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Liquid crystal mixtures with non-mesogenic dopants as optimized host matrices for functional nanoparticles

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Liquid crystal suspensions of 4CHCA with carbon nanotubes and laponite modified by introducing of lauric and decanoic acid as non-mesogenic dopants were considered. The homogeneity of the resulting systems was investigated by the methods of DSC, spectrophotometry, and polarizing optical microscopy. The possibility of varying the temperature range of the nematic mesophase of 4CHCA by changing the dopant concentration and its effect on the optical properties of the system is shown.

Keywords: nanoparticles, liquid crystals, differential scanning calorimetry, decanoic acid.

Рідкокристалічні суміші з немезогенними допантами як оптимізовані матриці-господарі для функціональних наночастинок. *С.С.Міненко, Н.А.Касян, О.М.Самойлов, Л.М.Лисецький*

Розглянуто рідкокристалічні суспензії 4CHCA з вуглецевими нанотрубками та лапонітом модифіковані шляхом внесення лауринової та деканової кислот як немезогенних допантів. Досліджено гомогенність утворюваних систем методами ДСК, спектрофотометрії та поляризаційної оптичної мікроскопії. Показано можливість варіювання температурними межами мезофази 4CHCA за рахунок зміни концентрації допанту та його вплив на оптичні властивості системи.

1. Introduction

One of the rapidly expanding fields in nanophysics and nanomaterials science is the development of composite systems in which nanoparticles (NP) are dispersed on the molecular level in a host matrix of soft matter nature. Among such matrices, one can note, e.g., polymers of different types, as well as still not-so-common anisotropic organic media, such as liquid crystals (LC). Dispersions of various nanoparticles in liquid crystals are at the cutting edge of research, judging from numerous reviews published quite recently [1–4] and breakthrough publications opening quite new directions of research in this field [5–9].

A multiplicity of possible practical applications of such composite nanomaterials requires a high-quality selection of a LC matrix for each type of nanoparticles which would ensure the best performance. As a characteristic example, one can consider luminescent nanoparticles (e.g., cerium, titanium, or zinc oxides [10–14]). In this case, the LC matrix used should not display bands of absorption or luminescence that would overlap with the excitation and emission bands of the nanoparticles. Another possible requirement is the possibility of varying the phase transition temperatures in a broad temperature range, since the change in luminescence characteristics or other important physical parameters at the nematic to isotropic transition could be a basis of various novel applications [8, 15]. Such requirements exclude most of the known LC systems, e.g., nematic mixtures conventionally used in electrooptics.

To avoid these drawbacks, we considered LC substances based on cyclohexanecarboxylic acids, such as 4-butylcyclohexanecarboxylic acid (4CHCA) and its hexyl homologue 6CHCA [16, 17]. Due to the absence of double bonds in their chemical structure, these mesogens show high transparency in the visible and near UV range. However, their nematic phase expands up to relatively high temperatures (38–91°C for 4CHCA), which makes it rather difficult to stabilize the temperatures close to the nematic to isotropic phase transition in conditions of most practical applications. Lowering the nematic range could be possible by adding non-mesogenic dopants with sufficiently high solubility that would not deteriorate the CHCA optical properties.

2. Experimental

Differential scanning calorimetry (DSC) studies were performed using a microcalorimeter Mettler DSC 1 (Mettler Toledo, Switzerland). The mixtures (~ 20 mg) were placed into an aluminum crucible and sealed, and thermograms were recorded in consecutive scans on heating and cooling (scanning rate 5°C/min). An experimental error was ±0.1°C for the isotropic transition temperature.

Polarizing optical microscopy studies were carried out using Micromed Polar 3 (Micromed).

Optical transmission spectra were measured in sandwich-type LC cells using a Shimadzu UV-2450 spectrophotometer (Shimadzu, Japan) within the spectral range of 300–900 nm. The measurements were carried out within a temperature range of 20–90°C both on heating and cooling, and the temperature values were changed in 0.2–0.5°C steps and stabilized using a flowing-water thermostat (±0.1°C).

To modify the CHCA matrix, aliphatic carboxylic acids, namely, dodecanoic (lauric) (LA) and decanoic (DA) were used. All carboxylic acids were re-crystallized from hexane and further purified by chromatography.

Nanoparticles were dispersed in the LC host by adding the appropriate weights of the carbon nanotubes or laponite to the LC solvent in the isotropic state with subsequent 1–2 min sonication of the mixture using a UZD-22/44 ultrasonic disperser (Ukrrospribor, Sumy, Ukraine).

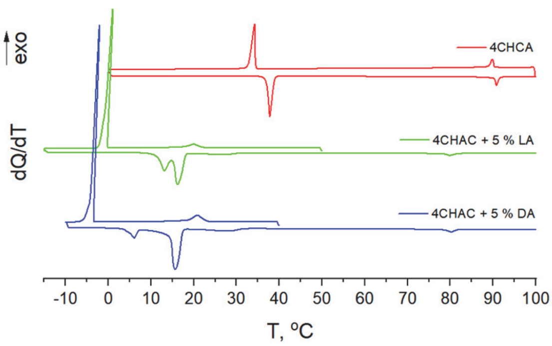

Fig. 1. DSC thermograms of 4CHCA (*1*), 4CHCA + 5 % LA (*2*) and 4CHCA + 5 % DA (*3*) on heating (endo) and cooling (exo). Cr, N and I correspond to crystalline, nematic and isotropic phases, respectively. Scanning rate 2 °C/min, sample mass 20 mg.

3. Results and discussion

The phase transition temperatures of 4CHCA (pristine and doped with 5 % LA or DA) were determined by means of differential scanning calorimetry (DSC) in the heating and cooling modes. The corresponding DSC thermograms are shown in Fig. 1.

The behavior of 4CHCA was typical for nematic LC, with a slight temperature hysteresis on cooling for both phase transitions. As could be expected, the introduction of LA or DA lowers the phase transition temperatures. At room temperature, after some time small crystals precipitated out from the nematic bulk. This was more pronounced for LA (probably because of its higher melting temperature), so, we carried out further experiments with DA due to its higher solubility.

DSC thermograms of the 4CHCA + DA system for different concentrations of the decanoic acid are shown in Fig. 2a, and the peaks of their nematic-isotropic phase transitions in Fig. 2b. Higher DA content leads to lower isotropic transition temperatures, the peaks are broadened, and additional peaks appear for the solid-nematic transitions. However, at DA concentration of 25%, the appearance of DSC thermograms is similar to those of pure compounds, suggesting the formation of a eutectic-like state. The DSC data are summarized in Fig. 3.

From the phase diagram (Fig. 3) it is clear that the mixture of 75 % 4CHCA + 25 % decanoic acid is really close to the eutectic. A theoretical estimate of the 4CHCA/DA eutectic obtained using our DSC data using Schroeder-van Laar equations [18, 19], gives the DA concentration of ~ 21 % and

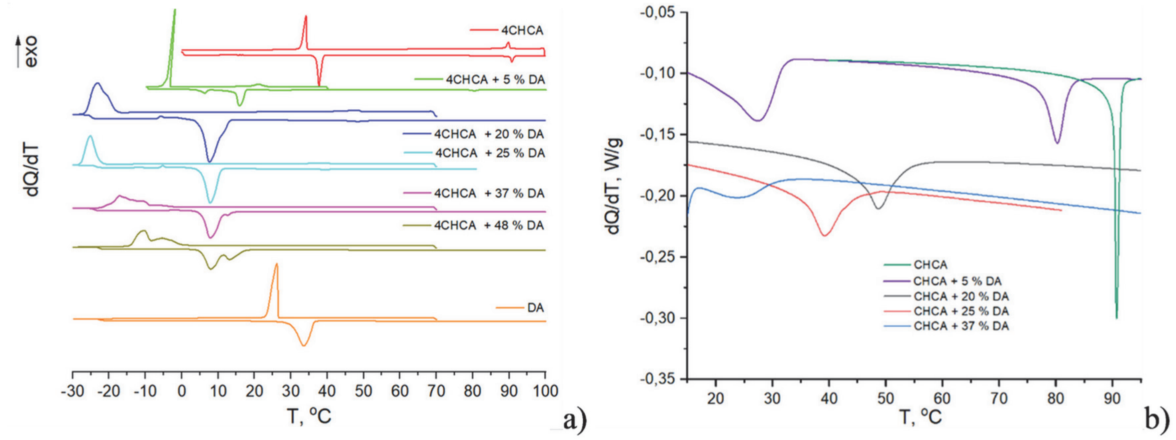

Fig. 2. DSC thermograms of 4CHCA + DA system for different concentrations of DA (a) and peaks of nematic-isotropic phase transitions (b)

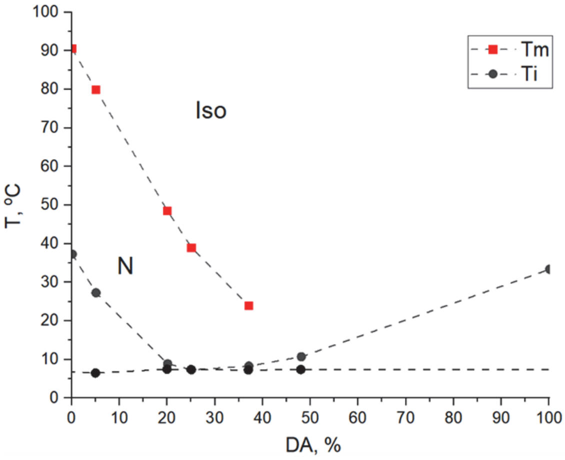

Fig. 3. Binary phase diagram of the system 4CHCA + decanoic acid

temperature ~ 4.3°C; thus, DA concentrations of 20–25 % seem to be optimal for the eventual use of CHCA + decanoic acid systems as a host matrices for nanoparticles.

To study the influence of nanoparticles on the LC matrix described above, we took, as an example, single-walled carbon nanotubes (SWCNT), which were widely studied earlier in different LC matrices [20]. By means of polarizing optical microscopy (POM), the textures of 4CHCA + 20 % DA + SWCNT were shown to demonstrate good homogeneity and uniform distribution of alloying impurities inside the matrix in the nematic phase and their aggregation in the isotropic phase (Fig. 4). The observed pattern is typical for nematic liquid crystals. This agrees with our DSC data, so, such systems could be used as hosts for nanoparticles.

As another viability test of the given paradigm, we used temperature variation of optical transmission measured according to the procedures used for LC systems with dispersed nanoparticles [21, 22]. The results are shown in Fig. 5. The transmission was measured at 800 nm in 20 μm thick cells. The investigated LC matrix shows the highest optical transparency. The introduction of CNT noticeably lowers the transmission, which undergoes a jump at the isotropic transition, suggesting efficient integration of the nanoparticles into the orientationally ordered nematic structure, like in other LC systems under similar conditions [21–24]. It is interesting to note that the introduction of laponite nanoparticles [23, 25] does not substantially lower the transmission, and the jump is not so obvious, suggesting its less efficient integration into the LC structure.

4. Conclusions

The results obtained can be generalized as an approach for optimization of liquid crystalline matrices as hosts of composite materials with dispersed nanoparticles. Mesomorphic characteristics of the matrix selected for a specified type of functional nanoparticles can be modified by introducing non-mesogenic dopants of similar chemical nature. Taking alkylcyclohexanecarboxylic acids as example, the homogeneity of the obtained systems doped with dodecanoic and lauric acid was studied by means of DSC, spectrophotometry and optical polarizing microscopy. It has been shown that matrices of this type could be applicable as hosts for dispersions of carbon nanotubes and other nanoparticles.

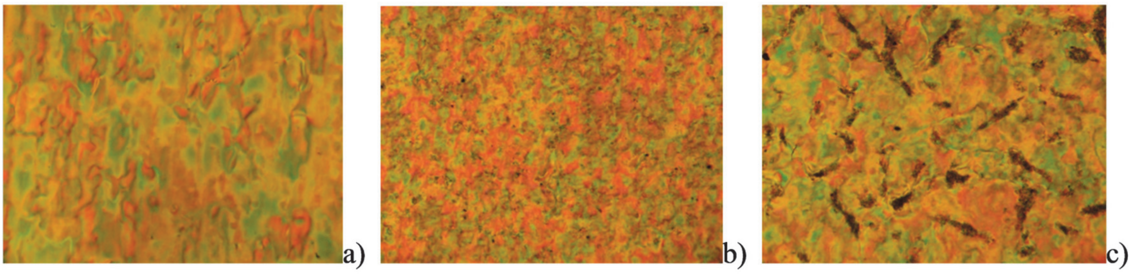

Fig. 4. Microphotographs of nematic liquid crystal textures 4CHCA + DA systems. Composition: a) 4CHCA + 20 % DA, b) 4CHCA + 20 % DA loaded with 0.05 % of SWNT in the nematic phase, c) 4CHCA + 20 % DA loaded with 0.05 % of SWNT in the isotropic phase. Cell thickness 20 μm, temperature 20°C, size of imaged area 500×500 μm, crossed polarizers

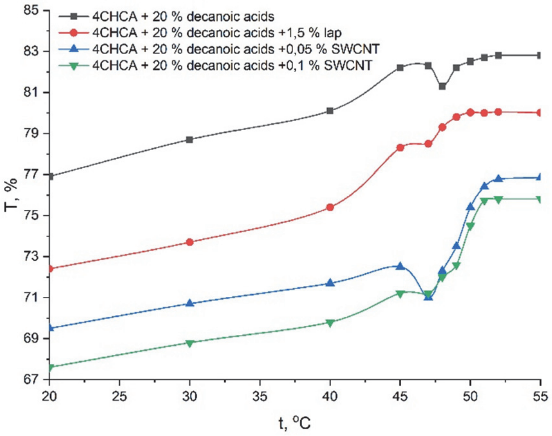

Fig. 5. Optical transmission at 4CHCA + 20 % DA doped with SWCNT and laponite

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