

TECHNOLOGICAL METHOD OF INCREASING PHOTOSENSITIVITY IN PHOTOCHROMIC LIQUID CRYSTAL POLYMER FILMS

L. Devadze, G. Petriashvili, A. Chanishvili, Ts. Zurabishvili,
N. Sepashvili, K. Chubinidze, Sh. Akhobadze, N. Ponjavidze

Georgian Technical University
Vladimer Chavchanidze Institute of Cybernetics
Tbilisi, Georgia
tsisanazurabishvili@yahoo.com

Accepted February 28, 2022

Abstract

Qualitatively new polymer films consisting of photochromic spiropyran doped in the liquid crystal nemato-chiral matrix has been obtained using the technological process of the microencapsulation method improved by the authors. Studies have shown that by controlling the microencapsulation process, technological characteristics of polymer films affect their photosensitivity. Reducing the microcapsules size, increasing the films thickness and their stretching result in the increased photosensitivity. The technological method of microencapsulation is proposed by the authors as one of the directions to increase the photosensitivity of photochromic liquid crystal polymer films.

1. Introduction

The placement of liquid crystal (LC) and photochromic molecules in one system makes it possible to combine synergistically their structural properties. Retaining their properties, the interaction between them gives this photochromic LC system special unique thermo-, photo- and electro-optical, as well as mechanical properties. Integration of such system with polymer enables the creation of new multifunctional polymer materials, which is very promising for the use of photochromic LC systems in modern photo-optically controlled devices to record, display and storage information.

A photochromic LC system is a composition that contains photochromic spiropyran (SP) dissolved in a cholesteric LC matrix. In such composition SP has high photosensitivity upon exposed to ultraviolet (UV) light irradiation.

This phenomenon is especially observed in a nematic-chiral LC matrix (a mixture of a spirally induced nematic LC substance with an optically active chiral additive) doped with SP. In obtained reversible SP photochromic LC system, exposure to UV light can be controlled not only by photochromic transformations but the structure of the LC matrix.

The authors studied the photosensitivity of compositions consisting of a nemato-chiral mixture doped by SP with different lengths of the alkyl radical [1]. A nemato-chiral matrix was chosen the helix pitch p of which weakly depends on the temperature T ($dp/dT \approx 0$). Such nemato-chiral mixture as a thermal indicator is characterized by an insignificant temperature shift of the selective reflection of the light wavelength (Bragg's reflection band) in the visible spectrum. If in the system the Bragg reflection band in the long-wavelength red region is distanced from the absorption band of the short-wavelength colored merocyanine form of SP, the process of coloration-decoloration caused by photo-induction can be observed [2].

From a practical point of view, it is very important to obtain polymer materials on the base of the photochromic LC composition. The polymer protects the integrated composition from external factors, preserves the photochemical stability and makes it possible to use multiple polymer material.

The photochromic LC system was introduced into the polymer by the method of microencapsulation [3, 4]. The basic principle of the method is obtaining a stable encapsulated emulsion in a dispersion system (composition-polymer solution), which is achieved by using an emulsifier. The method of encapsulation by the authors was improved by choosing glacial acetic acid as a suitable emulsifier, which does not chemically interact with SP, nematic and optically active substances and provides a stable dispersion system in polyvinyl alcohol (PVA), which contains dispersion phase-isolated, crushed compositions-aggregates of the microcapsules in the form dispersion medium of an aqueous solution of PVA [5].

In the polymer, the initial properties of the composition are fixed in a microcapsule that preserves these parameters as much as possible and ensures the production of thermochromic polymer films with high reflection intensity and photochromic LC polymer films with high photosensitivity.

Using the technological process of an innovative microencapsulation method was obtained:

- Thermochromic LC polymer films [6 – 8] consisting of a nemato-chiral mixture with different temperature ranges [9];
- An irreversible photochromic LC polymer film containing a nematic substance with a photosensitive optically active additive [10]; and
- Qualitatively a new reversible SPLC polymer films containing the nemato-chiral LC mixture doped with different lengths of the alkyl radical spiropyran SP [1, 11 – 13].

The present paper describes the technological process of the microencapsulation method of making SPLC polymer films and discusses the influence of technological characteristics of films (size of microcapsules, film thickness, stretched and non-stretched film) on their photosensitivity based on spectral and optical-microscopic studies.

The technological method of microencapsulation developed by the authors is proposed as one of the directions to increase the photosensitivity of photochromic SPLC polymer films.

2. Experimental

SPLC polymer films were obtained based on the composition consisting of an SP doped LC nemato-chiral mixture. Nemato-chiral mixtures with temperature dependence $dp/dT \approx 0$ was selected, which contains a certified nematic substance with a cyano-biphenyl group and a certified optically active additive with different ratios of components (wt.%). SP of the indoline series with different lengths of the alkyl radical at the nitrogen atom was doped in the mixture to obtain SP doped LC nemato-chiral liquid crystal composition.

Polymer films consist of one encapsulated layer containing the encapsulated composition and of two or one protective layers obtained based on different concentrations of an aqueous solution of PVA.

The technological process of making SPLC polymer films by the microencapsulation method consists of the following three stages.

2.1. Preparation of encapsulated emulsion

SP doped with a nemato-chiral composition, heated to an isotropic state, is poured in an aqueous solution of PVA. The emulsifier glacial acetic acid is added to the solution. The composition is encapsulated in a PVA solution stirring the emulsion at a constant temperature. Regulation of the stirring speed of the emulsion determines the size of the microcapsules. Encapsulated emulsion (layer) is obtained.

2.2. Obtaining of polymer film

Protective and encapsulated layers of a polymer film are obtained on the polished glass of a special drying device. An aqueous solution of PVA is poured on polished glass. After drying, a protective film layer is obtained. Then the encapsulated emulsion is poured onto the protective layer. After drying, a two-layer encapsulated polymer film is obtained. To obtain a three-layer film one protective layer is added. The thickness of the films is controlled by the concentration of the polymer and the thickness of the wire stretched over (on) the glass surface.

2.3. Stretching of polymer film

Polymer films are stretched in a special thermal chamber using a stretching device. Uniaxial deformation is carried out, after which the film sample is cooled to room temperature and removed from the stretching device.

3. Results and discussion

Elastic and homogeneous SPLC polymer films of various shapes and sizes are made following the practical requirements using the technological microencapsulated method. At all

stages of the process regulation of technological characteristics – sizes of microcapsules in film, the thickness of the film, non-stretched and stretched film – it became possible to obtain films with high photosensitivity.

The optical parameters of the polymer films were measured using a fiber-optic spectrometer Avantes–2048. Photoinduction by UV rays was performed with a lamp and filters. Microscopic investigation of the obtained films was carried out using a polarizing microscope.

Spectral and optical microscopic studies have shown that the technological characteristics of the films affect photosensitivity. In the samples of films of the same content, a change in the photosensitivity is noted by adjusting the size of the microcapsules, the thickness and the stretching of the films.

Microscopic studies of the films confirm that microcapsules in the polymer do not suffer disintegration upon the UV irradiation and temperature, which ensures maximum preservation of the properties of the composition in microcapsules (**Figures 1 and 2**). Hence the optical parameters of SPLC polymer films do not change.

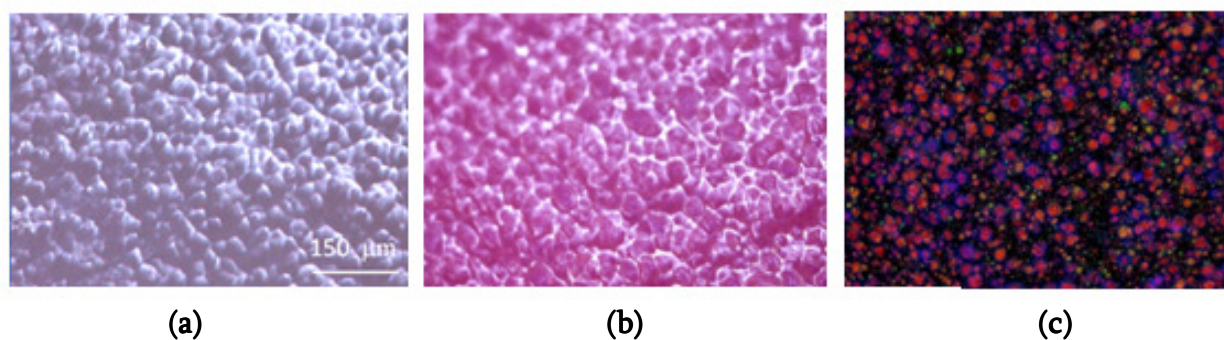


Figure 1. Microcapsules (150×) in SPLC polymer films: (a) non-irradiated, (b) irradiated with UV light and (c) in light transmission mode.



Figure 2. Non-irradiated (light) and irradiated (dark) areas in SPLC films (60×).

The encapsulated layer of SPLC polymer films was obtained on the stage of the technological process of preparing the encapsulated emulsion. By controlling the stirring speed, during the preparation process of the encapsulated emulsion, it is possible to change the size of the microcapsules containing the films, which has a significant impact on the photosensitivity of the SPLC films.

Spectral and microscopic studies have shown that a decrease in the size of the microcapsules increases both: the peak of absorption characteristic of the colored form of the SP and the intensity of reflection of the nemato-chiral matrix. Photosensitivity of polymer films of the same content, but differing in the size of the microcapsules, exhibit different

photosensitivity. The absorption peak of the films with a small size of microcapsules is significantly higher than of the films with large microcapsule, sizes – see **Figure 3**.

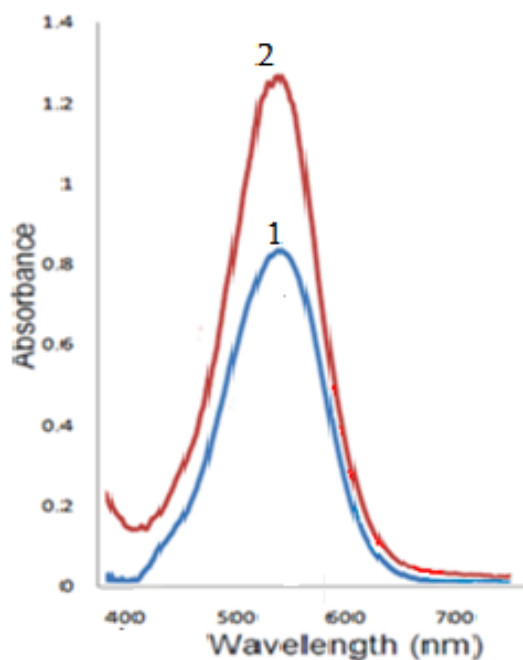


Figure 3. Absorption spectra of SPLC polymer films with same thickness (100 μm) and different sizes of microcapsules after irradiated with UV light. Films with size of microcapsules of (1) 40 – 50 and (2) 20 – 25 μm .

The phenomenon is explained by the fact that a large microcapsule of radius R can form 8 small microcapsules with a radius of $R/2$, the sum of the surface area of which is twice the area of one large microcapsule. If the whole area of large macromolecules is occupied by absorbing centers (SP molecules), the rest of the molecules cannot be activated, since only the upper layers are activated during irradiation.

A decrease in the size of microcapsules, increases their total surface. Accordingly, much more molecules are able to reach the upper layer and become activated under the influence of UV irradiation. If all parameters (extinction, concentration, film thickness) are constant and only the size of the microcapsule decreases, then at the same irradiation dose the absorption peak of films containing smaller microcapsules compared to films with the large microcapsules is caused an increase in photosensitivity of SPLC polymer films.

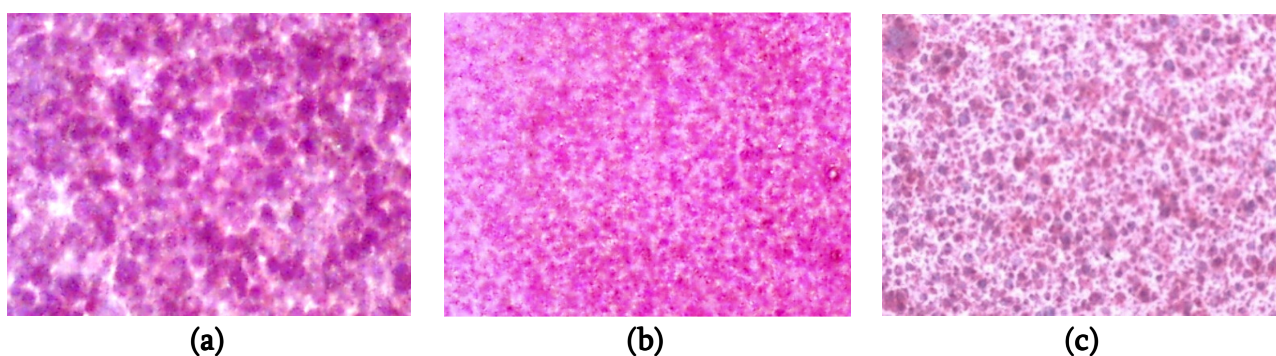


Figure 4. SPLC polymer films (200 \times) irradiated with UV light with size of microcapsules of (a) 40 – 50, (b) 30 – 35 and (c) 20 – 25 μm .

Reducing the sizes of microcapsules (**Figure 4**) enhances the contrast between irradiated and non-irradiated areas of the film which shows the increase in photosensitivity. The change of photosensitivity in polymer films with different sizes of microcapsules is well demonstrated upon information recording of SPLC polymer films under the influence of UV light (**Figure 5**).

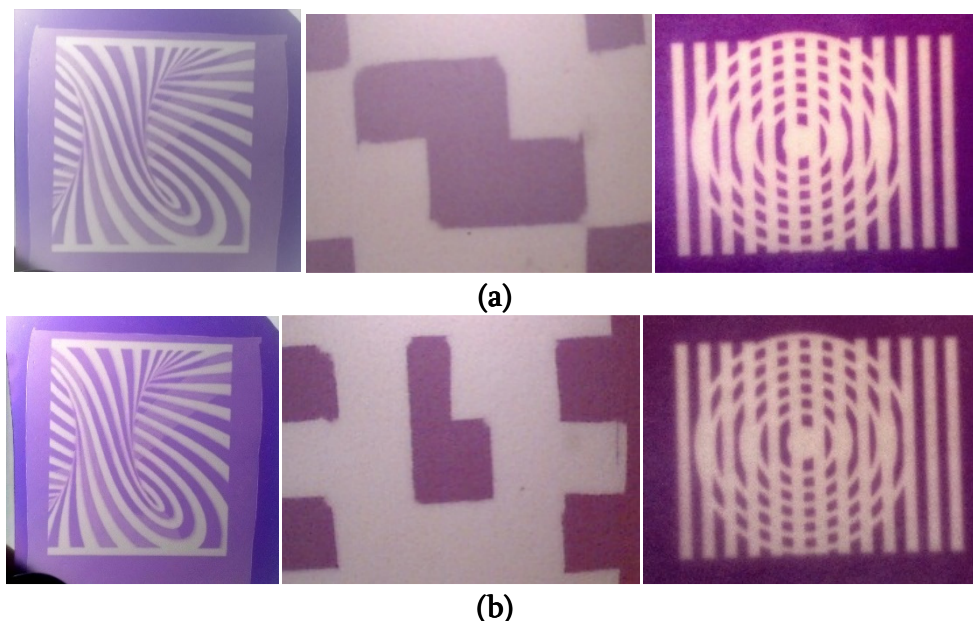


Figure 5. Optical recording images by UV light in SPLC polymer films with size of microcapsules of **(a)** 40 – 50 and **(b)** 20 – 25 μm .

SPLC polymer films of different thicknesses were obtained on a special drying device. Optical studies showed that an increase in thickness significantly increases the absorption peak characterized the photosensitivity of the polymer films and does not affect the intensity of selective reflection of the nematic-chiral matrix (**Figure 6**).

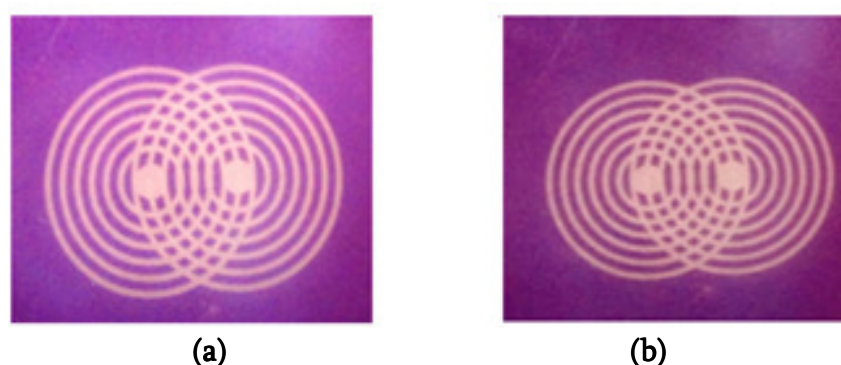


Figure 6. Optical recording images by UV light in SPLC polymer films with thickness of **(a)** 75 and **(b)** 100 μm .

At the stage of stretching of polymer films, uniaxial deformation of the SPLC polymer films occurs. By stretching of the films the uniaxially oriented polymer is formed, the macromolecules of which, straightened by their axes, are oriented predominantly along one direction, which together with the macromolecules causes the ordering orientation of the microcapsules (**Figure 7**).



Figure 7. Stretched SPLC polymer films with microcapsules.

Stretching film samples leads to the formation of a planar configuration of the oriented texture of PVA macromolecules, which ensures the production of polymer films with improved optical properties in comparison with non-stretched films of the same composition and thickness: stretching-orientation significantly increases the selective reflection of the nemato-chiral matrix [6] and improves the photosensitivity of SPLC polymer films (**Figure 8**).

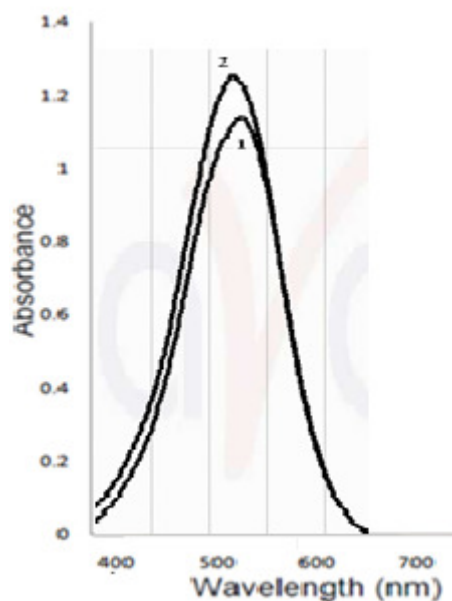


Figure 8. Absorption spectra of SPLC polymer films with same thickness (75 μm) after irradiated with UV light: (1) non-stretched and (2) stretched films.

The improvement in photosensitivity of stretched polymer films shown upon optical recording images by the UV light (**Figure 9**). The change of photosensitivity of SPLC polymer films with the different technological characteristics is clearly shown upon the recording of optical information with UV rays. Spectral and microscopic studies have shown that the sharp contrast in films that have the highest photosensitivity are stretched films containing microcapsules with a size of 20 – 25 μm and the thickest films with a thickness of 100 μm (**Figure 10**).

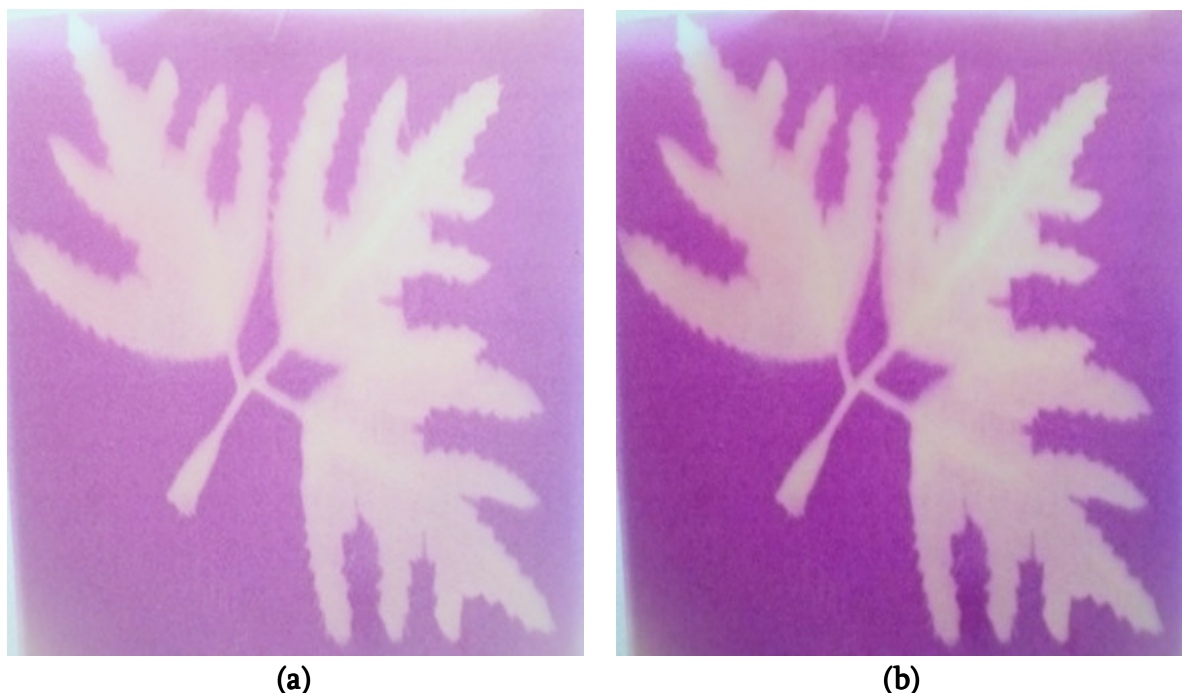


Figure 9. SPLC polymer films after irradiated by UV light: (a) non-stretched and (b) stretched film.



Figure 10. Optical recording images with high contrast by UV light in SPLC polymer films.

4. Conclusions

Spectral and microscopic studies have confirmed that using the innovative technological microencapsulation method, qualitatively new SPLC polymer films consist of doped photochromic SP the LC nemato-chiral matrix has been obtained.

In the films produced, the properties of the composition are fixed in the microcapsules, which ensure maximum preservation of the optical properties of polymer films. Microcapsules in the polymer films do not suffer disintegration destruction under the influence of UV radiation, temperature and stretching.

By regulating the microencapsulation process technological characteristics affect the photosensitivity of polymer films: reducing the size of microcapsules, increasing film thickness significantly increases it and film stretching improves the photosensitivity of SPLC polymer films. The change of photosensitivity in polymer films is well demonstrated upon information recording in films under the influence of UV light [14, 15].

The technological process of microencapsulation can be used as one of the methods for increasing the photosensitivity of SPLC polymer films.

The received SPLC polymer films are photochemically stable-over time, the reflection intensity and photosensitivity of the films does not change. In contrast to the composition, multiple uses of polymer films are possible, which is very important for their practical application.

The presented SPLC polymer films with improved photosensitivity and high spatial resolution produced by authors open new prospects for creating multifunctional photosensitive rewritable materials for the development of high-performing optically photonic devices such as real-time UV irradiation dosimeters, real-time holograms, light-controlled molecular and fluorescent switches.

References

- [1] K. Japaridze, L. Devadze, J. Maisuradze, G. Petriashvili, Ts. Zurabishvili, I. Mzhavanadze, N. Sepashvili. Bull. Georgian Natl. Acad. Sci., 2013, 7, 3, 57-62.
- [2] K. G. Japaridze, L. V. Devadze, J. P. Maisuradze, I. A. Mzhavanadze, Ts. I. Zurabishvili, N. O. Sepashvili, G. Sh. Petriashvili. Georgian Eng. News, 2010, 4, 72-75.
- [3] J. R. Guigly, H. J. Benton. Mol. Cryst. Liq. Cryst., 1977, 42, 43-45.
- [4] A. P. Makhotilo, S. V. Shevchuk, V. P. Tkachenko, V. G. Tischenko. USSR Invention Certificate # 531835, 1976.
- [5] Ts. Zurabishvili, K. Japaridze, Z. Elashvili, G. Chelidze. Georgia Patent # P 2683, 2002.
- [6] K. G. Japaridze, Z. M. Elashvili, G. Sh. Chelidze, Ts. I. Zurabishvili, Z. Ya. Vashakidze, G. Sh. Petriashvili, S. P. Tavzarashvili, K. G. Tevdorashvili. Crystallography Rep., 1997, 42, 2, 300-302.
- [7] K. Japaridze, Z. Elashvili, C. Zurabishvili, G. Chelidze. Georgian Chem. J., 2006, 6, 4, 461-463.
- [8] K. G. Japaridze, G. S. Chilaya, Z. M. Elashvili, Ts. I. Zurabishvili, G. Sh. Petriashvili, G. Sh. Chelidze. Georgian Eng. News, 2008, 1, 63-67.
- [9] G. S. Chilaya, Z. M. Elashvili, S. P. Ivchenko, K. D. Vinokur. Mol. Cryst. Liq. Cryst., 1984, 106, 67-69.
- [10] K. Japaridze, Ts. Zurabishvili, G. Petriashvili. Georgia Patent # P 5232, 2011.
- [11] K. G. Japaridze, Ts. I. Zurabishvili, G. Sh. Petriashvili. Georgian Eng. News, 2009, 3, 129-130.
- [12] K. G. Japaridze, L. V. Devadze, J. P. Maisuradze, Ts. I. Zurabishvili, G. Sh. Petriashvili, N. O. Sepashvili, I. A. Mzhavanadze, Sh. A. Akhobadze, M. T. Gugava. Georgian Eng. News, 2011, 1, 94-98.

- [13] K. G. Japaridze, L. V. Devadze, J. P. Maisuradze, G. Sh. Petriashvili, Ts. I. Zurabishvili, I. A. Mzhavanadze, N. O. Sepashvili. *Nano Studies*, 2013, 7, 261-266.
- [14] G. Petriashvili, M. P. de Santo, L. Devadze, Ts. Zurabishvili, N. Fonjavidze, N. Sepashvili, R. Gary, R. Barberi. *Macromol. Rapid Commun.*, 2016, 37, 500-505.
- [15] G. Petriashvili, L. Devadze, A. Chanishvili, Ts. Zurabishvili, N. Sepashvili, N. Ponjavidze, M. P. de Santo, R. Barberi. *Opt. Mater. Express*, 2018, 8, 12, 3708-3716.