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Phase Diagram of Systems: Block Copolymer-Preferential Solvent of One Block†

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Abstract—We have studied by small angle X-ray scattering and differential scanning calorimeter different systems block copolymer/preferential solvent of one block.

For copolymers owning two amorphous blocks such as polystyrene-polybutadiene, in solution in toluene, we have only one liquid-crystalline structure which disappears at about 180 °C; this structure is lamellar if the copolymer contains between 35 and 60% of polybutadiene.

For copolymers owning an amorphous and a crystallizable block such as polystyrene-polyethyleneoxide, we have found two liquid-crystalline structures L.C. and L.L., which are both lamellar but differ by the state of the polyethyleneoxide chains. Below about 50 °C we have found the structure L.C. with crystallized polyethyleneoxide chains; between 50 and about 170 °C, we have found the structure L.L. with liquid polyethyleneoxide chains. The field of the structure L.C. is smaller with nitromethane which is a preferential solvent of polyethyleneoxide than with diethylphtalate which is a preferential solvent of polystyrene.

1. Introduction

At the Second International Liquid Crystal Conference, we have described the different liquid-crystalline structures exhibited by block copolymers in solution in a preferential solvent of one block. We have also shown the influence on the structural types and structural parameters of different factors: concentration and nature of the solvent, molecular weight and composition of the copolymer, nature of the blocks.⁽¹⁾ In this paper we shall study the influence of the temperature on binary systems: block-copolymer/preferential solvent of one block and describe the phase diagrams of these systems.

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

The interest of such a study is both practical and theoretical. First it allows the determination of the stability of the liquid-crystalline structures and the discovery of eventual phase transitions. Then it may allow the evaluation of the role played by the configurational entropy of the macromolecular chain in liquid crystalline structures and may help the explanation of the formation of these structures in a theoretical point of view.

Three cases are possible for the binary systems block-copolymer/solvent of one block. The first one is a copolymer with two amorphous blocks in solution in a preferential solvent of one block; the second one is a copolymer with an amorphous block and a crystallizable block in solution in a preferential solvent of the amorphous block; the third one is a polymer with an amorphous block and a crystallizable block in solution in a preferential solvent of the crystallizable block. We shall take as example of the three cases the following systems:

—copolymer polystyrene-polybutadiene/toluene (PS-PB/Tol.)
—copolymer polystyrene-polyethyeneoxide/diethylphtalate (PS-POE/Diet. Phtal.)
—copolymer polystyrene-polyethyleneoxide/Nitromethane (PS-POE/Nit)

For studying these systems, we have used simultaneously X-ray diffraction and differential scanning calorimeter; DSC has allowed us to determine both phase transitions and boundaries of the domains of stability of pure phases. X-ray diffraction has allowed us to perform the detailed determination of the structure of the different phases and the study of the variation of the structural parameters with temperature and concentration.

2. Experimental

Polystyrene-polybutadiene(PS-PB) and polystyrene-polyethylene-oxide(PS-POE) block copolymers were prepared by anionic polymerization, under high vacuum, in an all glass apparatus, in THF solution with cumyl potassium as initiator.

Molecular weights of copolymers were measured by light scattering, osmometry and Gel Permeation Chromatography (Table I).

TABLE 1 Molecular Weights and Compositions of the Copolymers Studied

Cop.	M_w *PS*	% *PS*	M_w total
SP. 3	16.500	41	40.200
SB. 1	71.000	61	117.000

G.P.C. curves and fractionation experiments have shown that our copolymers are free of homopolymers.

The D.S.C. experiments were performed with a Perkin-Elmer Differential scanning Calorimeter, type DSC 1B, equipped with tight cells.

X-ray diffraction measurements were performed with 3 different cameras: a Debye-Scherrer camera for studying large Bragg angles and 2 focusing cameras (one for middle angles and one for small angles). The two focusing cameras operating in vacuum, were equipped with both a bent quartz monochromator and a device for recording the diagrams of samples heated at high temperatures (kept constant to ± 0.5 °C).

3. Structures

All X-ray diffraction patterns from pure liquid-crystalline phases can be indexed (in the small-angles region) as a series of three (001) reflections, typical of a layered structure.

Therefore, the structure is lamellar and consists of a set of plane, parallel, equidistant sheets; each sheet results from the superposition of two layers; one formed by the insoluble block, the other by the solution in the preferential solvent of the soluble block. The inter-sheet spacing d is directly given by X-ray experiments; the thickness d_A of the soluble layer, the thickness d_B of the insoluble layer and the average area S available to a molecule are calculated by the following formulae based on simple geometry:

$$d_B = d\left[1 + \frac{\rho_B}{\rho_{AS}}\frac{1 - CX_B}{CX_B}\right]^{-1}$$

$$S = \frac{2M_B}{Nd_B\,\rho_B}$$

$$\rho_{AS} = \rho_A \cdot \rho_S(1 - CX_B)\,[\rho_A + c(\rho_S - \rho_A - X_B\rho_s)]^{-1}$$

with c = polymer concentration in the solution
X_B = concentration of the insoluble block in the copolymer
M_B = molecular weight of the insoluble block
ρ_A = density of the soluble block
ρ_B = density of the insoluble block
ρ_S = density of the solvent.

From the examination of the wide Bragg angles region of the diffraction diagrams we have established the existence of two types of lamellar structure: the type L.C. characterized by sharp lines situated in the region of large Bragg angles and resulting from folded and crystallized macromolecular chains; the type L.L. characterized by a diffuse halo characteristic of amorphous or melt macromolecular chains.

3.1. System Polystyrene-Polybutadiene/Toluene

(1) *Phase diagram*

By heating from −50 to +250 °C (at 20 °C/mn) mesomorphic gels containing less than 45% of toluene, one obtains on the thermogram: at first a signal in shape of step stairs, then an exothermic pike (Fig. 1).

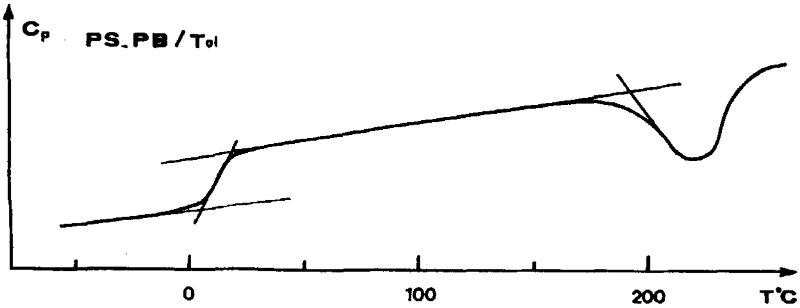

Figure 1. Example of thermogram of the system PS–PB/Tol.

The first signal results from the glass transition of the polybutadiene block and shows that toluene is a solvent of polystyrene and does not enter the polybutadiene regions.⁽²⁾

The exothermic pike takes place at temperatures lower than 185 °C. As it is demonstrated by X-ray diffraction, this pike results from the disparition of a mesomorphic lamellar structure through a reversible transition.

Such thermograms obtained for different solvent concentrations have allowed us to draw the phase diagram pictured in Fig. 2.

This diagram exhibits only one mesomorphic phase with a lamellar structure of L.L. type.

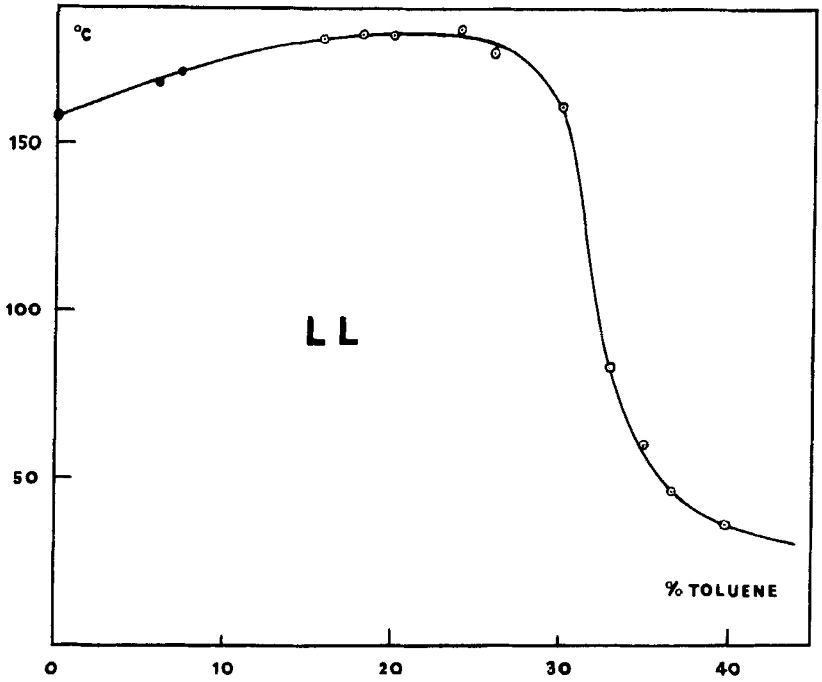

Figure 2. Phase diagram of the system PS–PB/Tol.

(2) *Influence of the temperature on structural parameters*

The variation of the structural parameters (calculated from X-ray diffraction patterns) versus temperature is pictured in Figs. 3 and 4.

The Fig. 3 where we have plotted the structural parameters versus temperature, for a constant concentration of toluene (25%) shows that, when temperature increases:

—the inter-sheet spacing d, the insoluble polybutadiene layer thickness d_B, and the soluble polystyrene layer thickness d_A decrease,

—the specific surface S increases.

In Fig. 4, we have plotted the structural parameters versus concentration for 4 constant temperatures: 25, 75, 125 and 170 °C.

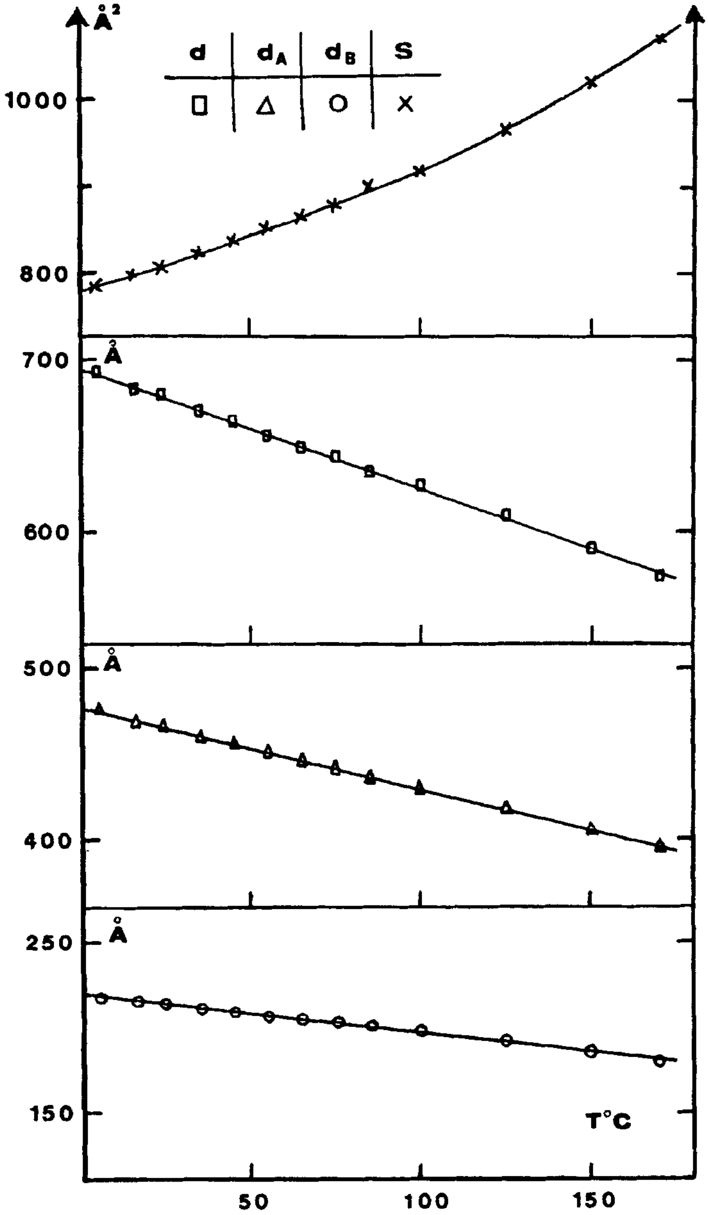

Figure 3. Variation of the parameters of the lamellar structure of the copolymer SB.I at a constant concentration of toluene (25%), versus temperature.

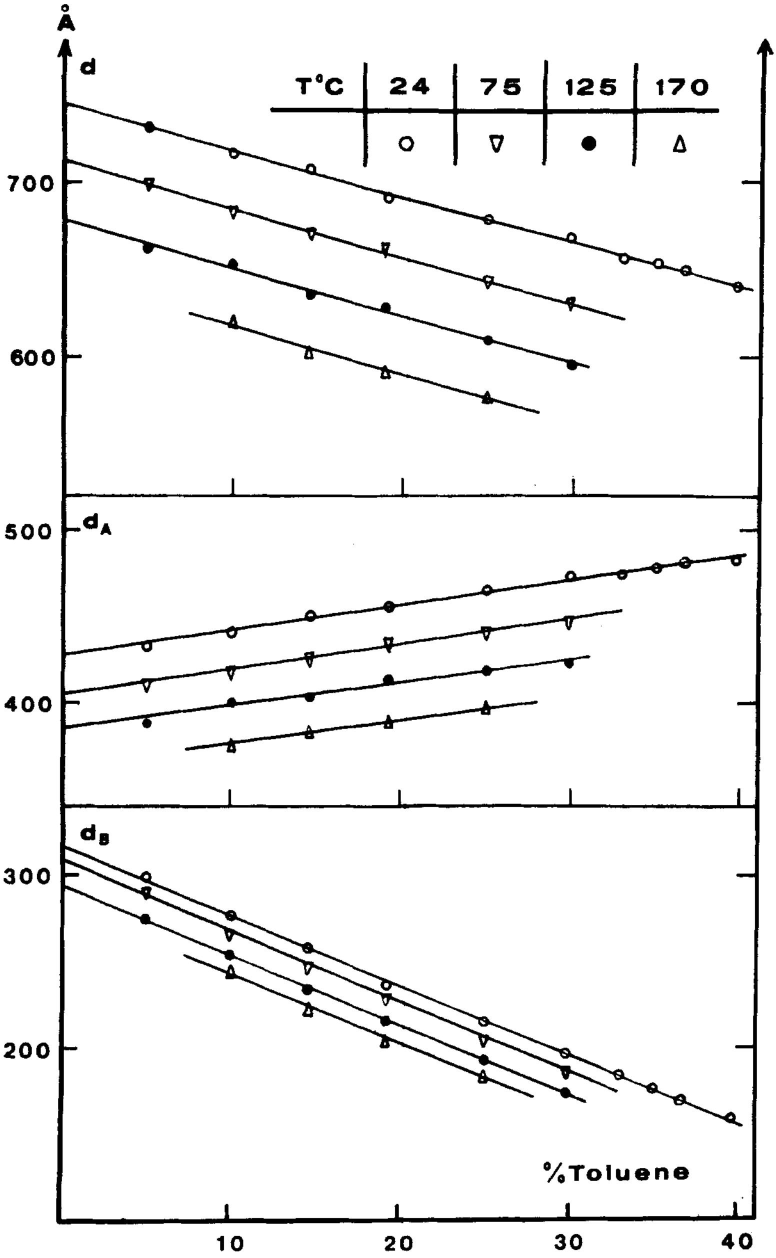

Figure 4. Variation of the parameters of the lamellar structure of the copolymer SB.I versus toluene concentration.

For a given temperature, the variation of the structural parameters versus concentration is nearly independent of the temperature (the straight lines are nearly parallel).

3.2. SYSTEM POLYSTYRENE-POLYETHYLENEOXIDE/DIETHYLPHTALATE

Samples of this system (in which diethylphtalate is a solvent of polystyrene) were prepared by direct weighing of the constituents. After homogenizing by heating at 80 °C, they are crystallized at 24 °C.

For such samples, with diethylphtalate content varying from 0 to 70%, the thermograms show 2 peaks (Fig. 5).

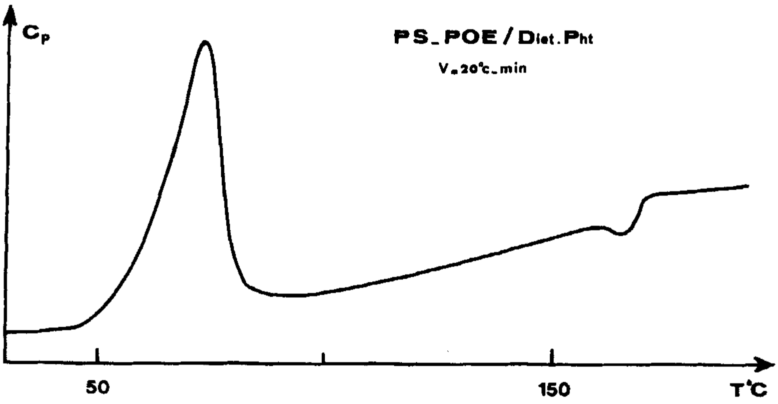

Figure 5. Example of thermogram of the system PS–POE/Diet. Phtal.

The first peak, corresponding to an endothermic transition, takes place at about 50 °C and results from the melting of the POE chains.⁽³⁾ Why does this transition result from the melting of the POE block? For three reasons:

—First, the endothermic peak takes place in the temperature vicinity of the melting point of the corresponding homopolyethyleneoxide,

—Then, the spherulitic texture observed at room temperature, by examination in polarization microscopy disappears at the temperature where the endothermic peak appears,

—Finally, the sharp lines characteristic of the monoclinic structure of the crystallized chains of polyethyleneoxide, in the region of large Bragg angles of the diffraction patterns, disappear at this temperature and give place to a diffuse halo characteristic of melt polyethyleneoxide chains.

Therefore, the first transition coincides with the change from a lamellar structure L.C. with folded and crystallized POE chains to a lamellar structure L.L. with melted POE chains.

The second peak, generally found at about 175 °C, results from the disappearance of the mesomorphic phase L.L. with melted POE chains, as it is proved by X-ray diffraction.

The phase diagram (concentration/temperature) pictured in Fig. 6, exhibits two mesomorphic phases, both with a lamellar structure but differing by the state of the polyethyleneoxide chains: folded and crystallized at room temperature in the structure L.C., melt at high temperature in the structure L.L.

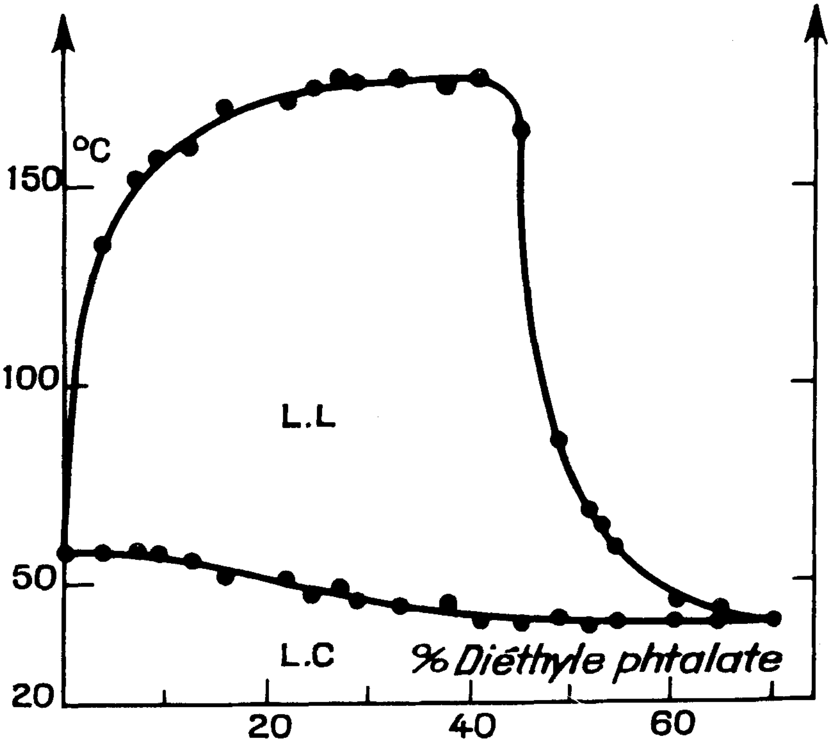

Figure 6. Phase diagram of the system PS–POE/Diet. Phtal.

3.3. SYSTEM POLYSTYRENE-POLYETHYLENEOXIDE/NITROMETHANE

(1) *Phase diagram*

Samples of PS-POE/Nit. system were prepared in a manner similar to those with diethylphtalate.

Thermograms from samples with nitromethane content between 0 and 25% show two peaks: an endothermic peak at about 40 °C and an exothermic peak at high temperature (Fig. 7).

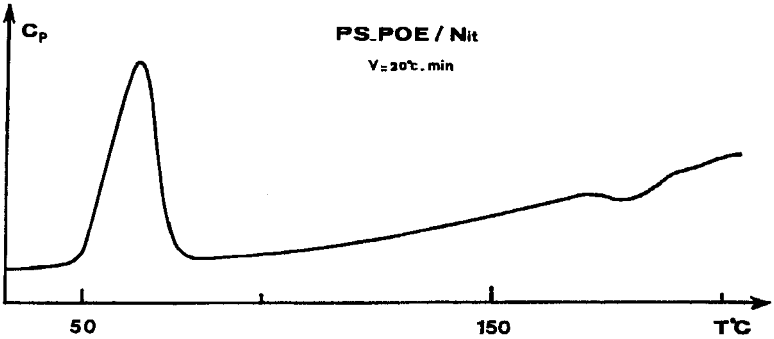

Figure 7. Example of thermogram of the system PS–POE/Nit.

Thermograms from samples with nitromethane content between 25 and 40% show only the exothermic peak.

For the same reasons as in the case of the system PS-POE/diethylphtalate, the endothermic peak results from the disappearance of the crystallinity of the POE chains and the exothermic peak from the crash of the mesomorphic structure L.L.

The phase diagram of the system PS-POE/NM presents two mesophases (Fig. 8). In the domain of nitromethane concentrations smaller than 25% and of temperatures lower than about 40 °C, the mesophase exhibits the lamellar structure L.C. with folded and crystallized POE chains. In the domain of higher nitromethane concentrations and higher temperatures, the mesophase exhibits the structure L.L. with POE chains dissolved in nitromethane.

(2) *Structure L.C.*

The structure L.C. needs come comments in the case of PS-POE/NM systems. We must recall that their X-ray diffraction patterns are characterized by:

—in the small angles region: sharp lines (001) typical of a layered structure,

—in the large angles region: sharp lines characteristic of crystallized POE chains.

(a) *Variation of the structural parameters with concentration.*

It is interesting to examine the variation of the structural parameters versus concentration at room temperature (this variation is plotted in Fig. 9). We note a discontinuity in the variation of the intersheet spacing at the nitromethane concentration of 25% where the structure L.C. disappears and where the endothermic peak also

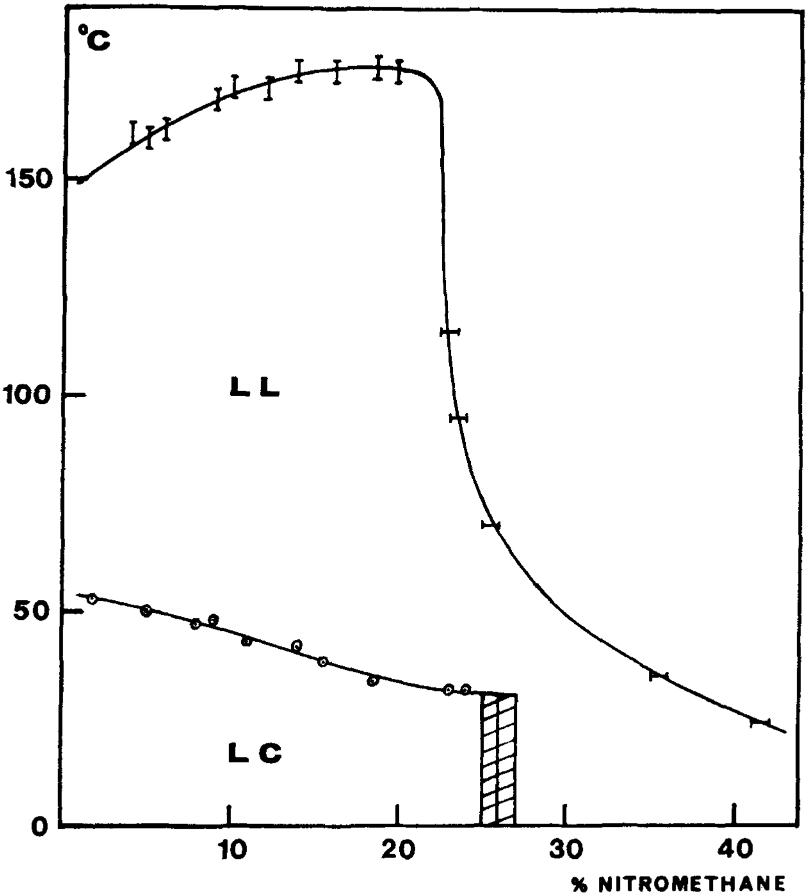

Figure 8. Phase diagram of the system PS–POE/Nit.

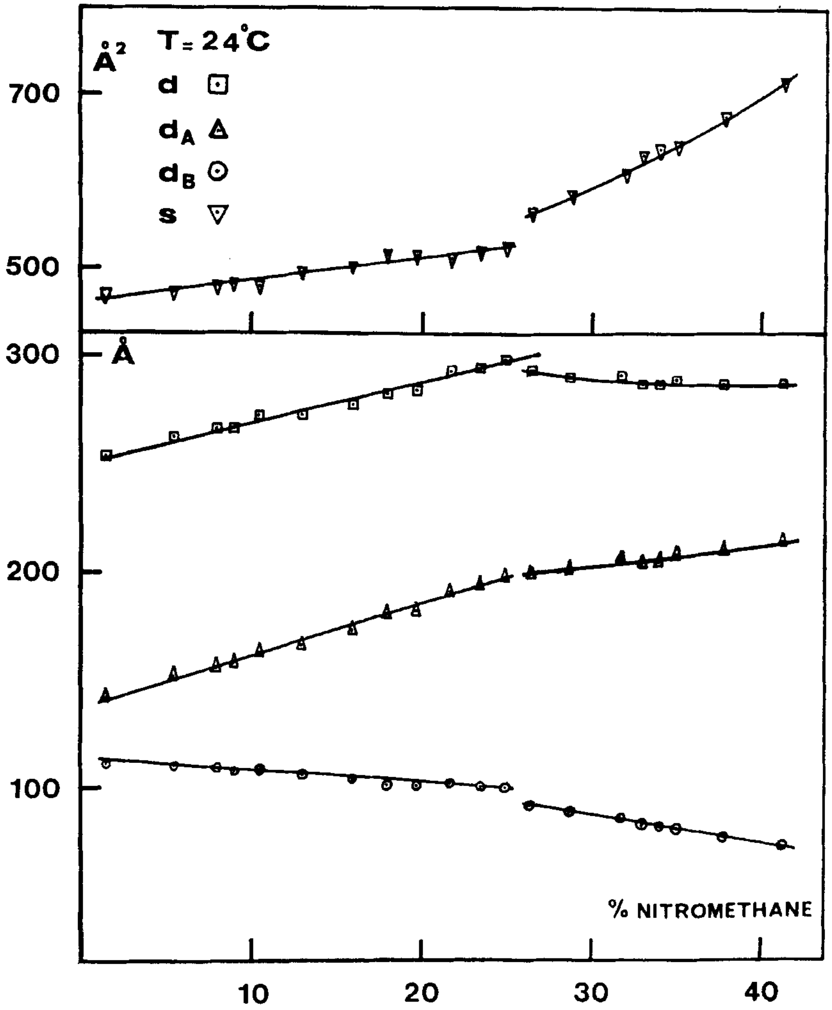

Figure 9. Variation of the parameters of the lamellar structure of the copolymer SP.3 versus Nitromethane concentration.

disappears. We also see that, when the nitromethane concentration increases from 0 to 25%:

—the intersheet spacing *d* linearly increases,

—the thickness d_A of the layer containing the POE chains and the nitromethane increases,

—*the thickness* d_B *of the layer containing the insoluble* polystyrene chains decreases,

—the average surface S available for a molecule increases.

(b) *Localization of the nitromethane*

The layer d_A contains both the POE folded and crystallized chains and the nitromethane. What are the respective positions of POE chains and nitromethane in the layer d_A? How can the coexistence of the POE crystallized chains with the nitromethane in this layer and the variation of the thickness d_A with concentration be explained?

One can think that the layer d_A results from the superposition of two layers: one formed by the crystallized POE chains, the other by the nitromethane. If this hypothesis is true, one must find a constant thickness for the POE layer and a thickness of nitromethane increasing with the solvent concentration.

With this hypothesis:

$$d_{\mathrm{POE}} = d_A\left[1+\frac{1-c^1}{c^1}\frac{\rho_{\mathrm{POE}}}{\rho_{\mathrm{Nit}}}\right]^{-1} \quad \text{with} \quad c^1 = \frac{\mathrm{Nit}}{\mathrm{POE}+\mathrm{Nit}} \text{ in weight.}$$

The results of such calculations are pictured in the Fig. 10.

One can see that, when the nitromethane concentration increases:

—the thickness of the POE layer remains constant and equal to the thickness of the POE in the dry copolymer, till Nit/POE = 0.22, where there is a change in the number of folding of the POE chains$^{(4)}$

—the nitromethane layer thickness increases linearly.

Therefore, our hypothesis is true and we can infer the following model: the layer d_A results from the superposition of 3 layers; two layers of equal and constant thickness, formed by crystallized POE chains are separated by a nitromethane layer. When the nitromethane concentration increases, the nitromethane layer thickness increases separating the POE layers but without dissolving the POE chains. When the nitromethane layer thickness reaches a value incompatible with the stability of the structure, the POE chains melt in nitromethane and give to the structure L.L.

4. Comments

It is interesting to compare the influence of the nature of the blocks (crystallizable or amorphous) and of the nature of the solvent

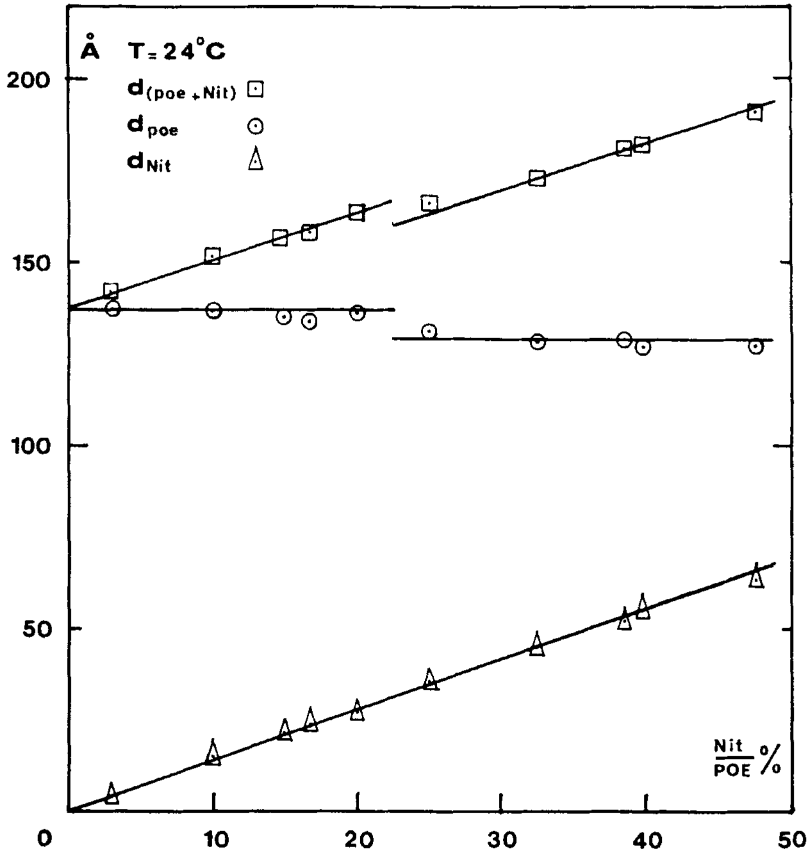

Figure 10. Variation of the thickness of the layers of Polyetyleneoxide and Nitromethane with Nitromethane concentration.

(preferential of the crystallizable block or of the amorphous block), on the thermic behavior of binary systems: block copolymers/ preferential solvent of one block. Block copolymers possessing two amorphous blocks exhibit only one mesophase whose structure is of the lamellar type L.L. when lengths of the two blocks are comparable. Block copolymers with an amorphous block and a crystallizable block exhibit two mesophases; both with a lamellar structure but differing by the state of the crystallizable block (melt in the structure L.L., but crystallized in the structure L.C.). If the nature of the blocks settles the number of the mesophases, the nature of the solvent only determines the domain of stability of the mesophases: the lamellar structure L.C. disappears at lower solvent concentrations and at lower temperatures if the solvent used is a solvent of the crystallizable block than if it is a solvent of the amorphous block.

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