Synthesis and mesomorphic behaviour of comb-like polymers based on lipopeptides with two hydrophobic chains

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Synthesis and mesomorphic behaviour of comb-like polymers based on lipopeptides with two hydrophobic chains

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Polymerizable lipopeptides with two hydrophobic chains were synthesized and transformed into comb-like polymers by radical polymerization. The structure of dry polymerizable lipopeptides and comb-like polymers and of their aqueous solutions was determined by X-ray diffraction. Comb-like polymers exhibit both thermotropic and lyotropic properties. Three types of mesomorphic structure were resolved: smectic B, smectic A and cylindrical hexagonal. The domains of stability of the mesophases and the values of their structural parameters were established.

1. Introduction

If thermotropic properties of polymers [1, 2] generally result from the presence in the molecule of rigid mesogenic groups identical or similar to those found in low molecular weight liquid crystals [3], some years ago we showed that liquid crystalline structures can be obtained with comb-like polymers that do not contain such mesogenic groups, but exhibit a microphase separation at the molecular level [4–6]. Our comb-like polymers were formed by a polyacrylamide or polymethacrylamide main chain and lipopeptidic side chains and exhibited both thermotropic and lyotropic behaviour [4–6].

Then, to analyse the influence of the nature of the amino acid on the liquid crystalline properties of comb-like polymers, we synthesized and studied polymers with polyacrylamide or polymethacrylamide main chains and lipoamino-acid side chains [7]. We showed that the nature of the amino acid governs the number, the nature and the domains of stability of the mesophases and the values of their geometrical parameters [7, 8].

Recently we showed that liquid crystallinity is a general property of comb-like polymers with polyvinylic main chains and lipopeptidic side chains, and we established the influence of the nature of the main chain on their mesomorphic behaviour [9].

Until now, all our comb-like polymers were based on lipopeptides with one hydrophobic lipidic chain. In order to examine the influence of the molecular characteristics of the lipidic chains on the liquid crystalline properties of comb-like polymers, we have prepared recently polymerizable lipopeptides with two hydro-phobic chains (a polymerizable one and a non-polymerizable one) and a polar head formed by an amino acid residue NH–CH(R)–COOH with a hydrophilic side chain R. They correspond to the general formula:

$$H_2C{=}CH{-}CO{-}NH{-}(CH_2)_n{-}Z{-}(CH_2)_q{-}CH{-}CO{-}NH{-}CH{-}COOH$$
$$H{-}(CH_2)_p{-}Z \qquad\qquad R$$
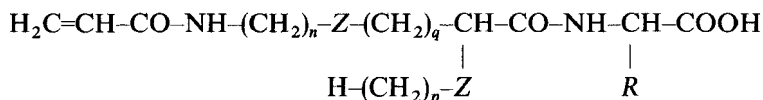
with $Z{=}CO{-}NH$ or $NH{-}CO$ and $R{=}CH_2{-}COOH$, $CH_2{-}CH_2{-}COOH$ or $CH_2{-}OH$.

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In this paper we will describe the synthesis and the liquid crystalline behaviour of polymerizable lipopeptides with an aspartic acid residue (R=CH$_2$–COOH) as the polar head, and the derived comb-like polymers.

2. Synthesis

2.1. *Principle of the synthesis*

How do we obtain these comb-like-polymers?

We start from an amino acid with a functional group at the end of its side chain and proceed as follows:

(i)   in a first step, we link the hydrophobic chain bearing the polymerizable group at the end of the side chain of the amino acid;

(ii) in a second step we link the second hydrophobic chain to the amino acid;

(iii) in a third step we link an amino acid with a hydrophilic side chain to the functional group remaining free;

(iv) in a fourth step we transform the polymerizable lipopeptide with two hydrophobic chains into a comb-like polymer by radical polymerization.

2.2. *Synthesis of the polymerizable lipopeptides*

To illustrate our method of synthesis, we describe the case of the polymerizable lipopeptides VLKD with two hydrophobic chains and an aspartic acid head group. They are synthesized in six steps, using L-lysine as starting material (see figure 1).

(i)   In the first step, taking advantage of the difference in reactivity of the ε and α-amino functions of lysine, the first hydrophobic chain bearing the polymerizable group is linked to the ε-amino function of lysine by interaction with 11-(acryloylamino)undecanoylsuccinimidyl ester. The reaction occurs in a acetone/water mixture, in the presence of TEA, at 0°C.

(ii) In the second step, in order to increase the reactivity of the α-amino function of (I), the carboxyl function of the lysine is transformed into its methyl ester by action of dimethoxypropane (DMP). The reaction occurs in DMP solution at 50°C.

(iii) In the third step, the second hydrophobic chain is linked to the lipolysine methyl ester (II) by the action of laurylsuccinimidyl ester on the α-amino function. The reaction occurs in chloroform solution, in the presence of TEA, at room temperature.

(iv) In the fourth step, the methyl ester of (III) is hydrolyzed by sodium hydroxide, at 40°C, in a mixture of methanol/water.

(v)   In the fifth step, the carboxyl function of (IV) is activated as its succinimidyl ester by the action of N-hydroxysuccinimide, in THF solution, at 4°C, in the presence of a coupling agent (DCC).

(vi) In the sixth step, aspartic acid is linked to (V) by aminolysis of the succinimidyl ester by the α-amino function of the aspartic acid. The reaction occurs in a mixture of ethanol/water, in the presence of TEA, at room temperature, and the polymerizable lipopeptide VLKD (VI) is obtained.

All the steps in the synthesis were followed by FTIR spectroscopy. The products obtained at each step were characterized by FTIR and NMR spectroscopy and their purities verified by thin layer chromatography.
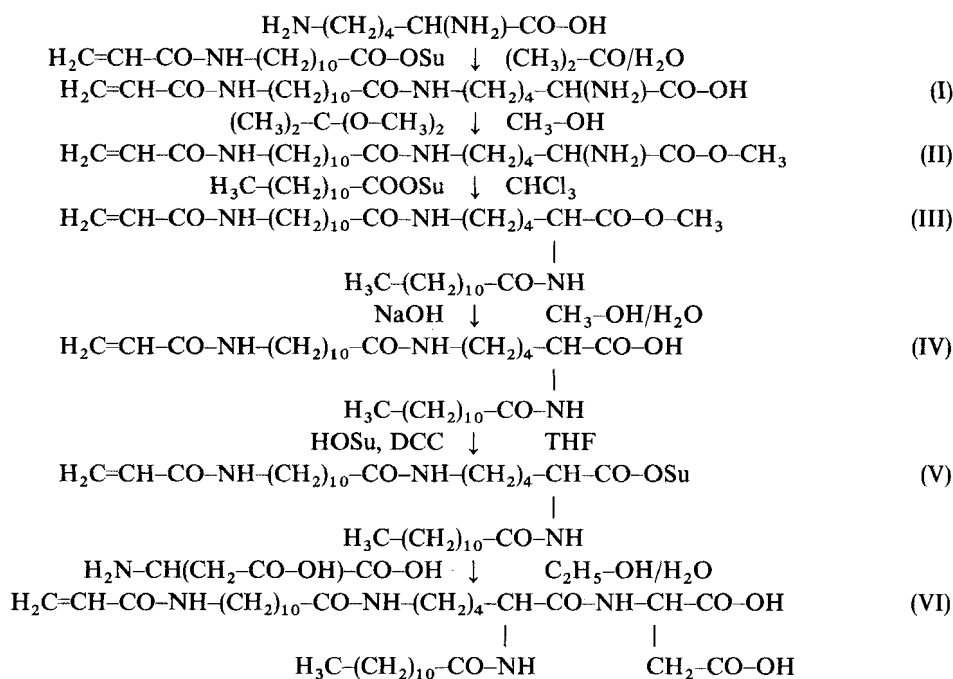
$$H_2N\text{-}(CH_2)_4\text{-}CH(NH_2)\text{-}CO\text{-}OH$$

$$H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}CO\text{-}OSu \quad \downarrow \quad (CH_3)_2\text{-}CO/H_2O$$

$$H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}CO\text{-}NH\text{-}(CH_2)_4\text{-}CH(NH_2)\text{-}CO\text{-}OH \tag{I}$$

$$(CH_3)_2\text{-}C\text{-}(O\text{-}CH_3)_2 \quad \downarrow \quad CH_3\text{-}OH$$

$$H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}CO\text{-}NH\text{-}(CH_2)_4\text{-}CH(NH_2)\text{-}CO\text{-}O\text{-}CH_3 \tag{II}$$

$$H_3C\text{-}(CH_2)_{10}\text{-}COOSu \quad \downarrow \quad CHCl_3$$

$$H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}CO\text{-}NH\text{-}(CH_2)_4\text{-}CH\text{-}CO\text{-}O\text{-}CH_3 \tag{III}$$
$$|$$
$$H_3C\text{-}(CH_2)_{10}\text{-}CO\text{-}NH$$

$$NaOH \quad \downarrow \quad CH_3\text{-}OH/H_2O$$

$$H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}CO\text{-}NH\text{-}(CH_2)_4\text{-}CH\text{-}CO\text{-}OH \tag{IV}$$
$$|$$
$$H_3C\text{-}(CH_2)_{10}\text{-}CO\text{-}NH$$

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

$$H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}CO\text{-}NH\text{-}(CH_2)_4\text{-}CH\text{-}CO\text{-}OSu \tag{V}$$
$$|$$
$$H_3C\text{-}(CH_2)_{10}\text{-}CO\text{-}NH$$

$$H_2N\text{-}CH(CH_2\text{-}CO\text{-}OH)\text{-}CO\text{-}OH \quad \downarrow \quad C_2H_5\text{-}OH/H_2O$$

$$H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}CO\text{-}NH\text{-}(CH_2)_4\text{-}CH\text{-}CO\text{-}NH\text{-}CH\text{-}CO\text{-}OH \tag{VI}$$
$$|\qquad\qquad\qquad |$$
$$H_3C\text{-}(CH_2)_{10}\text{-}CO\text{-}NH \qquad CH_2\text{-}CO\text{-}OH$$

Figure 1. Scheme for the synthesis of the polymerizable lipopeptide VLKD.

2.3. *Synthesis of the comb-like polymers*

The polymerizable lipopeptides (VI) were transformed into the comb-like polymers by radical polymerization in methanol solution at 65°C using AIBN as initiator. Then the aspartic acid terminal residues in the side chains were transformed into their sodium salts by action of sodium hydroxide. Average degrees of polymerization were between 50 and 100 [8].

3. Liquid crystalline properties

The structures of the polymerizable lipopeptide VLKD and the comb-like polymer PLKD have been studied in the dry state and in concentrated aqueous solution, between room temperature and 200°C, by X-ray diffraction.

3.1. *Description of the structures*

Four types of X-ray diagrams were obtained with the focusing camera.

(i) The first family of X-ray diagrams was obtained with the polymerizable lipopeptide VLKD. They exhibit in the low angle region a set of sharp lines with reciprocal spacings in the ratio 1, 2, 3 characteristic of a lamellar structure, and in the wide angle region a set of sharp lines characteristic of crystallized lipidic chains. Such X-ray diagrams correspond to a lamellar crystalline structure.

(ii) The second family of X-ray diagrams was obtained only with the comb-like polymer PLKD. They exhibit in the low angle region at set of 2 or 3 sharp lines with reciprocal spacings in the ratio 1, 2, 3 characteristic of a lamellar structure, and in the wide angle region a sharp line characteristic of a hexagonal packing of the side chains. Such X-ray diagrams correspond to a

smectic structure with a hexagonal organization in the planes of the lamellae [10]. We will see later that the smectic structure is smectic B for the dry polymer and smectic F or I in the presence of water.

(iii) The third family of X-ray diagrams was obtained only with the comb-like polymer PLKD. They exhibit in the low angle region a set of 2 or 3 sharp lines with reciprocal spacings in the ratio 1, 2, 3 characteristic of a lamellar structure, and in the wide angle region a diffuse band characteristic of the absence of periodic order in the planes of the lamellae. Such X-ray diagrams correspond to a smectic A structure [7, 10, 11].

(iv) The fourth family of X-ray diagrams was obtained only with the comb-like polymer PLKD. They exhibit in the low angle region as set of 3 to 5 sharp lines with reciprocal spacings in the ratio 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$ characteristic of a bidimensional hexagonal array, and in the wide angle region a diffuse band characteristic of the liquid state of the lipidic chains. Such X-ray diagrams correspond to a cylindrical hexagonal structure [7, 11].

The repeat unit of the comb-like polymer PLKD can be divided into two parts: a hydrophilic part A: $CO-NH-CH(CH_2-COONa)-COONa$ and a hydrophobic part B: $H_2C-CH-CO-NH-(CH_2)_{10}-CO-NH-(CH_2)_4-CH-NH-CO-(CH_2)_{10}-CH_3$. The two parts are incompatible and give rise to a microphase separation at the molecular level. Therefore, we can describe the lamellar and hexagonal mesomorphic structures as follows:

(i) The lamellar structure consists of plane, parallel, equidistant sheets; each sheet, of thickness d, results from the superposition of two layers: one, of thickness d_A, contains the hydrophilic sodium aspartate moieties and the water, while the other, of thickness d_B, contains the polymer main chain and the lipidic side chains (see figure 2).

(ii) The hexagonal structure consists of long, parallel cylinders of radius R, assembled in a hexagonal array of side 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 hydrophilic sodium aspartate moieties and the water (see figure 3).
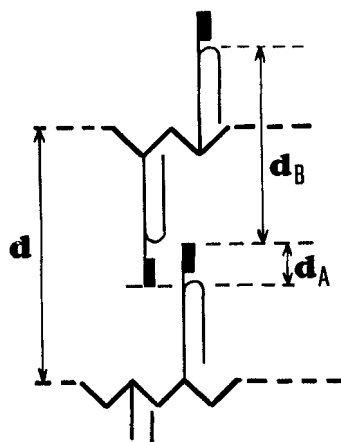

Figure 2. Schematic representation of the lamellar structure: polyacrylamide main chain ∧∨∨, lipidic chains ⊃⊂, aspartic acid polar head ▂▄ .

The lattice parameters: total thickness d for the lamellar structure and distance D between cylinders 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 repeating unit at the interface for the lamellar and hexagonal structures, respectively) were obtained using the following formulae based on simple geometrical considerations:

$$d_B = d \left(1 + \frac{CX_A V_A + (1 - C)V_S}{C(1 - X_A)V_B} \right)^{-1}, \tag{1}$$

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

$$S_L = 2M_B V_B / N d_B, \tag{3}$$

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

$$S_H = 2M_B V_B / N R, \tag{5}$$

where C is the weight content of lipopeptide or comb-like polymer in solution, X_A is the weight fraction of the hydrophilic moiety A, V_A is the specific volume of the hydrophilic moiety A ($V_A = 0.445\,\text{cm}^3\,\text{g}^{-1}$), V_B is the specific volume of the hydrophobic moiety B ($V_B = 0.998\,\text{cm}^3\,\text{g}^{-1}$), V_S is the specific volume of the water, and M_B is the molecular mass of the hydrophobic moiety ($M_B = 520$).

It was said previously that the X-ray diagrams with a set of sharp lines (with reciprocal spacings in the ratio 1, 2, 3) in the low angle region and a sharp line in the wide angle region, correspond to a smectic B phase in the dry polymer and to a smectic F or I phase in the presence of water. Why? If we compare the lengths L_B and L_A of the hydrophobic and hydrophilic moieties of the repeat unit of the comb-like polymer, measured using CPK molecular models, with the thicknesses d_B and d_A of the hydrophobic and hydrophilic layers, we see (see table 1) that for the dry polymer

$$d_B = 2L_B, \quad d_A = L_A \quad \text{and} \quad d = L_A + 2L_B.$$

Therefore the side chains are perpendicular to the planes of the lamellae and the structure is of the smectic B type; the hydrophobic layer of thickness d_B consists of a bilayer of hydrophobic lipidic chains, while the hydrophilic layer of thickness d_A consists of a monolayer of polar heads.

When water is added to the polymer, d_B decreases and becomes smaller than $2L_B$; the lipidic chains become tilted and the perpendicular smectic B structure becomes a tilted smectic structure (F or I).

3.2. *Domain of stability of the structures*

Now that the different structures are known, what are their domains of stability?

In order to establish the domains of stability of the mesophases, we have studied by X-ray diffraction, as a function of temperature, the dry polymer PLKD and its aqueous

Table 1. Comparison between the parameters d, d_A and d_B of the lamellar structure and the lengths L_A and L_B of the hydrophilic and hydrophobic parts of the repeat unit of the polymer PLKD.

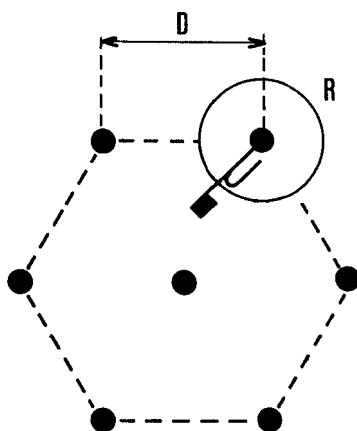| d_A Å	L_A Å	d_B Å	$2L_B$ Å	d Å	$L_A + 2L_B$ Å
7·2	8 ± 1	41	40 ± 1	48·2	49 ± 1

Figure 3.   Schematic representation of the hexagonal structure. Key as for figure 2.
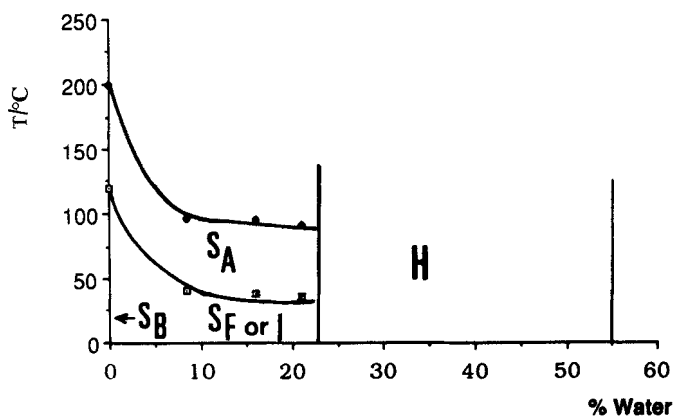

Figure 4.   Phase diagram temperature/water concentration for the comb-like polymer PLKD.
S_B = smectic B phase, S_F or S_I = smectic F or I phase; S_A = smectic A phase; H = cylindrical
hexagonal phase.

solutions of fixed concentrations. In the figure 4, the phase diagram is plotted as
temperature versus concentration of water for the comb-like polymer PLKD. The X-
ray results give the domains of stability for 4 mesophases:

(i)   a smectic B mesophase for the dry polymer at temperatures less than 110°C;
(ii)   a tilted smectic mesophase (F or I), for concentrations of water smaller than
       about 22 per cent and temperatures smaller than a limiting value that
       decreases from 110°C to 40°C when the concentration of water increases up to
       22 per cent;
(iii) a smectic A mesophase, for concentrations of water smaller than about 22 per
       cent, with temperature ranges varying from between 40°C and 90°C to 110°C
       and more than 200°C when the concentration of water decreases to 0 per cent;
(iv)   a cylindrical hexagonal structure for concentrations of water between about
       22 and 55 per cent.

The smectic A structure can be frozen in at room temperature by cooling, as demonstrated by X-ray diffraction (diffuse band at wide angles), although no glass transition could be observed by DSC.

Similar studies on the polymerizable lipopeptide VLKD have shown that VLKD gives only crystalline structures at temperatures where no spontaneous polymerization or degradation can occur.

3.3. *Factors governing the structural parameters*

As the factors governing the nature and the domain of stability of the mesophases are the concentration of water and the temperature, we will examine their respective influence on the structural parameters.

3.3.1. *Influence of concentration of water*

The concentration of water has two types of influence: (i) on the nature of the mesophases, and (ii) on the values of their structural parameters.

(i) *Influence of the nature of the mesophases*

As in the case of block copolymers [12], the type of structure is determined by the ratio of the volumes of the hydrophilic and hydrophobic domains. The addition of
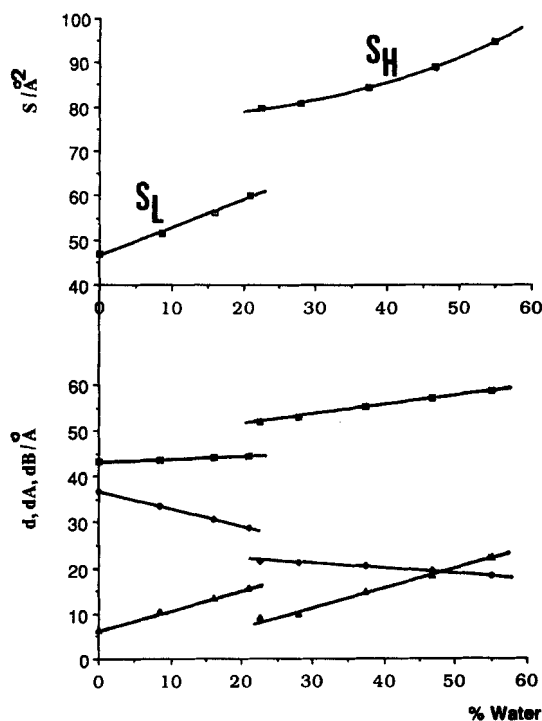

Figure 5. Variation of the geometrical parameters of the smectic B, smectic F or I and cylindrical hexagonal structures of the comb-like polymer PLKD with water concentration at room temperature: $\square$ total thickness of a sheet d, $\triangle$ thickness of the hydrophilic layer d_A, $\diamond$ thickness of the hydrophobic layer d_B, $\square$ average surface S_L, $\blacksquare$ distance between neighbouring cylinders D, $\blacklozenge$ radius of the cylinders R, $\blacktriangle$ distance between the surfaces of the cylinders $D\text{-}2R$, $\blacksquare$ average surface S_H.

water to comb-like polymers increases the relative volume of the hydrophilic domains and is therefore able to transform a lamellar structure (smectic) into one that is cylindrical hexagonal (see figure 4).

(ii) *Influence of the structural parameters*

We have plotted, as a function of the concentration of water, the variation, at room temperature, of the geometrical parameters of the smectic (B, F or I) and the cylindrical hexagonal structures in figure 5, and of the smectic A and the cylindrical hexagonal structures in figure 6.

We can see that the transition between the lamellar and the hexagonal structure involves a discontinuity in the variation of the structural parameters with concentration of water, whereas within the domain of stability of each mesophase, the structural parameters vary in a continuous way wih concentration of water.

For the lamellar structure, when the concentration of water increases, the total thickness d of a sheet, the thickness d_A of the hydrophilic layer and the average surface S_L per repeat unit at the interface all increase, whereas the thickness d_B of the hydrophobic layer decreases. How can we explain the decrease of d_B? In the smectic B phase (see figure 5), in the absence of water, the side chains are perpendicular to the layer; when water is added to the polymer, the hydrophilic moiety of the side chains swells, the surface S for a repeating unit at the interface increases, and to occupy all the
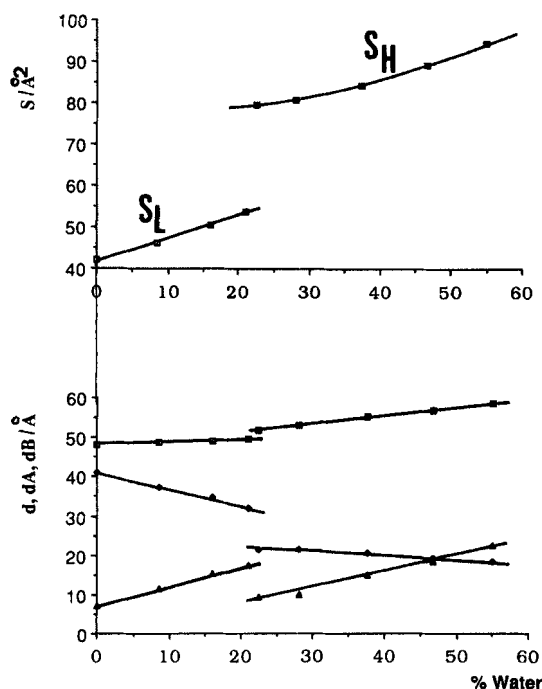
Figure 6.   Variation of the geometrical parameters of the smectic A and cylindrical hexagonal structures of the comb-like polymer PLKD with water concentration at room temperature: □ total thickness of a sheet d, △ thickness of the hydrophilic layer d_A, ◇ thickness of the hydrophobic layer d_B, □ average surface S_L, ■ distance between neighbouring cylinders D, ◆ radius of the cylinders R, ▲ distance between the surfaces of the cylinders D-$2R$, ■ average surface S_H.

available surface, the paraffinic chains are forced to tilt, and their tilt angle increases with the water content of the system until the lamellar structure disappears and is replaced by a cylindrical hexagonal structure, therefore the addition of water to the dry polymer transforms the perpendicular smectic B structure into a tilted smectic structure (F or I), and the tilt angle increases with water concentration. In the case of the smectic A phase (see figure 6) the hydrophobic chains are liquid and when the hydrophilic domains swell the paraffinic chains contract to keep a constant density.

For the hexagonal structure, when the concentration of water increases, the distance D between the cylinders, the distance $(D\text{-}2R)$ between the surfaces of the neighbouring cylinders and the average surface area S_H all increase, whereas the radius R of the hydrophobic cylinders decreases to allow the hydrophobic chains to keep a constant density.

3.3.2. *Influence of temperature*

We have already seen that increase of temperature is able to transform a smectic B structure into a smectic A structure, and that the smectic A phase can be frozen in at room temperature by cooling.

Comparison of figures 5 and 6 shows that, at the transition smectic B–smectic A, the total thickness d of a sheet, the thickness of d_A of the hydrophilic layer and the thickness d_B of the hydrophobic layer decrease, while the average surface S increases because the lipidic chains become liquid.

4. Experimental

4.1. *Materials*

α-amino acids, dicyclohexylcarbodiimide (DCC), N-hydroxy succinimide (HOSu), acryloyl chloride and dimethoxypropane (DMP) were purchased from Fluka. 11-Amino-undecanoic acid was purchased from Merck. AIBN and silica gel (Si 60) on aluminium plates for thin layer chromatography were purchased from Merck. Solvents were purified by classical methods.

4.2. *Methods*

Synthesis of 11-acryloylamino-undecanoic acid was performed by a modification of the method of de Winter and Marien [13], using aqueous KOH solution as the reaction solvent and toluene as the recrystallization solvent (yield 70 per cent). Synthesis of 11-acryloylamino-undecanoylsuccinimidyl ester was performed by an adaptation of the method of Paquet [14] using tetrahydrofuran (THF) as the reaction solvent (yield 85 per cent). Synthesis of the lauroylsuccinimidyl ester was carried out by the method of Paquet [14].

4.3. *Synthesis of the polymerizable lipopeptide* (VI)

Synthesis of (*I*): 0·09 mol of lysine hydrochloride was dissolved in 450 ml of water and 90 ml of TEA added. This solution was slowly poured into a solution of 0·075 mol of 11-acryloylamino-undecanoylsuccinimidyl ester in 450 ml of acetone and a suspension was obtained. After 18 h at room temperature, with agitation, the suspension was filtered, and the solid was dissolved in a minimum of methanol saturated with NaOH and reprecipitated with acetone. The precipitate of (I) was purified by dissolution in concentrated HCl at 0°C and reprecipitated with NaOH (1 M). Yield 54 per cent. $R_f = 0.55$ in n-propanol/NH$_3$ (7/3).

Synthesis of (II): 0·1 mol of (I) was dissolved in 100 ml of methanol and 30 ml of concentrated HCl added. This solution was poured into 300 ml of dimethoxypropane (DMP) and a suspension obtained [15]. After 6 h at 50°C with agitation (the formation of the ester (II) was followed by IR at 1750 cm^{-1}), the methyl ester (II) was isolated by addition of a large amount of diethyl ether and filtration. Then (II) was purified by successive dissolution and precipitation using the system methanol/diethyl ether. Yield 77 per cent. $R_f = 0.91$ in *n*-propanol/NH$_3$ (7/3).

Synthesis of (III): 0·022 mol of (II) was dissolved in 450 ml of chloroform and 7·2 ml of TEA added. Then 0·024 mol (1·1 equivalent) of lauroylsuccinimidyl ester was added. After 24 h at room temperature with agitation, most of the chloroform was evaporated under vacuum at 40°C. Then (III) was precipitated twice using acetonitrile and recrystallized from methanol at 4°C. Yield 45 per cent. $R_f = 0.40$ in MeOH/CH$_3$Cl (1/9).

Synthesis of (IV): 0·01 mol of (III) was dissolved in 130 ml of methanol; then 130 ml of water were added with agitation, and finally NaOH was added. The reaction was carried out at 40°C for 24 h. After cooling, HCl (1 M) was added until the pH is as 4 and agitation was continued for 0·5 h. The precipitate of (IV) was filtered off and washed twice with chloroform. Then (IV) was recrystallized from THF. Yield 90 per cent. $R_f = 0.4$ in MeOH/CH$_3$Cl (2/8).

Synthesis of (V): 0·007 mol of (IV) was dissolved in 400 ml of THF at 60°C. Then the solution was cooled to 0°C and 0·01 mol of HOSu and 0·007 mol of DCC were added. After about 24 h at 4°C (until the IR absorption of DCC at 2100 cm^{-1} had disappeared) with agitation, the DCU was precipitated by cooling at −20°C overnight and filtered off. A large amount of the THF was eliminated by evaporation and the oily solution of (V) was poured into cold water at pH = 7. The precipitate of (V) was filtered off and dried. Yield 85 per cent. $R_f = 0.3$ in MeOH/CH$_3$Cl (2/8).

Synthesis of (VI): To a solution of 6 mmol of (V) in 200 ml of acetone was added a solution of 10 mmol of aspartic acid in 200 ml of water and 40 ml of TEA; a suspension was obtained. After 18 h with agitation at room temperature, the acetone was evaporated off under vacuum. Then (VI) was precipitated out by addition of dilute HCl until the pH was 2. After filtration and drying, (VI) was purified by preparative thin layer chromatography. Yield 40 per cent.
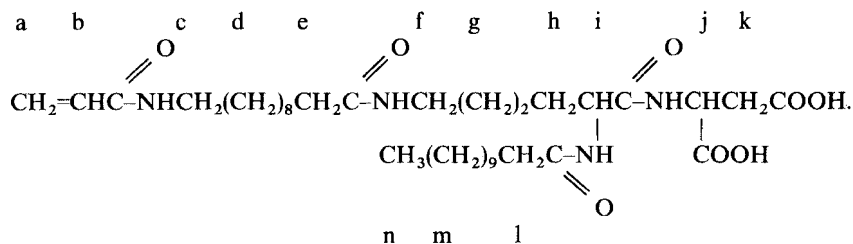
At each step of the synthesis the products were characterized by IR and NMR spectroscopy (250 MHz) (see table 2), and their purity was checked by TLC.

4.4. *Synthesis of the comb-like polymers* (VII)

1·5 g of (VI) were dissolved in 20 ml of methanol and, after elimination of oxygen by bubbling nitrogen into the solution, 120 mg of AIBN were added. The sealed system was maintained at 65°C with agitation for 72 h. Methanol was then eliminated under vacuum. The polymer was purified by dissolution in methanol and precipitation using acetonitrile (twice). Average degrees of polymerization were between 50 and 100 [8].

4.5. *Preparation of mesomorphic gels*

Comb-like 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.

Table 2. Proton chemical shifts of the monomer VLKD in CD_3OD,

$$\text{a} \quad \text{b} \quad\quad \text{c} \quad \text{d} \quad \text{e} \quad\quad\quad \text{f} \quad \text{g} \quad\quad \text{h} \quad \text{i} \quad\quad\quad \text{j} \quad \text{k}$$

$$\overset{O}{\overset{\parallel}{}} \quad\quad \overset{O}{\overset{\parallel}{}} \quad\quad\quad \overset{O}{\overset{\parallel}{}}$$

$$CH_2{=}CHC{-}NHCH_2(CH_2)_8CH_2C{-}NHCH_2(CH_2)_2CH_2CHC{-}NHCHCH_2COOH.$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad CH_3(CH_2)_9CH_2C{-}NH \quad\quad COOH$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \overset{\diagdown}{}$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O$$
$$\quad\quad\quad\quad\quad\quad\quad \text{n} \quad\quad \text{m} \quad\quad \text{l}$$

Identification of protons of VLKD. After polymerization, the proton chemical shifts of carbon a and carbon b of VLKD disappear, and in the polymer PLKD they appear at $\delta = 3\cdot7$ ppm and $\delta = 2\cdot2$ ppm respectively.

δ ppm	Proton number	Carbon symbol
6·1–6·2	2	a
5·7–5·6	1	b
4·6–4·4	1	i
4·4–4·2	1	j
3·3–3·1	4	c, f
2·7–2·6	2	k
2·3–2·1	4	e, l
1·9–1·7	2	h
1·7–1·1	38	d, g, m
1·0–0·8	3	n

5.5. *X-ray diffraction studies*

X-ray diffraction studies were performed under vacuum with a Guinier type focusing 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.

Dry comb-like polymers were also studied with a pin hole camera, operating under vacuum and equipped with a device recording the diffraction patterns from samples held at various temperatures (between 20 and 200°C) with an accuracy of 1°C.

5. Concluding remarks

Comb-like polymers exhibit both thermotropic and lyotropic properties. The thermotropic character is revealed by the existence of smectic B and smectic A structures for dry polymers as a function of temperature. The lyotropic character is evidenced by the existence of different mesomorphic structures as a function of the water concentration. When water is added to the polymer at room temperature, the smectic B structure transforms into a tilted smectic structure (F or I) that maintains the hexagonal lateral order, but is characterized by an angle of tilt that increases with the water concentration until the lamellar structure disappears and is replaced by a cylindrical hexagonal structure. When water is added to the smectic A structure, a swelling of that structure is observed until the ratio of the volumes of the hydrophilic and hydrophobic domains becomes too large and involves the appearance of a cylindrical hexagonal structure. On the contrary the polymerizable lipopeptide VLKD exhibits only crystalline structures.

Our comb-like polymers with polyvinyl main chains and lipopeptidic side chains containing two hydrophobic lipidic chains form a new class of liquid crystalline polymers with both thermotropic and lyotropic properties. Studies of similar comb-like polymers with different polar heads are now in progress. In a forthcoming paper we will compare their liquid crystalline properties with those of model lipopeptides with two hydrophobic chains and with comb-like polymers with lipopeptidic side chains containing only one hydrophobic lipidic chain.

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