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The H₂-phase of the lyotropic liquid crystal sodium 3,4,5-tris(ω -acryloyloxyundecyloxy)benzoate

R. RESEL*, U. THEISSL, C. GADERMAIER, E. ZOJER, M. KRIECHBAUM†, H. AMENITSCH‡, D. GIN‡, R. SMITH‡ and G. LEISING

Institut für Festkörperphysik, Technische Universität Graz, A-8010 Graz, Austria

†Institut für Biophysik und Röntgenstrukturforschung,

Österreichische Akademie der Wissenschaften, A-8010 Graz, Austria

‡Department of Chemistry, University of California, 94720 Berkeley CA, USA

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The phase behaviour of the lyotropic liquid crystal sodium 3,4,5-tris(ω -acryloyloxyundecyloxy)benzoate was investigated by small angle X-ray scattering. The water content of the lyotropic liquid crystal phase was varied between 8 and 20 wt % and the investigations were performed in a temperature range up to 70°C. A reversed hexagonal structure (H₂-phase) as well as the isotropic phase were observed. The lattice constant of the H₂-phase was found to be independent of the water content. An extremely small dependence on temperature could be found. Based on the shape of the molecules and the observed structural properties, a model for the arrangement of the molecules within the H₂-phase is given. The transition temperature from the H₂-phase to the isotropic phase decreases significantly from 60°C for the sample with 8 wt % water content to 30°C for the sample with 20 wt % water content.

1. Introduction

Nanocomposites are an interesting new class of materials with outstanding physical properties. Highly photoactive materials can be achieved by the combination of luminescent molecules with a nanostructured matrix. The matrix isolates the luminescent molecules from each other. As a consequence of this isolation, the optical properties differ considerably from their bulk properties [1]. Non-linear optical materials and micro-sized optically pumped lasers have already been realized [2, 3].

One possibility for obtaining such nanocomposites is the combination of luminescent molecules with lyotropic liquid crystals [4]. The lyotropic liquid crystals in their reversed hexagonal phase (H₂-phase) serve as matrix, and the water cores of this structure can be used for inclusion of water soluble luminescent molecules. Polymerization of the matrix yields a stabilized assembly of the lyotropic liquid crystals with isolated luminescent molecules [5, 6]. The polymerization is achieved by opening carbon-carbon double bonds which are associated directly with the lyotropic monomer molecules and/or given additives, and photochemical reactions initiate the polymerization process [7–9].

The material used in this study is suitable for obtaining such polymerized lyotropic liquid crystals; its chemical composition is sodium 3,4,5-tris(ω -acryloyloxyundecyloxy)benzoate. The chemical structure is depicted in figure 1. Mixing this salt with about 8 wt % water forms the H₂-phase. To allow the polymerization of the matrix, additionally a 2 wt % mixture of photoinitiator in *p*-xylene is added to the lyotropic liquid crystal phase. When the viscous liquid crystal phase is pressed between two silica plates, and polymerization is initiated by irradiation with UV light, thick free standing films of high optical quality are obtained [4, 5]. Structural investigations on the polymerized films have already been performed [10]. The ideal conditions for the formation of the H₂-phase should be found, to optimize the preparation procedure of these nanostructured, polymerized films. Within this paper we give a detailed characterisation of the H₂-phase

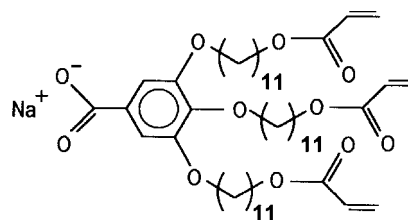


Figure 1. Molecular structure of the lyotropic liquid crystal sodium 3,4,5-tris(ω -acryloyloxyundecyl-oxy)benzoate.

* Author for correspondence
 e-mail: f513rese@mbox.tu-graz.ac.at

behaviour. The structural properties of the monomeric (unpolymerized) lyotropic liquid crystal phase are studied as a function of water content and temperature by small angle X-ray scattering (SAXS).

2. Methods

The structure of the H_2 -phase (figure 2) consists of water cores arranged in a two-dimensional hexagonal lattice. The water cores are located in the centre of hexagonal Wiegner-Seitz unit cells as depicted in figure 2. The distance between two adjacent water cores is given by the value $2r$. The monomer molecules are assembled around each water core with polar, hydrophilic head groups pointing towards the centre of the water core and the hydrophobic tails (sketched by zig-zag lines) forming the bulk in between. The thickness of one monomer monolayer within the H_2 -phase is between d_{min} and d_{max} . The diameter of the water core (d_w) can be calculated as a function of the water content (ϕ_w) in the core channels by using the equation $d_w = 2d(\phi_w \sqrt{3}/2\pi)^{1/2}$ [11]. In this formula, ϕ_w has to be given in vol %. For conversion from wt % to vol %, a density of 1 g cm^{-3} is taken for the monomer material which is in agreement with the densities of other comparable systems [11].

Before the preparation of lyotropic liquid crystal phases, the sodium 3,4,5-tris(ω -acryloyloxyundecyloxy)-benzoate salt was dried for 4 h in high vacuum at ambient temperature. The lyotropic liquid crystal phases were prepared by mixing the monomer with water; water contents of 8, 11, 14, 17 and 20 wt % were used. To make our studies under the same conditions as for films which are subsequently polymerized, a 2 wt % mixture of 2-hydroxy-2-methylpropiophenone (photoinitiator) dissolved in *p*-xylene was added. The mixtures were stirred mechanically. The resulting lyotropic liquid crystal

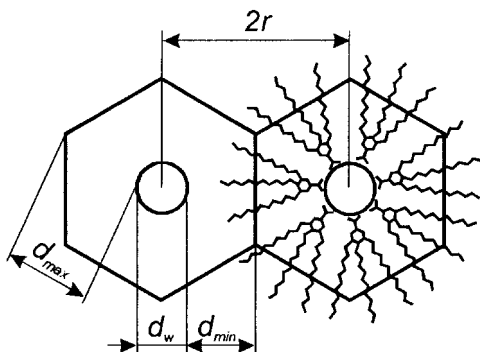


Figure 2. Two Wiegner-Seitz unit cells of the two-dimensional hexagonal lattice of the H_2 -phase; the water core channels are located in the centre. The lattice constant $2r$, the diameter of the water core channels d_w , and the minimum d_{min} and maximum d_{max} thickness of one monolayer are denoted. The arrangement of the molecules within the unit cell is depicted schematically.

phases have high viscosity for the sample with 8 wt % water content; which reduces systematically to a more fluid-like behaviour for the sample with 20 wt % water content.

Small angle X-ray diffraction experiments were carried out at the SAXS-beamline at the synchrotron Elettra, Trieste [12]. The primary beam with a cross section of $2 \times 0.5 \text{ mm}^2$ was highly collimated and monochromatized at a wavelength of 1.55 \AA . The diffraction patterns were taken with a one-dimensional detector with an exposure time of 50 s for each measurement. Silver behenate was used as the calibration standard [13]. The samples were filled into a temperature controlled sample holder (A. Paar, Austria). The samples were enclosed in an aluminium frame between two thin mica plates (thickness $40 \mu\text{m}$), sealed with a rubber ring and mounted in a thermostable steel cuvette holder. An external Pt100 resistor monitored the temperature of the sample holder. In order to check the reversibility of the structural transition, the samples were heated during the SAXS measurements to their isotropic phase at 70°C and subsequently cooled to ambient temperature at a rate of 1°C min^{-1} . The same results were obtained for measurements performed by increasing and by decreasing the temperature.

3. Experimental results

All X-ray diffraction patterns show three strong diffraction peaks. The interplanar distances of these three reflections follow the sequence $1:1\sqrt{3}:1/2$, which is characteristic for a two-dimensional hexagonal lattice. Due to the low water content, a reversed hexagonal phase (H_2 -phase) can be assumed for all the lyotropic liquid crystal phases investigated. The distance between two core channels ($2r$), which is also the lattice constant of the H_2 -phase, can be calculated easily from the position of the 10-diffraction peak ($h = 1, k = 0$) located at the interplanar distance d_{10} , by $2r = \sqrt{4/3} d_{10}$ [14].

Figure 3 shows the 10-diffraction peak at different temperatures for the sample prepared with 8 wt % water. At $T = 30^\circ\text{C}$ the 10-diffraction peak corresponds to an interplanar distance $d_{10} = 36.10 \text{ \AA}$ ($2\theta = 2.46^\circ$). Thus we obtain a distance between the core channels of $2r = 41.7 \text{ \AA}$. This peak shows an extremely small shift with increasing temperature. At $T = 60^\circ\text{C}$, the d_{10} -value decreases only by about 0.1 \AA . Above $T = 60^\circ\text{C}$, the 10-diffraction peak disappears. We conclude that the H_2 -phase melts at about 60°C , i.e. above this temperature only an isotropic liquid phase is present.

Another feature of the diffraction pattern in figure 3 is the development of a broad amorphous peak (a correlation peak) with increasing temperature. At $T = 30^\circ\text{C}$, only the 10-diffraction peak and no clear correlation peak can be observed. With increasing temperature, the

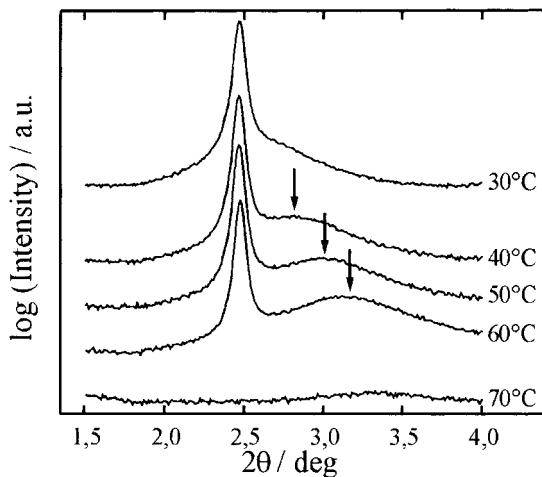


Figure 3. X-ray diffraction patterns of the lyotropic liquid crystal phases of a sample prepared with 8 wt % water content at different temperatures. For clarity, the experimental curves are vertically shifted relative to each other; the intensities are given in logarithmic scale. The positions of the correlation peaks are marked with arrows.

correlation peak becomes more and more pronounced. Finally at 70°C only a weak correlation peak remains. It should be noted that the position of the correlation peak shifts from $2\theta = 2.88^\circ$ at $T = 40^\circ\text{C}$ to $2\theta = 3.4^\circ$ at $T = 70^\circ\text{C}$.

Figure 4 shows the change of the 10-diffraction peak of the hexagonal structure for samples with different water contents at $T = 30^\circ\text{C}$. Two different observations are made from this series of measurements: (i) there is no change in the position of the 10-diffraction peak

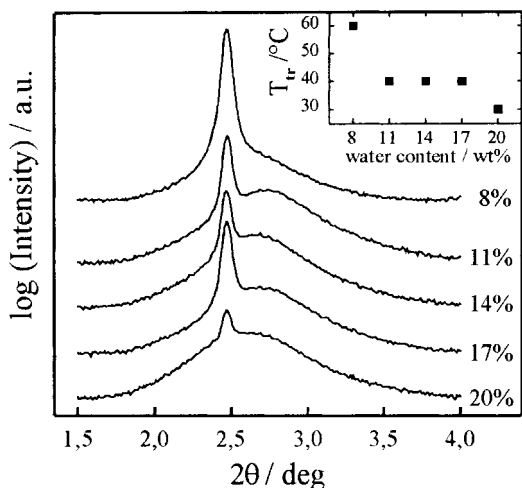


Figure 4. X-ray diffraction patterns of the lyotropic liquid crystal phases at 30°C prepared with different water contents. For clarity the experimental curves are vertically shifted relative to each other; the intensities are given in logarithmic scale. The inset gives the transition temperature (T_{tr}) from the H₂-phase to the isotropic phase as a function of water content.

for different water contents; (ii) the intensity of the 10-diffraction peak decreases with the water content, while the correlation peak becomes more pronounced relative to the diffraction peak.

The inset of figure 4 gives the transition temperature (T_{tr}) from the H₂-phase to the isotropic phase as a function of the water content. The sample with 8 wt % of water shows a value for T_{tr} slightly above 60°C. T_{tr} decreases to 30°C at 20 wt % of water.

Some general trends can be deduced from the experimental results. The lattice constant $2r$ does not show any dependence on the water content in the samples; only a very small change is observed with temperature. With increasing temperature and increasing water content, the intensity of the correlation peak increases dramatically. An increase in the intensity of the correlation peak is observed close to the transition temperature, which indicates melting of the H₂-phase.

4. Discussion

Three main questions arise from the experimental results. The first is the reason for the apparent insensitivity of the $2r$ -values to the water content of the samples. The second is the reason for the small temperature dependence of the lattice constants. The third is whether the intensity of the correlation peak has any relation to the stability of the H₂-phase.

We compare our system to lipid systems, which show similar structural properties. These lipid systems have revealed two distinct trends in the lattice constant $2r$ as a function of water content [11]. High water content during sample preparation yields lattice constants independent of the water content, whereas a strongly decreasing lattice constant is observed at lower water contents. Above a certain amount of water—the excess water point—no additional water can be included in the H₂-phase. The excess of water is probably located between the domains of the H₂-phase. Since in our system $2r$ is independent of the water content, we conclude that the system is above the excess water point. This means that our system is already fully hydrated at 8 wt % water. From an excess water point of 8 wt % and geometric parameters of the unit cell, an upper limit for d_w of 12 Å, and lower limits for d_{min} and d_{max} of 15 Å and 17 Å, respectively, can be given.

The length of the lyotropic molecule calculated in an all-*trans*-conformation is 26 Å. By comparing this length with d_{min} and d_{max} , we conclude that the hydrophobic tails of the molecules from neighbouring unit cells overlap and/or that the all-*trans*-conformation of the tails is not maintained. Since the σ -bonds of the tails have high rotational freedom, considerable folding/bending of the tails can be assumed for filling the interstitial space between the water channels.

In contrast to the investigated system, lipid systems show a strong dependence of the lattice constants on temperature [15]. In our system the lattice constant decreases only about 0.1 Å upon heating the sample from 25 to 70°C. The small change can be explained by the well defined conformation of the monomer molecules, which has a tapered shape of the benzoate head group [16]. This shape and the rigid bonds in the benzoate head group 'fix' the present packing in the hexagonal lattice and do not allow large changes in the arrangement of the molecules.

In respect of the molecular shape, we developed a packing model of the monomer molecules within the H₂-phase. A good volume packing of seven benzoate groups is obtained around a water core with a diameter of 10 Å. Within that model, the phenyl rings of the benzoate units are arranged parallel to the plane of the two-dimensional hexagonal lattice (perpendicular to the direction of the water core channels). As a consequence of this arrangement of the benzoate groups around the water core channel, the phenyl rings have to stack above each other in the direction of the water core channels. To support the present model, the theoretical volume of one monomer molecule is compared with the available volume of the hexagonal unit cell. The volume of the monomer molecule was estimated from characteristic volume increments of atomic groups of the molecule using the van der Waals radii of the atoms [17, 18]. The theoretical volume of the monomer molecule is 810 Å³. The volume of seven monomer molecules arranged in the two-dimensional hexagonal unit cell leads to a stacking distance of the benzoate units of about 3.8 Å. This is slightly larger than the stacking distance of aromatic molecules within crystal structures [17].

Besides the diffraction peaks of the H₂-phase, a much broader peak of less intensity—a correlation peak—is observed. It represents a typical distance of about 28 Å. The correlation peak arises for the isotropic phase of the lyotropic liquid crystals as well as for the H₂-phase. Higher temperatures cause the intensity of the correlation peak to increase, combined with a decreasing intensity of the 10-diffraction peak (figure 3). This behaviour indicates melting of the H₂-phase. The correlation peak is also observed at 30°C for samples with different water contents. The intensity, as well as the peak width, increases with higher water content in the system (figure 4). We conclude that the fraction of isotropic phase rises with higher water content. The transition temperature from the H₂-phase to the isotropic phase occurs for the sample with 8 wt % water at $T_{tr} = 60^\circ\text{C}$ and decreases with increasing water content (inset of figure 4). From these three experimental facts, we conclude that higher temperature as well as higher water content pushes the system

closer to the stability boundary of the H₂-phase. This boundary is represented by the transition temperature T_{tr} . The closer the system is situated to the transition temperature, the more the H₂-phase is destabilized.

5. Conclusion

The phase behaviour of the lyotropic liquid crystal sodium 3,4,5-tris(ω-acryloyloxyundecyloxy)benzoate was investigated as a function of temperature (25–70°C) and water content (8–20 wt %). The formation of the reversed hexagonal phase (H₂-phase) and an isotropic phase was observed.

The lattice constant of the H₂-phase, which is the distance between two core channels, was found to be 41.7 Å. Since the lattice constant does not change with water content, we conclude that the H₂-phase is already fully hydrated at 8 wt % water content. As a consequence, the diameter of the water core channels is smaller than 12 Å. We present a structural model for the arrangement of the molecules within the H₂-phase. In this model seven monomer molecules are arranged in one plane around the water core channel.

The isotropic phase is drastically reduced for the sample with 8 wt % water content at a temperature of 30°C. The transition from the H₂-phase to the isotropic phase is promoted by increasing temperature and increasing water content. Therefore, a water content of about 8 wt % can be suggested for preparing of the H₂-phase in order to obtain high quality polymerized films.

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