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THERMOTROPIC BEHAVIOUR OF THE COMPLEX LIQUID CRYSTAL SYSTEM CONTAINING 8CB [4-CYANO-4'-(*n*-OCTYLBIPHENYL)] AND ORGANIC FERROFLUID

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A ferronematic liquid crystal (FNLC) system containing 8CB (4-cyano-4'-[*n*-octylbiphenyl]) and magnetite particles was prepared by using the two steps method. The magnetite particles were dispersed in the organic (liquid crystalline) media by using toluene. However, the toluene affected the thermotropic and structural behaviour of the pure basic (8CB) substance, drastically. The product was stable as no any sedimentation and coagulation has been observed during several weeks after the preparation. However, the distribution of magnetite particles was found not to be homogeneous in the nm size range.

Keywords: *8CB, DSC, ferrofluids, ferronematic liquid crystal (FNLC), freeze fracture, SAXS*

Introduction

Recently, the complex systems containing nanoparticles gained a great scientific interest in the field of colloid chemistry of complex fluids. Especially, the ferronematic liquid crystals (FNLC) exhibit complex features [1–4]. These systems are thermotropic liquid crystals, in which magnetic particles are suspended colloidally. In presence of a magnetic field the liquid crystal molecules are easily oriented when the material is doped with magnetic particles. Number of features has been attributed to a coupling between the magnetic particles and the liquid crystal director [5]. To obtain structural and thermotropic information on the FNLC system we have executed different types of investigations (e.g. differential scanning calorimetry (DSC) [6], small angle X-ray scattering (SAXS), and freeze-fracture [7]). The main purpose of our study is devoted to the changes in the thermotropic behaviour of the liquid crystal matrix occurred by the addition of the different chemical components used for the FNLC preparation. Since an adequate distribution of the magnetite particles is required to yield a homogeneous FNLC product, therefore freeze fracture electron microscopy was also used to study the homogeneity of the sample.

The magnetite particles prepared in our laboratory, were dispersed in a well known thermotropic liquid crystal matrix, the 8CB (4-cyano-4'-[*n*-octylbiphenyl]) [8] by using novel method for the preparation of FNLC systems.

The formation of colloidal dispersion of finely-divided magnetic particles in organic carriers, such as biphenyl based liquid crystals and the sufficient stability of these compositions are possible if suitable adsorption layer structure is built on the surfaces of the particles, which ensure the continuous transition between the surface of the particles and the bulk phase.

Conventionally, stable organic ferrofluid compositions may be prepared by surface-active molecules or macromolecules. Theoretically, there are two ways to produce stable magnetite ferrofluid composition in organic media. In the one step method the ferrofluid is stabilized by the selected surface-active molecules or macromolecules which are dissolved in the organic carrier [9]. In the two steps method the magnetic particles are prepared in aqueous media then the particles are transferred from the aqueous media into the organic one by using a surfactant. After the procedure the hydrophobic magnetic particles are suspended colloidally in the organic carrier [10]. In our work the more complicated two steps method was chosen to avoid the excess of tenzide molecules which could strongly affect the phase transition of 8CB.

Experimental

Samples and methods

Preparation of FNLC

The suspension of ultrafine magnetite particles was formed by a conventional co-precipitation method [11]. Aqueous $FeCl_3$ (1.2 M) and $FeCl_2$ (0.7 M) solution was mixed with identical volumes. Magnetite par-

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ticles were flocculated with concentrated NaOH solution (pH=11). After removing supernatant liquid, the resulting magnetite slurry was washed with water, adjusting the pH to 5.5. The sediment was dispersed with 1 M HCl.

In order to produce stable suspension of magnetite particles in a biphenyl based liquid crystal sodium-dodecyl-benzene-sulphonate (SDBS) surfactant and toluene were chosen as the organic media. Surfactant solution was added to the diluted aqueous magnetite ferrofluid. SDBS molecules adsorbed onto the particles with their strong polar group and resulted in the flocculation of the magnetite particles. The sediment was dispersed in toluene. Water was removed and the concentration of organosol was increased by vacuum distillation. The particle concentrations were determined by the dry mass method.

Organic ferrofluid was mixed with 4-cyano-4'-8-alkylbiphenyl (8CB) liquid crystal, which was in its isotropic phase. Sedimentation or coagulation has not been observed during several weeks. Phase separation of toluene/8CB mixture was not observed, too.

Methods

The calorimetric scans were performed by using a DSC 2920 instrument (TA Instruments, US) operating at a scan rate of 2.5 K min^{-1} in the temperature range from 0 up to 50°C. The reference pan was empty. The DSC curves were recorded in the heating direction in all cases. The temperature at the peak maximum was defined as the transition temperature. The calibration of the calorimeter was carried out by using a pure indium sample (T_{onset}=156.6°C).

The SAXS study of the magnetic particles of the ferrofluid was performed on the Jusifa apparatus of the Doris III synchrotron radiation source in Hasylab/DESY (Hamburg, Germany). A two-dimensional detector was used and the range of the scattering variable, s (defined as $s=(2/\lambda)\sin\Theta$, where Θ is the half of the scattering angle, λ is the wavelength of the X-ray) from about 0.0015 up to 0.15 $Å^{-1}$ was covered.

The SAXS studies of the liquid crystal systems were carried out by using a modified compact Kratky camera (Anton Paar, Graz, Austria). The camera was supplied with a linear, one dimensional position-sensitive device (Mbraun, Garching, Germany) for the exposure of the nonoriented SAXS patterns in the range of the scattering variable, s from 0.003 up to 0.15 $Å^{-1}$. The X-ray was a Ni-filtered CuK_α radiation (λ=1.542 Å). The SAXS curves were corrected considering the geometry of the X-ray beam profile in order to obtain point-focused data. The Kratky camera had an open section in the middle of the camera for the sample holder block which was made of aluminium. This block was thermally controlled by water flow using a thermostat. The actual temperatures were constant within less than 0.1°C as controlled by a thermocouple.

For the X-ray measurements the systems were transferred into thin walled quartz capillaries (Hilgenberg, Germany) with a diameter of 1 mm. The capillaries were sealed with a two-component synthetic resin and transferred into metal capillary holders placed into the aluminium sample-holder block.

The gold specimen holders used in freeze-fracture were preincubated at 26°C. Samples of small volume (about 1–2 μL) were taken out and were placed into the gold holders, which were then immediately plunged into partially solidified Freon for 20 s freezing and then placed and stored in liquid nitrogen. Fracturing was carried out at –100°C in a Balzers Freeze-Fracture Device (Balzers AG, Liechtenstein). The fractured faces were etched for 30 s at –110°C. The replicas, prepared by platinum–carbon shadowing, were cleaned with distilled water. From pure water, the replicas were picked up on 200 mesh copper grids. The electron micrographs were taken with an electron microscope (Jeol JEM-100 CX II, Japan).

Results

Characterization of FNLC by DSC

8CB is a well established smectic liquid crystal. The pure 8CB system has shown three transitions according to the DSC curves. Melting point was found to be 21.1°C where the crystalline (Cr) state passes into smectic A (SmA). The smectic A phase transforms into nematic (N) at 33.5°C, and further into the isotropic (I) liquid at 40.5°C [8].

Melting point between the crystalline and smectic A mesophase can only be detected when the sample has been kept for several hours between 0 and 4°C. The two other transition temperatures were detected in every case in the temperature range from 0 to 50°C. The measurements were reproducible e.g. the curves were the same after the repeated scans.

Four types of samples were investigated. The composition of the samples, except of pure 8CB, is summarized in Table 1. The addition of non-mesomorphic substances to a liquid crystal generally caused a minor decreasing in the value of the phase transition temperatures. We have found change of phase transition temperatures in the presence of the different components added (toluene and toluene based magnetite sol). Distinction of the magnitudes of the transition signals are serious; therefore melting peaks are presented separately (Fig. 1) from the other two transitions (Fig. 2). The characteristic parameters of the phase transition peaks are summarized in Table 2. Neither toluene nor the magnetite sol

Table 1 Properties of synthesized samples; 'Other materials' means the sum of the toluene and ferrofluid

	8CB/ g	Other materials/ mass/mass%	Magnetite content/ %
8CB and toluene (A)	0.1995	0.30	0
8CB magnetite sol with low concentration (0.5 mass/mass%) (B)	0.2382	0.67	0.0035
8CB and magnetite sol with high concentration (17.2 mass/mass%) (C)	0.2548	0.43	0.074

Table 2 Characteristic parameters of the phase transitions

Crystalline undergoes to smectic A			
Sample	T_{os}/°C±0.1	T_{trans}/°C±0.1	ΔH/J g^{-1}±1.0
pure 8CB [6]		21.1	
pure 8CB	20.2	22.3	86.5
A	19.2	21.5	87.2
B	18.7	21.3	85.1
C	19.2	21.4	86.5
Smectic A undergoes to nematic			
Sample	T_{os}/°C±0.1	T_{trans}/°C±0.1	ΔH/J g^{-1}±0.05
pure 8CB [6]		33.5	
pure 8CB	32.7	33.0	0.32
A	31.9	32.2	0.32
B	31.4	31.7	0.31
C	31.8	32.1	0.33
Nematic undergoes to isotropic			
Sample	T_{os}/°C±0.1	T_{trans}/°C±0.1	ΔH/J g^{-1}±0.3
pure 8CB [6]		40.5	
pure 8CB	39.9	40.2	3.0
A	38.9	39.2	2.9
B	38.2	38.6	2.9
C	38.8	39.2	2.8

affected the transition enthalpies significantly. Temperatures of the melting point and of the nematic-to-isotropic transition are decreased significantly by toluene. The smectic-to-nematic transition temperature is only slightly shifted to a smaller value in the presence of toluene.

The main conclusion is that the liquid crystalline structures remain in the presence of toluene or toluene based organic sol. Transition temperatures are decreased, but by less than 1.0–1.5°C.

SAXS studies

The scattering curve of the magnetic particle was recorded in their organic-sol states in a wide range of the scattering variable corresponding to a particle size interval from about 5 up to 1000 Å. The scattering of the diluted system of the magnetic particles can be interpreted as the sum of the scattering of each particle. The most important parameter for the size characterization, the Guinier radius, R_G can be obtained from the initial section of the SAXS curve with the assumption of $R_G s<2\pi$. In the case of the monodisperse spherical particles the log(intensity) *vs*. s^2 plot is linear. The SAXS curve of the magnetic particles does not show a straight line in this plot, therefore the particles can be described only as a heterodisperse system. The particle size distribution is characterized by the method of Shull and Roess [12]. The characteristic diameter of the particles is 42 Å which is significantly smaller than the value (110 Å) obtained by transmission electron microscopy (TEM). The difference can be explained by the size increasing originating in the aggregation of the particles. The latter was always observed in the electronmicrographs.

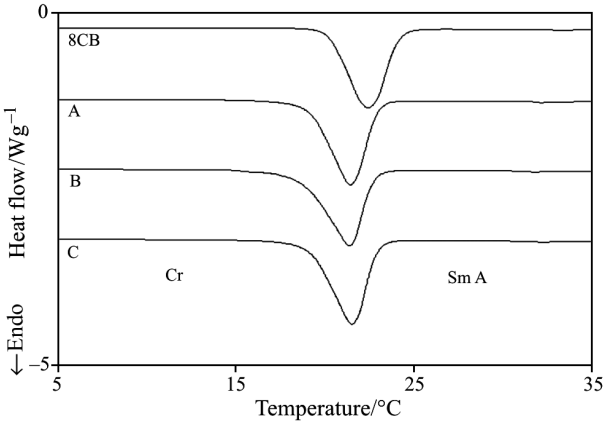

Fig. 1 DSC curves of melting in the pure and the filled systems

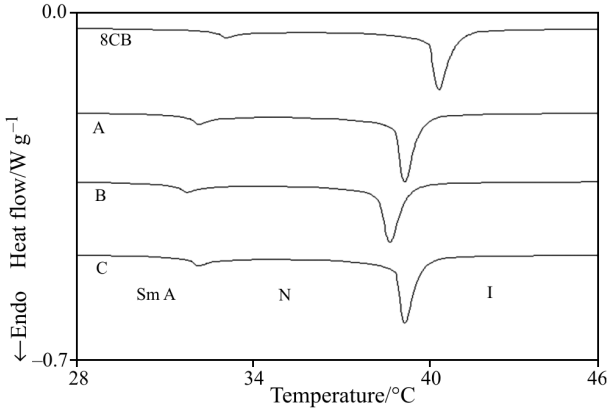

Fig. 2 DSC curves of smectic-to-nematic and nematic-to-isotropic transitions in the pure and the filled systems

Both pure and filled systems were investigated at 16, 26, 36 and 46°C which are the characteristic temperature values for the crystalline, smectic A, nematic and isotropic liquid phases, respectively. The pure 8CB liquid crystal exhibits different SAXS patterns corresponding its mean feature in the different phases, as it can be followed in Fig. 3. In the crystalline and smectic A phases very sharp Bragg reflection appears as it was supposed for the typical layer ordered structures. However, the layer distances are the same, about 30 Å in the thermally adjacent smectic phases. At 36°C the Bragg reflection is destroyed drastically, indicating that in the nematic phase the lamellar arrangement no longer holds. At 46°C the Bragg peak disappears corresponding to an isotropic, liquid-state.

The addition of toluene to the 8CB liquid crystal causes significant reduction of the Bragg peaks in all liquid crystalline states. This change indicates that the lamellar arrangement is not so typical as in the pure system as presented in Fig. 4. Moreover, a broadening of the Bragg reflections appears, which reflects the reduction of the number of the parallel layers in the domain of the stacks.

The SAXS curves of the ferronematic liquid crystal systems prepared with low and higher magnetite content are similar as it can be observed in Figs 5 and 6. Bragg peaks can only be observed in the crystalline and smectic A phases, but they are strongly diminished. The changes in the SAXS patterns related to the pure 8CB are rather due to the toluene than to the magnetite content (see the concentrations in Table 1).

Freeze fracture

The homogeneity of the FNLC sample (having the highest magnetite content) was checked by using freeze fracture and electronmicroscopy. The electron-

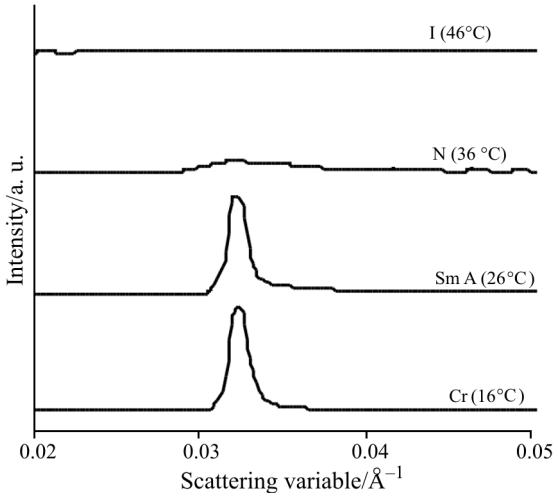

Fig. 3 Bragg profiles of the pure 8CB liquid crystal

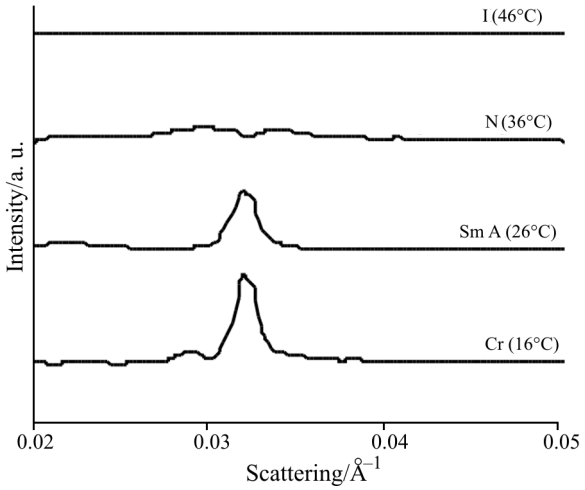

Fig. 4 Bragg profiles of the 8CB+toluene system

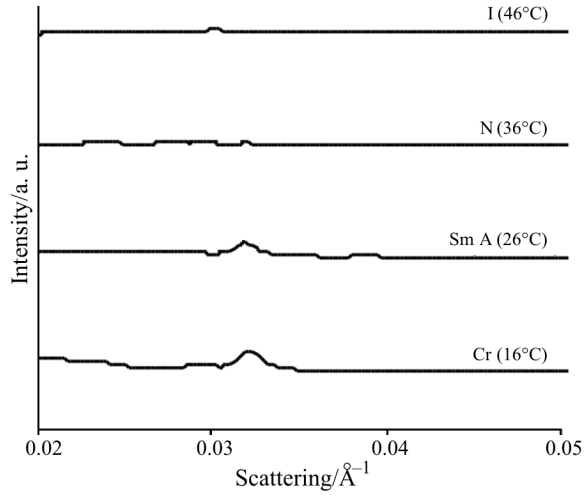

Fig. 5 Bragg profiles of the FNLC with lower magnetite content

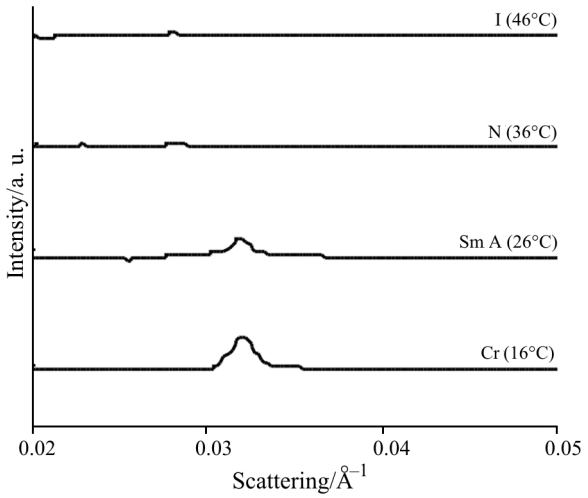

Fig. 6 Bragg profiles of the FNLC with higher magnetite content

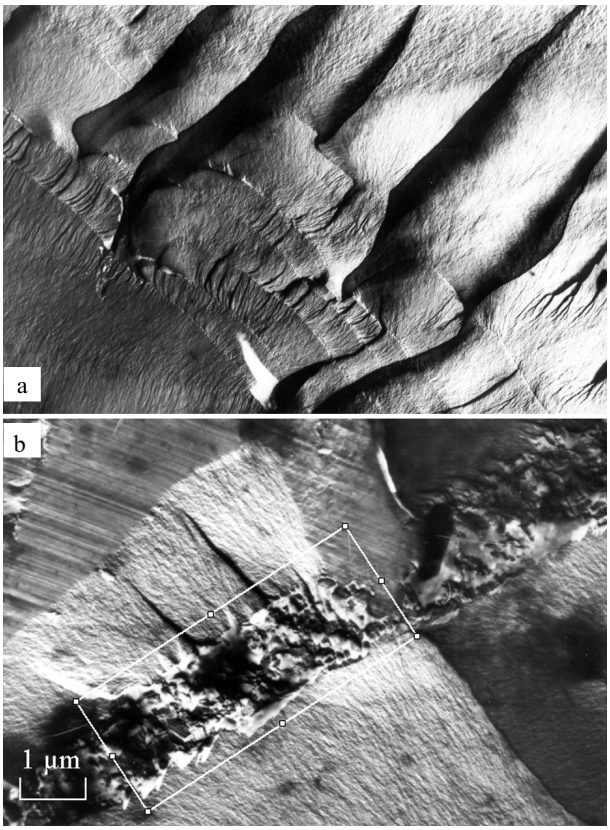

Fig. 7 Freeze fracture electron micrographs of the FNLC at 26°C in steady state

micrographs obtained after the freeze fracture procedure at 26°C (smectic A) revealed the typical lamellar structure of the smectic phase. Giant domains appear in the pictures. The fractured surfaces are not smooth as it can be observed in Fig. 7a. Beside the typical parts some aggregates of small units are embedded in the liquid crystalline matrix indicating that the homogenization of the magnetite particles was not entirely

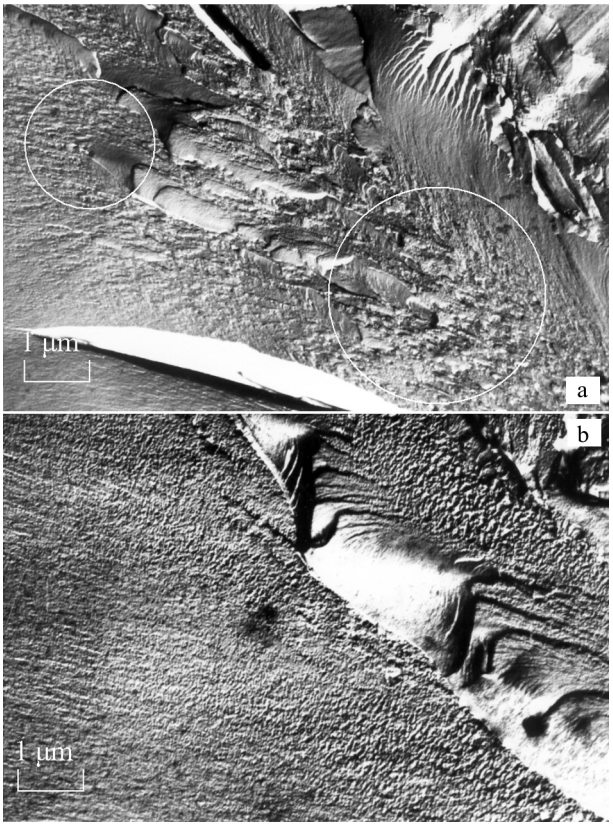

Fig. 8 Freeze fracture electron micrographs of the FNLC at 26°C after 0.5 h of shear

(Fig. 7b). The size range of the smallest fractured units of aggregates is from 200 up to 600 Å, approximately. As the TEM images showed an average size of 110 Å we have concluded that these small domains appeared in the fractured surface morphology are the stacks of the magnetite particles. The homogenization of the magnetite particles was increased by using a shear cell [13]. After half an hour of shear at 26°C (smectic A) the sample was quenched immediately and the freeze fracture procedure was carried out. After this kind of the homogenization no any aggregation was observed in the electronmicrographs (Figs 8a and b). However, after the shear the large domains are dissected into smaller domains which are not more typical for the liquid crystalline system with smectic phase.

Conclusions

The drastic reduction of the Bragg reflections indicates that in the presence of magnetite particles the ordered lamellar arrangement is extremely destroyed. The destruction of the lamellar structure was due to the toluene which is a fundamental chemical component of the preparation. No homogeneous distribution of magnetite particles in the liquid crystalline matrix has been found in the size range of submicrons.

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