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# NEW CARBAZOLE BASED MATERIALS: SYNTHESIS AND SPECTRAL CHARACTERIZATION

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*In this paper two new carbazole and azo-derivative based materials are presented. Although they are similar in composition, they differ by structure. The obtained materials were characterized by FT-IR and NMR spectroscopy in order to confirm the designed structure. 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**: Solvatochromic study, Carbazole based materials, Azo-derivative

## 1. Introduction

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

Among 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.

It is well known that carbazole based materials [1] as well as azo-chromophores [2] have already been proven to have good NLO properties. Therefore, it is expected that materials containing both types of sequences (carbazole and azo) will reveal enhanced NLO properties.

In this respect, we synthesized new monomers with carbazole sequence and azo-benzene 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 azo-benzene groups are already used for materials in NLO applications like holography and dichroism due to their isomers' stability and quick interconversion [3, 4]. To make these materials suitable for polymerization a methacrylate group was inserted.

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In this paper two different materials are obtained by the same proposed method and a solvatochromic study for these polymers is presented.

## 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 diethyl ether. All solvents were purchased from Sigma-Aldrich and were used as received (analytic purity).

In the monomer synthesis 9H-carbazole, epichlorohydrin and methacryloyl chloride purchased from Sigma-Aldrich were used as received, while 4-[(4-hydroxyphenyl)diazenyl]benzo-R (HPDB-R) was synthesized [5]. Potassium hydroxide (KOH), triphenyl phosphine (Ph3P), 4-dimethylaminopyridine (DMAP) and triethylamine (TEA) were purchased from Sigma-Aldrich and used as received.

### 2.2. Synthesis

Two new monomers obtained by the same synthesis method are presented.

This method leads to monomers with similar sequences but different structures. Our aim was to understand how the different substituent and the interest groups influence the properties of the final materials.

The method used follows the classic steps of synthesis and polymerization [6]. Fig. 1 shows the synthesis reaction of Monomers 1 and 2 (*M 1* and *M 2*).

The synthesis starts by heating a mixture of 9H-carbazole and epichlorohydrin in THF in the presence of KOH at 80-90 $^{o}$C. The reaction flask was sparged with nitrogen. The obtained intermediate compound 1 (*IC 1*) was separated and washed and then used to obtain intermediate compounds 2 and 3 (*IC 2* and *IC 3*) by reacting with HPDB-R in the presence of $Ph_3P$ at 120 $^{o}$C for almost 18 hours. The *IC 2* and *IC 3* were 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* and *IC 3* with methacryloyl chloride in the presence of TEA and DMAP (widely used as a hypernucleophilic acylation catalyst) at room temperature for 3-4 hours.

The obtained monomers 1 and 2 (*M 1* and *M 2*) were chromatographically separated and polymerized (*M 1*) in 1,4-dioxan using BP as initiator. The resulting polymer 1 (*P 1*) was precipitated in diethyl ether and washed several times before drying under vacumm at 40 $^{o}$C for 48 hours [7-9].

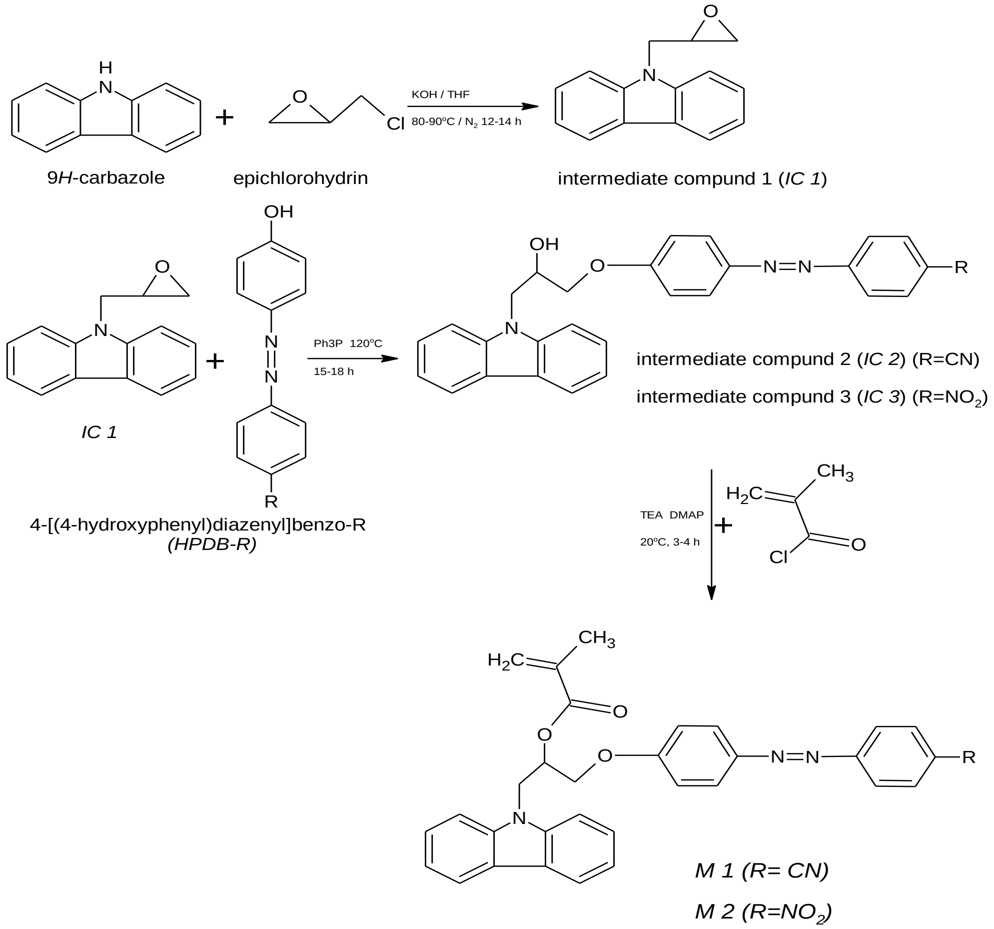

Fig. 1. The synthesis reactions of the monomers where R is CN for the monomer *M1* and $NO_2$ for monomer *M2*

### 2.3 FT-IR Spectroscopy

In order to confirm the designed structure of the synthesized materials FT-IR spectroscopy was performed. For this characterization a Brucker VERTEX 70 instrument, equipped with a Harrick MVP2 diamond ATR device apparatus have been used. The specific vibrational peaks of the contained groups were assigned for each material.

The specific peaks of *M 1* (Fig. 2) are found at: 2929-3053 $cm^{-1}$ (Ar-CH stretching vibration), 2227 $cm^{-1}$ (C≡N stretching vibration), 1598 $cm^{-1}$ (Ar-C=C stretching vibration), 1453 $cm^{-1}$ ($CH_3$ deformation), 1139 $cm^{-1}$ (CO stretching vibration) 1028 $cm^{-1}$ (O-H stretching vibration) and 1720 $cm^{-1}$ (C=O stretching vibration in the methacrylic group).

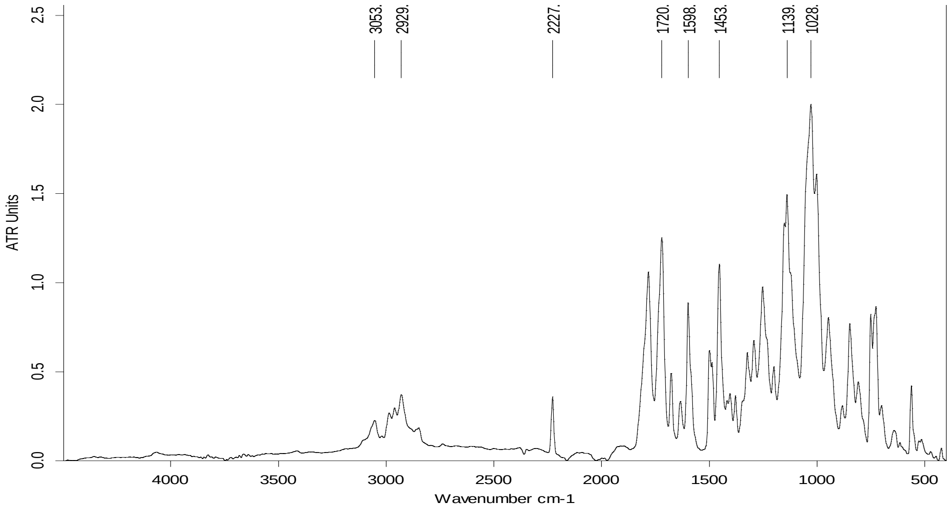

Fig. 2. FT-IR spectra of *M 1*

Relevant FT-IR peaks for the *M 2* (Fig. 3) can be observed at: 3453-3526 cm$^{-1}$ (O-H stretching vibration), 2931-3104 cm$^{-1}$ (Ar-CH stretching vibration), 1590 cm$^{-1}$ (Ar-C=C stretching vibration), 1520 cm$^{-1}$ ($NO_2$ stretching asymmetric vibration), 1320 cm$^{-1}$ (NO2 stretching symmetric vibration), 1453 cm$^{-1}$ ($CH_3$ deformation), 1137 cm$^{-1}$ (CO stretching vibration), 1493 and 1004 cm$^{-1}$ (O-H stretching vibration). Beside the peaks mentioned before, the characteristic peaks for the methacrylic group can be also observed at 1732 cm$^{-1}$ (C=O stretching vibration) and 1635 cm$^{-1}$ (C=C stretching vibration).

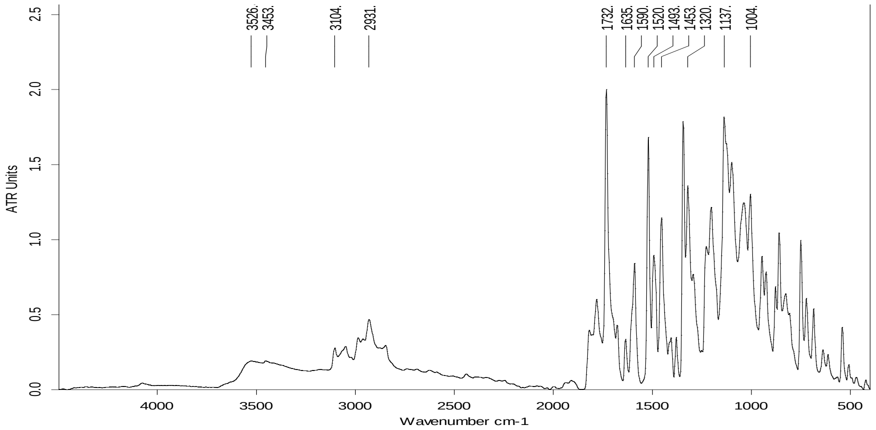

Fig.3. FT-IR spectra of *M 2*

### 2.4. NMR Characterization

A more specific structure determination is given by NMR investigation and, therefore, $^{1}$H-NMR spectra have been obtained in dimethylsulphoxide with a

Bruker Avance DRX 400 Instrument. For each monomer, $^1$H-NMR spectra were performed in order to determine its structure. In Figs. 4 (M 1) and 5 (M 2) the representative spectra are presented and the peak attribution for each monomer is described in each figure caption [10-12].

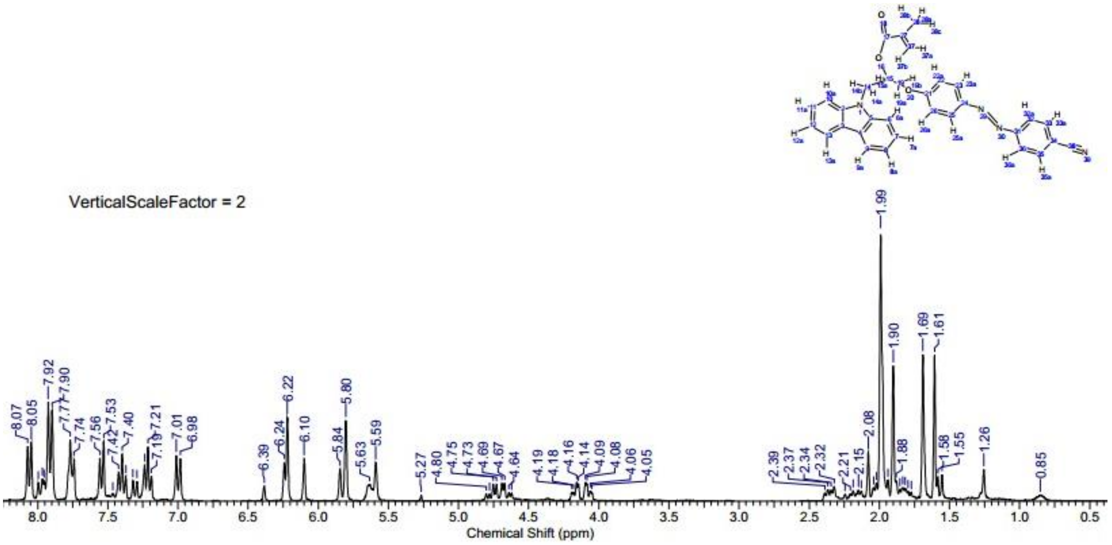

**Fig. 4.** $^1$H NMR spectra (DMSO-$d_6$) of *M 1* ): δ1=8.07 (d, 1H, aromatic), δ2=7,92 (s, 1H, aromatic), δ3=7.77 (d, 1H, aromatic), δ4=7.56 (t, 1H, aromatic carbazole), δ5=7.21 (t, 1H, aromatic carbazole), δ6=8.05 (d, 1H, aromatic carbazole), δ7=4.67 (t, 2H), δ8=1.61 (s, 3H), δ9=5.80 (s, 1H) ppm.

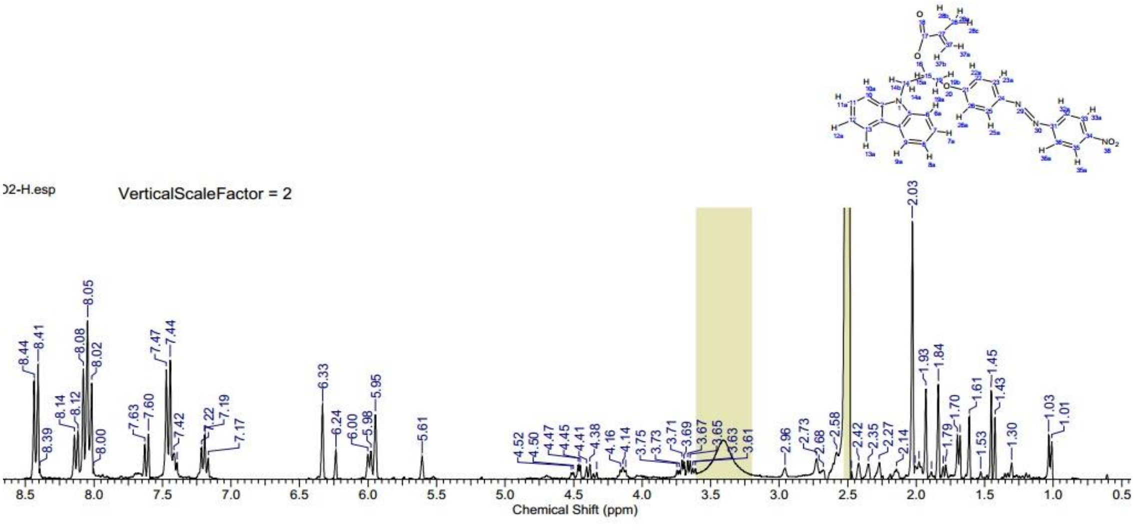

**Fig. 5.** $^1$H NMR spectra (DMSO-$d_6$) of *M 2*: δ1=8.44 (d, 1H, aromatic), δ2= 8.41 (d, 1H aromatic), δ3=8,05 (d, 1H,aromatic carbazole), δ4=7.63 (d, 1H aromatic carbazole), δ5=7.60 (d, 1H, aromatic carbazole), δ6=7.44 (t, 1H, aromatic carbazole), δ7=7.22 (t, 1H, aromatic carbazole), δ8=8.05 (d, 1H, aromatic carbazole), δ9=4.41 (t, 2H,), δ10=3.71 (t, 2H,) , δ11=1.61 (s, 3H,), δ12=5.61 (s, 2H) ppm.

### 2.5. UV-VIS Characterization

Comparing the UV-Vis spectra of *IC 2* and of *M 1* (Fig. 6) in different solvents, 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.

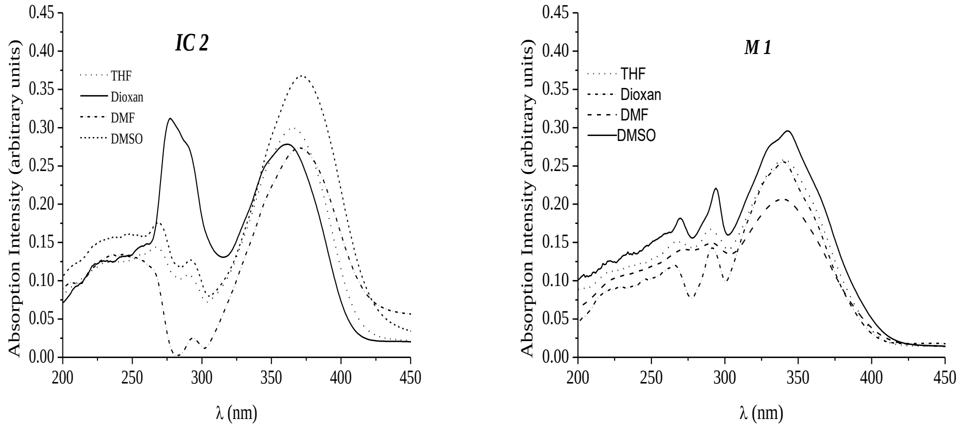

Fig. 6. UV-Vis spectra for *IC 2* and *M 1* in different solvents: THF, 1,4-dioxane, DMF and DMSO

It can be observed, from Fig. 6, 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 relation to solvent polarity: 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 compound *M 2* (Fig. 7) it is observed that for all solvents the specific absorption peaks for each constitutive sequence are defined. Only in 1,4-dioxane the specific peak of the modified carbazole appears as a shoulder at 340 nm. Another difference appears for the specific peak of azoic sequences absorption of $\pi$-$\pi^*$ transition around 280 nm. Comparing with the rest of the solvents, the peak at 280 nm is higher in intensity and wider. The *IC 3* presents the same behavior in all the used solvents with no major differences. Only a small shift of the carbazole ring specific absorption can be observed when DMSO was used.

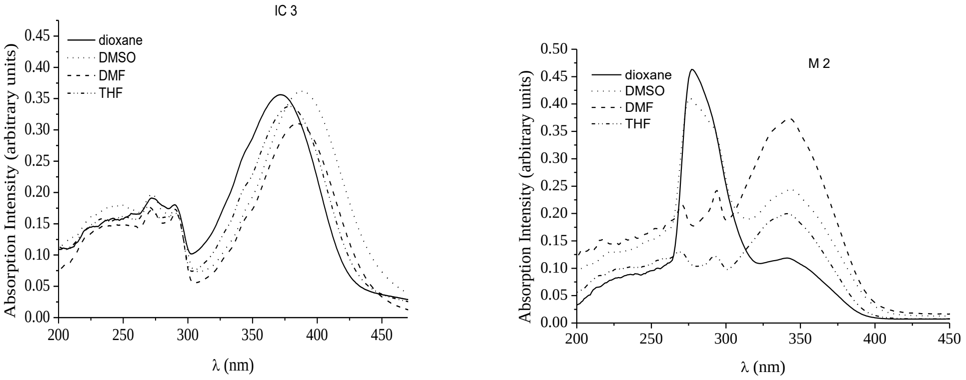

Fig. 7. UV-Vis spectra of IC 3 and *M 2* in different solvents: THF, 1,4-dioxane, DMF and DMSO

The absorption intensity of compound *P1* (Fig. 8) is higher when the solvent polarity is lower (1,4-dioxane and THF), and comparing with the maxima of the monomer, a hypsochromic shift is observed.

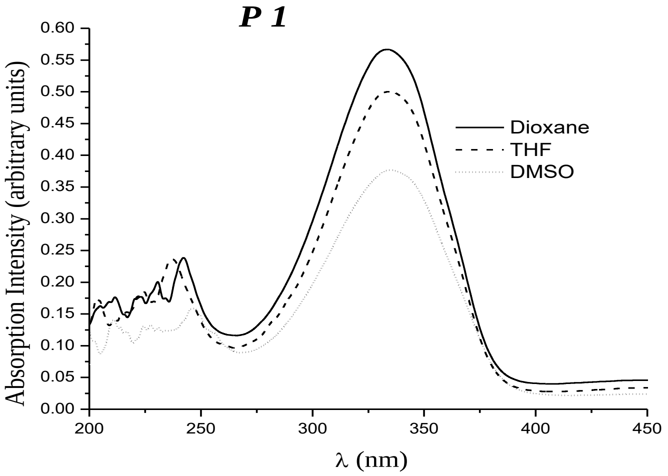

Fig. 8. UV-Vis spectra of *P 1* in different solvents: THF, 1,4-dioxane and DMSO

The use of solvents with different polarities showed for the two synthesized monomers a different behavior concerning the specific absorption of the $\pi$-$\pi^*$ transition of the azo-derivative and of the carbazole groups (Fig. 9).

For the compound *M 2* the spectra in different polarity solvents (Fig. 9) shows the same behavior when THF, 1,4-dioxane and DMF were used as solvents. A hyperchromic effect can be observed in all three spectra. The difference appears in the shape of the spectra in the cases of 1,4-dioxane and

DMSO where the specific absorption of the azo sequence is higher than the one of the carbazole ring.

In the case of *M 1,* the shape and the intensity proportionality between the specific peaks remains the same regardless the solvent polarity. Another observation can be made on each spectrum: increasing the polarity index of the solvent a small bathochromic effect is induced. The polarity of the solvents has the same effect on the spectra and a red shift appears.

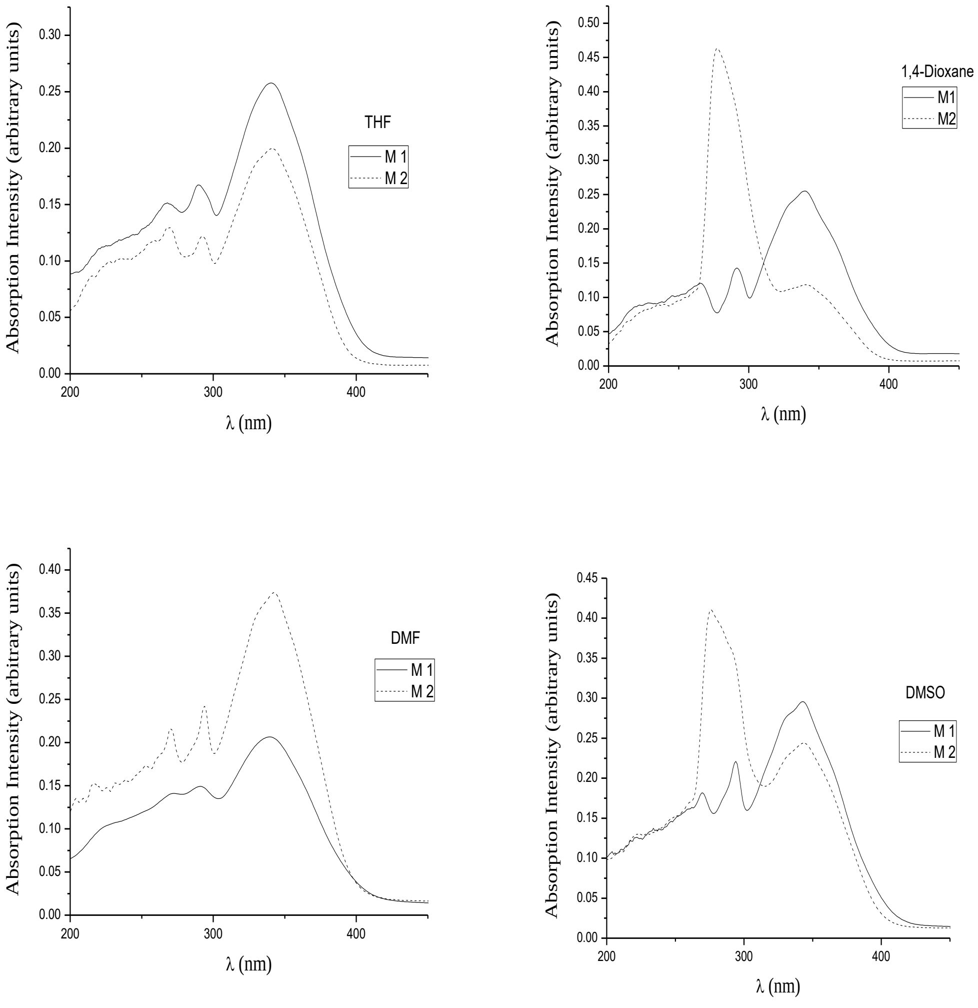

Fig. 9. Comparative UV-Vis spectra of *M 1* and *M 2* in different solvents: THF, 1,4-dioxane, DMF and DMSO

## 3. Conclusions

The presented synthesis method leads to monomers with designed structure. The advantage of this method is the fact that the resulting polymer has a precise structure even though there are more steps and strict conditions. The method yield is small, and the monomer hardly polymerizes because of its bulky substituents.

The positions of the UV-Vis bands are not strongly affected by the length of the $\pi$ conjugate bridge or by the electronic nature of the substituent groups. The solvent polarity affects the width and the intensity of the absorption peaks. At the same time the peaks are shifted to higher wavelengths.

Comparing the absorption spectra of the synthesized materials we observed in the case of *M2* an increase of the absorbance with the increase of solvent polarity which suggests a higher mobility and thus a better reorganization of the alkyl chain around the carbazole ring.

This study can be useful as a tool for explaining the properties-structure correlation for these new polymers, more structural and compositional investigation will be performed in order to prove the properties-structure dependence.

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

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