



## Synthesis of New Unsaturated Copolyesters Based on Dibenzylidene-4-phenylcyclohexanone Moiety

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### ABSTRACT

A series of four linear-unsaturated copolyesters **IX-XII** in 73% to 88% yield were synthesised by interfacial polycondensation technique of 1,3-bis(4-hydroxy-3-methoxybenzylidene)-4-phenylcyclohexanone **I** or 1,3-bis(4-hydroxybenzylidene)-4-phenylcyclohexanone **II** with 3,3'-isophthalate dibenzoyl chloride **V** or 4,4'-terephthalate dibenzoyl chloride **VI**. Initially, the monomers **I**, **II**, **V** and **VI** were synthesised in excellent yields by following a literature procedure [1-4]. In addition, the model compounds **VII**, **VIII** were also synthesised by reacting **I** or **II** with benzoyl chloride in 76% and 89% yield respectively [1]. The chemical structure of the monomers, model compounds and copolyesters have been confirmed by elemental and spectral analysis as stated in. Finally, studying the solubility of the copolyesters showed that most of them were insoluble in most common organic solvents. **Key-words:** Interfacial polycondensation, copolyester, solubility.

### INTRODUCTION

Unsaturated polyesters are one of the most important matrix resins for composite applications. Unsaturated polyesters possess a wide range of properties and are used in marine, automobile, construction, sport, and they have also led to the need and development of high-performance unsaturated polyesters [5-8]. Unsaturated copolyesters, also called polyester resins, are based on macromolecules with a polyester backbone in which both a saturated acid or unsaturated acid are condensed with a dihydric alcohol [9]. Several researches have reported the preparation of unsaturated copolyesters by the polycondensation of dicarboxylic acids; acid anhydrides or diacid chlorides with diols, where at least one of the monomers contains an unsaturated carbon-carbon double bond (C=C). Unsaturated polyesters are generally difficult to perform because of their limited solubility in common organic solvents and their high-melting point or high glass-transition point by virtue of their rigid structures [10-12].

As a continuation of our study on the synthesis and properties of new polyesters and copolyesters, a new series of unsaturated copolyesters based on dibenzylidene-4-phenylcyclohexanone in the main chain has planned to synthesis and characterize in this work. Moreover, the solubility of the synthesised copolyesters has also been examined and discussed.

### EXPERIMENTAL

#### Instrumentation

Melting points were determined on a Barnstead Electrothermal IA 9100. All melting points were uncorrected. Infrared spectra were recorded on a Perkin Elmer Para-

gon RX I FT-IR spectrophotometer accompanied with ATR accessory. The <sup>1</sup>HNMR spectra was recorded on a JEOL ECA-500 II spectrometer. The elemental analysis was carried out on an elemental analyzer, Model 2400, Perkin Elmer instrument.

### 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 [13].

### Synthesis of monomers I, II, V, VI

#### General procedure A for the synthesis of diphenols I, II

A mixture of (0.02 mol) 4-hydroxy-3-methoxybenzaldehyde or 4-hydroxybenzaldehyde and (0.01 mol) 4-phenylcyclohexanone was dissolved in (30 ml) ethanol. A catalytic amount of concentrated HCl was added and the resulting mixture was refluxed for four hours. 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 [1]. By using the above general procedure, the following diphenols **I** and **II** were obtained.

#### Synthesis of 1,3-bis(4-hydroxy-3-methoxybenzylidene)-4-phenylcyclohexanone I

Obtained by following the general procedure **A** and by using 4-hydroxy-3-methoxybenzaldehyde, as brown crystals; yield 75%, mp 161 – 163 °C (lit. [1] 160 – 163 °C). IR  $\nu_{\max}$  (cm<sup>-1</sup>) 3525, 3183, 1642, 1575 [1].

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

Obtained by following the general procedure **A** and by using 4-hydroxybenzaldehyde, as brown powder; yield 87%, mp 140 – 142 °C (lit. [1] 140 – 143 °C). IR  $\nu_{\max}$  (cm<sup>-1</sup>) 3200, 1643, 1570 [1].

#### General procedure B for the synthesis of diacid chlorides V, VI

A solution of (0.01 mol) terephthaloyl dichloride or isophthaloyl dichloride in (25 ml) CCl<sub>4</sub> was added slowly to a mixture of (0.05 mol) 4-hydroxy benzoic acid in (0.1 mol, 4 gm NaOH in 100 ml of H<sub>2</sub>O) and (100 ml) CCl<sub>4</sub>. 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'-terephthalate dibenzoic acid **IV**). The formed diacid **III** or **IV** was refluxed for 6 hr 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** [2-4].



### Synthesis of 3,3'-isophthalate dibenzoyl chloride V

Obtained by following the general procedure B and by using 3,3'-isophthalate dibenzoic acid III, as a white precipitate; yield 89%, mp 189 – 190 °C (lit. [4] 189 – 190 °C). IR  $\nu_{\max}$  (cm<sup>-1</sup>) 3104, 3075, 1776, 1737, 1596 [4].

### Synthesis of 4,4'-terephthalate dibenzoyl chloride VI

Obtained by following the general procedure B and by using 4,4'-terephthalate dibenzoic acid IV, as a white precipitate; yield 90%, mp 229 – 230 °C (lit. [4] 229 – 230 °C). IR  $\nu_{\max}$  (cm<sup>-1</sup>) 3160, 1780, 1737, 1598 [4].

### Synthesis of models VII, VIII

#### General procedure C

Benzoyl chloride (0.002 mol) was added in 20 minutes to a mixture solution of Monomer I or II (0.001 mol) and 50 ml of an aqueous sodium hydroxide solution (0.002 mol) and 25 ml of dichloromethane. The reaction mixture was then left to stir at room temperature for an hour. At the end of the reaction time, a solid product precipitated. The solid product was filtered off, washed with water and ether, dried and recrystallized from ethanol.

#### Synthesis of 1,3-bis(4-hydroxy-3-methoxybenzylidene)-4-phenylcyclohexanone dibenzoate (VII)

Obtained by following the general procedure C and by using 1,3-bis(4-hydroxy-3-methoxybenzylidene)-4-phenylcyclohexanone I, as a yellow powder; yield 76%, mp 141 - 143 °C (lit. [1] 142 °C). IR  $\nu_{\max}$  (cm<sup>-1</sup>) 1732, 1658, 1583 [1].

#### Synthesis of 1,3-bis(4-hydroxybenzylidene)-4-phenylcyclohexanone dibenzoate (VIII)

Obtained by following the general procedure C and by using 1,3-bis(4-hydroxybenzylidene)-4-phenylcyclohexanone II, as a yellow powder; yield 89%, mp 168 - 170 °C (lit. [1] 168 °C). IR  $\nu_{\max}$  (cm<sup>-1</sup>) 1732, 1671, 1598 [1].

### Synthesis of copolyesters IX – XII

#### General procedure D

A 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)-4-phenylcyclohexanone I or 1,3-bis(4-hydroxybenzylidene)-4-phenylcyclohexanone II, and a solution of (0.002 mol NaOH in 50 ml distilled water) and 25 ml CH<sub>2</sub>Cl<sub>2</sub>. A solution of (0.001 mol) of 3,3'-isophthalate dibenzoyl chloride V or 4,4'-terephthalate dibenzoyl chloride VI in (25 ml) CH<sub>2</sub>Cl<sub>2</sub> was added over two minutes period at room temperature. The reaction mixture was left to stir for an hour whereby an orange solid separated out. The solid was filtered off, washed with water, alcohol and dried under reduced pressure (1 mm Hg) at 100 °C for two days. By using this general procedure, the following copolyesters IX – XII were synthesised.

### Synthesis of copolyester IX

Obtained by following the general procedure **D** and using 1,3-bis(4-hydroxy-3-methoxybenzylidene)-4-phenylcyclohexanone **I** and 3,3'-isophthalate dibenzoyl chloride **V** as an orange powder in 88% yield. IR  $\nu_{\max}$  (cm<sup>-1</sup>) 1742, 1664, 1601, 1251, 1156. Found: C, 73.48%; H, 4.61%. Calc. for (C<sub>50</sub>H<sub>36</sub>O<sub>11</sub>): C, 73.88%; H, 4.46%.

### Synthesis of copolyester X

Obtained by following the general procedure **D** and using 1,3-bis(4-hydroxy-3-methoxybenzylidene)-4-phenylcyclohexanone **I** and 4,4'-terephthalate dibenzoyl chloride **VI** as an orange powder in 75% yield. IR  $\nu_{\max}$  (cm<sup>-1</sup>) 1733, 1650, 1602, 1257, 1156. Found: C, 73.51%; H, 4.59%. Calc. for (C<sub>50</sub>H<sub>36</sub>O<sub>11</sub>): C, 73.88%; H, 4.46%.

### Synthesis of copolyester XI

Obtained by following the general procedure **D** and using 1,3-bis(4-hydroxybenzylidene)-4-phenylcyclohexanone **II** and 3,3'-isophthalate dibenzoyl chloride **V** as an orange powder in 73% yield. IR  $\nu_{\max}$  (cm<sup>-1</sup>) 1738, 1652, 1602, 1260, 1150. Found: C, 76.10%; H, 4.33%. Calc. for (C<sub>48</sub>H<sub>32</sub>O<sub>9</sub>): C, 76.59%; H, 4.28%.

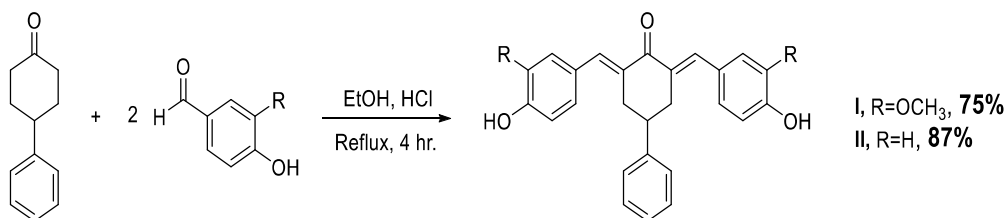
### Synthesis of copolyester XII

Obtained by following the general procedure **D** and using 1,3-bis(4-hydroxybenzylidene)-4-phenylcyclohexanone **II** and 4,4'-terephthalate dibenzoyl chloride **VI** as an orange powder in 80% yield. IR  $\nu_{\max}$  (cm<sup>-1</sup>) 1737, 1670, 1601, 1256, 1158. Found: C, 76.28%; H, 4.19%. Calc. for (C<sub>48</sub>H<sub>32</sub>O<sub>9</sub>): C, 76.59%; H, 4.28%.

## RESULTS AND DISCUSSION

### Synthesis of diphenols I, II

1,3-bis(4-hydroxy-3-methoxybenzylidene)-4-phenylcyclohexanone **I** and 1,3-bis(4-hydroxybenzylidene)-4-phenylcyclohexanone **II** have been synthesised by the condensation of two equivalents of 4-hydroxy-3-methoxybenzaldehyde or 4-hydroxybenzaldehyde with one equivalent of 4-phenylcyclohexanone at reflux for 4 hours in the presence of ethanol as solvent and a catalytic amount of hydrochloric acid as a catalyst (Scheme 1). The structure of these monomers was confirmed by IR which was in accordance with the literature [1].

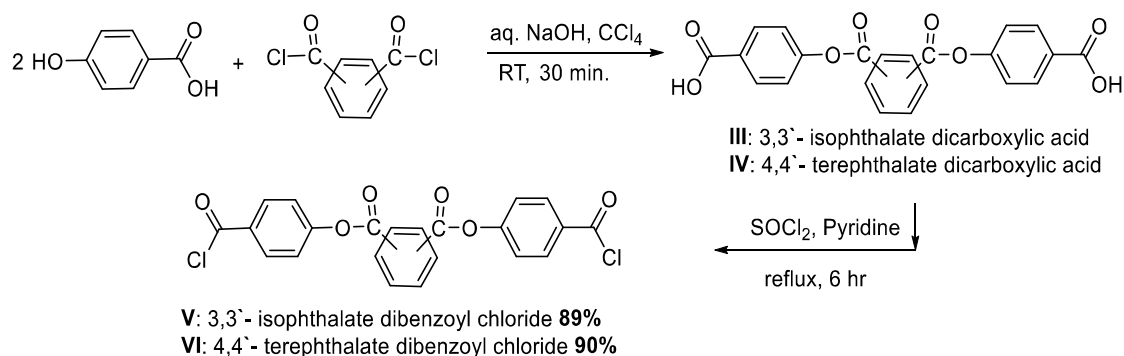


Scheme 2. Synthesis of diphenols I, II



### Synthesis of diacid chlorides V, VI

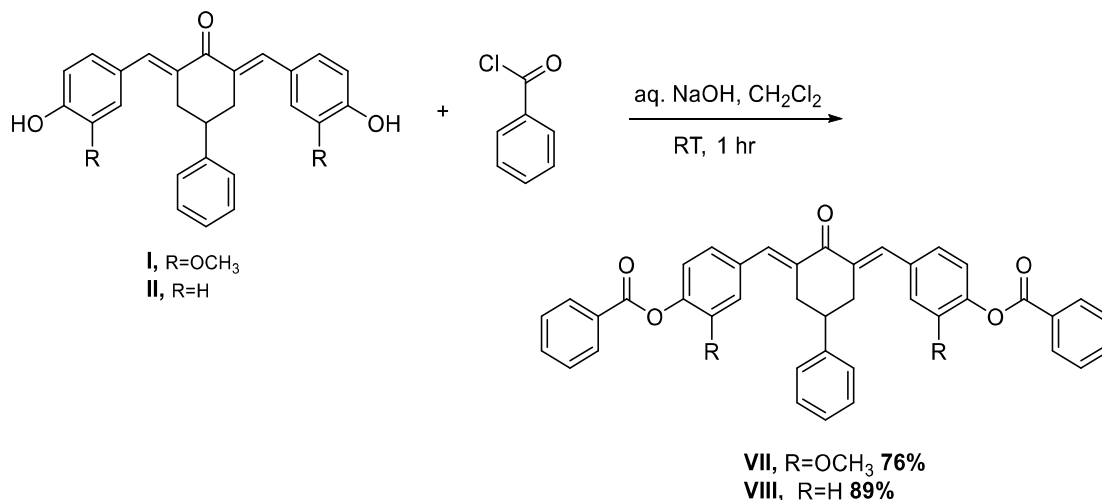
The synthesis of 3,3'-isophthalate dibenzoyl chloride **V** and 4,4'-terephthalate dibenzoyl chloride **VI** was carried out in two steps. In the first step, dicarboxylic acids **III**, **IV** have been synthesised by reacting two equivalents of 4-hydroxybenzoic acid with one equivalent isophthaloyl chloride or terephthaloyl chloride respectively. The next step was the synthesis of the diacid chlorides **V**, **VI** by reacting the corresponding crude dicarboxylic acid **III** or **IV** with an excess of thionyl chloride in the presence of pyridine (Scheme 2). The structure of the diacid chlorides was confirmed by IR which was in accordance with the literature [4].



**Scheme 3.** Synthesis of the diacid chlorides **V**, **VI**

### Synthesis of models VII, VIII

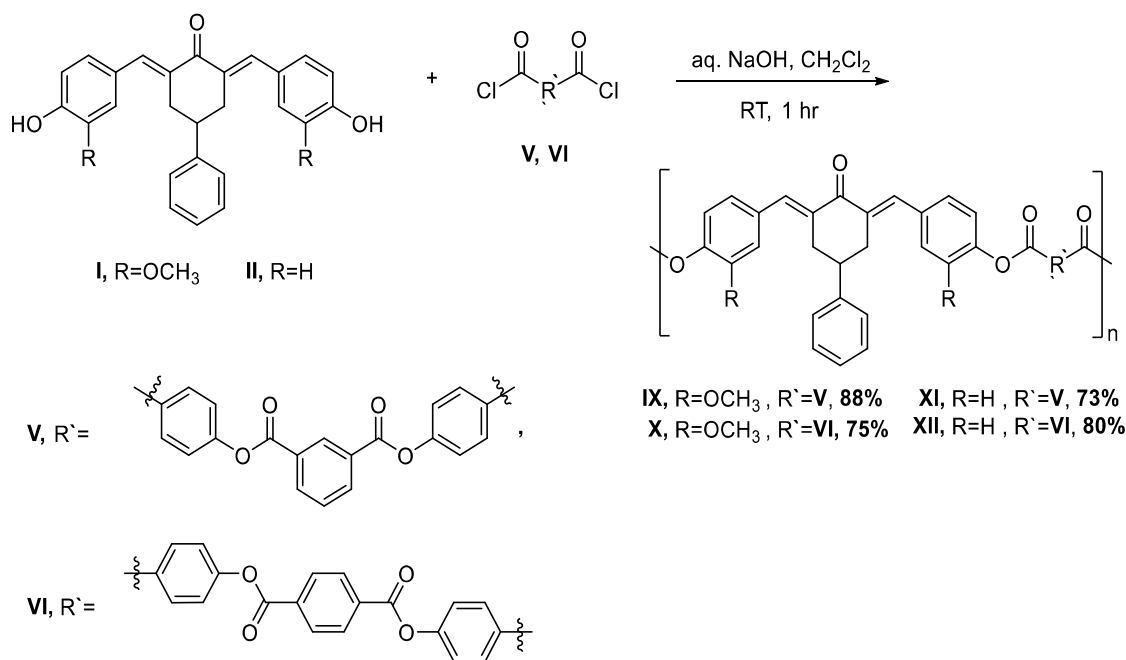
Before attempting the polymerisation step, model compounds **VII** and **VIII** were synthesised in excellent yields by the interaction of diphenols **I** and **II** with benzoyl chloride in NaOH solution and  $\text{CH}_2\text{Cl}_2$  (Scheme 3). The structure of the resulting models was confirmed by IR analysis which was in accordance with the literature [1].



**Scheme 3. Synthesis of models VII, VIII**

**Synthesis of copolyesters IX-XII**

An unreported class of unsaturated copolyesters were synthesized by the polycondensation of 3,3'-isophthalate dibenzoyl chloride **V** or 4,4'-terephthalate dibenzoyl chloride **VI** with 1,3-bis(4-hydroxy-3-methoxybenzylidene)-4-phenylcyclohexanone **I** or 1,3-bis(4-hydroxybenzylidene)-4-phenylcyclohexanone **II** using an interfacial Polycondensation technique at room temperature (Scheme 4).



**Scheme 4. Synthesis of copolyesters IX-XII**

Infrared and elemental analysis confirmed the structure of the 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 1733 – 1742  $\text{cm}^{-1}$  for the ester carbonyl groups and 1650 – 1670  $\text{cm}^{-1}$  for the carbonyl groups and at 1601 – 1602  $\text{cm}^{-1}$  for C=C groups and at 1251 – 1260  $\text{cm}^{-1}$  for C-O ester 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 [14].

**Study the solubility of copolyesters IX-XII**

The solubility of the copolymers was determined using 0.02 g of copolymer in 3 ml of solvent at room temperature. Most of the copolyesters were insoluble in most of the used solvents except copolyester **IX**, which showed a partial solubility in some



polar solvents. This could be attributed to the effect of the methoxy group, that increase the polarity of the polymer chain (Table 1).

Solvent	Copoly.IX	Copoly.X	Copoly. XI	Copoly.XII
Acetone	-	-	-	-
Chloroform	±	-	-	-
1,4 Dioxane	±	±	-	-
CCl <sub>4</sub>	-	-	-	-
THF	-	-	-	-
DCM	±	-	-	-
DMF	±	-	-	-
DMSO	-	-	-	-
Formic acid	-	-	±	-

**Table 1.** Solubility characteristics of copolyesters IX-XII

(±) Partially Soluble & (-) Insoluble

### CONCLUSION

Preparation of new copolyesters based on dibenzylidene-4-phenylcyclohexanone moiety in the main chain was achieved by the reaction of dibenzylidene derivatives with different diacid chlorides, using an interfacial polycondensation technique, with excellent yields (73% - 88%). Concerning the solubility, it was noticed that most of them were insoluble in most of the used solvents while the copolyester **IX** was partially soluble in some polar solvents.

### REFERENCES

- [1] Alkskas, I. A. and Esbata, A. A. *J. Macromole. Sci. Part A.* **2008**, 45, 218-220.
- [2] Tomlinson, M, L. *J. Chem. Soc.* **1946**, 756, 39-42.
- [3] Srinivason, M. and Jayalakshmi, G. *Chem. Ind.* **1985**, 339-343.
- [4] Shahram, M. A. and Leila A. F., *Chinese Journal of Polymer Science* **2011**, 29 (1), 93-95.
- [5] Vijayakumar, C. T.; Sivasamy, P. and Rajkumar, T. *Eur. Polym. J.* **2007**, 43, 3028.
- [6] Han, H. and Bhowmik, P. K. *Prog. Polym. Sci.* **1997**, 22, 1431.
- [7] Li, H.; Wang, D.; Fan, L. and Yang, S. *Eur. Polym. J.* **2006**, 42, 534.
- [8] Murali, M. and Samui, A. B. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, 44, 51.
- [9] Boenig, H. V. "Unsaturated polyesters," Elsevier, Amsterdam, **1964**.
- [10] Podkoscielny, W. and Rudz, W. *Eur. Polym. J.* **1993**, 29, 1115.
- [11] Elsunaki, T. M.; Ghaith, S. H. and Aboras, H. M. *Journal of Academic Research (Applied Science)* **2020**, 16, 1-4.

[12] Morgan, P. W. Condensation Polymers by Interfacial and Solution Methods; Interscience: New York, 1965.

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

[14] Kamal, I. A.; Ahmed, S. H. Shaban, M. R. and Mona, A. A. *International Journal of Basic & Applied Sciences IJBAS-IJENS* **2011**, 11, 14-22.