Synthesis and Characterisation of New Unsaturated Polyesters Based on 4,4'-Dihydroxy Dibenzylideneacetone

Abdulali B. Ben Saleh[a], Tareg M. Elsunaki[b], Mohamed A. Abd-Alla[c]

[a] Chemistry Department, Faculty of Education, Misurata University, Libya.

[b] Chemistry Department, Faculty of Science, Misurata University, Libya .

[c] Chemistry Department, Faculty of Science, Assiut University, Egypt.

Abstract 1,3-Bis (4-hydroxybenzylidene)acetone **I** was used as starting material for preparing new unsaturated polyesters. These polyesters were synthesized by utilizing interfacial polycondensation technique of 1,3-bis (4-hydroxy benzylidene) acetone **I** with adipoyl, sebacoyl, isophethaloyl, terephethaloyl and 4,4'-diphenic dichloride. In order to characterize these polymers, the necessary model compound **II** was prepared by reacting **I** and benzoyl chloride. The structure of **I**, **II** and produced polyesters were confirmed by elemental and spectral analysis. Additionally, solubility, reduced viscosity of the polyesters in the range of (0.52 - 0.76 dl/g) were determined. The thermal properties of the polymers were evaluated by thermogravimetric analysis and correlated with their structural units. The crystallinitiy of some polyesters were tested.

1. Introduction

In recent years increasing 'high-tech' applications make ever-increasing demand for materials in both terrestrial and extra-terrestrial environments use. High temperature resistant polymers are in great demand for high-speed aircraft structures and as structural components of space vehicles. Resin systems are currently attracting increasing attention as high-performance thermosetting resins and they can be used as the matrices for high performance composites due to their superior mechanical properties which are used in the electronic devices, high-temperature adhesive and aerospace industries.[1-5] They also can be utilised as a good strength, low dielectric constant, radar transparency, low water absorption, and superior metal adhesion.[6,7] Moreover, unsaturated polyesters find use in a variety of applications where their low cost chemical resistance and thermal stability are key factors.[8,9] A survey of the scientific literature reveals that unsaturated polyesters can be synthesised by the condensation of unsaturated carboxylic acid with dihydric alcohols or unsaturated diols with saturated acids.[10,11] Recently, unsaturated polyesters and poly(ester-amid)s have been synthesized by interfacial polycondensation of diphenol derivatives with diacids chloride.[12-15] The work reported here outlines the synthesis and characterization of new diarylideneacetone based on aliphatic and aromatic polyesters. The solubility, viscosity, thermal stability and crystallinitiy were examined.

2. Experimental

2.1.1. Measurements

The Elemental analyses were carried out on a Perkin-Elmer 240 C instrument. IR spectra's were recorded on a Pye Unicam PU9712 infrared spectrophotometer using KBr pellet technique. ^{1}HNMR spectras were run on a Bruker 11.1HO 100 MHz NMR spectrometer in DMSO using TMS as the internal reference. The inherent viscosity of the polymer solutions (0.5 % w/v) in conc. sulphoric acid were determined at 25 °C using an Ubbelohde suspended level viscometer. The solubility of the polymers was examined using (0.02 g) of polymer in (3-5 ml) of solvent at room temperature. X-ray diffractgraphs were obtained using an XD-610 Shimadzu X-ray Diffractometer, with nickel-filtered Cu Kα radiation. Thermogravimetric analysis (TGA) was carried out on a Shimazu TGA-50H Thermal analyzer, at a heating rate of 10 °C min^{-1}.

2.2. Reagents and Materials

4,4'-diphenic dichloride was prepared according to the literature.[16] All other chemicals were of high purity and further purified by standard methods.[17]

2.3. Synthesis of (1,3-Bis(4-hydroxybenzylidene) acetone I

A mixture of (0.02 mol) 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 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 (1:3) methanol-water. Yellow needles were obtained; yield 85 %, mp 236 – 238 °C. Found: C, 76.24 %; H, 5.41%. Calc. for $C_{17}H_{14}O_3$: C, 74.67 %; H, 5.29 %. IR (KBr)/ cm^{-1} 1618 (C=C), 1647 (C=O), 3504 (OH). ^{1}HNMR (100 MHz; DMSO-d6) δH 6.7 - 7.1 (8H, m, Ar-*H*), 7.5 - 7.8 (4H, m, C*H*=C*H*), 10.1 (2H, s, O*H*).

2.4. Synthesis of Model Compound (4,4'– Dibenzylidene acetone dibenzoate) II

1,3-Bis (4-hydroxybenzylidene) acetone **I** (0.005 mol) was dissolved in NaOH solution (0.01 mol, 0.4 g/20 ml H_2O) and stirred at room temperature before the addition of benzoyl chloride (0.01 mol) within 30 min. At the end of the reaction time, a yellow solid product precipitated. The solid product was filtered off, washed with water then ether,dried in *vacuo* at room temperature and recrystallised from ethanol.

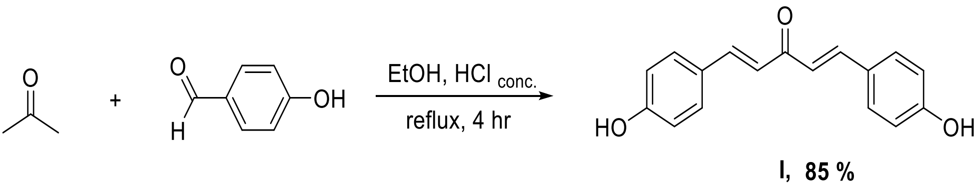
Yellow crystals were obtained; yield 83 %, mp 170 – 172 °C. Found: C, 77.87 %; H, 5.01 %. Calc. for $C_{31}H_{22}O_5$: C, 78.47 %; H, 4.66 %. IR (KBr)/ cm^{-1} 1610 (C=C), 1645 (C=O), 1710 (C=O of ester group). ^{1}HNMR (100 MHz; DMSO-d6) δH 7.2 – 7.9 (18H, m, Ar-*H*; C*H*=C*H*), 8.0 – 8.3 (4H, m, Ar-*H*).

2.5. Synthesis of Polyesters III – VII

A thee-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) diarylideneacetone (I), (0.002 mol) of NaOH solution in (50 ml) water and (25 ml) methylene chloride. Diacids chloride (0.001 mol) in (25 ml) methylene chloride was added over a 2 min period at room temperature and vigorously stirred. After completing the addition of diacids chloride, the reaction mixture was left to stir for 60 min whereby a highly-yellow 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. The synthesized polyesters, their yield, elemental analysis and some of their properties are listed later in Table 1.

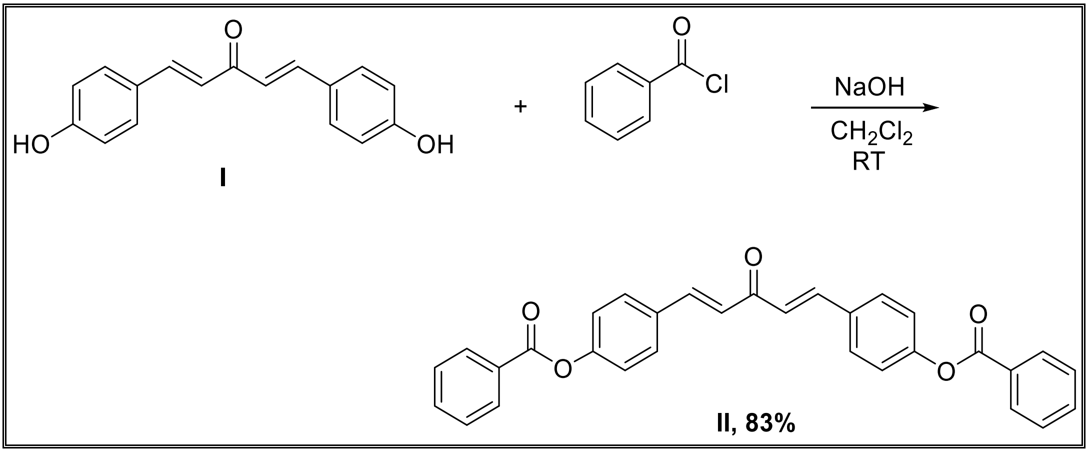
3. Results and discussion

Diphenol **I** was synthesised by the condensation of 4-hydroxybenzaldehyde (0.02 mol) with acetone (0.01 mol) in the presence of ethanol and a catalytic amount of conc. HCl (Scheme 1). The structure of this monomer was confirmed by elemental and spectral analysis (see section 2).



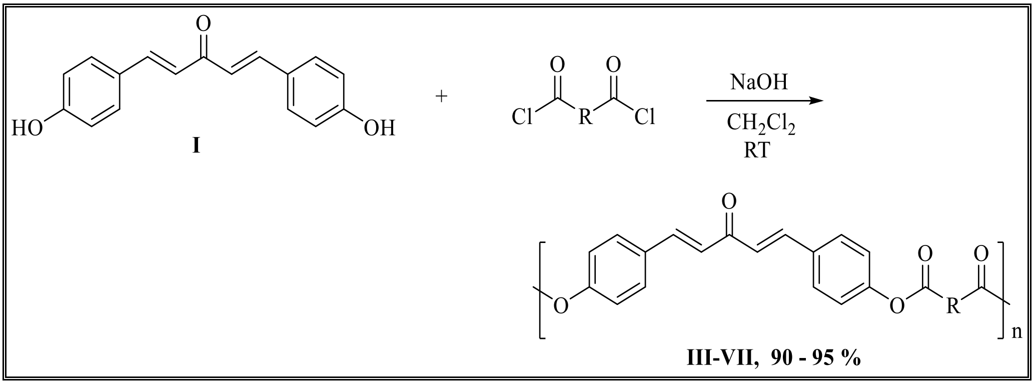
Scheme 1. Synthesis of monomer I

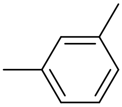
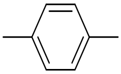
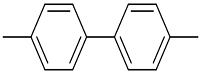
Before attempting polymerization, the model compound **II** was synthesised by the interaction of monomer **I** with benzoyl chloride in NaOH solution and CH_2Cl_2. The structure of this model was confirmed by elemental and spectral analysis (see section 2). The reaction is illustrated as shown in scheme 2.



Scheme 2. Synthesis of model compound II

A new class of liner unsaturated polyesters based on diary lidene acetone **I** was synthesized using interfacial poly condensation of monomer **I** with adipoyl, sebacoyl, isophethaloyl, terephethaloyl and 4,4’- diphenic dichloride (Scheme 3).



Polyester	**III**	**IV**	**V**	**VI**	**VII**
R	$-(CH_2)_4-$	$-(CH_2)_8-$			

Scheme 3. Synthesis of Polyesters III – VII

The resulting polyesters **III – VII** were characterized by IR spectroscopy, elemental analysis, viscosity, TGA and X-ray analysis. The yield, elemental analysis and reduced viscosity of the polyesters are listed in Table 1. The elemental analysis of all different polyesters coincided with the characteristic repeating units of each polymer. It needs to be mentioned that in the elemental analysis, the difference between the calculated and found ratio is sometimes reached 0.9 %. However, It is not uncommon for polymers, especially those of high molecular weight, to trap solvent molecules within the polymer matrix, and these polymers contain polar groups which are capable of hydrogen bonding with solvent molecules.[18]

Table 1. The elemental analysis, yield, appearance and reduced viscosity of the polyesters III –VII

Polyesters	C %		H %		Yield %	Appearance	ηred dL/g
	Calc.	Found	Calc.	Found			
III	73.39	73.55	5.35	5.44	90	Powder (yellow)	-
IV	74.98	74.12	6.51	6.09	92	Powder (yellow)	0.72
V	75.75	75.08	4.06	4.87	95	Powder (yellow)	0.60
VI	75.75	74.98	4.06	4.01	94	Powder (yellow)	0.52
VII	78.80	77.93	4.26	4.66	91	Powder (yellow)	0.76

*Reduced viscosity measured in conc. H_2SO_4

The IR spectra support the structural assignments for all polyesters; the data obtained indicated the disappearance of the characteristic absorption band of the OH group and the appearance of new absorption bands at 1725 – 1754 cm^{-1} characteristics of the carbonyl groups of esters, at 1645 – 1650 cm^{-1} for the carbonyl groups of acetone moieties and at 1590 – 1605 cm^{-1} for C=C groups. In addition, other characteristic absorption bands, due to specific groups present in the various polymers, were also evident in the IR spectra.

The solubility characteristics of polyesters **III – VII** were tested in various solvents such as, acetone, formic acid, 1,4-dioxane, 1,2-dichlorobenzene, THF, DMSO, CH_3Cl, CH_2Cl_2, conc. H_2SO_4 and a mixture of CH_3Cl:CH_2Cl_2 and CH_3Cl:CCl_4. It was found that, the majority of the polyesters are soluble in halogenated solvents such as $CHCl_3$, CH_2Cl_2, CCl_4, 1,2-dichlorobenzene, CH_3Cl:CH_2Cl_2 and CH_3Cl:CCl_4 as well as THF. It also was found that all polymers are completely soluble in conc. H_2SO_4 giving deep reddish-violet color. In DMSO, polyesters **III**, **IV** are completely soluble. However, polyesters **VI**, **VII** are insoluble. Moreover, the majority of the polyesters are partially soluble in formic acid. Generally, it should be noted that the presence of methylene groups in the polymers chain **III**, **IV** increases the solubility.[19,20]

The thermal behavior of polyesters **III – VII** were evaluated by TGA in air at a heating rate of 10 °C /min. Table 2 gives the temperatures for various percentage weight losses. The temperature for 10 % weight loss is considered to be the polymer decomposition temperature and it ranges between 237 – 362 °C. Therefore, the data in table 2 indicated the thermal stabilities of these polymers are in the order **VI** > **VII** > **V** > **IV** > **III**. It should be noted that the aliphatic based polymer **III**, **IV** are less thermally stable than the aromatic based polymers.

Table 2. Thermal Stabilities of Polyesters III – VII

Polyesters	**Temperature (°C) for various % decom positions**				
	10 %	**20 %**	**30 %**	**40 %**	**50 %**
III	237	342	390	503	588
IV	240	303	388	462	500
V	300	329	383	455	507
VI	362	404	442	470	503
VII	351	407	444	477	509

X-ray diffractography of polyesters **III – VI** in Figure 1 showed amorphous halo patterns in the region of $2\theta = 5 - 55°$ and this indicated a low degree of crystallinitiy. However, polyesters **VI** showed a few reflections of sharpness peaks intermediate between crystalline and amorphous interference and this indicated a some degree of crystallinitiy.[21,22]

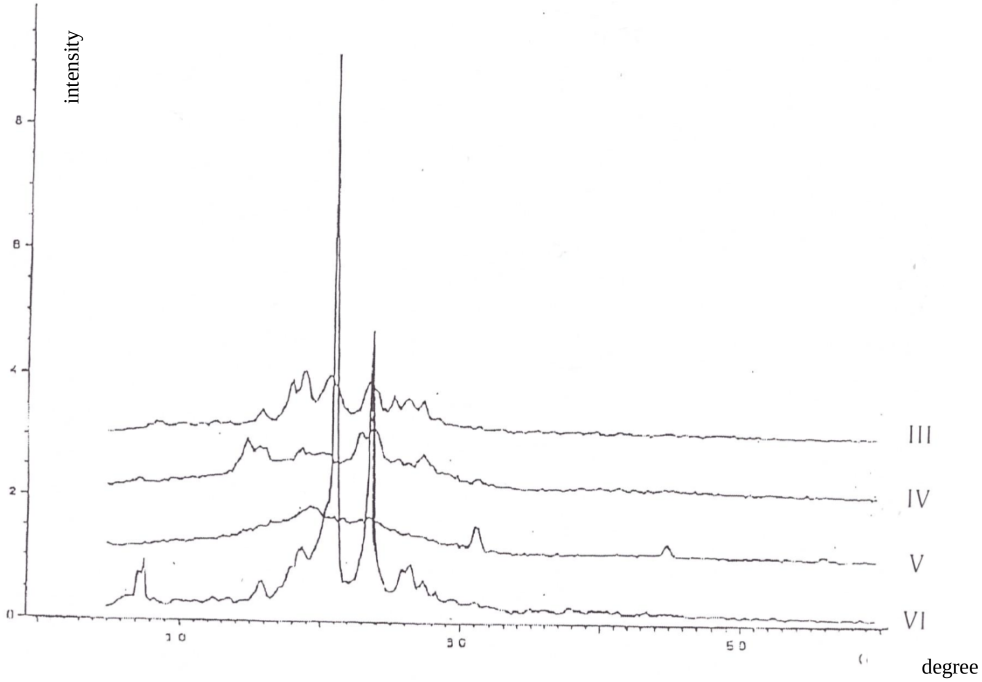


Figure 1. X-ray Diffraction Patterns of Polyester **III – VI**

4. Conclusions

Unsaturated polyesters based on diarylideneacetone **III – VII** have been prepared by interfacial polycondensation technique. Polyesters that have methylene groups linkage were more soluble than those connected through aromatic rings linkage. Thermogravimetric analysis showed that the aliphatic based polymers were less thermally stable than the aromatic based polymers. X-ray diffraction analysis indicated a low degree of crystallinitiy except polymer **VI** which showed a some degree of crystallinitiy.

5. References

[1] Fang, T. and Shimp, D. *Prog. Polym. Sci.,* 20, 61 – 118, **1995**.

[2] Fan, J.; Hu, X. and Yue, C. J. *Polym. Sci, Part B. Polym. Phys.,* 41, 1123 – 1134, **2003**.

[3] Herr, D.; Nikolic, N. and Schultz, R. *High Performance Polymers,* 13, 79 – 100, **2001**.

[4] Hamerton, I. and Hay, J.; *Polymer International*, 47, 465 – 473, **1998**.

[5] Hamerton, I. and Hay, J. N. *High Performance Polymers*, 10, 163 – 174, **1998**.

[6] Shimp, D. and Chin, B. *Chem. & Techn.,* 230 – 257, **1994**.

[7] Nair, C.; Mathew, D. and Ninan, K. *Adv. Polym. Sci.,* 155, 1 – 99, **2001**.

[8] Wende, a.; Priede, H. and Deutch, K. *Proceeding of 2nd international symposium on glass reinforced plastics*, Berlin, **1967**.

[9] Parkyn, B.; Lamb, F. and Clitton, B. V. *Polyesters. Vol. 2, Unsaturated polyesters and polyester plasticizers*, American Elsevier, New York, **1967**.

[10] Zhu, J.; Cai, J.; Xie, W.; Chen, P.; Gazzano, M.; Scandola, M. and Gross, R. A. *Macromolecules*, 46, 796 – 804, **2013**.

[11] Gaina, C.; Gaina, V. and Cozan, V. *Eur. Polym. J.* 37, 79 – 84, **2001**.

[12] Al-Muaikel, N. S. *Eur. Polym. J.* 39, 1025 – 1033, **2003**.

[13] Murali, M. and Samui, A. A. *J. Polym. Sci. Part A: Polym, Chem.,* 44, 51 – 57, **2006**.

[14] Alkskas, I. A. and Esbata, A. A. *J. Macromole. Sci. Part A.,* 45, 218 – 224, **2008**.

[15] Khairou, K. S.; Abd-Alla, M. A.; Aly, K. I.; Nahas, N. M. and Al-Bonian, A. M. *Arabian Journal of Chemistry*, 2, 65 – 71, **2009**.

[16] Kornblum, N. and Kendall, D. L. *J. Am. Chem. Soc.* 74, 5782 – 5782, **1952**.

[17] Perrin, D. D.; Armarego, W. L. F. and Perrin, D. R. *Purification of laboratory chemicals, 2nd ed. , Pergamon,* New York, **1980**.

[18] Ali, K. I. and Geies, A. A. *High Performance Polymers*, 4, 187 – 195, **1992**.

[19] Abd-Alla, M. A. and Aly, K. I. *High Performance Polymers*, 2, 235 – 243, **1990**.

[20] Abd-Alla, M. A.; Kandeel, M. M.; Aly, K. I. and Hammam, A. S. *J. Macromole. Sci. Part A.,* 27, 523 – 538, **1990**.

[21] Mandelken, L. *Crystallisation of Polymers, McGraw-Hill*, New York, **1964**.

[22] Abd-Alla, M. A.; Aly, K. I. and Hammam, A. S. *High performace polymers*, 1, 223 – 237, **1989**.