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Liquid Crystal-in-Water Emulsion Stabilized by Layer-by-Layer Adsorption of Polyelectrolytes and Magnetite Nanoparticles

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Abstract—We propose a method for stabilizing and modifying the dispersed phase of a liquid crystal-in-water (LC/water) emulsion using the sequential adsorption of polyelectrolytes and magnetite nanoparticles, which leads to the formation of LC-filled nanocomposite microcapsules. The obtained samples were studied by optical microscopy and Raman spectroscopy. It is established that the LC-filled nanocomposite microcapsules can move under the action of an external magnetic field.

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Liquid crystal (LC) composite materials represent ensembles of LC droplets with dimensions ranging from hundreds of nanometers to tens of microns dispersed in a polymer matrix [1, 2]. These composites are widely used in display technology [3] due to their unique electrooptical properties, which can be controlled by external factors (electric and magnetic fields, temperature, deformation) [1, 2]. The optical properties of LC composites are determined by the orientation of LC molecules at the LC–polymer interface. This orientation depends to a considerable degree on the chemical composition of the polymer and/or the interface, which makes it possible to use LCs in chemical and biological sensors [4]. LC composites can be obtained by various methods, in particular, based on the phase separation of an initial LC–polymer mixture [1, 2] into LC droplets and a polymer matrix; an alternative method is based on the filling of porous materials (glasses, polymers, silicon, etc.) by LCs [2].

In recent years, method for layer-by-layer adsorption of polymers on solid and liquid cores have been developed, which can be used to obtain stable polymer microcapsules [5, 6]. Lockwood et al. [7] sequentially deposited polyelectrolyte layers on thermotropic LC droplets dispersed in water and obtained stable microcapsules containing LC molecules with bipolar orientation. Using a method for the inclusion of magnetic nanoparticles into polyelectrolyte shells developed in [8–10], it is possible to obtain microcapsules that can be displaced and concentrated by an external magnetic field. It was also shown [11, 12] that the permeability of polyelectrolyte microcapsules can be controlled by a variable magnetic field.

This Letter presents the results of experiments on the stabilization of an LC/water emulsion by sequential adsorption of polyelectrolytes and magnetite nanoparticles. The samples were studied by optical microscopy, Raman spectroscopy, and confocal Raman microscopy. Experimental data were interpreted by comparison to the results of theoretical calculations of the Raman spectra of LC molecules.

The experiments were performed with emulsions of a nematic liquid crystal (NLC) of the ZhK-807 type, representing a five-component mixture of R-oxycyanobiphenyls (R = methyl, amyl, propyl, hexyl, heptyl) [13] obtained from the Research Institute of Organic Semiproducts and Dyes (Russia), solutions of poly(sodium styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) purchased from Sigma-Aldrich Co., and an aqueous sol of magnetite (Fe_3O_4) nanoparicles stabilized with citric acid (Sigma-Aldrich Co.). Figure 1 shows the typical image of magnetite nanoparticles examined by transmission electron microscopy (TEM), which shows that the average size of nanoparticles is within 10–20 nm and the particles form aggregates which are typical of magnetite nanoparticles.

Encapsulation of the NLC emulsion in water was performed by the method of Lockwood et al. [7] using solutions of the anionic (PSS) and cationic (PAH) polyelectrolytes. The emulsions were prepared by

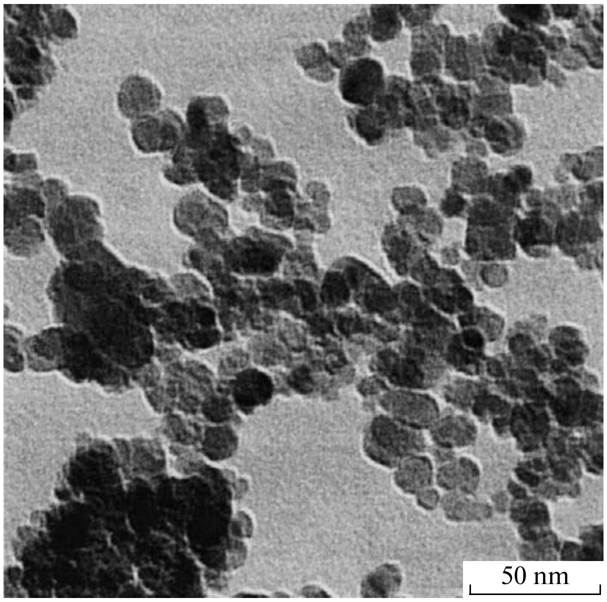

Fig. 1. TEM image of magnetite nanoparticles.

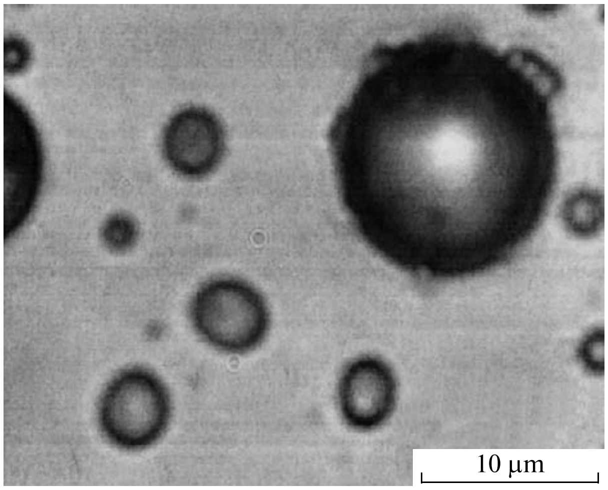

Fig. 2. Optical micrograph of NLC droplets in an emulsion stabilized by nanocomposite layers.

mixing 0.2 ml of the initial NLC and 0.8 ml of an aqueous PSS solution with a concentration of 4 mg/ml. The mixture was ultrasonically treated on a URSK N070 setup (Russia) for 1 min at a frequency of 27 kHz and a power density of 3.5 W/cm^2. To this mixture was added 1 ml of a solution of PAH (2 mg/ml) in 0.5 M sodium chloride solution and the polyelectrolyte adsorption was carried out for 15 min after which the excess polyelectrolyte was removed by rinsing in deionized water.

It was experimentally established that the formation of a PSS/PAH polyelectrolyte bilayer is the main condition necessary for the stabilization of NLC droplets in the emulsion. The PAH molecules adsorb at the NLC/aqueous PSS solution interface and interact with PSS molecules present on the surface of spherical NLC droplets, which leads to the formation of a polyelectrolyte complex. Monitoring of the state of the initial emulsion with NLC droplets containing no adsorbed PAH layer showed that this mixture separated into two phases with the time. This behavior indicates that the presence of only a layer of adsorbed PSS is insufficient to stabilize the NLC emulsion.

In the following experiments, multilayer polyelectrolyte shells on NLC droplets were formed by the method of layer-by-layer adsorption. According to this, PAH and PSS molecules were sequentially adsorbed from their 2 mg/ml solutions in 0.5 M aqueous NaCl solution. The time of incubation in each polyelectrolyte solution was 15 min. After each adsorption stage, the emulsion was triply rinsed in deionized water. Nanocomposite coatings on NLC droplets were obtained using an aqueous sol of magnetite (Fe_3O_4) nanoparticles. Since the nanoparticles were only stabilized by citric acid, the particle surface was negatively charged. Magnetite nanoparticles were adsorbed on the surface of NLC droplets after the adsorption of a cationic polyelectrolyte (PAH). The structures and compositions of nanodimensional shells formed on the surface of NLC droplets are presented in the table.

Samples of NLC emulsions were examined in an optical microscope (Olimpus LX71, Japan). Figure 2 shows the typical image of NLC droplets stabilized by a nanocomposite layer. The diameters of NLC particles varied within 2–15 μm. This spread is explained by the polydisperse character of the initial NLC emulsion in an aqueous PSS solution.

The chemical composition of emulsions was studied using the methods of Raman spectroscopy and confocal Raman microscopy (NTEGRA Spectra, NT-MDT, Russia). Figure 3a (curve *1*) shows the typical Raman spectrum of NLC in an emulsion, which was measured using laser excitation at a wavelength of 473 nm, a power of 35 mW, and a response signal accumulation time of 1 s.

In order to interpret the experimental data, we have calculated the Raman spectra of pentoxycyanobiphenyl using a PC GAMESS/Firefly program package [14] and imaged the results using GaussSum routine

Structures and compositions of shells on NLC droplets in emulsions stabilized by polyelectrolyte and nanocomposite layers

Sample no.	Shell structure and composition	Total number of layers
1	$(PAH/PSS)_3$	6
2	$(PAH/PSS)_2(PAH/Fe_3O_4)(PAH/PSS)$	8
3	$(PAH/PSS)_3(PAH/Fe_3O_4)$	8

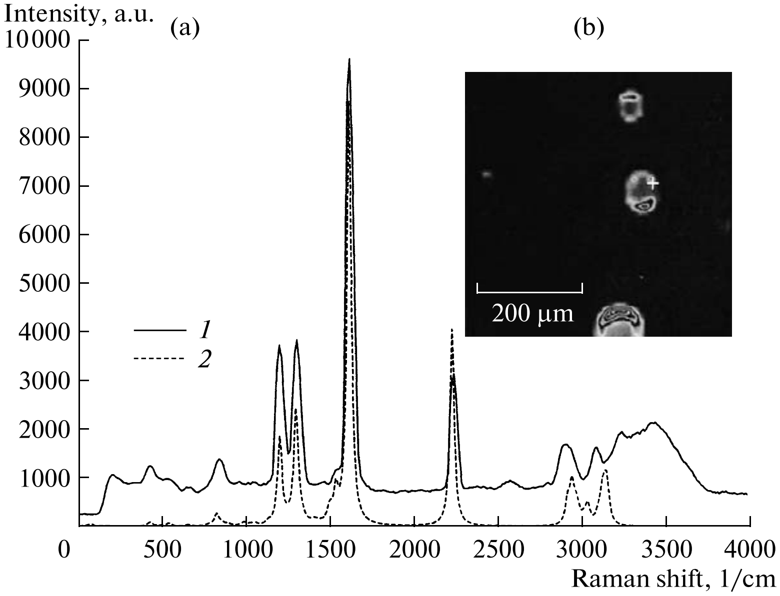

Fig. 3. Results of studying NLC emulsions by Raman scattering techniques: (a) experimental (curve *1*) and theoretically calculated (curve *2*) Raman spectra; (b) confocal Raman micrograph (bright/dark contrast encodes the 1600 cm^{-1} line intensity and the cross indicates the point where the spectrum presented in Fig. 3a was measured).

[15] for the total spectrum and wxMacMolOlt routine [16] for the molecular vibrational modes corresponding to separate spectral lines. The initial molecular geometry was set and the preliminary optimization was carried out by the molecular dynamics methods (for a Tripos 5.2 force field) using the Ghemical routine [17]. Calculations were performed using methods of the density functional theory on a B3LYP/6-31G level. The theoretical spectrum is presented for comparison in Fig. 3a by curve *2*, the intensity of which was normalized to the most intense peak in the experimental spectrum and frequency shift coefficient was set at 0.97. The most intense lines in the Raman spectrum correspond to the following vibrational modes of the NLC molecule: 1600 cm^{-1} (symmetric vibrations of carbon atoms in the benzene ring); 2300 cm^{-1} (stretching vibrations of C≡N bonds); 1300 cm^{-1} (stretching vibrations of C–C bonds between two benzene rings); 1330 cm^{-1} (stretching vibrations of C–C≡N bonds).

Figure 3b shows an image of the NLC droplets in the emulsion studied by the method of confocal Raman microscopy, where the bright/dark contrast encodes the intensity of the most intense line (~1600 cm^{-1}) in the Raman spectrum. This image was obtained using excitation with laser radiation at a wavelength of 473 nm and a power of 35 mW. The number of points in the scanned region was 50 × 50 and the signal accumulation time at each point was 0.1 s. The image clearly reveals the NLC contained inside microcapsules. It was also established in our experiments that NLC droplets with nanocomposite shells can be transferred along magnetic field lines under the action of a constant external magnetic field.

Based on the results presented above, we conclude that the proposed method can be used to obtain stable aqueous emulsions of NLC droplets and to modify the NLC droplets by magnetite nanoparticles. It is experimentally established that nanocomposite-coated microcapsules can be transferred by applying a constant external magnetic field.

We believe that aqueous NLC emulsions stabilized by the method of sequential adsorption of polyelectrolytes and magnetite nanoparticles can be used for the creation of biological and chemical sensors. The possibility of using NLC droplets with said coatings in data display and processing technology requires additional investigations.

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