Liquid Crystals

Influence of the size and the attached organic tail of modified detonation nanodiamond on the physical properties of liquid crystals

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For the functionalisation of the detonation nanodiamond (DND), we attached via grafting carboxylate groups, leading to only one of such groups per 5000–6000 carbon units. Activation of the COOH-surface functionalised groups allowed the attachment of various organic tails. Dielectric and electro-optical properties of nematic liquid crystalline mixtures (LCMs) doped with modified DND (MDND) have been investigated. It is established that the effect of MDND on the dielectric properties of the LCMs depends on the size of the nanoparticles and the type of rod-like elongated organic molecules attached to the MDND. It was found that nanoparticles of small size (4–5 nm) do not significantly affect the parameters of LCMs. At the same time, the conglomerates based on MDND of about 50 nm or about 100 nm in diameter can increase or decrease the dielectric anisotropy and the response time of LCMs to about 1.5–2.5 times, depending on the polarity of the tails.

1. Introduction

The investigation of the influence of nanoparticles on the properties of liquid crystals (LC) has become a continuous scientific interest in recent years.[1] The composition of liquid crystalline mixture (LCM) with dielectric,[2] semi-conducting [3] and metallic [4] nanoparticles has been investigated. It has been shown that small amounts of nanoparticles to a great extent modify dielectric, optical and magneto-optical properties of LC hosts.[5] But out of all the nanomaterials, diamond nanoparticles (DNPs) and carbon nanotubes (CNTs) seemed most promising in this regard. This is due to the fact that the nanotubes having elongated shape similar to that of the LC molecules can be orientationally ordered by the nematic matrix.[6,7] This led to some effects, such as changes of the viscosity of the LCMs, an improvement of the threshold and the dynamic characteristics [8,9] and the emergence of the electro-optic memory.[10] All these effects are related to dielectric properties of LC-CNT composites. Interesting investigations of the dielectric characteristics in order to understand the unique properties of LC-CNT compositions were presented by Dierking et al. [6,8] It was shown that the dielectric relaxation time increases with the CNT concentration. This suggests a strong interaction between LC molecules and CNT as well as an increase of the viscosity. Remarkably, the spectra for $c \geq 0.05$ wt.% could not be fitted using the Debye equation due to the essential electron polarisation of samples introduced by CNT.[11]

DNP is also an attractive material for scientific and technological applications. Its high chemical and mechanical resilience, high surface stability and high thermal conductivity make diamond a promising candidate in the field of electrochemistry.[12] In contrast to the tubes, DNPs have a spherical form. DNPs greatly influence the conductivity of LCs as well as modify their electro-optical response. It was found that the insertion of DNPs may result in significant ionic rectification of LCMs because of trapping of the ionic impurities by the nanoparticles. In parallel, at sufficiently high loading, such a doping essentially increases the permittivity of the LC layers, mainly due to randomisation of the LC alignment.[13] This makes these objects rather suitable for the improvement of their operating characteristics.

Detonation of oxygen-deficient explosives in an inert medium produces ultra-fine diamond particles having diameters of 4–5 nm. This has been done four decades ago, but this novel form of diamond has never been isolated as pure product thereafter. One reason for this might be core aggregates having a diameter of 100–200 nm are extremely tight and could not be broken up by any known methods of de-aggregation. After a number of futile attempts, Krüger et al. [14] was able to obtain primary particles using the recently emerging technique of stirred-media milling with micron-sized ceramic beads. The

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milled aqueous slurry of nanodiamond gave a stable, thick and dark-coloured colloidal suspension. After soft sonication, dynamic light scattering measurements showed a sharp distribution in the single-digit nano-range, and high-resolution transmission electron microscopy resulted in a average diameter of 4.4 nm for separate particles in agreement with X-ray results, leading to 4–5 nm.

Basically one can differentiate between three major steps, leading to the conversion of carbon-containing explosives to modern DND products, namely synthesis, postsynthesis processing and modification. The processing includes separation of the detonation soot from metallic impurities and non-diamond carbon impurities. Typically, this has to be done during process admixture; for example, the diamond carbon powder is subjected to thermal oxidation via nitric acid under pressure, allowing the separation of the diamond phase.[15] While the primary DND particle size is 4–5 nm, they are tightly and loosely bound forming aggregates. The typical commercial polydispersed DND powder subjected to powerful ultrasonic treatment exhibits average aggregate sizes of 200–400 nm.[16]

Nanodiamonds are unique among the class of carbon nanoparticles because of their intrinsic hydrophilic surface. The surface contains a complex array of chemical groups, including carboxylic acids, esters, ethers, lactones and amines. Alteration in DND surface can lead to a bunch of chemical functionalities, compared with nanoscale diamond powders, since almost 15% of all atoms in the DND primary particle are located on the surface and therefore are solvent accessible. Oxidation of the soot or further oxidation of DND containing non-diamond carbons can be based on singlet oxygen in liquid media, oxygen or ozone [17] in a gas phase. This results in a rather advanced oxidation, leading to predominant carboxylic acid groups on the DND surface. Although the surface of bulk diamond has been considered to be chemically inert, DNDs contain numerous oxygen-containing surface functional groups (i.e., –COOH, –OH) introduced during purification and modification stages.[18] Due to various methods of surface functionalisation, DNDs can be readily incorporated into other matrices useful for attaching organic groups.

DND shows potential for applications in energy storage, composites and catalysis. Further DND can be used in electroanalysis, electrochemical double-layer capacitors and batteries. Other potential biomedical applications include the use of nanodiamonds as supporters for solid-phase peptide synthesis and as sorbents for detoxification and separation.[19]

Our interest was devoted to the characterisation of suspensions using a special class of nanodiamond material of sizes 4–5 nm, often called in the literature as 'ultradispersed diamond' or 'detonation nanodiamond' (DND), produced via the detonation of carbon-containing explosives.[15] The studies were directed to attach functionalised organic groups to the surface of the DNDs. Dielectric and electro-optical investigation of LCMs doped with modified DND (MDND) of small size (4–5 nm) and doped with conglomerates of MDND of about 50 and 100 nm in size with different polar groups at the surface has been conducted. Our primary goal was to compare dielectric and electro-optical properties of conglomerates of MDND dispersed in LCMs with those of small-size MDND.

2. Materials and methods

For further functionalisation of the DND, we focused on the attachment of several carboxylate groups. DND via oxidation with nitric acid comprises (back-titration method) one carboxylate group per 5000–6000 carbon units, not enough for further chemical modification. The oxidation of external non-diamond carbon atoms leads to formation of hydroxyl groups, carbonyl groups or groups with isolated double bonds and esters, amides and nitriles, which can be used for further functionalisation of nanodiamond. The peculiarity of the oxidation process is to obtain an appropriate activity for many standard oxidation reagents ($KMnO_4$, CrO_3). Sometimes heavy metals are adsorbed on the DND, leading to complications in the preparation of pure samples. To increase the number of carboxylate groups, we used the technique of the ozonolysis of the sp^2 hybridised carbon atoms on the surface of the DND.

Some details of the ozonolysis will be highlighted: Suspension of DND with concentration 5 g per litre (water) were transferred into an apparatus producing ozone at a flow rate of 10–15 ml/second, leading to 3–5% of ozone in the gas mixture. Before using, the prepared ozone was purified by washing in the flask with concentrated sulphuric acid and then passed over granulated potassium hydroxide. The last one is able to oxidise the intermediate-formed ozonide to a carboxyl group, whereas hydrolysing the ester group leads to a carboxylate group. About 0.1 g of caustic soda was added to the suspension of DND in water under stirring; thereafter, ozone is passed for 2 hours (more than 300 times in excess). The final oxidation has been reached by adding 30 ml hydrogen peroxide (30%) while incubating the mixture for 1 hour. Then, 10% aqueous hydrochloric acid was added until pH 2–6 acidification, held for 1 hour. Finally, the upper clear layer was carefully decanted and the precipitate was centrifuged followed by washing with water 8–10

times. Residual water was removed by washing two times with dioxane. After drying overnight at room temperature, the content of carboxyl groups was determined. This procedure led to a two to three times increase in the content of carboxylate groups. The molecular weight (excluding the sorption of water) was between 1300 and 1560, depending on the kind of experiments.

The next step is the activation of the COOH-surface functional groups by acylchloride obtained by boiling nanodiamond with $SOCl_2$:
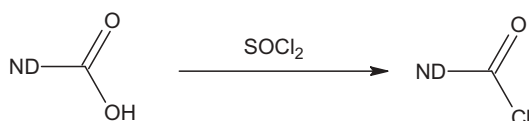

Acid chloride DND. To 2 ml thionylchloride, 1 g suspension of ozonised DNA in 30 ml dichloroethane was added and heated for 1 hour under reflux. After cooling, the product was separated by decantation and washed two times with dichloromethane.

Dicyano-4-4'-diphenyl DND. A mixture of 1 g DND chloride and 0.1 g 4-hydroxy-4'-cyanobiphenyl dissolved in 20 ml pyridine was heated at 25°C for 3 hours. Then, the ester of DNA was separated and washed with distilled water, twice with dimethylformamide (DMF) and three times with dichloromethane. The resulting ester was dried in air at 60°C for 3 hours.
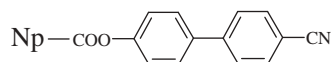
4-Octylphenyl DND. A mixture of 1 g chloride of DND and 0.1 g of 4-octylphenol in 20 ml of pyridine was heated at 25°C for 3 hours. Then, the ester of DNA was separated and washed with distilled water, twice with DMF and three times with dichloromethane. The resulting ester was dried in air at 60°C for 3 hours.
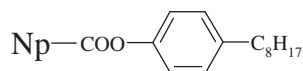
For the LC host, two mixtures with different polar liquid crystalline compounds were prepared. **M-1** is the mixture based on the compound with the CN end group and **M-2** is the mixture based on the compound with the OCF_3 end group. The selection of two mixtures was done in order to verify the effect of MDND on the parameters of LCMs with different polar groups. For further experiments, dicyano-4-4'-diphenyl DND of small size (4–5 nm) (**N-1**) and the conglomerates on the basis of dicyano-4-4'-diphenyl DND with size about 50 nm (**N-2**) and about 100 nm (**N-3**) were investigated. The conglomerates based on 4-octylphenyl DND with size about 50 nm lead to (**N-4**). The particles and LC's at certain proportions were manually mixed and then subjected to ultrasonic agitation for 20 min in EMMI-20. Then, in the mixtures **M-1 and M-2,** respectively, 0.5% of **N-1, N-2, N-3** and **N-4** was added, leading to the compositions **NLH-1, NLH-2, NLH-3, NLH-4** and **NLH-5, NLH-6, NLH-7, NLH-8,** respectively. For a more detailed study of the influence of the number (amount) of conglomerates of MDND on the dielectric properties of LCM, 0.2%, 0.4%, 0.6%, 0.8% and 1% of **N-3** and **N-4** have been added to the **M-1,** thereby the compositions **NLH-3a, NLH-3b, NLH-3c, NLH-3d** and **NLH-4a, NLH-4b, NLH-4c, NLH-4d** were, respectively, obtained. The dispersions prepared in such way were filled in the cells with a thickness of 7 µm. The quality of LC alignment and the sample morphology were studied using polarising optical microscope (Olympus BX-51P) interfaced with CCD camera at 100× in the transmission mode, under crossed polarisers using convergent white light. Electro-optical parameters were measured using the set-up consisting of a He–Ne laser ($\lambda = 632.8$ nm), rotating table, Linkam LTS 350 hot stage coupled with the temperature controller Linkam CI 94 (with an accuracy ±0.1°C), function generator HP 33, 120A and the digital oscilloscope HP Infinium. The frequency and the voltage of the sinusoidal electric field were 1 kHz and 10 V for all the electro-optic measurements. Dielectric measurements were carried out by impedance analyser 4192A at frequency 1 kHz.

3. Results and discussion

After explosion, DND products appear with different shapes. Separation of the fractions with a different size is carried out via the deposition time of DND from slurry of agglomerates in the solvent. During the oxidation of the saturated groups at the surface of nanodiamonds, mainly carboxylate groups [20] appear to have a high amount of oxygen. Those carboxylate groups are more susceptible at the vertex of the anisometric particles. It is plausible to assume that during the agglomeration nanoparticles end up in rod-like shapes.[21]

Intermolecular interaction via ionic and van der Waals forces facilitates the formation of agglomerates; moreover, there are condensation processes via
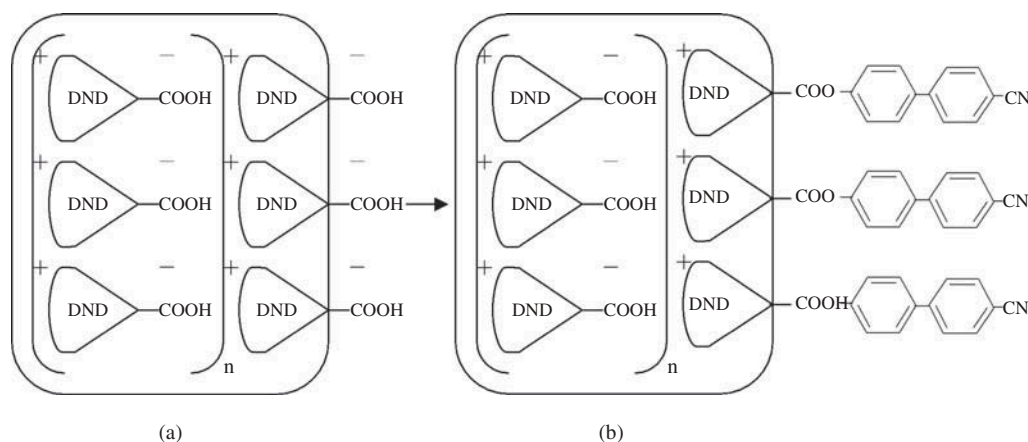
Figure 1. Conglomerates of DND (*n* > 15) before (a) and after (b) modification.

the carboxylate groups.[21] This preserves the symmetry of the diamond structure and the preferential location of carboxyl groups on one side of the elliptical structure (Figure 1a). As a model, the functionalised carboxylate groups will mainly sit on one side of the ellipse polycrystal (Figure 1b).

The choice of the used MDND was motivated by the fact that small particles will be easily dispersed into the LCMs and will be stabilised by the tail-like organic molecules that prevent their premature precipitation. Conglomerates of MDND can so be fixed inside the volume of LCMs during a few hours.

Interesting for us was to study the impact of different MDND on the dielectric characteristics of LCMs. Figure 2 shows the results of measurements of the dielectric permittivities for LCM with MDND and conglomerates of MDND modified dicyano-4-4′-diphenyl. It is seen that small MDND had no effect on these parameters independently on the magnitude of the dielectric anisotropy of LCMs. The 0.5% of any

polar dopant cannot change the parameters of the LC matrix.

Dielectric permittivities of pure LCMs and of LC nanocolloids containing conglomerates (50 nm, 100 nm in diameter) of MDND were different. We think this is due to the fact that the long-chain conglomerates of MDND have a permanent dipole moment parallel to the surface. This assumption is based on the fact that the functionalised organic groups attached on the surface of the DNDs and carried (with) a permanent dipole moment are oriented parallel to the planar aligned molecules of LC. This alignment is the result of elastic interactions between the LC molecules and the molecules of functionalised organic groups. In this case, the long-chain conglomerates of MDND are able to change the polarisability anisotropy of the mixtures, namely the perpendicular component has been increased. It is thinkable when the electric field has been applied, conglomerates of MDND become not reoriented
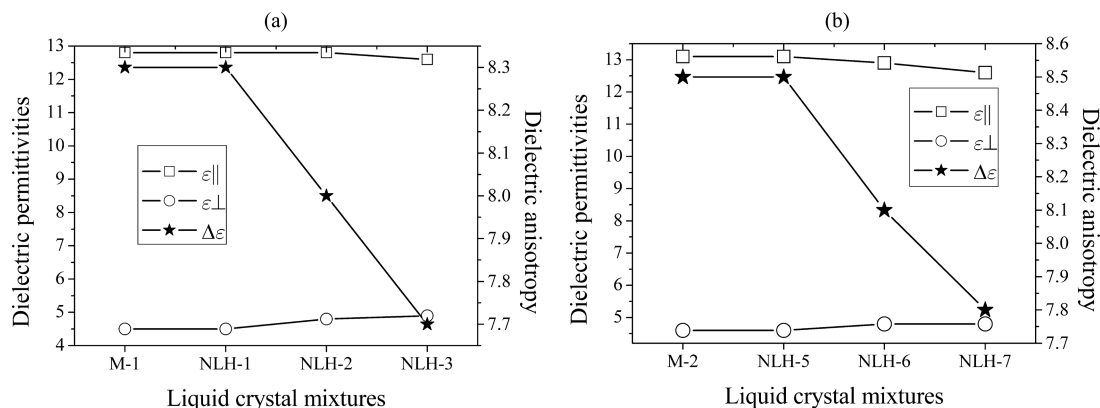

Figure 2. Dependence of dielectric permittivities and dielectric anisotropy of M-1 (a) and M-2 (b) on the size of nanoparticles; lines are guides for the eye.

like the LC molecules do, rather their organic tails on the surface became a little bit tilted; therefore, parallel dielectric permittivities and consequently the magnitude of the dielectric anisotropy have been decreased (Figure 2).

One should note that the influence of MDND on the parameters of LCMs with different polar compounds was the same. Naturally, the decrease of the dielectric anisotropy led to an increase of the switching times, especially fall time. Figure 3 shows that for LCMs with small MDND, the switching times remained virtually unchanged, and for LCMs with conglomerates of MDND, the switching time was reduced 1.5–2.5 times.

Similar studies were conducted with LCMs in which conglomerates of MDND with non-polar tails have been added. The effect of such conglomerates was opposite compared to those with the conglomerates MDND having polar tails. Of course, dielectric permittivities for pure LCMs and LCM nanocolloids with **N-4** were also different. This behaviour can be explained, assuming such particles are formed into long chains. In this case, they have a permanent dipole moment, which is directed at an angle to the long chain of **N-4**. Under this assumption, one can explain that the value of the dielectric anisotropy of the LCMs has been reduced. The polarisability anisotropy of mixtures, namely the perpendicular component, has been decreased. In the case where the electric field was applied, we assume **N-4** is not totally reoriented together with the LC molecules, and therefore parallel dielectric permittivity is slightly increased and consequently the magnitude of the dielectric anisotropy is increased (Table 1). The results presented in Table 1 have shown that the switching time decreased for compositions with **N-4** as expected.

At the end of this work, we performed experiments with LCMs in which different concentrations of **N-3** and **N-4** were added. Figure 4 shows that the

Table 1. Dependence of dielectric permittivities, dielectric anisotropy and electro-optical parameters of M-1 and M-2 on the conglomerates of N-4.

Mixture	$\varepsilon_\parallel$	$\varepsilon_\perp$	$\Delta\varepsilon$	V_{10}, V	V_{90}, V	τ_{rise}, ms	τ_{fall}, ms
M-1	12.8	4.5	8.3	1.50	2.07	0.71	24.27
NHL-4	13.0	3.9	9.1	1.42	2.03	0.55	18.04
M-2	13.1	4.6	8.5	2.00	2.47	1.42	29.28
NHL-8	13.4	3.9	9.5	1.79	2.22	0.82	15.33

strong influence of conglomerates of MDND on the main parameters of LCMs was observed at concentrations below 0.75% equivalent to the saturation of related parameters.

4. Conclusions

It is established that the effect of DND on the mesomorphic, dielectric and electro-optical properties depends on the size of nanoparticles and the type of tail-like organic molecules.

As expected, nanoparticles of small size (4–5 nm) do not significantly affect the physical properties of LCMs regardless of the value of their dielectric anisotropy. The addition of particles slightly increased the phase transition temperature of LCMs.

At the same time, the conglomerates of larger size (50 and 100 nm) can, depending on the polarity of the tails, increase or decrease the dielectric anisotropy and the response time of LCMs to about 1.5–2.5 times. Dicyano-4-4′-diphenyl DND and 4-octylphenyl DND decreased and increased, respectively, the dielectric anisotropy and switching time of LCMs. The change of the dielectric anisotropy and the switching time goes in line with the increase of the amount of DND particles.

Experiments with nanoparticles need to pay great attention to cleanliness to ensure reproducibility of
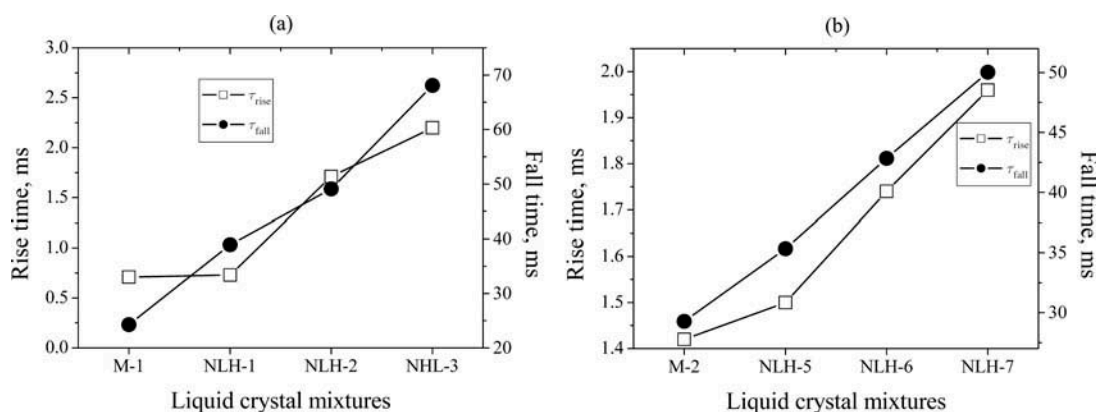

Figure 3. Dependence of the switching time of M-1 (a) and M-2 (b) on the size of nanoparticles; lines are guides for the eye.
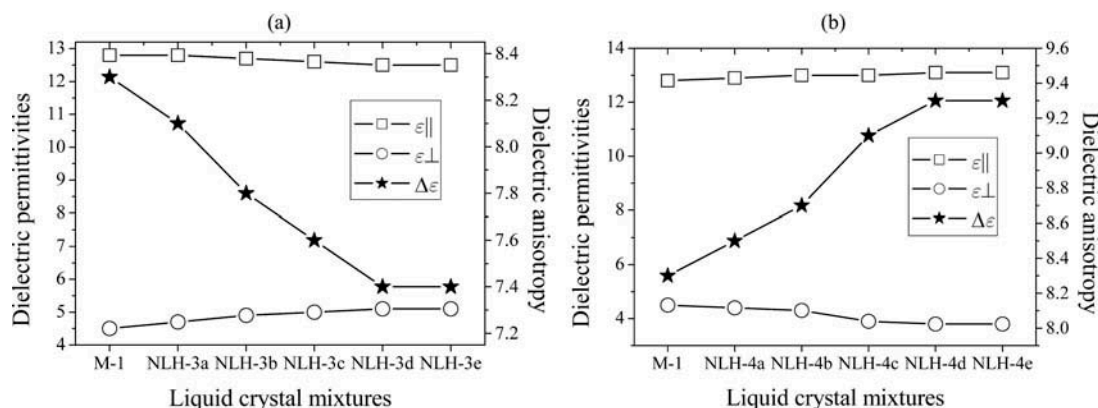
Figure 4. Dependence of dielectric permittivities and dielectric anisotropy of M-1 on the concentration of N-3 (a) and N-4 (b); lines are guides for the eye.

the results. It should be noted that each experiment was performed in three different cells. Extension in the measurements was less than 5%.

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