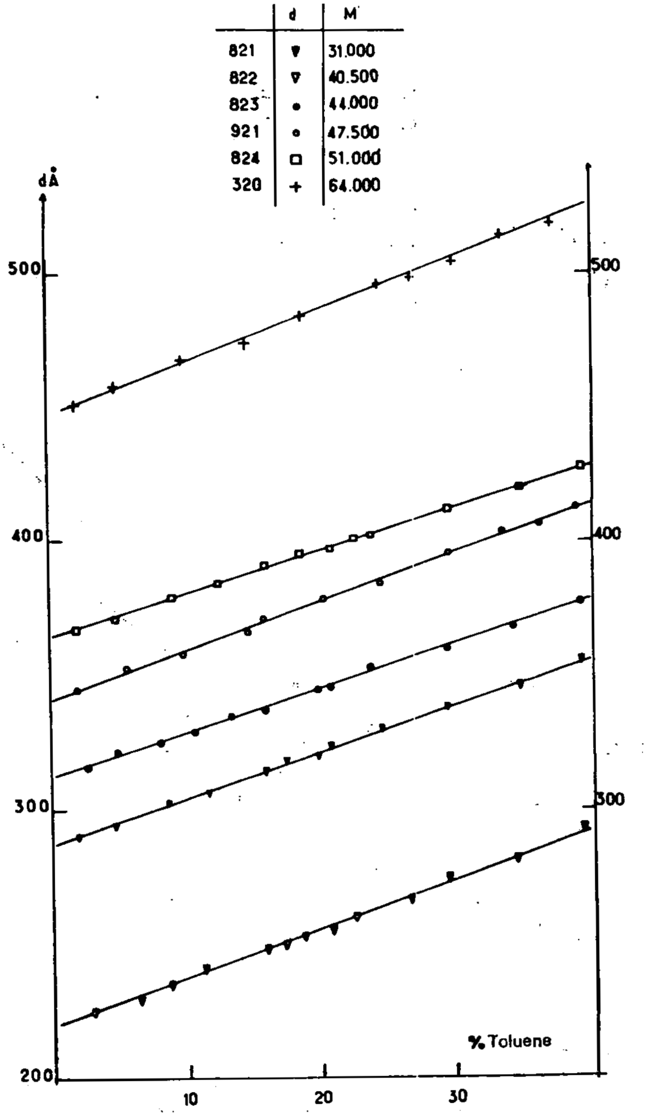

d
M
821 ▼ 31.000
822 ▽ 40.500
823 ● 44.000
921 ∘ 47.500
824 □ 51.000
320 + 64.000
dÅ
500
400
300
200
10
20
30
% Toluene

FIGURE 11

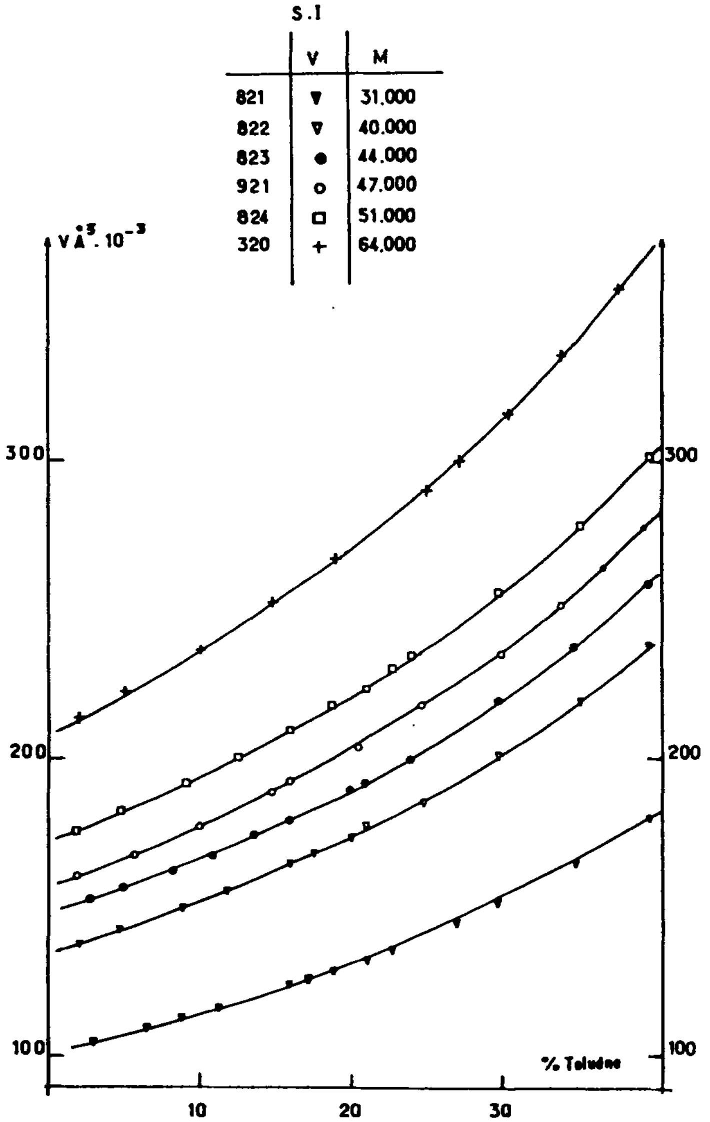

S.I
V
M
821 ▼ 31.000
822 ▽ 40.000
823 ● 44.000
921 ○ 47.000
824 □ 51.000
320 + 64.000
V Å³ . 10⁻³
300
200
100
300
200
100
10
20
30
% Toluene

FIGURE 12

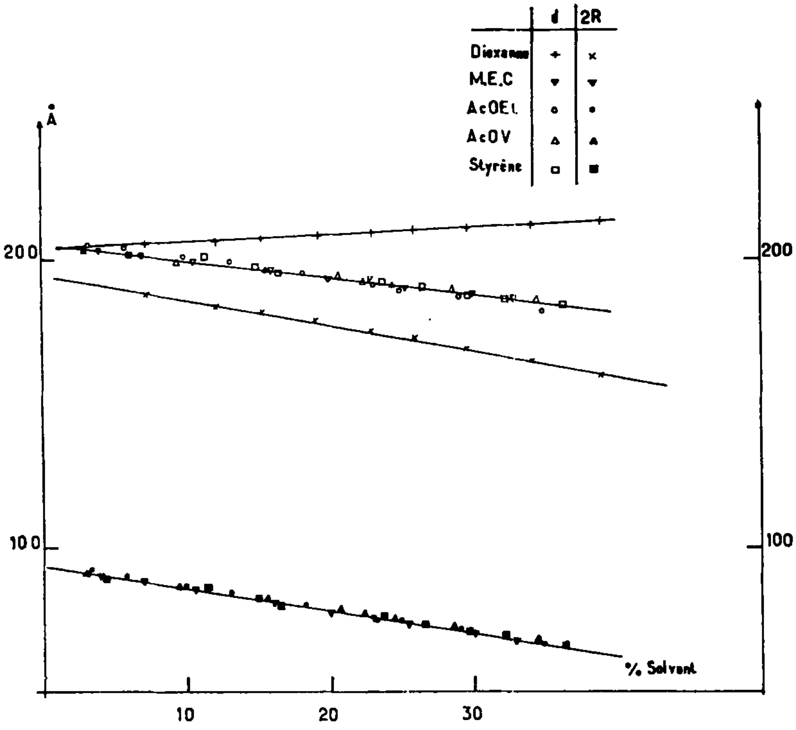


FIGURE 13

2. *Case of the Lamellar Structure*

To perform the study of the influence of the nature of the preferential solvent on the structural parameters of the lamellar structure, we have prepared a block copolymer polystyrene-polybutadiene whose average molecular weights are 71,000 for the polystyrene block and 46,000 for the polybutadiene block.

We have used the seven following preferential solvents of the polystyrene block: styrene, toluene, methyl ethyl Ketone (MEC), benzene, vinyl acetate (AcOV), ethyl acetate (AcOEt), and ethyl benzene.

It is shown in Fig. 14, where we have plotted the characteristic parameters of the lamellar structure (inter-sheet spacing d, thickness d_A of the layer of the solution of the polystyrene block, thickness d_B of the layer of the insoluble polyisoprene block) *versus* solvent concentration that all the points concerning the seven different solvents take place on only one line for each parameter.

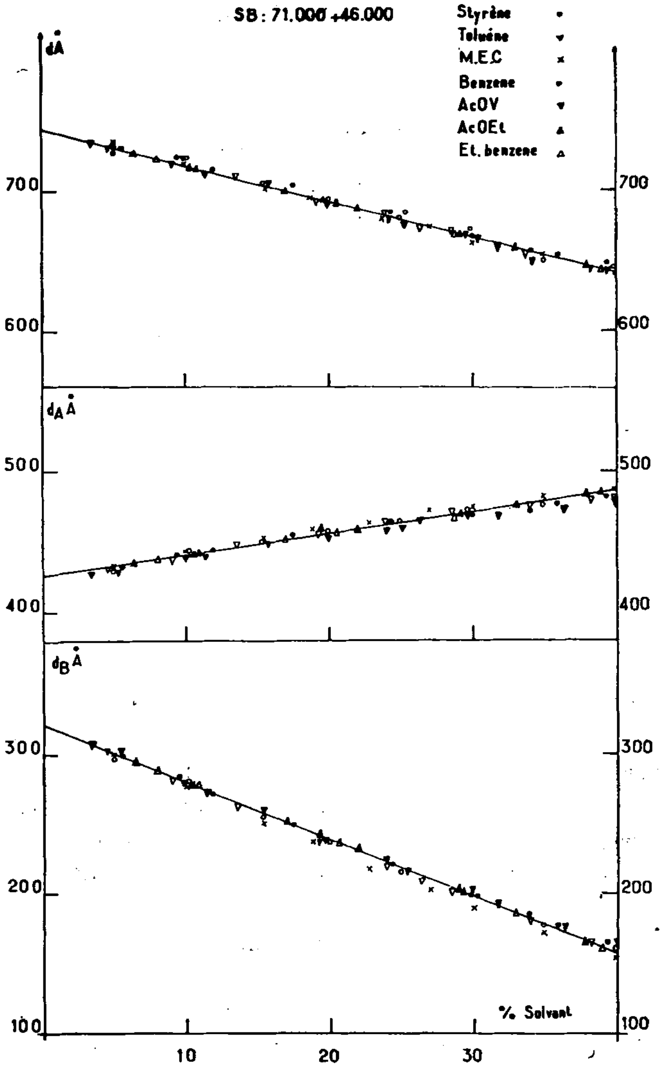


Figure 14

Discussion

We have established the existence of three types of liquid-crystalline structures for amorphous block copolymers: lamellar, hexagonal and cubic. We have studied the influence of different factors, such as concentration and nature of the preferential solvent, molecular weight and composition of the copolymer on structural types and structural parameters of liquid crystalline phases of amorphous block copolymers.

By studying the influence of the concentration of the solvent, we have shown that, when the concentration of the preferential solvent increases, there is:

—a cubic dilatation of the molecule of copolymer (Fig. 12)

—a linear and a cubic dilatation of the soluble block (Figs. 9 and 15)

—a linear contraction of the insoluble block (Fig. 7), this linear contraction taking place at constant volume (Figs. 4 and 6).

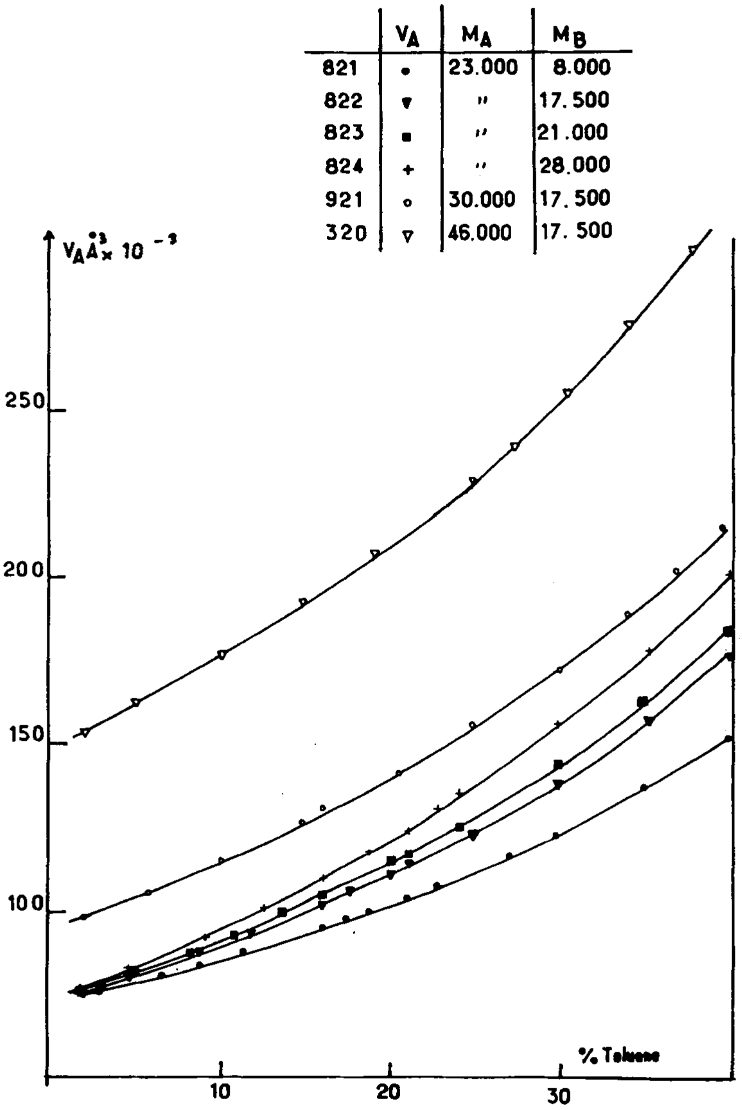
By using different preferential solvents, we have shown that the nature of the solvent is without influence on the structural parameters, as long as the different solvents used remain preferential solvents of the same block (Fig. 14). Nevertheless, if the solvent used becomes a preferential solvent of the other block, the structural parameters change (Fig. 13) and an inversion of the structure may take place (if we put a polyisoprene-poly-2-vinylpyridine block copolymer in solution in a preferential solvent of the polyisoprene block we obtain an hexagonal structure in which cylinders are filled by the poly-2-vinylpyridine block, while if we put the same copolymer in solution in a preferential solvent of the poly-2-vinylpyridine block the cylinders are filled by the polyisoprene block).

By varying the molecular weight and the composition of the copolymer we have shown that:

—the length and the volume of the molecule increase with the molecular weight of the copolymer (Figs. 11 and 12)

—the length and the volume of the soluble block increase with the molecular weight of this block (Figs. 9 and 15)

—the length of the insoluble block increases linearly with its



	V_A	M_A	M_B
821	•	23.000	8.000
822	▼	"	17.500
823	■	"	21.000
824	+	"	28.000
921	∘	30.000	17.500
320	▽	46.000	17.500

FIGURE 15

molecular weight (Fig. 8) but is independent of the molecular weight of the soluble block (Fig. 10).

The fact that the characteristic parameter of the insoluble block increases linearly with its molecular weight but is independent of the molecular weight of the soluble block on one hand, along with the fact that the nature of the solvent is without influence on structural parameters on the other hand, suggest that the

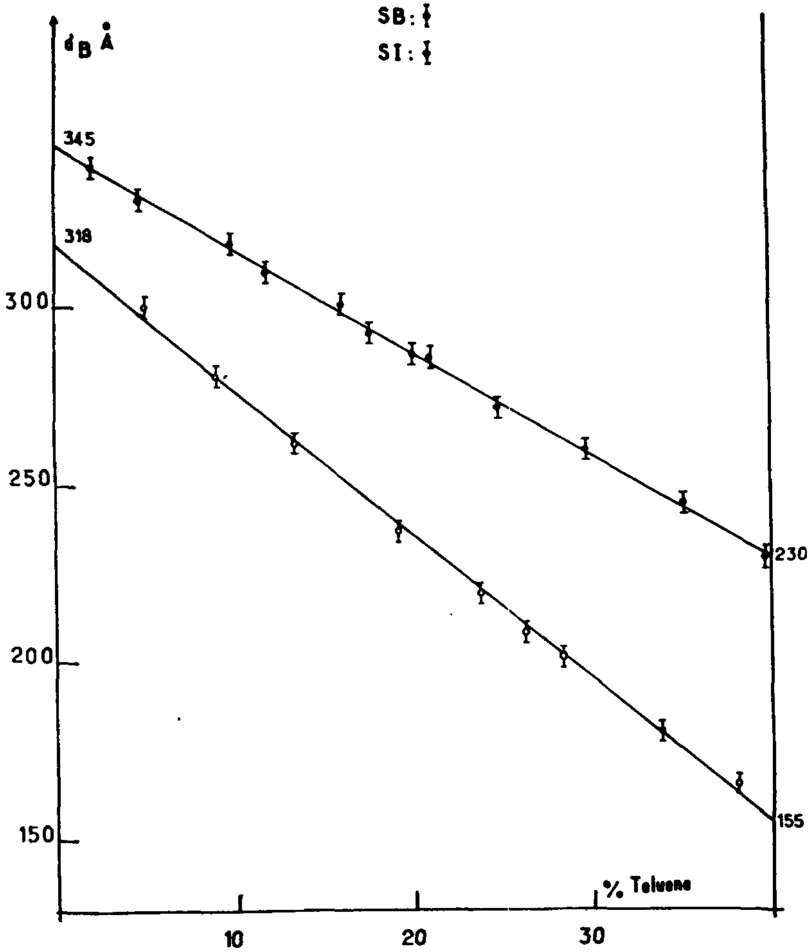


FIGURE 16

insoluble block of the molecule could play the leading part in liquid-crystalline structures of block copolymers.

Furthermore, if we compare two block copolymers (polystyrene-polyisoprene : SI and polystyrene-polybutadiene : SB) owning the same soluble block (polystyrene), giving the same structure (lamellar) in solution in the same solvent (toluene), we obtain (Fig. 16) two different lines for the variation of the thickness d_B of the insoluble block *versus* toluene concentration, although the molecular weight of the insoluble block is the same (46,000) in the two cases.

To definitely resolve the problem of the influence of the insoluble block in liquid-crystalline structures of amorphous block copolymers, we must study two block copolymers with the same insoluble block and two different soluble blocks. This study is in progress with polystyrene-polybutadiene1,2 and poly-2-vinylpyridine-polybutadiene1,2 block copolymers on one hand and with polystyrene-polyisoprene1,4cis and poly-2-vinylpyridine-polyisoprene1,4cis block copolymers on the other hand.

REFERENCES

1. Luzzati, V., Mustacchi, H., Skoulios, A. and Husson, F., *Acta. Cryst.* **13**, 660 (1960).
2. Husson, F., Mustacchi, H. and Luzzati, V., *Acta. Cryst.* **13**, 668 (1960).
3. Skoulios, A. and Finaz, G., *J. Chimie Physique*, 473 (1962).