

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Liquid-crystalline comb copolymers with lipoamino acid side chains Synthesis and structure study

Bernard Gallot^{ab}, Brigitte Marchin^a

^a Centre de Biophysique Moléculaire, C.N.R.S., Orléans Cedex 2, France ^b Laboratoire des Matériaux Organiques, Vernaison, France

To cite this Article Gallot, Bernard and Marchin, Brigitte(1989) 'Liquid-crystalline comb copolymers with lipoamino acid side chains Synthesis and structure study', *Liquid Crystals*, 5: 6, 1719 — 1727

To link to this Article: DOI: 10.1080/02678298908045682

URL: <http://dx.doi.org/10.1080/02678298908045682>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Liquid-crystalline comb copolymers with lipoamino acid side chains Synthesis and structure study

by BERNARD GALLOT† and BRIGITTE MARCHIN

Centre de Biophysique Moléculaire, C.N.R.S., 45071 Orléans Cedex 2, France

In order to obtain liquid-crystalline polymers without using classical mesogenic groups, comb copolymers consisting of a polyacrylamide main chain and lipoamino acid side chains have been synthesized. These copolymers were obtained by the polymerization of lipoamino acid macromonomers. These macromonomers were obtained from α,ω -aliphatic amino acids by linking a polymerizable group at the amino end and an α -amino acid at the carboxyl end. The macromonomers were then transformed into comb copolymers by free-radical polymerization. These comb copolymers exhibit mesophases both in aqueous solution and in the anhydrous state. The range of stability and the structures of the mesophases were determined by X-ray diffraction. Two types of structures were found, corresponding to the lyotropic lamellar and hexagonal mesophases. The influences of the nature of the amino acid and the water concentration on the domain of stability and the geometrical parameters of the mesomorphic structures were investigated.

1. Introduction

The liquid-crystalline behaviour of polymers generally results from the presence, in the polymer main chain [1] or side chains [2], of mesogenic groups identical or similar to those found in low molecular weight thermotropic liquid crystals [3]. Recently Gallot and Douy showed that liquid-crystalline structures can be obtained with comb copolymers that do not contain such mesogenic groups [4-6]. Our liquid-crystalline polymers were formed by polyacrylamide or polymethacrylamide main chains and lipopeptidic side chains; they exhibited both thermotropic and lyotropic behaviour [5, 6].

In order to examine the relationship between the liquid-crystalline properties of these comb copolymers and the nature of their side chains, we prepared comb copolymers with lipoamino acid side chains. In this paper we describe the synthesis and the liquid-crystalline behaviour of comb copolymers with a polyacrylamide main chain and lipoamino acid side chains containing one of the following amino acids: glycine (Gly), L-alanine (Ala) and L-tyrosine (Tyr).

2. Experimental

2.1. Materials

α -Amino acids, dicyclohexylcarbodiimide (DCCI), N-hydroxysuccinimide (HOSu) and acryloyl chloride of the highest purity available were purchased from Fluka. 11-Amino-undecanoic acid was purchased from Merck. Silica-gel Si60 on aluminium plates for thin layer chromatography was purchased from Merck. Solvents were purified by classical methods.

† Permanent address: Laboratoire des Matériaux Organiques, B.P. 24, 69390 Vernaison, France.

2.2. Synthesis

Synthesis of 11-(acryloylamino)-undecanoic acid was performed by a modification of the method of de Winter and Marien [7] 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 [8] using tetrahydrofuran (THF) as the reaction solvent (yield 85 per cent).

Synthesis of polymerizable lipoamino acids was performed by the method described by Paquet for the synthesis of N-palmitoylamino acids [8, 9]. The yields were 75 per cent for lipoglycine, 88 per cent for lipoalanine and 67 per cent for lipotyrosine.

Polymerization of lipoamino acids was performed in a 5 per cent methanol solution, at 60°C, under vacuum, using α, α' -azoisobutyronitrile (AIBN) as initiator.

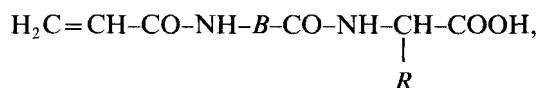
2.3. Measurements

The comb copolymers were dissolved in a small excess of water and when total homogeneity had been achieved the desired concentration was obtained by very slow evaporation at room temperature. The samples were then left at room temperature in sealed cells to ensure that equilibrium was reached. After X-ray experiments the concentration of each sample was checked by evaporation to dryness under vacuum.

X-ray diffraction was performed under vacuum with a Guinier type focussing camera equipped with a bent quartz crystal monochromator giving a linear collimation and a device for recording the diffraction patterns from samples held at various temperatures with an accuracy of $\pm 1^\circ\text{C}$.

3. Synthesis

The comb copolymers were obtained through the synthesis of macromonomers followed by the free-radical polymerization of these macromonomers. The macromonomers are polymerizable lipoamino acids of general formula



with $B = (\text{CH}_2)_{10}$ and R is the side chain of the amino acid: $R = \text{H}$ for Gly, CH_3 for Ala and $\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$ for Tyr.

3.1. Synthesis of macromonomers

Starting from α, ω -aliphatic amino acids, macromonomers were prepared in three steps: fixation of the polymerizable group at the amino end of the α, ω -aliphatic amino acid, activation of the acid group of the polymerizable acid and coupling between the activated polymerizable acid and the α -amine group of the α -amino acid. The products obtained at each step were characterized by infrared spectroscopy and their purity was checked by thin layer chromatography.

(a) Fixation of the polymerizable group

The 11-amino-undecanoic acid was reacted at 0°C in aqueous KOH solution with acryloyl chloride and the polymerizable 11-(acryloylamino)-undecanoic acid obtained

was recrystallized in toluene



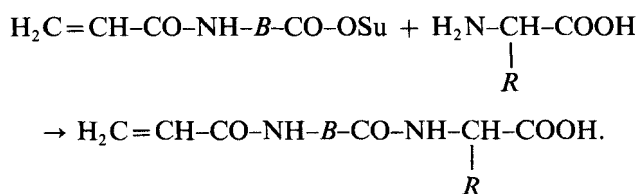
(b) *Activation of the polymerizable acid*

The polymerizable acid was activated in the form of its succinimidyl ester by the action of HOSu in THF solution at 0°C in the presence of a coupling agent (DCCI)



(c) *Coupling of the α -amino acid*

The polymerizable lipoamino acid was obtained by aminolysis of the polymerizable succinimidyl ester by the α -amine function of the α -amino acid in a water/acetone solution, at room temperature



3.2. *Synthesis of comb copolymers*

Comb copolymers were obtained by free-radical polymerization of the polymerizable lipoamino acids in methanol solution at 60°C, using AIBN as initiator. At the end of the polymerization the carboxyl groups of the amino acids were transformed into sodium salts by the addition of sodium hydroxide, and the comb copolymers were isolated by lyophilization.

Gel permeation chromatography, performed in aqueous solution and using polyoxyethylene standards for calibration, gave molecular weight values between 20 000 and 31 000, polymerization degrees between 70 and 100 and polydispersity index between 1.35 and 1.46.

4. **Structural study**

At room temperature these comb copolymers exhibit mesophases in aqueous solution for water concentrations lower than about 45 per cent. The structures of the mesophases and of the dry copolymers obtained by slow evaporation were determined by X-ray diffraction.

4.1. *Description of the structures*

All of the X-ray patterns show the diffuse wide angle band characteristic of liquid paraffinic chains [10] but, depending on the nature of the amino acid and the concentration, their low angle regions exhibit a set of reflections with Bragg spacings in the ratio $1 : \frac{1}{2} : \frac{1}{3} : \frac{1}{4}$ characteristic of a lamellar structure, or in the ratio $1 : 1/3^{1/2} : 1/4^{1/2} : 1/7^{1/2} \dots$ characteristic of a hexagonal structure.

As the repeating unit of the polymers can be divided into a hydrophobic part $B = \text{CH}_2-\text{CH}-\text{CO}-\text{NH}-(\text{CH}_2)_{10}$ and a hydrophilic part $A = \text{CO}-\text{NH}-\text{CHR}-\text{COONa}$, the lamellar and hexagonal structures can be described as follows.

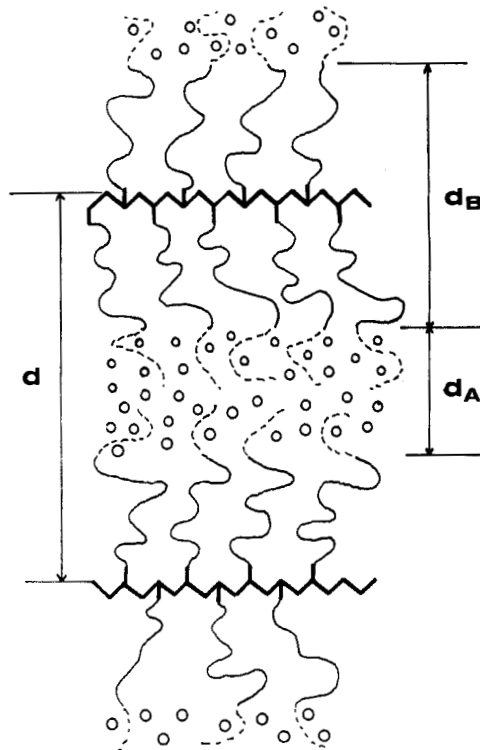


Figure 1. Schematic representation of the lamellar structure. \sim , Polyacrylamide main chain; \wedge , paraffinic chain; --- , amino acid; $\circ\circ\circ\circ$, water.

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_B , contains the polymer main chain and the lipidic side chains, whereas the other, of thickness d_A , contains the amino acid sodium salts and the water (figure 1).

The hexagonal structure consists of long, parallel cylinders of radius R , assembled in a hexagonal array of parameter D . They are filled with the polymer main chain and the lipidic side chain, and the space between the cylinders is occupied by the amino acid sodium salts and water (figure 2).

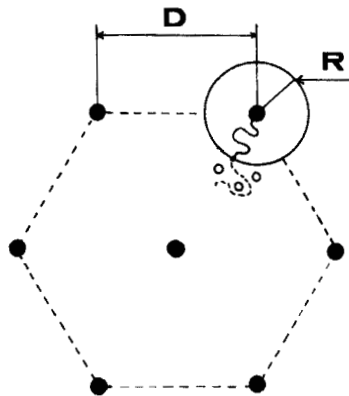


Figure 2. Schematic representation of the hexagonal structure. Key as for figure 1.

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 , and S_L and S_H (the average surface occupied by a chain at the interface for the lamellar and hexagonal structures, respectively)—were obtained using the following formulae based on simple geometrical considerations:

$$d_B = d \left(1 + \frac{cX_A v_A + (1-c)v_S}{cX_B v_B} \right)^{-1}, \quad (1)$$

$$d_A = d - d_B, \quad (2)$$

$$S_L = 2M_B v_B / N d_B, \quad (3)$$

$$R^2 = \frac{D^2 3^{1/2}}{2\pi} \left(1 + \frac{cX_A v_A + (1-c)v_S}{cX_B v_B} \right)^{-1} \quad (4)$$

and

$$S_H = 2M_B v_B / NR, \quad (5)$$

where c is the weight content of copolymer in solution, X_A and X_B are weight fractions of hydrophilic and hydrophobic chains, respectively, v_A is the specific volumes of the hydrophilic chains ($v_A = 0.54 \text{ cm}^3 \text{ g}^{-1}$ for Gly, $0.63 \text{ cm}^3 \text{ g}^{-1}$ for Ala and $0.61 \text{ cm}^3 \text{ g}^{-1}$

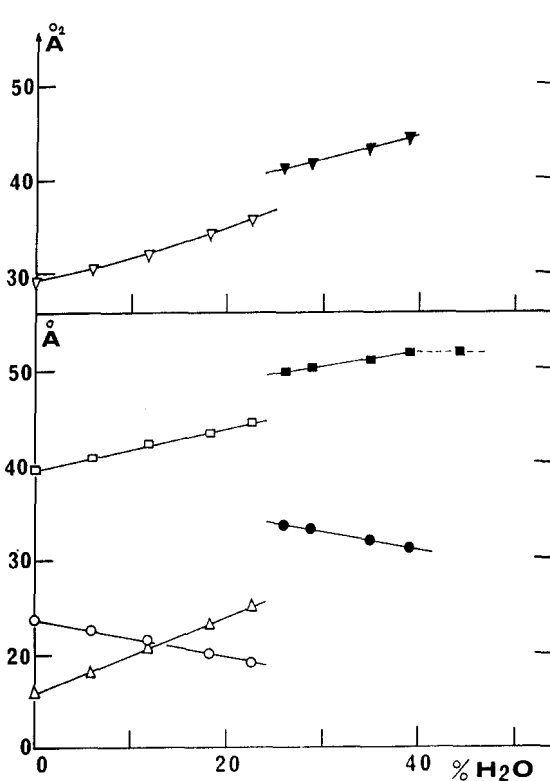


Figure 3. Variation with water concentration of the structural parameters of the lamellar and hexagonal structure exhibited by comb polymers with lipotyrosine side chains. □, d ; △, d_A ; ○, d_B ; ▽, S_L ; ■, D ; ●, $2R$; ▼, S_H .

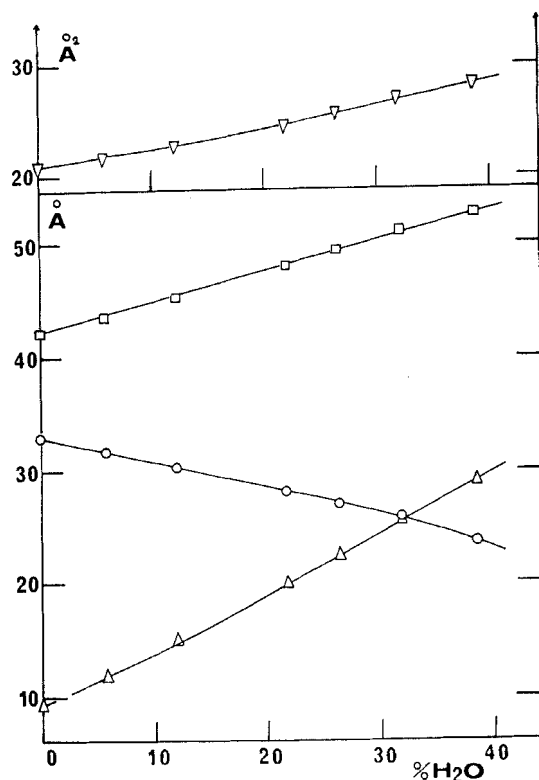


Figure 4. Variation with water concentration of the structural parameters of the lamellar structure exhibited by comb polymers with lipoglycine side chains. □, d ; △, d_A ; ○, d_B ; ▽, S_L .

for Tyr), $v_B = 0.933 \text{ cm}^3 \text{ g}^{-1}$, v_S is the specific volume of the solvent, $M_B = 210$ and N is the Avogadro number.

4.2. Influence of the water concentration

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

(a) Influence on the nature of the mesophases

As in the case of block copolymers [11], the type of structure is determined by the ratio of the volumes of the hydrophilic and hydrophobic domains. The addition of water to comb copolymers increases the relative volume of the hydrophilic domains and is therefore able to transform a lamellar structure into a cylindrical hexagonal one, as observed in the case of polymers with lipotyrosine side chains (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

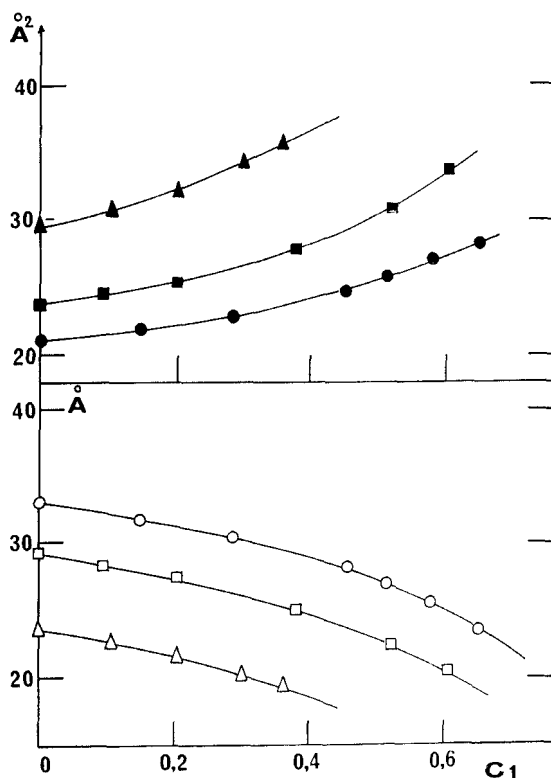


Figure 5. Influence of the nature of the amino acid on the thickness d_b of the hydrophobic lamellae and on the surface S for the lamellar structure of comb polymers. d_b (Å): ○, Gly; □, Ala; △, Tyr. S (Å²): ●, Gly; ■, Ala; ▲, Tyr.

mesophase the structural parameters vary in a continuous way with the concentration (figures 3 and 4).

For the lamellar structure (figures 3 and 4), when the water concentration increases, the total thickness d of a sheet, the thickness d_A of the hydrophilic layer and the average surface S_L per chain at the interface all increase, whereas the thickness 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

4.3. Influence of the nature of the amino acid

In order to analyse the influence of the nature of the amino acid we compared the behaviour of three comb copolymers with different amino acid side chains: a hydrogen atom for Gly, a methyl group for Ala and a 4-hydroxyphenyl group for Tyr.

First, the Tyr-containing polymer with the bulkiest amino acid side chain forms a lamellar and a hexagonal mesophase, whereas the Ala- and Gly-containing polymers form only lamellar mesophases. The structural parameters of the lamellar mesophases also vary with the nature of the amino acid. This is illustrated in figures 5 and 6, where the variation of the structural parameters of the lamellar structure

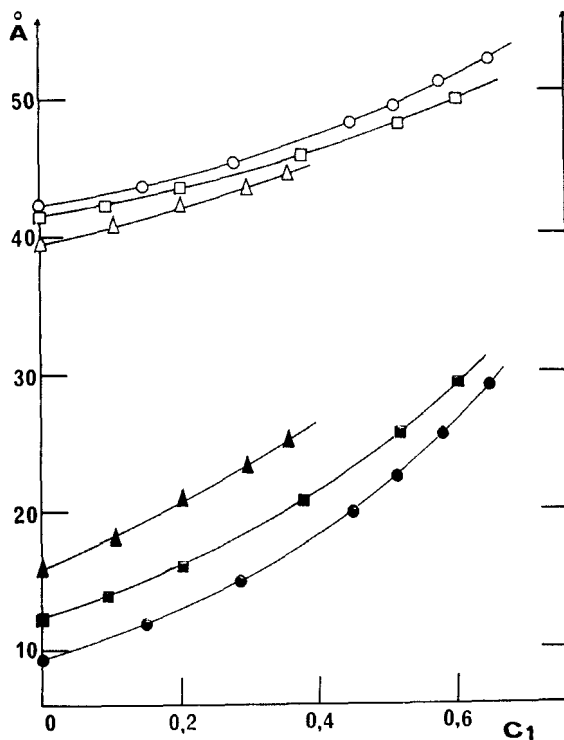


Figure 6. Influence of the nature of amino acid on the total thickness d of a sheet and on the thickness d_A of the hydrophilic lamellae for the lamellar structure of comb copolymers. d (Å): ○, Gly, □, Ala; △, Tyr. d_A (Å): ●, Gly; ■, Ala; ▲, Tyr.

of the three copolymers are plotted as a function of the water content:

$$c_1 = \frac{1 - c}{1 - c + cX_A} \quad (6)$$

It can be seen that when the volume of the amino acid side chain increases from Gly to Ala to Tyr, the surface area available for a chain at the interface increases in a parallel way, while the thickness d_B of the hydrophobic lamellae decreases to allow the density of the hydrophobic chains to remain constant. However, Figure 6 shows that the thickness d_A of the hydrophilic lamellae also increases with the volume of the amino acid side chain. The increase of both S and d_A suggests the existence of a tilt angle between the average direction of the side chain and the interface. Such a tilt angle is in accord with molecular models.

Figure 6 also shows that there is a small variation of the total thickness d of a sheet, resulting from the difference of variation between d_A and d_B .

4.4. Influence of the temperature

The influence of the temperature on the lamellar mesomorphic structure of dry comb copolymers obtained by slow evaporation of the water of the lamellar mesophases has been studied by X-ray diffraction between 20 and 200°C.

For comb copolymers with lipoglycine or lipoalanine side chains the lamellar structure remains stable up to at least 200°C. For comb polymers with lipotyrosine

side chains a transition occurs at about 150°C. This transition is characterized by the appearance in the low angle region of X-ray patterns of a diffuse band replacing the set of sharp reflections observed at lower temperatures. Such X-ray diagrams suggest the existence of a nematic mesophase that remains stable until at least 200°C.

References

- [1] LENZ, R. W., 1985, *Pure appl. Chem.*, **57**, 1537.
- [2] FINKELMANN, H., and REHAGE, G., 1984, *Adv. polym. Sci.*, **60/61**, 99.
- [3] GRAY, G. W., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press).
- [4] GALLOT, B., and DOUY, A., 1985, French Patent 8 511 121.
- [5] GALLOT, B., and DOUY, A., 1987, *Molec. Crystals liq. Crystals*, **153**, 367.
- [6] GALLOT, B., and DOUY, A., 1989, *Makromolek. Chem., Macromolec. Symp.*, **24**, 321.
- [7] DE WINTER, W., and MARIEN, A., 1984, *Makromolek. Chem., rap. Commun.*, **5**, 593.
- [8] PAQUET, A., 1976, *Can. J. Chem.*, **54**, 733.
- [9] PAQUET, A., 1980, *Can. J. Biochem.*, **58**, 573.
- [10] LUZZATI, V., MUSTACCHI, H., SKOULIOS, A., and HUSSON, F., 1960, *Acta crystallogr.*, **13**, 660.
- [11] GALLOT, B., 1978, *Liquid Crystalline Order in Polymers*, edited by A. Blumstein (Academic Press), Chap. 6.