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Preparation of New Azo-polyesters containing Chalcone Moiety in the main chain

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Abstract

A series of four azopolyesters were synthesized by the interfacial Polycondensation technique of a chalcone diphenols; (*E*)-1،3-bis(4-hydroxyphenyl)prop-2-en-1-one **I** or(*E*)-3-(4-hydroxy-3-methoxyphenyl)-1(4hydroxyphenyl)prop-2-en-1-one **II** with diacid chlorides namely 3,3'-Azo dibenzoyl chloride **III** and 4,4'-Azo dibenzoyl chloride **IV**. Initially, the two chalcone moieties **I, II** were prepared by reacting two equivalents of 4-hydroxy benzylidene or 4-hydroxy-3-methoxy benzaldehyde with one equivalent of 4-Hydroxy acetophenone in the presence of a catalytic amount of concentrated HCl and EtOH as a solvent at reflux. The resulting azopolyesters were characterized by elemental analyses and IR spectroscopy.

INTRODUCTION

Chalcones (*α,β*-Unsaturated ketones) are biogenetic precursors of flavonoids [1]. Chemically, chalcones are 1,3diaryl-2-propen-1-ones in which two aromatic rings are joined by a three-carbon bridge having a carbonyl moiety and *α,β*-unsaturation. Chalcone moieties are available in natural as well as synthetic compounds and are found to display a variety of pharmacological activity such as antibacterial, anti-tumor [2], anticancer [3], anti-tubercular, anti-inflammatory [4], antioxidant [5], anti-malarial [6], anti-ulcerative [7], etc.

Unsaturated azopolyesters are based on macromolecules with a polyester backbone in which both a saturated acid and unsaturated acid are condensed with a dihydric alcohol [8]. Several researches have reported the preparation of unsaturated azopolyesters by the polycondensation of dicarboxylic acids or acid anhydrides with diols, where at least one of the monomers contains an unsaturated carbon–carbon double bond (C=C). Unsaturated azopolyesters are generally difficult to perform because of their limited solubility in organic solvents and their high-melting temperature or high glass-transition temperature by virtue of their rigid structures [9,10,11].
The objective of our study is to synthesize four azo-polyesters by incorporating the chalcone moieties in the azo-polyester main chain by polycondensation process, then characterizing them analytically.

EXPEREMENTAL

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. ^{1}H-NMR spectra, in DMSO solution, were recorded on GEMINI-200, H1, 199.9785043 MHz**.** The solubility of the copolymers was determined using 0.02 g of copolymer in 3 ml of solvent at room temperature.

Reagents and materials

All chemicals were of high purity and further purified by standard methods. With the exception of thionyl chloride, which was purified by simple distillation by mixing it with quinoline (5:1) respectively. It was collected at boiling point (76.7 °C) and stored in a sealed bottle.

Synthesis of the chalcone diols

General procedure A [12]

A mixture of (0.01 mol) 4-hydroxybenzylidene or 4-hydroxy-3-methoxy benzaldehyde and (0.01 mol) 4-Hydroxyacetophenone was dissolved in (30 ml) ethanol. A catalytic (3 ml) of conc. HCl was added and the resulting mixture was refluxed for 4 hr. At the end of the reaction time, a yellow 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 chalcone **I** and **II** were obtained.

Synthesis of (*E*)-1,3-bis(4-hydroxyphenyl)prop-2-en-1-one I

Obtained by following the general procedure **A** and by using 4-hydroxybenzylidene and 4-Hydroxy acetophenone as yellow crystals; yield **71%**, mp 202 – 203 °C (lit. [13] 205 – 206 °C). IR: (ATR, cm^{-1}) 3301, 1648, 1583. ^{1}H NMR (300 MHz; DMSO) δH 6.80 (2H, d, *J* 8.6, Ar-*H*), 6.86 (2H, d, *J* 8.6, Ar-*H*), 7.58 (1H, d, *J* 15.3, COC*H*=CH), 7.66 (1H, d, *J* 15.3, COCH=C*H*), 7.67 (2H, d, *J* 8.6, Ar-*H*), 8.00 (2H, d, *J* 8.6, Ar-*H*), 10.00 (1H, br. s, O*H*), 10.32 (1H, br. s, O*H*) [12].

Synthesis of (*E*)-3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one II

Obtained by following the general procedure **A** and by using 4-hydroxy-*3-methoxy*benzylidene and acetophenone; as yellow powder; yield **85%**, mp 232 – 234 ºC (lit. [14], 229 ºC). IR: (ATR, cm^{-1}) 3320, 1655. ^{1}H NMR (300 MHz; DMSO) δH 3.87 (3H, s, OCH_3), 6.83 (1H, d, *J* 8.4, Ar-*H*), 6.90 (2H, d, *J* 8.4, Ar-*H*), 7.24 (1H, dd, *J* 8.4 and 1.5, Ar-*H*), 7.48 (1H, d, *J* 1.5, Ar-*H*), 7.61 (1H, d, *J* 15.3, COC*H*=CH), 7.73 (1H, d, *J* 15.3, COCH=C*H*), 8.06 (2H, d, *J* 8.4, Ar-*H*), 9.59 (1H, br. s, O*H*), 10.33 (1H, br. s, O*H*) [12].

Synthesis of the diacid chlorides

General procedure B [15]

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 pole yellow precipitate which soon dissolved to give a dark brown solution. The solution was cooled to room temperature before air was drawn through to afford a buff precipitate, filtration, washing three times with distilled water and drying afforded the azobenzene dicarboxylic acid. The formed diacid was refluxed for 24 hr 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 corresponding diacid chloride.

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

Obtained by following the general procedure **B** starting with 3-nitrobenzoic acid as an orange needle; yield **90%**, mp 98 – 100 °C (lit [15]. 100 – 101 °C). IR: (ATR, cm-1) 3073, 1747, 1696, 1584, 1472. IR was in accordance with the literature [15].

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 [15]. 164 – 165 °C). IR: (ATR, cm-1) 3099, 1770, 1733, 1696, 1575, 1473. IR was in accordance with the literature [15].

Synthesis of the models

General procedure C [16]

Monomer **I** or **II** (0.001 mol) was dissolved in aqueous sodium hydroxide solution (0.002 mol/L in 25 ml water and 0.3 ml methylene chloride) with stirring at 25 °C. then was added benzoyl chloride (0.002 mol/L) to the reaction mixture. At the end of reaction time, the solid product was filtered off, washed with water and ether.

Synthesis of model (V)

Obtained by following the general procedure **C** and by using (*E*)-1,3-bis(4-hydroxyphenyl)prop-2-en-1-one **I** and benzoyl chloride as yellow powder; yield **80 %**, mp = 133 – 135 °C. IR: (ATR, cm^{-1}) 1737, 1662, 1119. ^{1}H NMR (300 MHz; DMSO) δH 7.42 (2H, d, *J* 8.7, Ar-*H*), 7.53 (2H, d, *J* 8.7, Ar-*H*), 7.61 – 7.66 (4H, m, Ar-*H*), 7.75 – 7.79 (2H, m, Ar-*H*), 7.82 (1H, d, *J* 15.6, COC*H*=CH), 8.01 (1H, d, *J* 15.6, COCH=C*H*), 8.04 (2H, d, *J* 8.7, Ar-*H*), 8.15 – 8.19 (4H, m, Ar-*H*), 8.31 (2H, d, *J* 8.7, Ar-*H*). MS (EI) calc. for $[M]^+$ ($C_{29}H_{20}O_5$) m/z 448.47 found 448.25 and 105 base peaks.

Synthesis of model (VI)

Obtained following the general procedure **C** by using (*E*)-3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl) prop-2-en-1-one **II** and benzoyl chloride as yellow swollen precipitate; yield **70%**, mp = 138 – 140 °C. IR: (ATR, cm-1) 1737, 1662, 1119. 1H NMR (300 MHz; DMSO) δH 3.84 (3H, s, OCH_3), 7.31 (1H, d, J 8.1, Ar-*H*), 7.45 – 7.50 (3H, m, Ar-*H*), 7.58 – 7.63 (4H, m, Ar-*H*), 7.68 – 7.77 (3H, m, Ar-*H*), 7.76 (1H, d, *J* 17.4, COC*H*=CH), 7.95 (1H, d, *J* 17.4, COCH=CH), 8.09 – 8.16 (4H, m, Ar-*H*), 8.23 – 8.27 (2H, m, Ar-*H*). MS (EI) calc. for $[M]^+$ ($C_{30}H_{22}O_6$) m/z 478.59 found 478.30 and 105 base peaks.

Synthesis of azo-polyester

General procedure D [17]

Two-necked flask, equipped with a mechanical stirrer (500 rpm), and dropper was charged with a mixture of (0.001 mol*)* (*E*)-1,3-bis(4-hydroxyphenyl)prop-2-en-1-one **I** or (*E*)-3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl) prop-2-en-1-one **II**, and a solution of (0.002 mol NaOH in 50 ml distilled water) and (25 ml) CH_2Cl_2. A solution of (0.001 mol) of 3,3'-isophthalate dibenzoyl chloride **III** or 4,4'-terephthalate dibenzoyl chloride **IV** in (25 ml) CH_2Cl_2 was added over a (5 min) period at RT. The reaction mixture was left to stir for (1 hr) whereby an orange solid separated out. The solid was filtered off, washed with water, hot alcohol and dried under reduced pressure (1 mm Hg) at 100 °C for 2 days. By using the above general procedure, the following copolyesters **VII – X** were obtained.

Synthesis of azo-polyester VII

Obtained by following the procedure **D** and using (*E*)-1,3-bis(4-hydroxyphenyl)prop-2-en-1-one **I** and azobenzene-3,3'-dicarboxylic acid chloride **III** as a yellow prittle film in **77%** yield. IR: (ATR, cm^{-1}) 1732, 1662, 1598, 1152. Found C, 72.93%; H, 3.71%; N, 5.81%. Calc. for ($C_{29}H_{18}N_2O_5$): C, 73.41%; H, 3.82%; N, 5.90 %.

Synthesis of azo-polyester VIII

Obtained by following the general procedure **D** (*E*)-1,3-bis(4-hydroxyphenyl)prop-2-en-1-one **I** and azobenzene-4,4'-dicarboxylic acid chloride **IV** as an orange prittle film in **87%** yield. IR: (ATR cm^{-1}) 1733, 1658, 1597, 1122. Found C, 72.80%; H, 3.74%; N; 5.78 %. Calc. for ($C_{29}H_{18}N_2O_5$): C, 73.41%; H, 3.82%; N, 5.90%.

Synthesis of azo-polyester IX

Obtained by following the general procedure **D** and using (*E*)-3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxy phenyl)prop-2-en-1-one **II** and azobenzene-3,3'-dicarboxylic acid chloride **III** as a Yellow prittle film in **87%** yield. IR: (ATR ‹cm^{-1}) 1732, 1661, 1597, 1150. Found C, 70.90%; H, 3.84%; N, 5.39%. Calc. for ($C_{30}H_{20}N_2O_6$): C, 71.42%; H, 4.00%; N, 5.55%.

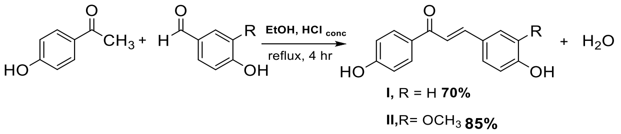
Synthesis of azo-polyester X

Obtained by following the general procedure **D** and using (*E*)-3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxy phenyl)prop-2-en-1-one **II** and azobenzene-4,4'-dicarboxylic acid chloride **IV** as an orange powder in **85%** yield. IR: (ATR ‹cm^{-1}) 1733, 1639, 1597, 1110. Found C, 70.84%; H, 3.90%; N, 5.53%. Calc. for ($C_{30}H_{20}N_2O_6$): C, 71.42%; H, 4.00%; N, 5.55%.

RESULTS AND DISCUSSION

Synthesis of chalcone monomers

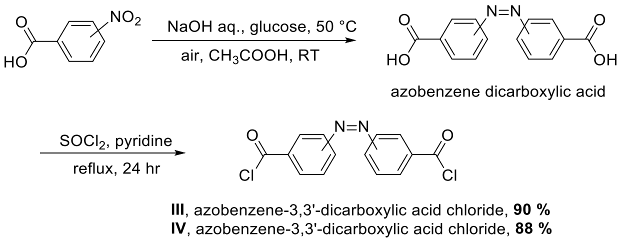
(*E*)-1,3-bis(4-hydroxyphenyl)prop-2-en-1-one **I** or (*E*)-3-(4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one **II** has been synthesised by the condensation of one equivalent of 4-hydroxy-3-methoxybenzaldehyde or 4-hydroxybenzaldehyde with one equivalent of 4-Hydroxy acetophenone **(Scheme 1)**. The structure of these monomers was confirmed by IR and ^{1}H NMR.



Scheme 1. Synthesis of the chalcone **I, II**

Synthesis of azobenzene dicarboxylic acid chlorides

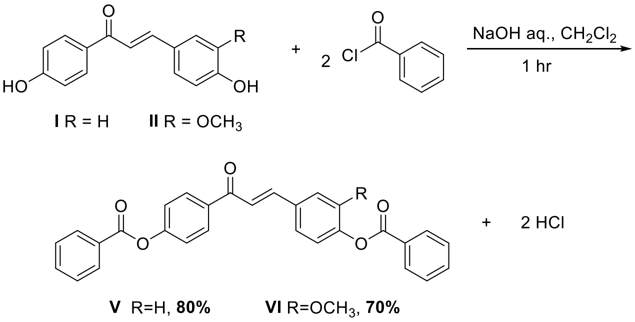
The synthesis of azobenzene-3,3'-dicarboxylic acid chloride **III** and azobenzene-4,4'-dicarboxylic acid chloride **IV** were achieved in two steps. Firstly, azobenzene dicarboxylic acids have been synthesised starting with 3-nitrobenzoic acid or 4-nitrobenzoic acid. The next step was the synthesis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



Scheme 2. Synthesis of Diacid chlorides **III**, **IV**

Synthesis of model compounds

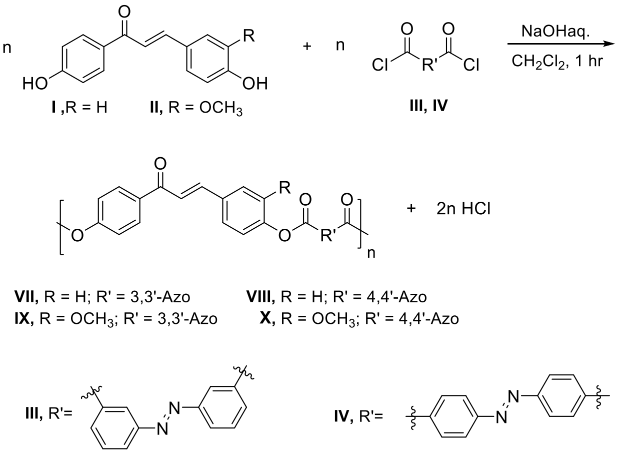
Before attempting the polymerization, the model compounds were synthesized by the reacting one equivalent of chalcone derivatives **I** or **II** and two moles of benzoyl chloride. (**Scheme 3)**.



Scheme 2. Synthesis of models **V- VI**

Synthesis of azo-polyesters VII-X

New azopolyesters **VII-X** were obtained by reacting one equivalent of chalcone derivatives **I** or **II** with one equivalent of diacid chlorides containing the azo group **III** or **IV** at room temperature (**Scheme 4**).



Scheme 4. Synthesis of models **V- VI**

IR and elemental analysis confirmed the structure of prepared azopolyesters. Firstly, IR spectra for all azopolyesters showed the disappearance of the characteristic absorption band of the OH group and the appearance of new absorption bands at 1733 – 1742 cm^{-1} for the ester carbonyl groups and 1664 – 1670 cm^{-1} for the carbonyl groups and at 1581 – 1601 cm^{-1} for C=C groups and at 1251 – 1260 cm^{-1} for C-O ester groups. The elemental analysis of all azopolymers coincided with the characteristic repeating units of each. It should be noted that the elemental analysis of these polymers deviated up to 0.5% from the theoretical values.

CONCLUSION

Preparation of new azopolyesters containing Chalcone Moiety in the main chain were achieved by the reaction of chalcone diols with different diacid chlorides, using an interfacial polycondensation technique, with excellent yields (**77% - 87%**).

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