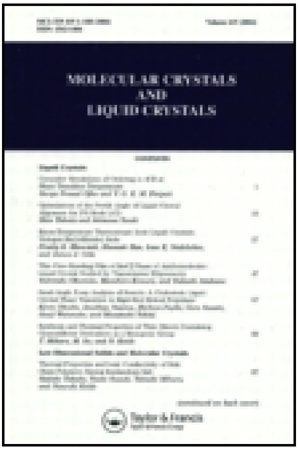

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Comb Copolymers with Thermotropic and Lyotropic properties Synthesis and Structural Study

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COMB COPOLYMERS WITH THERMOTROPIC AND LYOTROPIC PROPERTIES SYNTHESIS AND STRUCTURAL STUDY

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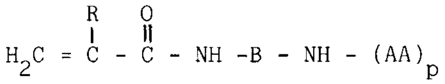
Abstract Comb copolymers with polyacrylamide or polymethacrylamide main chains and lipopeptidic side chains were synthesized in two steps : synthesis of a polymerizable lipopeptide followed by radical polymerization of the lipopeptidic macromonomer. X ray diffraction and DSC studies showed that comb copolymers exhibit both a thermotropic and a lyotropic behaviour. The influence of the nature and the degree of polymerization of the peptidic chains on the type (smectic, nematic or cholesteric) and the domain of stability of the liquid-crystalline structures was established. In the case of smectic structures, the influence of the solvent concentration and the degree of polymerization of the peptidic chains on the distances between the smectic planes was also established.

INTRODUCTION

Copolymers with different polymeric main chains and side chains formed by mesogenic groups linked to the main chain through a spacer generally show thermotropic properties[1]. On the contrary, amphipatic lipopeptides exhibit a lyotropic behaviour[2]. In order to obtain liquid-crystalline polymers that exhibit both thermotropic and lyotropic properties comb copolymers with lipopeptidic side chains were synthesized[3,4]. This paper describes the synthesis and the liquid-crystalline structures of comb copolymers consisting of polyacrylamide or polymethacrylamide main chains and oligopeptide or polypeptide side chains linked to the main chains through an aliphatic spacer containing from 6 to 12 carbon atoms.

SYNTHESIS

In order to obtain liquid crystalline comb copolymers, at first was synthesized a macromonomer that is a polyerizable lipopeptide of general formula :



$$H_2C = \overset{\overset{R}{|}}{C} - \overset{\overset{O}{\|}}{C} - NH - B - NH - (AA)_p$$

with R = H or CH_3, B = $(CH_2)_n$ and AA = amino acid residue,

then the macromonomer was polymerized by radical polymerization.

A) Synthesis of polymerizable lipopeptides

The synthesis of polymerizable lipopeptides is performed in two steps. In the first step a polymerizable group is linked at one end of our α,ω-bifunctional lipid ; in the second step, the functional group remainded free is used to link, at the other end of the lipid, a peptidic chain and obtain a polymerizable lipopeptide.

1) Synthesis of polymerizable lipids

Starting from an α,ω-diamine $H_2N-B-NH_2$ the synthesis of the polymerizable lipid is performed in three steps : protection of an amine function of the aliphatic diamine, linkage of the polymerizable group and elimination of the protecting group.

a) Protection of an amine function. In the first step di-tert-butyldicarbonate is reacted for 12 hours with the diamine $H_2N-B-NH_2$ in solution in a water/methanol mixture (50/50 in volume) in the presence of NaOH to keep constant the pH ; after precipitation by water, the protected lipid is purified by column chromatography

$H_2N - B - NH_2 + \text{di Boc} \longrightarrow \text{Boc} - NH - B - NH_2.$

b) Fixation of the polymerizable group. In the second step a reaction of amidation is performed between the free amine function of the protected lipid and a small excess of acryloyl chloride or methacryloylchloride in THF solution and in the presence of triethylamine

$\text{Boc-NH-B-NH}_2 + H_2C\text{=CR-CO-Cl} \rightarrow \text{Boc-NH-B-NH-CO-CR=CH}_2.$

c) Elimination of the protecting group. In the third step, the protecting group Boc is eliminated by action at first of HBr and then of NaOH

$\text{Boc-NH-B-NH-CO-CR=CH}_2 \longrightarrow H_2\text{N-B-NH-CO-CR=CH}_2$

2) Synthesis of polymerizable lipopeptides

The synthesis of polymerizable lipopeptides is performed by two methods and the choice of the method depends on the degree of polymerization wanted for the peptidic chains.

a) N-carboxyanhydride method. When a degree of polymerization p higher than one of the amino acid AA is wanted the polymerization of the N-carboxyanhydride of the amino acid is initiated by the primary amine function of the polymerizable amine and the polymerization is performed in THF or chloroform solution depending upon the nature of the amino acid side chain[3], then the lipopeptide is fractionated and the degree of polymerization of each fraction is determined by titration of the terminal function or by NMR.

b) Peptide coupling method. When a degree of polymerization p = 1 for the amino acid AA is wanted a coupling reaction between the amine function of the polymerizable amine and the α-carboxylic acid function of the amino acid protected on all its other reactive functions[3], is performed in THF solution in the presence of N-hydroxysuccinimide and dicyclohexylcarbodiimide ; then the protecting groups are eliminated.

B) Synthesis of comb copolymers

Polymerizable lipopeptides are transformed into comb copolymers by radical polymerization of their acrylamide or methacrylamide groups. The polymerization solvent and the polymerization initiator depends upon the solubility of the polymerizable lipopeptides. In the case of lipopeptides with hydrophilic peptidic chains such as polysarcosine, the radical polymerization is performed in water solution at room temperature with potassium persulfate as initiator.

In the case of lipopeptides with hydrophobic peptidic chains such as poly(γ-benzyl-L-glutamate), poly(N^{ε}-trifluoroacetyl-L-lysine), poly(N^{ε}-benzyloxycarbonyl-L-lysine)... the polymerization or the copolymerization with N-alkylacrylamide or N-alkylmethacrylamide with a long paraffine chain is performed in THF solution, at 60°C, with AIBN as initiator.

STRUCTURE

The study of the structure of comb copolymers in the dry state and in concentrated solution in different solvents and the study of their phase diagram temperature/concentration have been performed by X-ray diffraction and differential scanning calorimetry (DSC). 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 for recording the diffraction patterns from samples held at various temperatures with an accuracy of ± 1°C. It has been demonstrated that our comb copolymers exhibit the rather exceptional property of being liquid crystalline polymers both thermotropic and lyotropic.

A) Hydrophilic copolymers

Comb copolymers obtained by radical polymerization of lipopeptides with a peptidic chain of polysarcosine illustrate the behaviour of hydrophilic polymers. X-ray patterns exhibited by hydrophilic comb copolymers both in the anhydrous state and in concentrated water solution show the existence of two liquid-crystalline structures : a smectic A structure and a nematic structure. The smectic A structure is characterized by the presence in the low angle region of X-ray diagrams of a set of 2 or 3 sharp reflections with Bragg spacings in the ratio 1,2,3, and by the presence in the wide angle region of a large band. The nematic structure is characterized by the presence on X-ray diagrams of a diffuse band.

The Figure 1 gives an example of phase diagram temperature/concentration. It corresponds to a comb copolymer with a polyacrylamide main chain and liposarcosine side chains formed by polysarcosine chains with an average degree of

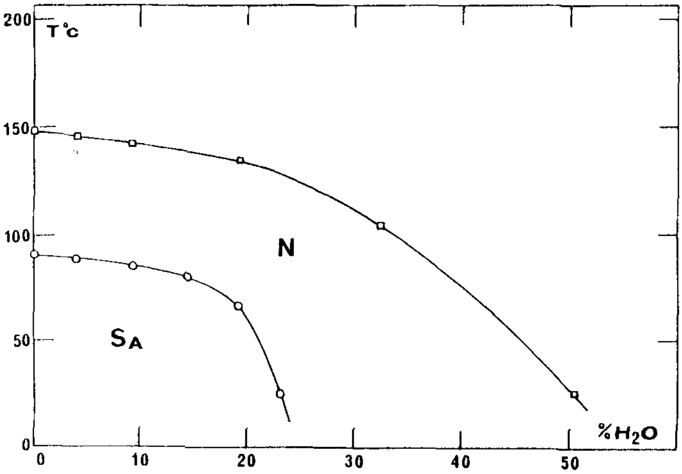


Fig. 1

polymerization p = 6,5 linked to the main chain by an aliphatic spacer with 12 carbon atoms. The phase diagram presents two mesophases ; a smectic A and a nematic mesophases and illustrates the fact that our comb copolymers are both thermotropic and lyotropic polymeric liquid crystals. The smectic A phase is observed for water concentrations between 0 and 23 % and for temperatures lower than 90°C. The nematic phase is observed for water concentrations between 23 and 52 % at room temperature, and in the dry state for temperatures between 90 and 150°C.

The influence of the water concentration and the degree of polymerization of the peptidic chains on the structure of the mesophases was also studied. When the water concentration increases the distance d between the smectic planes increases as illustrated by figure 2 that corresponds to

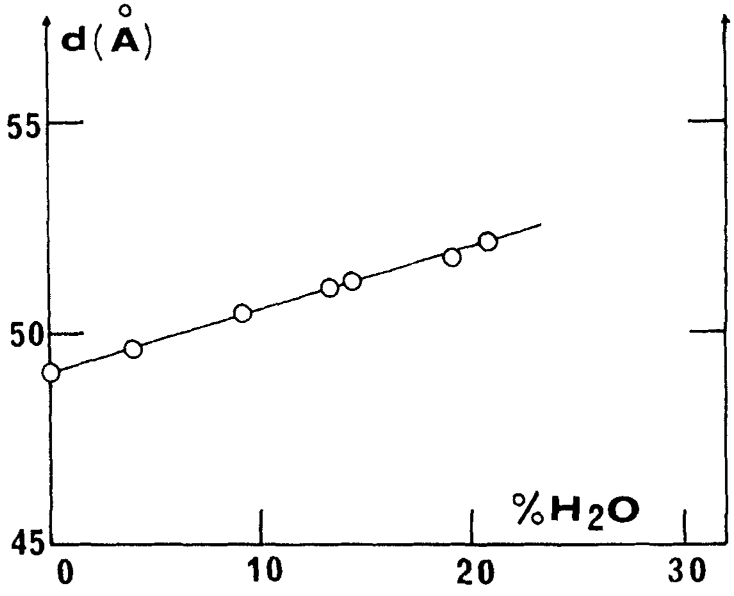


Fig. 2

the same comb copolymer as in figure 1. When the degree of polymerization of the peptidic chains increases the distance d between the smectic planes also increases.

B) Hydrophobic copolymers

Hydrophobic copolymers obtained by copolymerization of N-alkylacrylamide with a long paraffinic chain and acrylamide macromonomers with hydrophobic peptidic chains exhibit nematic and cholesteric mesophases as a function of the nature and the concentration of the solvent.

For instance, comb copolymers with peptidic chains of poly-trifluoroacetyl-lysine exhibit nematic structures in ethyl acetate and dioxane solution and nematic and cholesteric structures in methanol solution ; comb copolymers with polybenzylglutamate peptidic chains exhibit nematic structures in dioxane solution.

REFERENCES

1. H. Finkerlmann and G. Rehage, Adv. Polym. Sci. 60/61, 99 (1984).
2. A. Douy and B. Gallot, Makromol. Chem. 187, 465 (1986).
3. B. Gallot and A. Douy, French Patent n° 85.111.21.
4. B. Gallot and A. Douy, European Patent n° 86.401.603.5.