Protein-Dispersed Liquid Crystals

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SYNOPSIS

Nematic liquid crystals (LC) were embedded in a highly structured gelatin film as the discrete phase in the form of droplets. Thereby, the gelatin matrix forces a preferred orientation of the LC molecules in the droplets, initiated by the interaction between the triple helices of gelatin and the LC at the interface protein/LC. This is explained on a molecular level by the formation of a supramolecular structure at the interface, which is a germ for the continued preferred orientation of the mesogenes inside the droplets.

INTRODUCTION

Liquid crystals (LC) are components of modern optoelectronic modules in technology and of biosensors in medicine and life sciences.[1] They have the ability of spontaneous self-organization characterizing the anisotropic liquid-crystalline state. Biopolymers can also spontaneously form highly organized structures.

We embedded LC as a discrete phase in a highly structured biopolymer. Therefore, gelatin was used. It forms a triple-helical tertiary structure[2] and is an excellent film former. Thus, we have found a preferred orientation of the LC molecules in the droplets of the gelatin layer.[3] In the present work, an explanation will be given for this preferred orientation. The latter is based upon the interaction between the two structures at the interface biopolymer/LC. Thereby, a new structure, a supramolecular one, has been formed.

EXPERIMENTAL

Gelatin

A low-molecular gelatin (from Gelatinewerk Calbe, Germany) was used. As raw material, we used bones of cattle, degreased with hot water and demineralized, then treated with saturated lime for 53 days. The gelatin was extracted from the limed precursor with water at 48°C.

Liquid Crystals

A cyano-biphenyl mixture (E 5, Fa. Merck, Germany) was used.

Molecular Mass Distribution of the Gelatin

The molecular mass distribution of the gelatin was measured by gel permeation chromatography. The column, 20 cm in length and 2 cm in diameter, was filled with Sepharose CL-4B (Pharmacia AG, Sweden). For the sample, 3 mL of gelatin solution (1.5% w/w) was used. The elution was done at 38°C with a NaCl–water solution (6% w/w) at an elution velocity of 60 mL/h, an elution time of 3.5 h, and a pressure level of 250 kPa. The column effluent was monitored for absorbance at 254 nm. The column was calibrated with gelatin molecular mass standards (Serva, Germany).

Gelatin Layers

Gelatin, 7.5 g, was stirred in 92.5 g of water, soaked overnight at 8°C, and then melted at 40°C to give an aqueous solution. To 15 mL of this gelatin solution, 0.35 g E 5 was added dropwise under stirring at 40°C with a high-speed mixer, forming a finely dispersed emulsion. The emulsion was poured into a Teflon cup.

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- Cold-dried layer: For cooling and setting, the Teflon cup was kept at room temperature for 2 h and then at 4°C for 24 h, followed by drying in an air current at 12°C.
- Hot-dried layer: Without a cooling and setting phase, the content of the Teflon cup was immediately evaporated on a hot plate at 50–55°C to yield a film.

All the layers were optically clear and had a thickness of about 20 μm.

Conoscopic Measurements

The layers were investigated as described in Ref. 3 in a conoscopic ray using an amplifying microscope.

RESULTS AND DISCUSSION

We have formed the gelatin layers from aqueous solution via the gel condition and subsequent cold drying of the gel (drying temperature < 20°C). It is known that under these conditions highly structured triple-helical domains are formed in the layer.[2] The *trans*-conformation in the gly-(HO) pro bond is the steric prerequisite for the spontaneous organization of triple-helical domains.

For the manufacture of the gelatin/LC layers, a low-temperature extracted gelatin was used. Their molecular mass distribution is shown in Table I. The low-temperature extracted gelatin has a comparatively large portion of gelatin molecules with a molecular mass between 30,000 and 425,000 Daltons as well as low portions of oligomers and microgel. If cold-dried gelatin layers are produced with such gelatins, then the quantity of triple-helical domains is especially high because our measurements have shown that in contrast to conventional wisdom only gelatin molecules between 30,000 and 425,000 Daltons are imbued with the *trans*-conformation in the gly-(HO) pro bond and that, in particular, the higher molecular mass fractions characteristic of oligomers and microgel lack such *trans*-conformation and, therefore, lack a triple-helical structure.[4]

Table I Molecular Mass Distribution of the Gelatin

Peptides	<30 kD	21.2%
Peptides	30–80 kD	38.5%
α-, β-, and γ-strands and α-, β-, and γ-peptides	80–340 kD	30.7%
Oligomers	340–900 kD	7.8%
Microgel	>900 kD	1.8%

Table II Tilt Angle φ of the Ordered Structure of Gelatin Layers

Gelatin Layer	φ/Degree
Cold-dried layer	16
Cold-dried layer + E 5	16
Hot-dried layer	No orientation measurerable
Hot-dried layer + E 5	
Type B, cold dried layer	
No salt content	9.3[a]
1.8% NaCl	4.6[a]
2.0% $CaCl_2$	19.4[a]
Type A, cold-dried layer	
No salt content	5.0[a]
1.8% NaCl	10.1[a]
2.0% $CaCl_2$	6.7[a]

Type A: acid-processed gelatin; type B: lime-processed gelatin.
[a] See Ref. 5.

The spontaneous organization of triple-helical domains in the microscopic molecular field has an effect even on the macroscopic range of the gelatin layer: The conoscopic measurements show (Table II) that the triple-helical domains in the cold-dried layer are not arranged without order, but that they have a preferred orientation in the solid layer. The optical axis of the triple helices forms an angle (tilt) of 16° in relation to the substrate normal. However, the tilt angle is not a constant value. If there was salt contained in the gelatin layer or if different gelatins were used for the formation of layers, other tilt angles were measured (Table II).

In the case where the LC was mechanically dispersed in the aqueous gelatin solution and a cold-dried layer was produced, two points are remarkable:

1. The LC molecules in the gelatin film were not distributed homogeneously, but heterogeneously as a discrete phase in form of droplets.
2. The triple-helical structure of the gelatin film was not destroyed by the embedded LC, not even at the relatively high LC concentration in our measurements (35 wt % LC related to gelatin quantity). On the contrary, as our conoscopic measurements show (see Table II and Ref. 3), the LC molecules in the droplets are arranged nematically so that their long molecular axis is adjusted parallel to the op-

tical axis of the gelatin film. Thus, the gelatin matrix forces a preferred orientation of the LC molecules, as schematically demonstrated in Figure 1.

On the other hand, hot-dried gelatin layers (drying temperature > 40°C, no triple-helical structure[2]) with embedded LC do not provide an interference figure in the conoscopic ray and, therefore, hot-dried gelatin films do not show the structural discrimination as in the cold-dried gelatin film with embedded LC (Table II).

Hence, it follows that for the preference of LC orientation in the cold-dried film the triple-helical domains are essential. A new structure quality, a supermolecular structure, is formed by the interaction between gelatin matrix and LC. This was indicated by the higher thermal stability of this supramolecular structure in comparison with the gelatin and LC structure measured separately.[6]

How can this supramolecular structure be explained on a molecular level? It is well known[7] that the triple-helical domains of the gelatin are composed of three left-handed single-strand helices with a pitch of 8.5 Å and pro and (HO) pro in *trans*-conformation. Shifted by $\frac{1}{3}$ pitch, the helices are further twisted as strands of a rope round a threefold axis into a right-handed triple helix. That results in a molecular architecture of high symmetry. The triple-helix strand is stabilized by a multitude of intramolecular hydrogen bonds starting in each case from the part —NH— of a peptide bond. Two of the three NH groups in each turn of the chain are linked to the oxygen of either of the other two chains by hydrogen bonds, the NH···O distance being 2.8 Å.

Also, on the surface of the triple helix, the hydrogen bonds occur in a short, symmetrical interval. Individual hydrogen bonds on the surface of the triple helix can join intermolecularly without the triple helix being broken. It is easy to understand that at the interface triple helix/LC droplet these hydrogen bonds can correlate with the electron donors of the LC molecules, thus forcing LC molecules into the space position of the triple helix, as shown schematically in Figure 2. This superstructure at the interface can be regarded as the germ for the continued preferred orientation of the mesogens inside the droplet. In this way, the preferred orientation of the LC molecules in the discrete droplets in the gelatin matrix can be explained.

CONCLUSION

In the system consisting of nematic LC embedded in the triple-helical gelatin matrix, the LC droplets exist in a discrete, homogeneously orientated condition already without external excitation. Starting from this state, they transform into another condition by external influence. This discloses a new possibility for the application of LC displays.

The external excitation can comprise a wide variety of possibilities, such as light, sound, mechanical pressure, and heat as well as electric and magnetic fields. Two of the possibilities, the excitation in the electric field and by light, have been included in our investigation and we will report on these measurements in the near future.

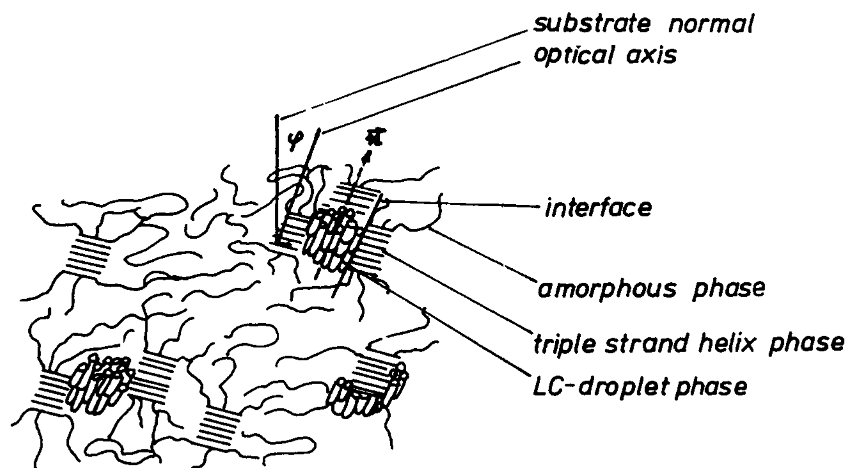

Figure 1 Cyanobiphenyl mixture (E 5, Fa. Merck) embedded in the gelatin matrix as discrete phase (droplets) with a tilt angle φ of the nematic director $\vec{n}$ inside the droplets.

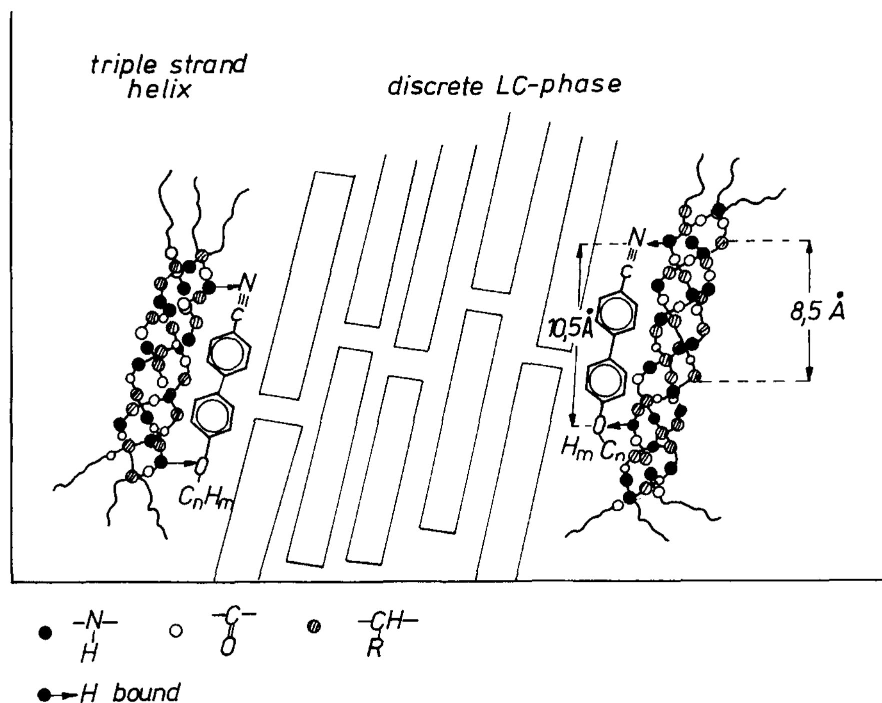

Figure 2 Formation of the superstructure on the interface triple helix/liquid crystals and the preferred orientation of the liquid crystals inside the droplets. Model of collagen structure that has been built with a repeating sequence —NH—CO—CHR— (R = amino acid residue) is used. A repeat distance of 8.5 Å is marked.

REFERENCES

1. H. Ringsdorf, B. Schlarb, and J. Venzmer, *Angew. Chem.*, **100**, 117 (1988).
2. D. D. Macsuga, *Biopolymers*, **11**, 2521 (1972).
3. A. Seeboth and H. Hermel, *Thin Solid Films*, **173**, L 119 (1989).
4. H. Hermel, H.-J. Wappler, R. Wetzel, E. Buder, H. Legutke, and H. Herbrich, *J. Imag. Sci.*, **35**, 305 (1991).
5. H. Hermel, A. Seeboth, B. Kersten, and H. Legutke, *J. Imag. Sci.*, **35**, 87 (1991).
6. A. Seeboth, H. Hermel, and G. Kretzschmar, *Thin Solid Films*, **201**, 197 (1991).
7. A. Rich and F. H. C. Crick, *J. Mol. Biol.*, **3**, 483 (1961). F. H. C. Crick and J. C. Kendrew, *Adv. Protein Chem.*, **12**, 133 (1957).

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