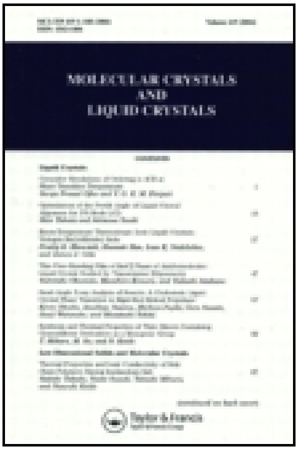


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Structural Patterns in Polymer-Dispersed Liquid Crystal Films

S. J. Kłosowicz [a] , O. Francescangeli [b] & S. Di Bella [b]

[a] Institute of Applied Physics, Military University of Technology, Kaliskiego 2, Warsaw, Poland

[b] Dipartimento di Scienze del Materiali e della Terra and Istituto Nazionale per la, Fisica della Materia, Università di Ancona, Via Brecce Bianche, I-60131, Ancona, Italy

Version of record first published: 24 Sep 2006

To cite this article: S. J. Kłosowicz, O. Francescangeli & S. Di Bella (1999): Structural Patterns in Polymer-Dispersed Liquid Crystal Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 326:1, 139-148

To link to this article: http://dx.doi.org/10.1080/10587259908025410

Mol. Cryst. Liq. Cryst., Vol. 326, pp. 139-148
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Structural Patterns in Polymer-Dispersed Liquid Crystal Films

S. J. KŁOSOWICZ[a], O. FRANCESCANGELI[b,*] and S. DI BELLA[b]

[a] *Institute of Applied Physics, Military University of Technology, Kaliskiego 2, Warsaw, Poland;*
[b] *Dipartimento di Scienze dei Materiali e della Terra and Istituto Nazionale per la, Fisica della Materia, Università di Ancona, Via Brecce Bianche, I-60131, Ancona, Italy*

(Received 10 June 1998; In final form 15 July 1998)

Different methods for the creation of structural patterns in Polymer Dispersed Liquid Crystals (PDLC) are discussed and compared, with a special attention to the recent techniques of induced director pre-orientation and inhomogeneities creation in PDLC films. Examples of the periodic structural patterns obtained by means of different methods adopted during the PDLC preparation are reported. These PDLC with intrinsic structure patterns are very promising for the realization of both active and passive devices such as switchable light modulators, controlled diffraction gratings and switchable couplers for fiber optic systems.

Keywords: Polymer dispersed liquid crystals; diffraction gratings; electro optics

1. INTRODUCTION

Polymer-dispersed liquid crystals (PDLCs) can be used for the realization of optical devices much more advanced than the simple light shutter which was the very first application of PDLCs [1,2 and references therein]. In fact, these composites may find application as materials for electrically controlled devices in laser and integrated optics, *e.g.*, fast modulators, switches, couplers and variable focal length lenses, moreover, for sensor systems, specialized displays, optical data storage and optical computing. However, the mentioned tasks require a more effective processing of the light beam,

---

*Corresponding author. Tel.: 39 71 220 4734, Fax: 39 71 220 4714.

which can be obtained only if areas with different optical properties are realized over the same PDLC film. This means, for instance, that different areas should scatter the incident light to different extents. In this way, an optical pattern for the light beam passing through the film is realized. Gratings of this kind can be obtained either by temporary disturbance of the PDLC optical properties or by preparation of a permanent structural pattern in a PDLC film. The former may be observed as consequence of an interaction of the PDLC with a profiled laser beam or consequence of selective driving by means of electrodes of suitable shape. The second effect implies that areas containing LC droplets of different concentration, size and shape are embedded in one PDLC film during its preparation. The change of structure between adjacent areas can be either continuous or discrete. The electro-optical properties of such PDLCs also become inhomogeneous and can be used for the light beam processing.

In this contribution different methods of preparation of structural patterns in PDLC are discussed and compared, starting with the well established holographic technique but with a special attention to the recent and very promising techniques of induced director pre-orientation and inhomogeneities creation in PDLC films.

1.1. Holographic Gratings

There are two main ways of obtaining differentiated structure in a polymer-dispersed liquid crystal composite by holographic methods. Both have been extensively studied in the past few years. The first method consists in the realization of a grating in the form of microscopic voids in a photocurable holographic material. Those voids are infused by a liquid crystal (LC) material in a separate process [3]. The second way [4–9] is a modification of the well known photopolymerization induced phase separation method (PIPS) of PDLC. This method consists in the preparation of a homogeneous mixture of a LC and a photocurable polymer (dopants of a different kind may be also included). The mixture is deposited between two glass plates with a conductive coating (in case of active, *i.e.*, electrically driven, device) and suitable spacers. Then the system is exposed to laser radiation of suitable wavelength, which creates a holographic pattern in the sample. The information is written in the form of an alternation of bright fringes, where the polymer is cured and phase separation occurs, and dark fringes, where either the polymer is not cured at all or is cured only due to the second order effects caused by the diffusion of free radicals from the illuminated areas. The mechanism of prepolymer curing in the dark fringes involves an increase of miscibility of LC and polymer in comparison with the bright areas. For this reason, the concentration of LC droplets is usually close to zero in the dark areas. Due to solidification of the system the structure so obtained is stable in time. The effectiveness of the grating depends, amongs others, on the PDLC film thickness, the curing ratio (the faster is the curing the lower is the LC droplet diameter) and the material properties of the PDLC system.

1.2. Induced Director Pre-orientation

The very first method used to fix the orientation of the director in LC droplets embedded in a polymer matrix was the introduction of a low-molecular aligning dopant, *e.g.*, Lecithin [10], which enforces the radial anchoring conditions in the polymer cavities. This method, however, can be applied to relatively large areas of the PDLC, so it is not useful for pattern formation. Nevertheless, it may be used to adjust the properties of the whole PDLC film.

A more interesting method of director pre-orientation consists in the application of a bias electric field during polymeric matrix curing [11]. An example is shown in Figure 1. This effect depends on the LC dielectric anisotropy. For nematic LC with $\Delta\varepsilon > 0$, molecules of a nematogen tend to align parallel to the field. This enforced alignment is "frozen" by the cured polymer after removal of the field. So, in the normal mode of operation of the electro-optical PDLC device (*i.e.*, electrically induced transmission), areas which are transparent in off-state are introduced into PDLC film. This effect is enhanced by a longitudinal deformation of the LC droplets along the field (for $\Delta\varepsilon > 0$) due to the electric contribution to the LC deformation free energy. Accordingly, scattering and non-scattering areas are obtained after curing. In the case of nematic LC with negative $\Delta\varepsilon$, the electric field aligns the molecules perpendicular to itself and as consequence the intensity of light scattering increases. This technique offers also the possibility of a two-frequency driving of the device when the LC exhibits a dispersion of $\Delta\varepsilon$, *i.e.*, director pre-orientation of the LC by a high-frequency field ($\Delta\varepsilon < 0$) and driving of the obtained structure by a low-frequency field ($\Delta\varepsilon > 0$).

The above method can be applied only for those preparations which do not include a solvent, *i.e.*, polymerization- (PIPS) or thermally- (TIPS) induced phase separation. The photochemical curing of a prepolymer is strongly preferred, however, due to the easy control of LC droplet diameter. The shape of a particular area is determined by the shape of electrodes on the supporting glass plates. In this way, complex structural patterns can be easily obtained. The spatial resolution of this technique is of the order of 10 μm for a typical PDLC thickness, *i.e.*, 10–20 μm. The best results have

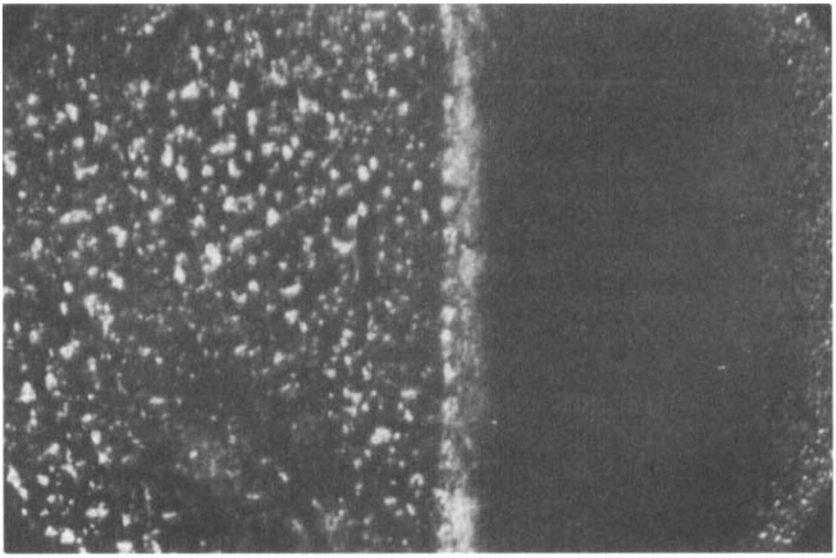


FIGURE 1 Microscopic view between crossed polarizers of a PDLC aligned by an electric field. The external electric field has been applied to the dark side during photocuring of the prepolymer, the bright side has not been pre-oriented.

been obtained with alternating voltages because high constant electric fields may deform the droplet shape or even change the conditions for droplet nucleation in an uncontrolled way. An example of the boundary region between pre-oriented and not pre-oriented parts of a PDLC film is reported in Figure 1. Adopting fast-curing prepolymers one can obtain structural gratings even in relatively thin samples, *i.e.*, thinner than 10 µm.

The reported method is fundamentally different from the creation of temporary optical patterns by the application of special space distributions of electric field. In fact, in the former case the pattern is electrically driven during the curing process by a suitable choice of the aligning electric field and it results to be permanent, while in the latter case the pattern is created by the application of the field to the cured PDLC and vanishes after removal of the field.

1.3. Creation of Inhomogeneities in PDLC Films

This technique consists in a local change of the PDLC structure without any director alignment. It is based on the introduction of different conditions for nucleation of the LC droplets in different areas of the same PDLC film [11, 12]. In the case of phase separation, both the solubility of a LC material in the cured polymer and the conditions for droplet nucleation depend on the curing temperature. For the PIPS method this means that number and size of droplets are lower in the areas where the temperature is higher. For the TIPS method, the number of droplets is larger while their size is smaller for higher cooling ratio. In this way, number and mean diameter of LC droplets (and so light scattering) can be adjusted in selected areas of the PDLC by the introduction of a transversal temperature gradient. Temperature gradient is limited by heat conductivity and allows to introduce only a continuous change of droplet nucleation conditions. For this reason, the spatial resolution of the temperature-induced inhomogeneities is rather poor.

In the case of PIPS method, the so called selective polymerization can be adopted. This method consists in the illumination of a prepolymer-LC mixture by UV light through a mask with a suitale pattern of black areas. Curing of the polymer and usual phase separation take place in the illuminated regions. On the other hand, in the dark areas either the prepolymer remains uncured, when relatively large areas are involved ($>1\ \mathrm{mm}^2$), or polymerization takes place due to free radical diffusion, in the case of smaller areas. The latter is a second order effect and the conditions of droplet nucleation are anyway different from those in the illuminated areas. This mechanism is similar to that observed in the case of holographic gratings and its resolution is up to 10 μm for PDLC thicknesses of about 20 μm.

It is also possible to change the PDLC structure by droplet shaping, *i.e.*, deformation of spherical LC droplets to ellipsoidal shape, which results in a change of light scattering intensity [13]. This effect may be achieved by shearing during the curing process (droplets elongated parallel to cell walls), elongation of plastomer-based PDLC with mutual local thermal stress or application of a high electric field during phase separation (droplets elongated according to their dielectric anisotropy). Only the latter method allows to introduce structural pattern into the PDLC by means of shaped electrodes, moreover, it is always present in case of electrically induced director pre-orientation. This method can be used in combination with shearing in the case of PDLC containing ferroelectric SmC* LC phase. Elongation of plastomer has been adopted in the case of PVA based systems. All these methods have given rather poor results so they may be used only for additional adjustment of PDLC structural patterns.

2. EXPERIMENTAL

The studied PDLC systems and the preparation methods are summarized in Table I.

TABLE I PDLC samples studied in present work

No.	*Polymer*	*Nematic LC*	*Preparation*	*LC content [% bw]*
1	PVA PA-18 (Shin Etsu)	W-486, ZLI-2457 (Merck)	Encapsulation	30 ÷ 50
2	PMMA, toluene	W-486	SIPS	30 ÷ 50
3	PMMA, monomer (Ubichem)	W-486, PCB (BDH)	PIPS	15 ÷ 20
4	PVCH	W-486, ZLI-2457 (Merck)	TIPS	25 ÷ 30
5	NOA-65 (Norland)	W-486, W-801	PIPS	25 ÷ 50

Here SIPS, TIPS and PIPS stand for solvent, thermally and polymerization induced phase separation, respectively. PVA, PMMA, PVCH and NOA-65 stand for polyvinyl alcohol, polymethyl methacrylate, polyvinyl cyclohexanal and commercial photocurable glue (Norland Optical Adhesives), respectively. The details of the different PDLC preparation methods are described elsewhere [12, 14–16]. The thickness of the different PDLC films was either 9, 14 or 20 μm. Most of the studies have been done for photocured NOA-65 resin and W-486 mixture system 9 μm thick. This system has been chosen because of the easy preparation and control of the parameters, and the negligible miscibility of the components after polymer curing.

W-486 is a mixture of nematic derivatives of cyclohexane benzene isothiocyanate. W-801 is a mixture based on nematic alkyl and alkoxycyanobiphenyls; its solubility with uncured NOA-65 is very good but it also dissolves in cured NOA-65 up to 20 per cent in weight. For this reason it significantly changes the PDLC properties. These mixtures were prepared at the Institute of Chemistry of the University of Technology, Warsaw, Poland.

3. RESULTS AND DISCUSSION

Some selected examples of the results obtained with the different techniques previously described are reported in the following.

Figure 2 shows the structural pattern created in a PDLC film by applying an external electric field during the LC droplet nucleation with the NOA-65 + W-486 system. The high concentration of small LC droplets in the bright areas and the small number of large LC droplets, due to coalescence, in the dark areas are clearly visible.

The photo reported in Figure 3 shows the spatial change of the LC droplet distribution obtained by means of a temperature gradient using the TIPS method starting the PVCH + ZLI-2457 system.

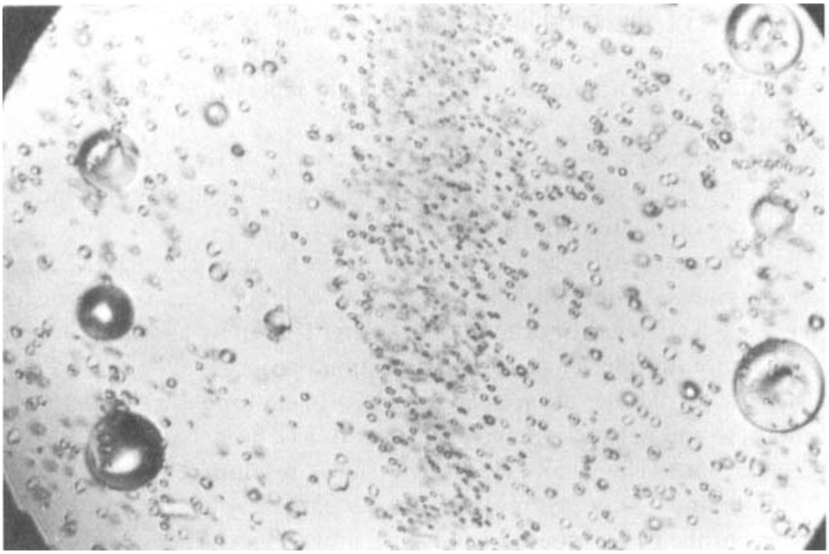


FIGURE 2 Structural pattern in a PDLC layer created by an external electric field applied during the LC droplet nucleation in the NOA-65 + W-486 system.

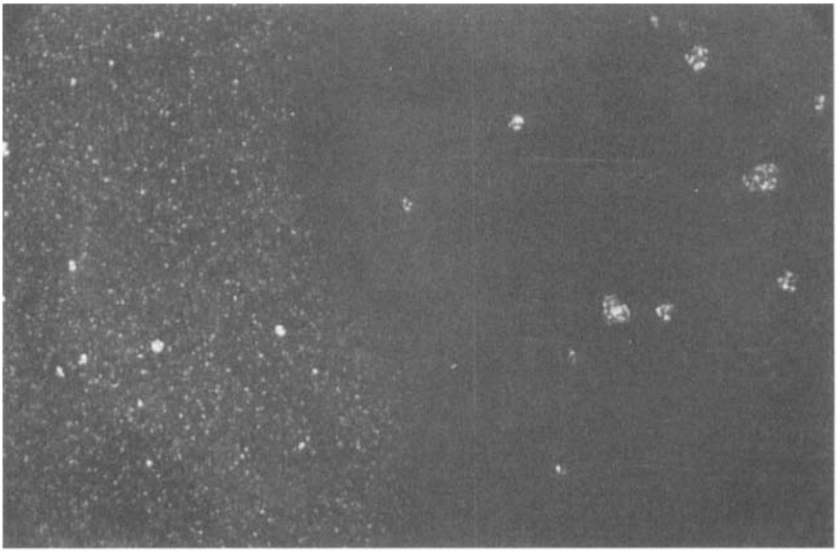


FIGURE 3 Spatial change of a distribution of LC droplets in a PDLC structure obtained by temperature gradient with TIPS preparation method in the PVCH + ZLI-2457 system.

Examples of the periodic structural patterns obtained in the NOA-65 + W-486 system by selective polymerization with mask and by director pre-orientation with pattern of electrodes are reported in Figure 4(a) and (b), respectively.

As one can see, significant differentiation of PDLC structure with reasonable resolution can be obtained by means of electrically induced director pre-orientation and selective polymerization.

The occurrence of large LC droplets in dark areas of a PDLC film is probably caused by the much slower increase of prepolymer viscosity which makes easy a coalescence of the LC droplets. This effect has been observed for LC concentrations close to the saturation one.

The best spatial resolution obtained was ≈10 μm for electric director pre-orientation and selective polymerization. It has been limited by droplet diameter, film thickness and electrode or mask resolution.

The obtained patterns revealed to be extremely stable in time: no variation of their properties was observed over 2 years. They are also stable against periodic electric, thermal and mechanic shocks if the polymer structure is not destroyed.

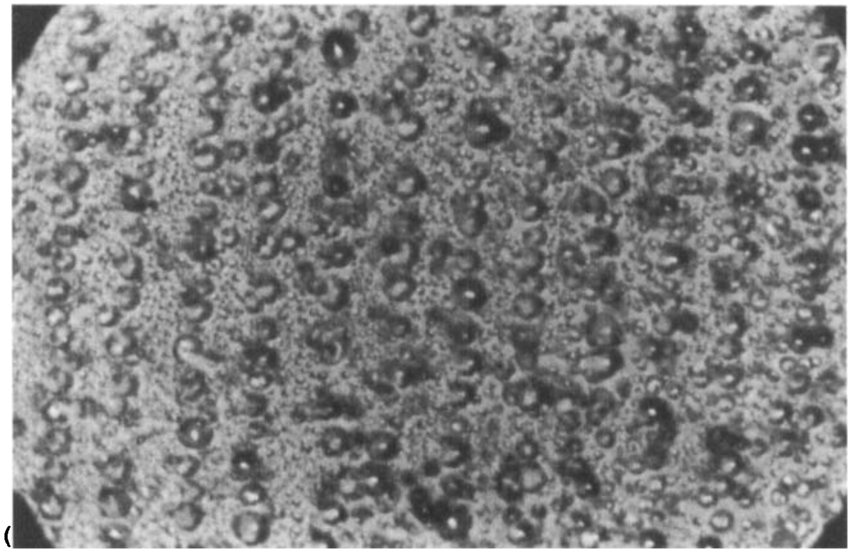
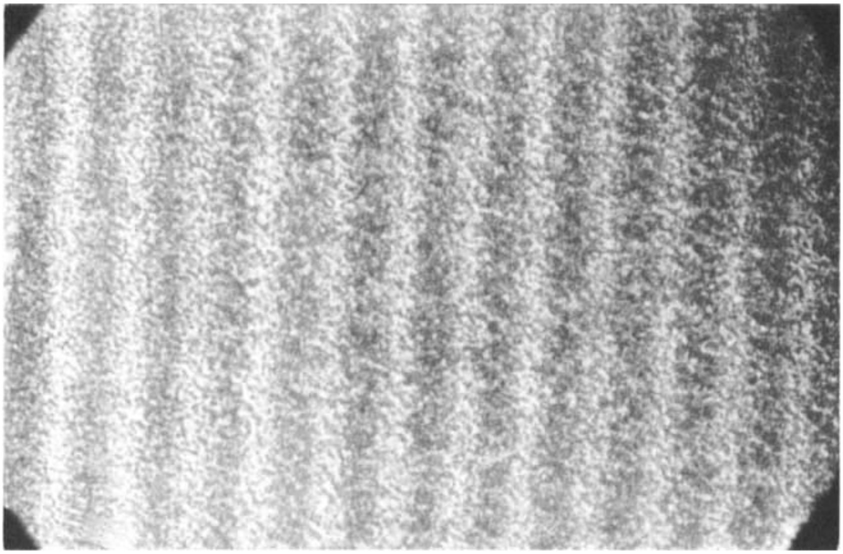


FIGURE 4 Examples of periodic structural patterns obtained by (a) selective polymerization and (b) director pre-orientation in the NOA-65 + W-486 system.



(b)

FIGURE 4 (Continued).

As examples of application of the obtained structures a LC adjustable phase-amplitude diffraction grating [17] and switchable couplers for fiber optic systems [18] may be given.

On the base of the presented results, the following main conclusions can be drawn.

Structural patterns, either discrete or continuous, can be obtained in PDLC film by means of different methods adopted during the PDLC preparation. Besides the holographic method, profiled electric fields, temperature gradient and selective polymerization may be also successfully adopted for this purpose. Especially PIPS and to the some extent TIPS methods of PDLC preparation are useful to obtain structural patterns in PDLC. Other methods, *e.g.*, doping by low-molecular compounds or droplet shaping may additionally adopted for an adjustment of the properties of whole PDLC film.

The presence of a structural pattern results in an optical pattern for the incident light, *i.e.*, the light scattering is different for different parts of the PDLC film. The parameters of the optical pattern may be adjusted by controlling the conditions of PDLC preparation (mean droplet diameter, film thickness, pattern resolution). The electric driving of such patterns depends on the LC and the method of preparation.

PDLC with intrinsic structure patterns can be applied to realize both active and passive devices affecting the light beam parameters, *e.g.*, switchable light modulators, controlled diffraction gratings and switchable couplers for fiber optic systems.

Acknowledgements

This work has been supported by the Polish State Committee for Scientific Research (Poland – Italy International Co-operation Research Grant no. C/11786/96). The authors wish to thank Professor R. Dabrowski for delivering liquid crystal samples.

References

[1] J. W. Doane, In: "*Liquid Crystals Applications and Uses*", Ed. B. Bahadur, Singapore, World Scientific, 1991, Chap. 14.

[2] H. S. Kitzerow, *Liq. Cryst.*, **16**, 1 (1994).

[3] R. T. Ingwall and T. Adams, *Proc. SPIE*, **1555**, 279–290 (1991).

[4] R. L. Sutherland, L. V. Nataranjan, V. P. Tondiglia, T. J. Bunning and W. W. Adams, *Proc. SPIE*, **2152**, 303–313 (1994).

[5] R. L. Sutherland, V. P. Tondiglia, L. V. Nataranjan, T. J. Bunning and W. W. Adams, *Appl. Phys. Lett.*, **64**(9), 1074–1076 (1994).

[6] R. L. Sutherland, V. P. Tondiglia, L. V. Nataranjan, T. J. Bunning and W. W. Adams, *Proc. SPIE*, **2532**, 309–318 (1995).

[7] R. L. Sutherland, V. P. Tondiglia, L. V. Nataranjan, T. J. Bunning and W. W. Adams, *Proc. SPIE*, **2404**, 132–143 (1995).

[8] V. P. Tondiglia, L. V. Nataranjan, R. L. Sutherland, T. J. Bunning and W. W. Adams, *Opt. Lett.*, **20**(11), 1325–1327 (1995).

[9] T. J. Bunning, L. V. Nataranjan, V. P. Tondiglia, R. L. Sutherland, D. L. Veziet and W. W. Adams, *Polymer*, **36**(14), 2699–2708 (1995).

[10] A. V. Kovalchuk, M. V. Kurik, O. D. Lavrentovich and V. V. Sergan, *Mol. Cryst. Liq. Cryst.*, **193**, 217– (1990).

[11] S. J. Kłosowicz, *Opto-Electronics Review*, **2'94**, 31–35 (1994).

[12] S. J. Kłosowicz, *Proc. SPIE*, **2372**, 343–349 (1995).

[13] S. J. Kłosowicz, *Opto-Electronics Review*, **4**(1–2), 62–68 (1996).

[14] S. J. Kłosowicz, E. Nowinowski and J. Żmija, *Mol. Cryst. Liq. Cryst.*, **215**, 253 (1992).

[15] S. J. Kłosowicz, E. Nowinowski-Kruszelnicki and J. Żmija, *Proc. SPIE*, **1845**, 545-548 (1993).

[16] S. J. Kłosowicz, *Molecular Materials*, **4**, 277–281 (1994).

[17] S. J. Kłosowicz and E. Nowinowski-Kruszelnicki, *Proc. SPIE*, **2372**, 367–371 (1995).

[18] S. J. Kłosowicz, E. Nowinowski-Kruszelnicki and L. Jaroszewicz – to be published.