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# Synthesis and Characterization of Schiff Base Polymer Dyes Containing Electron-Withdrawing and Electron Releasing Groups

# Elektron Salıcı ve Electron Çekici Grup İçeren Schiff Bazı Polimer Boyaların Sentez ve Karakterizasyonu

Research Article

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## ABSTRACT

New thermally stable water soluble azo dye and azo-Schiff base polymer dyes were synthesized via condensation reaction of 4-methyl pyridine and poly-(4,4′-diamino)biphenyl-2,2′-disulfonic acid with substituted azo-coupled 2-hydroxy-5-((4-nitrophenyl)diazenyl) benzaldehyde. For the structural analyses of synthesized substances FT-IR and NMR analysis, florescence and UV-Vis measurements for optical properties and the thermal behavior (TG-DTA) of the prepared dyes have been determined using thermogravimetric technique. Azomethine dyes (AZOBMS and AZOBMSP) have relatively higher thermal durability in comparison to azo dye (AZOBM). The solvatochromic studies of the prepared dyes in DMSO, DMF, $CH_3CN$ and THF. In addition, spectrophotometric and spectrofluorometric studies showed that these dyes were good absorbent and fluorescent. The effect of various organic solvents with different polarities on the UV-Vis spectra and fluorescence analyses of the dyes has been also studied.

**Key Words**
Imine polymers, synthesis, characterization and thermal analysis, azo-azomethine dyes.

## ÖZ

4-Metil piridin ve poli(4,4′-diamino)bifenil-2,2′-disülfonik asit ile 2-hidroksi-5-((4-nitrofenil4)diazenil) benzaldehit bileşiği ile yeni ısıl kararlı suda çözünebilen azo boyaları ve azo-Schiff baz polimeri boyaları sentezlendi. Sentezlenen maddelerin yapısal analizleri FT-IR ve NMR, optik özellikleri için floresans ve UV-Vis ölçümleri, termogravimetri tekniği kullanılarak ısıl davranışları (TG-DTA) ölçüldü. Azometin boyaların (AZOBMS ve AZOBMSP) solvatokromik çalışmaları DMSO, DMF, $CH_3CN$ ve THF de yapıldı. Ayrıca farklı organik çözücülerde spektrofotometrik ve spektrofloremetrik çalışmaları sonucunda iyi absorban ve floresan özellik gösterdiği gözlendi.

**Anahtar Kelimeler**
İmin polimerler, sentez, karekterizasyon ve ısıl analiz, azo-azometin boyalar.

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## INTRODUCTION

Schiff base products are usually known as azomethine compounds because of the presence of azomethine bond [1]. Azo compounds are the oldest and largest class of industrial synthesized organic dyes because of their versatile application in various fields, such as biomedical studies, advanced application in organic synthesis, high technology areas such as electro-optical devices, and dyeing textile fibers [2]. The most common dyestuff among these are azo-group (-N=N-) containing dyes. These dyestuffs are commonly used in areas such as textile, lac-dyes, polyography, elastic, leather, plastic materials, dying of synthetic fibers and other industrial areas [3,4]. Azo moieties are relatively robust and chemically stable, and therefore they prompted extensive studies of azobenzene-based structures as colorants and dyes [5]. Aromatic azo products are key chromophores in the chemical industry as pigments and dyes, indicators, food additives, radical reaction initiators and therapeutic agents. They are known to be involved in various fields such as dyeing of textile fibers, coloring of different materials such as wood, wool and leather [6]. Aldehyde group containing azo dye stuff, as a result of condensation with primer amines are known to synthesize many azomethine bond containing azo dyes. These dyestuffs are used by textile industry to dye various fabrics. Imine group containing azo dyes, apart from textile industry, have significant importance to photochemistry science. It is widely known that -C=N- or -N=N- containing structures can form complexes with numerous metals efficiently, so that they can be used as metal sensors [7]. Considerable attentions have been paid to the study of azo-azomethine dyes containing hydroxyl groups in recent years. Intermolecular proton transfer of this class of dyes has important consequences on their electronic structure which may be exploited for their photochromic and/or thermochromics behavior [8]. All colors of dye are available in azo dyestuff: yellow, red, purple, blue, green, brown, and black) As the amount of azo-groups increases, the intensity of the color increases. In addition, the color intensity increases when groups such as -OH, $-NH_2$, $-N(CH_3)_2$, $-CH_3$ and halogens are abundant and when naphthalene derivatives, instead of benzene derivatives, are used. [9]. Therefore, it is remarkable that azomethine containing azo dyes are forming complexes with certain metals. Obtained metal complexes are used as nonlinear optic materials. The crucial point of nonlinear optic material synthesis, is the highly polarizable characteristic of the molecule to be synthesized. To provide this, substituent groups of different characteristics must be conjugated to the structure [10]. These groups are compelled to be good electron donors and acceptors, so that the polarizability of the molecule increases [11]. At the same time, the compound whose linearity is disrupted becomes favorable for energy-transfer processes [12,13].

Taking this information into consideration, in this study, two groups are compared: azo-azomethine dye containing electron donor methyl ($-CH_3$) and the formerly synthesized electron accepting containing ($-SO_3H$) azo-azomethine polymers

## MATERIALS and METHODS

### Chemicals

While all solvents (N,N-dimethylformamide (DMF), tetrahydrofurane (THF), dimethylsulfoxide (DMSO), ethanol, chloroform ($CH_3Cl$), hexane) and chemicals (4,4′-diamino-2,2′-bifenil sulphonic acid, 2-hydroxybenzaldehyde, KOH, HCl, NaOH, $NaNO_2$, $Na_2CO_3$, NaCl) were provided from Merck (Germany) Company, only sodium hypochlorite (30%) was purchased from Paksoy Chemicals Company. They are used in experiments without the need of initial purification.

### Instruments

The infrared and ultraviolet-visible spectra were measured by Perkin Elmer FT-IR Spectrum one and Perkin Elmer Lambda 25 (USA), respectively. The FT-IR spectra were recorded using universal ATR sampling accessory (4000-550 $cm^{-1}$). $^1H$ and $^{13}C$-NMR spectra (Bruker AC FT-NMR spectrometer (Netherlands) operating at 400 and 100.6 MHz, respectively) were also recorded by using deuterated DMSO-d6 as a solvent at 25°C. The tetramethylsilane was used as internal standard. Thermal data were obtained by using a

Perkin Elmer Diamond Thermal Analysis system (USA). TG-DTA measurements were made between 10-1000°C (in $N_2$, rate 10°C/min).

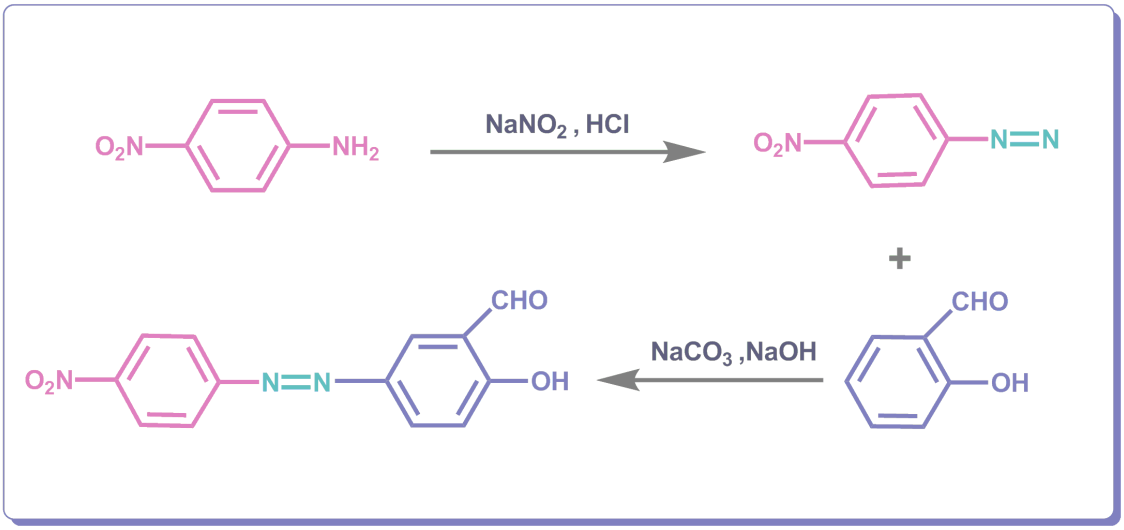
Ultraviolet-visible (UV-Vis) spectra were measured by Analytikjena Specord 210 Plus (United Kingdom) at 25°C. The absorption spectra were recorded by using DMSO at 25°C.

A Shimadzu RF-5301PC spectrofluoro photometer (Japan) was used in fluorescence measurements. Emission and excitation spectra of the synthesized compounds were obtained in solution forms in DMF for monomers and polymers. Measurements were made in a wide concentration range between 3.125-100 mg/L to determine the optimal fluorescence concentrations. Slit width in all measurements was 5 nm.

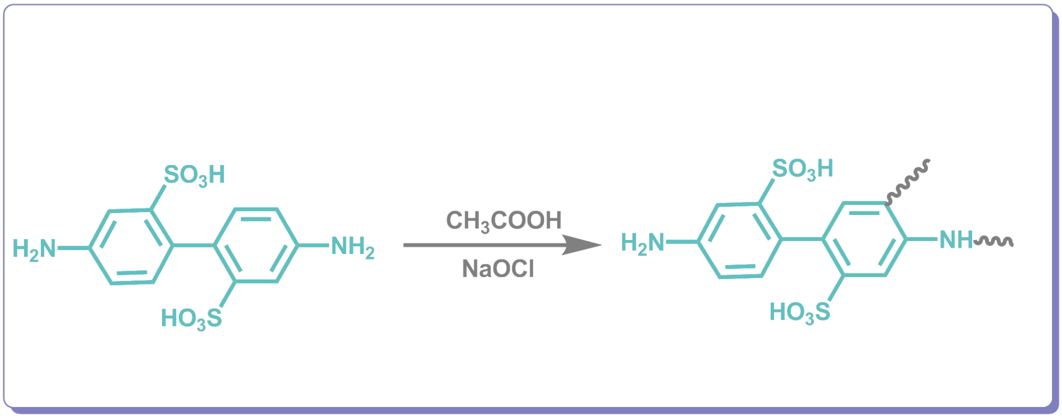
### Azo Dyestuff Synthesis

4-Nitroaniline 1.38 g (0.01 mol) was put into a two-neck reaction flask with a volume of 100 ml and 18% HCl was added. Then, mixture was refluxed for 30 minutes in the water bath of 70°C, under condenser until 4-nitroaniline dissolved. And then it was placed in ice-water medium after it was cooled down to 25-30°C. Meanwhile, 0.69 g $NaNO_2$ was dissolved in distilled water. In 0-3°C ice-water medium, $NaNO_2$ solution was added to the 4-nitroaniline solution, stirred rapidly, yielding a yellow-colored diazo compound. 1.22 g 2-hydroxybenzaldehyde was placed into a 500 ml beaker, 0.4 g and 4.24 g $Na_2CO_3$ was added and then dissolved by 20 mL distilled water in ice-water medium. Thus, 2-hydroxybenzaldehyde solution in basic medium was prepared. Prepared diazo compound solution was added at 5-6 intervals into the basic 2-hydroxybenzaldehyde solution which is placed in an ice-water medium of 0-1 °C and the solution was stirred rapidly for 30 minutes. The color of the solution changed into orange-pink. And then the beaker containing the solution was closed with watch-glass and left overnight stirring moderately at room temperature. The next day the light orange-colored compound was filtered by a water trompe and washed in vacuum with 10 % 100 mL NaCl solution. The purity of the product was controlled with thin layer chromatography (TLC). N-hexane: ethyl acetate (3:2) was used as the most appropriate solvent system. Then, the product was dried at 40°C for a day in the vacuum incubator [2,14]. The obtained dye molecule was abbreviated as AZOBM (2-hydroxy-5-((4-nitrophenyl)diazenyl)benzaldehyde) (Scheme 1).

AZOBM: $^1$H-NMR (DMSO): δ ppm, 11.86 (s, $^1$H, -CHO), 10.22 (s, 1H, -OH), 8.35 (d, 2H, -HA), 8.19 (s, $^1$H, HD), 8.08 (d, 1H, HC), 8.00 (d, 2H, HB), 7.22 (d, 1H, HE). AZOBM: $^{13}$C-NMR (DMSO) : δ ppm, 190.56 (C11-H), 165.26 ( C8-ipso), 155.00 (C4-ipso), 148.61 (C1-ipso), 145.17 (C5-ipso), 130.52 (C6-H), 125.60 (C2-H), 123.79 (C3-H), 123.33 (C10-H), 119.29 (C7-H), 117,81 (C9-H).



**Scheme 1.** Synthesis of Azo dye.



**Scheme 2.** Synthesis of poly-(4,4′-diamino-2,2′-biphenyl sulphonic acid) (polyamine).

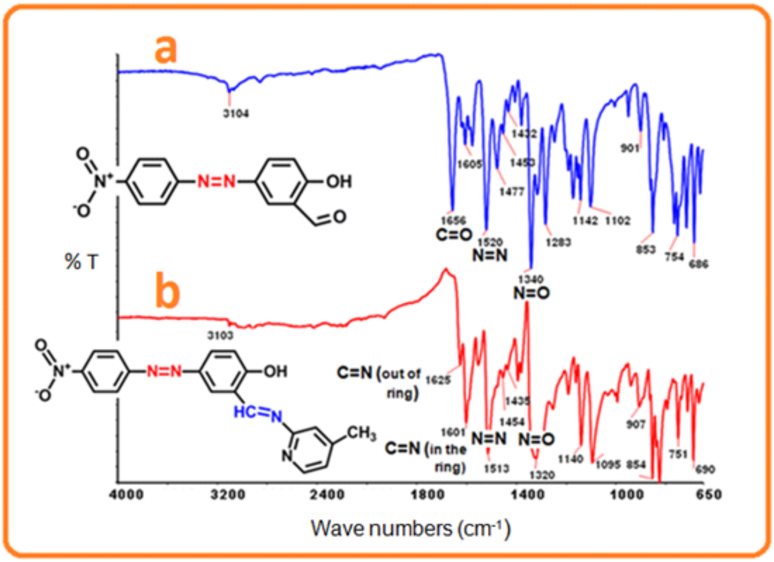


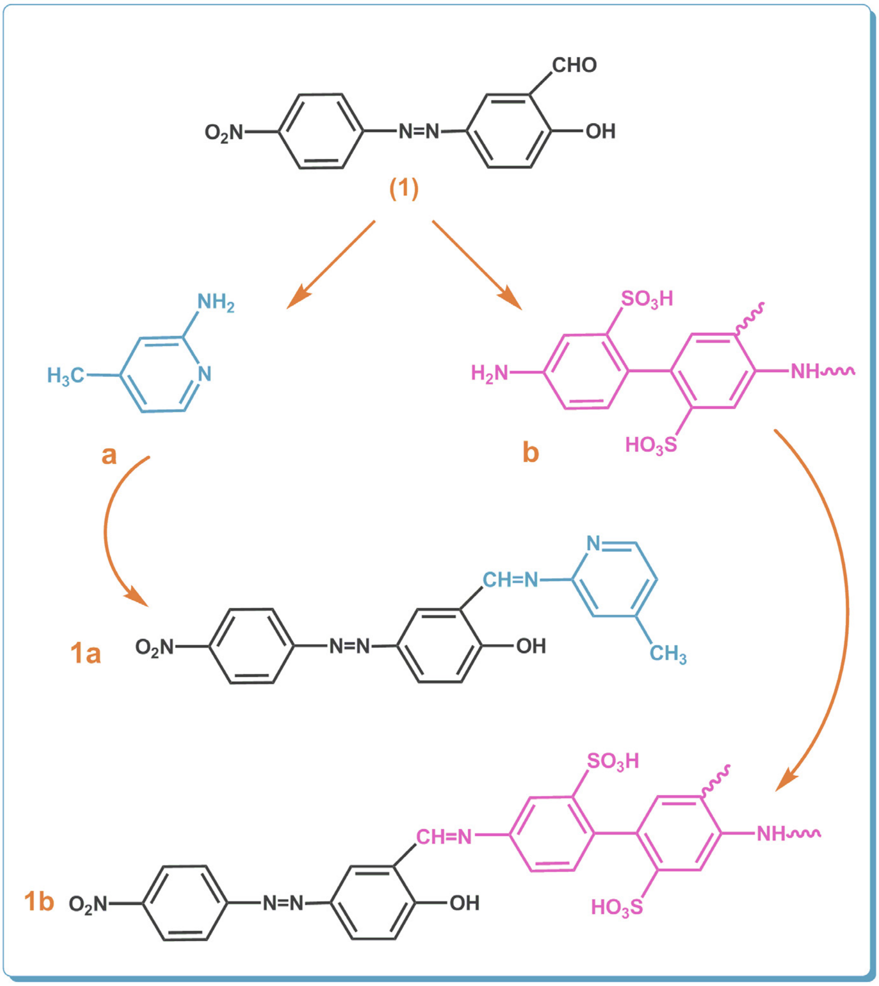
**Figure 1.** IR Spectra of AZOBM (a) and AZOBMS (b).

### Azo-Azomethine Dyestuff Synthesis

2.71 g azo dye was dissolved in 20 ml ethanol and put in reaction flask. 1.08 g 2-amino-4-methylpridine was dissolved in ethanol and added to the dye. Then it was refluxed for 16 hours at 60°C, later its solvent was evaporated in a petri dish. The compounds were dried in incubator at 35°C for one day. The obtained Azo-azomethine dyestuff was shortened as AZOBMS (2-((4-methylpyridin-2-ylimino)methyl)-4-((4-nitrophenyl)diazenyl) phenol). The same process was carried out with 2.71 g azo dye and 3.44 g 4,4′-diamino-2,2′-biphenyl sulphonic acid polymer (2,8). Azo-azomethine dye polymer was abbreviated as AZOBMSP (Poly-(4-amino-4′-(2-hydroxy-5-((4-nitrophenyl)diazenyl)benzylideneamino) biphenyl-2,2′-disulfonic acid) (Scheme 3).

Oxidative polycondensation (OP) reactions of 4,4′-diamino-2,2′-biphenyl sulphonic acid were carried out in aqueous alkaline medium (0.1 M KOH) as suggested for aromatic amine compounds, as in the literature [15].

AZOBMS: $^1H$-NMR (DMSO): δ ppm, 10.26 (s, 1H, -OH), 9.62 (s, 1H, -CH=N), 8.50 (d, 1H, HD), 8.40 ( d, 1H, HC), 8.33 (d, 1H, HJ), 8.06 (d, 2H, HA), 8.01 (d, 2H, HB), 7.36 (s, 1H, HI), 7,21 (d, 1H, HK), 7.12 (d, 1H, HE), 2,36 (s, 3H, $-CH_3$). AZOBMS: $^{13}C$-NMR (DMSO): δ ppm, 163.76 ( C8-H), 161.95 (-HC=N), 160.55 (C11-ipso), 155.79(C4-ipso), 150.8 (C1-ipso, C15 -H), 148.34 (C13-ipso), 144.93 (C5-ipso), 128.66



**Scheme 3.** The synthesis of azo-containing Schiff-base dyes: 1a (AZOBMS), 1b  (AZOBMSP)

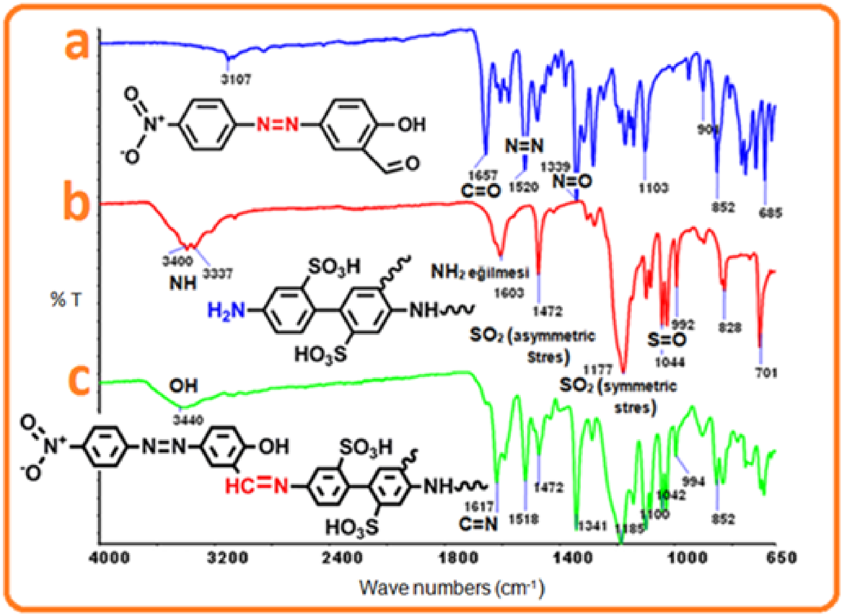


**Figure 2.** IR Spectra of AZOBM (a) P-DABSA (b) and AZOBMSP (c).

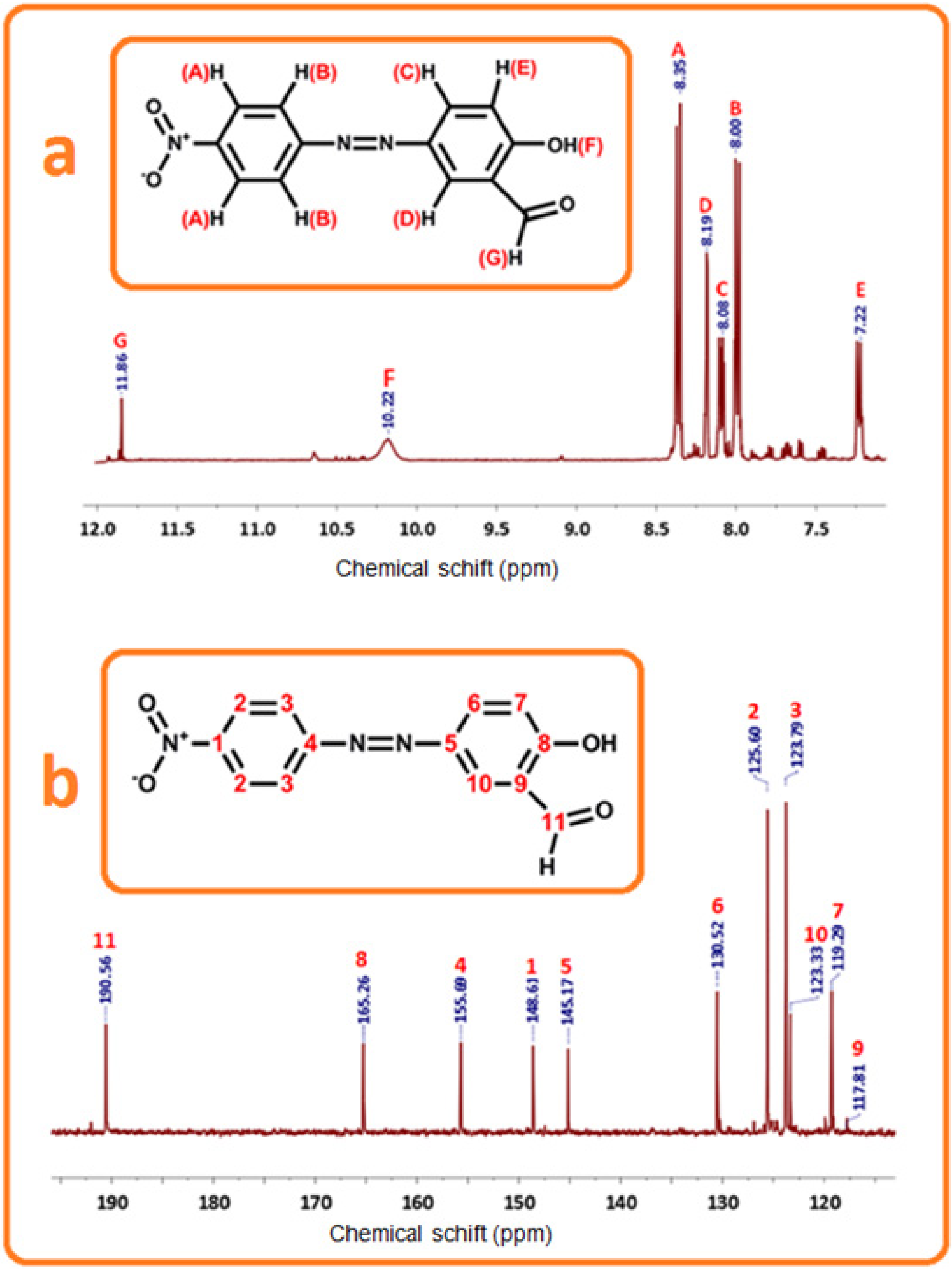


**Figure 3.** $^{1}$H-NMR spectra of AZOBM (a) $^{13}$C-NMR spectra of AZOBM (b).

(C6-H, C14-H), 126.00 (C2-2H), 123.37 ( C10-H), 119.25 (C3-2H), 115.12 (C9-ipso, C12-H ), 113.72 (C7-H), 21.11 (-CH3). AZOBMSP: $^{1}$H-NMR (DMSO d6 ): ppm, 10.55 (s, 1H, -OH), 10.21 (s, 2H, -SO3H), 9.22 (s, 1H, -CH=N), 8.41-6.38 ( aromatic-H), 4.99 (s, 1H, -NH). AZOBMSP: $^{13}$C-NMR (DMSO) : $\delta$ ppm, 162.29 ( C8-H), 161.77 (-HC=N), 155.96 (C4-ipso, C11-ipso), 148.46 (C1-ipso), 146.61 (C5-ipso), 145.55 (C14-ipso), 144.83 (C18-ipso), 133.15 (C16-ipso), 130.35 (C15-H), 127.92 ( C19-H), 125.97 (C6-H, C12-H, C21-H), 123.79 (C2-2H, C10-H, C17-ipso, C13-H), 120.98 (C3-2H), 119.78 (C20-H), 117.00 (C9-ipso), 113.46 (C7-H).

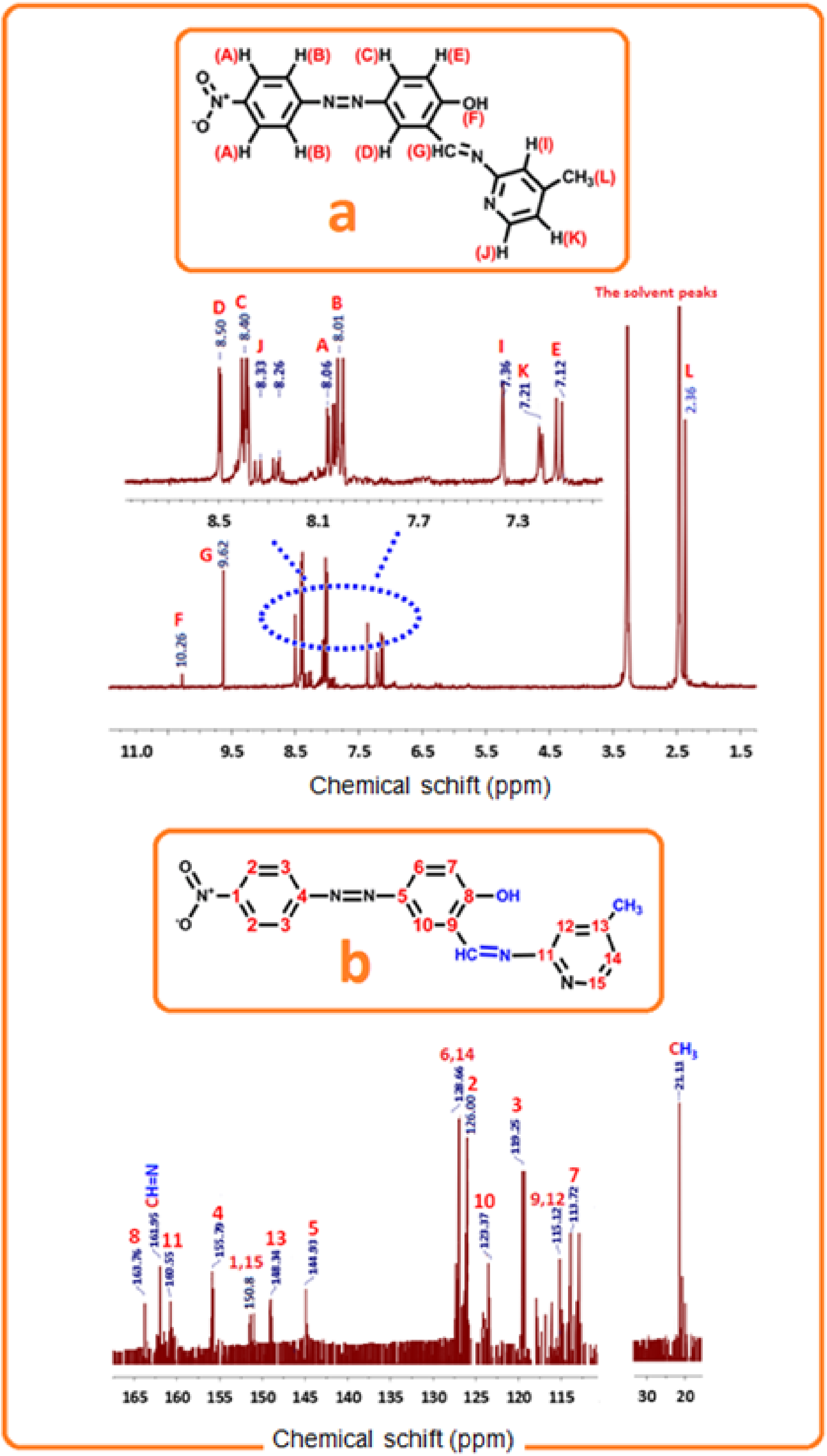


**Figure 4.** ¹H-NMR spectra of AZOBMS (a) ¹³C-NMR spectra of AZOBMS (b).

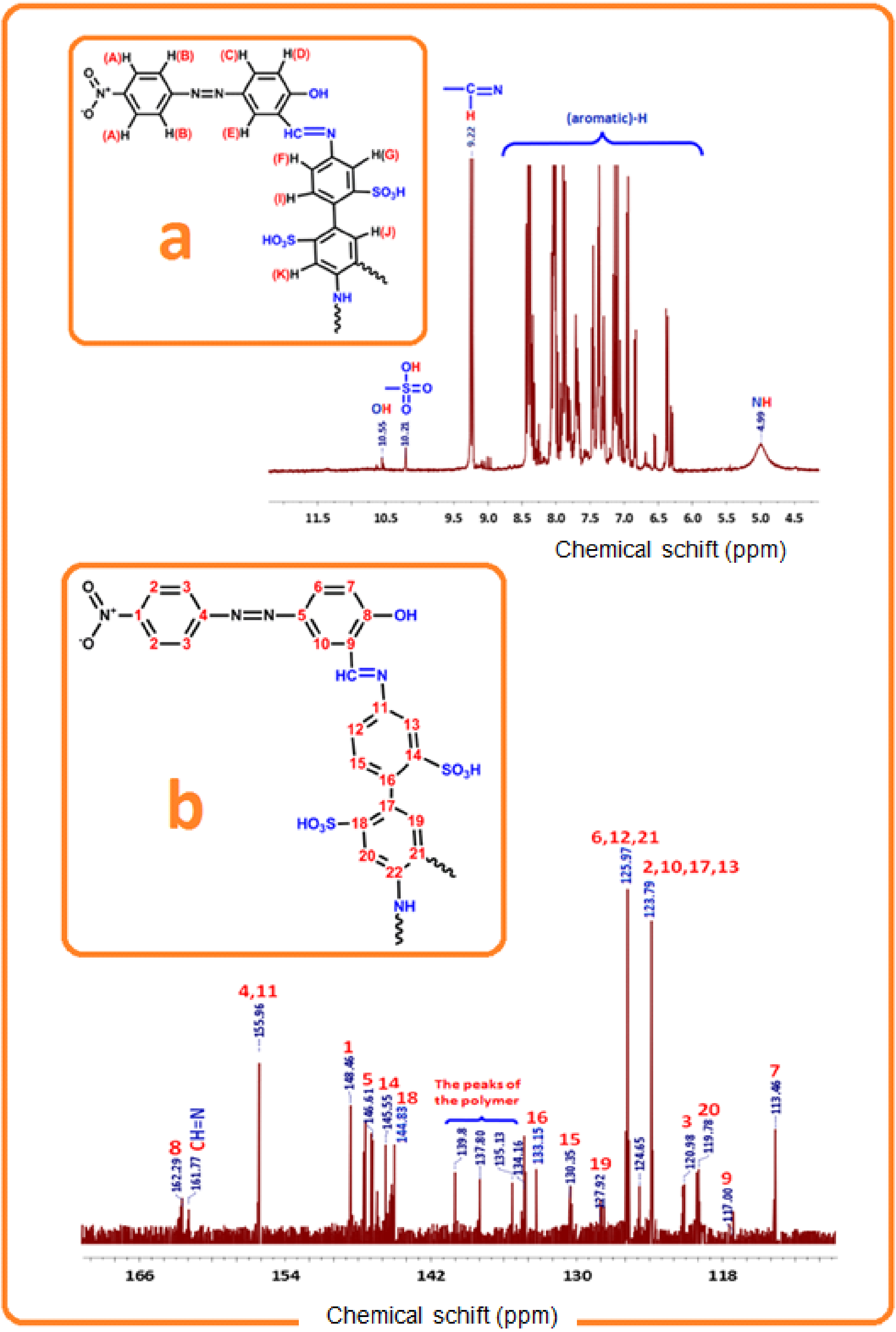


**Figure 5.** $^1$H-NMR spectra of AZOBMSP (a) $^{13}$C-NMR spectra of AZOBMSP (b).

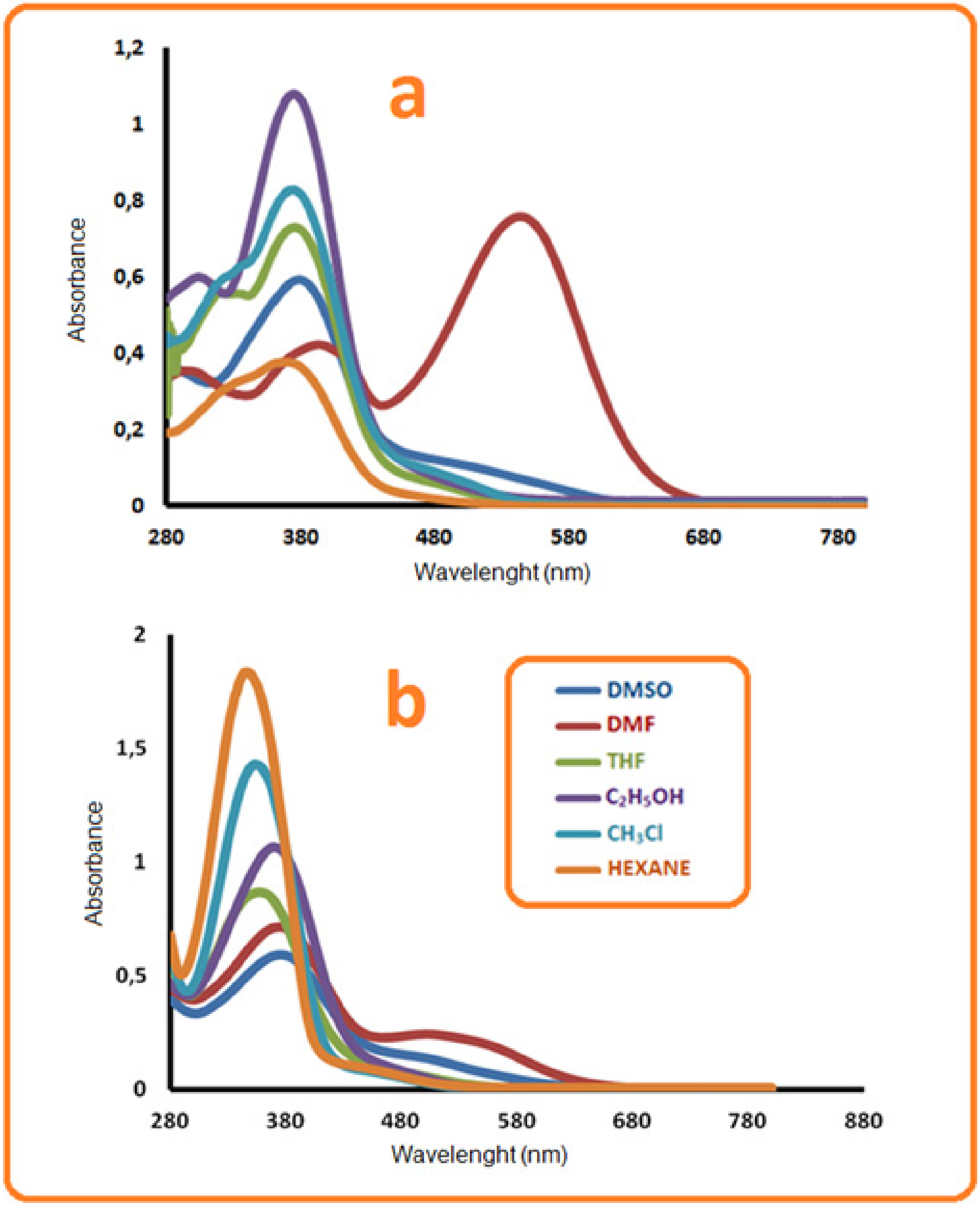


**Figure 6.** UV-Vis absorption spectra of the synthesized compounds in different solvents.

## RESULTS and DISCUSSION

Structures of synthesized monomer and polymers were explained with FT-IR, UV-Vis, $^1$H-NMR and $^{13}$C-NMR analyses. In Figure 1a, the characteristic peaks of azo dyestuff are shown, with carbonyl peak (C=O) at 1656 cm$^{-1}$, azo group (N=N) at 1520 cm$^{-1}$ and nitrogen oxide (N=O) peak at 1340 cm$^{-1}$. In Figure 1b the stretching vibrations of 2-amino-4-methyl pyridine underwent a condensation reaction with dye are shown, peaking at 1625 and 1601 cm$^{-1}$ for imine (CH=N) in the ring and out of the ring, respectively imine. Azo-dye characteristic peaks were discussed in Figure 2a. In Figure 2b, FT-IR Spectrum for 4-4′-diamino-2,2′-biphenyl disulphonic acid polymer was examined: peaks of NH$_2$ group at 3400-3337 cm$^{-1}$, bending of NH$_2$ at 1603 cm$^{-1}$, asymmetric stretching of SO$_2$ at 1472 cm$^{-1}$, symmetric stretching of SO$_2$ at 1177 cm$^{-1}$ and S=O stretching at 1044 cm$^{-1}$ were observed. In Figure 2c, the stretching vibe vibrations of imine (CH=N) and OH were seen at 1625 cm$^{-1}$ and 3440 cm$^{-1}$, was a result of the condensation reaction between the dye and 4,4′-diamino-2,2′-biphenyl disulphonic acid polymer [16].

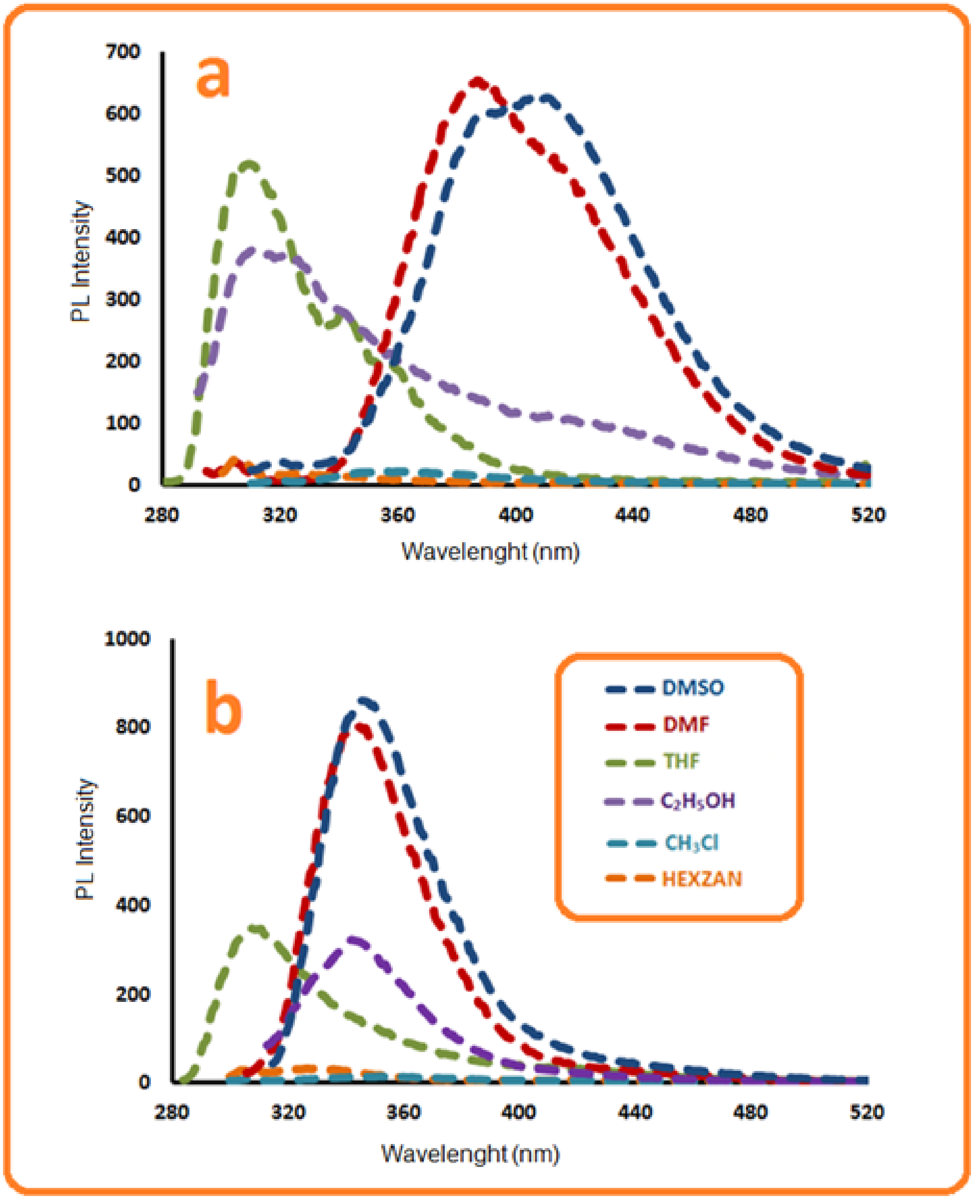


**Figure 7.** AZOBMSP (a) AZOBMS (b) Emission spectra of the synthesized compounds in different solvents.

Chemical shifts of $^1$H-NMR and $^{13}$C-NMR spectrum of the synthesized compounds are given in Figures 3-5. $^1$H-NMR spectrum of azomethine and aromatic proton signals of the AZOBMS were observed at 9.62 and 8.52-7.12 ppm, respectively. In the $^{13}$C-NMR spectrum of hydroxyl, azomethine, methyl and aromatic carbon signals are observed at 163.76, 161.95, 21.11 and 160.55-113.72 ppm range, respectively. $^1$H-NMR spectrum of hydroxyl peaks of sulphonic acid and hydroxyl groups of the AZOBMSP were discovered at 10.55 and 10.71 ppm, respectively. Furthermore, the proton signals of azomethine and -NH group were observed at 9.22 and 4.99 ppm, respectively. $^{13}$C-NMR spectrum of hydroxyl, azomethine and aromatic carbon signals of the AZOBMSP were ascertained to be 162.22, 161.77 and 148.46-113.46 ppm, respectively. New peaks of the polymer were observed at 137.80, 135.13, 139.8 and 134.16 ppm.

Figure 6a (AZOBM), 6b (AZOBMS) and 6c (AZOBMSP) display the distinctive solvent colors for the same concentration. No color changes were observed under the UV lamp, although UV-vis spectrum observations showed that azo and azomethine chromophore and additionally molecules containing the entire dye molecules gave off π →π* shift a large amount of cis isomer photo stationary state in 330-400 nm range, n→π* shift a trans isomer-rich photo stationary state in 460-600 nm range only for DMF solvent [17]. Except for the DMF absorption bands, all absorption bands were highly similar and gave off one maximum. In addition, binding of $-CH_3$ to the benzene ring caused a bathochromic shift in the long wavelength of DMF. Polar and basic characteristics of DMF are more related to an ionization equilibrium than an azo-hydrosol tautomeric equilibrium. o-Hydroxyl electron delocalization of azo-azomethine dye depends on: 1) Selective disassociation. 2) Solvent's ability to form strong H-bans with intermolecular tautomeric form. 3) Intramolecular H-bands formation of C=N, N=N and -OH groups. In the absorption spectra of azo groups found in aromatic compounds, it is stated that the absorption bands lay in shorter wavelengths (e.g. azomethine band at 222-342 nm), where the azo group is an powerful chromophore and when bound to aromatic systems, absorption bands shift to the visible wavelength (400-700 nm) [18]. In general, there is a shift towards the red in the absorption spectra with increasing solvent polarity [17]. It is well known that cis–trans isomerization behavior of azobenzene compounds depends on the solvent [19].

In the emission spectrum amongst all compounds, similar spectral shifts were seen except for DMF and DMSO as in UV-vis spectrum. Both of the dyes were prepared separately in different solvents. Effects of the polarity of different solvents were examined with fluorescence spectrum. According to the polarity index, DMSO is highly polar solvent while the hexane is nonpolar. As the polarity increased, the red shift was observed. This increase in polarity was particularly more efficient in DMF and DMSO. Additionally, structure of the dyes is important in this case. İndeed, the change in solvent polarity changes caused by shifts in emission bands are called solvatochromic shifts and are experimental evidence of changes in salvation energy. Solvent increases, the relaxed state energy decreases and the red shift of the emission spectrum increases. A red transition (bathochromic) is observed, as the polarity of solvent increases to result in a positive solvatochromism and proving that a relaxed intramolecular charge transfer state is completed.

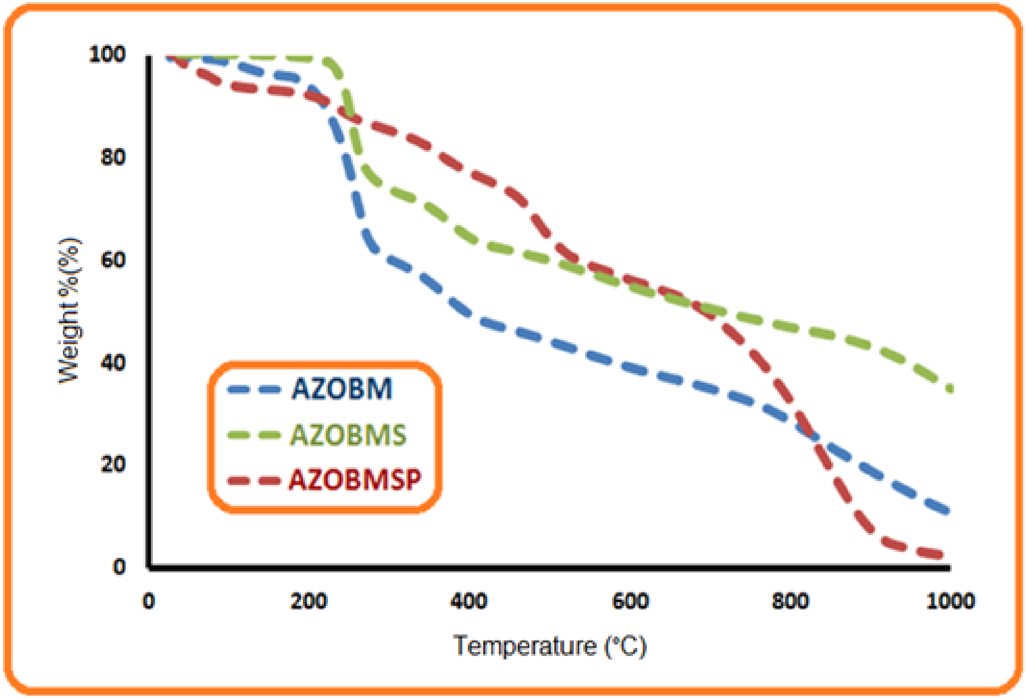


**Figure 8.** TG curves of the synthesized compounds.

TG curves of the synthesized AZOBM, AZOBMS and AZOBMSP are given in Figure 8. Initial decomposition temperature (Ton) of AZOBM was marked as 224°C, additionally $T_{20}$ and $T_{50}$ temperatures was were measured obtained as 250°C and 450°C, respectively. Residue level at 1000°C was calculated as 15%. Thermally, AZOBM decomposes in three steps: (164-304°C, $T_{max1}$= 36.12%, 304-435°C, $T_{max2}$= 12.69%, 435-1000°C, 36.58%). Initial decomposition temperature (Ton) for AZOBMS was measured as 237°C, $T_{20}$ and $T_{50}$ measured as 264°C and 717 C, respectively. Residue level at 1000°C was calculated as 35%. AZOBMS thermally decomposes in two steps. (160-321°C, $T_{max1}$= 27.38%, 321-1000°C, $T_{max2}$= 37.32%). Initial decomposition temperature ($T_{on}$), $T_{20}$ and $T_{50}$ for AZOBMSP were obtained as 206 , 453 and 747°C, respectively. Residue level

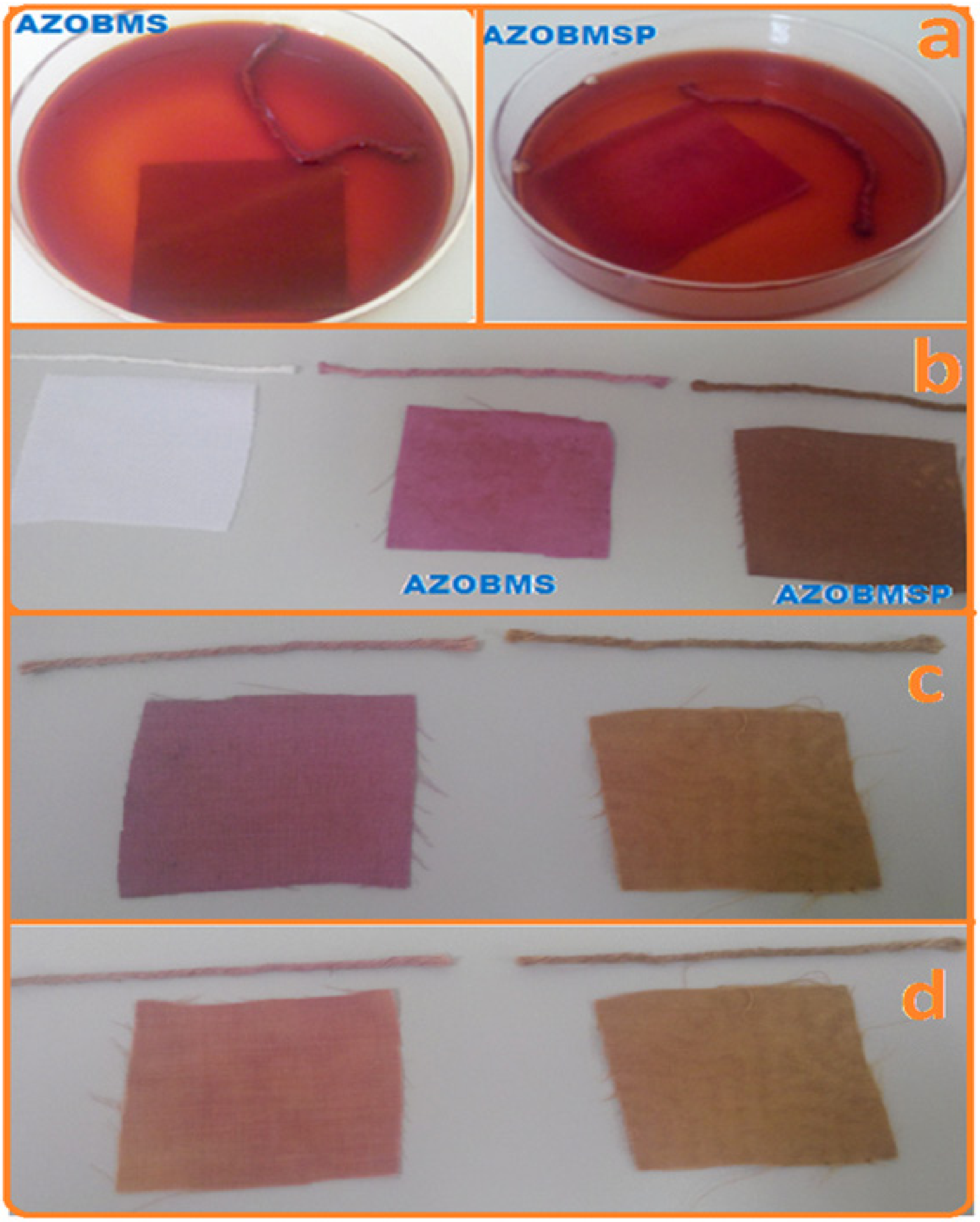


**Figure 9.** in aqueous alkaline media (a) after dyeing (b) after washing (c) After standing in the light of day (d).

at 1000°C was calculated as 10 %. AZOBMSP thermally decomposes in four steps. (151-286°C $T_{max1}$= %7.19, 286-423°C $T_{max2}$= %10.44, 423-588°C $T_{max3}$= %18.71, 588-1000°C $T_{max4}$ = % 54.12). Initial decomposing temperature for AZOBMS is higher compared to that of AZOBMSP. According to the TGA results, the initial degradation temperatures ($T_{on}$) of the polymers are lower than those of their monomers indicating that the synthesized polyphenols have lower thermal stabilities than their monomer species. This is because of the formation of C-O etheric bond during the oxidative polycondensation reaction (C-O-C coupling). This weak bond is easily broken at moderate temperatures and makes the polymer thermally unstable [20]. Thermal data suggest that azophenol polymers synthesized by oxidative polycondensation (OP) are highly thermally stable and the OP method can be used for the preparation of thermally stable azophenol polymers [17].

To dye a material with a dimension of 16 cm x 10 cm, 1 g of carrier, 1 g of dispersant and 0.5 g of urea were added in 250 mL of water then, 0.13 g of azo dye was mixed at 40°C. The reaction was maintained for 15 min under reflux at 85°C. After the material boiled for 1 h was removed from the bath and rinsed with hot water, it was placed in 250 mL of water containing a little amount of soap and boiled for 30 min. Then, the mixture was rinsed several times with cold water and dried at room temperature to perform the dyeing process. The dyeing materials could be dissolved in acidic or basic solutions to eliminate the solubility problems [21]. Based on this procedure, fabrics and fibers were held for one day in petri dishes after soaking in aqueous basic media of AZOBMS and AZOBMSP prepared with KOH as shown in Figure 9a. In Figure 9b, after dyeing process, materials were dried and photographed. Dried fabric and fiber were washed in water filled petri dish for washing fastness test. Re-dried materials are shown in Figure 9c. For light fastness test, the materials were held in direct sunlight. The results are shown in Figure 9d. Afterwards, dyed fabrics and fibers were compared to their first state shown in Figure 9b, both for washing and light fastness.

## CONCLUSIONS

This study reported the preparation and spectroscopic properties of novel dyes containing electron-withdrawing ($-CH_3$) and electron-releasing ($-SO_3H$) groups. It was found that these dyes exhibited both significant absorption and high fluorescence intensity. Further, results of the photo stability study suggested that these compounds had high photo stability in terms of their susceptibility to photo bleaching. Thus, these dyes can be used in gas chromatography or in high temperature reactions. Fluorescence polarity study data of the dyes introduced that electron-withdrawing ($-CH_3$) dye was sensitive to the polarity of the microenvironment induced by different solvents. The solvatochromic studies of the prepared dyes in DMSO, DMF, $CH_3CN$ and THF was indicated that the low energy of $\pi\rightarrow\pi$ band or the dyes shows bathochromic shift as the polarity of solvent was raised. Moreover, solvatochromic shifts were observed in fluorescence and UV-vis spectra of these dyes upon changing solvent polarities, indicating that these compounds can be used as solvatochromic surveying. The polymers obtained were also thermally stable with high decomposition temperature. The azophenol polymers showed reversible trans–cis isomerization on irradiation with UV and visible light in solution. These properties of the polymers could be promising for their technological use. Furthermore, in the light of this study, the OP method can be regarded as a new environmentally friendly and economic way for the preparation of macromolecular azo dyes. Finally, the preparation and spectroscopic evaluation of these dyes may show a considerable promise in a range of different applications, including analytical, biological and environmental.

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