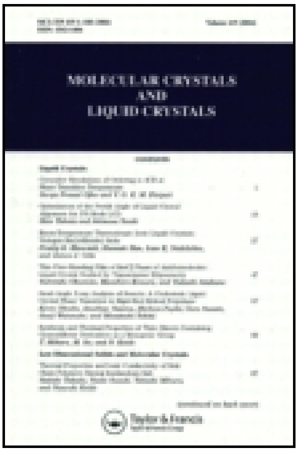

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Agglomeration of Silica Nanoparticles in Filled Nematic Liquid Crystals

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Agglomeration of Silica Nanoparticles in Filled Nematic Liquid Crystals

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The large memory effect of about 95 per cent was achieved in nematic liquid crystal filled with big hydrophilic silica nanoparticles (d=40 nm) and low surface area 50±15 m^2/g. We have measured the temperature dependence of transmittance and heat flow of this system. We have found a small but clearly positive shift of the nematic liquid crystal-isotropic liquid transition temperature with the increase of concentration of nanoparticles. The main origin of the large memory effect is the orientational influence of surface of the silica nanoparticle agglomerates. Agglomeration of nanoparticles is induced by orientational elastic forces of liquid crystal. This effect can be used to form regular or complex microstructures from silica nanoparticles. Applications of such a mixture also include 2-dimensional pressure imaging.

Keywords: agglomeration; silica nanoparticles; nematic liquid crystal

INTRODUCTION

The idea of combining interactions in the design of new synthetic materials and formation of desired structures with controlled ordering at different length scales was discussed recently.[1,2] The new self-organized materials can be produced on different length scales by balancing organizing forces. Several guideline principles and approaches have been proposed which include phase and microphase separation, surface segregation, mesophase formation, adsorption and crystallization. The dispersions of small nanoparticles in anisotropic fluids are one of such subject of interest for a long time,[3–6] where surface interactions strongly influence the orientational ordering of liquid crystal (LC). The first application of nematic liquid crystal, filled with small microparticles (FNLC) for light shutter

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was proposed by Hilsum in 1976.[6] A nematic LC was dispersed with micron-size soda glass spheres. Light scattering was caused by the refractive index mismatching of the liquid crystal with that of the soda glass. In 1991, R. Eidenschink and W. H. De Jeu have introduced new liquid crystal display technique, based on FNLC.[3] They found out that solid nanoparticles of pyrogenic silanised silica, dispersed in the nematic material cause the static light scattering not because of refraction index mismatching as in PDLC or in micron-size soda spheres dispersed in LC but due to strong variation of the local orientation of the nematic director. After application of voltage the dispersion turns into transparent state because of almost perfect homeotropic alignment of liquid crystal. M. Kreuzer and co-workers proposed to use such a mixture for high resolution laser-addressed display with spatial resolution better than 2 μm.[4] M. Kreuzer proposed the following mechanism to explain the bistability of this system.[4] Reorientational forces of liquid crystal break hydrogen bonds between both the aerosil nanoparticles and the aerosil nanoparticles and liquid crystals during the electric poling process. New hydrogen bonds are formed. After removal of electric field the new network of aerosil nanoparticles with new internal interfaces stabilizes the homeotropic alignment.[7] This proposed mechanism was questioned by A. V. Glushchenko and co-workers.[8] Their results of study of FNLC by ultrasonic spectroscopy implied the aggregate structure of silica nanoparticles rather than nematic LC domains in 3-dimensional network of silica nanoparticles.

On the other hand, there is a great interest in finite-size effects on the behavior of anisotropic LCs incorporated into a silica aerogel matrix.[9–11] It has been shown that the observed rise in the nematic liquid crystal-isotropic liquid transition temperature (T_{NI}) can be explained not by size effects but by the orienting influence of the surface on the field, thus stabilizing the orientational order.[10] The adhesion energy of a nematic LC to the silica aerogel surface has been estimated about 1 erg/cm^2.[10] Recently, such studies have been expanded to FNLC system.[11, 12] A high-resolution calorimetric study has shown the shift of N-I transition to lower temperatures with the introduction of the aerosil particles and this shift was independent on aerosil surface treatment at low silica concentrations.[11] The theoretical model for light scattering from a distorted uniaxial material has been developed and the power law dependence of nematic correlation length ζ on the volume concentration Φ with exponent $Y \approx 1.60$ has been obtained. The maximum possible optical turbidity has been estimated $\tau_{max}=0.54\ \mu m^{-1}$.[12]

We have studied the nematic liquid crystal mixture filled with big hydrophilic silica nanoparticles (d=40 nm) and low surface area 50±15 m^2/g. We have found the large memory effect of about 95 per cent for this system. Here we show that the main origin of the large memory effect is the aerosil nanoparticle agglomeration induced by orientational elastic forces of liquid crystal and how it can be used to make regular or complex microstructures from silica nanoparticles.

EXPERIMENTAL

To make FNLC mixture we used nematic LC mixture BL011 (Merck Ltd.) with positive dielectric anisotropy $\Delta\varepsilon = +16.2$ (1 kHz), low threshold voltages $U_{(10,020)} = 1.24$ V and $U_{(90,020)} = 1.67$ V and the following other parameters at 20 °C: $T_{NI} = +62$ °C, viscosity $\nu = 63$ cSt, $\varepsilon_0 = 22.4$, $\Delta n = 0.2779$ and $n_0 = 1.5351$ (589 nm). Two types of hydrophilic silica nanoparticles were used: AEROSIL A380 and OX50 (Degussa, Germany) with particle sizes of 7 nm and 40 nm, BET surface areas of 350 ± 15 m^2/g and 50 ± 15 m^2/g correspondingly. Aerosil nanoparticles were used without any additional treatments as supplied by Degussa Corp. One-hour stirring has been used to ensure spatial homogeneity of FNLC mixtures. The concentration of nanoparticles was varied in the range 3 ~ 27 weight %. Stable dispersions with very high volume ratio for the nematic LC phase are achievable. Sandwich structures with FNLC between two glass plates with transparent ITO coatings were made for transmission-voltage measurement. Spacer particles of size 8 μm were used to control the cell gap. The sample transmittance ($T = I_{out}/I_{in}$) was measured using He-Ne laser as a light source and a photodiode for detection of transmitted light. Transmittance-voltage (T-V) dependence of filled nematic cell has been measured upon application of the ac voltage U = 0 ~ 170 V at frequency of 1 kHz.

The heat flow-temperature dependence was measured by differential scanning calorimetry. The heating and cooling rate was less than 0.05 K/min.

RESULTS

Strong scattering of visible light from mixture BL011+AEROSIL was observed in the nematic phase due to large optical anisotropy of BL011 ($\Delta n = 0.2779$ at 589 nm and 20 °C). Upon application of ac electric field the dispersion has become transparent at threshold voltage of about 20~30 V at aerosil concentration of 10~18 wt %. The threshold voltage corresponds to the energy to break up the hydrogen bonds both between the aerosil particles and between the aerosil particles and LC during the electric poling process due to orientational forces of liquid crystal. Upon increasing the electric field aerosil aggregates comprising the existing aerosil network were broken up and the optical transmittance curve went to saturation. This transparent state was memorized because new network of aerosil particles was formed. The memory parameter M was calculated from the ratio $M=(T_r\text{-}T_0)/(T_s\text{-}T_0)$, where T_0 is initial transmittance, T_r – remained transmittance, T_s – saturated transmittance. Small memory effect was observed at first scanning in the mixture with AE380 (Figure 1a). The memory parameter is about 21%. But after first scanning the T-V curve can be repeatedly measured with very small hysteresis.

The strong memory effect ($M \approx 95$ %) was observed in nematic LC filled with big hydrophilic nanoparticles OX50 ($d = 40$ nm) and low surface area (50 ± 15 m^2/g) (Figure 1b). There is a threshold voltage for memory effect. If electric field doesn't overcome the threshold value the memory parameter would be lower. The threshold voltage for memory effect is about 50–100V depending on concentration of aerosil nanoparticles. In nematic liquid crystals the substrate can exert their influence to distances up to several thousands of angstroms. Multidomain structure of FNLC was proposed by M. Kreuzer.[4] T. Bellini and co-workers have found that the microscopic structure of the nematic LC (8CB) in silica aerogel matrix is a polydomain structure induced by the 8CB – silica surface interaction with orientational correlations (ξ_{max}~180Å) comparable to the aerogel pore size (ξ_p~175 Å).[9e, 13]

TEM pictures of nematic LC filled with AE380 (a) and OX50 (b) hydrophilic nanoparticles in scattering state are shown in Figure 2 for comparison. After mechanical stirring the hydrophilic aerosil nanoparticles form a 3-dimensional sophisticated necklace structures (Figure 2b) with liquid crystal domains in empty spaces.

In Figure 3 the temperature dependencies of optical transmittance and of heat flow of nematic LC filled with hydrophilic aerosil nanoparticles OX50 (16 W. %) are shown. The mixture BL011+AEROSIL OX50 strongly scatters the visible light in the nematic phase due to large LC birefringence. At $T \gtrsim T_{NI}$ we have observed the sharp change from strong scattering state to weak scattering in the isotropic phase. Therefore, the strong turbidity in nematic phase is not because of optical inhomogeneity or molecular scattering of light.[10] We didn't find the optical hysteresis when light transmittance was measured as a function of temperature.

We observed the small but clear positive shift of T_{NI} with the increase of concentration of aerosil nanoparticles. For LC in micropores this shift is given by [10]:

$$\Delta T_{NI} = T_{NI}{}^{R} - T_{NI} = (T_{NI}/q_{NI}\rho)\,(S/V)\,(W - \sigma_{NI}) \qquad (1)$$

where S/V – specific surface area, W – adhesion energy of LC to substrate, $\rho \approx 1\ g/cm^3$ – the density of nematic LC, q_{NI} – the heat of the transition from

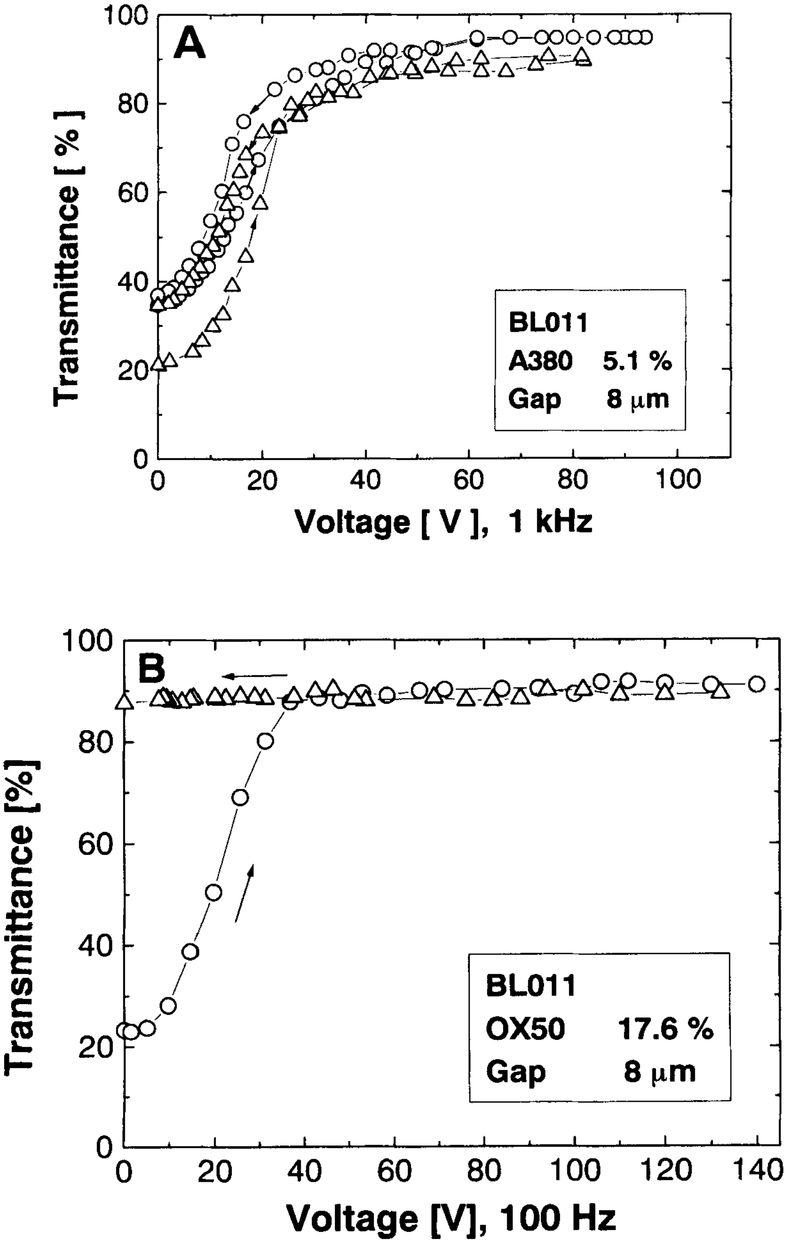

FIGURE 1 T-V dependence of nematic LC filled with small AE380 (a) (Δ - 1st scanning, O – 2nd scanning) and big OX50 (b) hydrophilic nanoparticles

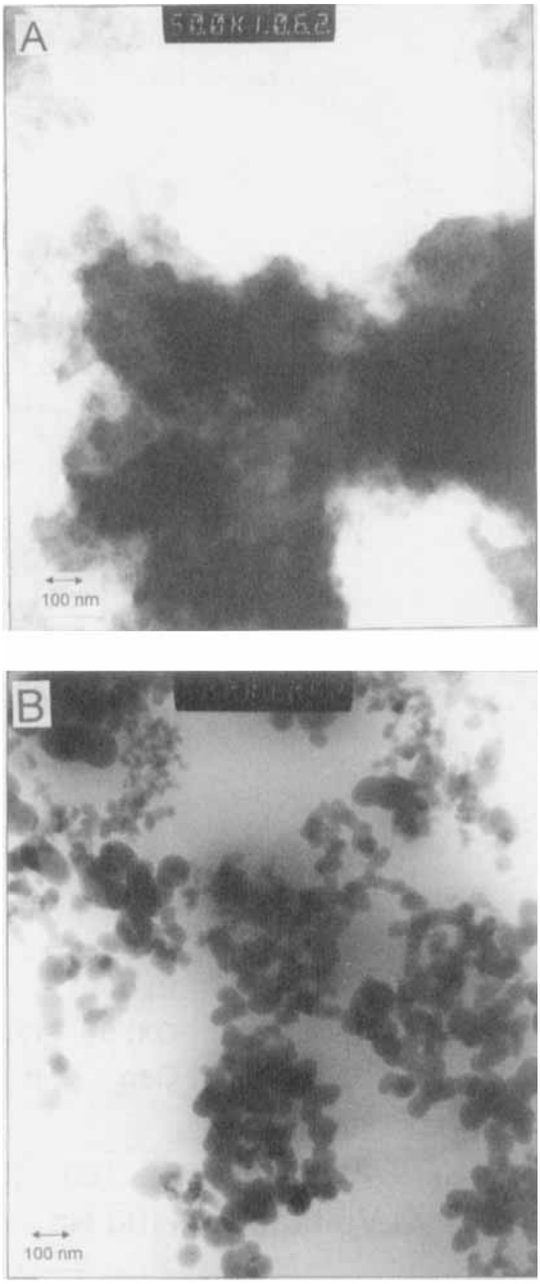

FIGURE 2 TEM micrographs of nematic LC filled with AE380 (a) and OX50 (b) hydrophilic nanoparticles

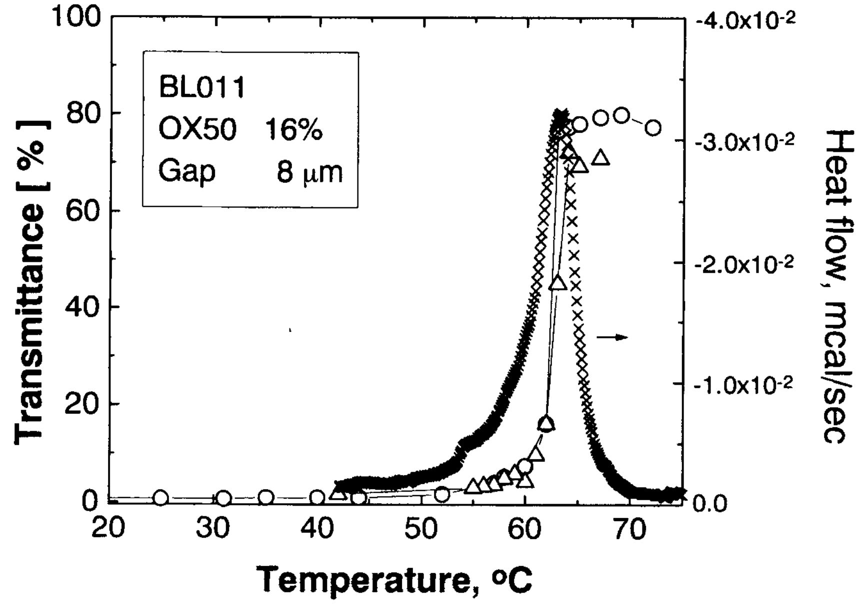

FIGURE 3 Transmittance-temperature dependence (O – heating, Δ – cooling) and heat flow-temperature dependence (× – heating) of nematic LC filled with hydrophilic aerosil nanoparticles OX50 (16 %)

nematic to isotropic phase. At high concentration of 16~24 w. % the typical values for nematic liquid crystals are $q_{NI} \approx 2\times10^7$ erg/g, $\sigma_{NI} = \sigma_N - \sigma_I \approx 10^{-2}$ erg/cm^2, $T_{NI} = 335$ K and $\Delta T_{NI} \approx 2$ K. In the approximation of cylindrical pore S/V=2/R where R is the mean pore radius. Taking into account that W $\approx$ 1erg/cm^2,[10] we obtain very reasonable values for S/V $\approx$ 12 m^2 per cm^3 and the mean pore size about 0.17 μm. We should note that the shape of broad NI transition region of BL011 mixture didn't change. LC mixtures are characterized by broad diffusive peak and up to several peaks can be observed.[14]

Unfortunately, the absence of accurate data for temperature dependence of refraction index for BL011 mixture does not allow us to fit our experimental data according to the theoretical model for light scattering from a distorted uniaxial material[12] and obtain exact value for nematic correlation length in our case. However, it was assumed[12] that the aggregates of aerosil nanoparticles are fractals with dimension 2 and nematic correlation length can be expressed as $\zeta \propto \langle p \rangle^{1.6}$ where <p> is the mean pore size within the aggregate. So we can estimate ζ from this expression as ζ~590 Å using the value of <p> obtained above from the positive shift T_{NI}.

We can qualitatively explain the positive shift of T_{NI} by the following way. Different parts of LC mixture have different transition temperatures because of orienting influence of non-uniformly distributed aerosil nanoparticles, which can be described as spatially distributed aligning surfaces. Such orienting influence of the aerosil nanoparticles surface on the director field stabilizes and enhances the local orientational order of liquid crystal.[10] The phase transition properties of nematic liquid crystals aligned by a short range, arbitrary strength substrate potential have been studied theoretically and predicted the existence of boundary layer phase transition at higher temperatures.[15] This phenomenon has been verified experimentally.[16] It is worth to mention that the addition of surfactant can cause the decrease of transition temperature up to 9 K.[17] It means that the effect of aerosil particle surface treatment is of great importance. More experimental and theoretical studies of this effect are needed.

We have used the UV-curable photopolymer (5w.%) to prevent aerosil nanoparticle agglomeration by formation of polymer network before electric field was applied to FNLC mixture. Polymer network strongly limits the movements of aerosil nanoparticles. The memory effect was diminished to very small value <1% (see Figure 4). It means that the main origin for memory effect is the re-organization of aerosil nanoparticles network to a new system with new internal interfaces due to agglomeration of hydrophilic aerosil nanoparticles by means of orientational elastic forces of liquid crystal and the hydrogen bonding and its stabilization after removal of electric field. We should note that UV-irradiation must be sufficient for complete polymerization which was at first studied by R. Yamaguchi and coworkers.[18] In case of insufficient UV irradiation prepolymer monomers remain in the system but in the case of excessive UV irradiation the photopolymer and LC may be decomposed.

DISCUSSION

In our experimental studies of nematic thermotropic liquid crystal filled with big hydrophilic silica nanoparticles we have found the following facts: 1. The hydrophilic aerosil nanoparticles form a 3-dimensional sophisticated necklace structures with liquid crystal domains in empty spaces, 2. The strong memory effect and its disappearance in the presence of polymer network, 3. The small but clearly positive shift of T_{NI}. All these facts indicate the importance of the orienting influence of the surface of the aerosil nanoparticles to the LC and its stabilization effect on the orientational order. These facts generally support the model proposed by M. Kreuzer.[4] Hydrophilic aerosil nanoparticles form a 3-dimensional network after mechanical stirring. This 3-d network presents colloidal

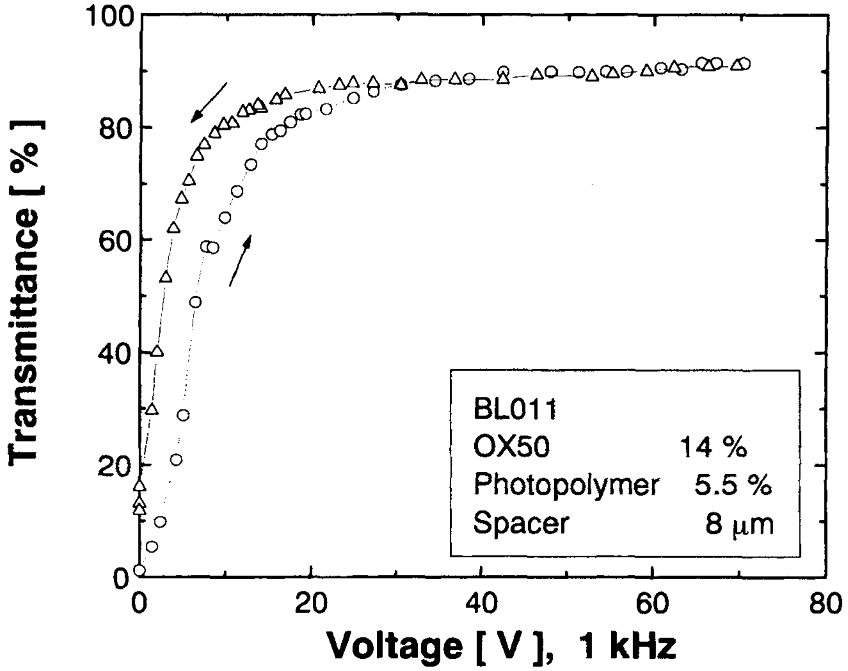

FIGURE 4 Transmittance-voltage dependence of nematic LC filled with big hydrofilic nanoparticles OX50 and with photopolymer

structural networks with sophisticated necklace structures and liquid crystal domains in empty spaces. We can consider aerosil nanoparticles in nematic LC as a porous gel-like medium with a set of aerosil nanoparticles networks bound by weak hydrogen bonds. The hydrogen bonds in LC+Aerosil system was carefully studied recently by IR spectroscopy.[19] The formation of weak hydrogen bonds between the aerosil hydroxyl groups and π-electrons of LC has been also shown. Near homeotropic orientation of 5CB dimers was changed to a chaotic one upon addition of aerosil nanoparticles due to planar orientation of LC molecules bonded to aerosil surface. The parallel alignment of LC molecules to fused silica surface have been also measured by optical second harmonic generation.[20] Re-orientational forces of liquid crystal break hydrogen bonds both between the aerosil nanoparticles and between the aerosil particles and LC molecules during the electric poling process. New hydrogen bonds are formed. The network of aerosil nanoparticles is re-organized to a new one with new internal interfaces and stabilizes the homeotropic alignment after removal of electric field.[7]

Small aerosil nanoparticles are involved in fluid flow. The larger particles due to their inertia can not follow the fast oscillatory motion of LC molecules. The effect of isotropic fluid forces on the aerosol agglomeration has been studied by J. Magill.[21] There is the extreme dependence of agglomeration rate on particle diameter. The change of a factor 2 in the particle radius results in a change of more than one order of magnitude in the agglomeration rate. The very strong dependence of force anisotropy on the particle size was obtained theoretically by R. W. Ruhwandl and E. M. Terentjev.[22] They have calculated the long-range pair potential between spherical colloid particles in a uniform liquid crystal and shown that the interaction potential has the form $U \sim R^8/d^5$, where R and d are the radius of spherical particle and the distance between two colloid particles, correspondingly. This anisotropic interaction potential leads to aggregation of particles in a colloid system. The particle size effect can explain the larger memory effect in liquid crystals filled with relatively big OX50 nanoparticles. After application of ac electric field to the FNLC mixture confined between the two ITO electrodes, the big nanoparticles are organized to large micron-sized agglomerates of different shapes with oriented internal interfaces due to orientational fluid forces. These agglomerates are invisible in optical microscope due to memory effect but can be made visible due to distortion of LC alignment around agglomerates by short heating at temperatures $\leq T_{NI}$ (see Figure 5a). Thus, the peculiarity of FNLC system with big nanoparticles is its behavior under influence of electric field. The micron-sized agglomerate structures with aligning surfaces are formed rather than a continuous 3-d network.

Figure 5b shows the regular microstructure made by application of ac electric field (50~100 V and 0.01 ~ 1kHz) to FNLC mixture (BL011 + OX50 (16%)) confined between the bottom glass substrate with comb-like patterned interdigital in-plane ITO electrode and top glass plate without ITO. The comb shaped ITO electrodes of 10 μm width are separated by a distance of 10 μm. The regular aerosil nanoparticles stripes (darker stripes on Figure 5b) of about 10 μm width separated by liquid crystal were prepared. More complex patterns of desired structure can be made by using special electrode configurations and fixed by photopolymer. This principle could be used in future nanoarchitecture with nanoparticles as building blocks and orientational elasticity of liquid crystal as building force.

The free energy of hydrogen bond formation between silica particles is very low and comparable with thermal energies at room temperatures[23]: $\Delta G \sim$ 1.2 kJ/mole for $OH\cdots$ (π system), 3.9 kJ/mole for $OH\cdots O$, 4.2 kJ/mole for $OH\cdots N$ and $kT \sim 2.5$ kJ/mole. So the aerosil nanoparticle agglomerates can be locally destroyed by heating with laser light[4] or by pressure[17] and which causes the static light scattering because of strong variation of the local orientation of

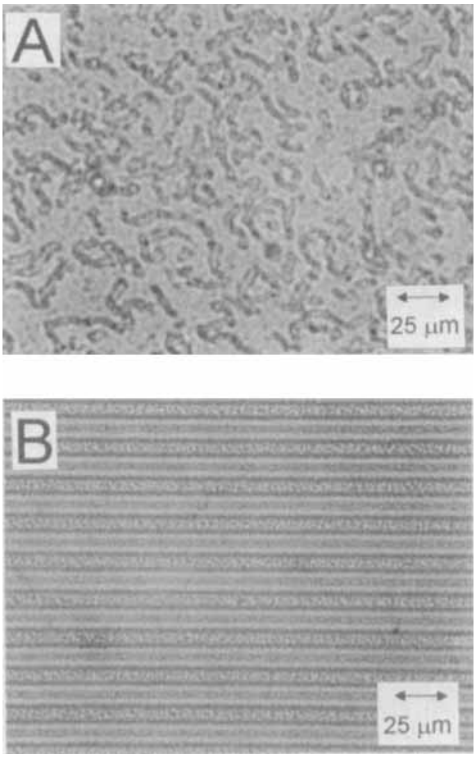

FIGURE 5 Optical micrographs of agglomerates of OX50 nanoparticles in nematic LC after application of ac electric field: a) non-patterned ITO electrodes, b) in-plane interdigital ITO electrodes

the nematic director. Upon increasing pressure the more aggregates are destroyed and scattering effect is also increasing. The nanoparticles can be repeatedly agglomerated by electric field and the mixture turns back to transparent state.[17] This effect might be used for 2-dimensional pressure imaging.

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