Polarizing properties of a stretched film of a polymer-dispersed liquid crystal with a surfactant dopant

M. H. Egamov, V. P. Gerasimov, M. N. Krakhalev, O. O. Prishchepa,[a)] and V. Ya. Zyryanov

L. V. Kirenskiĭ Institute of Physics, Krasnoyarsk Science Center, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia

V. A. Loiko

B. I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, Belarus

(Submitted February 21, 2013)
Opticheskiĭ Zhurnal **81**, 67–71 (July 2014)

The transmittance anisotropy of a composite polymer–liquid-crystal film has been studied as it varies with the degree to which it is elongated. The composite film includes polyvinyl alcohol, the nematic liquid crystal 4-n-pentyl-4′-cyanobiphenyl, and the surfeiting cetyltrimethylammonium bromide, which initiates homeotropic adhesion of the nematic to the surface of the polymer. It is shown that, when the film is uniaxially stretched, the transmittance of the orthogonally polarized component of directly transmitted radiation and accordingly the degree of polarization abruptly increase, reaching saturation when it is stretched to twice its length. Such variation of the film's macroscopic optical properties can be caused by an orientational–structural transition to a homogeneous configuration of the director in deformed droplets of the nematic and makes it possible to substantially improve the optical characteristics of light polarizers based on such composite media. © *2014 Optical Society of America.*

OCIS codes: (260.5430) Polarization; (160.3710) Liquid crystals.
http://dx.doi.org/10.1364/JOT.81.000414

INTRODUCTION

Devices for obtaining plane-parallel optical radiation (light polarizers) can be based on anisotropic properties inherent to various effects of the interaction of light with matter: reflection, refraction, absorption, scattering, etc.[1] In modern optical and optoelectronic technologies in the visible region of the spectrum, the most widely used polarizers are thin-film devices based on absorption anisotropy (polaroid films) or prism polarizers based on anisotropy of the total internal reflection (for example, Glan prisms).[2]

Thermoplastics with additives of dichroic molecular dyes or needle-shaped microcrystals are often used to fabricate a polaroid film. In this case, it is sufficient to heat the polymeric film to the plastic state, subject it to uniaxial stretching to order the dichroic elements, and cool it. One component of the transmitted radiation—for instance, that polarized parallel to the stretching direction—is virtually totally polarized in such a medium, whereas the orthogonally polarized light is partially transmitted. Polaroid films are distinguished by simple and inexpensive production technology, and their area is limited only by the possibilities of the process equipment. A substantial disadvantage of such films is that they cannot be used in powerful light fluxes, which, because of strong absorption, can cause them to be thermally destroyed. Prism polarizers are free from this disadvantage, but their aperture is usually restricted to several centimeters, they have greater mass and size, and they are much more expensive than thin-film polarizers.

It is interesting that the main advantages of the polarizers enumerated above can be simultaneously obtained in composite films that polarize optical radiation because of anisotropy of the light scattering. An example of such structures is a uniaxially stretched film of polymer-dispersed liquid crystals (PDLCs). Optical anisotropy in uniaxially stretched cholesteric PDLC films was first detected in Ref. 3 by selective scattering of light. The possibility of using the anisotropy of light scattering in uniaxially deformed (by stretching or shearing) PDLC nematic films to fabricate polarizers has been patented.[4] Such a polarizer is a polymeric film with an encapsulated ensemble of stretched ellipsoidal droplets of nematic liquid crystal (LC) whose long axes are predominantly oriented in the stretching direction (Fig. 1). Because of the tangential adhesion of the nematic to the polymer, the LC director inside the drops forms a bipolar configuration, with the lines of the director passing along the meridians of the ellipsoid and collected together at singular points—topological defects (boojums) that coincide with the poles of the ellipsoid.[5] The composition of the composite is chosen so that the orthogonal component of the refractive index $n_\perp$ of the nematic is equal to the refractive index n_p of the polymeric

 1070-9762/14/070414-04$15.00/0

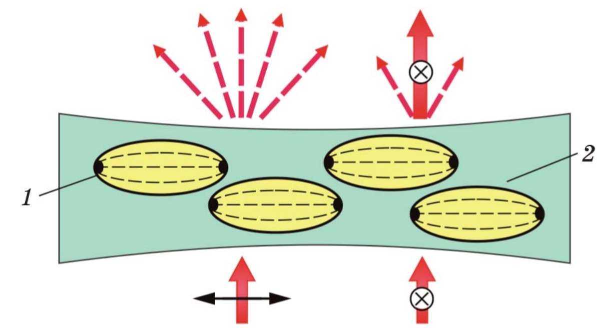

FIG. 1. Polarization of light transmitted through a uniaxially stretched PDLC film. Light with parallel (relative to the stretching direction) polarization is intensely scattered, and the orthogonally polarized component of the light is transmitted, being only weakly scattered. 1—LC droplets, 2—polymer. The dashed lines inside the droplets show the local direction of the director, while the dark semicircles show the topological defects.

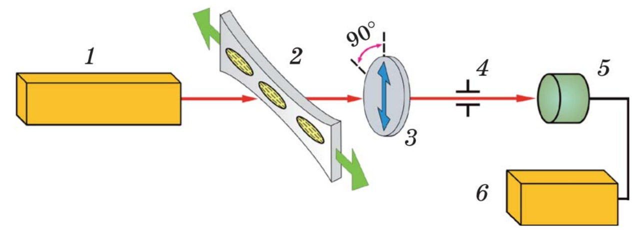

FIG. 2. Layout of apparatus for studying the polarizability of a PDLC film when it is uniaxially stretched. 1—He–Ne laser ($\lambda = 0.633$ μm), 2—test sample, 3—polarizer, 4—circular stop, 5—photodetector, 6—digital signal recorder.

matrix, $n_\perp \cong n_p$, while the birefringence $\Delta n = n_\parallel - n_\perp$ of the LC is a maximum. Here the symbols $\parallel$ and $\perp$ denote polarization of light parallel and perpendicular to the LC director, respectively.

In this case, the light polarized parallel to the film-stretching direction is intensely scattered as a consequence of the large refractive-index gradient $(n_\parallel - n_p)$ at the polymer–LC interface. The orthogonally polarized component of the light should apparently be transmitted without experiencing scattering because of the relationship $n_\perp \cong n_p$. However, detailed studies[6,7] carried out for uniaxially ordered PDLC films showed that orthogonally polarized light is partially scattered because of the inhomogeneous configuration of the director field and the presence of topological defects in the drops of the nematic. This both degrades the polarizability of the PDLC films and appreciably reduces the transmittance of directly transmitted radiation polarized perpendicular to the scattering direction.

The goal of these studies is to develop polarizing PDLC films with improved optical characteristics by using a specially matched surface-active substance—a surfactant.

THE OBJECT OF STUDY

The well-known nematic 4-n-pentyl-4′-cyanobiphenyl (5CB), which has transition temperatures T crystal–(22°C)–nematic–(35°C)–isotropic liquid, was chosen for investigation. At $T = 22$°C and with radiation having $\lambda = 0.633$ μm, the refractive indices of 5CB are $n_\parallel = 1.717$ and $n_\perp = 1.530$.[8] Polyvinyl alcohol (PVA) was used as a matrix. This polymer possesses high mechanical strength and is impermeable to gas, as well as being transparent in the visible region. The refractive index n_p of various kinds of PVA varies in the range 1.49–1.53 at $T = 22$°C,[9] and this makes it possible to choose a composition of components that satisfy the relationship $n_\perp \cong n_p$. To increase the elasticity, the PVA was plasticized with glycerin.

To modify the surface adhesion, the cationic surfactant cetyltrimethylammonium bromide (CTAB) was used on the polymer–LC interface in this project. By dissolving it in the LC, it decomposes into a negatively charged Br^- ion and a positively charged surface-active ion of cetyltrimethylammonium CTA^+.[10] The orienting influence of the CTAB surfactant depends on its concentration at the interphase boundary. Thus, at a low concentration, the CTA^+ cations arrange themselves into long active chains predominantly parallel to the interphase boundary and provide planar adhesion of the LC molecules to the polymer. At high concentration, active chains of CTA^+ oriented perpendicular to the surface of the polymer ensure homeotropic boundary conditions.[11]

The samples of PDLC films were fabricated by emulsifying the nematic in an aqueous solution of a mixture of polymer, glycerin, and surfactant, followed by evaporation of the solvent. The mass ratio of the components was PVA : glycerin : 5CB : CTAB = 1 : 0.3 : 0.2 : 0.006. This composition was subjected to mechanical mixing with the mixer rotating at 2500 rpm for 30 min. The heterophase mixture was deposited on the surface of a glass substrate, followed by drying in air at 23°C. The resulting PDLC films have fairly uniformly distributed drops of nematic in the volume of the polymer matrix and are 45 μm thick. The drops of LC in the plane of the film had a circular shape, and their mean size, determined using an Axio Imager.A1m polarization microscope (Carl Zeiss), was 4 μm.

MEASUREMENT TECHNIQUE

Rectangular plates of size 5 × 10 mm were cut from the resulting composite film and, by attaching them to a specially developed device, were subjected to uniaxial stretching. The measurement apparatus shown in Fig. 2 was used to investigate how the polarized components of the light-transmitting PDLC film depend on the elongation coefficient.

The circularly polarized beam of helium–neon laser 1 passed through sample 2, polarizer 3, and circular stop 4 and was incident on photodetector 5, the signal from which was recorded by voltmeter 6. The direction of the polarizer was oriented either horizontally to measure the transmittance $T_\parallel$ of the parallel-polarized component or vertically to measure $T_\perp$. The diameter of the opening of the stop, 10 cm away from the sample, corresponded to a diameter of the transverse cross section of the laser beam and was 1 mm. The stop thus cut off the light scattered at an angle, making it possible to measure the intensity of only the directly transmitted radiation.

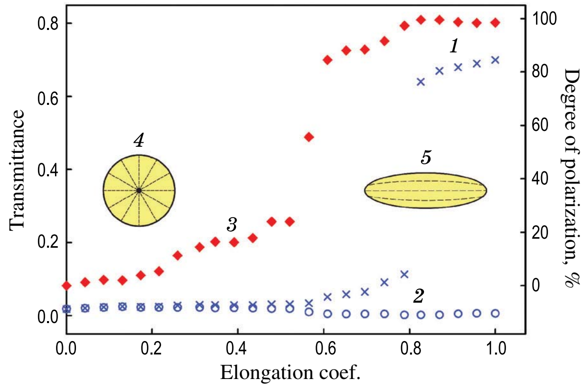

FIG. 3. Transmittance of orthogonally (1) and parallel (2) polarized components of the light, as well as the degree of polarization (3) versus the elongation coefficient of a PDLC film with PVA:glycerin:5CB:CTAB mass ratio of 1:0.3:0.2:0.006. The initial thickness of the film is 45 μm. 4—Initial radial configuration, 5—defect-free structure of the director.

RESULTS AND DISCUSSION

Figure 3 shows how the transmittance of the orthogonally polarized ($T_\perp$) and parallel polarized ($T_\|$) components of the directly transmitted radiation, as well as the degree of its polarization, defined by the ratio $P = (T_\perp - T_\|)/(T_\perp + T_\|)$, depend on the elongation coefficient $\Delta l/l_0$ of the composite film, where $l_0 = 10$ mm is its initial length. The PDLC film possesses no polarizing property in the original state: Its transmittance is independent of the polarization of the radiation and equals about 0.02. The transmittance remains virtually isotropic to a value of $\Delta l/l_0 \cong 0.22$; when it exceeds this, a smooth increase of $T_\perp$ begins, supplemented by a small decrease of component $T_\|$ when $\Delta l/l_0 > 0.52$. When $\Delta l/l_0 \cong 0.8$, this is followed by a sharp increase of the transmission of the orthogonal component $T_\perp$ by about a factor of 8. In this case, $T_\|$ reaches its minimum and then begins to smoothly increase; as shown in Ref. 6, this is explained by the decrease of the thickness of the scattering medium.

The abrupt transmittance increase of the orthogonally polarized component when $\Delta l/l_0 \cong 0.8$ is probably caused by transformation of the initial radial configuration of the director (4, Fig. 3) into a defect-free, virtually homogeneous orientational structure (5, Fig. 3). The possibility of forming such a defect-free structure was shown earlier[12] for drops of the nematic 5CB with an additive of lecithin—a nonionogenic surfactant that also induces homeotropic orientation of the LC. The character of the variation of the degree of polarization and of the perpendicular component of the transmittance when the composite film is stretched makes it possible to assume an even more complex sequence of orientational–structural transitions in deformed drops of the nematic. However, special studies that go beyond the framework of this paper are needed to explain the physical mechanisms that determine these features.

Having about an equal degree of polarization $P \geq 0.99$, the $T_\perp$ value of the PDLC test film with a surfactant reaches a value of 0.70, which substantially exceeds the analogous parameter of $T_\perp = 0.61$ achieved in Ref. 6 in a composite film not doped with surfactant, with the same twofold elongation. Further improvement of the technology for fabricating composite films and optimizing their composition will apparently make it possible to increase their transparency even further while maintaining a high degree of polarization of the directly transmitted radiation.

CONCLUSION

Unlike prism polarizers, uniaxially stretched PDLC films are also easy to fabricate and compact, like polaroid films. However, they have clear advantages over the latter. First, a PDLC film can be used to polarize much more powerful radiation, since a polaroid film absorbs more than half of the incident radiation and breaks down from heating, while a composite film only scatters light and is consequently heated much less. Second, PDLC films are capable of polarizing transmitted radiation in the entire region of transparency of the components being used (the visible and the near-IR regions), whereas polaroid films operate only in their own absorption band or that of the dichroic dye dissolved in them. One more important advantage of PDLC films should be mentioned, based on the possibility of controlling the degree of their polarization in the range from 0 to 1 by applying an electric field[13,14] or magnetic field.[15,16] However, a feature of polarizers based on light-scattering anisotropy should be pointed out that substantially restricts the region in which they can be used: They are promising only in optical devices where the scattered light can be cut off by stopping down the directly transmitted radiation—for example, in projection displays, laser systems, etc.

The studies carried out in this paper showed the possibility of substantially improving the optical characteristics of light polarizers based on uniaxially oriented PDLC films, achieved by introducing a specially chosen surfactant into a nematic. In the given situation, the surfactant additive, along with stretching of the composite film, results in the formation of the inhomogeneous boundary conditions needed to obtain a defect-free, homogeneous configuration of the director in the droplets of nematic. This in turn makes it possible to sharply reduce the stray scattering of light polarized orthogonal to the stretching direction and thereby to substantially increase the transmittance of the film for directly transmitted radiation.

ACKNOWLEDGMENTS

This work was carried out with the partial support of Grant 12-03-00816 of the Russian Foundation for Basic Research, Grants 24.32 and 24.29 of the Presidium of the Russian Academy of Sciences, and joint project 30 of the Siberian Section of the Russian Academy of Sciences (SO RAN), and a joint project of the SO RAN and the National Scientific Council of Taiwan.

[a]Email: p_oksana@iph.krasn.ru

1W. A. Shurcliff, *Polarized Light: Production and Use* (Harvard University, Cambridge, Massachusetts, 1962; Mir, Moscow, 1965).

2E. F. Ishchenko and A. L. Sokolov, *Polarization Optics* (MÉI, Moscow, 2005).

[3] A. S. Sonin and I. N. Shibaev, “Structural ordering and properties of cholesteric pseudo-encapsulated films,” Zh. Fiz. Khim. **55**, 1263 (1981).

[4] J. L. West, J. W. Doane, and S. Zumer, “Liquid-crystal display material comprising a liquid-crystal dispersion in a thermoplastic resin,” U.S. Patent 4,685,771, Int.Cl. G02F 1/13 (8/11/1987).

[5] G. E. Volovik and O. D. Lavrentovich, “Topological dynamics of defects: boojums in nematic drops,” Zh. Eksp. Teor. Fiz. **85**, 1997 (1983) [Sov. Phys. JETP **58**, 1159 (1983)].

[6] V. Ya. Zyryanov, S. L. Smorgon, and V. F. Shabanov, “Elongated films of polymer-dispersed liquid crystals as scattering polarizers,” Mol. Eng. **1**, 305 (1992).

[7] V. G. Nazarov, A. M. Parshin, A. V. Gunyakov, V. Ya. Zyryanov, and V. F. Shabanov, “Optical anisotropy of uniaxially oriented films of polymer-encapsulated liquid crystals,” Opt. Zh. **72**, No. 9, 28 (2005) [J. Opt. Technol. **72**, 675 (2005)].

[8] V. Ya. Zyryanov and V. Sh. Épshteĭn, “Measuring the refractive indices of a liquid crystal using a tunable source of coherent IR radiation,” Prib. Tekh. Eksp. No. 2, 164 (1987).

[9] A. F. Nikolaev, *Synthetic Polymers and Plastics Based on Them* (Khimiya, Leningrad, 1966).

[10] Zh. Kon’yar, *Orientation of Nematic Liquid Crystals and Mixtures of Them* (Universitetskoe Izd., Minsk, 1986).

[11] J. E. Proust, L. Ter-Minassian-Saraga, and E. Guyon, “Orientation of a nematic liquid crystal by suitable boundary surfaces,” Solid State Commun. **11**, 1227 (1972).

[12] O. O. Prishchepa, M. Kh. Égamov, V. P. Gerasimov, M. N. Krakhalev, and V. A. Loĭko, “Light polarizers based on polymer–LC–surfactant composites films as anisotropic scattering media,” Izv. Vyssh. Uchebn. Zaved. Fiz. **56**, No. 2/2, 258 (2013).

[13] V. Ya. Zyryanov, V. V. Presnyakov, S. L. Smorgon, and V. F. Shabanov, “Electrooptic properties and orientational–structural transformations in an ensemble of ellipsoidal drops of cholesterics,” Dokl. Ross. Akad. Nauk **354**, No. 2, 178 (1997) [Phys.–Dokl. **42**, 235 (1997)].

[14] V. V. Presnyakov, S. L. Smorgon, V. Ya. Zyryanov, and V. F. Shabanov, “Volt-contrast curve anisotropy in planar-oriented PDChLC films,” Mol. Cryst. Liq. Cryst. **321**, 259 (1998).

[15] O. O. Prishchepa, A. V. Shabanov, V. Ya. Zyryanov, A. M. Parshin, and V. G. Nazarov, “Friedericksz threshold field in bipolar nematic droplets with strong surface anchoring,” Pis’ma Zh. Eksp. Teor. Fiz. **84**, 723 (2006) [JETP Lett. **84**, 607 (2006)].

[16] O. O. Prishchepa, A. M. Parshin, A. V. Shabanov, and V. Ya. Zyryanov, “Magnetooptical study of Friedericksz threshold in polymer-dispersed nematic liquid crystals,” Mol. Cryst. Liq. Cryst. **488**, 309 (2008).