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Effect of polymer-dispersed liquid crystal morphology on its optical performance

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The effect of the preparation method and its parameters and system composition on the polymer-dispersed liquid crystal morphology are described including size, shape, and concentration of liquid crystal droplets. Three different methods of polymer-dispersed liquid crystal preparation – encapsulation, solvent-induced phase separation, and photopolymerization-induced phase separation have been studied. It has been confirmed that the mean size of liquid crystal droplets is proportional to the liquid crystal concentration and approximately inversely proportional to the solidification rate. Depending on the preparation parameters it is possible to obtain, from the same components, a composite in which liquid crystal droplets' size differs by four orders of magnitude. The driving voltage decreases while switching time increases with a size of liquid crystal droplets. The composites containing elongated liquid crystal droplets exhibit different electrooptical properties than those containing spherical droplets. Generally, changing composite morphology one can adjust electrooptical performance of polymer-dispersed liquid crystal.

Keywords: polymer-dispersed liquid crystals, morphology, electrooptical properties.

1. Introduction

Polymer-dispersed liquid crystals (PDLC) are composites in which liquid-crystalline droplets (diameter from 10^{-8} up to 10^{-4} m) are embedded in a solid polymer matrix. Curvilinear geometry of confined liquid crystal (LC) and the pronounced anchoring effects [1,2] result in application possibilities. The main electrooptical effect observed in nematic-containing PDLC is called electrically-induced light transmission [3] and consists in a transition from scattering to transparent state or *vice versa* induced by electric field due to a change of intrinsic LC molecular arrangement, hence optical properties of the composite. PDLCs containing chiral nematics may exhibit colour effects [4] caused by the change of helical pitch. In PDLC containing ferro- or antiferroelectric smectics, the bistable and tristable electrooptical switching are observed, respectively [5,6].

The PDLCs morphology, i.e., concentration, size, and shape of LC droplets, and the director field inside them, depends on the properties of components and a preparation process, and crucially affects electrooptical behaviour of PDLC composites. The concentration and mean size of LC droplets, affecting driving voltage, switching time, and optical contrast of the PDLC electrooptical cell, depend mainly on LC weight fraction and the droplet nucleation (polymer solidification) ratio.

LC droplets are usually spherical due to the surface tension. Such systems can be used in many applications, e.g., light valves or holographic devices [7]. However, the systems containing ellipsoidal droplets are also of great interest because optical axes of droplets are aligned in one direction. Moreover, LC droplets elongated and/or flattened in the cell plane increase optical filling of the sample cross-section by LC improving optical contrast of light valves based on electrically-induced transmission, especially in the reversed mode [8]. Such composites exhibit also unique effects, e.g., PDLC film being a monolayer of flat LC droplets exhibits very high optical contrast due to interference effects [9]. PDLC with deformed LC droplets can be adopted as effective non-absorbing light polarizers, i.e., one component of light beam is transmitted while the second one is intensively scattered [10]. They are also used in advanced holographic applications [11]. Moreover, to achieve multistable electrooptical switching of PDLC containing ferro- or antiferroelectric smectics the direction of spontaneous polarization vector of all LC droplets should be the same [12,13] what can be obtained only for elongated droplets.

In the presented paper, the effect of preparation on the morphology and electrooptical properties of PDLC containing nematic and chiral nematic LC is described. The aim of this work was to develop preparation of PDLC with morphology wanted from an application point of view, especially for electrically driven light modulators, another optical devices and information displays.

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2. Experimental

Both general methods of PDLC preparation have been studied. In the case of encapsulation, the system is heterogeneous during the whole process. LC is dispersed in a polymer solution, the solvent of which does not dissolve LC. The solvent evaporation stabilizes the obtained composite structure due to polymer solidification. The mean droplet size depends mainly on intensity of the system stirring. Morphology of the system is poorly controlled due to a coalescence of droplets.

In the case of a phase separation, the system containing LC and prepolymer or polymer is initially homogeneous. The nucleation of LC droplets takes place due to binder solidification. There are three modifications of this method depending on the factor causing phase separation: solvent-induced phase separation (SIPS), thermally-induced phase separation (TIPS) and polymerization-induced phase separation (PIPS) [3]. In PDLC obtained by phase separation, the LC droplet diameter is approximately inversely proportional to the polymer solidification rate [14].

Taking into account the results of former studies [4,14,15] and possible PDLC applications, three preparation methods have been tested. The details of used procedures have been described elsewhere [16,17].

2.1. Encapsulation

Poly(vinyl alcohol) – PVA has been chosen as the PDLC binder. It has been dissolved in distilled water, the cheapest and the most environment friendly solvent. Ethanol and/or acetone have been added to the system to decrease its viscosity and to increase the solvent evaporation rate. PVA has been modified by hardeners, plasticizers, and other dopants. From 10–40% by weight of LC, with relation to the dry polymer, has been added to the solution and the system has been vigorously stirred. The friction increased temperature up to 60–70°C decreasing the system viscosity and improving homogenization. The obtained mixture has been deposited onto a substrate poly(ethylene terephthalate) foil coated with an indium-tin oxide (ITO) conductive layer. The film thickness has been adjusted by shifting glass rod on plastic strings of different thickness (20–200 μm). Then, the solvent has been evaporated under laminar flux of purified air. Usually evaporation rate was sufficiently fast to reduce the coalescence of LC droplets. The obtained films have been laminated to the second conductive foil forming electrooptical cell or carefully separated from the substrate for microscopic studies. The method is simple and cheap but time consuming and requires lamination therefore it is not suitable for preparation of glass cells.

2.2. Solvent-induced phase separation

Poly(vinyl acetate) (PVAC) has been selected [4] as the polymer binder. At first, the solution of PVAC in ethyl acetate and/or butyl acetate has been prepared (20–50% by weight). Then LC mixture has been added (10–40% by weight with relation to the dry polymer). The obtained solution has been deposited onto ITO coated glass plate or a substrate foil in the same way as the above and the solvent has been evaporated; at first under laminar flux of purified air, then under lowered pressure and elevated temperature. The evaporation rate has been controlled by the intensity of air flux and the choice of the solvent composition. The obtained PDLC film has been laminated to the second conductive foil or separated from the substrate for microscopic studies. The method is also time consuming and not convenient for a preparation of glass cells.

2.3. Photopolymerization-induced phase separation

Two commercial poly(mercaptoesters) NOA-65 and NOA-68 (Norland Optical Adhesives), often used for PDLC preparation due to the excellent adhesion to glass, high elasticity, and refractive index close to the refractive index of glass, have been adopted as binder prepolymers. LC material (10–40% by weight) and the prepolymer have been mixed to obtain homogeneous system, then a drop of the obtained mixture has been placed onto a glass plate coated with ITO layer, covered by the same glass plate and weighed to obtain a uniform thickness of the prepolymer-LC film fixed by the glass spacers 6–18 μm thick. The prepolymer has been cured by UV radiation. The curing rate has been adjusted by changing UV flux from 1 up to 100 mW/cm^2.

2.4. PDLC containing elongated LC droplets

There are three ways to obtain elongated LC droplets by the phase separation. The first one consists in preparation of the composite film based on thermoplastic by SIPS or TIPS. Then, the PDLC film is stretched above the plastic deformation and therefore LC droplets are deformed and elongated. Local heat stress enhances the effect. The mean aspect ratio of the elongated droplets is usually from 2 to 4. Droplets deformed by this method are flattened and cannot be treated as ellipsoids of revolution.

The second way consists in application of electric field during a phase separation. The electric contribution to the LC elastic deformation free energy enforces droplets elongation, either parallel or perpendicular to the field depending on the sign of LC dielectric permittivity $\Delta\varepsilon$. LCs with $\Delta\varepsilon < 0$ are of special interest because an electric field elongates their droplets in the main cell plane. The droplet elongation obtained by this way is rather small due to possible film breakdown. A solvent cannot be adopted in this case, so only TIPS or PIPS can be used for PDLC preparation.

The third method adopts shearing during curing the polymer binder. The deformed droplets are stabilized by a cured polymer. Photopolymerization-induced phase separation (PPIPS) is the best method of PDLC preparation in this case, because of its simplicity and good control of the polymer curing ratio. Droplets are ellipsoids of revolution if their size is smaller than the film thickness.

2.5. Materials and measurements

Liquid-crystalline materials have been prepared at the Institute of Chemistry MUT and they are described in detail elsewhere [4,16,17]. In general, the LC mixtures have been designed to meet typical requirements: matching refractive indices of polymer and LC, and very low solubility of LC in cured polymer. Both nematic and chiral nematic materials have been studied. Commercially available polymers have been adopted as PDLC binders.

The mean size of LC droplets has been found by microscopic observation in the polarized light. Electrooptical measurements have been performed in a small-angle geometry by the standard setup using semiconductor laser, photodiode, and positioning stage. Colour effects in PDLC containing chiral nematics have been studied visually on the black heating stage and spectrophotometrically to find the maximum wavelength λ_{max} of the selective reflected light.

3. Results and discussion

In Figs. 1 and 2, the examples of the preparation effect on the morphology of PDLC obtained by encapsulation are presented. Both graphs include the results for spherical droplets, however, droplets of more complicated shape caused by coalescence have been also observed. The distribution of droplets diameter has been usually wide. The most uniform distribution has been obtained for low LC concentration, however, in this case the electrooptical contrast ratio and intensity of selective reflected light were low. PDLC exhibiting the selective light reflection should not contain too small LC droplets to avoid milky scattering of light, contrary to another electro-optical applications.

In Figs. 3 and 4, the examples of the preparation effect on the morphology of PDLC obtained by SIPS are presented, while Figs. 5 and 6 show similar examples for PDLC obtained by PPIPS. As one can see, the distribution of LC droplet diameter is narrower for these preparation methods.

In Fig. 7, the microscopic images of PDLC structures obtained by different methods are given, while Fig. 8 shows microscopic images of LC droplets of extremely different size obtained for the same LC and polymer. Figure 8(a) presents a very large nematic drop of irregular shape obtained by coalescence of smaller droplets during slow curing from a concentrated LC solution. Such systems can be adopted in fiber-optic systems [18]. Figure 8(b) presents PDLC containing nanosize droplets obtained by high photocuring rate and designed for holographic applications, e.g., optical information storage [7]. This example shows that adjusting the preparation process parameters one can change the size of LC droplets at least by four orders of magnitude.

Figure 9 presents the example of an effect of the morphology of PDLC film on its electrooptical parameters. The results obtained for another studied systems are qualitatively the same.

The effect of morphology of PDLC containing chiral nematics on its optical properties is given in Fig. 10. Intensity of the selectively reflected light increases with the droplets' concentration due to the better optical filling of the sample cross-section by LC. It has been confirmed that to obtain high intensity of the selectively reflected light, the size of LC droplets should be sufficiently large.

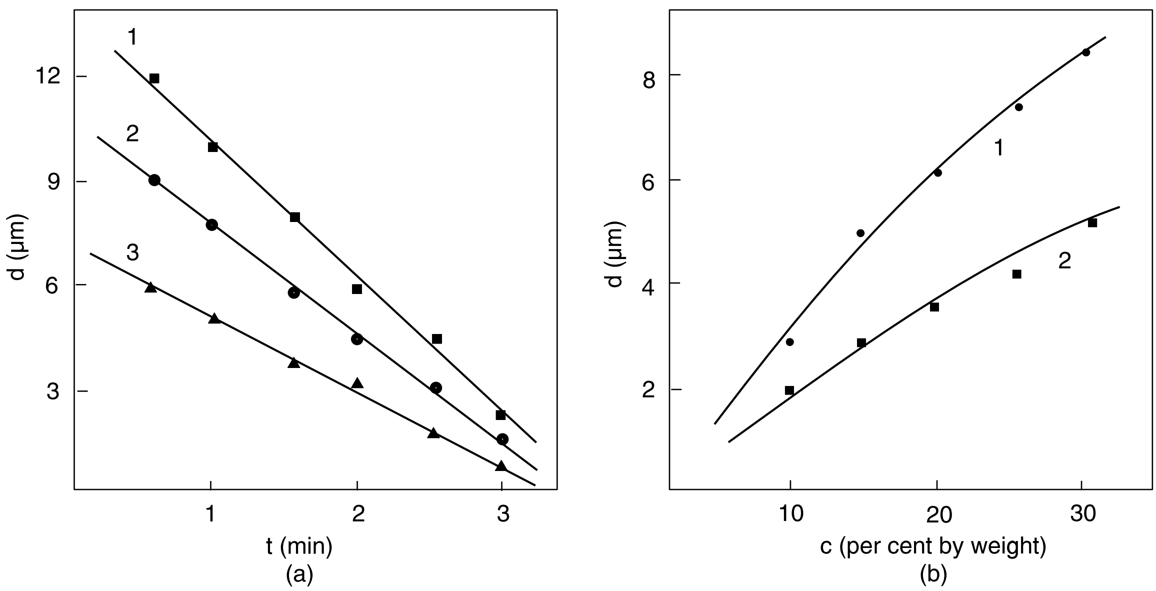

Fig. 1. Mean diameter of droplets of nematic mixture W-486 in the PVA plasticized by dibutyl phthalate: a) the effect of homogenization intensity; 1 – 1000 rpm, 2 – 5000 rpm, 3 – 10000 rpm, LC weight fraction 20 per cent; b) the effect of LC concentration with relation to the dry polymer; homogenization intensity: 1 – 2000 rpm for 3 min, 2 – 4000 rpm for 2 min.

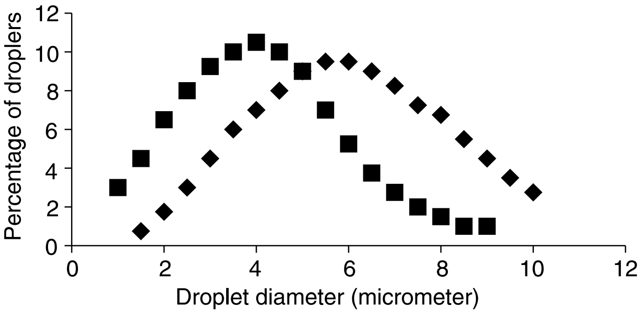

Fig. 2. The distribution of LC droplet diameter for different homogenization rates: ■ – 12000 rpm, ♦ – 10000 rpm; nematic mixture W-486 in the PVA, 20 per cent by weight.

As one can see, in the composites obtained by encapsulation, LC droplets of non-spherical shape are usually present and moreover the distribution of droplets' diameter is wide. SIPS produces spherical droplets but the distribution of their size is also relatively wide. The range of diameter of droplets obtained by both methods is limited to about 1–10 μm. However, they can be adopted in numerous applications, in which a droplets size should be close to the wavelength of visible light, e.g., optical shutters or devices using selective light reflection. Both methods can be adopted for preparation of the electrooptical cells using elastic polymer substrates.

PPIPS gives the best control of droplets' size, moreover the distribution of their diameter is the narrowest. Using this method, PDLC film can be obtained directly between the glass plates forming the electrooptical cell. Therefore it can be adopted for preparation of PDLC composites used in information displays, devices for optical beam processing or holographic systems.

The examples of microscopic images of PDLC films containing deformed LC droplets are presented in Fig. 11. The left picture shows the view of PDLC systems containing elongated and flattened LC droplets obtained by SIPS method, the central one the ellipsoidal LC droplets obtained by PPIPS method, while the right one the magnified image of the single LC droplet with the aspect ratio of about 5. The effect of droplets elongation on the electrooptical properties of PDLC composites is presented in Fig. 12. As one can see, a saturation voltage increases with droplet aspect ratio due to the stronger LC anchoring on the surface of deformed polymer cavity because the shorter axis of an ellipsoid decreases in comparison with a diameter of respective spherical droplet. For the same reason a switching time decreases with the droplet aspect ratio. Optical contrast ratio is higher for elongated droplets due to larger light scattering in off-state caused by larger difference of polymer and LC refractive indices in comparison with spherical droplets. In the tops of the deformed droplets, anchoring can be so strong that electric field does not switch LC optical axis at all.

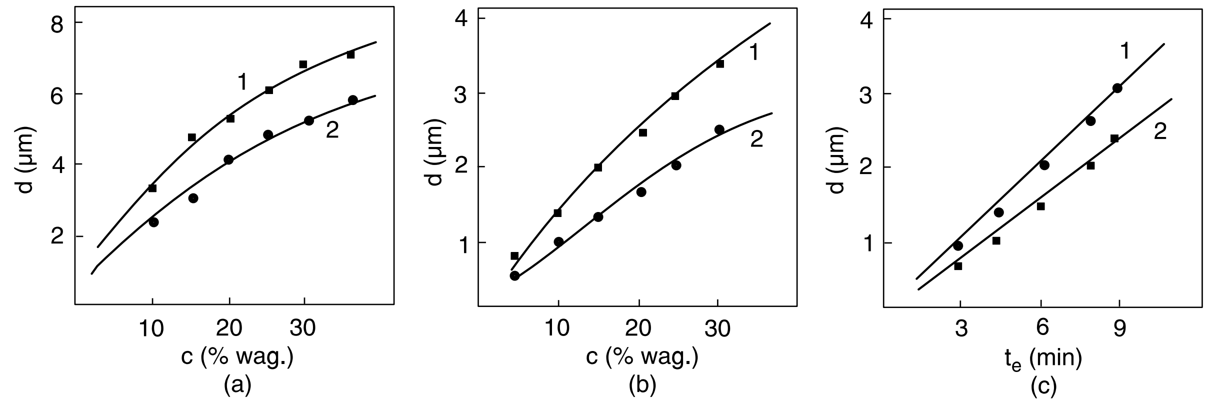

Fig. 3. Mean droplet diameter of nematic mixtures W-486 (a) and W-756 (b) vs. their concentration in PVAC (1 and 2 stand for 10 and 20 per cent bw of LC, respectively) and (c) different solidification time for PDLC containing 25 per cent bw of LC: 1 – W-486 and 2 – W-756.

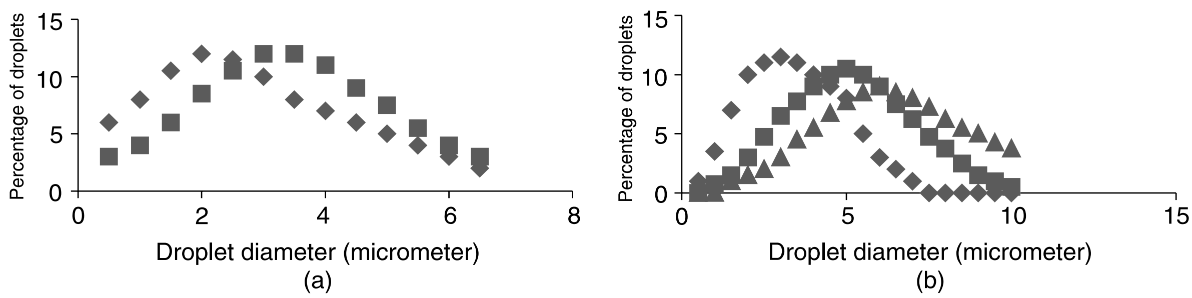

Fig. 4. The distribution of LC droplet diameter obtained by SIPS vs.: a) solvent (30 per cent bw): ■ – butyl acetate, ♦ – ethyl acetate; 20 per cent bw of W-756 in PVAC; solidification time 6 min; b) LC concentration (related to the dry polymer): ■ – 10 per cent bw, ♦ – 25 per cent bw, ▲ – 40 per cent bw; W-756 in PVAC, ethyl acetate + butyl acetate (1:1).

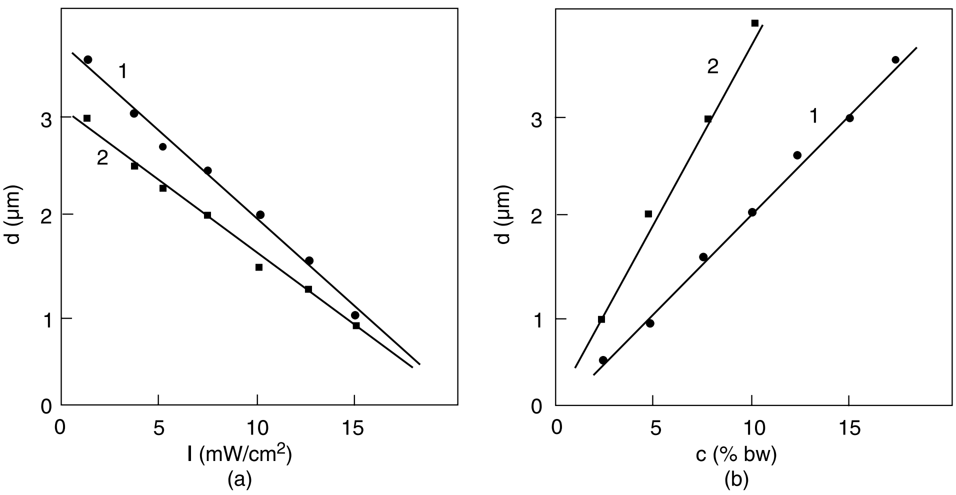

Fig. 5. Mean diameter of nematic droplets vs: a) photocuring rate of 1 – NOA-65 and 2 – NOA-68; LC mixture W-756, 20% by weight, b) LC concentration; 1 – W-486, 2 – W-756 in NOA-65; UV flux 10 mW/cm^2.

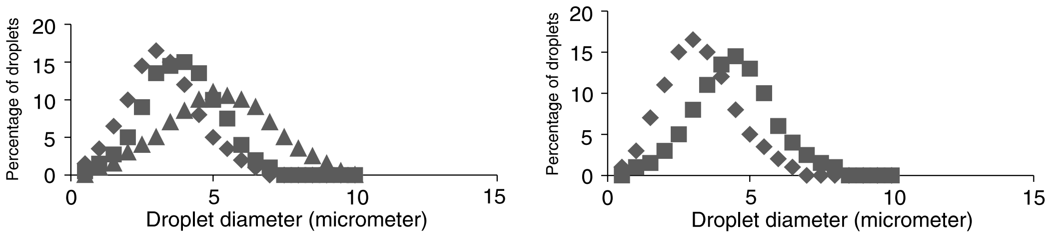

Fig. 6. The distribution of droplet diameter obtained by PPIPS vs.: a) concentration of LC (related to cured polymer) ■ – 10 per cent,, ♦ – 20 per cent, ▲ – 30 per cent; b) polymer binder – NOA-65, ■ – NOA-68, LC fraction 20 per cent by weight; UV flux – 5mW/cm^2.

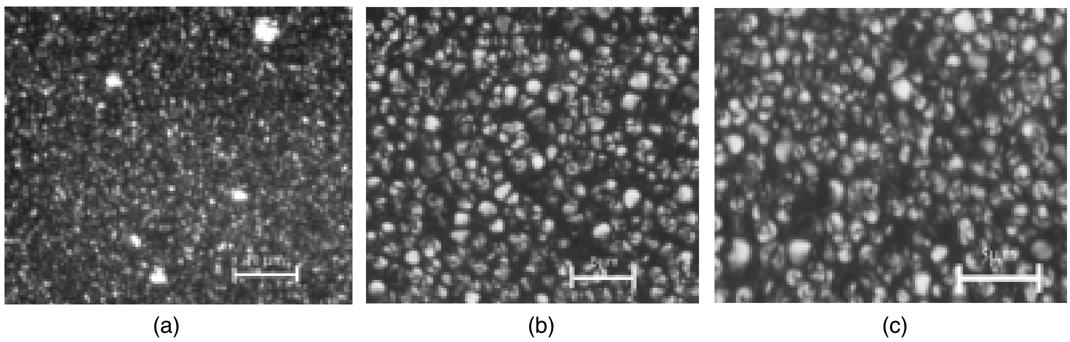

Fig. 7. Microscopic images in polarized light of PDLC obtained by: a) encapsulation, different size of LC droplets is clearly visible; b) SIPS, the distribution of droplets' diameter is more uniform than in case of encapsulation; c) PPIPS, the distribution of droplet diameter is close to the monodispersion.

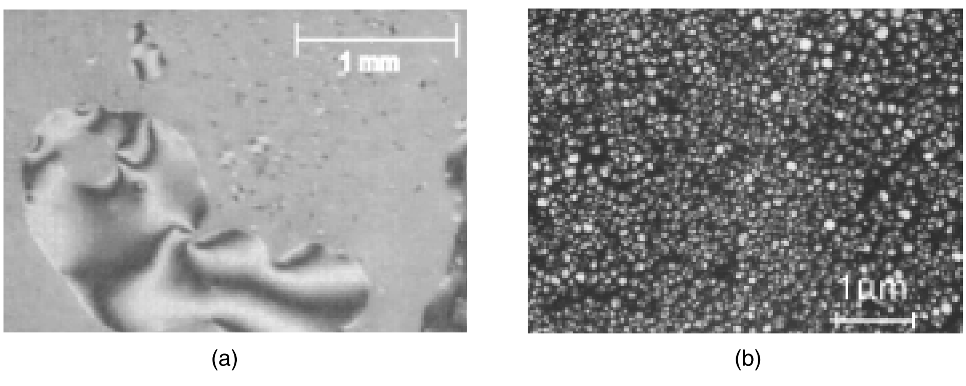

Fig. 8. Microscopic images in polarized light: a) very large nematic drop formed due to coalescence of smaller droplets in PDLC system containing 50% bw of W-756 mixture in NOA-65, UV flux 0.1 W/cm^2, b) nanosize nematic droplets obtained for the same polymer-LC system; LC fraction 20 per cent by weight, UV flux 100 W/cm^2.

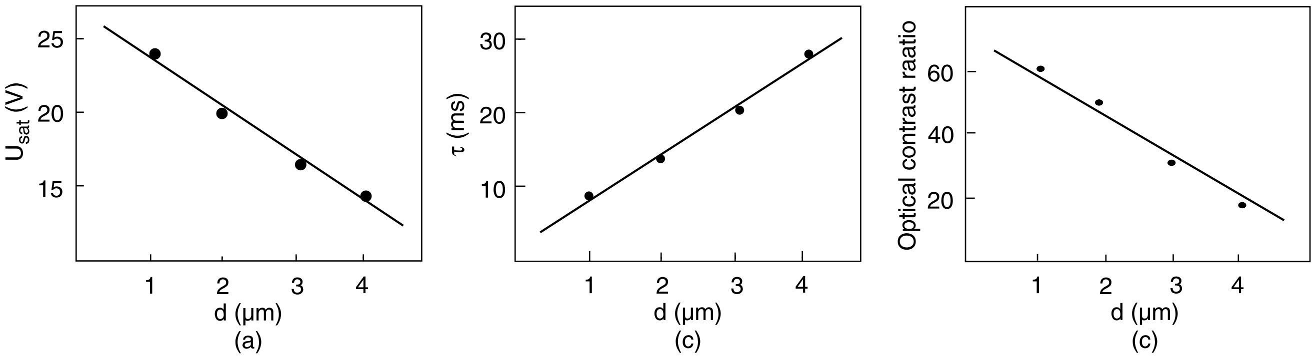

Fig. 9. The effect of mean LC droplet diameter on: a) saturation voltage, b) total switching time and c) optical contrast ratio of the PDLC cell; W-756 in NOA-65, 30 per cent bw, cell thickness 14 μm.

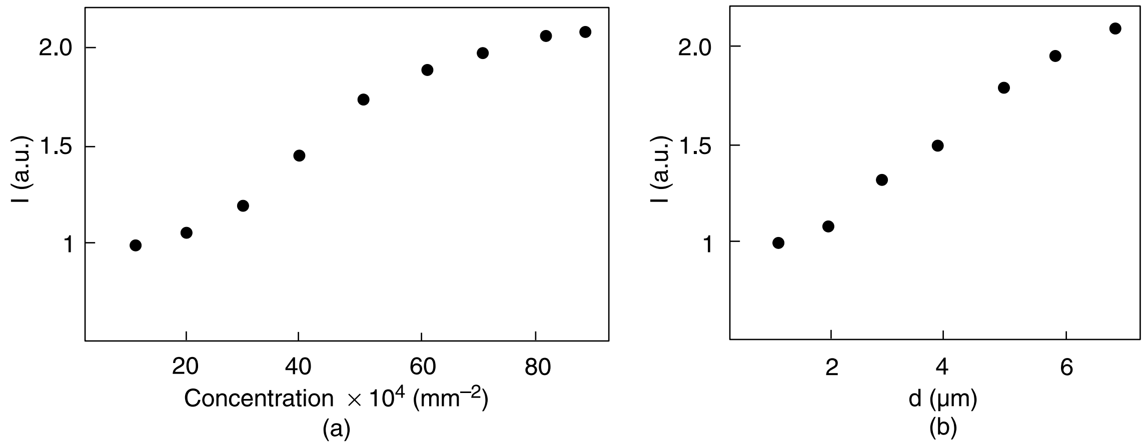

Fig. 10. The dependence of intensity of selectively reflected light on the morphology of PDLC obtained by SIPS: a) concentration of LC droplets, b) mean droplet diameter; Ch21 chiral nematic mixture in PVAC, 40 per cent bw.

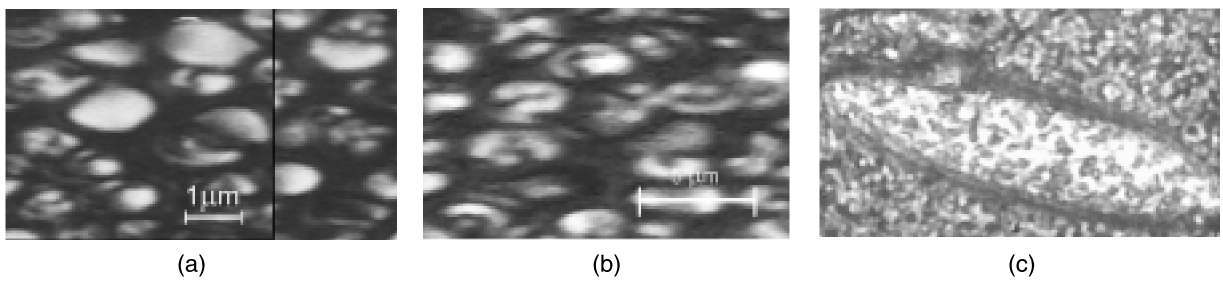

Fig. 11. Microscopic images in polarized light of PDLC containing elongated LC droplets: a) PVAC based composite obtained by SIPS and stretched with mutual heat stress, b) NOA-65 based composite obtained by shearing during PPIPS, c) the shape of LC ellipsoidal droplet obtained by shearing during PPIPS; W-756 LC mixture in NOA-65.

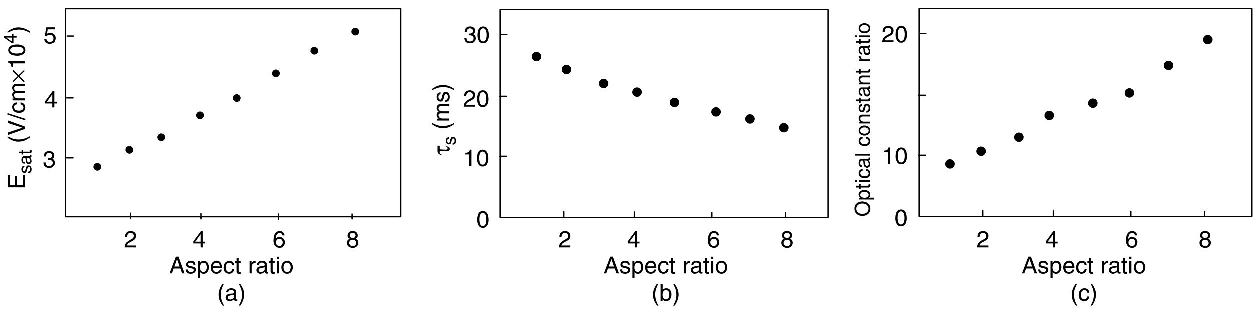

Fig. 12. The effect of the mean aspect ratio of elongated LC droplets in PDLC obtained by shearing during PPIPS on: a) saturation bias electric field E_{sat}, b) total switching time τ_s, c) optical contrast ratio; 30 per cent bw of W-756 LC mixture in NOA-65, sample thickness 14 μm.

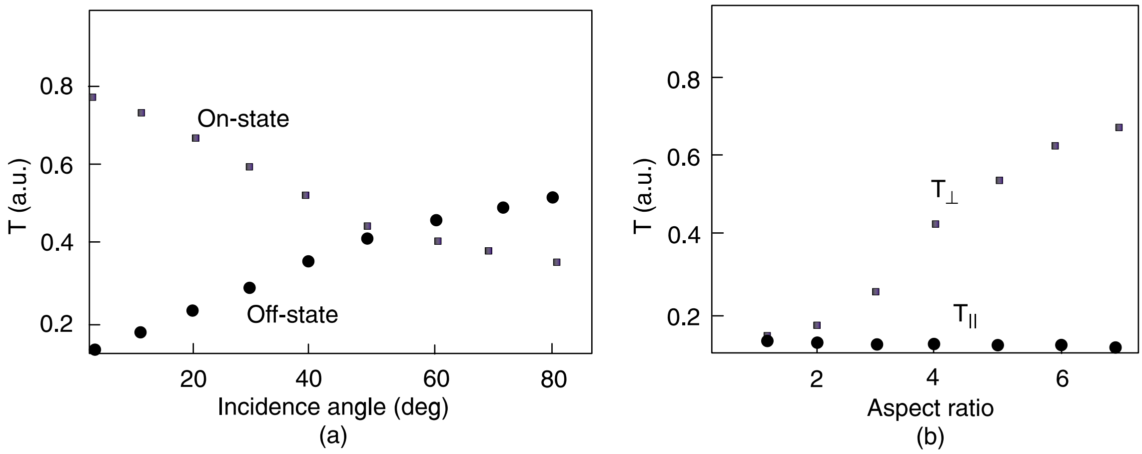

Fig. 13. The example of the optical anisotropy of PDLC sample containing elongated LC droplets; PVAC based composite stretched with mutual heat stress, W-756 mixture, 30 per cent bw, mean droplet aspect ratio 4, film thickness ~20 micrometers.

Such PDLC films are optically anisotropic because the mean refractive index of LC droplets depends on the direction of incident light. In the case of droplets flattened in the main cell plane the effect is more pronounced because the effective refractive index of the droplet is closer to the extraordinary one. The examples of the effect of droplets' optical anisotropy on PDLC properties are given in Fig. 13. The highest intensity of a transmitted beam is about 80% due to absorption and reflection of light by the cell glass plates. The obtained results are in good accordance with those published recently by Zyryanov [10] for another stretched PDLC system.

For PDLC with chiral nematics, showing selective light reflection, increase in optical homogeneity of the film and intensity of the reflected light have been observed [see Fig. 14(a)] due to the better optical filling the sample cross-section by elongated, especially flattened droplets. In many cases, when normal incidence and observation of light is adopted, e.g., fiber optic or sensor systems, this feature is very interesting. However, optical anisotropy of such droplets has caused significant angular dependence of the maximum wavelength of the selective reflected light, being a disadvantage in several applications [see Fig. 14(b)].

In any case, PDLC containing elongated, especially flattened, LC droplets exhibit behaviour similar to thin-layer LC cells.

4. Conclusions

1. Preparation process has the crucial effect on the PDLC morphology, especially the size and concentration of LC droplets. The droplet size increases with the LC weight fraction in the composite and is approximately inversely proportional to the solidification rate of the polymer binder.
2. The most uniform and the best controlled distributions of droplets' size have been obtained for relatively low LC concentration, high polymer solidification rate and PPIPS method.
3. Adjusting parameters of the preparation process one can change LC droplets' diameter in the wide range from tens of nanometers up to 1 millimetre.

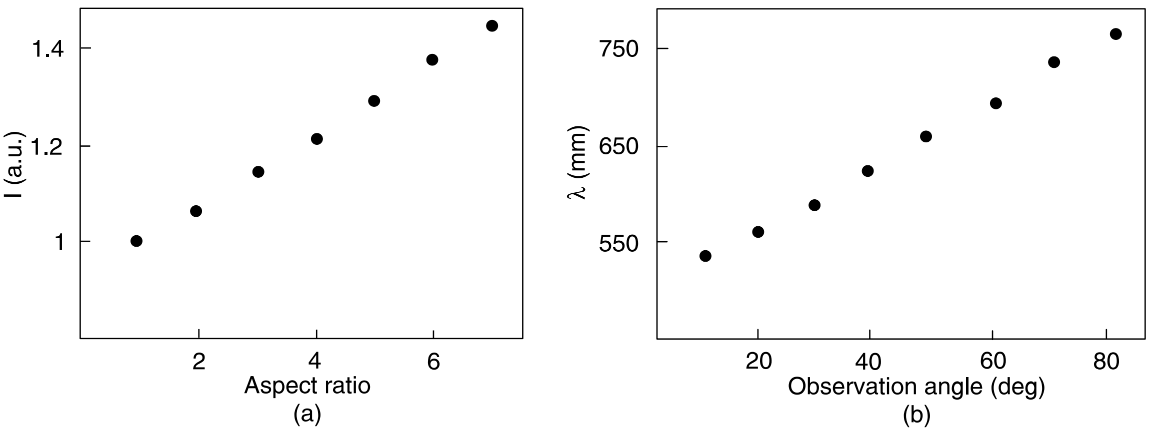

Fig. 14. a) The intensity the selective reflected light *I* on the mean LC droplet aspect ratio, b) angular dependence of the maximum wavelength λ_{max} of the selective reflected light for PDLC containing elongated LC droplets and normal incidence of 540 nm beam; PVAC based composite obtained by SIPS and stretched with mutual heat stress; 30 per cent bw of LEX1 mixture, mean droplet aspect ratio 4, film thickness ~20 micrometers.

4. Electrooptical parameters of PDLC can be effectively controlled by its morphology.
5. Elongation of LC droplets is an effective way to improve optical properties of PDLC containing nematics or chiral nematics and working in electrically-induced transmittance or selective light reflection modes. PDLC films containing elongated LC droplets exhibit larger optical contrast ratio and shorter switching times but require larger driving voltages due to more pronounced effect of anchoring of LC on the surface of polymer cavity. The optimal aspect ratio of LC droplets is 2–4 due to the extremely strong anchoring effects observed in tops of more deformed droplets.

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