Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Gallot, Bernard and Marchin, Brigitte(1989) 'Synthesis and liquid-crystalline behaviour of liposaccharide based comb polymers', Liquid Crystals, 5: 6, 1729 — 1735
To link to this Article: DOI: 10.1080/02678298908045683
URL: http://dx.doi.org/10.1080/02678298908045683

LIQUID CRYSTALS, 1989, VOL. 5, NO. 6, 1729–1735

Synthesis and liquid-crystalline behaviour of liposaccharide based comb polymers

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In order to investigate the relationship between the liquid-crystalline state and the biological properties of polymers, we synthesized and studied liquid-crystalline comb polymers with a polyacrylamide main chain and three types of liposaccharidic side chains. These comb polymers were synthesized in four steps: first the polymerizable group was linked to the amino end of an α,ω-aliphatic amino acid; in the second step the ω-carboxylic acid function was activated in the form of an N-hydroxysuccinimidylester; in the third step the active ester was aminolysed by the amine function of the saccharide (N-methyl-D-glucamine, 2-amino-2-deoxy-β-D-glucose or 1-amino-1-deoxy-β-D-galactose) and a polymerizable liposaccharide was obtained; finally the liposaccharides were transformed into comb polymers by free-radical polymerization. Comb polymers exhibit mesophases in concentrated aqueous, ethanol or dimethylsulphoxide solution, and their mesomorphic character remains after the slow evaporation of the solvent. X-ray diffraction studies have shown that the mesophases have smectic or nematic ordering, depending upon the nature of the saccharidic residues of the liposaccharidic side chains.

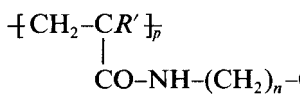
1. Introduction

In the framework of our research programme on lyotropic systems of biological interest, we have previously synthesized and studied peptidosaccharides [1], liposaccharides [2–4] and phospholiposaccharides [5, 6] in which the saccharidic chains are glycannic chains extracted from glycoproteins. These lyotropic species exhibit lamellar, hexagonal and cubic structures [1–6], depending upon the nature of both the hydrophobic chains and the hydrophilic saccharidic chains.

In order to examine the relationship between the chemical structures of mesomorphic polymers and their liquid-crystalline and biological properties we have recently synthesized comb copolymers with polyvinylic main chains and lipopeptidic [7, 8], lipoamino acid [9] and liposaccharidic side chains.

Comb polymers with liposaccharidic side chains have the general formula

(I)



In the present paper we describe the synthesis and the structure of comb polymers with acrylamide main chain ($R' = H$) and liposaccharidic side chains where $n = 10$ and where $HNR–X$ is one of the saccharides 1-amino-1-deoxy-β-D-galactose, 2-amino-2-deoxy-β-D-glucose or N-methyl-D-glucamine.

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0267-8292/89 $3.00

2. Experimental

2.1. *Materials*

N-methyl-D-glucamine, dicyclohexylcarbodiimide (DCCI), N-hydroxysuccinimide (HOSu) and acryloylchloride were purchased from Fluka. 11-Amino undecanoic acid was purchased from Merck. 1-Amino-1-deoxy-β-D-galactose and 2-amino-2-deoxy-β-D-glucose were purchased from Sigma.

Silica-gel Si60 on aluminium plates for thin layer chromatography was purchased from Merck. Solvents were purified by classical methods.

2.2. *Synthesis of polymerizable liposaccharides*

(*a*) *11-(Acryloylamino)-undecanoic acid*

An equivalent amount of acryloyl chloride was added dropwise to 11-amino-undecanoic acid in KOH aqueous solution at 0°C. After neutralization with HCl, filtration and recrystallization from toluene, the polymerizable acid was obtained with a yield of 85 per cent.

(*b*) *11-(Acryloylamino)-undecanoylsuccinimidylester*

11-(Acryloylamino)-undecanoic acid was reacted with an equivalent of HOSu and an equivalent of DCCI in tetrahydrofuran (THF) solution at 0°C for 6 h. After elimination of the precipitate of the dicyclohexylurea formed, the polymerizable succinimidylester was recovered by precipitation in water at pH 7 (yield 85 per cent)

(*c*) *Polymerizable liposaccharides*

To obtain the 11-(acryloylamino)-undecanoyl N-methylglucamine, 0·01 mol of the succinimidylester in solution in 100 ml of acetone was reacted with 0·02 mol of N-methylglucamine in solution in 50 ml water in the presence of 2 equivalents of triethylamine for 6 h. Then the acetone was evaporated off, 50 ml of water was added and the solution was acidified with HCl. The precipitate was filtered, washed with cold water and cold acetone, and dried. Finally the liposaccharide was dissolved in methanol, precipitated with ether and dried (yield 60 per cent).

To obtain the 11-(acryloylamino)-undecanoyl amino galactose or the 11-(acryloylamino)-undecanoylamino glucose, the corresponding amino saccharide was reacted with 11-(acryloylamino)-undecanoyl-succinimidylester under the same conditions as the N-methylglucamine (but the purification was carried out using as solvent an ethanol : water 3 : 1 (v/v) mixture followed by precipitation by NaOH in aqueous solution). Yields were 65 per cent for amino-galactose and 72 per cent for amino-glucose.

2.3. *Synthesis of comb polymers*

The polymerization of the liposaccharides was performed under vacuum at 60°C, using α,α′-azoisobutyronitile (AIBN) as initiator, in methanol solution for lipo-N-methyl-glucamine and lipoamino-galactose and in dimethylsulphoxide (DMSO) solution for lipoamino-glucose.

2.4. *Preparation of mesomorphic gels*

The comb polymers were dissolved in a small excess of solvent (water or ethanol) and, when total homogeneity was achieved, the desired concentration was obtained

by slow evaporation at room temperature. The samples were then left at room temperature in sealed cells until equilibrium was reached. After the X-ray studies the concentration of each sample was checked by evaporation to dryness under vacuum.

2.5. *X-ray measurements*

X-ray diffraction was performed under vacuum, with a Guinier-type camera equipped with a bent quartz monochromator giving well-focussed and monochromatic X-rays (Cu-K_{α_1}) and a device for recording the diffraction patterns from samples held at various temperatures (between +20 and +200°C) with an accuracy of ±1°C.

3. Synthesis

Comb polymers were synthesized in four steps.

The α,ω-aliphatic amino acid (**II**) was first transformed in a polymerizable ω-aliphatic acid (**III**) by fixing a polymerizable group at its amino end:

$$\underset{\textbf{II}}{H_2N\text{-}(CH_2)_{10}\text{-}COOH} + H_2C{=}CH\text{-}CO\text{-}Cl \rightarrow \underset{\textbf{III}}{H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}COOH}.$$

The polymerizable acid (**III**) was then activated in the form of its succinimidylester (**IV**) by reaction with HOSu:

$$\textbf{III} + HOSu \rightarrow \underset{\textbf{IV}}{H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}CO\text{-}OSu}.$$

The active ester (**IV**) was next aminolysed by the amine function of the saccharide ($HNR\text{-}X$) and a polymerizable liposaccharide (**V**) was obtained:

$$\textbf{IV} + HNR\text{-}X \rightarrow \underset{\textbf{V}}{H_2C{=}CH\text{-}CO\text{-}NH\text{-}(CH_2)_{10}\text{-}CO\text{-}NR\text{-}X}.$$

The polymerizable liposaccharide (**V**) was finally transformed into a comb polymer (**I**) by free-radical polymerization.

3.1. *Synthesis of the polymerizable acid (III)*

The polymerizable acid (**III**) was obtained by a modification of the method used by de Winter and Marien to obtain polymerizable surfactants [10]. Acryloylchloride was reacted with 11-amino-undecanoic acid at 0°C in aqueous KOH solution.

3.2. *Synthesis of the active ester (IV)*

The succinimidyl active ester (**IV**) was obtained by action of HOSu on the polymerizable acid (**III**) in THF solution at 0°C in the presence of a coupling agent (DCCI) [11].

3.3. *Synthesis of the polymerizable liposaccharides (V)*

The polymerizable liposaccharides (**V**) were obtained by aminolysis of the succinimidylester (**IV**) by the amine function of the aminosaccharides ($NHR\text{-}X$) at room temperature in a water–acetone solution.

3.4. *Synthesis of comb polymers (I)*

Comb polymers were obtained by free-radical polymerization of the liposaccharides (V). The polymerization was always performed under vacuum, at 60°C, using AIBN as initiator, but the polymerization solvent varied with the solubility of the liposaccharides; for lipo-N-methylglucamine and lipoamino-galactose the solvent used was methanol, whereas for lipoamino-glucose methanol was replaced by DMSO.

3.5. *Characterization*

The products obtained at each step of the synthesis were characterized by infrared spectroscopy and their purity was checked by thin layer chromatography.

Comb polymers were characterized by gel permeation chromatography in aqueous solution, using polyoxyethylene standards for calibration. Molecular weights between 21 000 and 30 000 and polydispersity indices lower than 1·5 were found.

4. Liquid-crystalline structures

Comb polymers with polyacrylamide main chains and liposaccharidic side chains exhibit mesophases in water, ethanol or DMSO concentrated solution and in the solvent-free state after slow evaporation.

4.1. *Comb polymers with lipo-N-methylglucamine side chains*

4.1.1. *Structure*

X-ray diagrams obtained at room temperature, for water concentrations lower than about 25 per cent, are characterized by the presence in the wide angle region of a diffuse band, characteristic of liquid paraffinic chains [12] and in the low angle region of a set of three sharp reflections with Bragg spacings in the ratio 1:2:3 characteristic of a lamellar structure.

The repeating unit of the comb polymer can be divided into a hydrophobic part $B = CH_2\text{–}CH\text{–}CO\text{–}NH\text{–}(CH_2)_{10}\text{–}CO\text{–}N(CH_3)\text{–}CH_2$ and a hydrophilic part $A = (CHOH)_4\text{–}CH_2OH$. 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 containing the penta-alcohol hydrophilic chains and the water, the other of thickness d_B containing the polymer main chain and the hydrophobic lipidic side chains (figure 1).

The total thickness of a sheet is obtained directly from X-ray diagrams. The values of d_A and d_B and of S, the average surface area occupied by a chain at the interface, are calculated using the following formulae which are based on purely geometrical considerations:

$$d_A = d\left(1 + \frac{cX_Bv_B}{cX_Av_A + (1 - c)v_S}\right)^{-1},$$

$$d_B = d - d_A$$

and

$$S = \frac{2M_Bv_B}{Nd}\left(1 + \frac{X_Av_A}{X_Bv_B} + \frac{(1 - c)v_S}{cX_Bv_B}\right),$$

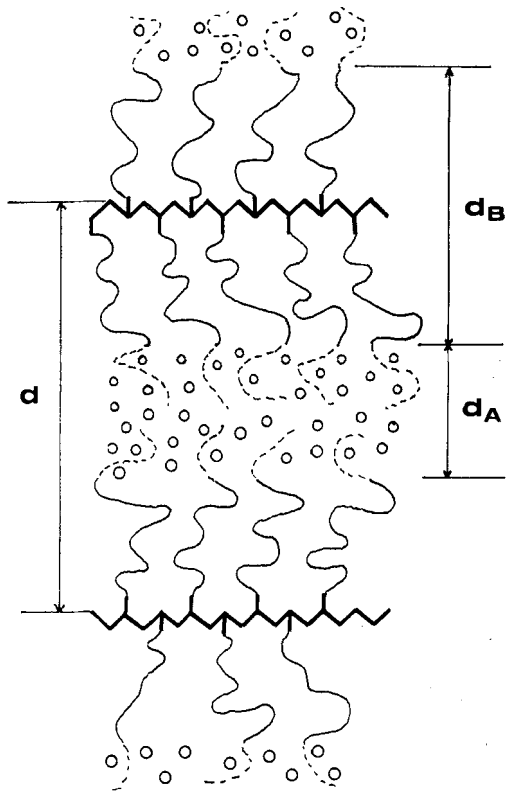

Figure 1. Schematic representation of the lamellar structure. ∧∧, Polyacrylamide main chain; ⌒, paraffinic chains; ⌒, saccharidic chains; OOOO, water.

where c is the weight content of copolymer in the solution, X_A and X_B are the weight fractions of the A and B parts of the repeating unit, v_A ($= 0{\cdot}654\,\text{cm}^3\,\text{g}^{-1}$) is the specific volume of the hydrophilic chains A, v_B ($= 1{\cdot}03\,\text{cm}^3\,\text{g}^{-1}$) is the specific volume of the hydrophobic chains B, v_S is the specific volume of the solvent, $M_B = 253$ and N is the Avogadro number.

4.1.2. *Influence of the water concentration*

We have plotted in figure 2 the variation of the geometrical parameters of the lamellar structure as a function of the water concentration of the mesophase. It can be seen that, as the water concentration increases, the total thickness d of a sheet, the thickness d_A of the hydrophilic layers and the average surface area per chain at the interface all increase, whereas the thickness d_B of the hydrophobic layer decreases in order to allow the hydrophobic chains to maintain a constant density.

4.2. *Comb polymers with lipo-amino-glucose side chains*

X-ray diagrams, obtained at room temperature, for DMSO concentrations smaller than about 40 per cent, are similar to those obtained with comb polymers with lipo-N-methylglucamine side chains, but the low angle reflections are rather diffuse, suggesting the existence of appreciable disorder in the lamellar structure.

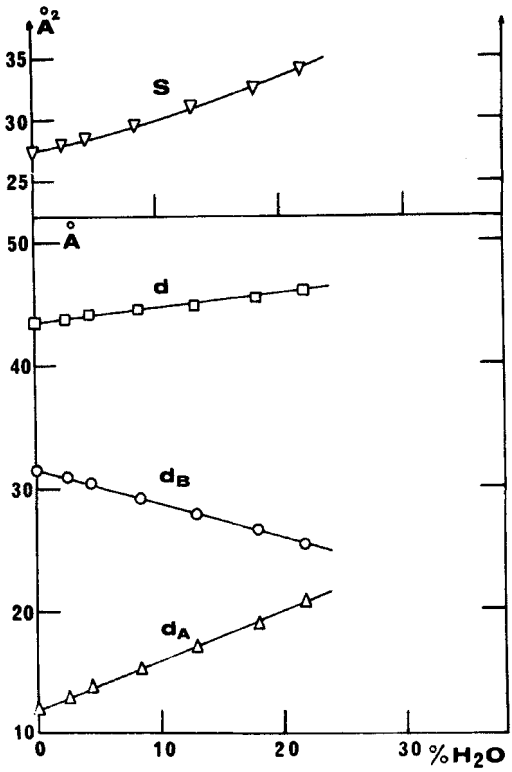

Figure 2. Variation with water concentration of the structural parameters of the lamellar structure exhibited by the comb polymer with lipo-N-methylglucamine side chains. □, intersheet spacing d; △, thickness of the hydrophilic layer d_A; ○, thickness of the hydrophobic layer d_B; ▽, average surface area per chain S.

The average thickness, d, of the sheets is about 45 Å and its variation with the DMSO content of the mesophases cannot be determined accurately.

4.3. *Comb polymers with lipoamino-galactose side chains*

X-ray diagrams, obtained at room temperature, for water or ethanol concentrations lower than about 30 per cent, exhibit a diffuse band in their wide angle region and another diffuse band in the low angle region. They are characteristic of a nematic structure.

5. Concluding remarks

In this paper we have described the synthesis of lyotropic comb polymers with a polyacrylamide main chain and three types of liposaccharidic side chains. We have shown that the structure of the mesophases varies with the nature of the saccharidic residue of the side chains: for N-methylglucamine a perfectly organized lamellar structure is obtained, for 2-aminoglucose a disordered lamellar structure is obtained and for 1-aminogalactose a nematic structure is obtained. The study by X-ray diffraction, polarization microscopy and differential scanning calorimetry of the influence of the temperature on the mesophases of these three comb polymers is now in progress. Furthermore, the study by the same techniques of the mesomorphic

behaviour of comb polymers with the same three liposaccharidic side chains but with polymethacrylamide main chains has been undertaken in order to establish the influence of the nature of the main chain. The results of these studies will be reported in the near future.

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