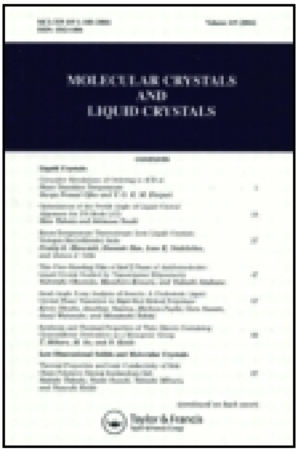

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Nano-size Polymer Dispersed Liquid Crystals for Phase-Only Optical Modulation

Daniele Eugenio Lucchetta [a] , Alessandro Manni [a] , Ridvan Karapinar [b] , Luigi Gobbi [a] & Francesco Simoni [a]

[a] Dipartimento di Fisica ed Ingegneria dei Materiali e del Territorio and Istituto Nazionale per la Fisica della Materia, Universita' di Ancona, Via Brecce Bianche, Ancona, I-60131, Italy

[b] Faculty of Arts and Sciences, Department of Physics, Yuzuncu Yil University, Van, 65080, Turkey

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Nano-size Polymer Dispersed Liquid Crystals for Phase-Only Optical Modulation

DANIELE EUGENIO LUCCHETTA[a],
ALESSANDRO MANNI[a], RIDVAN KARAPINAR[b],
LUIGI GOBBI[a] and FRANCESCO SIMONI[a]

[a]*Dipartimento di Fisica ed Ingegneria dei Materiali e del Territorio and*
Istituto Nazionale per la Fisica della Materia. Universita' di Ancona,
Via Brecce Bianche, I-60131, Ancona, Italy and
[b]*Yuzuncu Yil University, Faculty of Arts and Sciences,*
Department of Physics, 65080 Van, Turkey

In this work we report the preparation details and the electro-optical characterization of a new class of nanometer-sized PDLC obtained by using a multifunctional monomer in a pre-polymer mixture which is suitable for fast polymerization process. A systematic analysis of the sample morphology has been carried out on a large number of samples characterized by different values of the photoinitiator concentration and curing parameters. These samples have high transparency to the visible light. However, reorientation of the liquid crystal domains due to the application of a suitable voltage can affect the optical phase shift making these materials suitable as polarization independent "phase only" optical modulators.

Keywords: PDLC morphology; electro-optical properties; phase-only modulation;

Introduction

Polymer Dispersed Liquid Crystals (PDLCs) are composite materials in which nematic liquid crystals (NLC) are phase-dispersed as droplets in a polymer matrix. The mechanism of droplet formation is the phase separation of a starting prepolymer-LC or polymer-LC isotropic mixture induced by polymerization (PIPS), thermal quenching (TIPS) or solvent evaporation (SIPS) process [1]. A large variety of structures can be obtained depending on the components, component concentrations and curing techniques and parameters [2]. In particular photo-sensitive mixtures, when exposed to coherent or incoherent UV radiation can lead to PDLC samples characterized by well defined distribution functions of the liquid crystal (LC) droplets size [3] or to different morphologies (network structures, channels etc.) depending on the curing parameters. The classical droplet morphology is generally characterized by good mechanical and electro-optical properties whereas other morphologies show different and peculiar electro-optical behaviors which could find applications as self-ordering structures [4] and optical devices [5].

In typical PDLC systems the LC droplets are randomly distributed in the polymer matrix and their average size is close to the range of visible wavelengths. In the absence of an applied external field (electric, magnetic or mechanical) the droplet director N_d, which describes the average orientation of the LC director inside each droplet, is randomly oriented. In this situation the sample looks opaque because there is a refractive index mismatch between droplets and polymeric matrix which creates a strong scattering of visible light. When an external field is applied to the PDLC sample, the droplet director tends to align along the field. If, as usual, the ordinary refractive index of the

LC is chosen close to the one of the polymeric matrix, this collective alignment reduces the refractive index mismatch and the sample becomes transparent. Due to this peculiar behavior, PDLC materials have attracted wide interest for a large number of applications such as switchable windows and gratings, light shutters, displays etc.

By increasing the efficiency of the phase separation process, which depends on the components, components concentration and UV curing parameters, sub-micron (nano-sized) droplets can be obtained [6][7]. As a consequence the PDLC samples are characterized by low light scattering and high optical transmission. However by applying a suitable voltage (higher than in conventional PDLCs) it is possible to affect the LC orientation, thus changing the average refractive index of the sample. It is therefore expected that phase-only modulation is possible without any dependence on the light polarization. For this reason nano-sized PDLCs have a potential strong interest for development of innovative devices for optical communications.

In this article we report a detailed investigation performed on nanometer-sized PDLCs obtained by using a multifunctional monomer in a pre-polymer mixture which is suitable for fast polymerization process. In particular we have investigated the preparation methods, the morphologies and the electro-optical properties devoting special attention to the electrically-induced optical phase shift. This quantity was determined through an interferometric technique (Mach-Zehnder type) that allowed also getting information on the electro-optical response times. In the following we will describe in details the preparation methods used to obtain nano-domains of LC in the polymer matrix which have been characterized by Scanning Electron Microscopy

(SEM) connected to a professional image analysis system. The typical electro-optical response of these materials will be also presented.

Materials

Our pre-polymer mixture is a solution of the monomer dipentaerythritol pentacrylate (DPHPA), the photoinitiator benzophenone (BP), the solubilizer N-vinylpyrrollidone (NVP) and the liquid crystal E7 which is an eutectic mixture consisting of three cyanobiphenyls and a cyanoterphenyl. The chemical structures of the monomer and stabilizer can be found in the literature [6].

The monomer DPHPA has five acrylic functions on its backbone and it is suitable for giving fast polymerization kinetics [7]. After the photoactivation of the benzophenone/NVP system the two generated radicals are able to start the propagation step in which the pentacrylic monomer gives rise almost instantaneously to the formation of a cross-linked polymer and the phase separation takes place so that the LC molecules separate as a distinct phase in droplets whose mean diameter is in the nanometer range. For the details of the photo-polymerization process, the formation of the polymeric network is accomplished by UV irradiation of the mixture containing a small quantity of the photoinitiator benzophenone.

The photochemistry of benzophenone is well-known. The absorption of a UV radiation causes the formation of an unstable diradical. This very reactive species reacts with neighbouring molecules first by an electron transfer, which leads to a radical ion pair, and then by a proton transfer. The two radicals produced are able to initiate the polymerization reacting with the monomers present in the mixture.

Considering the components of the mixture used for the preparation of the PDLC films we notice that the polyacrylic compound used as monomer in the mixture is highly reactive and the formation of the propagating species is easy because the monomer are stabilized by resonance.

NVP has the function to reduce the viscosity of the solution. Since the polymerization developes in bulk, as the polymer grows, it is more difficult for the propagating species to meet unreacted monomers because of the increase of viscosity, and this brings to the formation of highly dispersed polymers with low masses. It is known that the polymer mass has a direct influence on the phase-separation process. Phase-separation is better accomplished if the polymer mass is high because in this condition the chemical differences between the liquid crystal and the matrix are magnified.

Experimentals

The PDLC samples were prepared using two conductive glasses (3 cm x 1.5 cm x 0.1 cm) filled by capillarity at about 65 °C, using the mixtures reported in Table I.

Mylar spacers were used to obtain cell thickness of 23 μm. The UV exposure time was varied from 10 to 30 minutes and the power of the incoherent UV light was fixed at 12.5 (low intensity), 24 (medium intensity) and 45 (high intensity) mW/cm^2 respectively.

Preparation, mixing and transfer of the mixtures into the glasses were done in the dark in order to avoid pre-curing effects due to the room light.

Mixture	E7	DPHPA	NVP	BP
C	35 %	49 %	15 %	1%
C*	35 %	49 %	15.5 %	0.5 %
C**	35 %	49 %	15.9 %	0.1 %

TABLE I: Summary of PDLC mixtures with different percentages of photoinitiator BP

The PDLC samples obtained at different curing times, curing intensities and made by different component concentrations were investigated by scanning electron microscopy (SEM). In our work a Philips XL20 SEM operating at 10 kV was used to study the morphology of the samples and to determine the droplet dimension. Liquid crystals domains ranging from about 45 nm to 250 nm were obtained by varying the curing parameters. However due to the limited resolution of our SEM apparatus it was not possible to carry out a detailed analysis of the effect of the concentration of the different components on the final morphology.

Figure 1a shows the distribution of the diameter of the LC droplets observed in a C** PDLC film polymerized at 24 mW/cm^2 for 10 min and Fig. 1b shows the correspondent fit made by a first order standard exponential decay function.

A professional Image Analysis Software Package (Image-Pro Plus by Mediacybernetics) has been used to perform spatial calibrations of the acquired SEM pictures, counts and statistical analyses on the droplets diameter distributions.

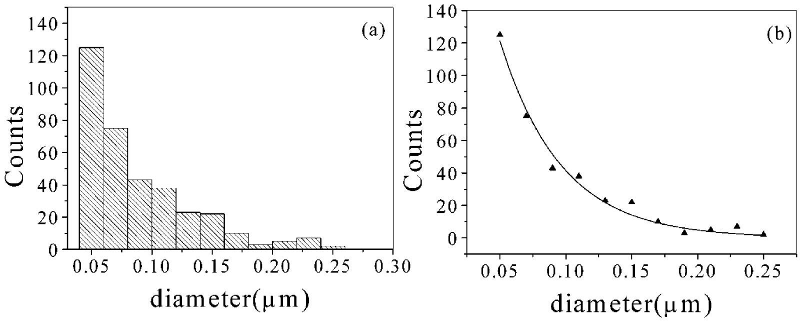

Figure 1: (a) Diameters distribution of a C** PDLC film polymerized at 24 mW/cm^2 for 10 min and (b) the corresponding first order exponential decay

Even if this procedure allows us a very detailed analysis of the image, it is still possible that small droplets are not counted due to the limited resolution of our SEM apparatus. However the exponential distribution shown in figs 1a, 1b is in agreement with our previous observations made on PDLC samples including larger droplets (>400 nm in diameter) falling within the SEM spatial resolution [3]. In fact we have already reported that while the particle size distribution (PSD) in UV cured PDLCs usually follow a log-normal behavior, by increasing the polymerization speed only an exponential tail is observed. Since our systems are characterized by a fast photo-polymerization process we may expect a similar exponential behavior of the PSD. Only in the case where limited SEM resolution affects the observed distributions, the left side cut-off of the curve is lost, thus overestimating the average droplet's diameter and this would occur for all the curves. Therefore our qualitative discussion on the reported data is still valid.

Changes in the percentage of photoinitiator can drastically affect the measured value of the average droplet's diameter. If we increase the percentage of photoinitiator a large number of free radicals will be obtained. These radicals are able to initiate the polymerization reaction by direct interaction with the monomers present in the mixture.

From a statistical point of view this interaction is highly favorable with the DPHPA monomer whose percentage in all the three mixtures is 49% (see Table I). It is well known that the termination step of the photopolymerization reaction depends on the square of the concentration of the reactive species whereas the propagation reaction depends linearly on concentration.

The large number of free radicals makes the termination step more favorable with respect to the propagation one. This behavior leads to the formation of low molecular weight structures (oligomers) in which the LC molecules are partially soluble. Unfortunately, as we wrote earlier, the phase-separation process is better accomplished if the polymer mass is high. In other words the presence of oligomers makes the phase separation process more difficult.

A reduction in the percentage of BF should lead to a better phase separation between LC and polymer which can originate into a larger number of LC droplets with a well defined droplets size distribution function. We found that the average value of the droplets diameter in all the three mixtures is in the range between 60 and 100 nm depending on the curing parameters. Only a particular set of C* nano-PDLC samples cured at 45 mW/cm^2 showed an inverted LC Polymer morphology characterized by a continuous two phase structure with very large LC domains and polymer spheres [1,8-9]. In these PDLC samples we measured LC domains larger than 100 nm.

While with our experimental setup it is not possible to get detectable differences in the total number of LC droplets between C and C* samples, the comparison between C and C**, both polymerized at 24 mW/cm^2 for 10 min show a considerable different behavior.

In fact, the total number of LC droplets, for an analyzed area of about 300 μm^2, in the C mixture is about 400 whereas a value of about 500 has been obtained in the case of the C** mixture. It is important to note that also the average value of the droplets diameter is higher for the C** mixture than for the C mixture (90 nm for C** versus 74 nm for C). This means that the corresponding volume fraction v_{lc} of the LC domains, in the C** samples, is higher than the one of the C samples or equivalently that a smaller quantity of LC still remains inside the polymeric matrix. In other words the phase separation process is more favorable in nano-PDLC samples made by the C** mixture.

As clearly reported in reference [3] the exponential behavior observed in our PSDs indicates a direct dependence of the average droplets dimension on the diffusion coefficient D of the activated species. The value of this coefficient decreases in time exponentially, as a result of the polymerization, towards a final value $D(I)$ which decreases by increasing the light intensity I [10]. This means that, in the general framework of the coarsening and phase separation theories, the LC droplet formation can be regarded as a time dependent diffusion controlled process which, in the case of small LC droplets, leads to the strongly asymmetric PSD experimentally observed. Fig. 2 reports the distribution function of a C** samples cured at high light intensity.

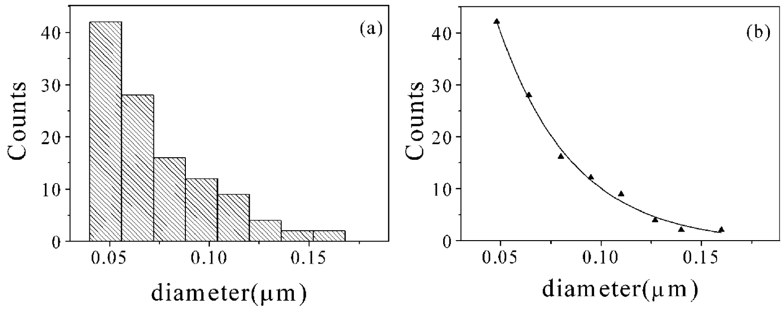

Figure 2: Distribution function (a) and first order exponential decay (b) for a C** nano-PDLC sample polymerized at 45 mW/cm^2 for 10 min

A value of 75 nm for the average droplets diameter has been derived from the data analysis. If we compare this value with the one obtained in the case of a C** sample polymerized at lower intensity we can easily conclude that for nano-PDLC samples the usual behavior in which the droplets size is smaller for PDLC samples polymerized at higher intensities is confirmed.

The electro-optical properties of these samples were studied by using as light source an He-Ne Laser beam (λ = 632.8 nm) running in a Mach-Zehnder interferometer geometry. In this way we determined the induced optical phase shift as a function of the applied electric field. Details of the experimental technique are given elsewhere [9]. A typical phase shift curve is shown in Fig. 3

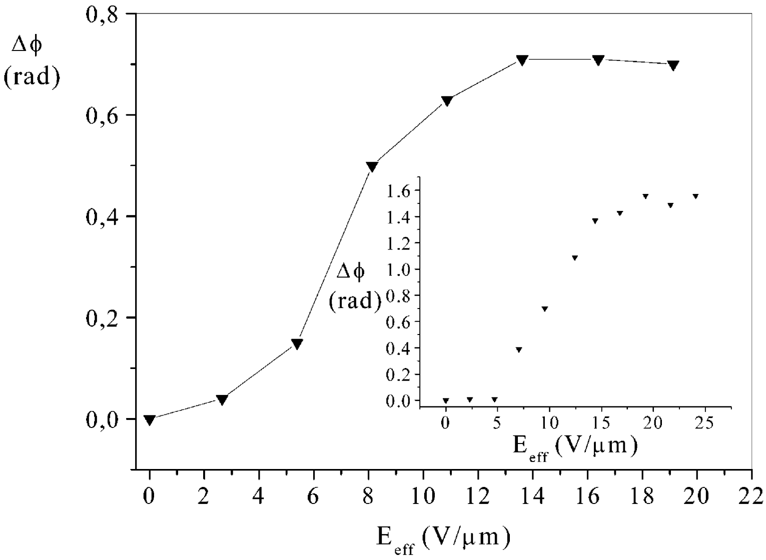

Figure 3: Electric-induced phase shift vs applied effective field for a C* nano-PDLC sample polymerised at high light intensity. The inset shows the possibility to obtain larger values of phase shift (up to π/2) by using different starting isotropic mixtures (see the text for details)

If we increase the LC concentration in our mixture up to 40% in weight, higher phase shifts can be easily obtained as reported in the inset.

In order to measure the effects due to the polarization of the incident light, the PDLC samples were mounted on a motorized goniometer inside one of the two arms of the interferometer, to be rotated in a plane normal to the incident beam. Measurements of the optical phase shift were taken for different orientations of the sample with respect to the incident linearly polarized beam. By rotating the sample no displacement of the interference pattern was detected. The measurements were performed with and without an applied electric field. The result was that any orientation of the sample produces the same phase shift, namely the electrically induced optical-phase modulation is polarization independent. The switching time of this modulation was found to be lower than 1 ms. The optical transmittance of these samples ranges from 80% to 90% due to the low scattering of the LC nano-domains for the visible wavelengths.

Conclusions

In this paper we have presented a morphological analysis and electro-optical characterization of nano-size PDLC materials prepared by rapid polymerization of a highly functionalized monomer. By reducing the percentage of photoinitiator benzophenone in the starting isotropic mixture it is possible to drive the phase separation process to obtain a final morphology characterized by a larger number of LC domains with bigger dimensions. This means that only a small amount of LC remains inside the polymeric matrix. The phase shift parameters and the electro-optic behavior of the PDLC samples were determined with an interferometric technique. Fast switching times and a “phase only” polarization independent modulation of the impinging light with phase shift values up to $\pi/2$ have been obtained. These main features make the nano-PDLCs interesting materials to design new photonic devices for telecom applications.

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