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IN VITRO ANTIOXIDANT EVALUATION OF SYNTHETIC COPOLYESTERS BEARING CHALCONE MOIETY IN THE MAIN CHAIN

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ABSTRACT

Five random copolyesters were synthesized using chalcone diols as monomers and aliphatic, aromatic diacid chlorides by Solution Polycondensation method. Their solubility with different solvents were checked and the viscosity of the copolyesters were also determined. The structures of the copolyesters were investigated using UV-Visible, FTIR spectroscopy. The Thermal stability of the copolyesters were studied by DSC and TGA. The polyesters were evaluated for their Antioxidant property by DPPH, Nitric oxide and FRAP method using Vitamin C as standard. The polymers exhibited good antioxidant activity.

Keywords *– Chalcones, Copolyesters, Antioxidants, DPPH, Nitric Oxide, FRAP.*

1. INTRODUCTION

Antioxidants are molecules that inhibit oxidation of other molecules. Antioxidants have diverse uses. They are used as preservatives in food and cosmetics where they help to counteract deterioration and as dietary supplements where they help to neutralize the adverse effects of oxidative stress by scavenging potentially damaging free radicals [1]. Antioxidants are used as oxidation inhibitors in fuels where they prevent the formation of engine fouling residues and prevent oxidative degradation of plastics, rubbers and adhesives thereby maintaining their strength and flexibility [2]. Phenolic acids and flavonoids possess good antioxidant activity. Chalcones are the precursors of flavonoids and are reported to have antioxidant property due to the reactive keto vinylenic group. Hydroxyl and phenyl substituents are associated antioxidant property [3]. Hence, this study aims to study the antioxidant property of synthetic random co-polyesters having chalcone moiety.

2. MATERIALS AND METHODS

AR grade Sigma-Aldrich samples of 4-hydroxy acetophenone, 4-hydroxy3-methoxy acetophenone, and ethyl vanillin were used for the synthesis of the two chalconediols. AR grade Sigma-Aldrich samples of succinyl chloride, glutaryl chloride, isophthaloyl chloride and terephthaloyl chloride were used for the five copolyesters synthesis. AR grade sample of Dimethyl acetamide (DMAc)

was used as a solvent for finding out inherent viscosity. Spectral grade DMSO-d_6 was used as internal standard for recording NMR spectra.

2.1 Synthesis of Monomer (Chalcone Diols)

The monomer chalcone diols were synthesized using Claisen-Schmidt Condensation reaction. The chalcone diols were synthesized and reported [4].

(*2E*)-1-(4-hydroxyphenyl)-3-(4-hydroxy-3-ethoxyphenyl) prop-2-ene-1-one (HHEP),

(*2E*)-1-(4-hydroxy-3-methoxyphenyl)-3-(4-hydroxy-3-ethoxyphenyl) prop-2-ene-1-one (MHEP)

2.2 Synthesis of Co-polyesters

The five co-polyesters were synthesized using two chalcone diols and four diacid chlorides namely (Succinyl Chloride, Isophthaloyl Chloride, Terephthaloyl Chloride, Gultaryl Chloride) by solution Polycondensation method.

2.3 Synthesis of PSGH

To 1g of HHEP in 100 mL R.B flask, added 10mL of dry DMF stirred till it is dissolved. Then added 0.2mL of succinyl chloride and 0.2mL of glutaryl chloride, raised the temperature to 120˚C. Left the reaction to proceed for 12 hours. After the reaction time, the reaction mixture was quenched in 50mL of n-hexane, filtered, dried and powdered. It was then reprecipitated using methanol.

Same method was adopted to synthesize other copolyesters [PIOH, POSH,PIOM,POSM] and reported [4].

The solubility of the copoyesters was checked in different solvents. The viscosity was measured by Ubbleholde Viscometer. The copolyesters were characterized by UV-Vis and FTIR spectroscopy. The Thermal stability of the copolyesters were studied by DSC and TGA.

2.4 Antioxidant Activity

2.4.1 DPPH Scavenging Activity

DPPH is a stable free radical that can accept an electron or hydrogen radical to become a stable diamagnetic molecule. Due to its odd electron, the methanolic solution of DPPH shows a strong absorption band at 517 nm. DPPH radical reacts with various electron donating molecules (reducing agents or antioxidants) and gets reduced. This results in the formation of the colourless 2,2'-diphenyl-1-picryl hydrazine. Reduction of the DPPH radicals can be estimated quantitatively by measuring the decrease in absorbance at 517 nm [5].

Procedure: 0.5 mL of DPPH was taken with 2.0 mL of polymer solution in ethanol, mixed well and kept in dark for 30 mins. The absorbance at 517 nm was measured. DPPH in ethanol served as control [5]. The test was also carried out with Vitamin C. The percentage of scavenging was calculated from the following equation

$$\% \text{ Scavenging} = \frac{(\text{Absorbance of Control} - \text{Absorbance of Test}) \times 100}{\text{Absorbance of Control}}$$

The % scavenging activity compared to Vitamin C was calculated using the formula

$$\frac{\% \text{ Scavenging activity of polymer}}{\% \text{ Scavenging activity of Vitamin-C}} \times 100$$

2.4.2 Nitric Oxide Scavenging Activity

Nitric Oxide (NO) is generated by sodium nitroprusside in solution. In the presence of an antioxidant or nitric oxide scavenger the amount of NO will be less. NO is estimated by using Griess reagent Nitric oxide gives a pink colour complex which is read at 540 nm [6].

Procedure: To 2mL of sodium nitroprusside 0.5 mL of polymer solution in ethanol was added. After incubation for 4 hours 0.5 mL of Griess reagent was added. The control tube had all the solutions except the polymer solution. The test was also done with Vitamin C. The % Scavenging and % scavenging activity compared to Vitamin C was calculated as mentioned in DPPH assay.

2.4.3 Ferric Ion Reducing / Antioxidant Power Assay

The antioxidants reduce Fe^{3+} to Fe^{2+}. This ion is then conjugated with the Ferricyanide ion to form a Prussian blue colored product, which is spectrophotometrically measured at 700 nm. The presence of SDS prevents the formation of turbidity in the solution.

Procedure: To 0.1 mL of the polymer solution added 0.9 mL 96% ethanol, 5 mL of distilled water, 1.5 mL of 1M HCl, 1.5 ml of 1% Potassium Ferricyanide, 0.5 mL of 1% SDS (Sodium dodecyl sulphate) and 0.2% Ferric chloride. Ascorbic acid is used as a reference. Boiled the mixture in a water bath at 50° C for 20 min, rapidly cooled and mixed well. The control tube had all the solutions except the polymer solution. The absorbance at 750 nm is measured [7]. The difference in OD of test and control was noted.

3. RESULTS AND DISCUSSION

3.1 Solubility

Solubility of the random copolyesters depends upon its crystallinity. The solubility decreases as the molecular weight increases. Copolyesters with aliphatic diacid chlorides in their polymeric chain are more soluble than the polymers with aromatic diacid chlorides. This is due to the presence of the rigid aromatic ring increases the molecular weight of the polymers, so the solubility is decreased.

All the polymers synthesized were soluble in aprotic polar solvents like DMF, DMSO, DMAc, and methanol and partially soluble in polar solvents like methanol and acetone but insoluble in non-polar solvents like n-hexane and benzene, this may be due to the intermolecular attraction between the polar solvents and the ester linkage present in the polymer molecule.

3.2 Viscosity

The inherent viscosity of the polymer increases with the length of the spacer group in the diacid chlorides and therefore the molecular weight also increases. The inherent viscosity of the polymer's ranges from 1.01 to 1.3.

3.3 Spectral Studies

3.3.1 UV-Visible Spectroscopy

The UV-Visible spectra of random copolyester (PSGH) was recorded at room temperature in methanol solution. The absorbance is shown in figure 1. The absorption maximum is 310 nm corresponding to the Chalcone group. Hence it is inferred that Chalcone moiety is incorporated in the polymer backbone. The peak absorption of the curves is mainly due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ transition and due to the excitation of C=O group of the molecule.

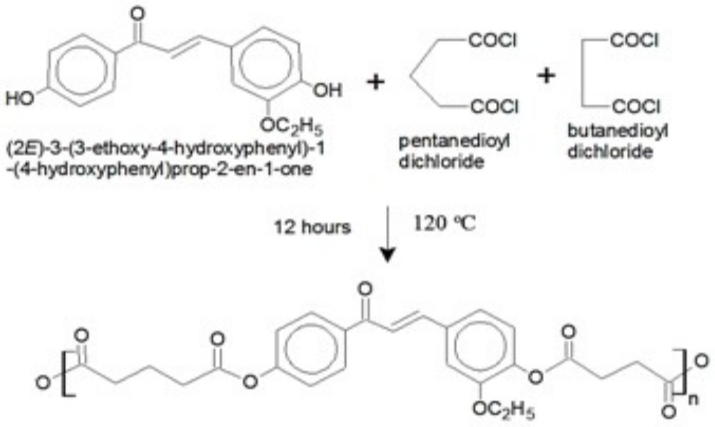
3.3.2 FTIR Spectroscopy

The FTIR spectra of the copolyesters were recorded in KBr pellet and the spectrum is shown in the figure 2. The C-H stretching appears at the range 2900-3160 cm^{-1} the olefinic double bond (-C=C-) stretching appears at 1500 -1532 cm^{-1}, the copolyesters showed the ester carboxyl stretching band from 1709 to 1759 cm^{-1}. The α, β unsaturated carbonyl stretching band is from 1583 to 1598 cm^{-1}. The C-O stretching of ester is denoted by 1210 cm^{-1}. The terminal OH stretching occurs at the range 3300 – 3800 cm^{-1}.

3.3.3 Thermal Properties of PSOH

The TGA curve of this polyester indicates that the PSOH is stable up to 377°C and it is shown in the figure 3. Thermal Stability of the copolyester PSOH was studied by thermogravimetric analysis in air and DSC Thermograms recorded in Nitrogen atmosphere at the scan rate of 10°/ min. The Glass Transition temperature is 94 °C and it is above room temperature and the melting point is at 236°C and it is shown in the figure 4. Other copolyesters are found to be thermally stable by DSC and TGA.

All the copolyesters were found to be having good antioxidant activity. Among the five PSOH and PSGH have higher activity than the others by DPPH and Nitric oxide Assay. But PSOM was found to be having better activity by FRAP method. The antioxidant effect of the chalcone based copolyesters may be due to the presence of the end hydroxyl group of the chalcone moiety in the copolyester backbone. Similar observations were reported by Pei-ze-Li et al [8].



Scheme-1: Synthesis of PSGH

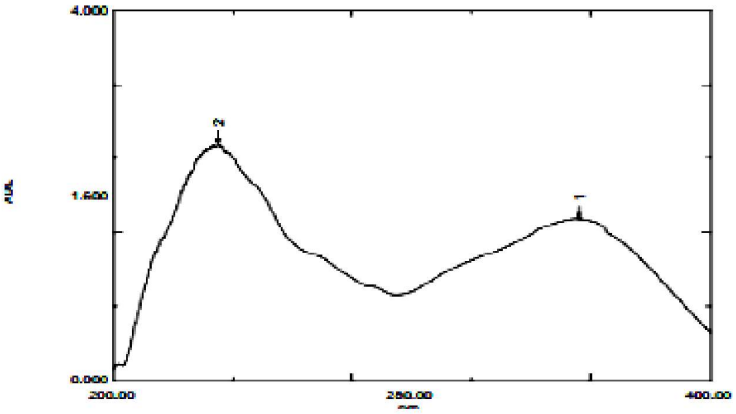


Fig. 1: UV-Visible spectrum of PSGH

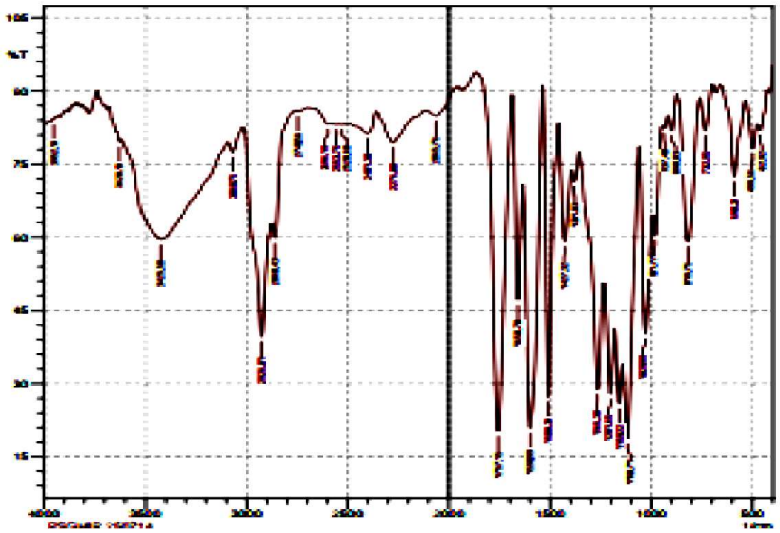


Fig. 2: FTIR Spectrum of PSGH

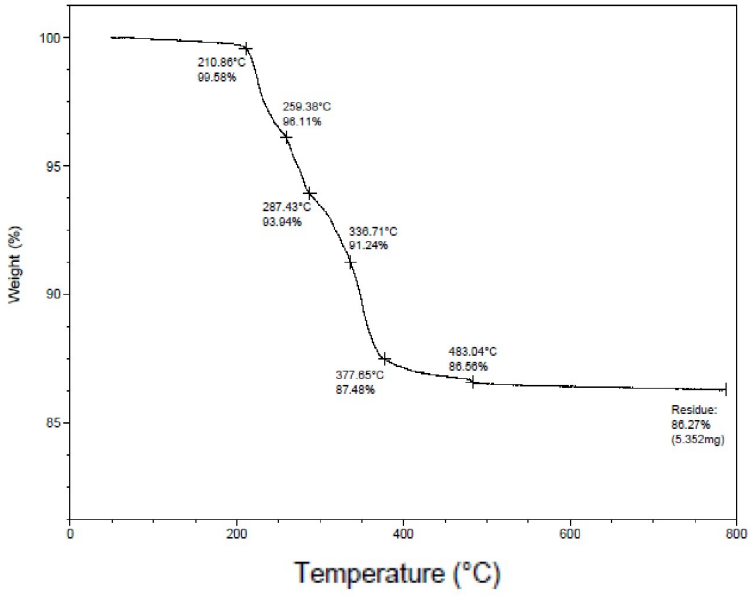


Fig. 3: TGA of PSOH

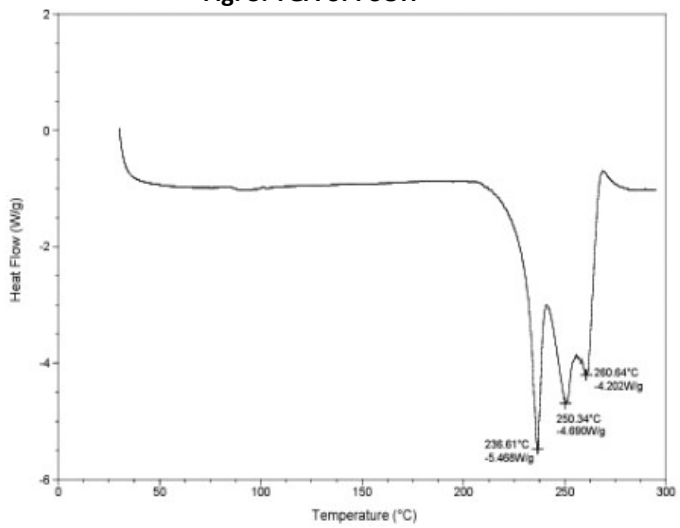


Fig. 4: DSC of PSOH

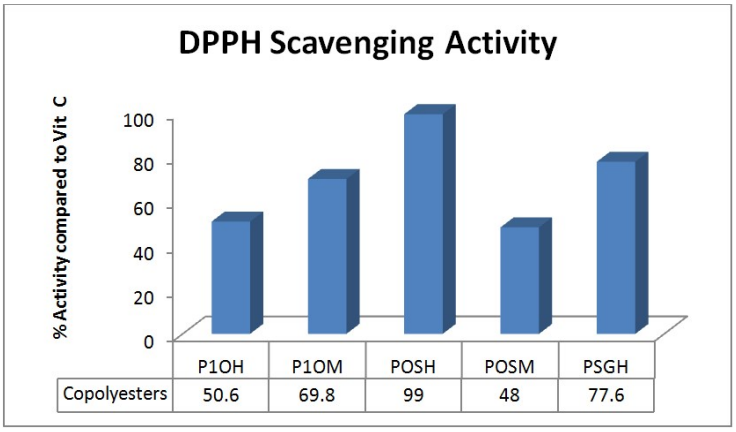


Fig. 5: DPPH - Values represent mean of three experiments

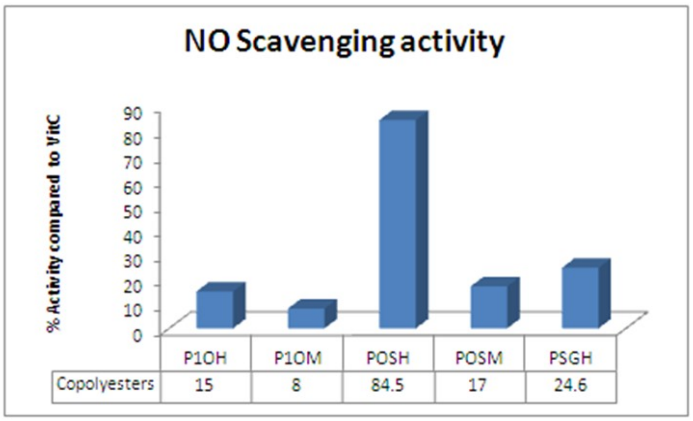


Fig. 6: NO - Values represent mean of three experiments

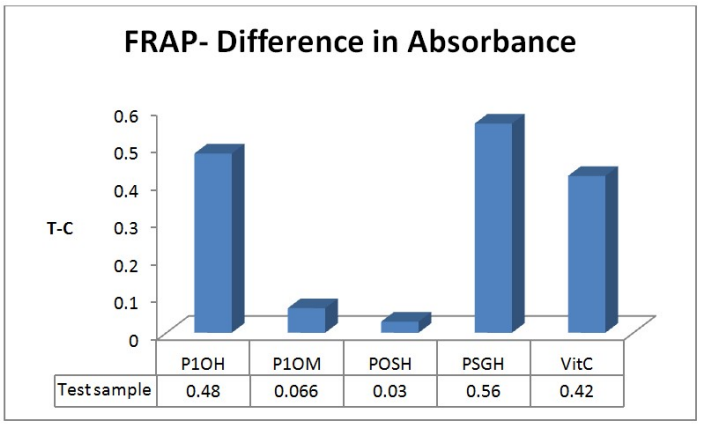


Fig. 7: FRAP - Values represent mean of three experiment.

4. CONCLUSION

We have synthesised five chalcone based random copolyesters and characterised them. The copolyesters were soluble in polar aprotic solvents. The inherent viscosity measured reveal that the copolyesters synthesised were of high molecular weight. The UV-Vis spectrum of copolyesters confirm the incorporation of chalcone moiety in polymer backbone and FT-IR spectra reveals the ester functionality. The thermal stability was ascertained by DSC and TGA. Among the five copolyesters PSOH, PSGH and PIOH has very good activity when compared to the reference vitamin C.

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