Impact of Surface-Functionalized CdSe Nanoparticles on Phase Transitions of 8CB And CE8 Liquid Crystals

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Impact of Surface-Functionalized CdSe Nanoparticles on Phase Transitions of 8CB And CE8 Liquid Crystals

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The impact of the surface–functionalised CdSe nanoparticles on various phase transitions of the two liquid crystals, 8CB and CE8, has been examined by means of high-resolution calorimetry. The addition of nanoparticles results in suppression of phase transitions and change in heat capacity anomalies. In contrast to silica aerosils CdSe nanoparticles do not form a rigid network. As a consequence, the impact of CdSe impurities on phase transitions resembles so called floppy phase regime, which exists at low concentrations of aerosils mixtures.

Keywords liquid crystals; nanoparticles; phase transition behaviour; high-resolution calorimetry

1. Introduction

Randomly perturbed liquid crystals (LCs) have attracted considerable interest in last decade [1, 2]. Suspensions of LCs and different nanoparticles (NPs) have been extensively studied for many years due to their potential applications on various subject areas. Some time ago it has been shown that the spontaneous onset of liquid crystal ordering could be a way to obtain very well aligned nanoparticles [1]. Aerogels, hydrophilic and hydrophobic silica aerosils, controlled porous glasses, and anopores were used as the agents of disorder [2, 3]. In addition, mixtures of ferroelectric and magnetic nanoparticles have been studied to show the electric and magnetic response. Such composite, i.e. ferroelectric LC and ferromagnetic NPs can be a candidate for a new soft magnetoelectric [4]. Recently, considerable attention was paid to liquid-crystalline blue phases (BPs) observed in chiral LCs. BPs exhibit exceptional potential for applications in photonics and display technologies [5]. Their application potential is mainly hindered by the narrow temperature range at which they appear. Hence, in the last years intensive research efforts are in progress in order to achieve stabilisation of

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these phases over a wide temperature range [6–8]. The blue phase III (*BPIII*) is especially of high technological interest [8]. It was demonstrated that the temperature range in which *BPIII* is stable is greatly enhanced in homogeneous mixtures of LCs and NPs of appropriate size and surface functionalisation [9–11]. The aerosil systems have already been studied in detail [12–17]. These particles in most cases form a responsive grid that can rearrange for strong enough elastic distortion imposed by a hosting LCs.

In this work the effect of hydrophobic spherical CdSe nanoparticles, which do not form a responsive grid, on various phase transitions of the two liquid crystal compounds is explored by means of high resolution calorimetry.

2. Experimental Methods

We experimentally investigated 8CB+CdSe and CE8+CdSe mixtures. The liquid crystal compound octylcyanobiphenyl (8CB) exhibits weakly first order isotropic-nematic (*I-N*), and nearly continuous nematic-smectic (*N-SmA*) phase transition, wherein SmA phase molecules are organized in bilayers [18]. The liquid crystal CE8 or 8SI* (4-(2-methyl butyl) phenyl 4-n-octylbiphenyl-4-carboxylate) has been supplied by Merck. The chemical structures of LC compounds, 8CB, and CE8 are shown at the top of Fig. 1. The typical diameter of CdSe nanoparticles was 4.5 nm [9–10]. CdSe have been synthesised at the National Centre for Scientific Research "Demokritos." NPs were surface treated with hydrophobic oleyl amine (OA) and tri-octyl phosphine (TOP). CdSe are highly soluble in non-polar solvent such as hexane, toluene and chloroform. Prior to mixing with LCs their solution was inserted in an ultrasonic bath in order to avoid any agglomeration. Further details about preparation have been described elsewhere [19]. A simple schema of CdSe particles is shown at the bottom of Fig. 1.

CE8

Cr-HexG*-HexJ*-HexI*-SmC*-SmA-N*-BPI-BPII-I

8CB

CdSe nanoparticles

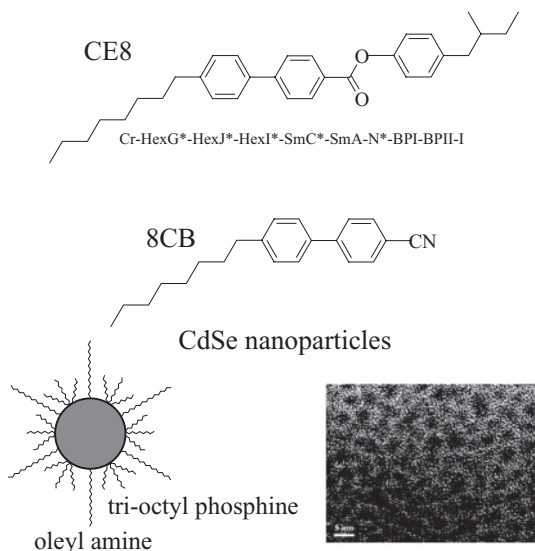tri-octyl phosphine

oleyl amine

Figure 1. The chemical formulae of the LCs CE8 (including its phase sequence) and 8CB can be seen at the top part. A simple schematic representation of the CdSe nanoparticles surface-treated with oleyl amine (OA) and tri-octyl phosphine (TOP) is presented at the bottom left part. On the bottom right a TEM image of CdSe NPs is shown.

The preparation of CE8 and NPs was as follows. The CE8 was dissolved in toluene together with the CdSe particles. The resulting solution was sonicated for five minutes and then stirred for one day at 85°C, until toluene had fully evaporated. After that mixtures were dried under vacuum for 24 h, while slowly stirring at 75°C [9]. In case of 8CB the same procedure was used, the difference was only that the 8CB was dissolved in acetone. We prepared mixtures of concentration $x = 0.05$ and $x = 0.15$ for 8CB, and $x = 0.07$ and $x = 0.20$ for CE8. Here $x = m_{NP}/(m_{NP} + m_{LC})$, where m_{NP} and m_{LC} denotes the masses of the NPs and the LC, respectively. Samples were placed in silver cells thermally linked to a temperature stabilised bath through supportive wires and air. The heat capacity was measured by a high-resolution computerised calorimeter [20]. The calorimeter is capable of operating in either ac or relaxation mode [21]. The comparison of data between these two modes of operation provides a quantitative determination of the released latent heat [20–22]. The uncertainty in the determination of latent heat is in the order 0.03–0.1 J/g for both 8CB+CdSe and CE8+CdSe systems.

3. Results and Discussion

In Fig. 2 we present temperature dependence of the ac specific heat C_p of 8CB+CdSe. The data were collected upon cooling the samples from the isotropic to *SmA* phase. By increasing the concentration of CdSe NPs, both *I-N* and *N-SmA* transition temperatures are shifted to lower temperatures and also both anomalies are broadened and suppressed. Temperature shifts of the transitions, *I-N* and *N-SmA* in comparison to the bulk 8CB, and width of the nematic phase ΔT_N are presented in Table 1. It has been found that with increasing concentration of CdSe the width of nematic phase decreases.
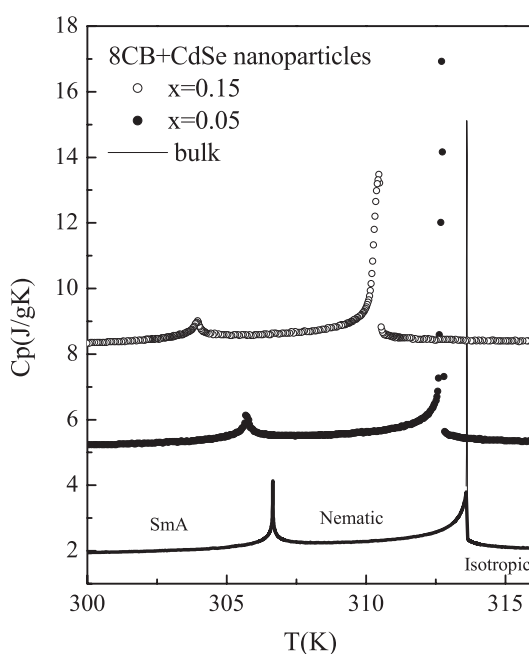

Figure 2. The temperature dependence of C_p data obtained in an ac mode for bulk 8CB and mixtures of 8CB+CdSe nanoparticles. The C_p data for $x = 0.05$ and $x = 0.15$ mixtures were shifted by a constant background value of 3 J/gK and 6 J/gK, respectively.

Table 1. Phase transition temperature shifts for 8CB+CdSe mixtures and pure 8CB. Phase transitions temperatures for bulk 8CB are: $T_{IN} = 313.67 K$ and $T_{NA} = 306.71 K$ [18]. Also shown is width of the nematic phase T_N

X	ΔT_{NA} (K)	ΔT_{IN} (K)	ΔT_N (K)
8CB bulk	0	0	7.03
0.05	0.93	1.03	6.96
0.15	3.21	2.75	6.50

The enthalpy changes and latent heat data are collected in Table 2. The total transition enthalpy for weakly first order transition is given by $\Delta H = \delta H + L$. Here δH denotes continuous contribution to the total enthalpy and L is a latent heat. The *I-N* phase transition remains weakly first order and rather sharp. In contrast to aerosil mixtures, no double peak feature was observed at *I-N* transition even at higher x. The latent heat decreases only slightly with increasing x. This indicates that the impact of CdSe NPs on phase transitions is similar to that observed in the floppy regime of aerosils mixtures observed at low concentrations (x < 0.01). Here, the moieties, that can potentially form the network, are essentially independent of each other. Consequently, the *N-SmA* phase transition remains continuous and rather sharp for both concentrations.

The second studied system was a mixture of chiral liquid crystal CE8 and CdSe nanoparticles. The impact of CdSe NPs on the phase transition temperatures of blue phases in such mixtures has already been studied [9–11]. Besides blue phases, we show in this work the impact of CdSe on smectic and cholesteric phase transition temperatures and enthalpies of all phases. The heat capacity data throughout the phase sequence from isotropic to smectic A for pure CE8 is given in [11]. The heat capacity data obtained in both relaxation and ac runs for two CE8+CdSe mixtures of $x = 0.07$ and $x = 0.20$ are shown in Figs. 3 and 4, respectively. Upper panels in Figs. 3 and 4 show the relaxation and ac data in the vicinity of the *I-BPIII* transition while lower panels show the range of temperatures about smectic A to cholesteric phase transition. It is observed that by increasing a concentration of CdSe nanoparticles the latent heat of the *I-BPIII* transition decreases significantly, however, the C_p anomaly of the *I-BPIII* phase transition remains sharp, i.e. first order even for the highest CdSe concentration. In contrast, increasing concentration of NPs suppress significantly the

Table 2. Enthalpy changes of the *I-N* and *N-SmA* phase transitions for bulk 8CB and 8CB+CdSe mixtures. Here ΔH_{IN} is the total enthalpy of the *I-N* transition, δH_{IN} is continuous contribution to the total *I-N* transition enthalpy and ΔL_{IN} is the latent heat. ΔH_{NA} denotes the total transition enthalpy of *N-SmA* phase in which case no latent heat is presented

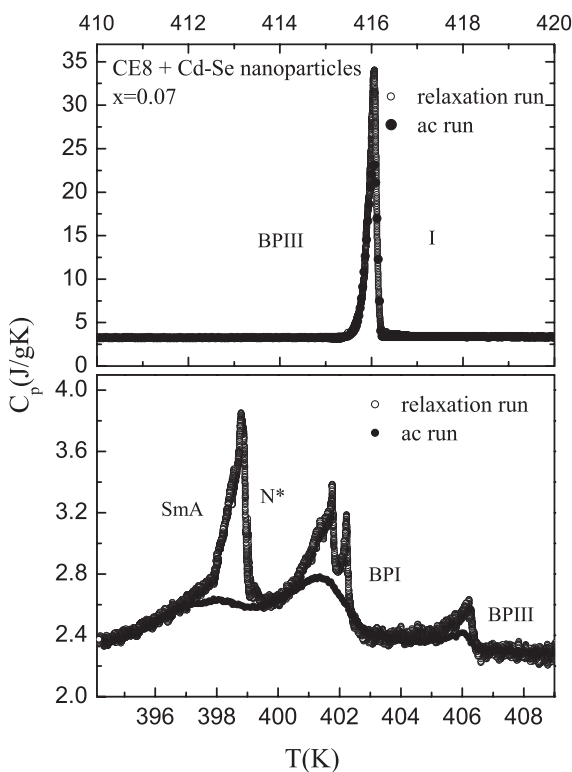| X	ΔH_{NA} (J/g)	δH_{IN} (J/g)	ΔH_{IN} (J/g)	L_{IN} (J/g)
8CB bulk	0.75	5.77	7.97	2.20
0.05	0.51	1.45	2.88	1.43
0.15	0.37	1.25	2.64	1.39

Figure 3. The heat-capacity temperature profiles for mixtures of CE8+CdSe nanoparticles with x = 0.07. The upper panel shows the C_p results obtained in both ac and relaxation runs about *I-BPIII* phase transition. The lower panel presents the ac and relaxation C_p data for the sequence of phases between *BPIII* and *Sm A* phase.

remaining low temperature *BPIII-BPI*, *BPI-N**, and *N*-SmA* phase transition C_p anomalies. The phase transition temperatures are shifted even for the lowest CdSe concentration, and all decreases with increasing x, except the *I-BPIII*, that remains close to the one of bulk CE8 for all the studied mixtures.

The enthalpy changes related to each of phase transition are listed in Table 3 for all studied samples. Because it is not possible to distinguish between the enthalpy changes

Table 3. Enthalpy changes for various phase transitions starting from I to SmA phase in bulk CE8 and CE8+CdSe mixtures. The enthalpy $\Delta H_{BPI-SmA}$ is a sum of enthalpies related to the *BPI-N** and *N*-SmA* phase transitions

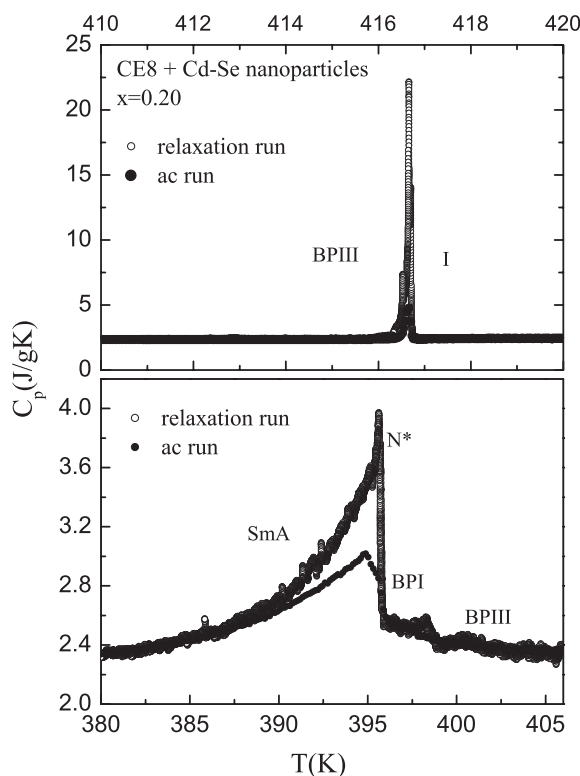| X	ΔH (I-BPIII) (J/g)	L (I-BPIII) (J/g)	ΔH (BPIII-BPI) (J/g)	L (BPIII-BPI) (J/g)	ΔH (BPI-SmA) (J/g)	L (BPI-SmA) (J/g)
CE8 bulk	0.17	0.05	0.35	0.08	6.73	4.63
0.07	7.99	6.87	0.22	0.14	2.52	0.96
0.20	1.65	1.59	0.11	0.10	2.46	2.01

Figure 4. The heat-capacity temperature profiles for mixtures of CE8+CdSe nanoparticles with x = 0.20 obtained in both ac and relaxation runs. The upper panel shows the C_p results about *I-BPIII* phase transition. The lower panel presents the C_p data for the sequence of phases between *BPIII* and *Sm A* phase.

related to the *BPI-N** and *N*-SmA* phase transitions in mixtures of CE8+CdSe, the total enthalpy $\Delta H_{BPI-SmA}$ is given. In comparison to the mixtures of Ce8+aerosils [11], stronger impact of CdSe nanoparticles on all phase transition temperatures below *I-BPIII* is observed similar to that in 8CB, however, the impact of CdSe nanoparticles on *I-BPIII* transition temperature remains to be very weak.

4. Conclusions

High resolution calorimetry measurements were conducted to study the impact of surface-functionalised CdSe nanoparticles on phase transitions in two liquid crystals, 8CB and CE8. In both 8CB+CdSe and CE8+CdSe mixtures the phase transition temperatures are shifted even for the lowest CdSe concentration except *I-BPIII* in CE8+CdSe mixtures. In case of 8CB+CdSe the *I-N* phase transition remains weakly first order, and the *N-SmA* phase transition remains continuous for both measured concentrations. In CE8+CdSe mixture is shown that by increasing a concentration of CdSe nanoparticles the C_p anomaly of the *I-BPIII* phase transition does not change significantly except for significant decrease of latent heat. For the other phase transitions *BPIII-BPI*, *BPI-N**, and *N*-SmA* already small amount of CdSe NPs strongly suppress the heat capacity values. Our results show that in contrast to silica

aerosils, the CdSe nanoparticles have significant impact on ordered phases, but little impact on disordered phase such as *BPIII* even for small CdSe concentration. This fact allows significant stabilization of *BPIII* phase by mixing functionalised CdSe nanoparticles [9].

Acknowledgments

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