

# Optical response of cyanoazomethine liquid crystal droplets in PDLC films based on a polysulfone matrix

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The optical behaviour of the liquid crystal 4-[4-(n-butyloxy)phenylene-imino-methylidene]benzointrile in composite films based on the polysulfone UDEL as polymer matrix was investigated by means of polarizing optical microscopy (POM), UV-vis and fluorescence spectroscopy. The composites were prepared by the solvent-induced phase separation (SIPS) and thermal-induced phase separation (TIPS) method. For some composite compositions, the formation of polymer dispersed liquid crystal systems was detected. POM observations of composites showed possible relations between morphological features and fluorescence characteristics, depending upon preparation conditions. The different fluorescence behaviour has been discussed in terms of differences in the aggregation degree of liquid crystal molecules arising from the dominant liquid crystal - liquid crystal, liquid crystal - polysulfone molecular interactions.

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## 1. Introduction

In recent years, fluorescent liquid crystals for electro-optical device utilization have intensively been investigated. Liquid crystals dispersed in a polymer matrix have attracted increasing interest over the recent years due to the new possibilities arising from the combination of liquid crystalline and polymeric properties, which cannot be found in low molar mass liquid crystals. The introduction of liquid crystals components into the polymer matrix results in enhanced self - support of display systems [1]. An important practical application are polymer-dispersed liquid crystals (PDLCs) obtained by phase separation. PDLCs are a relatively new class of materials that hold promise for many applications ranging from switchable windows to projection displays [2-4]. PDLCs consist of liquid crystal droplets that are dispersed in a solid polymer matrix. These tiny droplets (a few microns across for practical applications) are responsible for the unique behaviour of the material. The performance of the PDLCs strongly depends on the final morphology of the dispersed LC domains in the polymer matrix. The size, shape, and distribution of the LC domains are generally not only dictated by the thermodynamic phase equilibrium but also strongly dependent on the polymer and liquid crystal types used and on the interfacial interactions. The electro-optic properties of PDLCs were found to exhibit significant changes with material selection. The liquid crystal, as an important component of the polymer dispersed liquid crystals, has a great influence on the electro-optical properties. The CN - terminated liquid crystals are frequently used as components in the obtaining of the PDLC composites due to the fact that CN-containing liquid crystals are usually chemically stable, have low relaxation time and high dielectric anisotropy. They are materials widely used in liquid crystal displays [5]. The most popular are cyanobiphenyles, in which a CN as an electronodonor is joined to a biphenyl as an electronoacceptor. Inspired by the use of the

cyanobiphenyles as a component in obtaining the PDLC systems for high performance materials with tailor-made properties [6] we thought it interesting to investigate the formation of the PDLC systems with a cyanoazomethine liquid crystal and polysulfone UDEL as polymer matrix. We were the first to investigate the formation of this type of PDLC [7].

The present contribution reports the optical behaviour of this novel composite type comprising PDLC systems, obtained by the SIPS and TIPS methods. Information on the morphology and on the phase structure has been obtained by polarizing optical microscopy and X-ray diffraction measurements. The optical characterization of these materials has been performed by analysing their UV-vis absorption and photoluminescence emission as function of the aggregation degree of the liquid crystal.

## 2. Experimental

### 2.1. Materials and methods

For this study, polysulfone UDEL - 1700 (PSU), purchased from Merck was chosen as polymer matrix, due to its high- performance properties as engineering material [7]. As liquid crystal component we have chosen a single - component liquid crystal, namely 4-[4-(n-butyloxy)phenylene-imino-methylidene]benzointrile (**4CAz**) [8], synthesised by us, according to literature data [7, 9].

### 2.2. Films preparation

A solution of composite was prepared in vials by mixing the appropriate amounts of polymer and liquid crystal (see table 1) in a common solvent (chloroform) to form a 5% (w/v) solution. A small amount of mixture was casted onto a glass surface and kept in an enclosed case in order to induce the phase separation of the LC droplets from the polymer matrix by the SIPS method. In order to

obtain polymer dispersed liquid crystals by means of the TIPS method, the films were heated up to 180 °C (above the  $T_g$  value of the polysulfone) to achieve good mixing and then cooled at room temperature.

### 2.3. Test methods

The phase behaviour of the 4CAz liquid crystal and the PDLC composites were investigated by polarizing light microscopy, using an Olympus BH-2 microscope equipped with a Linkam THMS 600/HSF9I heating stage and TMS91 control unit.

Wide Angle X Ray Diffraction (WAXD) was performed on a Diffractometer Bruker D8 ADVANCE, using the Ni-filtered Cu-K $\alpha$  radiation ( $\lambda = 0.1541$  nm). A MRI-WRTC –temperature chamber (with nitrogen inert atmosphere) and MRI-TCPU1 - Temperature Control and Power Unit were used. The working conditions were 36 kV and 30 mA. All the diffractograms were investigated in the 1.5°÷40° (2 theta degrees) range, at different temperatures. All diffractograms are reported as observed.

UV–vis absorption and photoluminescence spectra were recorded on a Carl Zeiss Jena SPECORD M42 spectrophotometer and Perkin Elmer LS 55 spectrophotometer respectively, in very diluted solutions using 10 – mm quartz cells fitted with poly(tetrafluoroethylene) stoppers. The spectra maxima were automatically calculated by the Origin software.

### 3. Results and discussion

The PDLCs films were prepared by a combination of solvent - induced and thermally - induced phase separation processes. The SIPS process required both liquid crystal and polymer to be dissolved in a solvent. The solvent was then removed to begin the phase separation. In the TIPS method, the films obtained by the SIPS method were thermally heated, when a homogeneous mixture of liquid

crystal and a melted polymer was formed; liquid crystal droplets began to form as the polymer hardened. The droplets continued to grow until the glass transition temperature of the polymer was crossed. Well defined droplets dispersed in polymer matrix were obtained by the SIPS method for the composites containing a liquid crystal percent lower than 60 % (P4A6 – P9A1) (Fig. 1a, b), while for the composites containing 90, 80, 70 % liquid crystal (P1A9, P2A8, P3A7), the crystalline state was observed. By the TIPS method, PDLC films with high density of well defined droplets were obtained for the composites containing 80, 70, 60, 50 % liquid crystal (Fig. 1c, d), while the other composites present rare droplets (P6A4, P7A3) or do not show any droplet formation (P8A2, P9A1). Upon comparing the PDLC formation by the two methods, it can be observed that the PDLC systems of the composites containing 40, 30, 20 % liquid crystal formed by the SIPS method, disappear after the thermal treatment of the films (the TIPS method), while new PDLC systems appear for the composites corresponding to a liquid crystalline content of 80, 70 % (Table 1).

Table 1. Liquid crystal percent in the composite and the PDLC formation by the SIPS or TIPS methods

Code	4CAz %	SIPS	TIPS
P1A9	90	-	-
P2A8	80	-	F.D.
P3A7	70	-	F.D.
P4A6	60	F.D.	F.D.
P5A5	50	F.D.	F.D.
P6A4	40	F.D.	f.d.
P7A3	30	F.D.	f.d.
P8A2	20	F.D.	-
P9A1	10	F.D.	-

F.D.: fine droplets with big density; f.d.: fine rare droplets

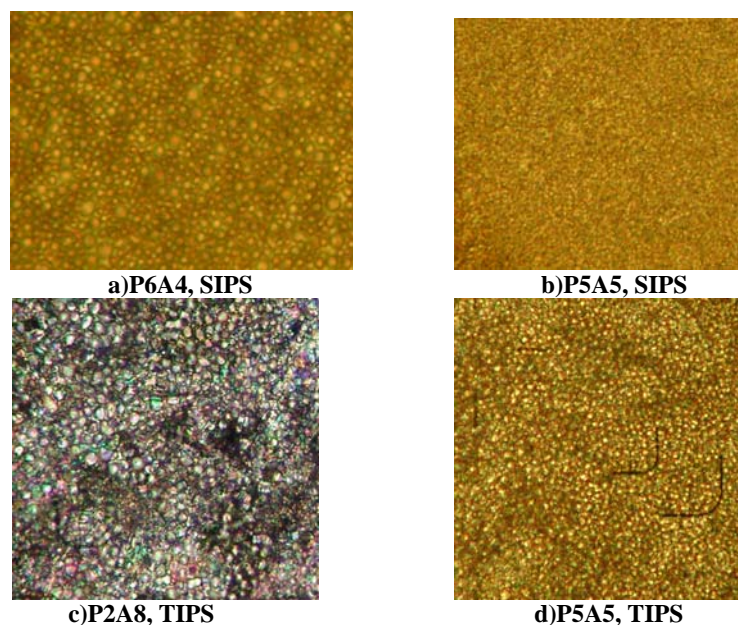


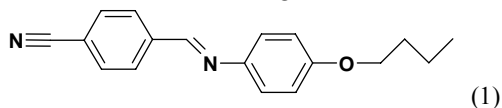
Fig. 1. Microphotographs of the PDLC composites, in optical polarized microscopy, crossed polarizers.

The explanation for this behaviour is that a complete separation of the two components does not result during the thermal treatment process and, inevitably, a liquid crystal fraction remains within the polymer matrix (P9A1, P8A2, P7A3) or a fraction of the polymer matrix remains in the liquid crystal (P1A9), PSU and 4CAz being more or less completely miscible [7].

The liquid crystal droplets have a round geometry and their domain size was estimated from the polarizing microscopic pictures (see Fig. 1), as being comprised in the 3 – 0.5  $\mu\text{m}$  range.

### 3.1 The UV-vis absorption behaviour

In order to identify the optical behaviour of composite films, the optical behaviour of the 4CAz liquid crystal in dilute solutions and films was investigated.



The electronic spectra of the 4CAz were detected in hexane and chloroform solution and also in solid thin films before and after a thermal treatment (Figure 2). Taking into account the structure of 4CAz (1) which contains lone pairs of electrons (N, O) and the multiple bonds (C≡N, CH=N) which allow an extent conjugation, from the theoretical point of view, the absorption of 4CAz is based on transitions of  $n$  and  $\pi$  electrons to the  $\pi^*$  excited state, with a major participation of the  $\pi$ - $\pi^*$  transitions. The UV-vis absorption spectrum of the 4CAz in nonpolar hexane solution is characterized by two absorption bands: an absorption band at longer wavelength in the 312 – 436 nm range (with a maximum at 353 nm and two shoulders at 339 and 368 nm) corresponding to the  $\pi$  -  $\pi^*$  transition of the conjugated molecules, while the shorter wavelength band ( $\lambda_{\text{max}}$  277 nm) originates in the electronic transition of the individual aromatic units. In chloroform solution, 4CAz shows a similar absorption spectrum to the hexane solution, with a better defined red-shifted band at 363 nm, indicative of the positive solvatochromism caused by the solute – solvent interactions [10]. According to the Franck-Condon principle, electronic excitation is much faster ( $\approx 10^{-15}$ ) than solvent reorganization around molecules ( $\approx 10^{-12}$  –  $10^{-10}$ ); therefore, the excited species have the same solvation pattern of their ground state. The red-shifting of the absorption band by the polar chloroform reflects the increased planarity of the azomethine molecules due to the increased resonance effect of the electron-withdrawing nitrogen which becomes stronger by “localization” of the electronic doublet by protonation [11]. The disappearance of the shoulders observed in the 4CAz hexane solution spectrum sustains this hypothesis; in hexane solution, the cyanoazomethine molecule is not entirely planar due to the nitrogen doublet which interferes to a certain extent with the conjugation through the molecule, thus leading to more conformers with different degree of conjugation. The transfer to a more polar solvent has the result the stabilizing of the extent conjugation state and thus the stabilizing of its excited state relative to its ground state and thus the new transition energy  $\Delta E$  is

lower than  $\Delta E'$  and an increases planarization of the molecules.

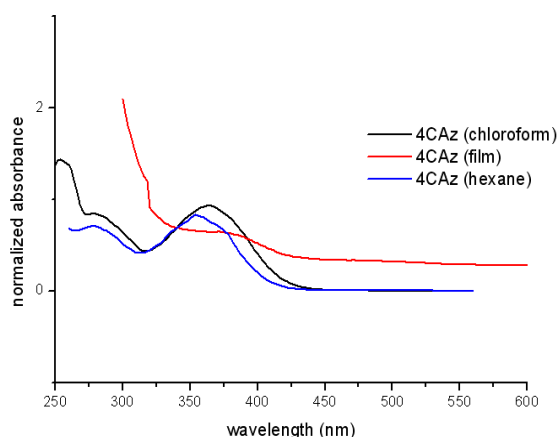


Fig. 2. UV-vis absorption spectra of 4CAz in  $\text{CHCl}_3$ , hexane, and solid-state.

In the electronic spectrum of the 4CAz untreated film obtained by casting from chloroform solution, the absorption maximum could not be recorded (probably due to the inhomogeneous thickness), while upon annealing of the film a considerable red shift of the UV-vis absorption maximum (to 371 nm) was observed, along with a decrease in the overall absorption intensity (Figure 2). This observation could indicate that the planar molecule conformations in chloroform solution were maintained in the film cast from the same solvent; moreover, the molecules have an increased planarity in solid state related to chloroform solution, induced by the stronger intermolecular interactions in the solid film versus the interactions with the solvent. These data are sustained by X-ray diffraction measurements which clearly show small distances among molecules and the formation of big crystallites after thermal treatment (see the X-ray diffraction measurements).

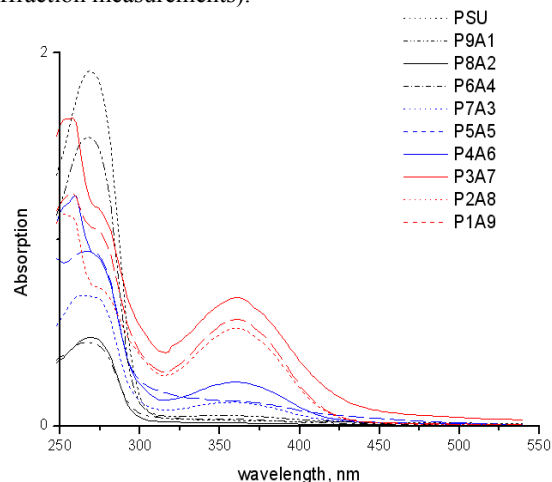


Fig. 3. The absorption spectra of chloroform solution composites.

The absorption spectra of the composite chloroform solutions are given in Fig. 3. Compared to the 4CAz chloroform spectrum, the solution composite spectra show small differences in the form and intensity of the both bands (the band originating in the electronic transition of the individual aromatic units and the band originating in the electronic transition of the chromophoric unit), depending on the composite composition.

As it can easily be observed, taking into account their UV-vis behaviour, the PA composites could be divided in three series. The first series includes the composites exhibiting high liquid crystal contents: P1A9, P2A8, P3A7 (red traces). Their absorption is the most intensive among PA composites and  $\lambda_{\text{max}}$  of their absorption is 361 nm, a medium value between the maxim absorption wavelengths of 4CAz solution in chloroform (364 nm) and hexane (354 nm), which reflects the influence of the PSU which acts as a non polar solvent. The second series comprises the composites with medium liquid crystal contents: P4A6, P5A5 and P7A3 (blue traces). Their absorption is less intensive than that of the first series and the  $\lambda_{\text{max}}$  is slightly blue shifted (359 nm), which reflects the decreasing liquid crystal quantity *versus* the greater amount of polymer, which hinders the polar solvent – liquid crystal interactions. Finally, the third series comprises the PSU and PA composites with the least 4CAz content; they do not present absorption due to the low chromophoric liquid crystal content. Thus, the UV-vis behaviour of the chloroform PA composite solutions reflects the influence of the PSU matrix, which acts as a non-polar solvent, and depends on the 4CAz composite amount.

### 3.2 The fluorescence behaviour

Since cyano-derivatives are known to be fluorescent compounds (fluorophores), the light – emitting ability of the 4CAz and its PA composites has been investigated on the basis of the photoluminescence (PL) spectra recorded for solutions or films, by exciting them with UV light having a wavelength equal to their maximum absorption peak.

The fluorescence spectra of the 4CAz were recorded in hexane or chloroform solutions and in treated and untreated film, by exciting them with UV light having various wavelengths, including the maximum absorption wavelength. While the hexane solution of 4CAz emitted UV, violet light, respectively, depending on the  $\lambda$  of the exciting light (see table 2), the 4CAz chloroform solution emitted blue light, without remarkable shifting of the  $\lambda$  maximum for different  $\lambda$  of the exciting light (Figure 4). This indicates that the 4CAz molecules in  $\text{CHCl}_3$  polar solvent are in the planar conformation due to the affinity of the lone pair of nitrogen electrons towards  $\text{CHCl}_3$  protons which increase the conjugation. On the other hand, the excited state of a molecule is more polarized than the fundamental one [12]. Therefore, we can assume that the 4CAz intrinsic fluorophore excited state manifests a propensity of interactions with neighboring polar solvent chloroform molecules, prior to their deactivation through the fluorescence pathway [13]. The interaction of the

4CAz molecules with the chloroform molecules decreases the energy of the excited states, thus engendering a red shift of the fluorescence spectrum and implicitly of its maximum, compared to the nonpolar hexane solution (Figure 4). The low concentrations of the 4CAz solutions exclude the intermolecular transformations and indicate that changes of the  $\lambda$  absorption maximum reflect an intramolecular process.

The untreated and treated 4CAz films emitted light on a large emission band with three maxima in the blue light domain and a maximum in the green light domain. This emission band with many maxima certainly reflects the aggregation in different amounts in the solid film and various excimer formations due to the different conformers (Figure 4). The emission behaviour of the 4CAz thermally treated film doesn't register significant modifications by exciting with UV light at different wavelengths (Figure 5), which indicates very stable aggregates [14].

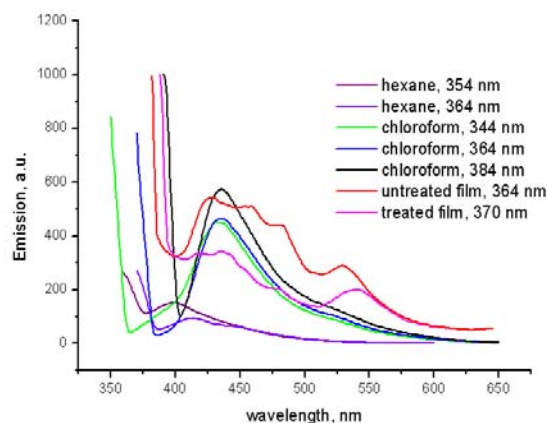


Fig. 4. Fluorescence spectra of 4CAz, in solution, excited with UV light of various wavelengths.

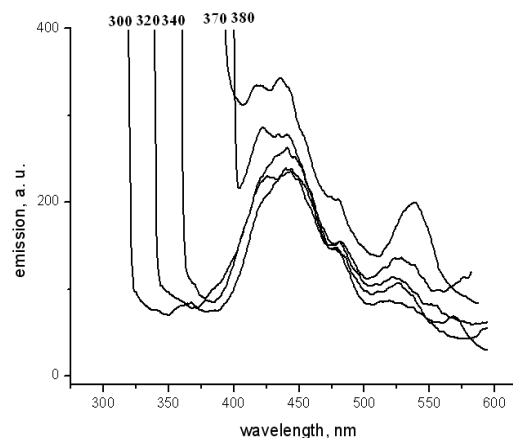


Fig. 5. Fluorescence spectra of 4CAz film, at various wavelengths.

The fluorescence spectra of the PA composites obtained by the SIPS method show a significant red shifting of the emission maxima compared to the untreated

4CAz film, which indicates a lower energy gap as a result of a higher conjugation of the 4CAz molecules in the PA composites, thus increasing planarity. Compared to the 4CAz film, the PA emission traces show less emission maxima: the PA composites which did not form PDLC systems show two emission peaks in the blue light emission domain (455, 480 nm, respectively) and one emission maximum in green light emission domain (526 nm); the other composites forming PDLC systems (except for P4A6) show only a maximum in the blue light emission domain (480 nm) and a maximum in the green light emission domain (520 nm). We can ascribe this phenomenon to the formation of small crystalline domains encapsulated in the polymer matrix, the emission profiles being influenced by the organization degree and thus by the planarity of the solid state molecules. As expected, the emission intensity decreases with the decreasing liquid crystal composite percent; the most intense peaks are observed for the P1A9, P2A8, P3A7 composites, which did not exhibit droplet formation under POM (Fig. 6).

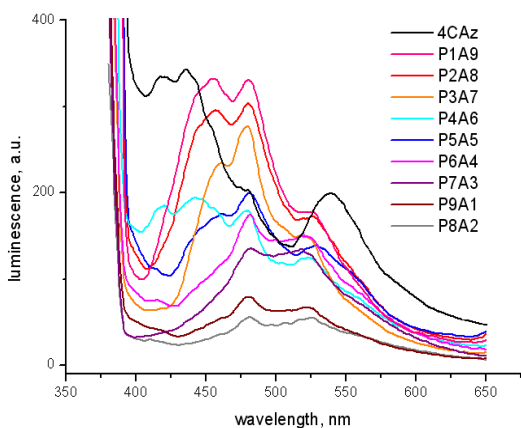


Fig. 6. Fluorescence spectra of SIPS PA composites.

Upon comparing emission of the SIPS and TIPS film traces, the shape of the latter show some modifications (Figure 7). Firstly, as it can easily be seen, the emission intensity decreases, due to the partial liquid crystal and polymer matrix miscibility [7], which ensures an intimate contact between the 4CAz molecules and the PSU chains, which seem to act as a quencher. The PL trace for the SIPS film of P4A6 composite, which is similar to that of 4CAz film, change in a trace similar to those of the PDLC composites for the TIPS film. As a general remark, the PDLC films obtained by the SIPS or TIPS methods have a

narrower emission band than the 4CAz or PA composites containing high 4CAz amounts. Generally speaking, a narrow emission band corresponds to the presence of the conformers with extent molecule conjugation. Taking all these into account it seems reasonable to assume that liquid crystalline droplet formation in the 4CAz/PSU composites provides droplets with better PL properties than the pure liquid crystal.

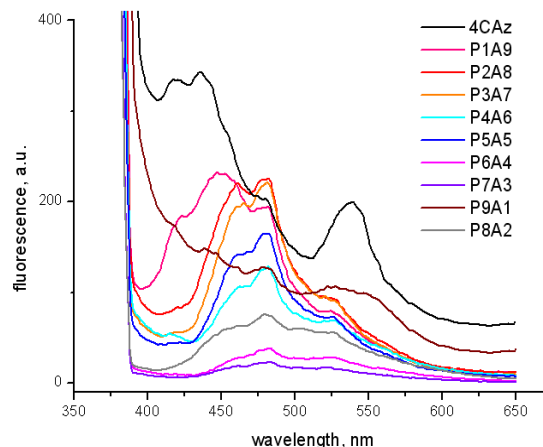


Fig. 7. Fluorescence spectra of TIPS PA composites

Stokes shift of the absorption and emission wavelengths is an important parameter which indicates the differences in compound properties and structures. The calculated Stokes shift values for 4CAz in hexane and chloroform solution, treated and untreated film, SIPS and TIPS composites indicated significant differences in the energy loss which occurred during transition from ground state ( $S_0$ ) to excited state ( $S_1$ ). The higher value was observed for the PA composites. The Stokes shift values were found to be higher for the 4CAz films in comparison with the ones in solutions, which illustrates that more energy loss occurred during the  $S_0$  to  $S_1$  transition in the solid state (Table 2). The optical band gaps ( $E_g^{opt}$ ) of the 4CAz are 3.5, 3.4 and 3.34 estimated from their absorption maxima. A decrease of the band gaps is evident for the 4CAz in the treated film *versus* the untreated film or solutions (Table 2). Similar optical band gaps were found for azomethine compounds with an extended conjugation [15, 16].

Table 2. Summary of photophysical properties of the 4CAz compound and the PA composites.

Compound	$\lambda_{abs,max}/nm$	$\lambda_{em,max}/nm$	Stokes shift/nm	$E_g^a$
4CAz, hexane	354	398	44	3.5
4CAz, chloroform	364	413	49	3.4
4CAz, untreated film	(364) <sup>b</sup>	427, 456, 481, 529	63, 92, 129, 165	-
4CAz, treated film	371	418, 435, 475, 537	47, 64, 104, 166	3.34
4CAz, PA composite	370	459, 480, 525	90, 110, 155	3.34

<sup>a</sup> HOMO – LUMO gap measured according to the UV absorption maximum;

<sup>b</sup> measured in chloroform solution

### 3.3 X-ray diffraction measurements

The X-ray diffraction pattern of the 4CAz compound was registered for the sample obtained by casting from chloroform solution (Figure 8a) and then thermally treated (heating up to the isotropic state and cooling at room temperature) (Fig. 8b).

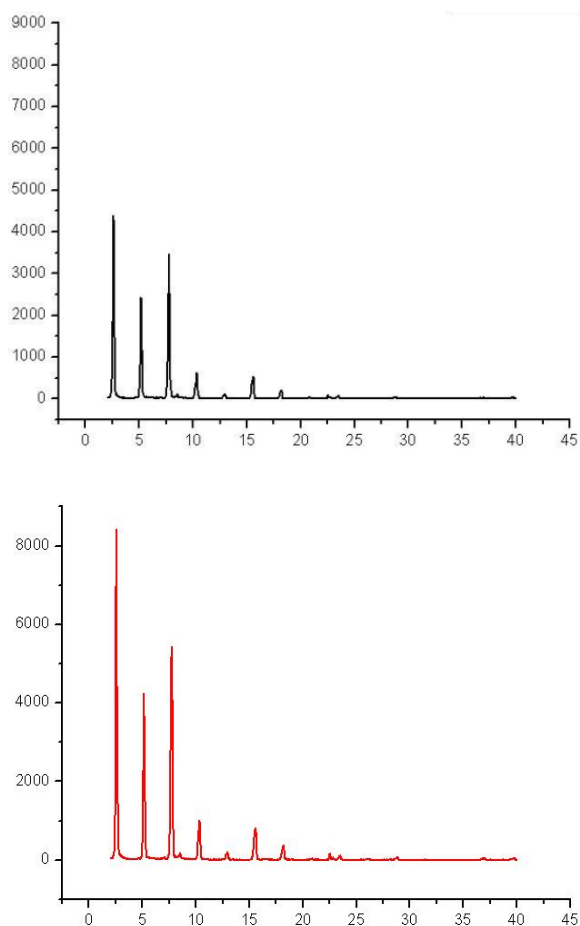


Fig. 8. X-ray diffraction pattern of the 4CAz, before (a) and after (b) the thermal treatment.

The X-ray patterns are typical for the crystalline state with high order degree, and more intense peaks can be easily observed for the thermally treated sample, in addition to the appearance of some new peaks at wider angles (Table 3).

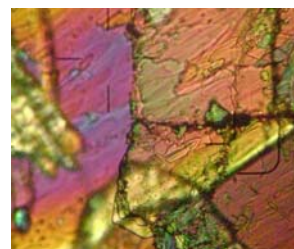
Table 3. The reflection angles and their intensity for the 4CAz compound, before and after a thermal treatment

$2\theta^a$	I	$2\theta^b$	I
2.51	466	2.51	8728
5.14	2637	5.06	4422
7.69	3677	7.69	5601
8.54	398	8.54	468
10.33	837	10.33	1215
12.87	353	12.87	442
15.6	815	15.5	977
18.14	490	18.14	603
20.77	284	20.87	362
22.47	376	22.47	468
23.41	353	23.41	387
		26.22	307
28.77	306	28.85	387
		36.92	336

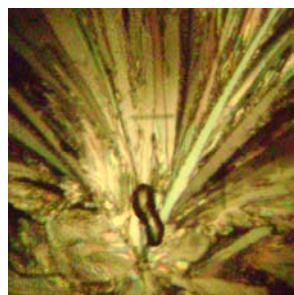
<sup>a</sup>before thermal treatment

<sup>b</sup>after thermal treatment

The latter peaks correspond to very small distances among molecules, probably due to the fact that the slow cooling from the melted state increases the trans conformer density, thus decreasing the distances among molecules. The more intense peaks for the thermally treated sample indicate larger crystallites, as it was proven by POM measurements (Fig. 9).



a)



b)

Fig. 9. POM microphotographs of the 4CAz before (a) and after (b) the thermal treatment.

#### 4. Conclusions

The optical behaviour of a cyanoazomethine liquid crystal was analyzed by polarizing microscopy, UV-vis and photoluminescence spectroscopy. X-ray diffraction measurements of the liquid crystal were performed in order to see the influence of crystallinity degree upon optical behaviour. It was established that the PDLC formation results in a narrowing of the emission band due to the small droplet formation with uniform alignment of the planar molecules. Also, it was established that the PSU acts as a quencher for the liquid crystal molecules dissolved in it.

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