



Synthesis, Characterization and *in vitro* Antimicrobial, Anticancer Activity of Random Copolyester using Orcinol

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In present study, a novel random copolyester *i.e.* poly(3-oxy-5-methylphenyl-4-oxynaphthal-1-yl)isophthalate (PONI) was synthesized through solution polycondensation methodology involving orcinol, 1,4-naphthalene diol and isophthaloyl chloride and its solubility in common solvents along with viscosity measurements were performed. The structure of the repeat units in the polyester chain were ascertained based on the spectral characterization of UV-visible, FTIR, ¹H & ¹³C NMR techniques. Thermal analysis of the copolyester were performed by TGA and DSC studies. The activation energy for thermal decomposition of polyester was estimated by well-known kinetic methods. The surface morphology and crystalline nature of the polymer were explored by employing SEM and WAXD methods. The antimicrobial efficacy of copolyester was assessed through well-diffusion method using a Gram-positive and a Gram-negative bacteria. The *in vitro* cytotoxicity of the polyester prepared was verified against HeLa cell line using MTT assay.

Keywords: Orcinol, Isophthaloyl chloride, 1,4-Naphthalene diol, Copolyester, Antimicrobial Activity, Anticancer activity.

INTRODUCTION

The colossal literature available on polyesters of terephthalic acid and relatively less work on isophthalates till date advocates that many new, exciting polymeric materials can be developed from these monomers involving diverse diols to build polymer chains and modify the repeat structure. Polyesters possessing only aliphatic moieties in the main chain have considerably lower melting temperatures along with higher solubility and ability to undergo biodegradation [1]. However, these shortcomings can be overpowered by the induction of aromatic units in the polymeric back bone [2]. Contemporary progresses in research have rekindled the interest in polyesters based on isophthalic acid and derivatives known for their superior thermal stability [3]. A meticulous choice of monomers is of paramount significance in the synthesis of a copolyester with desired properties like thermal stability, semi crystalline nature, biodegradability leading to wide range of applications.

As a result of exhaustive survey, orcinol as a unique monomer along with isophthaloyl chloride have been preferred to synthesize the random copolyester. Details on innovative copolyesters based on 5-(1-methoxy-*o*-carborane)dimethyl isophthalate

with outstanding neutron shielding properties for variety of applications ranging from environment to body protective substances are available in literature [4]. Reports on partial substitution of reasonably renewable random poly(butylene furoate) by isophthalate moieties reducing the crystalline nature of the polymer markedly are available [5]. Ubach *et al.* [6] studied the rate of crystallization being lessened due to augmentation in isophthalate units in a sequence of poly(ethylene terephthalate-*co*-isophthalate) polyesters along with decline in the enthalpy of the polyesters combined with lowering of melting temperatures and even leading to amorphous nature. Notable change in crystallization pattern and lowered rate due to attachment of isophthalate units into the polymeric backbones of distinct copolyesters based on 3,4'-bibenzoate, 4,4'-bibenzoate groups and ethylene glycol were observed by Edling *et al.* [7]. Literature devoted to exclusively aryl thermotropic copolyesters comprising 4,4'-biphenol derivatives along with isomers of naphthalene diols show that the inclusion of non-linear monomers leads to decline in the T_m values of polyesters [8]. Bagheri *et al.* [9] reported lowered rigidity among homologous copolyesters comprising of non-linear isophthalic acid moieties formulated by polycondensation of 4,4'-biphenyl analogs with

them. These polyesters reveal the significance of flexible spacers in the polymer chain to exhibit noteworthy odd-even effects. Enhancement in gas permeability owing to the presence of symmetric methyl substituents among aromatic polyesters encompassing perhydrocumyl cyclohexylidene units polycondensed with isophthaloyl chloride showing exceptional solubility in common organic solvents have been reviewed by Shingte *et al.* [10]. Recently investigation on completely bio-based poly-(butylene isophthalate) disclosed extremely sluggish crystallizing nature due to the *meta*-configuration among the esters groups containing isophthalate units leading to development of lamellar crystals and sizeable spherulites [11].

In recent times, copolymer containing poly(ricinoleic acid) with poly(propylene isophthalate) was found to acquire superior mechanical properties along with remarkable antibacterial activity has been obtained [12]. Outstanding mechanical properties combined with water resistance has been observed in branched water-soluble polyester concocted using sodium dimethyl isophthalate-5-sulfonate utilized as surface-sizing agents for cellulose fiber paper [13]. Karayannidis *et al.* [14] have proved that by progressively augmenting the proportion of ethylene-isophthalate units in PET results in diverse tensile mechanical features and thermal performance. As an extension of investigation in this domain, the current work encompasses the synthesis of a random copolyester having Orcinol as the key component in the main chain of the polyester along with isophthaloyl chloride and 1,4-naphthalene diol as the comonomers manufactured *via* polycondensation scheme followed by characterization involving precise analytical tools to yield polymeric materials with superior thermal characteristics coupled with ability to undergo biodegradation.

EXPERIMENTAL

Isophthaloyl chloride and orcinol were acquired from Merck, India while 1,4-naphthalenediol was procured from Avra synthesis Pvt. Ltd. India. AnalaR samples of solvents and chemicals were used as such in the present study. The inherent viscosity of the copolyester was ascertained in *o*-chlorophenol employing Ubbelohde viscometer, from the flow times achieved for the solution and pure solvent. The UV-visible spectrum was recorded with Shimadzu-UV-160A spectrophotometer employing acetone as solvent in the wavelength ranging from 200 to 800 nm and the FTIR spectrum of the polyester was documented by using Bruker FTIR Alpha spectrometer in the range 4000-450 cm^{-1} with the sample being integrated in KBr pellets. The ^1H NMR spectrum was obtained utilizing Jeol 500 spectrometer operating at 500 MHz employing CDCl_3 as solvent and tetramethyl silane (TMS) was used as the internal standard. The ^{13}C NMR spectrum was recorded with Varian 500 MHz using deuterated chloroform solvent. Chemical shifts are accounted in ppm from tetramethyl silane (TMS). Thermogravimetric analysis of the copolyester was carried out in N_2 environment by making use of SDT Q600 thermal analyzer. Approximately 10 mg of the polyester sample was heated from 50 to 800 $^\circ\text{C}$ at a heating rate of 20 $^\circ\text{C min}^{-1}$ and weight loss of the sample over the entire range of temperature utilized was detailed. Similar sample quantity and heating scan rate was

utilized in the DSC measurements which were done on NETZSCH STA 449 F3 Jupiter thermal analyzer. WAXD studies utilizing X'Pert Pro PW3050 diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) scanned over the 2θ range 10 $^\circ$ to 80 $^\circ$ were performed and the surface morphology was investigated using scanning electron microscope-Tescan Vega 3 with accelerating voltage 30 kV. The anti-proliferative effect of the polyester was experimented against HeLa (cervical carcinoma) cell line involving MTT method while the established Agar disc diffusion method on Mueller-Hinton agar (MHA) medium and Sabouraud dextrose agar (SDA) medium was employed to assess the antibacterial assay of the polyester sample.

Synthesis of random copolyester: Fluorinated polyarylates being prepared by high-temperature solution polymerization reaction involving refluxing of 4,4'-biphenyldicarbonyl chloride with substituted bisphenols in *o*-dichlorobenzene is given in the literature [15]. A comparative account of melt and solution polycondensation methodologies [16] utilized in the synthesis of aromatic polyesters possessing phenyl rings with non-coplanar conformation among the 2,2'-dimethyl substituted biphenylene units in the backbone of the polyester prepared using dicarbonyl dichloride and diol monomers at high temperatures has revealed higher inherent viscosity values by melt polycondensation technique. Rais *et al.* [17] have described the preparation of random copolyesters by polycondensation reaction involving a chalcone diol with isophthaloyl chloride. The synthesis of medium to reasonably high molecular weight aromatic copolyesters carrying suspended maleimide units from isophthaloyl chloride and substituted bisphenols through low temperature solution polycondensation technique have been reported by Nagane *et al.* [18]. Based on the literature cited above, it was decided to employ solution polycondensation methodology to obtain the copolyester in an analogous manner in the present research inquiry. The reaction flask was charged with 150 mL of 1,2-dichlorobenzene followed by orcinol (1.241 g, 0.01 mol), 1,4-naphthalenediol (3.2 g, 0.02 mol) and isophthaloyl chloride (6.09 g, 0.03 mol) in the mole ratio 1:2:3 and the contents in the vessel were refluxed thoroughly for about 40 h at 150 $^\circ\text{C}$ in nitrogen gas atmosphere with consistent swirling. The mixture was poured into 250 mL of petroleum ether after cooling and allowed to stand overnight and filtered. The crude sample was originally washed with deionized water then dissolved in minimum amount of acetone and finally poured into water. The solution was in due course evaporated to obtain pure polyester which was dried in vacuum over P_2O_5 . The yield of the copolyester obtained was around 69%. The solution polycondensation reaction is depicted in **Scheme-I**.

RESULTS AND DISCUSSION

Solubility and viscosity studies: Chemical structure of recurring groups and polarity of solvents are vital in the dissolution of polymers. Comparatively high molar mass aromatic polyesters comprising of naphthalene diols were reported by Tamami *et al.* [19] to be soluble or moderately soluble in solvents like chloroform and tetrahydrofuran. Recently in a literature on aromatic copolyesters, it was found that unique aromatic

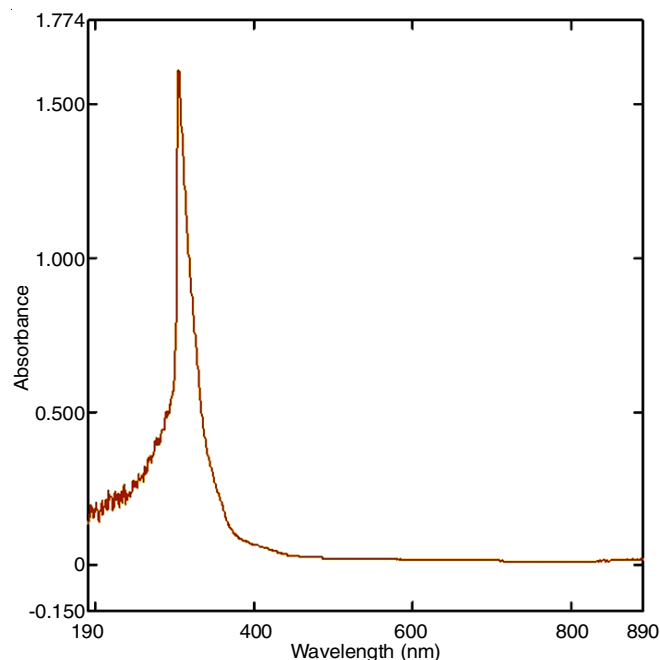
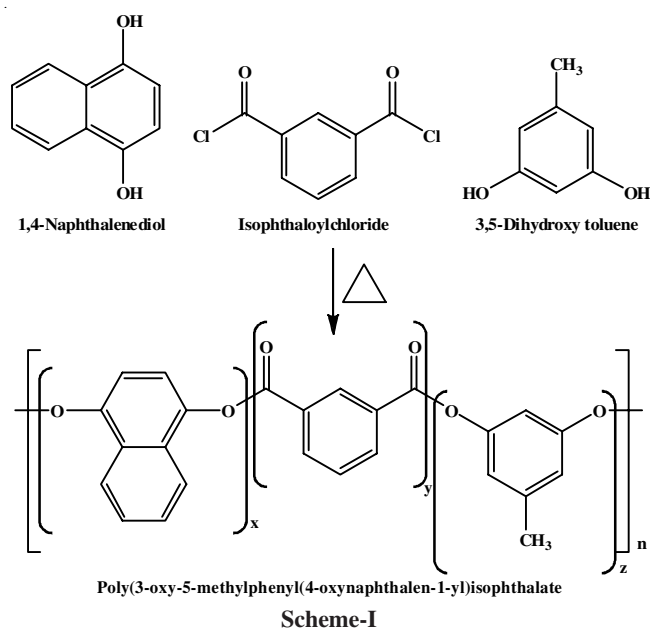


Fig. 1. UV-visible spectrum of PONI

polyesters involving (4-phenoxyphenyl)phenylmethene linkage with isophthaloyl chloride have been fabricated and the amorphous polyarylates prepared were noticed to be clearly soluble in organic solvents even at room temperature [20]. On the basis of the previous reports, the copolyester formed was examined for its solubility in various solvents like acetone, chloroform, DMF, DMSO, *o*-chloro phenol, methanol and THF in the present study. As expected the polyester was sparingly soluble in methanol compared to other solvents in which it was found to be considerably soluble.

Viscosity measurement is a crucial procedure in the determination of molecular weight of polymers. Macromolecules possessing exceptional molecular weight generally upgrade the viscosities of their solutions [21]. Inherent viscosity values ranging from 0.32 to 0.49 dL/g have been obtained in aromatic polyesters fabricated using isophthaloyl chloride with various cardo bisphenols through solution polycondensation route [22]. An innovative aromatic cardocopolyesters synthesized from novel bisphenols with reduced viscosities in the range 0.36 to 0.83 dL/g and inherent viscosity values of 0.19 to 0.25 dL/g among polyarylates containing tetraphenylfuran synthesized from isophthaloyl chloride are also observed [23,24]. Analogous to the previous observations, the inherent viscosity (η_{inh}) of the copolyester in the current study at 30 °C for 0.1 g/dL solution was estimated to be 0.24 dL/g based on the relative viscosity data attained from the flow time of copolyester solution and pure solvent (*o*-chloro phenol) by employing Ubbelohde viscometer.

UV-visible studies: The optical property and structural changes if any due to photochemical behaviour of polyesters can be studied by irradiating under UV light [25]. The UV-visible spectra of aromatic polyesters prepared by Chung *et al.* [26] revealed the absorptions at 260 to 320 nm due to the presence of aromatic groups. The electronic absorption spectrum of the copolyester synthesized in this study shown in Fig. 1, reveals a peak at around 310 nm as indicated by literature, which

is the testimony for highly conjugated system studied in the repeat unit of the copolyester.

FTIR studies: The FTIR spectrum of copolyester exhibited in Fig. 2 reveals the following characteristic absorption bands that are suggestive of aromatic polyesters: 1753 cm^{-1} (C=O), 1224 cm^{-1} (C–O), 1598 cm^{-1} , 1460 cm^{-1} (C=C arom.), which are confirmed by the study on polyarylates by Bucio *et al.* [27]. The broad band at 3450 cm^{-1} can be ascribed to the O–H stretching and another band around 3076 cm^{-1} , which may be due to aromatic C–H group as suggested by Hsiao *et al.* [28]. The spectrum exhibits bands near 717 cm^{-1} and 752 cm^{-1} arising from C–H out-of-plane bending mode of phenyl ring. This finding is consistent with the recent reports found in literature [29,30].

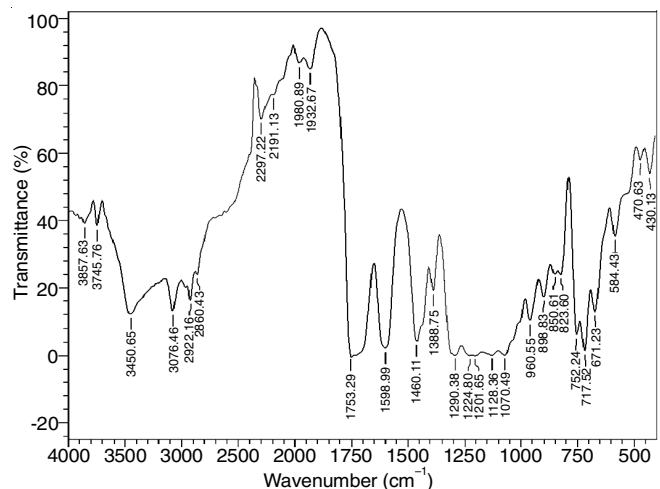
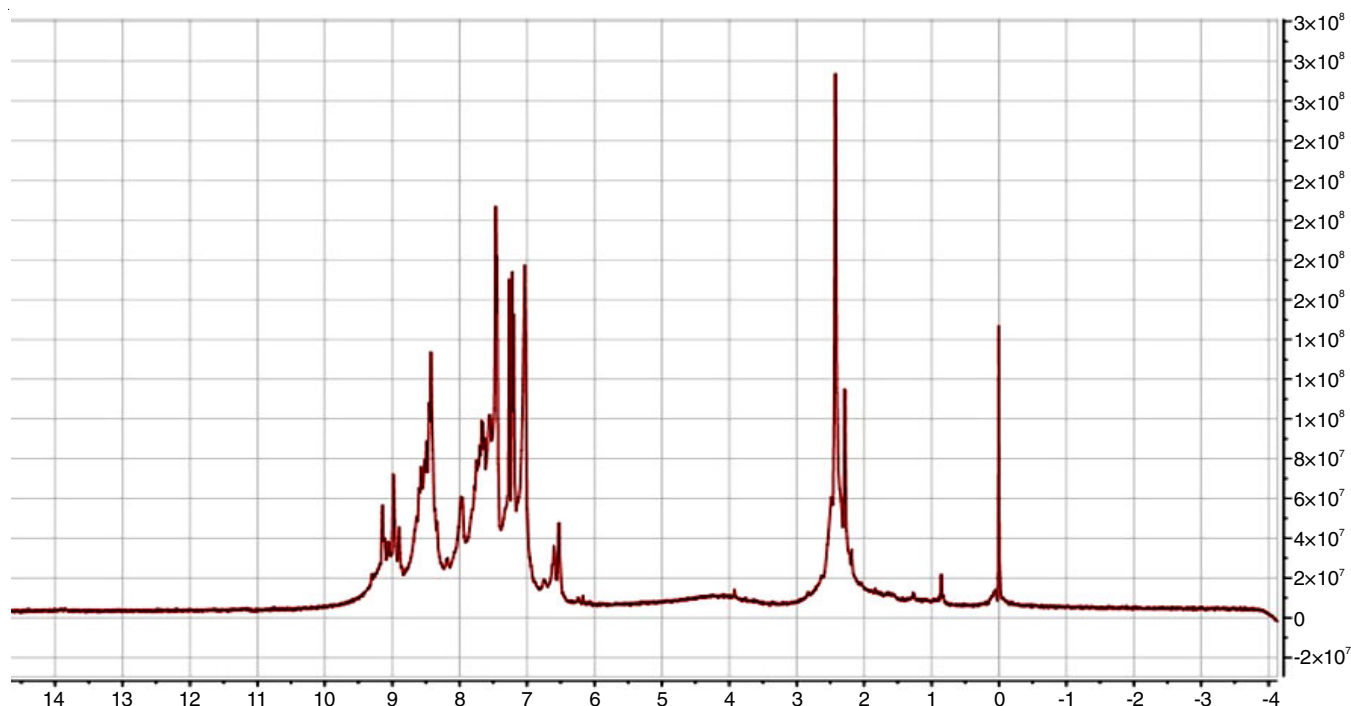


Fig. 2. FTIR spectrum of PONI

NMR studies: Fig. 3 displays the ^1H NMR spectrum of copolyester sample recorded at 500 MHz (CDCl_3 residual

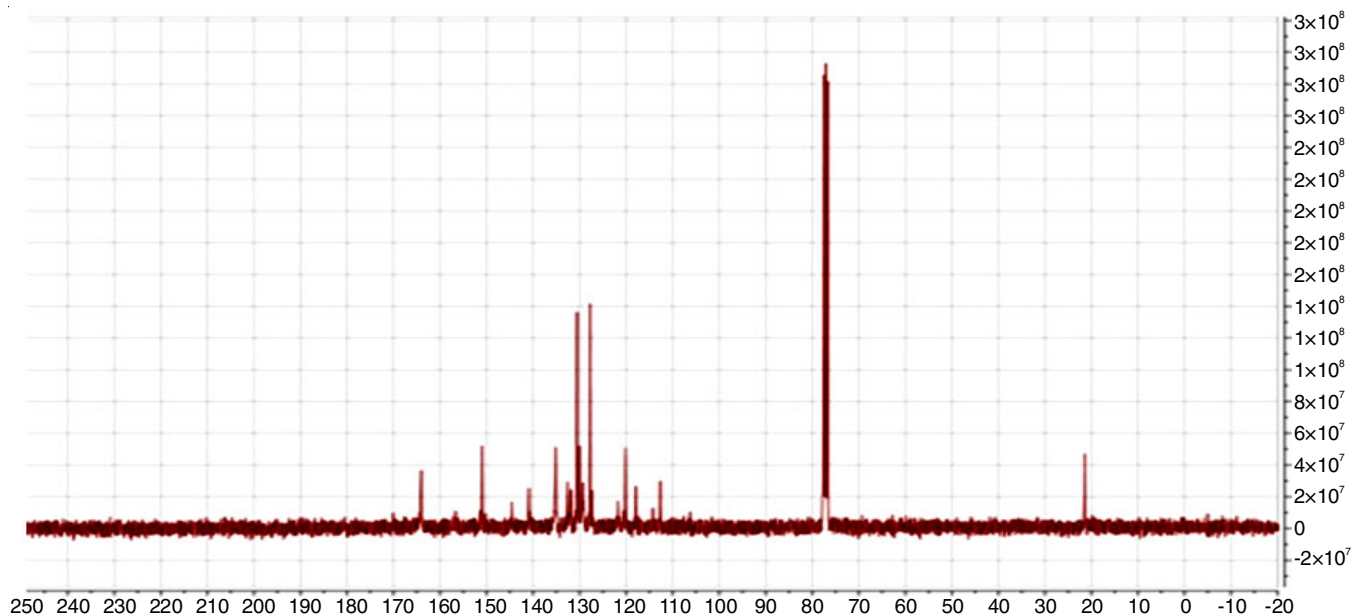
Fig. 3. ^1H spectrum of PONI

signal at 7.26 ppm). A resonance at $\delta = 2.3$ to 2.5 ppm is attributed to the protons of the methyl group bonded to phenyl rings in the polyester as suggested by Loría-Bastarrachea *et al.* [31]. The multiplet detected at $\delta = 6.5$ to 9.5 ppm is suggestive of the aromatic protons existing in the polyester, which is also established in the literature [32].

^{13}C NMR spectrum of the sample recorded at 500 MHz (CDCl_3 residual signal at 77.2 ppm) shows the characteristic resonances between 20 to 25 ppm and can be assigned to the methyl carbon attached to the aromatic units in the polyester and the peaks between 110 to 155 ppm were attributed to the aromatic carbon atoms [33,34] (Fig. 4). A singlet peak around

165 ppm can be credited to the carbonyl group in the polyester [35].

Thermal studies: To analyze the effect of temperature on the copolyester, the thermogram is presented in Fig. 5, which reveals that the polyester was thermally stable up to 580 °C (two stages of decomposition), which may be attributed to the presence of aromatic moieties in the main chain of polyester. These results are in synchronization with analogous observations on aromatic polyesters involving isophthaloyl chloride [36]. The first stage of decomposition involving about 18% weight loss was completed around 250 °C and almost entire quantity of polyester degraded in the next stage.

Fig. 4. ^{13}C spectrum of PONI

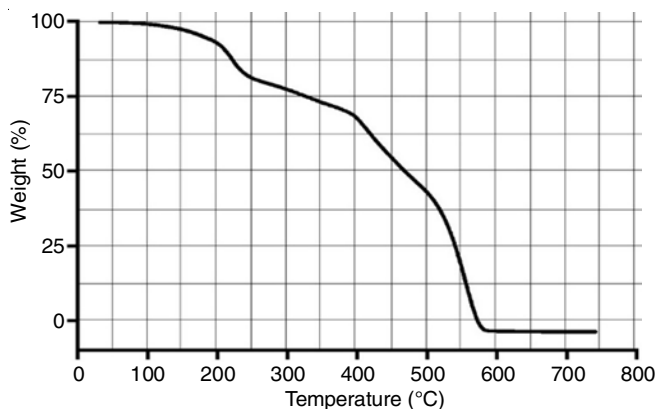


Fig. 5. TGA thermogram of PONI

Differential scanning calorimetry (DSC): There are plentiful reports on utilization of DSC analysis in the analysis of thermal characteristics of aromatic polyesters [37,38]. The DSC thermogram of PONI represented in Fig. 6 reveals a lower T_g value around 49.2 °C. This particularly low value for glass transition temperature in the copolyester may be due to the presence of naphthoyl units, which may disturb the linearity and thus make the polymer backbone less rigid [39]. T_m of this polyester was observed at 209.1 °C in accordance with reports on aromatic copolyesters in the literature [40].

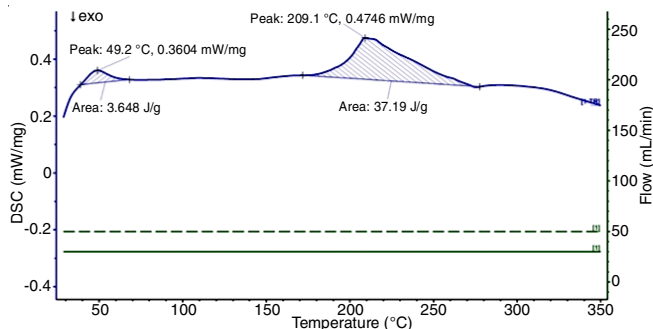


Fig. 6. DSC thermogram of PONI

Wide angle X-ray diffraction: The crystalline nature of the copolyester was analyzed by wide angle X-ray diffraction analysis. It was observed from the X ray diffractogram (Fig. 7) exhibited peaks around $2\theta = 20-70^\circ$, which suggests that the copolyester PONI was more amorphous indicative of moderate degree of crystallinity, which can be confirmed based on the observations by Hsiao & Chiou [40]. Charati *et al.* [41] also desc-ribed comparable results for aromatic polyesters based on isophthaloyl chloride. In addition, the copolyester reveals interplanar spacing ranging from 3.69696 to 1.38664 Å corresponding to 2θ values 24.0727° and 67.5558°, respectively as shown in Fig. 7.

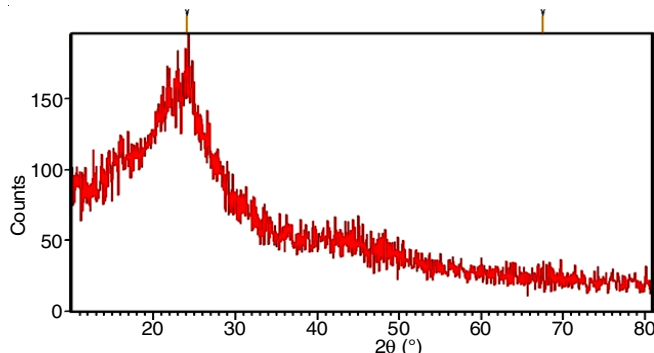


Fig. 7. X-ray diffraction of PONI

Scanning electron microscopy: The morphology of the copolyester was examined using SEM analysis. The scanning electron micrographs of copolyester (Fig. 8) portrays a considerable number of discrete imperfections found all over the surface. Upon magnification the copolyester surface reveals the features such as holes and pits as reported in the literature [42]. Cloud like pattern comprehensively found throughout the micrograph revealed the unique morphology reminiscent of micro voids.

Antimicrobial activity: The *in vitro* antimicrobial activity of the polyester was ascertained by well-diffusion method emp-

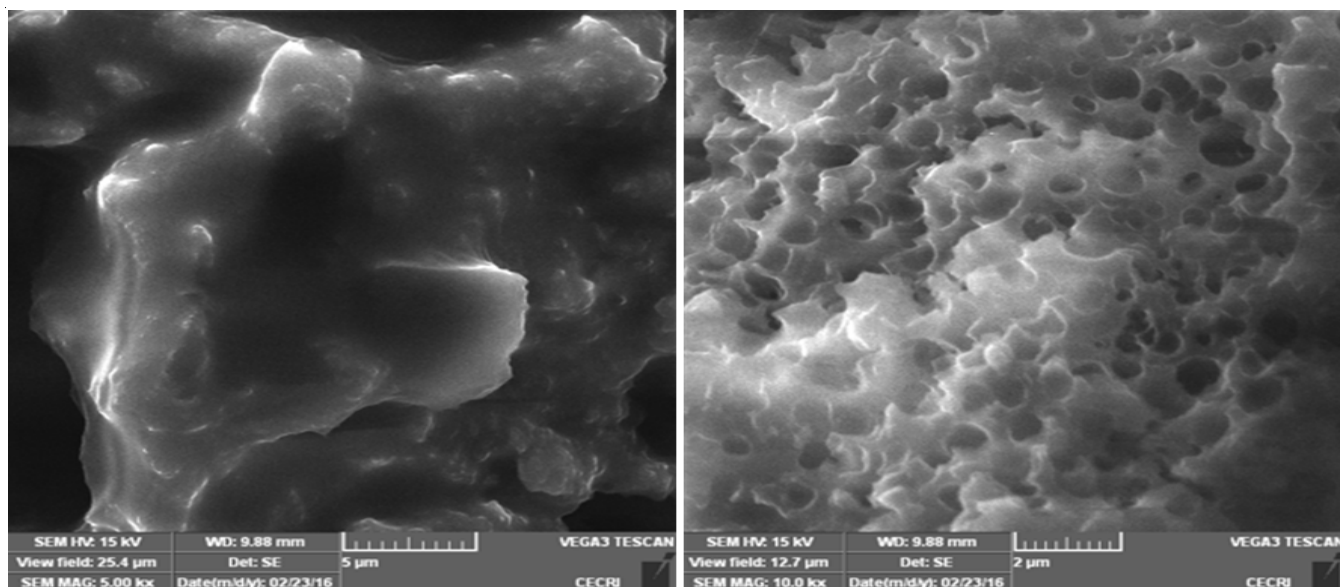


Fig. 8. SEM micrographs of PONI

loying Mueller Hinton Agar (MHA) medium against Gram-positive bacteria (*Bacillus cereus*) and Gram-negative bacteria (*Salmonella typhi*). The polyester demonstrated dissimilar antimicrobial activities against the pathogens with inhibition zones ranging from 8 to 14 mm (Table-1). Three concentrations (1, 2 and 3 mg/mL) of the copolyester were tested in the study and revealed diverse values of zone of clearance as reported by Kalpana & Nanthini [43].

Concentration (15 μ L)	Inhibition zone (mm)	
	<i>Bacillus cereus</i>	<i>Salmonella typhi</i>
1 mg/mL	–	10
2 mg/mL	–	13
3 mg/mL	8	14
Chloroform	–	5
Streptomycin	28	19

Anticancer activity: The MTT test results for HeLa cell viability in variety of substances has been examined and documented [44]. In present study, the anticancer activity of the copolyester PONI was tested against HeLa (cervical carcinoma) cell line using MTT assay [45]. The percentage cell viability of copolyester at different concentrations from 50 to 100 μ g/mL were determined. Three concentrations namely 50, 60 and 100 μ g/mL triggered 75 to 80% cell viability against HeLa cell line in comparison with 70 and 80 μ g/mL concentrations (Fig. 9). Thus, *in vitro* cytotoxicity experiments using HeLa cervical cancer cells showed considerable cytotoxic effect for the tested polyester.

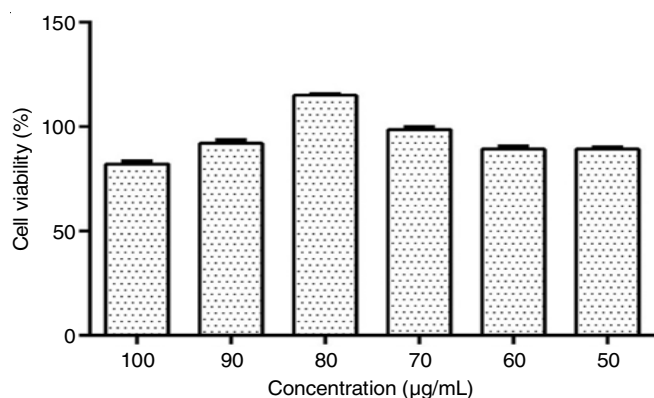


Fig. 9. Anticancer activity of PONI

Activation energy: Exhaustive survey of literature divulges the thermal performance of polyesters and their decomposition can be scrutinized by means of thermogravimetric analysis including kinetic processing of data involving methodologies given by Reich-Levi, Coats-Redfern, Flynn-Wall-Ozawa and Kissinger as reported by Hamciuc *et al.* [46]. The amalgamation of thermogravimetric analysis data with the kinetics involved in the decomposition phenomenon in a macromolecule has been observed [47]. The results of thermogravimetric analysis on copolyester in accordance with two representative common kinetic methods utilized to estimate the activation energy of thermal decomposition of polyesters is presented in Table-2. Figs. 10 and 11 depict the activation energy curves for the synthesized copolyester PONI by Murray & White and Coats & Redfern methods, respectively. The estimated values of activation energies based on the methods given above were found to be 9.98 and 10.96 K cal mol⁻¹, respectively which are in good agreement with each other and also in accordance with the previous findings in literature based on the comparison of activation energy data for thermal decomposition of polyesters involving different methodologies [48].

Conclusion

The copolyester PONI was synthesized *via* solution polycondensation method involving orcinol, 1,4-naphthalene

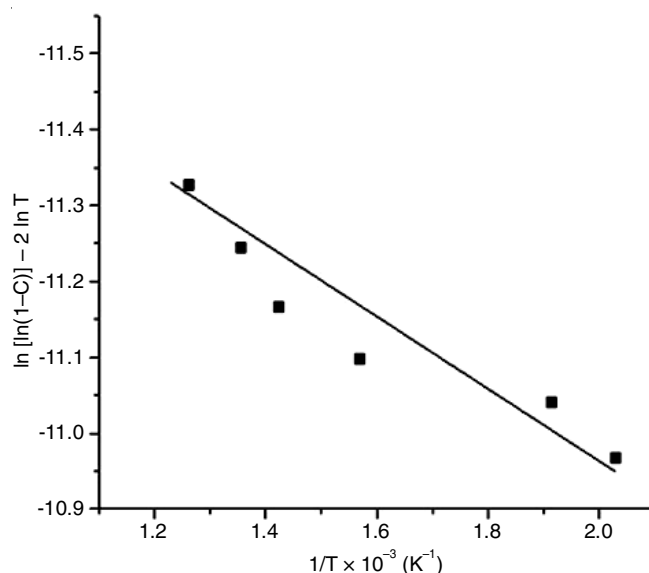


Fig. 10. Activation energy plot by Murray and White method of PONI

Degradation (%)	T (K)	$T^{-1} \times 10^{-3} K^{-1}$	1-C	2 ln T	T^2	ln (1-C)	log [ln(1-C)]	ln [ln(1-C)]	ln [ln(1-C)] - 2 ln T	log [ln(1-C)]/T ²
10	493	2.0283	90	12.4010	243049	4.49	0.652	1.501	-10.9678	2.68×10^6
20	523	1.9120	80	12.5191	273529	4.38	0.641	1.477	-11.0421	2.34×10^6
30	638	1.5673	70	12.9166	407044	4.24	0.627	1.444	-11.0987	1.54×10^6
40	703	1.4224	60	13.1107	494209	4.09	0.611	1.408	-11.1667	1.23×10^6
50	738	1.3550	50	13.2078	544644	3.91	0.592	1.363	-11.2448	1.08×10^6
60	793	1.2610	40	13.3516	628849	3.68	0.565	1.302	-11.3283	8.98×10^7
70	813	1.2300	30	13.4014	660969	3.40	0.531	1.223	-11.4282	8.03×10^7
80	823	1.2150	20	13.4259	677329	2.99	0.475	1.095	-11.5751	7.01×10^7
90	838	1.1933	10	13.4620	702244	2.30	0.361	0.832	-12.0752	5.14×10^7

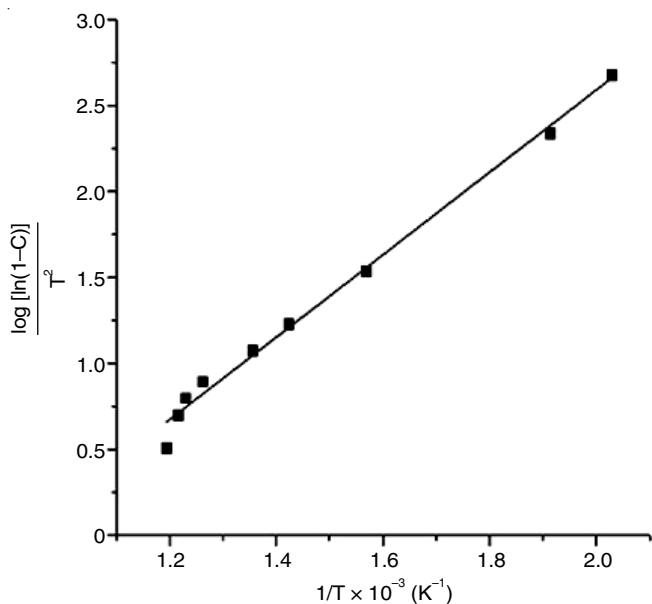


Fig. 11. Activation energy plot of PONI by Coats & Redfern method

diol and isophthaloyl chloride and found to be thermally stable up to 580 °C. The chemical structure was established using conventional spectral methods namely UV-visible, FTIR and ^1H & ^{13}C NMR spectroscopy. The band at 1753 cm^{-1} indicative of carbonyl stretching was observed in the FTIR spectrum of the polymer confirming the formation of the ester linkage. The spectral data obtained was in accordance with the chemical structure suggested for the repeat units in the polyester. The amorphous halo in the WAXD pattern of polyester confirmed its nature. The SEM micrograph indicates irregular surface morphology in the polyester. The thermal stability was confirmed by relatively higher activation energy values obtained by conventional kinetic methods for thermal decomposition in the polyester. The aromatic polyester exhibited antimicrobial and anticancer activities and can be recommended for additional experimental work to ascertain its diverse applications.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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