Influence of the Aldehyde Impurities on the Optical and Thermotropic Properties of a Liquid Crystalline Azomethine Dimer

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This paper presents the study of the influence of aldehyde impurities on optical and thermotropic behaviour of a liquid crystalline azomethine dimer. The survey has been realized by mixing a liquid crystalline azomethine dimer with controlled quantities of the aldehyde reagent which had been used for the synthesis of that dimer. The thermotropic behaviour was investigated by using polarized light microscopy (PLM), while optical properties were studied by using UV-Vis and photoluminescence spectroscopy. The aldehyde quenches the luminescence of mixtures due to the aggregation. Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM) measurements indicate that aggregate forming is directly connected with the content of aldehyde in the mixture.

Keywords: azomethine dimer, liquid crystal, aldehyde, aggregation, optical properties

Conjugated polymers are intensily studied for opto-electronic applications as organic light emitting diodes, field effect transistors, photovoltaic cells and so on [1-3]. The most used pathways to obtain conjugated polymers are coupling methods which use drastic reaction conditions and metallic catalysts that are difficult to be removed. An attractive alternative to current coupling methods is the azomethine forming which has the advantage of easy synthesis in mild reaction conditions, without metallic catalysts, with high yield and purity. Besides, the examination of polyazomethines as functional materials showed the properties which were suitable for working devices [4-6]. On the other hand, the obtaining of azomethines by condensation is a reversible reaction in humidity conditions that can contaminate the samples with small amounts of aldehyde reagent [7, 8]. This is why, we considered interesting to study the influence of the aldehyde reagent on the optical and thermotropic properties of an azomethine compound, being known the negative influence of keto defects upon luminescent behaviour [9-11]. The study was realized on a liquid crystal azomethine dimer which has the potential to acts as model for thermotropic polymers [12, 13]. To reach the proposed objective we used a liquid crystalline azomethine dimer synthesized and reported in our previous studies [14, 15]. Four mixtures of this dimer with different percents of aldehyde reagent were obtained and their thermotropic and optical behaviour was studied by using polarized light microscopy, UV-Vis and photoluminescence, dynamic light scattering and scanning electron microscopy.

Experimental part
Materials and methods
Reagents
-p-Cyano-benzaldehyde 97% (p-CB), dimethyl formamide (DMF) 99% and ethyl acetate 99% were purchased from Fluka and used as received. 1,2-Bis[2-(4-aminophenoxy)ethoxy]ethane was obtained and structurally characterized in our laboratory according to published procedures [16].

Synthesis of dimer

The liquid crystalline azomethine dimer (D) was synthesized by condensation reaction of p-cyanobenzaldehyde with 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane according to a procedure discussed elsewhere (Scheme 1) [14].

FTIR ν (cm⁻¹) (KBr): 3081–3041 (=C–H stretch of the aromatic rings), 2913–2878 (C–H stretch of the aliphatic chains), 2223 (-C≡N stretch), 1622 (-C=N- stretch), 1587, 1506, 1452 (C=C ring stretch), 1248 (C–O–C stretch), 841 (absorption band assigned to 1,4-phenylene ring).

1H – NMR (d-DMSO, δ ppm): 8.74 (s, 2H, CH=N), 8.07, 8.05 (d, 4H, ortho to-CN), 7.96, 7.94 (d, 4H, ortho to CH=N), 7.35, 7.33 (d, 4H, ortho to N=CH), 7.02, 7.00 (d, 4H, ortho to –O-), 4.12 (t, 4H, Ar–O–CH2–CH2–), 3.77 (t, 4H, Ar–O–CH2–CH2–), 3.64 (t, 4H, O–CH2–CH2–O).

Preparation of the controlled structural heterogenic mixtures of the dimer with p-cyanobenzaldehyde (p-CB)

For preparing homogeneous mixtures of the dimer (D) and p-cyanobenzaldehyde (p-CB) in various weight percentages (table 1) the compounds were dissolved in ethyl acetate and then the solvent was removed by heating up to 80°C. Finally, the mixtures were dried under low vacuum, at 60°C, for 8 h.

Measurements
Thermogravimetric (TGA) and differential scanning calorimetry (DSC) experiments were conducted on a Mettler TGA/SDTA 851e device. 3–3.5 mg of each sample were heated in Al₂O₃ crucibles with lids. In TGA mode, the samples have been heated from 30 to 600°C at a rate of 10°C/min, under nitrogen flow (5 mL/min), while in DSC measurements the samples were heated up to 200°C.

The thermotropic behaviour of the dimers and their mixtures was studied by observing the textures with an Olympus BH-2 polarized light microscope under cross polarizers with a THMS 600 hot stage and LINKAM TP92 temperature control system.

UV-Vis absorption and photoluminescence spectra were recorded on a Carl Zeiss Jena SPECCORD M42 spectrophotometer and a Perkin Elmer LS 55 spectrophotometer, respectively, in solution, using quartz cells of 10 mm thickness.
The particle size and size distribution were analyzed by dynamic light scattering (DLS) with a light scattering equipment Delsa Nano C, Beckman Coulter. These parameters were measured by using CONTIN method. The samples were prepared by dilution of the mixtures in pure DMF. The scattered light was measured at fixed angle 160°. The temperature was set to 25°C ± 0.1°C. Scanning electron microscopy investigation was performed on a Scanning Electron Microscope SEM EDAX – Quanta 200.

Results and discussions

A liquid crystalline azomethine dimer (D) has been synthesized by condensation reaction of p-cyano-benzaldehyde with 1,2-bis[2-(4-aminophenoxy) ethoxy]ethane (scheme 1) [14] and four mixtures of this dimer with the starting p-cyanobenzaldehyde (p-CB) reagent taken into different weight ratios were prepared (table 1).

<table>
<thead>
<tr>
<th>Code</th>
<th>D1</th>
<th>D5</th>
<th>D15</th>
<th>D30</th>
</tr>
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<tbody>
<tr>
<td>D%</td>
<td>99</td>
<td>95</td>
<td>85</td>
<td>70</td>
</tr>
<tr>
<td>p-CB%</td>
<td>1</td>
<td>5</td>
<td>15</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 1

The composition of the mixtures

The nematic mesophase appears from isotropic liquid in form of droplets with two and four brushes which coalesce to form a Schlieren texture. The crystalline – crystalline transition reveals a change of texture from spherulites to mosaic (fig. 1a, b).

To see how the thermotropic behaviour of the dimer changes because of the aldehyde presence, first, thermogravimetrical and differential scanning calorimetry curves have been recorded for each mixture. Figures 2a and 2b present typical curves for the mixture D30. The TGA trace shows two decomposition steps, starting at 100 and 410°C, respectively. The first decomposition step of the mixture was ascribed to the aldehyde sublimation, while the second one was attributed to the decomposition of dimer.

On TGA curve it can be seen, that the aldehyde sublimation is completed around 250°C, while at the full isotropization temperature (200°C) on DSC curve a small amount of aldehyde is still present. The DSC curve of the first heating scan recorded up to 200°C exhibits two endothermic steps: a broad one corresponding to the sublimation process and a sharper one corresponding to the melting. The next DSC heating scans (second and third)
reveal the appearance of the crystalline - crystalline peak, too. Comparing the three DSC heating scans it can be remarked that the sublimation peak became weaker and the melting peak became sharper as the number of heating scans increases, due to the aldehyde sublimation.

PLM observation of the mixtures shows some changes compared to the pure dimer compound, especially in the first scans. In the case of mixtures with small amount of aldehyde, the thermotropic behaviour remains relatively the same with that of the pure dimer, with only some small modifications like a slower crystallization (a larger domain of temperature). For the D15 mixture, in addition to the small changes mentioned, the crystalline - crystalline transition on the second heating scan is suppressed. The D30 mixture presents more significant modifications like a broader melting process (148-176°C), a spattered appearance in all the cycles (fig. 1c), the appearance of the crystalline state in form of fine granular texture instead clear spherulites of the pure dimer (fig. 1d). After 4-5 heating-cooling cycles, the behavior of the mixture is almost the same with that of the pure dimer, due to the complete sublimation of the aldehyde.

The introduction of more aldehyde reagent will lead to a complete suppression of the nematic mesophase. Therefore, the occurrence of the nematic mesophase and crystalline state is affected by the structural heterogeneity of the sample, especially in the first scan (table 2). Due to the relatively low temperature of the aldehyde sublimation, which is close to the isotropization temperature of the azomethine compound, this later compound is purified during the first heating scans.

Photophysical properties

Photophysical properties of the pure dimer and of the studied mixtures have been investigated by using ultraviolet-visible and photoluminescence spectroscopy in diluted solutions at certain concentrations, in order to better understand the influence of aldehyde presence upon optical behaviour. The electronic spectra of mixtures were obtained in diluted DMF solution (10⁻⁴ mol/L).

<table>
<thead>
<tr>
<th>Code</th>
<th>PLM transitions / °C</th>
<th>Observations</th>
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<tbody>
<tr>
<td>D</td>
<td>1H: Cr 176-179 I</td>
<td>Monotropic behavior, nematic mesophase</td>
</tr>
<tr>
<td></td>
<td>1C: I 166 N 140-139 Cr1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2H: Cr1 163-164 Cr2 178 I</td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>1H: Cr 176-178 I</td>
<td>Schlieren texture unaffected, slow crystallization</td>
</tr>
<tr>
<td></td>
<td>1C: I 168 N 143-132 Cr1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2H: Cr1 165-167 Cr2 177-178 I</td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>1H: Cr 179 I</td>
<td>Schlieren texture unaffected, slow crystallization</td>
</tr>
<tr>
<td></td>
<td>1C: I 166 N 148 Cr1</td>
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</tr>
<tr>
<td></td>
<td>2H: Cr1 165-166 Cr2 176-179 I</td>
<td></td>
</tr>
<tr>
<td>D15</td>
<td>1H: Cr 178 I</td>
<td>Crystalline-crystalline transition is suppressed</td>
</tr>
<tr>
<td></td>
<td>1C: I 167 N 140 Cr1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2H: Cr1 177-179I</td>
<td></td>
</tr>
<tr>
<td>D30</td>
<td>1H: Cr 150-170 I</td>
<td>Broader melting process</td>
</tr>
<tr>
<td></td>
<td>1C: I 168 N 155-137 Cr1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2H: Cr1 160-173 I</td>
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Table 2
PLM BEHAVIOUR OF THE PURE DIMER AND OF THE STUDIED MIXTURES
The UV-Vis absorption spectrum of the pure dimer in solution is characterized by two absorption bands: an absorption band at wavelength in the range of 310 - 430 nm that corresponds to the $\pi - \pi^*$ transition of the conjugated mesogens, while the second absorption band in the range of 280 – 295 nm, which is very weak, represents the electronic transition of the individual aromatic units [17, 18]. The UV-Vis spectra of the dimer and of mixtures in DMF solutions are shown in figure 3. All parameters obtained from these spectra are enclosed in table 3.

The controlled introduction of p-CB reagent led to a bathochromic shift of 10 nm from 348 nm to 358 nm (fig. 3) and a drastic decrease of absorption. Taking into consideration that all the parameters (concentration and dimension of the cuvette) were maintained constant, according to the Lambert-Beer law, we can say that molar extinction coefficient of mixtures is decreasing compared to that of pure dimer; it means that the absorption ability of chemical species in the mixtures is weaker than those of the pure dimer [19]. The cause of the absorbance decrease is, most probably, the formation of aggregates [20] between the dimer and the p-CB (reagent) (see DLS and SEM measurements). In the same time this aggregates lead to a conformational stiffness of the dimer which produces a red shift of the mixtures compared to the pure dimer D.

In photoluminescence spectra, the pure dimer shows only an emission peak in violet domain (410 nm), while the mixtures exhibit two emission peaks: an intense one in the violet region, similar to the pure dimer, and a second one in the green domain which can be ascribed to the aggregates formed by dimer and aldehyde. The spectra registered from time to time, reveal a decrease of emission intensity, most probably due to the aggregates growing (fig. 4).

<table>
<thead>
<tr>
<th>Code</th>
<th>UV-VIS: $\lambda_{\text{max}}$ (nm)</th>
<th>PL: $\lambda_{\text{max}}$ (nm)/ Intensity</th>
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</thead>
<tbody>
<tr>
<td>D</td>
<td>348</td>
<td>410/609</td>
</tr>
<tr>
<td>D1</td>
<td>292, 358</td>
<td>408/65; 523/42</td>
</tr>
<tr>
<td>D5</td>
<td>294, 358</td>
<td>418/243</td>
</tr>
<tr>
<td>D15</td>
<td>294, 358</td>
<td>408/70; 523/24</td>
</tr>
<tr>
<td>D30</td>
<td>294, 358</td>
<td>411/106; 528/219</td>
</tr>
</tbody>
</table>

To prove the formation of aggregates, dynamic light scattering (DLS) measurements have been performed for solutions of mixtures after 3 days. The particle size and their distribution determined by DLS are given in Table 4. All the samples clearly indicate the aggregate forming. As can be seen, while D1 mixture, containing a low percentage of aldehyde, shows in principal an aggregate diameter around 294 nm with a relative low polydispersity index, the increasing amount of aldehyde in mixture leads, in principal, to two kinds of aggregates corresponding to two aggregates diameters, with an increasing polydispersity index. It can be seen that all mixtures have a kind of aggregates with a submicrometric diameter (0.294 – 0.722 $\mu$m), while the mixtures having higher percentage of aldehyde (>5%) present additionally a kind of aggregates with micrometric diameter (7.077 – 28.406 $\mu$m).

The formation of aggregation was also investigated by using scanning electron microscopy (SEM). The SEM images of the dried solutions spread on glass plate show
the aggregates having the diameter close to those measured by DLS (fig. 5). The images reveal that, most probably, the aggregates with the largest diameter are formed by the aggregation of smaller aggregates.

Conclusions

A series of mixtures of a liquid crystal azomethine dimer with its aldehyde reagent were prepared and the modifications of thermotropic liquid crystalline and optical properties were investigated.

The thermotropic liquid crystalline behaviour is affected only when the mixtures contain a high amount of aldehyde (D15 and D30), but only for the primary cycles heating-cooling (2-3 cycles), till all the amount of aldehyde is sublimated.

The optical properties of azomethine dimer are drastically affected by the presence of aldehyde impurities, in this case aggregation occurs, which was demonstrated and analyzed by two different techniques DLS and SEM.

This study demonstrates that the presence of aldehyde as impurity affects in a negative way the thermotropic and especially optical properties, but their negative influence can be overcome by thermal treatment.

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References


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