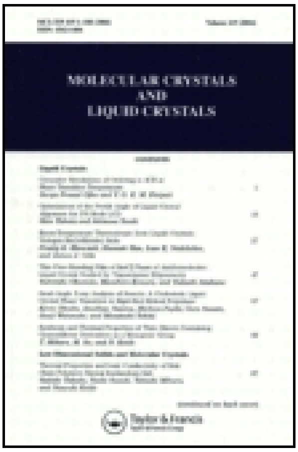

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Liquid-Crystalline Comb Polymers with Polystyrene Main Chain and Liposarcosine Side Chains

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In order to show that liquid-crystallinity is a general property of comb like polymers with polyvinylic main chains and lipopeptidic side chains we have synthesized comb like polymers with polystyrene main chains and liposarcosine side chains by polymerization of styryl-liposarcosine macromonomers. The macromonomers were prepared in 3 steps: in the first step, chloromethyl styrene was transformed into styrylacetic acid; in the second step, styrylacetic acid was linked at the α end of an ω protected α,ω-aliphatic diamine; in the third step, the unblocked ω-amino group was used to initiate the polymerization of the N-carboxyanhydride of sarcosine. Then the macromonomers were transformed into comb polymers by radical polymerization.

Our comb polymers exhibit mesophases in the dry state and in water concentrated solution. X-ray diffraction studies have shown that our comb polymers exhibit, in the absence of solvent a lamellar (Smectic A) mesophase, and in water concentrated solution two types of mesophases: lamellar and cylindrical hexagonal. The respective influence of the water concentration and the degree of polymerication p of the sarcosine on the type, the domain of stability and the geometrical parameters of the mesophases has been established. Comparison with comb polymers with polyacrylamide main chain and liposarcosine side chains has demonstrated the influence of the nature of the main chain.

Keywords: copolymers, structural, lipocosine, polystyrene

INTRODUCTION

Recently we synthesized and studied comb like polymers formed by polyacrylamide or polymethacrylamide main chains and lipopeptidic side chains and we showed that they exhibit smectic, nematic and cholesteric liquid-crystalline structures,[1] although they do not contain mesogenic groups identical or similar to those found in low molecular weight thermotropic liquid crystals.[2] Then we established the influence of the degree of polymerization of the peptide chains on the mesomorphic behaviour of comb like polymers using polymers with polyacrylamide main chains and liposarcosine side chains[3] and the influence of the nature of the amino acid on the structure and the geometrical parameters of the mesophases using comb like polymers with polyacrylamide main chains and lipoamino acid side chains.[4]

In order to show that liquid-crystallinity is a general property of comb like polymers with polyvinylic main chains and lipopeptidic side chains and to establish the influence of the nature of the main chain on their mesomorphic behaviour, we have synthesized comb like polymers with polystyrene main chains and liposarcosine side chains. In this paper we describe the synthesis and the liquid-crystalline behaviour of these polymers and we compare their mesomorphic properties with those of comb like polymers with polyacrylamide main chains and liposarcosine side chains.

EXPERIMENTAL PART

Materials

Sarcosine, dicyclohexylcarbodiimide (DCC), N-hydroxisuccinimide (HOSu) and 1,2-diaminododecane (DADD) were purchased from Fluka. Chloromethylstyrene was a gift from Dow Chemical. AIBN and Silica gel Si 60 on aluminium plates for thin layer chromatography were purchased from Merck.

Solvents were purified by classical methods.

Methods

N-*tert*-butyloxicarbonyl-1,2-diaminododecane Boc—NH—$(CH_2)_{12}$—NH_2 was prepared by reaction of di-*tert*-butyl-dicarbonate (diBoc) with 1,12-diaminododecane at room temperature in water/methanol solution.[5]

The Sarcosine N-carboxyanhydride (Sar-NCA) was obtained by the action of phosgene with sarcosine in tetrahydrofuran (THF) solution.[6]

Synthesis of the Polymerizable Amine (V)

1) Synthesis of (II). 9.7 g. of Magnesium and 35 ml. of diethylether were put in a flask fitted with a reflux condenser. 30.5 g. (0.2 mole) of chloromethylstyrene (I) were added dropwise. The speed of addition and the temperature of the flask were adjusted to maintain a small reflux. After 1 hour under reflux the system was diluted by addition of 35 ml. of diethylether, the viscous green solution was poured onto dry ice and acidified with sulfuric acid. The two phases obtained were separated and the organic phase was washed twice. After extraction with 60 ml. NaOH,1M (3 times), sulfuric acid (30 ml.) was added and the system was kept overnight to obtain a complete precipitation. The precipitate was filtered off, washed and dried. 17.5 g. of (II) were recovered (yield 54%).

2) Synthesis of (III). 16.2 g. (0.1 mole) of (II) were dissolved in 200 ml. of THF and the solution was cooled to 0°C. 12.7 g. (0.11 mole) of N-hydroxisuccinimide (HOSu) and then 20.6 g. (0.1 mole) of dicyclohexylcarbodiimide (DCC) were added by small amounts. The system was maintained at 0°C for 5 hours under agitation and overnight without agitation. The precipitate of DCU was filtered and washed with acetone. The filtrate was evaporated to dryness and a white solid was obtained. It was dissolved in ethanol and (III) was precipitated in water, filtered off and dried; 22 g. of (III) were recovered, (yield 85%).

3) Synthesis of (IV). 20.7 g. (0.08 mole) of (III) were dissolved in 200 ml. THF and 24.0 g. (0.08 mole) of Boc—NH—$(CH_2)_{12}$—NH_2 were added. After 24 hours

of reaction at room temperature the product (IV) was precipitated in water acidified by HCl, filtered off and dried. 36.4 g. of (IV) were recovered (yield 89%).

4) Synthesis of (V). The protective group (Boc) of (IV) was eliminated by addition of an excess of hydrobromic acid (HBr,4N) in acetic acid, followed by neutralization by sodium hydroxide. At pH = 9 the polymerizable amine (V) precipitated and was filtered off and dried. 25.4 g. of (V) were recovered (yield 90%).

At each step of the synthesis the products were characterized by Infrared Spectroscopy and NMR and their purity was checked by T.L.C.

Synthesis of Styryl-Lipopeptides (VI)

6.9 g. (0.02 mole) of the amine (V) were dissolved in 700 ml. of chloroform. Then, under strong agitation, 22.5 g. (0.2 mole) of Sar-NCA were added. After one hour of polymerization the solution was evaporated under vacuum and 19 g. of Styryl-liposarcosine (VI) were obtained.

The styryl-liposarcosine (VI) was fractionated by selective precipitation using the system solvent-non solvent Methanol-THF and the average number degree of polymerization p of the sarcosine of each fraction was determined by two methods: titration of the terminal amine function with perchloric acid in acetic acid and ultraviolet spectroscopy in ethanol solution.

Synthesis of Comb Polymers (VII)

5.0 g. of styryl-liposarcosine (VI) were dissolved in 100 ml. of methanol, after elimination of oxygen by bubbling nitrogen into the solution 150 mg. of AIBN were added, the system was maintained at 65°C under agitation for 72 hours. Methanol was eliminated under vacuum, the polymer was dispersed in water and recovered by lyophilization.

Preparation of Mesomorphic Gels

Comb polymers were dissolved in a small excess of water and when total homogeneity was realized, the desired concentration was obtained by very slow evaporation of the water. Then the samples were left at room temperature in tight cells to be sure that equilibrium was reached. After X-ray experiments the concentration of each gel was checked by evaporation to dryness in vacuum.

X-ray Diffraction Studies

X-ray diffraction studies were performed under vacuum with a Guinier type focussing camera equipped with a bent quartz monochromator giving a linear collimation and a device recording the diffraction patterns from samples held at various temperatures with an accuracy of 1°C.

RESULTS

Synthesis

The principle of the synthesis of comb like polymers with polystyrene main chains and liposarcosine side chains is similar to that of the synthesis of comb like polymers with polyacrylamide main chain and liposarcosine side chains. The synthesis involves two steps: preparation of a macromonomer from a α,ω-bifunctional lipid by fixation at one end of the polymerizable group and at the other end of the polysarcosine chain, followed by the transformation of the macromonomer into a comb like polymer by radical polymerization. Nevertheless the synthesis of styryl-lipopeptide macromonomers is longer and more difficult than that of acryloyl-lipopeptides because a styryl derivative with a carboxylic acid function has to be prepared while acryloylchloride and methacryloylchloride are commercially available.

Synthesis of Styryl-Liposarcosine

We performed the synthesis of styryl-liposarcosines in five steps

$$CH_2 = CH—C_6H_4—CH_2Cl \quad (I)$$

$$C_2H_5—O—C_2H_5 \quad \downarrow \quad \begin{matrix} Mg, \\ CO_2,\ H_2SO_4 \end{matrix}$$

$$CH_2 = CH—C_6H_4—CH_2—COOH \quad (II)$$

$$THF \quad \downarrow \quad HOSu,\ DCC$$

$$CH_2 = CH—C_6H_4—CH_2—CO—OSu \quad (III)$$

$$THF \quad \downarrow \quad Boc—NH—(CH_2)_{12}—NH_2$$

$$CH_2 = CH—C_6H_4—CH_2—CO—NH—(CH_2)_{12}—NH—Boc \quad (IV)$$

$$CH_3—COOH \quad \downarrow \quad HBr,\ NaOH$$

$$CH_2 = CH—C_6H_4—CH_2—CO—NH—(CH_2)_{12}—NH_2 \quad (V)$$

$$CHCl_3 \quad \downarrow \quad p.\ Sar—NCA$$

$$CH_2 = CH—C_6H_4—CH_2—CO—NH—(CH_2)_{12}— \\ NH—[CO—CH_2—N(CH_3)]pH \quad (VI)$$

In the first step chloromethylstyrene (I) is transformed into styrylacetic acid (II) by action at first of magnesium in diethylether and then of carbon dioxide and sulfuric acid.

In the second step (II) is activated under the form of its succinimidic ester (III) by action of N-hydroxisuccinimide (HOSu) in THF solution at 0°C in presence of a coupling agent (DCC).

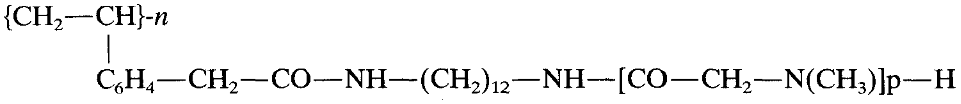
In the third step the succinimidyl ester (III) is reacted with the Boc α protected α,ω-dodecyldiamine in THF solution at room temperature and the protected amine (IV) is obtained.

In the fourth step the protecting group (Boc) of (IV) is eliminated by action at first of an excess of hydrobromic acid in acetic acid solution and then of sodium hydroxide and the polymerizable amine (V) is obtained.

In the fifth step the polymerizable amine (V) is used to initiate the polymerization of the N-carboxyanhydride of sarcosine (Sar-NCA) in chloroform solution and sytryl-liposarcosines (VI) are obtained. Then, in order to obtain styryl-liposarcosines with a small polydispersity the macromonomers (VI) are fractionated by selective precipitation using the system solvent-non solvent methanol-THF and the average number degree of polymerization *p* of sarcosine in each fraction of styryl-liposarcosine is determined by titration of the terminal amine function and by U.V. spectroscopy.

Synthesis of Comb Polymers

Styryl-liposarcosine macromonomers (VI) are transformed into comb like polymers (VII) by radical polymerization in methanol solution at 65°C using AIBN as initiator.



$$\begin{array}{l}\{CH_2\text{—}CH\}\text{-}n\\ \qquad\quad |\\ \qquad\quad C_6H_4\text{—}CH_2\text{—}CO\text{—}NH\text{—}(CH_2)_{12}\text{—}NH\text{—}[CO\text{—}CH_2\text{—}N(CH_3)]p\text{—}H\end{array}$$

LIQUID-CRYSTALLINE STRUCTURES

Comb copolymers exhibit in the dry state and in water concentrated solution (less than about 45% of water) mesomorphic structures at room temperature.

1) Description of the structures.

All the X-ray patterns of the mesophases show the diffuse wide angle band characteristic of liquid paraffinic chains.[7] But their low angle regions exhibit a set of 3 to 5 sharp reflections with Bragg spacings in the ratio 1:1/2:1/3:1/4:1/5 characteristic of a lamellar structure, or in the ratio $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}:1/\sqrt{9}$ characteristic of a hexagonal structure depending upon the water concentration.

The hydrophilic part A = $NH\text{—}[CO\text{—}CH_2\text{—}N(CH_3)]p$ and the hydrophobic part B = $CH_2\text{—}CH\text{—}C_6H_4\text{—}CH_2\text{—}CO\text{—}NH\text{—}(CH_2)_{12}$ of the repeating unit of the comb like polymers are incompatible and give rise to a microphase separation at the molecular level. So we can describe the lamellar and hexagonal structures as follows.

The lamellar structure consists of plane, parallel, equidistant sheets: each sheet, of thickness **d**, results from the superposition of two layers; one, of thickness $\mathbf{d_A}$, contains the polysarcosine hydrophilic chains and the water, while the other, of thickness $\mathbf{d_B}$ contains the polymer main chain and the lipidic side chains (Figure 1).

The hexagonal structure consists of long, parallel cylinders of radius **R**, assembled in a hexagonal array of parameter **D**. The cylinders are filled with the polymer main chain and the lipidic side chains, while the space between the cylinders is occupied by the polysarcosine hydrophilic chains and the water (Figure 2).

The lattice parameters d for the lamellar structure and D for the hexagonal structure were obtained directly from the X-ray patterns. The other parameters: d_A, d_B, R, S_L and S_H (the average surface occupied by a chain at the interface for

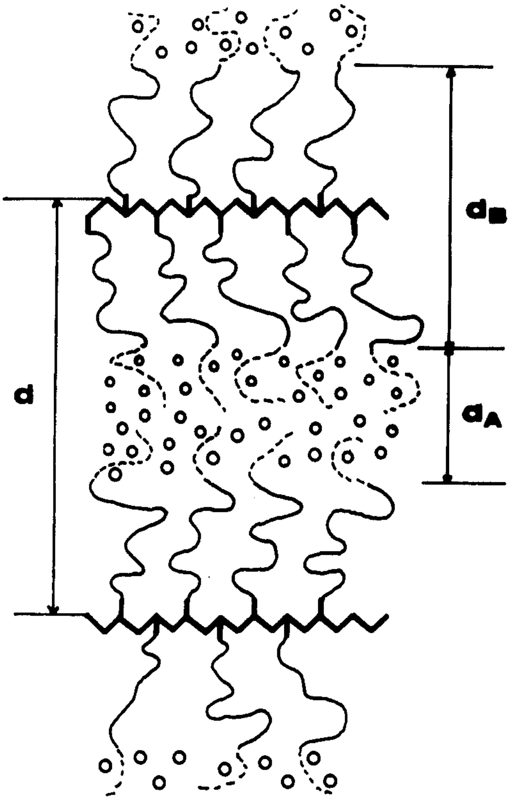


FIGURE 1 Schematic representation of the lamellar structure. 〰 polystyrene main chain, ∼ paraffinic chain ╌ polysarcosine chain, o o o o water.

the lamellar and hexagonal structures, respectively) were obtained using the following formulae based on simple geometrical considerations:

$$d_B = d\left[1 + \frac{CX_AV_A + (1 - C)V_S}{C(1 - X_A)V_B}\right]^{-1} \tag{1}$$

$$d_A = d - d_B \tag{2}$$

$$S_L = 2M_BV_B/Nd_B \tag{3}$$

$$R^2 = \frac{D^2\sqrt{3}}{2\pi}\left[1 + \frac{CX_AV_A + (1 - C)V_S}{C(1 - X_A)V_B}\right]^{-1} \tag{4}$$

$$S_H = 2M_BV_B/NR \tag{5}$$

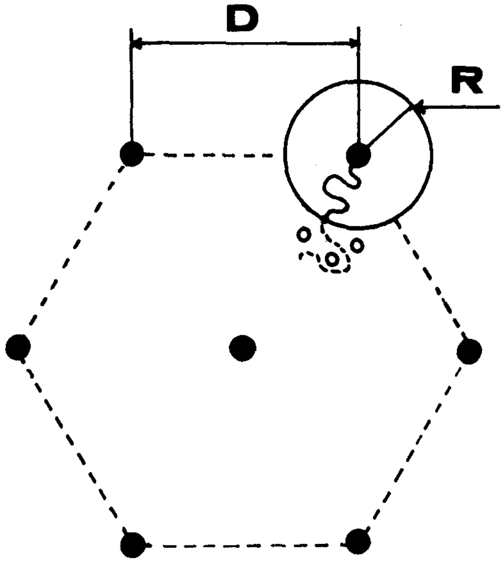


FIGURE 2 Schematic representation of the hexagonal structure.
〰 polystyrene main chain, ⌒ paraffinic chain
- - - polysarcosine chain, o o o o water.

where:

- C is the weight content of copolymer in solution,
- X_A is the weight fraction of hydrophilic polysarcosine chains in the polymer (Table)
- V_A is the specific volume of the hydrophilic chains A (V_A = 0.755 $cm^3\ g^{-1}$)
- V_B is the specific volume of the hydrophobic moiety B(V_B = 0.970 $cm^3\ g^{-1}$)
- V_S is the specific volume of the water
- $M_B = 328$
- N is the Avogadro number

2) Influence of the water concentration.

The water concentration has two types of influence: on the nature of the mesophases and on the values of their structural parameters.

a) Influence on the nature of the mesophases.

As in the case of block copolymers,[8] the type of structure is determined by the ratio of the volumes of the hydrophilic and hydrophobic domains. The addition of water to comb like polymers increases the relative volume of the hydrophilic domains and is therefore able to transform a lamellar structure into a cylindrical hexagonal one (Figure 3).

b) Influence on the structural parameters.

As can be seen in Figure 3, the increase of the water concentration involves a discontinuity in the variation of the structural parameters at the transition between the lamellar and the hexagonal structure, but within the domain of stability of each

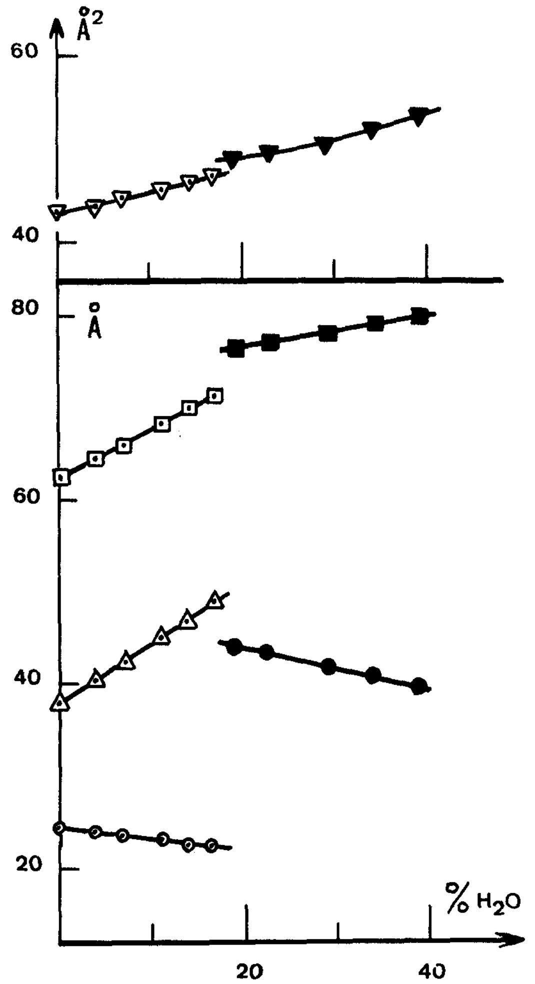


FIGURE 3 Variation with water concentration of the structural parameters of the lamellar and hexagonal structures exhibited by the comb like polymer PS12Sar9: □ = d; △ = d_A; ○ = d_B; ▽ = S_L; ■ = D; ● = 2R; ▼ = S_H.

mesophase the structural parameters vary in a continuous way with the water concentration.

For the lamellar structure (Figure 3), when the water concentration increases, the total thickness **d** of a sheet, the thickness $\mathbf{d_A}$ of the hydrophilic layer and the average surface S_L per chain at the interface all increase, whereas the thickness $\mathbf{d_B}$ of the hydrophobic layer decreases as the hydrophobic chains have to keep a constant density.

For the hexagonal structure (Figure 3), when the water concentration increases, the distance **D** between the cylinders and the average surface area S_H both increase, whereas the diameter **2R** of the hydrophobic cylinders decreases.

3) Influence of the degree of polymerization **p**.

In order to establish the influence of the degree of polymerization p of the peptidic

TABLE

Characteristics of polymers studied by X-ray diffraction

Polymer	P	X_A
PS12Sar18	18	0.798
PS12Sar14	14	0.755
PS12Sar9	9	0.666
PS12Sar6	6	0.574

p = Average number degree of polymerization of the polysarcosine chains.
X_A = Composition of the polymer in lipisarcosine.

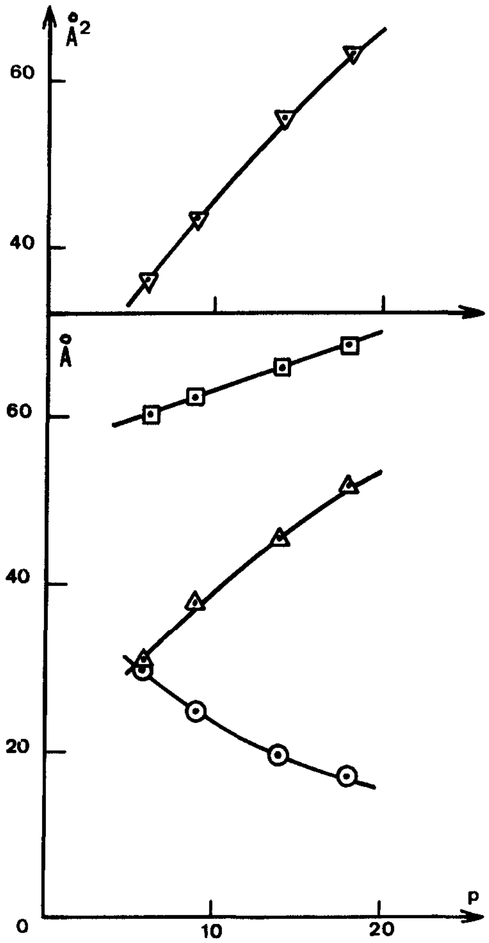


FIGURE 4 Variation, with the average number degree of polymerization p of the polysarcosine side chains, of the structural parameters of the lamellar structure exhibited by comb like polymers PS12Sarp: ▢ = d; △ = d_A; ○ = d_B; ▽ = S_L.

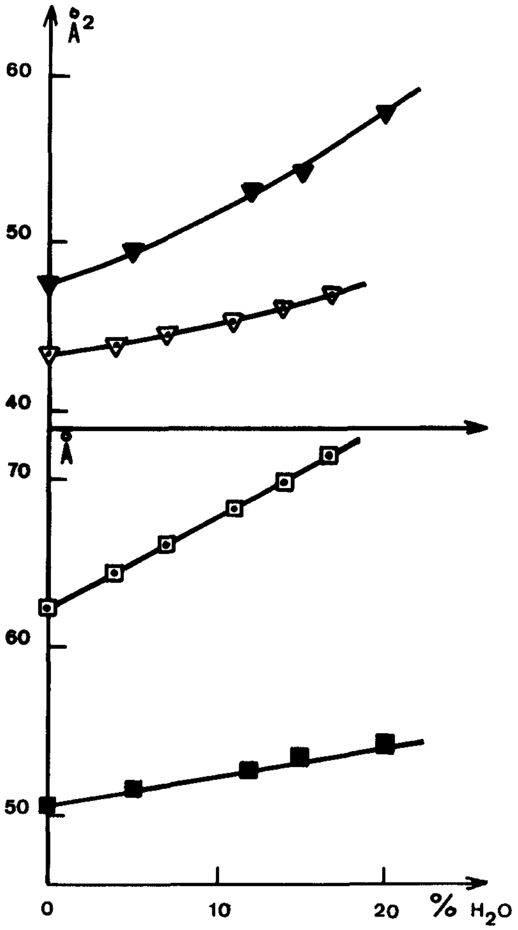


FIGURE 5 Variation with water concentration of the intersheet spacing d and the average surface SL of the lamellar structure exhibited by the polymers PAAm12Sar8.8: ■ = d; ▼ = S_L; and PS12Sar9: □ = d; ▽ = S_L.

chains on the structural parameters of the lamellar (Smectic A) mesophases, we have studied by X-ray diffraction a set of comb like polymers with the same polystyrene main chain and the same paraffinic spacer of 12 carbon atoms but different degrees of polymerization p of the peptidic polysarcosine chains (Table).

In the Figure 4 are plotted the variation of the parameters of the lamellar structure as a function of the number average degree of polymerization p of the sarcosine for a set of comb like polymers in the dry state. One can see that when p increases: the total thickness d of a sheet, the thickness d_A of the hydrophilic layer containing the polysarcosine chains and the average surface S_L all increase, whereas the thickness d_B of the hydrophobic layer decreases.

4) Influence of the nature of the main chain.

In order to establish the influence of the nature of the main chain on the structural parameters of the lamellar structure of comb like polymers we have performed, by X-ray diffraction, a comparative study of two comb like polymers with an

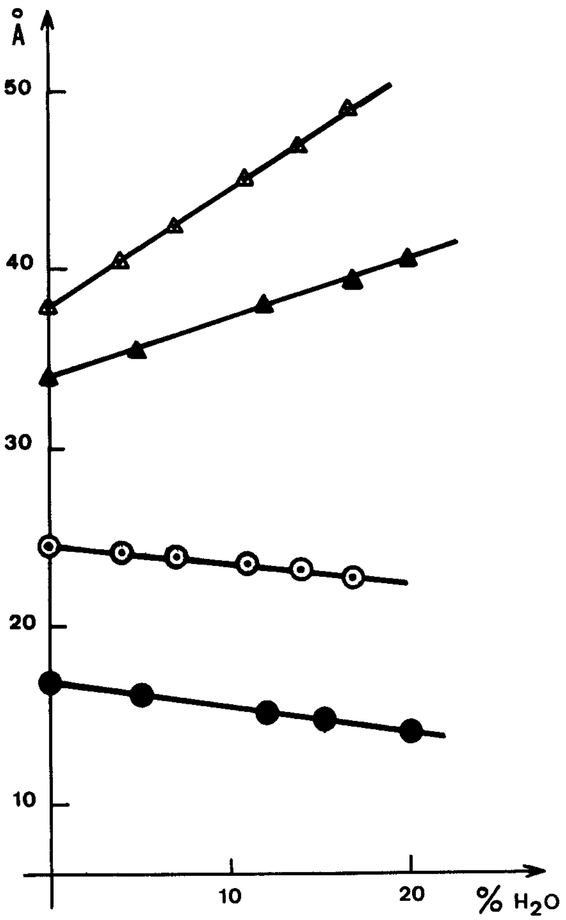


FIGURE 6 Variation with water concentration of the thicknesses d_A and d_B of the hydrophilic and hydrophobic layers of the lamellar structure exhibited by the polymers PAAm12Sar8.8: ▲ = d_A; ● = d_B and PS12Sar9: △ = d_A; ○ = d_B.

identical paraffinic spacer containing 12 methylene groups and with a polysarcosine chain with nearly the same degree of polymerization p of the polysarcosine chain (8.8 for the polyacrylamide polymer PAAm12Sar8.8 and 9 for the polystyrene polymer PS12Sar9), but differing by the nature of the main chain: polystyrene for the polymer PS12Sar9 and polyacrylamide for the polymer PAAm12Sar8.8.

On the Figures 5 and 6 are plotted the variation of the parameters of the lamellar structure of the two polymers as a function of the water concentration of the mesophases. One can see that the total thickness d of a sheet, the thickness d_A of the hydrophilic layer and the thickness d_B of the hydrophobic layer are all higher for the polystyrene polymer than for the polyacrylamide polymer, whereas the average surface S_L per chain at the interface between the hydrophilic and hydrophobic layers is smaller for the polystyrene polymer than for the polyacrylamide polymer.

CONCLUDING REMARKS

In this paper we have described the synthesis and the liquid crystalline behaviour of comb like polymers with polystyrene main chain and liposarcosine side chains. We have shown that these copolymers exhibit in the dry state and in concentrated solution mesomorphic structure as well as do comb like polymers with polyacrylamide, polymethacrylamide, polyacrylate or polymethacrylate main chains and liposarcosine side chains.[1,3,5] Therefore liquid-crystallinity is a general property of comb like polymers with polyvinyl main chains and lipopeptidic side chains. The mesomorphic behaviour of these polymers results from their amphiphilic character: their lipophilic parts formed by the polymer main chains and the aliphatic part of the lipopeptidic side chains on the one hand, and hydrophilic peptidic part of the side chains on the other hand tend to separate in space from one another with creation of interfaces. The hydrophilic and hydrophobic moieties tend to segregate into distinct microdomains having the shape of lamellae (Figure 1) or cylinders (Figure 2) alternatively juxtaposed and separated by defined boundaries.

Nevertheless, if the existence of mesophases is a general property of comb like polymers with polyvinyl main chains and lipopeptidic side chains, the nature of the main chain determines the type of mesophases obtained, their domain of stability and the values of their geometrical parameters. For example comb like polymers with polyacrylamide or polymethacrylamide main chains and liposarcosine side chains exhibit as a function of both the water concentration and the temperature Smectic A (lamellar) and Nematic mesophases[3]; while comb like polymers with polystyrene main chain and liposarcosine side chains exhibit at room temperature Smectic A (lamellar) and cylindrical hexagonal mesophases. The influence of temperature on the mesophases of comb like polymers with polystyrene main chains is now in progress to verify the existence of thermotropic properties.

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