Preparation of New Copolyesters Based on Dibenzylideneacetone Moiety

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***Abstract*—** A series of four unsaturated copolyesters were prepared by interfacial polycondensation technique of 1,3-bis(4-hydroxy-3-methoxybenzylidene) acetone **I** or 1,3-bis(4-hydroxybenzylidene) acetone **II** with 3,3\-isophthalate dibenzoyl chloride **V** and 4,4\-isophthalate dibenzoyl chloride **VI**. Initially, the two diphenols **I**, **II** were prepared by reacting two equivalents of 4-hydroxy-3-methoxybenzaldehyde or 4-hydroxy benzaldehyde with one equivalent of acetone in the presence of a catalytic amount of concentrated HCl and EtOH as a solvent at reflux. The resulting copolyesters were characterized by elemental analyses; IR; Solubility and Rate of water absorption**.**

***Keywords*: *Interfacial polycondensation, copolyester, solubility, water absorption*.**

I. INTRODUCTION

Polyesters showed interesting applications in various fields including wide commercial use as fibers. Unsaturated polyesters are coming into wider and wider use as matrices for composite materials for naval construction for economic reasons and because of their ease of processing. This has encouraged the synthesis of some new unsaturated copolyesters with the hope that they may find some interesting applications. Unsaturated copolyesters, also called polyester resins, are based on macromolecules with a polyester backbone in which both a saturated acid and unsaturated acid are condensed with a dihydric alcohol [1]. Some of the copolyesters were used in an American invention to create dyed fibers. These fibers were found to have a cohesive strength and heat resistance and stability against water. Unsaturated copolyesters from mixing unsaturated polyesters and styrene were used to laminate wood and paper for weather resistant surfaces [2-4]. A survey of the literature reveals that, different unsaturated copolymers could be prepared by the reaction of diacid chlorides containing an ester-group with aromatic diphenols [5]. Unsaturated copolyesters containing ester functional groups within the copolymer chain are obtained by polycondensation of dicarboxylic acids or diacid chlorides with different diphenols whereby at least one of the monomers contains an unsaturated carbon-carbon double bond [6]. Herein, a synthetic approach towards the synthesis of four unsaturated copolyesters by the interfacial polycondensation of diacid chlorides containing an ester-group with dibenzylidene acetone derivatives as diphenols. Some of the physical properties of these copolyesters (solubility, water absorption rate) were studied.

II. EXPEREMENTAL

A. Instrumentation

Melting points were measured on a Barnstead Electrothermal IA 9100. Infrared spectra were recorded on a Jasco FT/IR-4100 Fourier transform infrared spectrophotometer. Elemental analysis was performed using a Perkin-Elmer 2400 CHN elemental analyser.

B. 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 ^{o}C) and stored in a sealed bottle [7].

C. Synthesis of monomers

- General procedure A

A mixture of (0.02 mol) 4-hydroxy-3-methoxybenzaldehyde or 4-hydroxybenzaldehyde 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 hr. 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. Using this general procedure, diphenols **I** and **II** were obtained [8].

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

Obtained using the general procedure A with 4-hydroxy-3-methoxybenzaldehyde and acetone as brown crystals; yield **70%**. mp 102 – 104 °C (lit. [8] 99 – 100 °C). IR ν_{max} (cm^{-1}) 3395, 1640, 1616, 1165 [8].

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

Obtained using the general procedure A with 4-hydroxybenzylidene and acetone as brown powder; yield **75%**. mp 243 – 245 °C (lit. [8] 244 – 246 °C). IR ν_{max} (cm^{-1}) 3504, 1646, 1614, 1165 [8].

- General procedure B

A solution of (0.025 mol) terphthaloyl chloride or isophthaloyl chloride in (25 ml) CCl_4 was added slowly to a mixture of (0.05 mol) 4-hydroxy benzoic acid in (0.1 mol, 4 g NaOH in 100 ml of H_2O) and (100 ml) CCl_4, The mixture was continued stirring at RT for half an hour until a white precipitate was formed, the mixture then was acidified with HCl, filtered, washed three times with distilled water and dried to afford the dicarboxylic acid (3,3\-isophthalate dibenzoic acid **III** and 4,4\-terphthalate dibenzoic acid **IV**). The formed diacid **III**, **IV** was refluxed for 6 hrs with an excess of thionyl chloride (40 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 RT then was diluted with petroleum ether (60 – 80 °C). The crude precipitate was recrystallized from petroleum ether (60 – 80 °C) to afford the diacid Chlorides **V, VI** [9].

- Synthesis of 3,3\-isophthalate dibenzoyl chloride **V**

Obtained using the general procedure B with 3,3\-isophthalate dibenzoic acid **III** as a white precipitate; yield **89%**. mp189 – 190 °C (lit. [9] 189 – 190 °C). IR ν_{max} (cm^{-1}) 3104, 3075, 1776, 1737, 1596, 1497 [9].

- Synthesis of 4,4\-terephthalate dibenzoyl chloride **VI**

Obtained using the general procedure B with 4,4\-terephthalate dibenzoic acid **IV** as a white precipitate; yield **90%**. mp 229 – 230 °C (lit. [9] 229 – 230 °C). IR ν_{max} (cm^{-1}) 3160, 1775, 1737, 1596, 1496 [9].

D. Synthesis of Copolyesters

- General procedure C

Two-necked flask, equipped with a mechanical stirrer (500 rpm), 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**, 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 2 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, alcohol, acetone and dried under reduced pressure (1 mm Hg) at 100 °C for 2 days [10]. Using this general procedure, the following copolyesters **VII – X** were obtained.

- **Synthesis of Copolyester VII**

Obtained utilising the general procedure C with 1,3-bis(4-hydroxy-3-methoxybenzylidene) acetone **I** and 3,3\-isophthalate dibenzoyl chloride **V** as a Yellow powder in **80%** yield. IR ν_{max} (cm^{-1}) 1739, 1652, 1600, 1156. Found: C, 70.19%; H, 4.19%. Calc. for ($C_{41}H_{28}O_{11}$): C, 70.69%; H, 4.05%.

- Synthesis of Copolyester **VIII**

Obtained utilising the general procedure C and using 1,3-bis(4-hydroxy-3-methoxybenzylidene) acetone **I** and 4,4\-terephthalate dibenzoyl chloride **VI** as a Yellow powder in **79%** yield. IR ν_{max} (cm^{-1}) 1733, 1649, 1599, 1156. Found: C, 70.24%; H, 3.88%. Calc. for ($C_{41}H_{28}O_{11}$): C, 70.69%; H, 4.05%.

- Synthesis of Copolyester **IX**

Obtained utilising the general procedure C with 1,3-bis(4-hydroxybenzylidene) acetone **II** and 3,3\-isophthalate dibenzoyl chloride **V** as a yellow powder in **85%** yield. IR ν_{max} (cm^{-1}) 1732, 1651, 1581, 1150. Found: C, 73.13%; H, 3.97%. Calc. for ($C_{39}H_{22}O_{11}$): C, 73.58%; H, 3.80%.

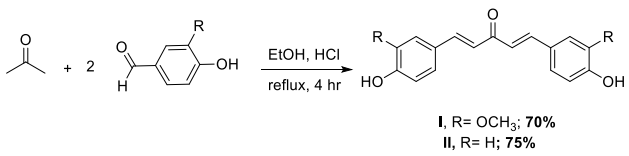
- Synthesis of Copolyester **X**

Obtained utilising the general procedure **C** with 1,3-bis(4-hydroxybenzylidene) acetone **II** and 4,4\-terphthalate dibenzoyl chloride **VI** as a Yellow powder in **80%** yield. IR ν_{max} (cm^{-1}) 1733, 1650, 1599, 1158. Found: C, 73.08%; H, 3.63%. Calc. for ($C_{39}H_{22}O_{11}$): C, 73.58%; H, 3.80%.

III. RESULTS AND DISCUSSION

A. Synthesis of monomers

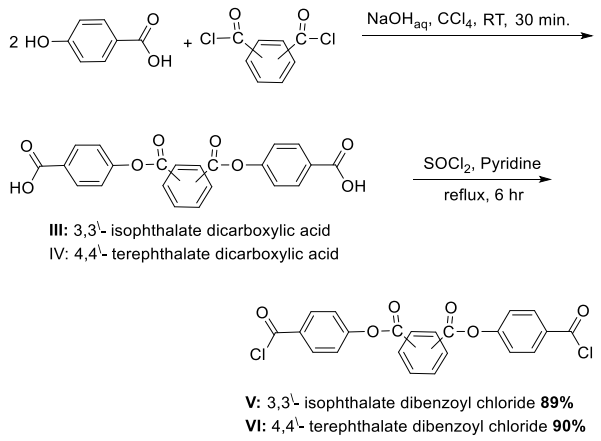
1,3-bis(4-hydroxy-3-methoxybenzylidene) acetone **I** and 1,3-bis(4-hydroxybenzylidene) acetone **II** have been synthesised by the condensation of two equivalent of 4-hydroxy-3-methoxybenzaldehyde or 4-hydroxy benzaldehyde with one equivalent of acetone (Scheme 1). The structure of these monomers was confirmed by IR.



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

B. Synthesis of Diacid Chlorides

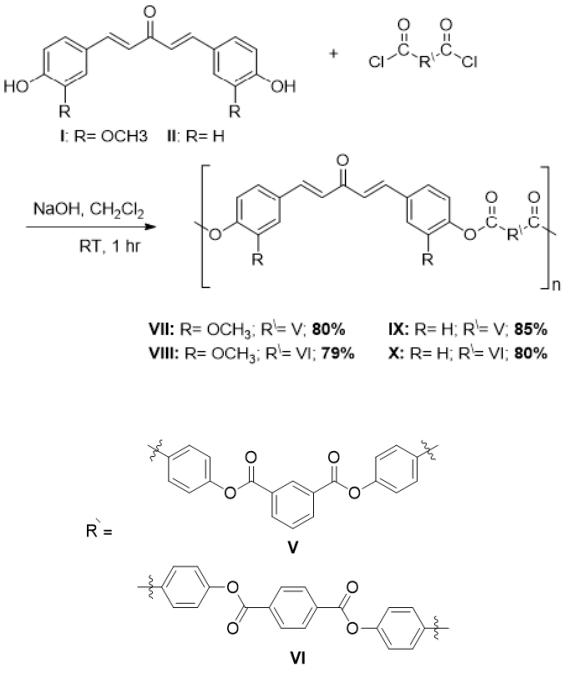
The synthesis of 3,3\-isophthalate dibenzoyl chloride **V** and 4,4\-terphthalate dibenzoyl chloride **VI** were achieved in two steps. Firstly, dicarboxylic acids **III, IV** have been synthesised starting with 4-hydroxybenzoic acid and isophthaloyl chloride or terphthaloyl chloride. The next step was the synthesis of the diacid chlorides **V, VI** by reacting the corresponding dicarboxylic acid with an excess of thionyl chlorvide at reflux (Scheme 2).



Scheme 2. Synthesis of the Diacid Chlorides **V**, **VI**

*C. Synthesis of Copolyesters **VII – X***

An unreported class of unsaturated Copolyesters were synthesized by the polycondensation of 3,3\-isophthalate dibenzoyl chloride **V** or 4,4\-terphthalate dibenzoyl chloride **VI** with 1,3-bis(4-hydroxy-3-methoxy benzylidene) acetone **I** or 1,3-bis(4-hydroxy benzbenzylidene) acetone **II** using an interfacial polycondensation technique at RT (Scheme 3).



Scheme 3. Synthesis of Copolyesters **VII- X**

IR and elemental analysis confirmed the structure of prepared copolyesters. Firstly, IR spectra for all copolyesters showed the disappearance of the characteristic absorption band of the OH group and the appearance of new absorption bands at 1732 – 1739 cm^{-1} for the ester carbonyl groups and 1650 – 1652 cm^{-1} for the carbonyl groups and at 1599 – 1620 cm^{-1} for C=C groups and at 1150 – 1158 cm^{-1} for C-O-C groups.

The elemental analysis of all copolymers coincided with the characteristic repeating units of each. It should be noted that the elemental analysis of these copolymers deviated up to 0.5% from the theoretical values. However, it is not uncommon for copolymers to trap solvent molecules within the copolymer matrix [1].

*D. Study the Solubility of Copolyesters **VII-X***

Room temperature solubility characteristics of copolyesters **VII** – **X** were tested using various solvents including: acetone, THF, DMF, DMSO, CH_2Cl_2, $CHCl_3$, CCl_4, 1,4-dioxane and formic acid (0.02 g of copolymer in 3 ml of solvent at room temperature). Concerning the solubility, it was noticed that most of them were insoluble in most of the used solvents while (**VIII, IX**) were partially soluble in concentrated formic acid (Table 1) [11].

Table 1. Solubility Characteristics of Copolyesters **VII-X**

Solvent	Copoly. VII	Copoly. VIII	Copoly. IX	Copoly. X
Acetone	-	-	-	-
1,4-Dioxane	-	-	-	-
THF	-	-	-	-
$CHCl_3$	-	-	-	-
CH_2Cl_2	-	-	-	-
CCl_4	-	-	-	-
DMF	-	-	-	-
DMSO	-	-	-	-
Formic acid	-	±	±	-

(±) partially soluble & (-) insoluble

*D. The Rate of Water Absorption of Copolyesters **VII-X***

The rate of water absorption of all prepared copolyesters was measured at 20 °C. The measurement was made at 65% humidity over 120 hrs in total, the rate of absorption rate (4.5 – 12.9%). It was found that copolyesters derived from terphthaloyl chloride have lower absorption rate of water than those derived from isophthaloyl chloride. Due to the difference in which the way of chain paching which reduces the possibility of aligning the chains of copolyesters and thus increase the rate of water absorption. It was also observed that copolyesters containing methoxy group have the highest absorption rate of water than that do not contain methoxy group which could be attributed to that, the methoxy group increases the cavities within the polymers by enlarging the distances between the pached chains (Figure 1) [12].

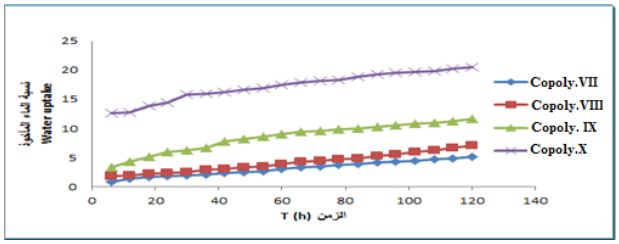


Figure 1: The Rate of water absorption of Copolyesters **VII – X**

IV. CONCLUSION

Preparation of new copolyesters based on dibenzylidene acetone moiety were achieved by the reaction of dibenzylidene derivatives with different diacid chlorides, using an interfacial polycondensation technique, with yields ranging from **79%** to **85%**. Concerning the solubility, it was noticed that most of them were insoluble in most of the used solvents while some of them were partially soluble in concentrated formic acid**.** The water absorption rate was also measured and it was ranged from 4.5% to 12.9%, for all synthesized copolymers.

V. ACKNOWLEDGMENTS

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VI. REFERENCES

[1] Kamal, I. A.; Ahmed, S. H.; Shaban, M. R.; and Mona, A. A. New Unsaturated Copolyesters Based on Diarylidenecyclopentanone. Optimum Conditions of Synthesis, Characterization and Morphology, *International Journal of Basic & Applied Sciences IJBAS-IJENS*, 2011, 11, 14 - 22**.**

[2] Al-Muaikel, N. S. Synthesis and Characterization of New Unsaturated Polyesters and Copolyesters Containing Azo Groups in the Main Chain, *European. Polym. Journal* 2003, 39, 1025 - 1033.

[3] Alkskas, I. A. and Esbata, A. A. J. Synthesis and Characterization of New Unsaturated Polyesters Containing 4-Phenylcyclohexane Moiety in the Main Chain, *Macromole. Sci. Part A.*, 2008, 45, 1 – 7.

[4] Elsunaki, T. M.; Arafat, S. A. and Abd-Alla, M. A. Synthesis and Characterization of New Polyesters Based on Diaryllidene-1-methyl-4-piperidone, *Al-satil*, 2013, 7, 39 - 49.

[5] Ben Saleh, A. B.; Elsunaki, T. M. and Abd-Alla, M. A. Synthesis and Characterization of New Unsaturated Polyesters Based on 4,4\-Dihydroxy Dibenzylidene-acetone, International Science and Technology Journal, 2017, 9, 405 - 419.

[6] Alkskas, I. A.; El-gnidi, B. A.; Ghalieo, K. M. and Azam, F. Synthesis and Characterization of Polyesters Based on Diethylketone Moiety, Chinese Journal of Polymer Science, 2014, 32, 1450 - 1459.

[7] Armarego, W.L. Purification of laboratory chemicals, Butterworth Heinemann, 2017, 476 - 480.

[8] Vogel, A. I. Text Book of Practical Organic Chemistry 4th Ed., Longman, London and New York, 1984, 610 - 613.

[9] Shahram, M. A. and Leila, A. F. Soluble Polyimides from A Semi-Aliphatic Diamine Containing Ester, Amide and Ether Groups, *Chinese Journal of Polymer Science*, 2011, 29, 93 - 100.

[10] Tareg, M. E.; Ghaith, S. A.; Hana, M. A. Synthesis of New Unsaturated Azo Polyesters Containing Diaryllideneacetone Moiety in the Main Chain, *ARPN Journal of Science and Technology*, 2017, 7, 47 - 50.

[11] Ben Saleh, A. B; Elsunaki, T. M. and Abd-Alla, M. A. Preparation and Characterization of New Thermally Stable Polyesters of 3,3\-Dihydroxy Dibenzylidene-acetone, *International Science and Technology Journal* 2017, 12, 1 - 14.

[12] Twaich, A. M. Preparation and Characterization of New Organometallic Unsaturated Polyesters Containing Ferrocene Moiety in the Main Chain, a Master Dissertation, Chem. Dept., Fac. Sci., Misrata. Univ., Misrata, Libya, 2014.