

SOLVATOCHROMIC STUDY OF NEW CARBAZOLE BASED MATERIALS

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In this paper two new materials with enhanced nonlinear optical properties (NLO), obtained from carbazole and an azoderivative, are presented. Although they are similar in composition, they differ in structure and synthesis. These materials were investigated individually, but also comparatively, through UV-Vis spectroscopy in order to determine the possibility of using them in applications requiring NLO properties.

Keywords: Carbazole, NLO.

1. Introduction

One of the most interesting domains of research remains the nonlinear optics (NLO) area. This is due to the applications requiring different type of materials from organic to inorganic and from small to supramolecular structures.

Between all these materials, polymers with NLO properties are of high interest. Some properties can be induced even during the synthesis and an important step is represented by the monomers choice.

In this respect, we synthesized a new monomer with carbazole sequence and azobenzen groups. We started with carbazole because of its known properties concerning the hole to hole conductivity, thermal and photochemical stability and for the possibility to control the structural modification on the carbazolyl ring. The azobenzene groups are already used for materials in NLO applications as holography and dichroism due to its isomers stability and quick conversion between them [1,2]. To make these materials suitable for polymerization a methacrylate group was inserted. All of these sequences are already used in NLO application and that is why we designed these polymers and undergone a UV-Vis study to see if those materials have the applicability we seek.

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The proposed work is based on previous studies of these types of materials and the aim of this paper is to conduct this synthesis in order to obtain new materials suitable for precise applications like NLOs.

2. Experimental

2.1. Materials

For the compounds synthesis and characterization, the following solvents were used: tetrahydrofuran (THF), ethanol, toluene, dimethyl formamide (DMF), 1,4-dioxane, dimethyl sulfoxide (DMSO) and ether ethylic. All solvents were purchased from Sigma-Aldrich and were used as received (analytic purity).

In the monomer synthesis were used as received 9H-carbazole, epichlorohydrin, methacryloyl chloride purchased from Sigma-Aldrich. The 4-[(4-hydroxyphenyl)diazenyl]benzotrile (HPDB) was synthesized. For the reaction medium potassium hydroxide (KOH), triphenyl phosphine (TPhPh), 4-dimethylaminopyridine (DMAP) and triethylamine (TEA) were added, all were purchased from Sigma-Aldrich and used as received.

In the second method sodium hydroxide (NaOH) and tetrabutyl ammonium bromide (TBAB) were used in order to modify the polymer obtained from vinyl benzyl chloride (VBC) and maleic anhydride (MA). The used initiators were benzoyl peroxide (BP) and azobisisobutyronitrile (AIBN). NaOH, TBAB, VBC, MA, BP and AIBN were also purchased from Sigma-Aldrich and used as received.

2.2. Synthesis

In this paper we present two methods for obtaining new polymers by different synthesis reaction.

These two methods lead to polymers with similar sequences but different structures. Our aim was to understand how the position of the interest groups influences the properties of the final materials.

The first method (Fig. 1) follows the classic steps of synthesis and polymerization. Fig. 1 shows the synthesis reaction of Monomer 1 (*M 1*).

The synthesis starts by heating at 80-90 °C 9H-carbazole and epichlorohydrin in THF in the presence of KOH. The reaction flask was sparged with nitrogen. The obtained intermediate compound 1 (*IC 1*) was separated and washed and then used to obtain intermediate compound 2 (*IC 2*) by reacting with HPDB in the presence of TPhP at 120 °C for almost 18 hours. The *IC 2* was separated and washed.

All products were purified by ethanol recrystallization.

The last step was the insertion of the polymerizable group. This was achieved by reacting *IC 2* with methacryloyl chloride in presence of TEA and DMAP (widely used as a hypernucleophilic acylation catalyst) at room temperature for 3-4 hours.

The obtained monomer 1 (*M 1*) was chromatographically separated and polymerized in 1,4-dioxan using BP as initiator. The resulting polymer 1 (*P 1*) was precipitated in ether ethylic and washed several times before drying under pressure at 40 °C for 48 hours [3,4,5].

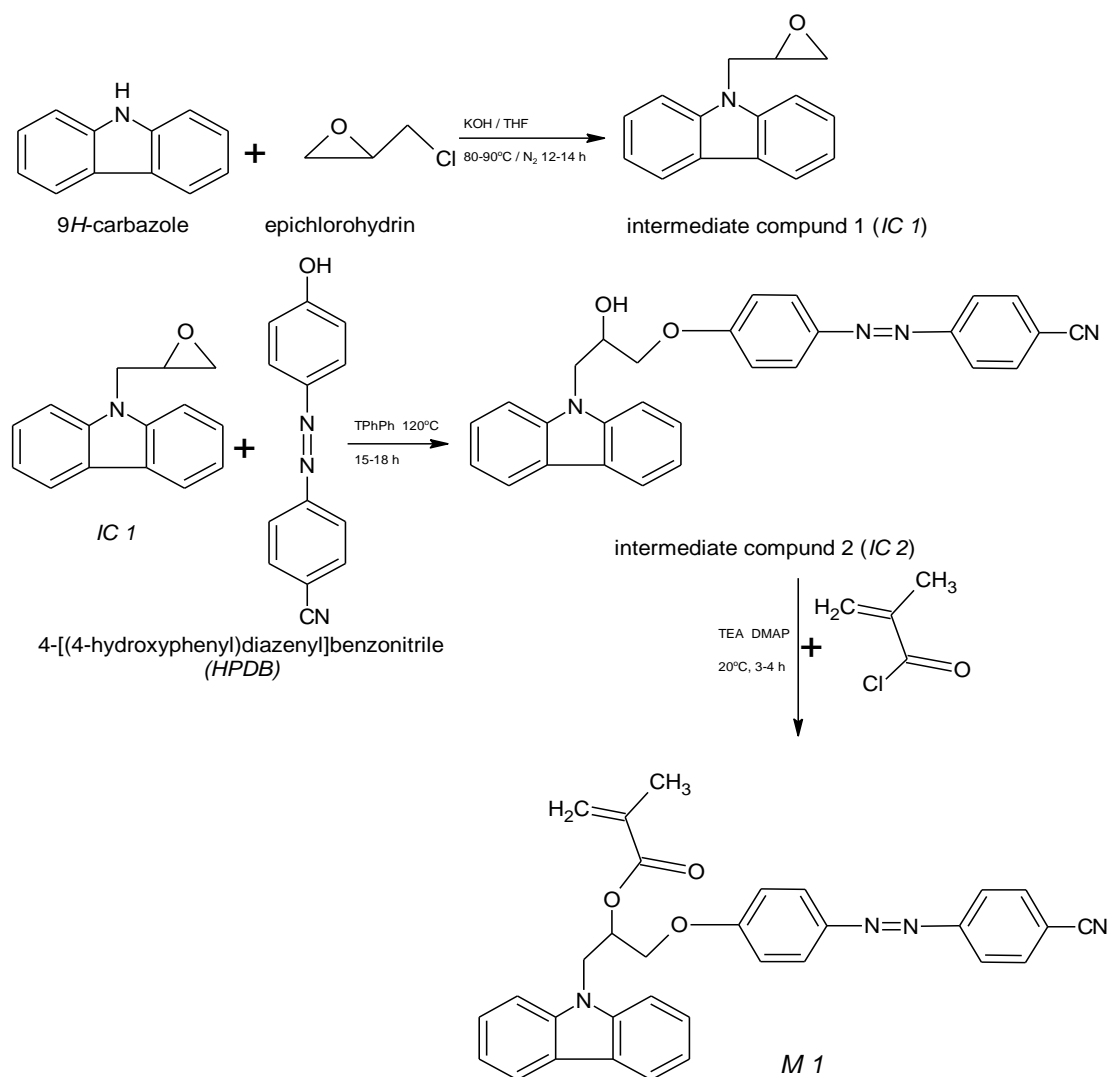


Fig. 1. The synthesis reactions of the *M 1*

The second obtained material has a different synthesis path (Fig. 2). First, vinyl benzyl chloride (VBC) and maleic anhydride (MA) were polymerized in toluene using AIBN as initiator. The obtained polymer (poly (VBC-MA)) was modified with carbazole sequences by dissolving them in DMF in presence of NaOH and TBAB. The resulted intermediate compound 3 (*IC 3*) was then reacted with HPDB in presence of TEA [5,6,7].

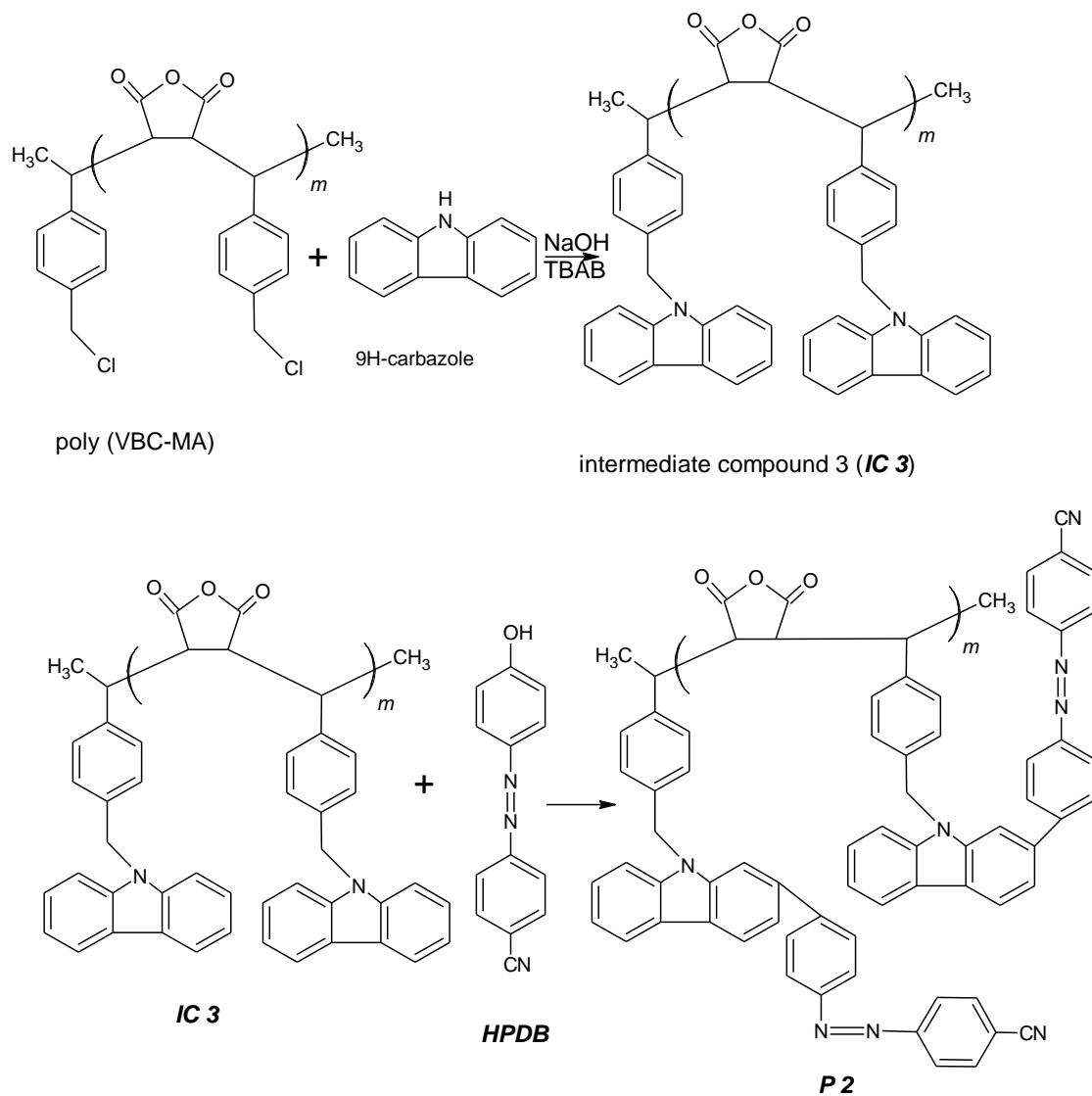


Fig. 2: The synthesis reaction of the *P 2*

The obtained compound *P2* was precipitated by the same method as *P1* in ether ethylic and washed several times before drying under pressure at 40 °C for 48 hours. In this case, the insertion of the azobenzene group was on the carbazolic ring.

2.3. UV-VIS Characterization

Comparing the spectra of the solution in different solvents of *IC 2* and of *M 1* (Fig. 3) the similar absorption maxima were observed: between 200-275 nm for the alkyl sequences, between 275-325 nm specific absorption maxima for $\pi-\pi^*$ transition of azoic sequences and between 325-450 nm specific absorption maxima for $\pi-\pi^*$ of the carbazole ring.

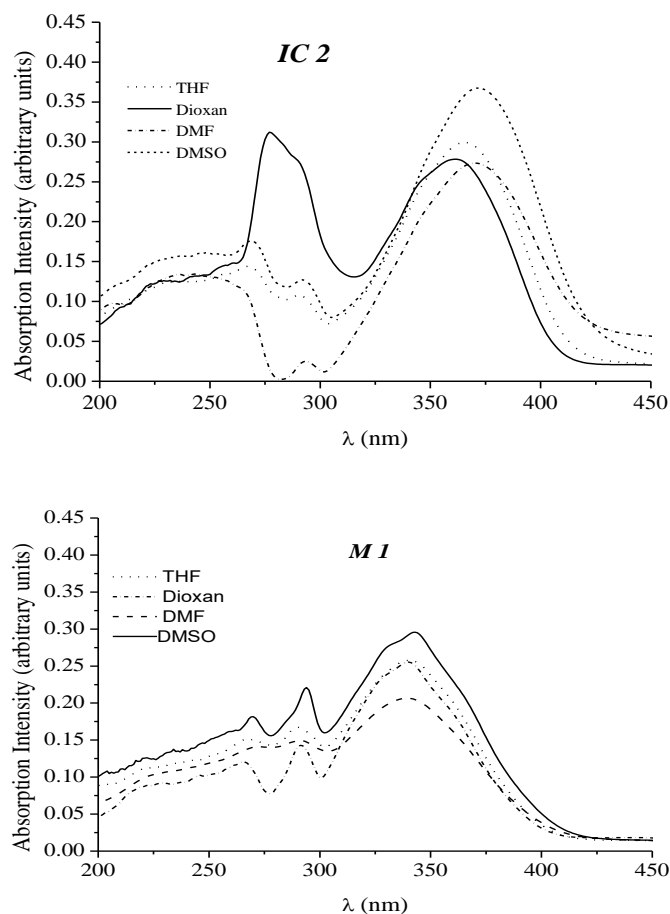


Fig. 3: UV-Vis spectra for *IC 2* and *M 1* in different solvents: THF, 1,4-dioxane, DMF and DMSO

It can be observed, from Fig. 3, that the solvent polarity modifies the behavior of the intermediate compound: 1,4-dioxane stimulates transition between 250-330 nm, while DMSO stimulates the specific transitions for the carbazole ring. For the monomer the same behavior was observed in all solvent polarities: the absorption maximum increases with the polarity increasing and the areas from 200 to 275 nm and from 275 to 330 nm are well defined.

In the case of *P2* compound (Fig. 4) it is observed that even when high polarity solvent is used (DMSO) the specific absorption peaks for each constitutive sequence are not well defined. Only for high dilutions a shoulder at 340 nm specific for the modified carbazole and some small and broad maxima around 521 nm appear. The same behavior is also seen for solutions obtained using DMF solvent, while when THF solvent was used an important absorption peak at 425 nm is highlighted. It can be noted that for the compound *P2* using solvents with low polarity (1,4-dioxane and THF) stimulates the appearance of excited species having as consequence absorption bands at 448 and 640 nm.

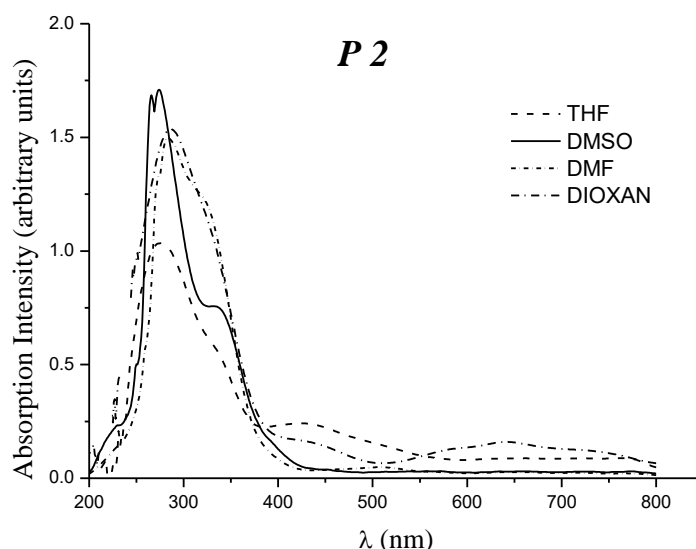


Fig. 4: UV-Vis spectra of *P 2* in different solvents: THF, 1,4-dioxane, DMF and DMSO

At the same time, the two synthesized materials have a complete different behavior concerning the specific absorption of the π - π^* transition of the azo-derivative and of the carbazole groups (Fig. 5 and 6).

In the case of *P1* compound (Fig. 5) the absorption intensity is higher when the solvent polarity is lower (1,4-dioxane and THF), while for *P2* compound the highest absorption intensity is obtained for DMSO solvent.

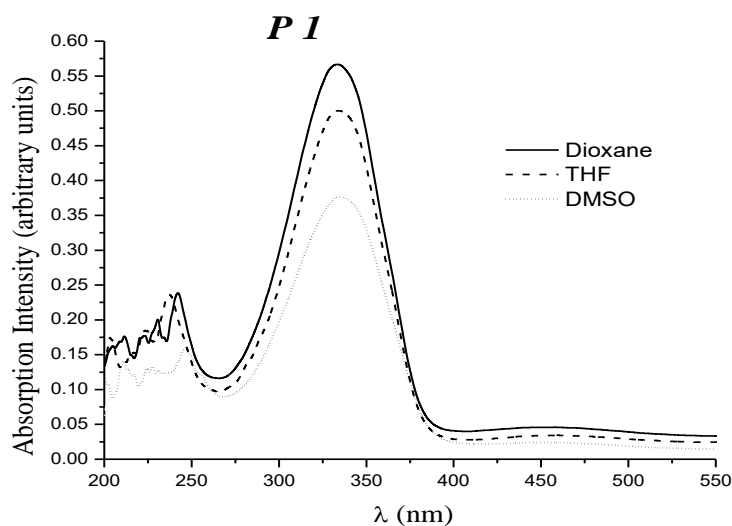


Fig. 5: UV-Vis spectra of *P1* in different solvents: THF, 1,4-dioxane and DMSO

For the compound *P2* the spectra of different concentration solution (Fig. 6) shows the same behavior for all the used solvents. A hyperchromic effect can be observed in all four spectra. The difference appears in the shape of the spectra. In the case of THF a clear peak appears around 430 nm, while for 1,4-dioxane the second peak has a low absorption intensity and a broad area. For DMSO the broad peak has a shoulder at a lower wavelength while for DMF there is only one broad peak at high wavelength.

Another observation can be made on each spectra: with the concentration dilution a hypsochromic effect is induced. The polarity of the solvents has the same effect on the spectra and a blue shift appears.

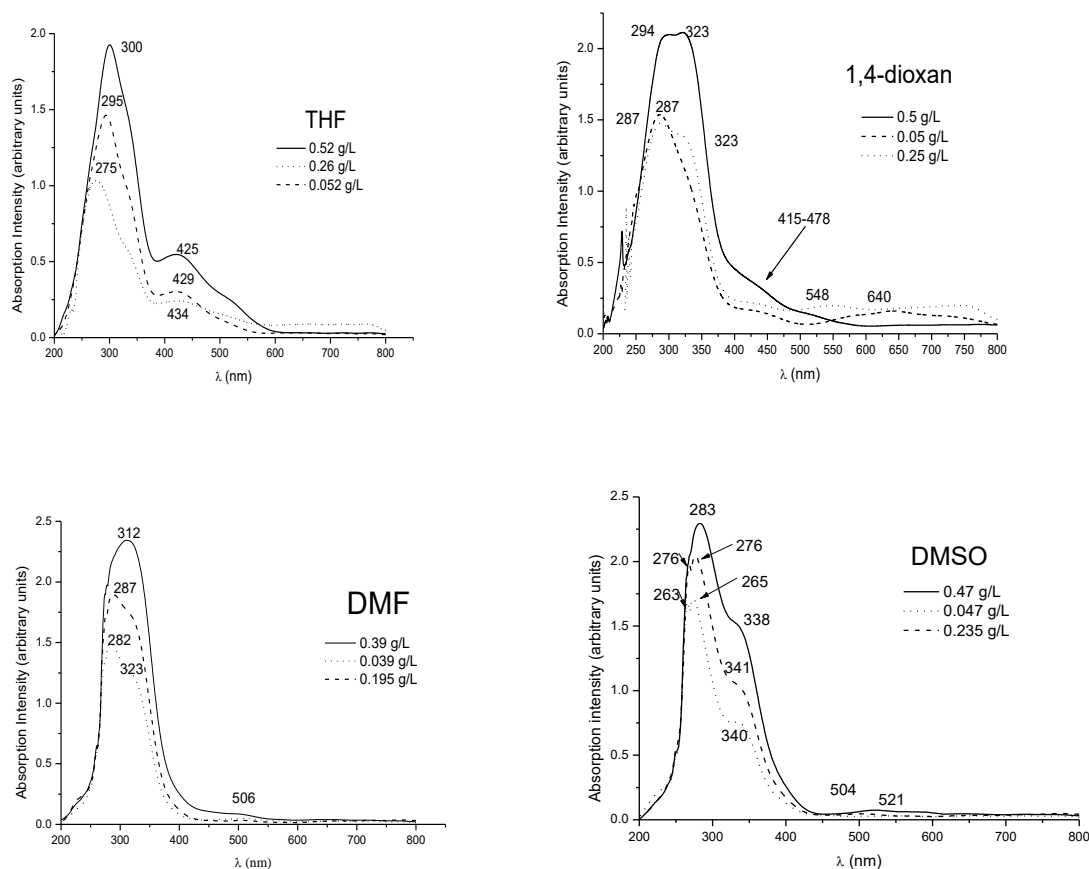


Fig. 6: UV-Vis spectra of *P 2* various concentration in different solvents: THF, 1,4-dioxane and DMSO

3. Conclusions

Both presented synthesis methods lead to polymers with designed structure. The first one has more steps and strict conditions and lead to a small amount of monomer which hardly polymerizes because of its bulky substituents. The advantage of this method is the fact that the resulting polymer has a precise structure.

The second synthesis has fewer intermediates which are easily separated. One problem that can appear in this case is the addition of the azobenzene

sequence because both pendant groups (carbazoyl and azobenzene) are voluminous and steric hindrance might occur.

The positions of the UV-Vis bands are strongly affected by the structure of compound, by the length of the π conjugate bridge and by electronic nature of the substituent groups. The solvent polarity affects the number, the width and the intensity of the absorption peaks shifting them to higher wavelengths.

Comparing the absorption spectra of the synthesized materials we observed in the case of *P2* an increase of the optical density with the increase of solvent polarity which suggests a higher mobility and thus a better reorganization of the alkyl chain around the carbazole ring.

These investigations represent the first step in optical characterization of the synthesized compounds. In the near future NLO characterization will be performed on these materials.

At the same time this study will be useful as a tool for explaining the correlation properties-structure for these new polymers.

More structure and composition investigation are following this study to prove the properties-structures dependence.

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