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PRELIMINARY COMMUNICATION

Surfactant bound polypeptides

II. Liquid-crystalline behaviour of triton X-100 bound poly-γ-benzyl-L-glutamate

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The liquid-crystalline behaviour of two polymers in which the non-ionic surfactant Triton X-100 was bound covalently to low molecular weight poly-γ-benzyl-L-glutamate (degree of polymerization 21 (TRG-I) and 26 (TRG-II)) was studied in five non-aqueous solvents. Cholesteric mesophases were observed, significantly, at as low a concentration as 5–8 per cent (w/v) in chloroform, dimethylformamide, dioxane and dichloromethane. The cholesteric pitch, however, is small (e.g. 1·1 μm in a 10 per cent (w/v) solution in dichloromethane). The polymer TRG-II exhibited cholesteric mesophases in the mixed solvent dioxane : dichloromethane (2 : 8 v/v) unlike the homopolymer poly-γ-benzyl-L-glutamate. Interestingly, in benzene solutions neat crystalline plates were formed.

Since Robinson [1] reported the liquid-crystalline phase of poly-γ-benzyl-L-glutamate (PBLG) in non-aqueous solvents, a prolific growth of interest on diverse aspects of the lyotropic liquid-crystalline phases of polypeptides was witnessed [2–6]. It is now established that a high degree of polymerization (DP > 60) and relatively high concentration (≥ 10 per cent w/v) are prerequisites for the formation of lyotropic polypeptide mesophases [2, 3].

Physicochemical studies on polypeptides linked to non-peptidic surfactants are under way in this laboratory. Our studies [7] on PBLG, of low degree of polymerization covalently linked to the non-ionic surfactant Triton X-100, revealed that the incorporation of the surfactant in the polymer chain markedly enhances the solubility of the peptide block in a number of non-aqueous solvents, and also affects its packing in the solid state. These polymers with rather low molecular weight surprisingly exhibited mesophases at rather low concentrations.

The synthesis of poly-γ-benzyl-L-glutamate bound covalently to octylphenoxy-polyethoxyethanol (Triton X-100) and its conformation are reported elsewhere [7]. The chemical formula of the polymer is

$$XY\text{COCH}R\text{NH}(\text{COCH}R\text{NH})_{n-1}\text{COO}^-\text{K}^+$$

X, octylphenoxy group, $(CH_3)_3CCH_2C(CH_3)_2C_6H_4O$; *Y*, decaethyleneoxy group, $(CH_2CH_2O)_{10}$; *R*, $(CH_2)_2COOCH_2C_6H_5$. The degree of polymerization (*n*) of the peptide block of two samples studied was determined by an N.M.R. method to be 21 (TRG-I) and 26 (TRG-II). The solvents for making polypeptide solutions were purified and 'dried' according to the literature [8].

The surfactant bound polypeptide samples were readily soluble in chloroform, dichloromethane, dioxane and dimethylformamide, but dissolved slowly in benzene over a period of 6–7 days; the homopolymer PBLG itself is well known to dissolve very slowly after going through a gel stage. Solutions of the polymers were allowed to equilibrate at room temperature (~25°C) for 2 days. They were then placed in 0·05 mm deep cavities on microscopic slides which were covered with a cover slip, and in some cases sealed with DPX mountant (BDH). A Reichert 347 polarizing optical microscope was employed for recording the textures. The optical rotation of the solutions as a function of polypeptide concentration was determined with a Jasco digital polarimeter DIP 360 at a wavelength of 589 nm.

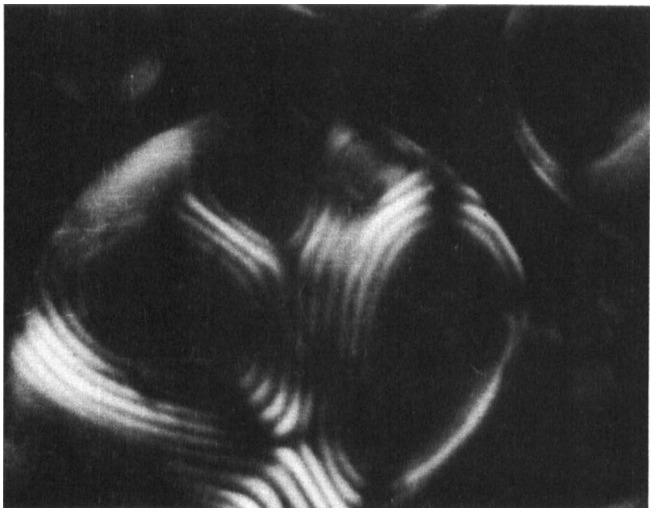

Figure 1. Cholesteric mesophases in dichloromethane of TRG-II (c = 5·0 per cent w/v) (600 ×).

Mesophases were observed at high polymer concentration in four of the five solvents studied and these mesophases persisted even on dilution. In fact, in dichloromethane a clear 'fingerprint' pattern, characteristic of cholesteric mesophases and depicted in figure 1, was observed in the birefringent component of the biphasic TRG-II solutions at as low a concentration as 5·0 per cent (w/v). In dioxane, chloroform and dimethylformamide (DMF) mesophases also appeared at rather low concentration (see table). However, in dioxane and DMF the well-delineated cholesteric textures could not be observed (cf. figure 2). In chloroform the texture was similar to that in dichloromethane. All of these solvents are considered to be helicogenic, and promote the formation of an alpha-helical polypeptide backbone. It may be expected, however, that the extent and nature of the interaction of the solvent with the non-peptidic surfactant moiety in the polymers would vary due to the considerable range of chemical properties among the solvents used.

It has been reported that high molecular weight PBLG (M = 300 000) has a cholesteric pitch of 31 μm in 20 per cent (w/v) solution in dioxane [1]. The cholesteric pitch is not expected to depend on molecular weight, but only on the concentration of the solution and the nature of the solvent [4]. However, the pitch of the present systems is roughly an order of magnitude less than that exhibited by the

homopolypeptide itself. The pitch, for example, was 1·10 μm at c = 10 per cent (w/v) in dichloromethane for TRG-II; the pitch did decrease as expected with increasing concentration (by 0·27 nm on doubling the concentration). Apparently, the pitch is quite small in dioxane and hence the distinct cholesteric retardation lines were not observed; similar observations were reported for the homopolymer by Robinson [1].

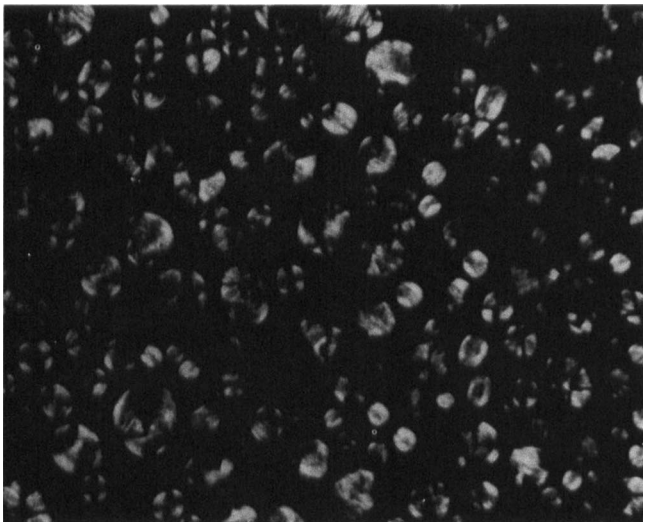

Figure 2. Cholesteric mesophases in dioxane of TRG-II (c = 5·4 per cent) (100 ×).

Mesophases observed in different solvents for Triton X-100 bound poly-γ-benzyl-L-glutamate, TRG-II (T = 20°C).

Solvent	Mesophase	Lowest percentage concentration (w/v) at which observed	Figure number
Dichloromethane	Cholesteric	5·0	1
Dioxane	Cholesteric	5·4	2
Dichloromethane: dioxane (8 : 2)	Cholesteric	5·7	—
Chloroform	Cholesteric	7·8	—
Dimethylformamide	Cholesteric		—
Benzene	Crystalline	5·5	3

In the mixed solvent containing dichloromethane (80 per cent) and dioxane (20 per cent) cholesteric textures were also seen at as low a concentration as 6 per cent (w/v). This observation is in contrast to the findings of Robinson [1], who found a solvent induced cholesteric compensation (nematic) in this mixed solvent for the homopolymer poly-γ-benzyl-L-glutamate. The solvent compensation was attributed by Robinson [1] to the supramolecular right-handed arrangement of the polypeptide rods in dioxane being compensated by the left-handed arrangement in dichloromethane. More recently Czarniecka and Samulski [9] have explained the same phenomenon on the basis of a variation in the apparent chirality of the helix surface: the arrangement of the side-chain benzyl groups changes in different solvents. In the present systems the cholesteric untwisting in the mixed solvent is perturbed by the incorporation of the surfactant moiety on the polypeptide. Hence in addition to sustaining the mesophasic order, the surfactant influences the cholesteric pitch.

The polymer exhibited crystalline aggregates in 5 per cent solutions in benzene (cf. figure 3). The homopolypeptide is reported to form smectic rather than cholesteric mesophases in this solvent. Powers and Peticolas [10] attributed the observed high specific viscosity and low effective dipole moment for PBLG in benzene solutions to be due to antiparallel side-by-side association of the macromolecules. A smectic mesophase is intrinsically more ordered and therefore exhibits more crystal-like features. The surfactant indeed augments this arrangement of the polypeptide rods in benzene leading to crystalline aggregates in our system. It is important to mention that these crystalline particles are observed only when the polypeptide is in the mother liquor; on gradual evaporation of the solvent, the crystal phases tarnish and eventually thorny aggregates are formed.

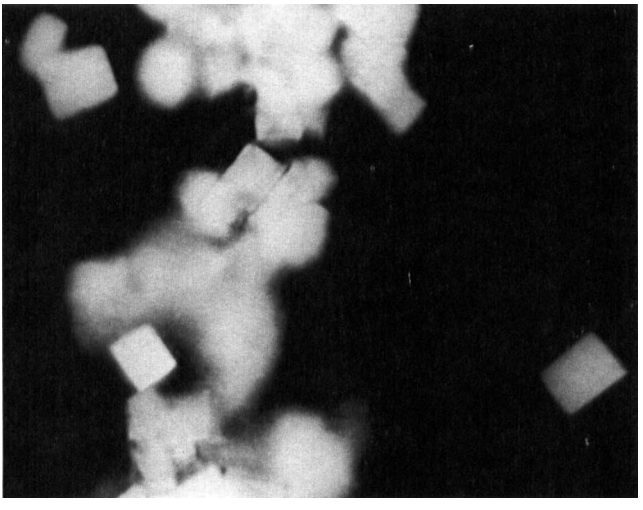

Figure 3. Crystalline aggregates in benzene for TRG-II (c = 5·5 per cent) (100 ×).

We also studied the specific rotation of the TRG-II system as a function of concentration. The specific rotation of TRG-II in chloroform decreased drastically from + 67° to 0° on reducing the concentration from 6·2 per cent to 3·5 per cent (w/v), and at lower concentrations the specific rotation changed sign (− 8° at 1·9 per cent (w/v)). Apparently, the formation of the mesophase is associated not only with an enhancement in the specific rotation, but also a change in the sign of the specific rotation. A reversal of the sign of 'form optical rotation' from negative to positive values on raising the temperature was reported by Patel *et al.* for poly-γ-benzyl-D-glutamate [11].

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