

# Synthesis of New Unsaturated Azo-Polyesters Containing Diarylideneacetone Moiety in the Main Chain

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## ABSTRACT

A series of four unsaturated azo-polyesters were prepared by interfacial polycondensation of 1,3-bis(4-hydroxy-3-methoxybenzylidene)acetone **I** or 1,3-bis(4-hydroxybenzylidene)acetone **II** with azobenzene-3,3'-dicarboxylic acid chloride **III** and azobenzene-4,4'-dicarboxylic acid chloride **IV**. Initially, the two diols were prepared by reacting two moles of vanillin or 4-hydroxy benzaldehyde with one mole of acetone in the presence of concentrated HCl as a catalyst and EtOH at reflux. In addition, two model compounds **V**, **VI** were also prepared using one mole of either diols and two moles of benzoyl chloride in the presence of NaOH as a catalyst. Structure of diols **I**, **II**, model compounds **V**, **VI** and all prepared azo-polyesters **VII** – **X** was confirmed by IR, elemental analysis. Study of physical properties for all azo-polyesters was also carried out; including solubility and viscosity.

**Keywords:** *Interfacial polycondensation, Azobenzene dicarboxylic acid chloride, Azopolyes*

## 1. INTRODUCTION

Fiber-reinforced plastics form a versatile class of materials that are increasingly replacing conventional structural materials such as metals, wood, and concrete in engineering applications. These materials, commonly termed FRP, offer a high strength-to-weight ratio, excellent corrosion resistance, ease of fabrication, and versatility of product design in comparison with metals. Although both thermosets and thermoplastics are used as matrix materials for fiber reinforcement, the thermosets constitute the major segment. Amongst the thermosetting resins, unsaturated polyesters and epoxies are the most commonly used matrix materials for FRP. The unsaturated polyester (UP) resins are thus commercially important for the reinforced plastics markets. In addition, their low cost, the UP resins can be tailor-made to meet specific requirements by proper choice of their chemical building blocks. The UP resins are formed by the reaction of diols and dicarboxylic acids with the unsaturation on either. The most commonly used diols: ethylene glycol (EG), propylene glycol (PG), and neopentyl glycol (NPG) [1]. Studies on polymers with different optical properties have attracted more attention due to their applications in the optical properties [2]. Azo dye the most important class of commercial dyes are intensively investigated due to its environmental stability, ease of preparation and its optical and electrical properties.

A survey of the literature reveals that, different unsaturated polymers could be prepared by the reaction of azobenzene dicarboxylic acid chlorides with aromatic diamines [3], aliphatic diamines and aliphatic diols [4], aromatic diols [5][6][7].

This work presents the synthesis of unsaturated azo-polyesters by the polycondensation of azobenzene diacid chlorides with diarylideneacetone derivatives as diols.

## 2. EXPERIMENTAL

### 2.1 Instrumentation

IR spectra were recorded on ATR-Unit Fourier Transform infrared spectrophotometer-FTIR. The elemental analysis was carried out on an elemental analyzer, Model 2400, Perkin Elmer instrument. <sup>1</sup>H NMR spectra were run on a Bruker 11.1HO 100 MHz NMR spectrometer in DMSO using TMS as the internal reference. Viscosity measurements were made in concentrated H<sub>2</sub>SO<sub>4</sub> at 25 °C using an Ubbelohde suspended level viscometer. The solubility of the polymers was determined using 0.02 g of polymer in 3 ml of solvent at room temperature.

### 2.2 Reagents and Materials

All chemicals were of high purity and further purified by standard methods [8].

### 2.3 Synthesis of monomers

#### 2.3.1 General Procedure A

A mixture of (0.02 mol) vanillin or 4-hydroxy benzaldehyde and (0.01 mol) acetone was dissolved in (30 ml) ethanol. A catalytic amount of conc. HCl was added and the resulting mixture was refluxed for 4 h. At the end of the reaction time, a light brown solid product precipitated after the addition of distilled water. The solid product was filtered off, washed with several portions of water, dried and recrystallized from a mixture of (3:1) methanol-water. By using the above general procedure the following diols **I** and **II** were obtained.

#### 2.3.2 Synthesis of 1,3-bis(4-hydroxy-3-methoxy benzylidene)acetone **I**

Obtained by following the general procedure **A** and by using vanillin and acetone as brown crystals; yield **70 %**, mp 102 – 104 °C (lit. [9], 99 – 100 °C). Found: C, 69.63 %; H, 6.05 %. Calc. for C<sub>19</sub>H<sub>18</sub>O<sub>5</sub>: C, 69.93 %; H, 5.56 %. IR: (ATR, cm<sup>-1</sup>) 3395, 1640, 1616, 1165. <sup>1</sup>H NMR (100

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MHz; DMSO-d<sub>6</sub>)  $\delta$ H 3.8 (6H, s, OCH<sub>3</sub>), 6.7 - 7.1 (6H, m, Ar-H; CH=CH), 7.6 - 7.8 (4H, m, Ar-H), 9.8 (2H, s, OH). <sup>1</sup>H NMR was in accordance with the literature [9].

### 2.3.3 Synthesis of 1,3-bis(4-hydroxybenzylidene)acetone II

Obtained by following the general procedure A and by using 4-hydroxybenzaldehyde and acetone as brown powder; yield **75 %**, mp 243 - 245 °C (lit. [9], 244 - 246 °C). Found: C, 74.24 %; H, 5.41%. Calc. for C<sub>17</sub>H<sub>14</sub>O<sub>3</sub>: C, 74.67 %; H, 5.29. IR: (ATR, cm<sup>-1</sup>) 3504, 1646, 1614, 1165. <sup>1</sup>H NMR (100 MHz; DMSO-d<sub>6</sub>)  $\delta$ H 6.7 - 7.1 (8H, m, Ar-H), 7.5 - 7.8 (4H, m, CH=CH), 10.1 (2H, s, OH). <sup>1</sup>H NMR was in accordance with the literature [9].

## 2.4 Synthesis of the di-acid chlorides

### 2.4.1 General procedure B

4-Nitrobenzoic acid or 3-nitrobenzoic acid (0.078 mol) was dissolved in a solution of NaOH (1.25 mol, 50 g in 225 ml of water) and warmed to 50 °C, then a solution of glucose (0.555 mol, 100 g in 150 ml of water) was added slowly and continued stirring until a pale yellow precipitate which soon dissolved to give a dark brown solution. The solution was cooled to room temperature before air was drawn through the brown solution for 5 h (until no further precipitate was formed) then was acidified with acetic acid to pH 6 to afford a buff precipitate, filtration, washing three times with distilled water and drying afforded the azobenzenedicarboxylic acid. The formed diacid was refluxed for 24 h with an excess of thionyl chloride (30 ml) in the presence of few drops of pyridine as a catalyst. At the end of the reaction time, the reaction mixture was left to cool to room temperature then was diluted with petroleum ether (60 - 80 °C). The crude precipitate was recrystallized from petroleum ether (60 - 80 °C) to afford the azobenzenedicarboxylic acid chloride [10].

### 2.4.2 Synthesis of azobenzene-3,3'-dicarboxylic acid chloride III

Obtained by following the general procedure B starting with 3-nitrobenzoic acid as an orange needles; yield **90 %**, mp 98 - 100 °C (lit [10], 100 - 101 °C). IR: (ATR, cm<sup>-1</sup>) 3073, 1747, 1696, 1584, 1472. IR was in accordance with the literature [10].

### 2.4.3 Synthesis of azobenzene-4,4'-dicarboxylic acid chloride IV

Obtained by following the general procedure B starting with 4-nitrobenzoic acid as a dark-red needles; yield **88 %**, mp 164 - 165 °C (lit [10], 164 - 165 °C). IR: (ATR, cm<sup>-1</sup>) 3099, 1770, 1733, 1696, 1575, 1473. IR was in accordance with the literature [10].

## 2.5 Synthesis of Model Compounds

### 2.5.1 General procedure

1,3-Bis(4-hydroxy-3-methoxybenzylidene)acetone I or 1,3-bis(4-hydroxybenzylidene)acetone II (0.005 mol) was dissolved in NaOH solution (0.01 mol, 0.4 g in 20 ml H<sub>2</sub>O) and stirred at room temperature before the addition of ben-

zoyl chloride (0.01 mol), then the reaction mixture was continued to stir for more one hour. At the end of the reaction time, a yellow solid product was precipitated. The solid product was filtered off, washed with water then ether, dried in *vacuo* at room temperature and recrystallized from ethanol.

### 2.5.2 Synthesis of 4,4'-Divanillylideneacetone dibenzoate V

Obtained by following the general procedure C and by using 1,3-Bis(4-hydroxy-3-methoxybenzylidene)acetone I and benzoyl chloride as yellow powder; yield **78 %**, mp 117 - 119 °C. Found: C, 73.15 %; H, 4.22 %. Calc. for C<sub>33</sub>H<sub>26</sub>O<sub>7</sub>: C, 73.41 %; H, 4.89 %. IR: (ATR, cm<sup>-1</sup>) 1710, 1665, 1618, 1110. <sup>1</sup>H NMR (100 MHz; DMSO-d<sub>6</sub>)  $\delta$ H 3.9 (6H, s, OCH<sub>3</sub>), 7.1 - 7.3 (16H, m, Ar-H; CH=CH), 8.1 - 8.3 (4H, m, Ar-H).

### 2.5.3 Synthesis of 4,4'-Dibenzylideneacetone dibenzoate VI

Obtained by following the general procedure C and using 1,3-Bis(4-hydroxybenzylidene)acetone I and benzoyl chloride as yellow crystals; yield **83 %**, mp 170 - 172 °C. Found: C, 77.87 %; H, 5.01 %. Calc. for C<sub>31</sub>H<sub>22</sub>O<sub>5</sub>: C, 78.47 %; H, 4.66 %. IR: (ATR, cm<sup>-1</sup>) 1710, 1645, 1610. <sup>1</sup>H NMR (100 MHz; DMSO-d<sub>6</sub>)  $\delta$ H 7.2 - 7.9 (18H, m, Ar-H; CH=CH), 8.0 - 8.3 (4H, m, Ar-H).

## 2.6 Synthesis of Azo-Polyesters

### 2.6.1 General procedure D

A three-necked flask, equipped with a mechanical stirrer (500 rpm), dry nitrogen inlet and outlet and dropper was charged with a mixture of (0.001 mol) 1,3-Bis(4-hydroxy-3-methoxybenzylidene)acetone I or 1,3-bis(4-hydroxybenzylidene)acetone II, (0.002 mol) of NaOH solution in (50 ml) distilled water and (25 ml) CH<sub>2</sub>Cl<sub>2</sub>, (0.001 mol) of azobenzene-3,3'-dicarboxylic acid chloride III or azobenzene-4,4'-dicarboxylic acid chloride IV in (25 ml) CH<sub>2</sub>Cl<sub>2</sub> was added over a 2 min period at room temperature and vigorously stirred. After completing the addition of diacid chloride, the reaction mixture was left to stir for 1 h whereby an orange solid separated out. Then, the solid was filtered off, washed with water, alcohol, acetone and dried under reduced pressure (1 mm Hg) at 100 °C for 2 days. By using the above general procedure the following azo-polyesters VII - X were obtained.

### 2.6.2 Synthesis of azo-polyester VII

Obtained by following the general procedure D and using 1,3-Bis(4-hydroxy-3-methoxybenzylidene)acetone I and azobenzene-3,3'-dicarboxylic acid chloride III as an orange powder in **94 %** yield. Found: C, 70.19 %; H, 4.48 %; N, 5.22. Calc. for C<sub>33</sub>H<sub>24</sub>N<sub>2</sub>O<sub>7</sub>: C, 70.71 %; H, 4.32 %; N, 5.00 %.

### 2.6.3 Synthesis of azo-polyester VIII

Obtained by following the general procedure D and using 1,3-Bis(4-hydroxy-3-methoxybenzylidene)acetone I and azobenzene-4,4'-dicarboxylic acid chloride IV as an orange in **93 %** yield. Found: C, 70.10 %; H, 4.46 %; N,

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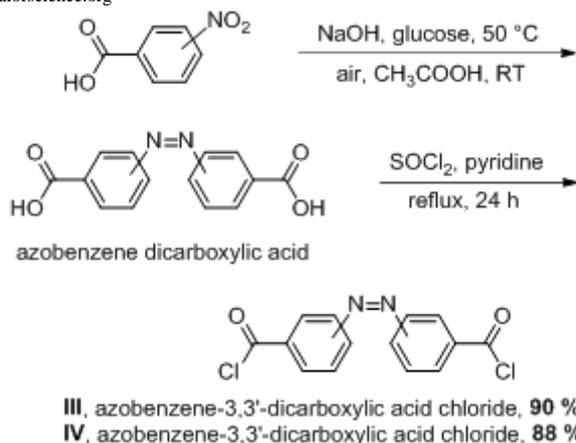
5.10. Calc. for  $C_{33}H_{24}N_2O_7$ : C, 70.71 %; H, 4.32 %; N, 5.00 %.

### 2.6.4 Synthesis of azo-polyester IX

Obtained by following the general procedure **D** and using 1,3-Bis(4-hydroxybenzylidene)acetone **II** and azobenzene-3,3'-dicarboxylic acid chloride **III** as an orange powder in **91 %** yield. Found: C, 73.83 %; H, 4.30 %, N, 5.39. Calc. for  $C_{31}H_{20}N_2O_5$ : C, 74.39 %; H, 4.03 %; N, 5.60 %.

### 2.6.5 Synthesis of azo-polyester X

Obtained by following the general procedure **D** and using 1,3-Bis(4-hydroxybenzylidene)acetone **II** and azobenzene-4,4'-dicarboxylic acid chloride **IV** as an orange powder in **90 %** yield. Found: C, 73.69 %; H, 4.28 %, N, 5.43. Calc. for  $C_{31}H_{20}N_2O_5$ : C, 74.39 %; H, 4.03 %; N, 5.60 %.

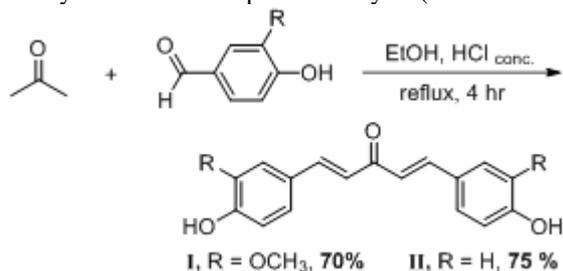


Scheme 2. Synthesis of the diacid chlorides

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis of monomers

1,3-Bis(4-hydroxy-3-methoxybenzylidene)acetone **I** and 1,3-Bis(4-hydroxybenzylidene)acetone **II** has been synthesised by the condensation of two moles of vanillin or 4-hydroxybenzaldehyde with one mole of acetone as depicted in Scheme 1. The structure of these monomers was confirmed by elemental and spectral analysis (see section 2).



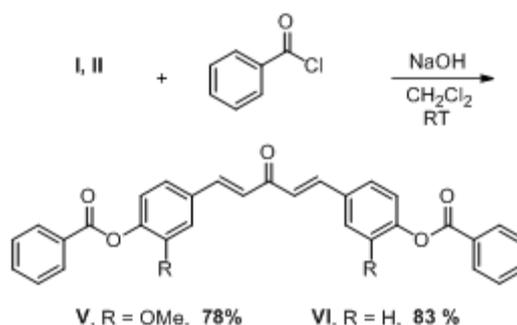
Scheme 1. Synthesis of the monomers

### 3.2 Synthesis of azobenzene dicarboxylic acid chlorides

The synthesis of azobenzene-3,3'-dicarboxylic acid chloride **III** and azobenzene-4,4'-dicarboxylic acid chloride **IV** were achieved in two steps. Firstly, azobenzene dicarboxylic acids have been synthesised starting with 3-nitrobenzoic acid or 4-nitrobenzoic acid. The next step was the synthesis of the diacid chlorides by reacting the corresponding dicarboxylic acid with an excess of thionyl chloride as depicted in Scheme 2.

### 3.3 Synthesis of model compounds

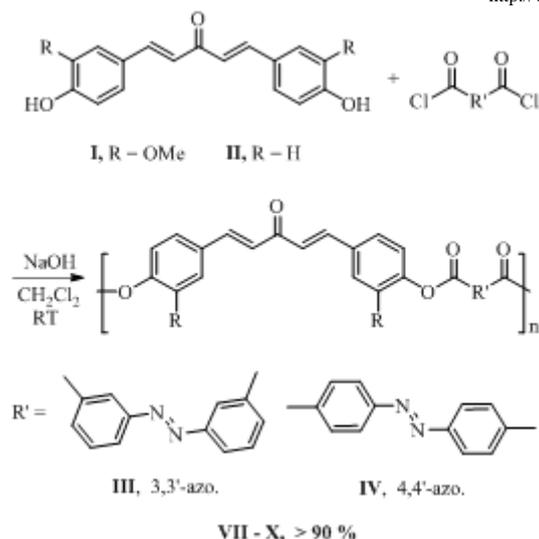
Before attempting the polymerization, the model compounds were synthesized by the interaction of two moles of benzoyl chloride and one mole of monomer **I** or **II**. This reaction was shown in Scheme 3.



Scheme 3. Synthesis of the model compounds

### 3.4 Synthesis of azo-polyesters VII – X

An unreported class of unsaturated azo-poly-esters were synthesised by the polycondensation of azobenzene-3,3'-dicarboxylic acid chloride or azobenzene-4,4'-dicarboxylic acid chloride with 1,3-Bis(4-hydroxy-3-methoxybenzylidene)acetone **I** or 1,3-Bis(4-hydroxybenzylidene)acetone **II** using an interfacial polycondensation technique at room temperature. The synthesis of these azo-polyesters is represented in Scheme 4.

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polymers	VII	VIII	IX	X
R	OMe	OMe	H	H
R'	3,3'-azo.	4,4'-azo.	3,3'-azo.	4,4'-azo.

#### Scheme 4. Synthesis of azo-polyesters

The resulting azo-polyesters were confirmed their structures by IR and elemental analysis (see section 2). The elemental analysis of all polymers coincided with the characteristic repeating units of each. It should be noted that the elemental analysis of these polymers deviated up to 0.7 % from the theoretical values. However, it is not uncommon for polymers to trap solvent molecules within the polymer matrix [11].

IR spectra for all polyesters showed the disappearance of the characteristic absorption band of the OH group and the appearance of new absorption bands at  $1730 - 175 \text{ cm}^{-1}$  characteristics of the carbonyl groups of esters, at  $1652 - 1654 \text{ cm}^{-1}$  for the carbonyl groups of acetone moieties and at  $1618 - 1624 \text{ cm}^{-1}$  for C=C groups and at  $1163 - 1202 \text{ cm}^{-1}$  for C-O-C groups. It should be pointed out that the -N=N- absorption band of the aromatic azo compound is difficult to identify in the IR spectra because of the interference of the C=C ring stretching vibration [12][13]. In addition, other characteristic absorption bands, due to specific groups present in the various polymers, were also evident in the IR spectra.

#### 3.5 Solubility

Room temperature solubility characterisation of azo-polyesters VII - X were tested using various solvents including: acetone, THF, DMF, DMSO,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , 1,4-dioxane, formic acid and conc.  $\text{H}_2\text{SO}_4$ . All azo-polyesters were insoluble in most solvents except polymer VIII which were partially soluble in DMSO, DMF, formic acid whereas polymer VII were just partially soluble in DMF. In a strong protic solvent such as  $\text{H}_2\text{SO}_4$ , all the synthesised azo-polyesters were freely soluble and gave reddish color.

**Table 1. Solubility characteristics of azo-polyesters**

Solvent	VII	VIII	IX	X
Acetone	IS	IS	IS	IS
$\text{CHCl}_3$	IS	IS	IS	IS
1,4-dioxane	IS	IS	IS	IS
$\text{CCl}_4$	IS	IS	IS	IS
$\text{CH}_2\text{Cl}_2$	IS	IS	IS	IS
THF	IS	IS	IS	IS
DMSO	IS	PS	IS	IS
DMF	PS	PS	IS	IS
HCOOH	IS	PS	IS	IS
conc. $\text{H}_2\text{SO}_4$	S	S	S	S

S = Soluble & PS = Partially Soluble & IS = Insoluble

#### 3.6 Determination of viscosity

The reduced viscosity of azo-polyesters VII - X was determined by Ubbelohde suspended level viscometer using concentrated  $\text{H}_2\text{SO}_4$  at  $25 \text{ }^\circ\text{C} \pm 0.5 \text{ }^\circ\text{C}$ , and this gave the values, 0.80, 0.77, 0.82 and 0.76 dl/g respectively.

#### 4. FUTURE WORK

Studies of other physical properties for all prepared azo-polyesters including: thermal analysis, crystallinity, electrical conductivity, are in progress in our lab and will be published soon.

#### 5. CONCLUSIONS

A new unsaturated azo-polyester VII - X containing diarylideneacetone moiety was prepared using interfacial polycondensation technique. The solubility test showed poor solubility behavior in most solvents except concentrated  $\text{H}_2\text{SO}_4$  which they were freely soluble and gave reddish color. Reduced viscosity of all azo-polyesters gave the values in the range of 0.76 - 0.82 dl/g.

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