



Synthesis, Characterization and Biocidal Properties of Some Random Copolyesters Containing Chalcone Diol Moiety

MOHD IMRAN RAIS^{1,*}, S.J. ASKAR ALI¹ and D. REUBEN JONATHAN²

¹PG and Research Department of Chemistry, The New College, Chennai-600 014, India

²Department of Chemistry, Madras Christian College, Chennai-600 059, India

*Corresponding author: E-mail: mimran186@gmail.com

Received: 8 March 2018;

Accepted: 18 April 2018;

Published online: 31 May 2018;

AJC-18953

A series of 8 random copolyesters were produced by polycondensation of chalcone diol with terephthaloyl chloride, isophthaloyl chloride, adipoyl chloride, oxalyl chloride, glutaryl chloride and succinyl chloride. The Claisen-Schmidt reaction in acidic medium was used to prepare chalcone diol. The characterization of prepared random copolyesters was done by checking the solubility in different solvents and viscosity measurements. FT-IR, ¹H- and ¹³C-NMR spectroscopic techniques were applied to study the structure of repeating units available in the polymer chain. Thermal analysis was done by DSC. The well-diffusion method was employed to establish the biocidal efficacy of these 8 copolyesters by using a Gram-positive and Gram-negative bacteria.

Keywords: Chalcone diol, Polycondensation, Copolyesters, Bactericidal activity, Fungicidal activity.

INTRODUCTION

Chalcones are α,β -unsaturated ketones and characterized as biogenetic precursors of flavonoids [1]. The most convenient method for the preparation of chalcones [2-4] is the Claisen-Schmidt condensation of equimolar quantities of aryl methyl ketone with aryl aldehyde in the presence of alcoholic alkali [5]. Naturally occurring chalcones are found mostly in the hydroxylated forms such as butein, licochalcone-A, isoliquiritigenin, xanthoangelol and flavokawan [6]. Chemically, these are 1,3-diphenyl-2-prop-en-1-one and have reported a wide range of biological activities including antileishmanial, antiinflammatory, antimitotic, modulation of P-glycoprotein-mediated multi drug resistance and antimalarial activities, etc. [7-12].

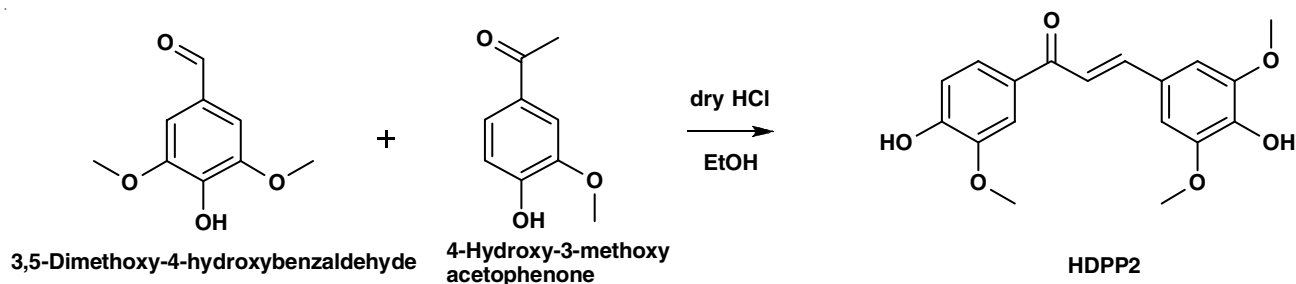
Polyesters are important plastics with monomers linked by ester moieties. Copolyesters obtained from a multiplicity of reactions having the component groups linked in random or statistical order are termed random copolyesters. However, the randomness of copolyesters depended mainly on the mixing time and not on the aromatic polyester content [13]. They are usually prepared by copolymerization of a mixture of comonomers. The copolymerization reaction and copolymer structure are controlled by the ratios and reactivity of reagents and catalysts [14]. The photo-cross linking property of polymer is owed to carbon-carbon double bond of α,β -unsaturated carbonyl groups which undergo [2+2] cycloaddition reactions under UV radiation [15].

As a continuation of research in this field, the present work comprises the novel synthesis of random copolyesters having chalcone as the main substance in the chain by the process of polycondensation, then characterizing them by utilizing appropriate analytical techniques and finally studying their bactericidal and fungicidal properties. Copolyesters are synthesized by the copolymerization of a diol with diacid chloride-1 and diacid chloride-2 in the mol ratio of 2:1:1. They are high molecular weight compounds containing ester linkages.

EXPERIMENTAL

All the compounds used in this study viz. 3,5-dimethoxy-4-hydroxy benzaldehyde, 4-hydroxy-3-methoxy acetophenone, terephthaloyl chloride, isophthaloyl chloride, adipoyl chloride, oxalyl chloride, glutaryl chloride and succinyl chloride were of analytical grade and procured from Sigma-Aldrich, USA.

Preparation of monomer (HDPP2): The monomer 2E-1-(4-hydroxy-3-methoxyphenyl)-3-(3,5-dimethoxy-4-hydroxyphenyl)prop-2-en-1-one was (HDPP2) prepared by reacting 3,5-dimethoxy-4-hydroxybenzaldehyde (100 mmol) and 4-hydroxy-3-methoxy acetophenone (50 mmol) in 100 mL of absolute ethanol with constant stirring in 250 mL of round bottom flask by passing dry HCl gas for 1 h (**Scheme-I**). The mixture then mixed with ice water where precipitate was filtered and recrystallized with absolute alcohol. Yield: 90 %, colour: green solid, m.p. 175 °C, IR (KBr, ν_{\max} , cm^{-1}): 3413 (OH), 1647 (C=O);



Scheme-I

^1H NMR ($\text{DMSO}-d_6$), 9.7 (s, 2H, -OH), 7.1-7.8 (m, 6H, aromatic), 6.9 (dd, 2H, -CH=CH), 3.8 (s, 2H, -OCH₃).

Synthesis of copolyester (PTA2): The monomer HDPP2 was dissolved in 10 mL DMF in a 100 mL round bottom flask. After 5 min, 1 mL of triethylamine was added and stirred. The monomer was allowed to dissolve completely in 15 min at room temperature then diacid chlorides terephthaloyl chloride and adipoyl chloride were added. The temperature increases to 80 °C and maintained at this with continuous stirring for 3 h. The mixture then poured into 100 mL of distilled water, where the copolyester was precipitated. It was filtered, allowed to dry in air.

Similarly, other copolyesters PTO2, PIA2, PIO2, PTG2, PTS2, PIG2 and PIS2 were synthesized by the same method using HDPP2 diol as shown in Table-1.

RESULTS AND DISCUSSION

Solubility: The synthesized eight random copolyesters are insoluble in least polar solvents, partially soluble in moderately polar solvents and soluble in highly polar solvents. Similar explanation was offered by Sidhartan and Amaladhas [16] in

a series of copolyesters. The results of solubility are presented in Table-2.

Viscosity measurements: The inherent viscosity of the resulting copolyesters was established in dimethyl acetamide solution at 30 °C using Ubbelohde viscometer. In every case 25 mg of pure dry copolyester sample was dissolved in 25 mL of dimethylacetamide, put aside for sometime with intermittent shaking. The η_{inh} was evaluated from the flow time measurements. The values of η_{inh} were found to be in the range 0.87 to 1.98 dL/g (Table-1). The statistics showed that the prepared copolyesters are of high molecular weight.

Spectral studies: The FT-IR data of diol and 8 random copolyesters was taken on Perkin-Elmer system. It shows characteristic absorptions in the range 1730 to 1756 cm^{-1} due to the presence of ester C=O stretching frequency for copolyesters. These observations were also made by Samuel *et al.* [17] in a series of copolyesters.

Bruker Advance instrument was used to record ^1H NMR at 400 MHz and ^{13}C NMR at 75 MHz. To record ^1H - and ^{13}C NMR spectra, all the four copolyesters *viz.* PTA2, PIA2, PTO2 and PIO2 are dissolved in $\text{DMSO}-d_6$ solvent. The aromatic protons were observed in the range δ 7.1 to 8.8 ppm carbonyl carbon

TABLE 1
MONOMER USED, COPOLYESTER CODES OF THE EIGHT COPOLYESTERS WITH
THEIR RESPECTIVE PERCENTAGE YIELD AND INHERENT VISCOSITIES

Random copolyester codes	Diol	Diacid chloride-I	Diacid chloride-II	Yield (%)	η_{inh} (dL/g)
PTA2	HDPP2	Terephthaloyl chloride	Adipoyl chloride	73	1.31
PTO2	HDPP2	Terephthaloyl chloride	Oxalyl chloride	72	0.87
PIA2	HDPP2	Isophthaloyl chloride	Adipoyl chloride	74	1.98
PIO2	HDPP2	Isophthaloyl chloride	Oxalyl chloride	75	1.65
PTG2	HDPP2	Terephthaloyl chloride	Glutaryl chloride	76	1.65
PTS2	HDPP2	Terephthaloyl chloride	Succinyl chloride	79	1.98
PIG2	HDPP2	Isophthaloyl chloride	Glutaryl chloride	77	0.87
PIS2	HDPP2	Isophthaloyl chloride	Succinyl chloride	74	0.87

TABLE-2
SOLUBILITY OF COPOLYESTERS IN SOME COMMON ORGANIC SOLVENTS

Random copolyester codes	DMSO	DMAc	DMF	C ₃ H ₆ O	C ₄ H ₈ O	CHCl ₃	EtOH	CH ₃ OH	C ₆ H ₆	C ₆ H ₁₄
PTA2	++	++	++	+-	+-	+-	--	--	--	--
PTO2	++	++	++	+-	+-	+-	--	--	--	--
PIA2	++	++	++	+-	+-	+-	--	--	--	--
PIO2	++	++	++	+-	+-	+-	--	--	--	--
PTG2	++	++	++	+-	+-	+-	--	--	--	--
PTS2	++	++	++	+-	+-	+-	--	--	--	--
PIG2	++	++	++	+-	+-	+-	--	--	--	--
PIS2	++	++	++	+-	+-	+-	--	--	--	--

soluble ++, partially soluble +- and insoluble --

TABLE-3
BIOCIDAL ACTIVITY DATA OF SOME RANDOM COPOLYESTERS CONTAINING CHALCONE DIOL MOIETY

Sample codes	Zone of inhibition (mm)							
	25 µg	50 µg	75 µg	100 µg	25 µg	50 µg	75 µg	100 µg
<i>Bacillus subtilis</i>					<i>Escherichia coli</i>			
PIA2	11	13	14	16	10	12	14	14
PIO2	10	11	14	14	12	15	16	16
PTA2	11	13	15	15	12	14	14	14
PTO2	10	13	14	16	14	16	16	17
Streptomycin (10 µg)	18				20			
<i>Candida albicans</i>					<i>Aspergillus niger</i>			
PIA2	11	15	18	18	-	-	-	18
PIO2	10	13	15	15	-	-	-	12
PTA2	10	15	17	17	-	-	-	9
PTO2	12	14	15	15	-	-	-	14
Fluconazole (25 µg)	28							
Clotrimazole (25 µg)					16			
– = Not active								

- = Not active

having vinylic protons were found in the range of δ 6.9-7.0 ppm. The chalcone moiety which have methoxy protons are shown between δ 3.4 to 3.9 ppm and δ 2.5 to 2.9 ppm is the range for methylene protons. Similar work was reported by Chitra *et al.* [18] in a series of copolyesters derived from chalcone diol. The indication of signals at δ 162-188 ppm in the ^{13}C NMR spectra indicates the carbonyl carbon of ester group as well as ketone carbonyl group. The aromatic carbon atoms are indicated by the signals at δ 130 ppm. Thus the proton decoupled ^{13}C spectrum of polymers indicates that polymer chain contains ester group. The copolymerization of these polyesters was attributed to their random placements along the polyester chain, which was also varified with ^{13}C NMR spectroscopy.

Thermal analysis: Thermal transition from DSC for the copolyester PTA2 (Fig. 1) showed a heating curve having endothermic melting peak (T_m) with the corresponding enthalpy (ΔH_m) [19].

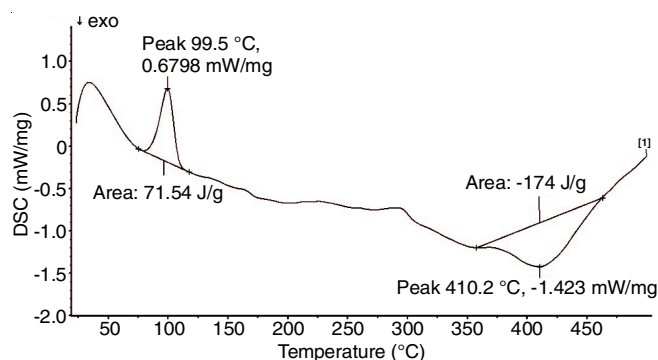


Fig. 1. Thermal analysis showing by random copolyester PTA2 by DSC

Antibacterial activity (disc-diffusion method): The antibacterial activities of four test compounds such as PIA2, PIO2, PTA2 and PTO2 were carried out by well diffusion method [20,21]. The concentrations of the test compounds (PIA2, PIO2, PTA2 and PTO2) were taken in DMSO and tested in different concentrations. The target microorganisms were cultured in Mueller-Hinton broth (MHB). After 24 h the suspensions were adjusted to standard sub culture dilution. The agar plates were seeded with freshly prepared different pathogens. Agar wells with diameter of 6 mm were made with the help of

a sterile stainless steel cork borer. The standard drug streptomycin (10 µg) was used as a positive reference standard to determine the sensitivity of each microbial species tested. Then the plates were incubated at 37 °C for 24 h. The diameter of the clear zone around the well was measured and expressed in millimeters [22,23]. It is apparent that the four copolyesters were found to be bactericidal in nature (Table-3). With increase of concentration of the copolyester material, the inhibition effect increased.

Antifungal activity (disc-diffusion method): The antifungal activity of synthesized random copolyesters PIA2, PIO2, PTA2 and PTO2 were assayed against *Candida albicans* and *Aspergillus niger*. It is found that clotrimazole and fluconazole suppressed the growth of *Candida albicans* and *Aspergillus niger*, respectively as shown in Table-3 and it is obvious that the four copolymers were found to be fungicidal in nature [24,25].

ACKNOWLEDGEMENTS

The authors are thankful to SAIF/IIT Madras, Chennai, India for providing the thermal analysis. The authors also thanks to the Principal and the Management of The New College, Chennai, India for their support.

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