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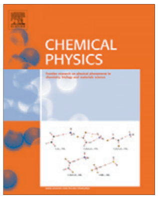

Self-assembly of gelator molecules in liquid crystals studied by ESR

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ABSTRACT

Thermotropic liquid crystal *trans*-4-heptylcyclohexanecarboxylic acid (**HCCA**) doped with 4-oxo-2,2,6,6,-tetramethyl-1-piperidinyloxy spin probe (Tempone) is investigated by electron spin resonance (ESR) spectroscopy in the presence of chiral bisoxalamide gelator **1** during both cooling and heating cycles. In the temperature range 295–383 K, where **HCCA** displays isotropic, nematic, smectic B and crystalline phases, the impact of **1** self-organization was detected via (non) homogeneous partitioning of the spin probe in the environments varying in the polarity, an effect dependent on the gelator concentration. In particular, the evidence of the onset of the gelator network self-assembly in the nematic phase was detected by ESR at higher temperatures than the ones reported so far by other experimental techniques. Additionally, the spectral analysis points to the switching of the polarity in the vicinity of the spin probe when the transfer of chirality from **1** to **HCCA** upon cooling of the sample from isotropic to chiral nematic phase appears and when the event of LC gelation results in the achiral nematic phase during chiral gel fibers formation. When the gelation proceeds in the smectic phase, the melting of the gelator network is studied in the nematic phase during the heating cycle. Furthermore, the event of **HCCA** crystallization is shown to be strongly affected by the presence of **1** as well. The experimental evidence is provided that gelator network confines the **HCCA** into the domains within the bulk crystalline matrix where the local molecular dynamics are still not frozen. Therefore, we propose that non-homogeneous polarity profile of molecular organization/packing within LC gels could be determinable for the physical properties of various LC gel phases.

1. Introduction

Liquid crystalline (LC) physical gels represent a new type of soft materials that possess induced or enhanced electro-optical [1–5], photochemical [6–9] and electronic [10–12] properties useful for the construction of supramolecular devices for advanced applications. Although verified with various experimental techniques these properties are still not understood at the fundamental level. The reason is that most of the techniques like calorimetry and microscopy detect macroscopic manifestation of gelation of different mesophases of LC molecules and respective phase transitions in the bulk. Therefore, the aim of this study was to apply electron spin resonance (ESR) spectroscopy, which provides information at the local level of incorporated reporter group, to gain insight into the structural properties at the interface between gelator network and layer of liquid crystalline molecules. Additional motivation for this approach is in the fact that ESR spectroscopy has been widely used to study liquid crystals [13,14], but there are very few studies presenting dynamic properties of gels [15,16] while to the best of the authors' knowledge there is no ESR study of LC gels so far reported in the literature.

In this study we are focused on organogelator molecules that are capable of self-assembling into long, fibrous structures of nanosize diameters through highly specific noncovalent interactions, such as hydrogen bonding, van der Waals, π–π stacking, electrostatic and charge-transfer interactions [17–19]. Noncovalent cross-links between the nanofibers and/or mechanical entanglements create a three-dimensional network, which entraps the solvent inside the interstices leading to gelation and loss of fluidity of the system. The basic structural requirement for a molecule to exhibit gelation properties is its self-complementarity and capability of unidirectional self-assembling into fibrous aggregates. It has been shown that in the case of liquid crystalline gels an LC phase was gelled as an ordinary solvent [20–23]. In such a system each species is capable of giving a different type of noncovalent supramolecular organization at a specific temperature. Usually, LC gels exhibit random or ordered phase-separated structures depending on the relation between sol–gel ($T_{\text{sol–gel}}$) and isotropic-LC ($T_{\text{iso-lc}}$) transition temperatures. When $T_{\text{iso-lc}}$ is higher than $T_{\text{sol–gel,}}$ the anisotropic LC media serve as a template for anisotropic growth of gelator fibers [24–27]. On the contrary, when LC media are isotropic ($T_{\text{sol–gel}} > T_{\text{iso-lc}}$), a randomly dispersed network of gelator fibres is formed.

In continuation of our studying oxalamide gelators which exhibit self-assembling property [28–34], here we present the

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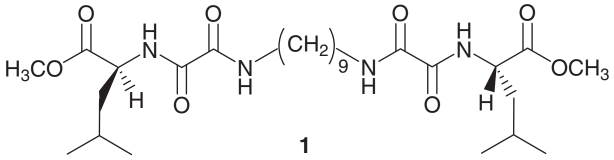
investigation of the chiral bisoxalamide gelator **1** (1,9-*N*,*N*′-bis [oxalyl-(L-leucin-methyl ester)] diaminononane) in the context of its gelling capacity of the nematic and smectic B mesophases of **HCCA** (*trans*-4-heptylcyclohexanecarboxylic acid), both shown in Scheme 1 [35,36]. Compound **1** is a supergelator of **HCCA** with gelation capability observed down to the concentrations of 0.025 wt.% in the smectic B mesophase, to our knowledge it is the lowest concentration of gelator in LC gels ever published [35].

The gelation of each mesophase depends on the concentration of chiral gelator **1**. When gelator **1** is present in concentrations higher than 0.55 wt.% (e.g. **G1**), **HCCA** on cooling transforms from the isotropic to chiral nematic phase. Upon further cooling a gelation of LC occurs, chiral gel fibers are formed while the nematic phase becomes achiral [35]. In contrast, when **1** is present in the concentration range of 0.025–0.5 wt.% (e.g. **G01**), neither chiral induction nor gelation of the nematic phase can be observed. However, at lower temperatures, the subsequent transition of nematic phase into homeotropically oriented smectic B phase triggers instantaneous self-assembly of gelator **1** molecules into aligned fibrous aggregates, i.e. gelation of mesophase.

In this study, the complex system of **HCCA** and **1** was studied using ESR spectroscopy during the temperature induced phase transition/self-assembly of liquid crystalline/gelator molecules. The advantage of the approach relies on the sensitivity of the method to detect changes in the local properties while reporting about dynamics on the time scale ranging from 10^{-11} s to 10^{-8} s [37]. Since neither **HCCA** nor gelator molecules are paramagnetic, the external reporter group in terms of the spin probe has to be incorporated in the system under investigation. In our previous study of the self-assembled noncovalent thermoreversible bis(leucine) oxalamide ethanol gels ESR spin probe technique was applied for the first time [38], indicating that the spin probe exhibiting hydrogen acceptor properties is the most appropriate one for this type of experiments. Following the same approach, here presented study made use of Tempone spin probe (4-oxo-2,2,6,6,-tetramethyl-1-piperidinyloxy) which allowed a direct interaction with gelator and/or **HCCA** to be investigated through its hydrogen bonding affinity. Therefore, we were able to detect changes in the local properties/dynamics in the vicinity of the spin probe, while **HCCA** underwent phase transitions in the presence of gelator molecules. In particular, the evidence of the onset of the gelator network self-assembly in the nematic phase for **G1** was detected by ESR at higher temperatures than the ones reported so far in the literature and based on other experimental techniques. In addition, the spectral analysis pointed to the switching of the polarity in the vicinity of the spin probe when the transfer of chirality from **1** to **HCCA** upon cooling of the sample from isotropic to chiral nematic phase appears and when the event of LC gelation results in the achiral nematic phase during chiral gel fibers formation. Regarding **G01** for which the gelation proceeds in the smectic phase, the gelator network could be studied in the nematic phase in which the **1** self-assembly pertains during the heating cycle. This allowed the comparison with **G1** and the onset of the melting of the **1** self-assembly network within the nematic phase to be assigned. The importance of the interplay between self-organization of **HCCA** and **1** was clearly shown in the event of **HCCA** crystallization which was strongly affected by the presence of **1**. We provide the experimental evidence that gelator network confines the **HCCA** into the domains within the bulk crystalline matrix where the local molecular dynamics are still not frozen. Therefore, we propose that non-homogeneous polarity profile of molecular organization/packing within LC gels could be determinable for the physical properties of various LC gel phases.



1

HCCA

Scheme 1. Structures of bisoxalamide gelator **1** and mesogen **HCCA**.

2. Materials and methods

2.1. Materials

The thermotropic liquid crystal **HCCA** (commercially available from Merck) exhibits phase transition temperatures as follows: Cr_2 31 (13.46 kJ/mol) Cr_1 54 (5.20 kJ/mol) B 77 (2.43 kJ/mol) N 104 (1.25 kJ/mol) [36]. **HCCA** was doped with a nitroxide paramagnetic spin probe Tempone (commercially available from Sigma–Aldrich) at the concentration of 0.7 mM. The chiral bisoxalamide gelator **1** (1,9-*N*,*N*′-bis [oxalyl-(L-leucin-methyl ester)] diaminononane) was prepared as reported previously [39]. Detailed study of **HCCA** and gelator **1** is provided in reference [35]. To obtain liquid crystal gels, **HCCA** was mixed with gelator **1** in two different amounts (0.1 wt.% in **G01** and 1.0 wt.% in **G1** sample, respectively). The experiments were started by heating the mixtures to the isotropic state (383 K) and then cooling the mixtures to the room temperature and reheating to the isotropic phase. All the samples were deoxygenated in an argon atmosphere.

2.2. Methods

The phase behavior of the samples was determined by differential scanning calorimetry (DSC), Perkin–Elmer Diamond and polarized optical microscopy (POM), Olympus System Microscope BX51TF equipped with a Linkam THMS 600 hot stage. The morphology of self-assembled fibers of gelator **1** formed in the LC phase was visualized by polarizing optical microscope and transmission electron microscope (TEM), Zeiss EM 10A, operated at an accelerating voltage of 60 kV. The samples were shaded with palladium and used for TEM investigation.

ESR spectra were recorded on a Varian 109 X-band spectrometer operating at 9.76 GHz and 100 kHz modulation. The microwave power (2 mW) and modulation amplitude (0.1 mT) were adjusted well below the saturation and distortion level of the spectra. The temperature was controlled using a variable temperature unit Bruker ER 4111 VT with a flow of cold nitrogen gas. Measurements of the samples were performed in a temperature range from 383 K to 295 K in steps of 5 K at a rate of 1 K/min.

The simulation of experimental data was performed using EasySpin program package, a MATLAB toolbox for simulating and fitting ESR spectra (Version 3.1.1.) [40]. The spectral analysis indicated that the paramagnetic reporter group undergoes fast isotropic Brownian motion with short correlation time of $\tau_c < 0.1$ ns so that elements of g and hyperfine A tensors taken from the literature [41] average out in such a way that differences between the various experimental data could be discussed in terms of isotropic hyperfine constant, $a_0 = (A_{xx} + A_{yy} + A_{zz})/3$.

3. Results and discussion

The complexity of the interplay between self-organization of **HCCA** and **1** was addressed using two-level approach with respect