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D. Markovitsi [a], A. Mathis [a], J. Simon [a], J. C. Wittman [a] & J. Le Moigne [a]
[a] Centre de Recherches sur les Macromolécules (CNRS) 6, rue Boussingault, 67083, Strasbourg, France
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ANNELIDES V : A NEW TYPE OF LYOTROPIC MESOMORPHIC PHASE.

D. MARKOVITSI, A. MATHIS, J. SIMON*, J. C. WITTMAN and
J. LE MOIGNE.
Centre de Recherches sur les Macromolécules (CNRS)
6, rue Boussingault 67083 Strasbourg, France.

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ABSTRACT : The Annelides represent a new class of surfactants able to selectively complex a predetermined metallic ion. They are shown to form a novel type of lyotropic phase. This phase is thoroughly characterized by polarizing microscopy and X-rays determinations. It is found to be lamellar with a transition at 32°C to an isotropic phase. The main geometrical parameters are determined, in particular, the surface available for each polar head is calculated.

Introduction

The Annelides represent a new class of surfactants characterized by a polar head able to selectively include a metallic ion and a hydrophobic part which ensures an amphiphilic character and allows the formation of ordered aggregates [1-4]. Previously, only micellar [1-7] or thermotropic liquid crystal phases [8-11] have been described with surfactants comprising a metallic cation. However, Gaspard et al. have reported a lyomesophase based on the phthalocyanine subunit, but it does not possess the Annelide type structure [12]. Ligand I (figure 1) has been synthesized and used to form a novel type of lyomesophase allowing the or organization of transition metal complexes, i.e. the formation of supermolecular transition metal assemblies.

* to whom correspondence must be addressed.

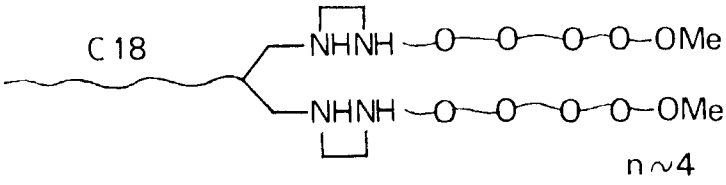

Figure 1 : Ligand synthesized.

Experimental Results

The synthesis of the ligand is detailed in a forthcoming paper [13]. It necessitates five steps starting from the diethylester of malonic acid. The number average molecular weight of the polyoxyethylene glycol chains is determined by ^{1}H NMR (reference -OMe group). It was found to be in agreement with the expected value (Polysciences). The polydispersity has been determined by gel permeation and mass spectrometry [13]. The cobaltic complex is formed from the free ligand by a well known procedure [14,15]. It is purified by chromatography over Sephadex CM-25 (eluent : HCl). The lyotropic phase is prepared by mechanically stirring the cobalt complex and the proper amount of water (0.83-0.17, w/w), the mixture is made homogeneous by heating at 50°C in a tightly closed vessel for 15 hours. Typical features of the lamellar organization is apparent by polarizing microscopy [16].

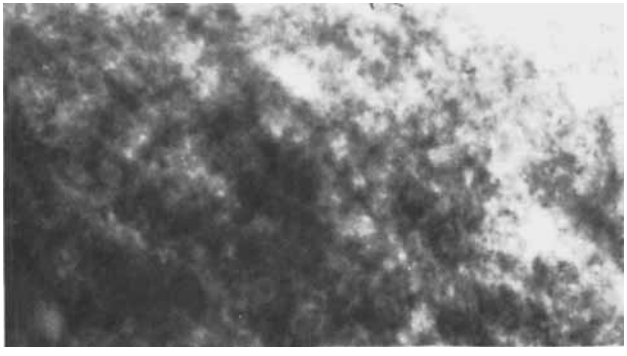

Figure 2 : Texture of the cobaltic lyotropic phase of ligand I.

The transition temperature to an isotropic solution is 32°C. This transition has been shown to be reversible by Differential Scanning Calorimetry.

X-rays determinations at low angle have been run on the same sample at room temperature. Four narrow lines of approximately equal intensities are seen with a spacing ratio of 1 : 1/2, characteristic of a lamellar system [17]. The periodicity parameter d is found to be 55 Å. The density has been determined (1.1036 g/ml) allowing the calculation of the main structural parameters [17]. The density of the hydrophobic part alone has been estimated from the literature [18]. From that it was possible to calculate the thickness of the hydrophobic part and the surface avalaible for each polar head [17].

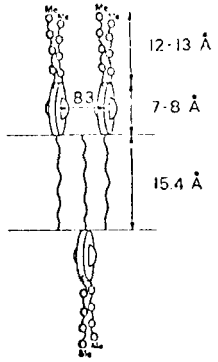

Figure 3 : Schematic representation of the Annelide lyotropic phase as determined by X-rays measurements.

The thickness of the paraffinic moiety is consistent with a single layer of octadecyl chains in a liquid state [19] (l = 15 Å). The size of the polar head can be accurately estimated from C.P.K. molecular models (7-8 Å), which leaves 12-13 Å per hydrated polyoxyethylene glycol chain. This value corresponds roughly to the end to end distance of a polyethyle glycol polymer in its random coiled conformation [20](10 Å) rather than in its fully extended one (18 Å). One is thus led to a monolayer like structure as schematically pictured in

figure 3. The surface avalaible for each paraffinic chain is 34.5 $\mathring{A}^2$ (69 $\mathring{A}^2$ per polar head), which is in good agreement with the value found in lamellar phases [17,21].

Conclusion

A new type of lyomesophase has been thoroughly characterized by polarizing microscopy and X-rays determinations. Work is in progress to study the original properties of these supermolecular systems. In particular the photochemical properties of the cobaltic complex are presently being examined.

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