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Lytotropic Liquid Crystals from Lecithin, Water, and Polyethylene Glycol

Lytotropic liquid crystals with lecithin as the amphiphile and with water/polyethylene glycol (PEG) solutions as the solvent were prepared with polyethylene glycol/water ratios from 182 to 0. The liquid crystals were lamellar and the interlayer spacing was independent of the solvent content for water/PEG ratios ≤ 1 but increased strongly with the water/PEG ratio. Higher ratios gave increased interlayer spacing with solvent content similar to the variation for liquid crystals with water as solvent but the absolute values of the spacing were higher.

INTRODUCTION

The area of polymers ordered into liquid crystalline patterns has attracted a pronounced attention in recent years partly due to the success of the Du Pont fiber spun from a liquid crystalline melt (1). Several symposia have been organized on the subject (2, 3) concentrating on thermotropic structures against their advantage of being one-component systems. Mesogenic side groups attached to a polymeric backbone have been shown to promote nematic, smectic, as well as cholesteric organization (4-11).

Polymerization in, or the inclusion of polymers into lyotropic liquid crystals, poses a greater problem because of the multicomponent nature of lyotropic systems. The conditions for polymerization in lyotropic liquid crystals have been stated (12) using the criteria for polymerization in crystalline structures (13-15). These criteria are (a) the chain period of the polymer must coincide with the translational period of the monomer crystalline lattice, (b) the overlapping volumes of monomeric units in the polymer chain should not appreciably differ from that of the monomer molecule, and (c) the volume contraction during the chain formation should not be in the direction of chain growth.

Polymers may also be used as the mesogenic agent in order to form liquid crystals with suitable solvent. In this area, the pioneering contributions by Samulski (16) should be mentioned as well as the extensive investigations on block copolymers (17, 18). The latter ones (19) have recently been reported (20) to give liquid crystals with extremely high solvent content.

An interesting relation between polymers and ordered amphiphilic structures is further found in the influence of polymers on the fusion of cells (21) and vesicles (22). It should be noticed that even small additions of polyethylene glycol have been demonstrated to have a pronounced effect on cell fusion (23).

This information indicated a considerable importance of structural relations between polymers such as polyethylene glycol, water, and lecithin in concentration ranges giving rise to liquid crystals. Earlier attempts to form lecithin/water liquid crystals containing proteins (24) have met with limited success, but our recent experience with

nonaqueous liquid crystals with oligomers of polyethylene glycol (25-27) provided some indication of a potential for liquid crystals with high concentrations of a low-weight polyethylene glycol.

The results reported in the present article not only showed a combination of lecithin and a low-molecular polyethylene glycol to give lamellar liquid crystals, but also that the polyethylene glycol could be replaced with water in all proportions. It appeared obvious that the experiments would provide further information on the site and interaction of the polymers with the amphiphilic molecules in the presence of and without water. We considered this information sufficiently novel and interesting, also from a biological point of view (21-23) to justify a report on the exploratory investigations.

Lecithin was combined with a low-molecular-weight polyethylene glycol/water solution and the geometrical dimensions determined as fraction of the solvent content for different water/polyethylene glycol ratios.

EXPERIMENTAL

1. Preparation of Materials

(a) *Lecithin.* Lecithin, Epikuron 200 (Lucas Meyer, Hamburg, Germany) was purified by fractionation over an alumina column (28). The eluant used was a solution of chloroform:methanol (9:1 vol/vol). The lecithin fractions, giving one spot on thin-layer chromatography were vacuum-distilled ($<50^{\circ}\text{C}$) under nitrogen atmosphere to recover a translucent and colorless lecithin. An antioxidant, *d*- α -tocopherol acetate (Sigma) was added to the lecithin fractions before distillation.

(b) *Solvents.* Polyethylene glycol (PEG), (M_w/M_n 540) Polysciences, Inc. The original water content was determined by Karl Fisher titrations and found to be 0.55% for polyethylene glycol.

Five series of samples were prepared with water/polyethylene glycol ratios according to the legend to figure 2.

The lecithin and the different polyethylene glycol solutions (I-V) were weighed into small glass vials with screw tops, flushed with nitrogen, and centrifuged. They were then mixed in a vortex vibromixer. Alternating mixing and centrifugation was continued until microscopically homogenous samples were obtained.

A small amount of the equilibrated sample was drawn in a fine glass capillary, then sealed for X-ray diffraction determinations of interlayer spacings in a Kessig low-angle camera from Richard Seifert. Ni-filtered Cu radiation was used and the reflections determined by a Tennelec position sensitive detection system (Model PSD-1100).

RESULTS AND DISCUSSION

The ratio between the spacings given by the low-angle X-ray diffraction data was 1:1/2 showing a lamellar structure (29). The optical pattern, Fig. 1, with their "oil streaks" and Maltesian crosses confirmed this structure and also served to prove the lamellar organization for those samples for which only one X-ray reflection could be detected.

The interlayer spacing versus solvent weight ratio for different PEG/water ratios are given in Fig. 2. The series with the least water content gave an interlayer spacing that was independent of the solvent ratio. The value of the spacing was $46.0 \pm 1.0 \text{ \AA}$ (95% confidence interval). An increase of the water content to a water/PEG ratio of 1.0 gave samples with considerably increased interlayer spacing but still identical value for different solvent in the total stability range. The interlayer spacing was now $56.1 \pm 0.7 \text{ \AA}$ (95% c.i.).

With water as the main component of the solvent, water/PEG weight ratio 3:1, the constant interlayer spacing was found only for solvent percentages less than 23%. For this range, Fig. 2 gives an interlayer spacing of $57.1 \pm 1.1 \text{ \AA}$ (95% c.i.). Composition with solvent percentages in excess of 23% resulted in an increase of interlayer spacing with

the solvent content; two straight lines intersecting at a solvent/lecithin ratio of 0.3 are an obvious feature in Fig. 2.

With the water/PEG ratio as high as 10 (Fig. 2) the interlayer spacing was dependent on the amount of solvent for the entire stability range. The slope of the line was now of the same magnitude as the one for pure water (marked in Fig. 2). A least squares calculation gave slopes of $29 \pm 3 \text{ \AA/solvent ratio}$ (95% c.i.) for the mixed solvent and $31.5 \pm 1.5 \text{ \AA}$ (95% c.i.) for the liquid crystal with water as a solvent with the same confidence interval.

In addition, the interlayer spacings extrapolated to zero solvent concentration were greater for the water/PEG ratio 10 than for liquid crystals with water only. The value was 51 \AA for the water/PEG ratio equal to 10 with a reduction to 41 \AA for 100% water. The maximum value for the extrapolated interlayer spacing was 57 \AA for a water/PEG ratio of 3. It is evident the value for interlayer spacing extrapolated to zero solvent content was increased, went through a maximum, and was reduced with increased water/PEG ratio.

These constant interlayer distances versus the amount of solvent may at first be interpreted as due to a two-phase part of the system. We are well aware of this possibility; the following comments may be of value for the discussion of such a possibility.

The low-angle X-ray diffraction patterns showed only the presence of a lamellar liquid crystal and the optical pattern was not characterized by the indistinct patterns typical of a mixture of two liquid crystals.

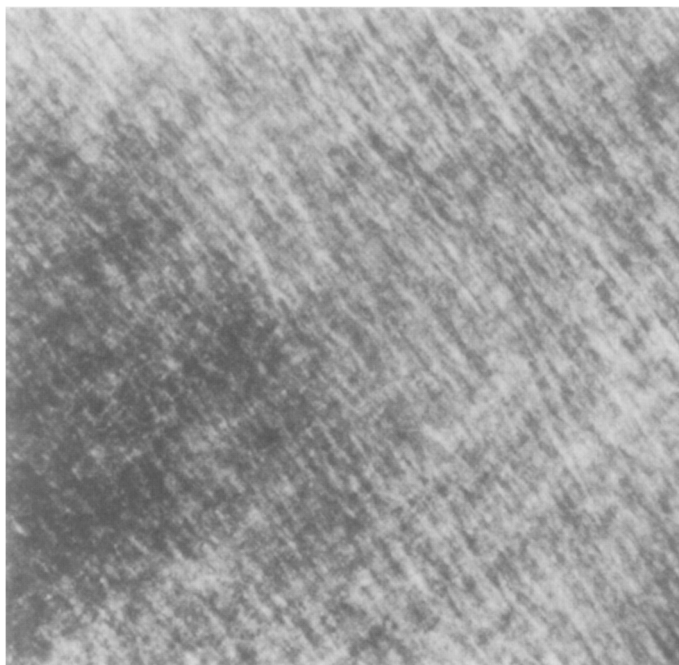


FIG. 1. The optical pattern in polarized light was typical of a lamellar liquid crystal.

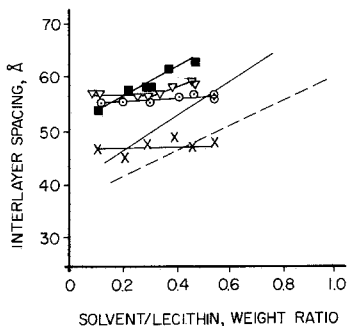


FIG. 2. The lamellar spacing as function of solvent/lecithin ratio.

Symbol	Series	PEG/water
(X)	I	181
(●)	II	1.0
(∇)	III	1/3
(■)	IV	1/10
(—)	V	0
(- - -)	VI	Ethylene glycol

A two-phase region of a lamellar phase and an isotropic liquid is not detectable from the X-ray patterns and the presence of the magnitude of 5% of the isotropic phase requires very careful observations of the microscopic pattern. In the present results, the ratio of the two components varies from 0.1 to 0.5. Hence, two-phase area for the entire range would involve a minimum of approximately 44% of the isotropic phase. It is difficult to have anyone unable to detect the presence of such a phase in the system. It would certainly be separated during the routine centrifugations, which are part of the standard procedure.

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