RESEARCH ARTICLE

A Study on the Synthesis, Characterization, and Biological Efficacy of Certain Copolyesters Containing Chalcone Moiety in the Main Chain

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Abstract

Aim: To synthesise random copolyesters containing chalcone moiety in the main chain, their characterization and biological activity. **Material and Methods:** A series of eight random copolyesters were synthesized by the polycondensation of a chalcone diol with two aromatic diacid chlorides and four aliphatic diacid chlorides. The two aromatic diacid chlorides used were terephthaloyl chloride and isophthaloyl chloride. The aliphatic diacid chlorides used were adipoyl chloride, oxalyl chloride, glutaryl chloride, and succinyl chloride. The chalcone diol was synthesized by acid catalyzed Claisen-Schmidt reaction. **Results and Discussions:** These copolyesters were characterized by qualitative solubility tests and viscosity measurements. The microstructure of the repeating units available in the copolyester main chain was established by Fourier transform infrared, ^{1}H-nuclear magnetic resonance (NMR), and ^{13}C-NMR spectroscopic techniques. DSC was apply to study thermal analysis. The well diffusion method was employed to establish the biological efficacy of these eight copolyesters by involving Gram-positive and Gram-negative bacteria. **Conclusion:** The presented work reports random copolyester preparation by polycondensation method and viscosity measurements tells about that the prepared compounds are of high molecular weight. others like FTIR, NMR, Solubility measurements and DSC characterize them. Biological properties was also studied.

Key words: Bactericidal, chalcone diol, copolyesters, fungicidal, polycondensation

INTRODUCTION

Aromatic compounds having α, β-unsaturated ketones are chalcones. They are present centrally in significant biological compounds and also exists in nature as precursors of flavonoids and isoflavonoids.[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] Chalcones are excellent models for studying photo-induced electron transfer processes which play a key role in different fields such as polymer, photo, optic, and laser physics.[6] They are used to synthesized several derivatives such as cyanopyridines, pyrazolines, isoxazoles, and pyrimidines having different heterocyclic ring systems.[7-10] Chalcone moieties are available in natural as well as synthetic compounds and are found to display a variety of pharmacological activity such as antibacterial, antitumor, anticancer, antituberculosis, anti-inflammatory, antioxidant, antimalarial, and anti-ulcerative.[11,12] The presence of reactive methoxy and hydroxyl groups in the chalcone backbone is responsible for their biological activity. Chitra *et al*. synthesized copolyesters containing bis(chalcone) moiety in the main chain and found that these polymers exhibit significant bactericidal activity against pathogenic bacteria.[13]

Polyesters are important plastics with monomers linked by ester moieties. Copolyesters obtained from a multiplicity

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of reactions having the component groups linked in random or statistical order are termed random copolyesters. 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-crosslinking property of polymer is owed to carbon-carbon double bond of α, β-unsaturated carbonyl groups which undergo [2+2] cycloaddition reactions under ultraviolet radiation.[15]

Our objective for the synthesis of these eight copolyesters containing chalcone moieties in the main chain is to characterize them and finally studying their biological activities. Copolyesters are high molecular weight compounds which contain ester linkages and are synthesized by the copolymerization of diol, diacid chloride-I, and diacid chloride-II in the ratio of 2:1:1.

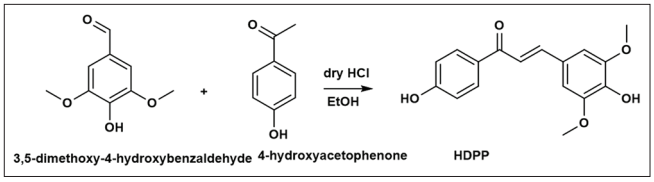
EXPERIMENTAL SECTION

Materials used as received

3,5-dimethoxy-4-hydroxybenzaldehyde, 4-hydroxyacetophenone, terephthaloyl chloride, isophthaloyl chloride, adipoly chloride, oxalyl chloride, glutaryl chloride, and succinyl chloride were used.

Preparation of monomer (HDPP)

The monomer (2E)-1-(4-hydroxyphenyl)-3-(3,5-dimethoxy-4-hydroxyphenyl)prop-2-en-1-one was prepared by 3,5-dimethoxy-4-hydroxybenzaldehyde(100 mmol) and 4-hydroxyacetophenone (50 mmol) in 100 ml of absolute alcohol with constant stirring in 250 ml of round bottom flask by passing dry HCl gas for 1 h as shown in Scheme 1. The mixture then mixed with ice water where precipitate was filtered and recrystallized with absolute alcohol. Green color solid we obtained Yield: 90%, MP=160°C, infrared (IR) (OH)=3493.05/cm, and Ketogenic group (C=O) = 1647.68/cm;^{1}H-nuclear magnetic resonance (NMR) (dimethyl sulfoxide [DMSO]-d_6) δ 9.7-10.3(s,2H, -OH), δ 7.0–8.0(m, 6H, aromatic), δ 6.8–6.9(dd, 2H, -CH=CH), and δ 3.4–3.8(s, 2H, -OCH_3).



Scheme 1: Reaction for the synthesis of diol

Synthesis of copolyester PTA1

The monomer HDPP 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.

The other copolyesters PTO1, PIA1, PIO1, PTG1, PTS1, PIG1, and PIS1, were synthesized by the same method using HDPP diol shown in Table 1.

RESULTS AND DISCUSSION

Solubility

The eight random copolyesters synthesized were soluble in highly polar solvents, partially soluble in moderately polar solvents and thoroughly insoluble in the least polar solvents. Similar explanation was offered by Sidhartan and coworkers in a series of copolyesters.[16] The results of solubility are presented in Table 2.

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)
PTA1	HDPP	Terephthaloyl chloride	Adipoyl chloride	75	1.65
PTO1	HDPP	Terephthaloyl chloride	Oxalyl Chloride	70	1.18
PIA1	HDPP	Isophthaloyl chloride	Adipoyl chloride	71	0.86
PIO1	HDPP	Isophthaloyl chloride	Oxalyl chloride	73	1.2
PTG1	HDPP	Terephthaloyl chloride	Glutaryl chloride	73	1.98
PTS1	HDPP	Terephthaloyl chloride	Succinyl chloride	74	1.98
PIG1	HDPP	Isophthaloyl chloride	Glutaryl chloride	72	1.65
PIS1	HDPP	Isophthaloyl chloride	Succinyl chloride	75	1.98

Viscosity measurements

The inherent viscosity of the resulting copolyesters was determined in dimethyl acetamide solution at 30°C using Ubbelohde Viscometer. In each case, 25 mg of pure dry copolyester sample was dissolved in 25 ml of DMAc, kept aside for some time with occasional shaking. The η_{inh} was calculated from the flow time measurements. The inherent viscosity values were found to be in the range 0.86–1.98 dL/g and are presented in Table 1. The data show that these copolyesters are of high molecular weight.

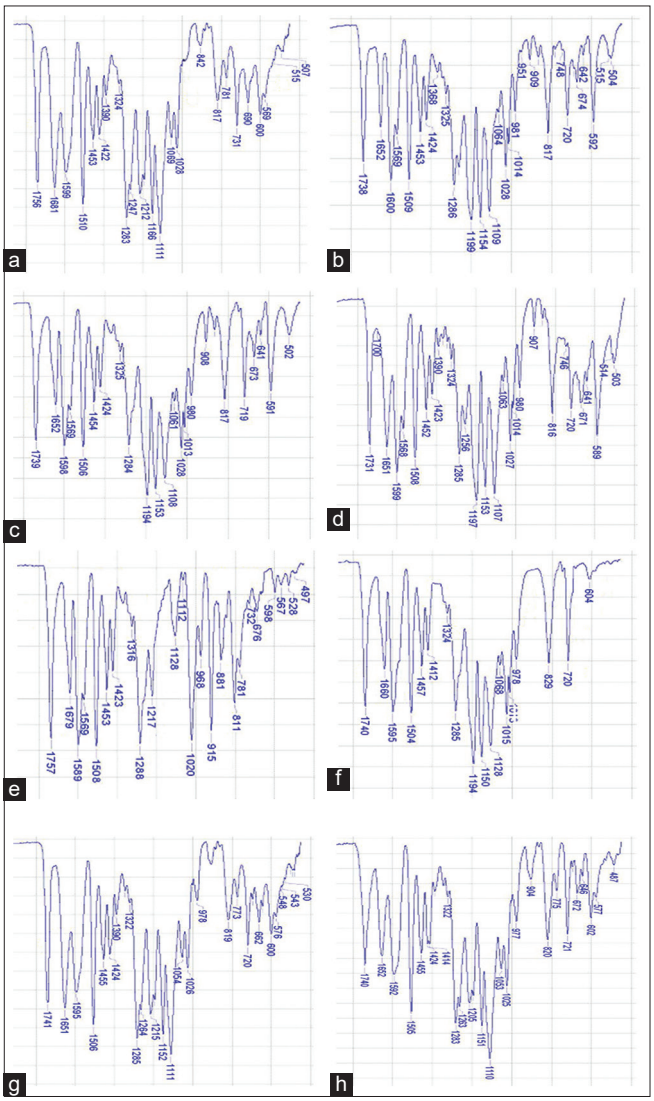


Figure 1: (a) Infrared (IR) data of PTA1. (b) IR data of PIA1. (c) IR data of PTO1. (d) IR data of PIO1. (e) IR data of PTG1. (f) IR data of PIG1. (g) IR data of PTS1. (h) IR data of PIS1

Spectral studies

Fourier transform IR(FT-IR) spectrum of diol and eight copolyesters on Perkin-Elmer System. It shows characteristic absorptions in the range 1730–1756 cm^{-1} due to ester C=O stretching frequency for copolyesters. Similar observations were made by Samuel *et al*.[17] in a series of copolyesters [Figure 1a-h].

Bruker advance instrument was involved to record ^{1}H-NMR at 400 MHz and ^{13}C-NMR at 75 MHz. To record ^{1}H-NMR and ^{13}C-NMR spectra, all the four copolyesters PTA1, PIA1, PTO1, and PIO1 are dissolved in DMSO-d_6 solvent. The aromatic protons were observed in the range δ 7.1–9.1 ppm. The vinylic protons attached to the carbonyl carbon were observed in the range δ 6.8–7.0 ppm. The methoxy protons in the chalcone moiety are shown between δ 3.4 and 3.9 ppm. The methylene protons were observed in the range δ 2.5–2.8 ppm [Figure 2a-d]. Similar observations were performed by Chitra *et al.* in a series of copolyesters derived from chalcone-diols. The signals at δ 163-188 ppm in the ^{13}C-NMR spectra indicate 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 the polymer chain contains ester group. The copolymerization of these polyesters was attributed to their random placements along the polyester chain, which was also verified with ^{13}C-NMR spectroscopy [Figure 3a-d].

Thermal analysis

Thermal transition from differential scanning calorimetry for the copolyester PTS1 [Figure 4] shows heating curve

Table 2: Solubility of copolyesters in some common organic solvents

Random copolyester codes	DMSO	DMAc	DMF	C_3H_6O	C_4H_8O	$CHCl_3$	EtOH	CH_3OH	C_6H_6	C_6H_{14}
PTA1	++	++	++	+ –	+ –	+ –	--	--	--	--
PTO1	++	++	++	+ –	+ –	+ –	--	--	--	--
PIA1	++	++	++	+ –	+ –	+ –	--	--	--	--
PIO1	++	++	++	+ –	+ –	+ –	--	--	--	--
PTG1	++	++	++	+ –	+ –	+ –	--	--	--	--
PTS1	++	++	++	+ –	+ –	+ –	--	--	--	--
PIG1	++	++	++	+ –	+ –	+ –	--	--	--	--
PIS1	++	++	++	+ –	+ –	+ –	--	--	--	--

++: Soluble, +–: Partially soluble and –: Insoluble. DMSO: Dimethyl sulfoxide

having an endothermic melting peak (T_m) at 105°C with the corresponding enthalpy (ΔHm) of 88.67J/g.[18]

BIOLOGICAL ACTIVITIES

Antibacterial property(disc-diffusion method)

The antibacterial activities[19,20] of the four test compounds such as PIA1, PIO1, PTA1, and PTO1 were carried out by well diffusion method. The concentrations of the test compounds (PIA1, PIO1, PTA1, and PTO1) were taken in DMSO and used in the concentration of 25, 50, 75, and 100 µg/mL. The target microorganisms were cultured in Mueller–Hinton broth. After 24 h the suspensions were adjusted to standard subculture dilution. The Petri dishes are containing Mueller–Hinton Agar medium. The agar plates were seeded with freshly prepared different pathogens. Agar wells with a 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

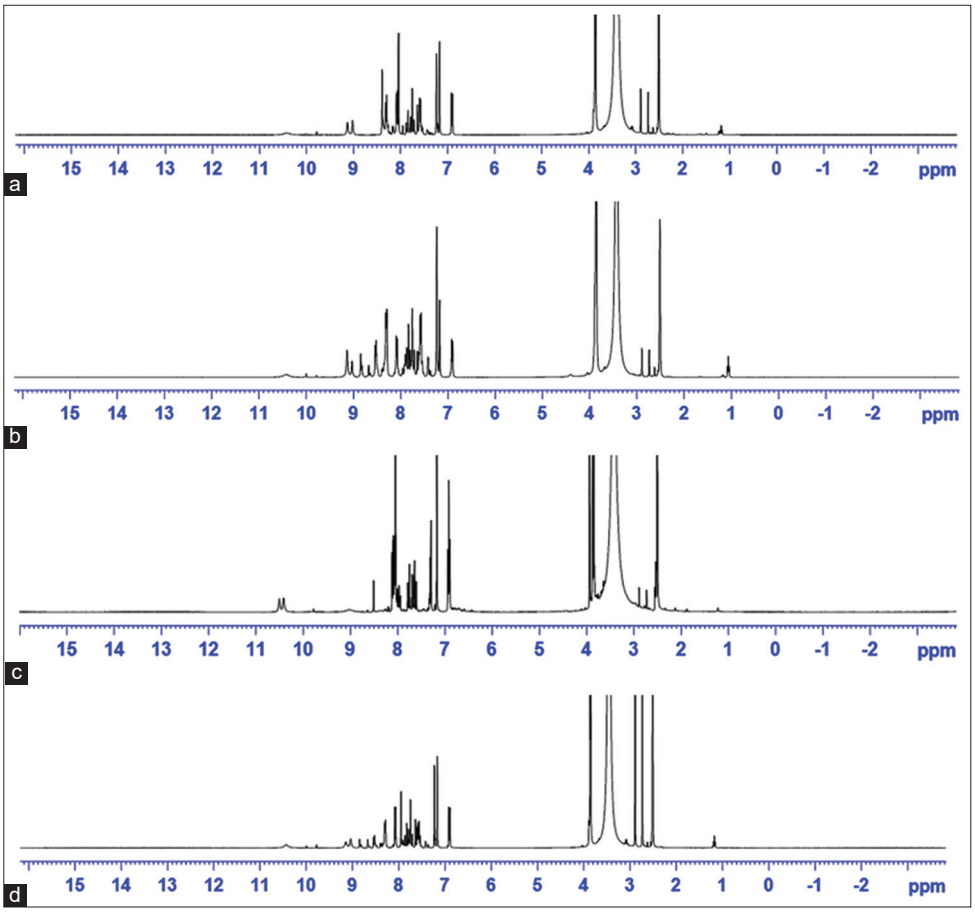


Figure 2: (a) 1H-nuclear magnetic resonance (^{1}H-NMR) data of PTA1. (b) ^{1}H-NMR data of PIA1c. (c) ^{1}H-NMR data of PTO1. (d) ^{1}H-NMR data of PIO1

Table 3: Inhibition effect of copolyesters on the growth of *Bacillus subtilis* and *Escherichia coli*

Sample code	Zone of inhibition (mm) and MIC µg/mL							
	Bacillus subtilis				Escherichia coli			
	25 µg	50 µg	75 µg	100 µg	25 µg	50 µg	75 µg	100 µg
PIA1	-	-	8	10	13	15	17	17
PIO1	-	-	7	9	10	13	16	17
PTA1	-	-	7	9	13	15	17	17
PTO1	-	-	8	10	-	-	10	11
Streptomycin (10 µg)	19				20			

-: Not active. MIC: Minimal inhibitory concentration

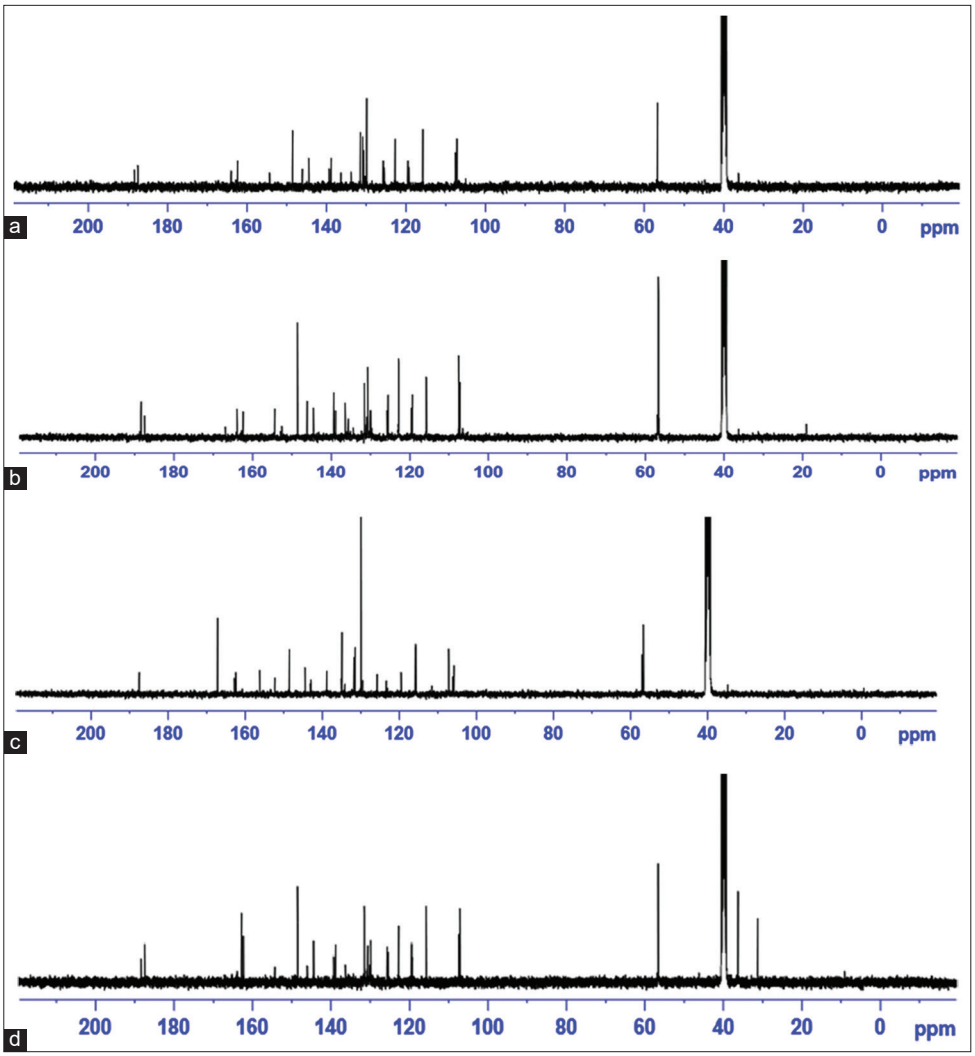


Figure 3: (a) ^{13}C-nuclear magnetic resonance (NMR) data of PTA1. (b) ^{13}C-NMR data of PIA1. (c) ^{13}C-NMR data of PTO1. (d) 13C-NMR data of PIO1

Table 4: Inhibition effect of copolyesters on the growth of *Candida albicans* and *Aspergillus niger*

Sample code	Zone of inhibition (mm)							
	Candida albicans				*Aspergillus niger*			
	25 µg	50 µg	75 µg	100 µg	25 µg	50 µg	75 µg	100 µg
PIA1	18	18	20	20	-	-	8	10
PIO1	17	17	19	19	-	-	-	-
PTA1	16	18	20	20	-	-	-	8
PTO1	14	16	18	18	-	-	-	-
Fluconazole (25 µg)					28			
Clotrimazole (25 µg)	16							

-: No activity. *C. albicans: Candida albicans, A. niger: Aspergillus niger*

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 as its antimicrobial activity[21,22] shown in Table 3.

Antifungal property (disc-diffusion method)

The antifungal activity of synthesized random copolyesters PIA1, PIO1, PTA1, and PTO1 were assayed again *Candida albicans* and *Aspergillus niger*. Clotrimazole and Fluconazole

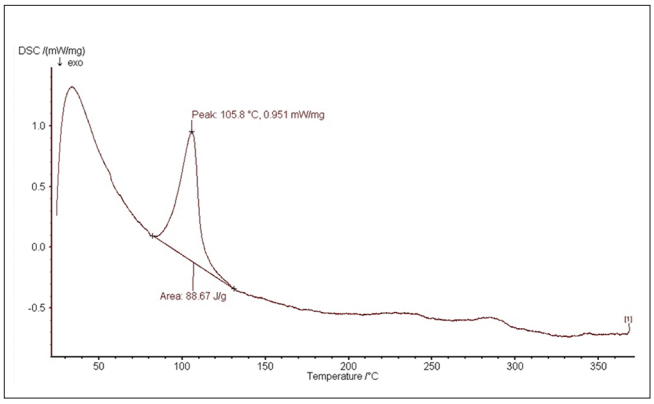


Figure 4: Thermal analysis showing by PTS1

suppressed the growth of *C. albicans* and *A. niger,* respectively, as shown in the table. Similar observations were made by Francis *et al*.[23] in the copolyesters and Sukanya *et al*.[24] in the *Phyllanthus emblica*, a medicinally valued plant shown in Table 4.

CONCLUSION

The research study reports the efficacious synthesis of random copolyesters by direct polycondensation method. Viscosity measurements reveal that the polymers synthesized are of high molecular weights. The synthesized polymers have been characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectral studies. The structural assignment of the polymers is supported by these spectral data. The copolyesters are highly soluble in polar organic solvents, characterized by solubility tests. Disc diffusion method was employed to establish and document the bactericidal and fungicidal activities of these copolyesters.

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