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Control of phase separation and morphology of thiol-ene based PDLCs by curing light intensity

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ABSTRACT

Polymer dispersed liquid crystals (PDLCs) based on nematic liquid crystal (LC) E7 and pre-polymeric composition NOA65 were formed via the photoinduced phase separation in a wide intensity range of the actinic UV light ($l = 0.5-40 \text{ mW cm}^{-2}$). The phase separation process was monitored by measuring transmittance kinetics of the composite layers. Increase of curing light intensity accelerates the phase separation and drastically influences the final structure of PDLC samples. Reduction of light intensity below 2 mW cm⁻² results in transition from the conventional PDLC morphology of fine monodispersed LC droplets (with a droplets' diameter $d \sim 1 \,\mu$ m) to the more complex morphology combining fine droplets ($d \sim 1 \,\mu$ m) with the large LC domains ($d \sim 10 \,\mu$ m) of irregular shape. The dual-size morphology is explained by essential contribution of both liquid–liquid and liquid–gel demixing processes at low intensities of curing light. This morphology causes unusual electro-optic response characterized by non-monotonic dependence of optical transmittance on the applied voltage, low driving voltage and high initial transmittance. It extends range of potential applications of thiol–ene based PDLCs.

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1. Introduction

Polymer dispersed liquid crystals (PDLCs) are the most extensively studied liquid crystal (LC) composites operating in a light scattering mode. In the most common case they consist of isolated or connected LC droplets dispersed in a rigid polymer matrix. In the initial state PDLC composites intensively scatter light because of the refractive index mismatch between LC and polymer binder, two adjacent droplets and within the droplets of LC [1]. A scattering intensity of the composites can be drastically decreased by application of electric or magnetic field due to alignment of LC within the droplets and matching the refractive indices of LC and polymer. Based on electrically controlled light scattering effect in PDLCs, big number of electro-optical devices is developed, such as smart windows, projection and direct view displays, optical valves, polarization-independent phase modulators and tunable LC lenses [1–3].

Most often PDLCs are formed through a polymerization-induced phase separation (PIPS). In this method homogeneous mixture of LC and pre-polymer composition (monomers, oligomers, initiators, etc.) is subjected to polymerization action such as light or e-beam irradiation, heating and polycondensation. The polymer phase hardening in a course of phase separation ejects LC that results in its microincapsulation.

The vast majority of pre-polymeric compositions used for PDLC formation through PIPS are based on free radical polymerization. Among them two classes are most widely used. The first class comprises thiol–ene mixtures undergoing step-growth polymerization under irradiation, while the other class includes acrylate compositions capable to polymerize via chain-growth radical polymerization [4].

Comparing with acrylate systems, the thiol-ene compositions provide better control of PDLC morphology (e.g., size and uniformity of LC drops) as well as practically remove undesirable aging effects. Besides, they are characterized by low toxicity and reduced nonuniform shrinkage. In holographic type PDLC the thiol-ene compositions provide higher diffraction efficiency and switching contrast [5]. This explains increasing interest to thiol and ene compositions as polymer binders for PDLCs.

Historically first and presently commonly used thiol–ene based PDLC systems are made of commercial optical adhesive NOA65 from Norland Products and the cyano-*n*-phenyl LC mixtures, usually E7 from BDH/Merck. The NOA65 pre-polymer is reportedly a UV curable pre-polymer mixture containing trifunctional thiol and a tetrafunctional urethane allyl ether (the ene) [6]. The ordinary refractive index of LC E7 and refractive index of NOA65 are

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favorably very close [7] so that the corresponding PDLC films become fully transparent in a field on state. The early studies of such



Fig. 1. Transmittance kinetic curves for UV light intensity 36 mW cm⁻² (a) and 0.8 mW cm⁻² (b). The arrows with marks on and off point the instants of time when the illumination and relaxation phases of T(t) curves are started. The insets present parts of T(t) curves corresponding to illumination phase on a logarithmic scale.



Fig. 2. Measured (filled squares) and fitted (continuous lines) T(t) curves corresponding to illumination phase. The fitting is provided by formula (1). The curves (1), (2), (3) and (4) correspond to UV light intensity equal to 36, 4, 2 and 0.8 mW cm⁻².

PDLCs were focused on maximal improvement of their electro-optic performance based on optimization of curing conditions (UV exposure, curing temperature, polymer concentration, etc.) [8-11]. The NOA65-E7 PDLC composites comprising dichroic dye has been considered by Malik and Raina in Ref. [12]. A deep insight in curing reactions and phase separation kinetics of NOA65-E7 composites was made by Koening's group using a real-time FTIR spectroscopy [13-15]. The fractions of LC in separated LC domains and polymer matrix were established for different curing conditions and concentrations in the initial LC-pre-polymer mixture. Recently, White et al. [16] considered effect of functionality of thiol and ene monomers on polymerization kinetics and morphology of PDLC composites. It was found that increasing monomer functionality (both thiol and ene) accelerates achievement of gelation point of thiol-ene pre-polymer and thus reduces size of LC droplets in PDLC samples. This gives additional way for optimization of thiol-ene based PDLCs.

We believe that essential gap for further improvement of NOA65–E7 composites still exists even without chemical modification of polymer mixture. This might be achieved by thorough optimization of the components' concentrations and processing parameters and, possibly, insertion of some additional components. In Refs. [17,18] we demonstrated that doping NOA65–E7 PDLCs with nanoparticles of inorganic materials may substantially reduce their off-axis haze. We also clarified morphological evolution of this system with a wide-range change of polymer concentration c_p [19]. In spite of monotonic decrease of sizes of LC domains, the electro-optic contrast of this composite was established to be a non-monotonic function of polymer concentration with a pronounced maximum at $c_p = 35-40$ wt.%.

A present study considers morphology and electro-optic characteristics of NOA65–E7 PDLCs as functions of curing light intensity. By using intensity range much wider than in the early studies of these composites [9,11] several types of PDLC morphologies characterized by different electro-optic behavior were realized. In situ monitoring of phase separation allowed us to determine parameters of this separation process and their dependence on the intensity of curing light.

2. Experimental

2.1. Samples

Nematic LC E7 (BDH/Merck), used as a LC component of PDLC samples, is a eutectic mixture of cyanobiphenyls. It contains 51% *n*-pentylcyanobiphenyl (5CB), 25% *n*-heptylcyanobiphenyl (7CB), 16% *n*-octyloxycyanobiphenyl (8OCB) and 8% *n*-pentylcyanoterphenyl. This mixture has nematic mesophase in the range -30 to 61 °C [13,14]. The UV curable optical adhesive NOA65 (Norland Products) used as a polymer binder in PDLCs is reported to be a mixture of trimethylolpropane diallyl ether, trimethylolpropane tris thiol, isophorone diisocyanate ester and a benzophenone photoinitiator [6,13]. Both LC E7 and photopolymer NOA65 were used as received.

A blend of 62 wt.% of E7 and 38 wt.% of NOA65 was automatically mixed over 10 h at room temperature and used as the initial reactive mixture for UV curing. Samples were prepared by sandwiching the initial reactive mixture between two glass plates containing transparent ITO electrodes. A gap between the substrates was $d = 26 \pm 2 \mu m$. The UV light source was a lamp LC3 from Hamamatsu. The curing light intensity, *I*, registered in the spectral range 250–400 nm was changed from 0.05 to 40 mW cm⁻². In the majority of experiments the time of UV exposure t_{exp} was fixed at 70 s.

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 Table 1

 Fitting parameters for T(t) curves corresponding to different intensities of curing light.

UV light intensity	Fitting J	Fitting parameters				
	Α	τ	β	T_0	$\langle \tau \rangle$	
0.48	0.92	24.2	4.4	0.088	20.4	
0.8	0.93	23.1	4.3	0.081	19.7	
1.2	0.94	1	4.0	0.062	18.6	
2	0.96	14.7	3.7	0.042	13.2	
4	0.97	7.5	2.6	0.035	6.9	
18	0.99	2.8	2.2	0.014	2.6	
36	1	1.5	1.8	0.008	1.27	



Fig. 3. Stretching parameter β (a), mean time of transmittance decay $\langle \tau \rangle$ (b), and saturation transmittance T_0 (c) as functions of UV light intensity. Symbols are experimental points, while the lines are just for eye guidance.

2.2. Experimental techniques

The optical and electro-optical studies were carried out by using experimental set up earlier described in Refs. [20,21]. The system detects transmission of PDLC samples for unpolarized He–Ne laser light at λ = 632.8 nm. The samples were set perpendicularly to the laser beam. The distance between the sample and the detector (silicon photodiode) was approximately 30 cm so that the collection angle of the transmitted light was about ±2°.

By measuring kinetics of optical transmittance *T* during phase separation the sample was exposed to UV light. The angle of incidence of UV light on the sample was about 30°. The light intensity was changed from 0.05 to 40 mW cm⁻² by changing distance between the UV source and the sample. The exposure process was launched 20 s after starting recording of sample transmittance. After 70 s of exposure the sample was monitored additionally 2550 s to clarify a post-deposition behavior.

For measuring sample transmittance T vs. applied voltage U curves, an external electric field was applied across the PDLC sample. In this process the sinusoidal voltage of frequency 145 Hz was stepwise increased up to a desired maximum value U_{max} and then decreased in the same manner. The whole voltage up and down ramp was preformed during 120 s, and an additional measuring time 60 s allowed us to study relaxation behavior of the transmission in the off-state.

The microscopic observations were carried out by using a polarizing optical microscope Olympus BX41 equipped with a digital camera conjugated with a PC.

3. Results and discussion

3.1. Transmittance kinetics

The optical transmittance as a function of exposure time was measured in a whole intensity range defined above. In what follows we are however focused on a narrower range, I = 0.5–40 mW cm⁻², corresponding to stable PDLC structures. The unstable and insufficiently stable samples realized at I < 0.5 mW cm⁻² will be briefly described in the next section. The detailed study of these samples is beyond the scope of the present paper.

Fig. 1 shows transmittance kinetics for two intensities roughly corresponding to limits of the intensity range $0.5-40 \text{ mW cm}^{-2}$. The arrows with marks on and off point the instants of time when the UV light is switched on and off. The parts of T(t) curves corresponding to illumination phase are collected in Fig. 2.

One can notice that the sample transmittance monotonically decays with the exposure time demonstrating trend of saturation. A higher intensity of UV light provokes a faster decay of *T*. This behavior is typical for PDLCs formed by PIPS [2,3].

In general, the measured transmittance vs. exposure time curves are too complex to be described by a single exponential function. Firstly, the T(t) curves for low intensities contain specific initial tail with a constant transmittance followed by a low rate of transmittance decay. Secondly, T(t) curves for high intensities usually undergo maximum in the final part of intensity decay (see inset in Fig. 1(a)), which might be caused by isotropic to nematic phase transition in LC droplets. Because this maximum is small, it will be ignored in the fitting process. Using this simplification, T(t) curves can be satisfactorily fitted by a stretched exponent commonly used to describe complex relaxation processes, such as relaxation in disordered systems [22]:

$$T = T_0 + A \exp\left(-(t/\tau_s)^\beta\right). \tag{1}$$

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Fig. 4. Microphotographs of PDLC samples obtained for different UV light intensities. The intensity is equal to 36, 18, 4, 2, 1.2 and 0.8 mW cm⁻² in case (a), (b), (c), (d), (e) and (f), respectively. The exposure time is 70 s.

In formula (1) T_0 is a transmittance value in saturation state, τ_s is a decay time, A is a value of transmittance decay and β is a stretching parameter. Fig. 2 demonstrates that function (1) fits experimental curves very well except last parts of these curves corresponding to final 10–15% of decay. The fitting parameters corresponding to different intensities of curing light are summarized in Table 1. This table also includes a mean decay time calculated as:

$$\langle \tau \rangle = \int_0^\infty dt \exp\left(-(t/\tau_s)^\beta\right),$$
 (2)

where τ_s and β are parameters preliminarily determined by fitting. As can be seen from Table 1, the values of $\langle \tau \rangle$ are close to τ_s .

Table 1 is supplemented by Fig. 3 showing $\beta(I)$, $\langle \tau \rangle(t)$ and $T_0(t)$ plots. It is obvious that growing of curing light intensity *I* results in monotonous decrease and saturation of T_0 , β and $\langle \tau \rangle$.

At high intensities, $\beta \rightarrow 1$ so that a photoinduced decay of *T* can be presented roughly by a single exponential function. In this case the decay of *T* starts practically instantly with illumination. On the contrary, lowering of *I* enhances stretching of *T*(*t*) curve; for intensities higher than 2 mW cm⁻² stretching parameter β exceeds 4. The pronounced tail observed in the initial phase of these curves means that response of *T* on illumination is essentially delayed.

The marked difference in the initial parts of T(t) curves can be explained assuming difference in the phase separation mechanisms for high and low intensities of curing light. At high intensities, the gel point of pre-polymer is quickly reached so that the phase separation occurs mainly via a liquid–gel separation process. At low *I*, much longer time is needed for reaching gel point of prepolymer at which intensive separation is launched. This might explain specific tail of T(t) curves detected for the samples prepared



Fig. 5. Diameter of LC drops as a function of curing light intensity obtained for exposure time fixed at 70 s. In case of dual-size morphologies realized at I < 2 mW cm⁻², the filled and open circles stand for droplets of smaller and bigger size, respectively. The lines are presented for eye guidance. A, B and C mark the intensity ranges corresponding to liquid dispersions, dual- and singe- size PDLC morphologies, respectively.

at low *I*. Since viscosity of pre-polymer binder changes slowly, one can assume that the initial transmittance decay, i.e., initial tail of T(t) curves, is caused by a liquid–liquid separation mechanism. This is supported by the fact that concentration of E7 in the mixtures is close to its solubility limit in NOA65 [15]. At longer exposure, the gel point is reached resulting in intensive liquid–gel separation. Decrease of $\langle \tau \rangle$ with the intensity of curing light reflects shortening of both gelation time and liquid–gel separation time. The difference in the initial separation process may explain essential difference in the morphology of PDLC samples discussed in the next section.

Decrease of T_0 with the intensity *I* implies enhancement of light scattering in a zero field. This leads to growing of electro-optic contrast as shown in Section 3.3. It is important to note that the increase of exposure time from 70 to 600 s did not essentially change the value of T_0 . This means that 70 s is the time sufficient for phase separation in our composites.

Finally we consider the part of transmittance kinetics (Fig. 1) after the electric field is off (the relaxation part). It is obvious that at I > 2 mW cm⁻² sample transmittance *T* does not practically change after the field is off. In case of lower light intensity, the transmittance *T* demonstrates insufficient change (10–15% of its maximal value) in the first 10–15 min after shutting down of UV light. Usually, *T* gets slightly down and then grows up and saturates as demonstrated in Fig. 1(b). The relaxation behavior and final level of *T* in case of 600 s exposure were rather similar to those in case of 70 s exposure. The observation of just illuminated

PDLC samples under polarizing microscope showed that the slow dynamics described can be caused by establishment of equilibrium director configuration within the big LC drops and also fusion of some of these drops.

The transmittance relaxation was also monitored in a large time scale (two weeks). We found that the level of *T* realized after first 10–15 min of relaxation did not noticeably change in a course of next days of sample storage. This implies sufficiently high stability of the induced morphologies.

3.2. PDLC morphologies

The microscopic structures of PDLC samples formed at I = 0.5–40 mW cm⁻² and $t_{exp} = 70$ s were reproducible and quite uniform (relative deviation of T_0 within one probe has not exceeded 20%). Fig. 4 illustrates typical structures corresponding to different values of *I*. The presented microscopic pictures were taken at about 30 min after finishing UV illumination accounting for a 15 min equilibration time for our samples. Same as in case of T(t) kinetics, two types of structures can be selected. When I > 2 mW cm⁻² the samples contain small LC drops (the average drops' diameter *d* is 0.5–5 µm) with high monodispersity (the single size structure). This is in good agreement with earlier studies of other groups [9,11] and our results obtained by SEM method [19]. In turn, when I = 0.5-2 mW cm⁻², along with small droplets, much bigger droplets (d = 20-50 µm) are formed (the dual-size structure). The *d* vs. *I* plot according to microphotographs from Fig. 4



Fig. 6. Microphotographs of PDLC samples obtained for different exposure times. The time is equal to 0, 10, 30, 50, 70 and 600 s in case (a), (b), (c), (d), (e) and (f), respectively. The curing light intensity is 0.5 mW cm⁻².

is presented in Fig. 5. The dual-size of LC drops at $I < 2 \text{ mW cm}^{-2}$ results in splitting of d(I) curve. Before the splitting, in the intensity range 4–40 mW cm⁻², the d(I) curve exhibits rather slow decrease, which, as in Refs. [9,11], can be considered as a quasilinear one.

The intensity decrease below 0.5 mW cm⁻² at $t_{exp} = 70$ s results in formation of unstable or insufficiently stable samples in a form of liquid dispersions (LC drops dispersed in a liquid pre-polymeric composition with a high content of LC). This intensity range is marked in Fig. 5 as a range A. It should be noted that the upper limit of this range, I = 0.5 mW cm⁻², drops with increase of t_{exp} above 70 s.

To clarify a structural evolution under UV irradiation, the exposure time dependence of samples morphology at fixed intensity I was analyzed. The microscopic pictures for a set of samples corresponding to I = 0.5 mW cm⁻² are presented in Fig. 6. There is evident that short exposure ($t_{exp} = 10$ s, Fig. 6(b)) initiates formation of small LC drops in the initially uniform mixture (Fig. 6(a)). The further increase of exposure time results in growing of LC drops (Fig. 6(c)) and formation of dual-size morphology (Fig. 6(d)). This morphology alters with further increase of t_{exp} to 70 s that is first of all apparent in deformation of large spherical drops (Fig. 6(e)). The following increase of exposure time to 600 s does not bring any visible morphological changes (Fig. 6(f)). Development of PDLC structures under high intensities $(I > 2 \text{ mW cm}^{-2})$ is much more simple; the fine monodisperse LC droplets initially appearing in some areas quickly cover all sample. The interruption of this intensive exposure in a very early phase ($t_{exp} = 0.5-5$ s, depending on the light intensity level) results in formation of liquid dispersions with the morphology shown in Fig. 6(b).

The observed difference in structural evolution and resultant morphologies for low ($I < 2 \text{ mW cm}^{-2}$) and high ($I > 2 \text{ mW cm}^{-2}$) intensity of curing light might be explained by different LC-polymer demixing mechanisms. At high intensities a gel point is rapidly reached so that LC and polymer separate mainly via the liquid-gel demixing at which the rate of pre-polymer conversion is high [15]. This leads to formation of fine monodispensed drops. In contrast, at low intensity of curing light the conversion process is slow. This means that the system arrives at a gel point slowly and thus, on the initial stage, the phase separation occurs via the liquid-liquid demixing. At sufficiently long expositions, this slow separation dynamics results in formation of big spherical LC domains capable to fuse in a course and after the illumination [23]. The corresponding structure is demonstrated in Fig. 6(c). Formation of the fraction of finer drops at later illumination stage (Fig. 6(d)) might be caused by reaching gelation point and thus occurrence of liquid-gel demixing. The gelation of pre-polymeric matrix results in deformation of large spherical drops and stabilization of the induced dualsize morphology (Fig. 6(e) and (f)).

The results presented in Figs. 4 and 6 demonstrate that, in a general case, the morphology of E7–NOA65 composites is not a function of exposure dose considered as a product of intensity I and exposure time t_{exp} . For instance, the dual-size morphology can not be reached at any time of exposure in case of high intensity irradiation. In turn, the fine droplet morphology is not realizable for low intensities. Because of this the structures are characterized by I and t_{exp} rather than the dose of exposure.

At the same time, the exposure dose determines purity of separated phases. The degree of contamination of LC and polymer phases in the formed composites was not investigated. Instead, we just demonstrated that the exposure time t_{exp} = 70 s is sufficient for induction of stable structures at any light intensity from the range 0.5 to 40 mW cm⁻². In other words, increasing of exposure time above 70 s, and thus improved purity of LC and polymer phases, did not result in any noticeable changes in sample morphology and its stability. This implies minor effect of the remained pre-polymeric impurity on sample stability. In big contrast, the morphologies of liquid dispersion were unstable. They altered under applied electric voltage, mechanical stress and even without any external actions at long time storage.

3.3. Electro-optic characteristics

Fig. 7(a) and (b) illustrates typical T(U) curves for the samples with the single size and dual-size morphologies, respectively. The samples with a single size structure demonstrate response typical for PDLC: the T(U) curve monotonically increases and saturates with a voltage ramp up and subsequently decreases to the initial value with the voltage ramp down. The observed hysteresis is also typical for PDLC systems and reportedly is connected with the LC layers at the LC–polymer interface responding differently to the external field than the LC bulk [3].

The T(U) curves for the samples with a dual-size structure are distinctly different; they demonstrate non-monotonic (oscillating) character. This phenomenon was earlier described in the works of Bouteiller et al. [24], Zyryanov et al. [25] and Barannik et al. [26]. Same as in our case, it was observed in the samples containing large LC domains comparable or bigger than the thickness of PDLC films. In Ref. [24] the origin of the minimum of T(U) curve is explained by sectional LC reorientation within large domains partially aligned in the initial state. This reorientation increases scattering losses within the LC domains due to the light scattering



Fig. 7. Transmittance vs. applied voltage curves for the samples obtained for curing light intensity 36 mW cm⁻² (a) and 0.8 mW cm⁻² (b). T_0 , T_{min} and T_s stand for initial, minimal and maximal (saturation) transmittance, respectively.

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Fig. 8. Microphotographs of the dual-size morphology sample subjected to electric voltage. The voltage is equal to 3, 7, 14 and 20 V in case (b), (c), (d) and (e), respectively. The photographs (a) and (f) correspond to zero voltage states before (a) and after (f) the voltage application.

on the border of reoriented and non-reoriented sub-domains. A sufficiently strong field is capable to reorient all LC within the domains. As result, the sub-domains disappear and scattering loses essentially decrease. The character of LC reorientation within large drops under applied voltage suggests that this mechanism is important for our samples (Fig. 8).

At the same time, Zyryanov et al. [25] and Barannik et al. [26] assume that minimum of T(U) curve has an interference origin and appears due to superposition of light beams passed through the LC droplets and surrounding them polymer matrix. The applied voltage changes phase difference of these beams that results in the oscillations of optical transmittance. This interference mechanism may contribute to the discussed oscillation effect in case of coherent testing light. However, the pronounced oscillation effect in our samples was also observed in experiments with a non-coherent white light. This allows us to believe that the interference mechanism plays a minor role in our systems.

The driving voltage U_{90} (the voltage at which transmittance changes in 90% comparing with its saturation value) as a function of UV light intensity *I* is shown in Fig. 9(a). The increase of U_{90} with *I* is in full accord with the decrease of drop diameter *d*, since U_{90} is theoretically inversely proportional to *d* [3]. Same as *d*(*I*) curve presented in Fig. 5, the $U_{90}(I)$ curve has a singularity point at about $I = 2 \text{ mW cm}^{-2}$. As mentioned above, this point marks a border between two types of PDLCs with the morphologies presented in Fig. 4(a)–(c) and Fig. 4(e) and (f), and the electro-optic curves T(U) shown in Fig. 7(a) and (b), respectively. According to Fig. 9(a), the dual-size PDLC structures require considerably lower driving voltage than the single size structures with the fine drops (10–15 V vs. 30–45 V). At the same time, they demonstrate substantially lower electro-optic contrast defined as a ratio of optical transmittances in saturation and zero field states (T_s and T_0 values, Fig. 7). According to Fig. 9(b), the contrast value for the single size structures exceeds 100, while the maximal value reached for the dual-size structures are 2–3 times higher if one considers the electro-optic contrast as a ratio of maximal and minimal transmittances (T_s and T_{min} values, Fig. 7). Fig. 9(b) presents data according to both definitions of electro-optic contrast.

The accurate and wide range controlling of PDLC morphology described above extends the application field of NOA65–E7 composites. For instance, the obtained results suggest unique solutions for a pattering of PDLC morphology and creation of high brightness LCDs operating in a low voltage regime [1,2].

4. Conclusions

In summary, the photoinduced phase separation in the E7– NOA65 composites was studied in a wide intensity range of actinic UV light ($I = 0.05-40 \text{ mW cm}^{-2}$). The phase separation process was monitored by measuring transmittance kinetics of the composites' layers. In general, the transmittance vs. exposure time curves can be successfully fitted only by a stretched exponent with the O. Yaroshchuk et al. / Optical Materials 32 (2010) 982-989



Fig. 9. Driving voltage U_{90} (a) and contrast ratio CR (b) of PDLC samples, as functions of curing light intensity *I*. In (b) the squares and open circles correspond to CR values calculated as T_s/T_0 and T_s/T_{min} , respectively. B and C mark the intensity ranges corresponding to dual- and singe- size morphologies, respectively.

stretching parameter β approaching 1 at high intensities of UV light. Increase of curing light intensity accelerates the phase separation and drastically influences final structure of PDLC samples. Reduction of light intensity below 2 mW cm⁻² results in the transition from the ordinary morphology of fine droplets to the dual-size morphology combining fine droplets and big droplets with the size comparable or bigger than the thickness of the composite layer. At any intensity from the range 0.05 to 40 mW cm⁻², below critical dose for polymer gelation, PDLC structures appear in the form of liquid dispersions.

The character of morphological transition from the liquid to solid dispersion considerably depends on the light intensity. In case of high intensities ($l > 2 \text{ mW cm}^{-2}$) the liquid dispersions are quickly solidified due to the reaching of gel point of pre-polymer. This means that a liquid–gel demixing mechanism dominates. On the contrary, if $l < 2 \text{ mW cm}^{-2}$, samples are in a liquid state relatively long so that a considerable part of mixture is separated via a liquid–liquid demixing. The LC separated on this stage forms relatively big drops ($d \sim 10 \text{ }\mu\text{m}$). Later on, on the stage of polymer gelation, fine drop fraction is formed ($d \sim 1 \text{ }\mu\text{m}$). This two-stage separation process results in the dual-size PDLC morphology.

The new morphology containing large LC domains determines unusual electro-optic response with a non-monotonic transmittance-voltage curve and reduced voltage of electro-optic switching. Because of the reduced role of scattering mechanism based on the refractive index mismatch, this morphology should yield low off-axis haze, i.e., wide viewing angle [2,27]. The obtained results also suggest an effective method for accurate controlling of PDLC morphology. This altogether extends variety of E7–NOA65 composites and field of their potential applications.

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