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SYNTHESIS AND CHARACTERIZATION OF CERTAIN NEW RANDOM COPOLYESTERS

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ABSTRACT

Three biodegradable aliphatic random copolyesters PMMC (Poly-Mannitol malonate-co-mannitol citrate), PPAC (Poly propylene azelate-co- propylene citrate), and PSGC (Poly sorbitol glutarate-co-sorbitol citrate) were synthesized by direct melt polycondensation using Titanium tetra isopropoxide as a catalyst. The biodegradable polymers Structural arrangement confirmed by FT-IR ,^{1}H NMR and ^{13}C NMR analysis. The crystalline nature of synthesized polyesters was determined by X-Ray Diffraction and Differential scanning calorimetry all the three synthesized polyesters having Biodegradability which was confirmed by weight loss methodology. The Synthesized biodegradable polyesters will be useful in drug delivery and biomedical application.

KEY WORDS

Biodegradable Polymers, Aliphatic Polyesters, D-Mannitol based polymers.

INTRODUCTION:

Polymers play an important role in the production of various commodity products ranging from mega sized products to nano sized products more than 110 million ton of plastics are produced in the world half of them are destroyed within a short time and remained in garages for decades. About 25 million tons plastics per year have accumulated in nature which may lead to severe environmental pollution [1-3]. To avoid such stagnation, it is necessary to produce recyclable and biodegradable polymers [3-8]. The simplest way for reducing bio resistant synthetic polymers is to produce biodegradable polymers. Biodegradation is an effective method for eliminating some polymeric wastes under composting and land filling conditions. Now a days a wide Varity of green polymers which show variation in their physical properties and mechanical properties along with biodegradability are in production [8-12]. Hence, the development of new biodegradable polymer systems has played vital role in the area of research. At present, different copolyesters have been synthesized and characterized direct melt poly condensation is a very useful method for production of biodegradable polyesters as it is environmentally safe, and it comes under green chemistry [8-15]. In this study, we dealt with the investigation on the synthesis, characterization as well as biodegradation properties of certain new random copolyesters which have aliphatic moieties in their polymer back bone. Biodegradable polymers used in drug delivery and biomedical application. Among synthetic polymers, biodegradable polymers have been paid more attention since they have the features of biodegradability and compatibility [16-21].

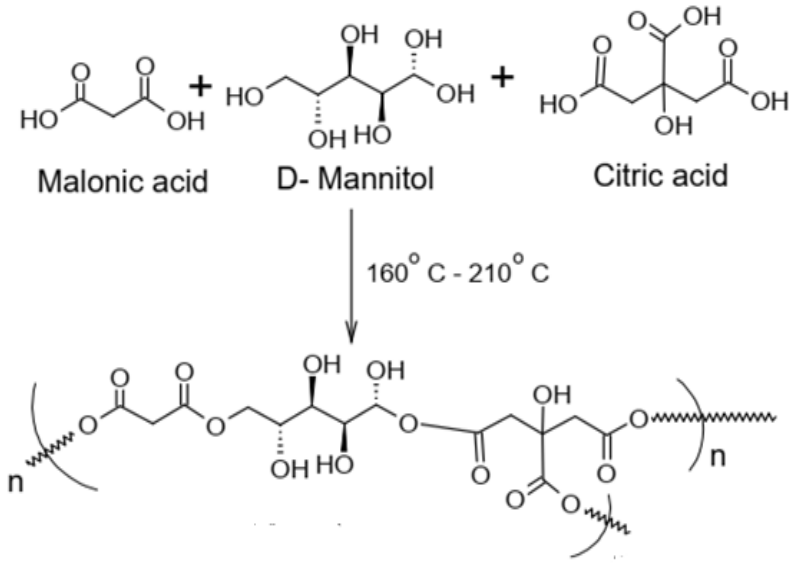
MATERIALS:

Malonic acid (M), Citric acid(C), Azelaic acid (A), Glutaric acid (G), 1.3 Propanediol (P) and D-mannitol (M)

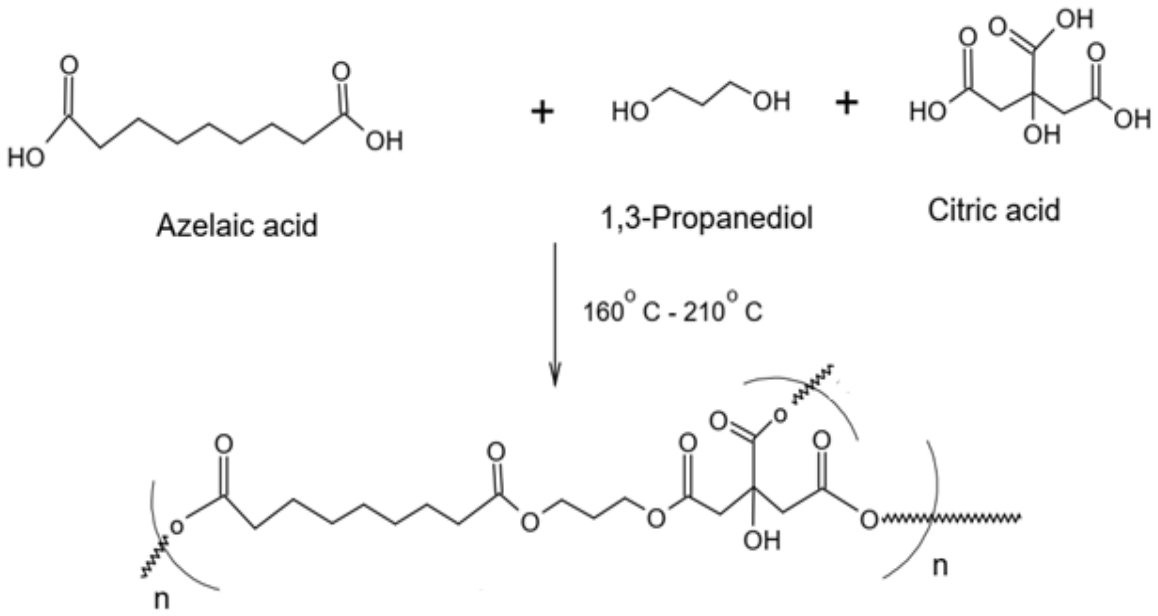
Sorbitol (S) were purchased from Sigma Aldrich used as such. Titanium Tetraisopropoxide (TiTPo), used as a catalyst was purchased from Lancaster. All other chemicals and solvents (AR Grade) were used as such.

Synthesis of copolyesters:

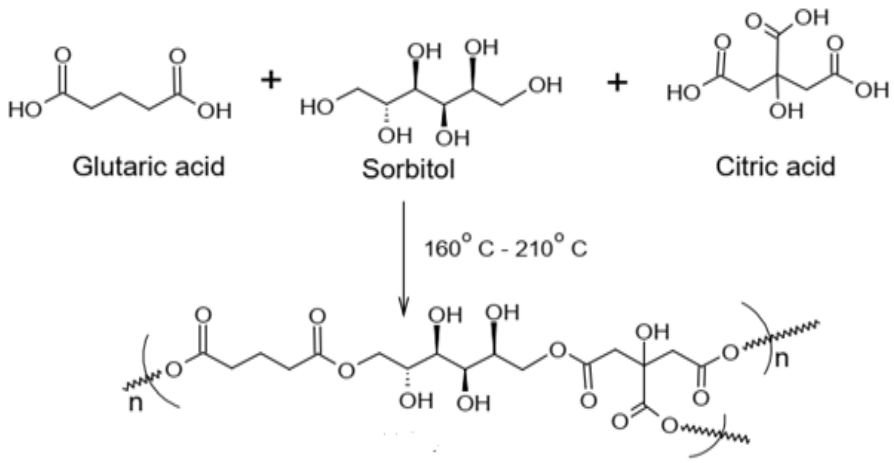
The biodegradable polyester PMMC was synthesized by predetermined amount of Malonic acid (M), Citric acid (C) and D-Mannital (M) was taken in the three-neck flask was slowly heated to 160°C- 210°C for 3 hours to remove water as by product. The prepolymer heated One hour under vaccum condition with the addition of 0.1mmol TiTPO catalyst to increase the molecular weight of the polyester. The synthesized polyester was dissolved in chloroform and separated using the 10-fold cold methanol solvent. The biodegradable polymer dried in vaccum and stored in the vaccum desiccator. The biodegradable polyesters PPAC and PSGC were synthesized by same procedure utilized in the above polymer by direct melt polycondensation. The scheme of the polyester synthesis is as follows



Scheme: 1 Synthesis of Poly mannitol malonate-Co-mannitol citrate (PMMC)



Scheme: 2 Synthesis of Poly propylene Azelate-Co- propylene Citrate (PPAC)



Scheme: 3 Synthesis of Poly Sorbitol glutarate-Co-sorbitol citrate (PSGC)

CHARACTERIZATION OF COPOLYESTERS:

Solubility Studies:

The solubility of the polymers was determined in various organic solvents, 10mg of the polyester sample was taken in a small Stoppard test tube and 1ml of the solvent was added. The solubility of copolyesters were analyze and recorded.

Infrared Spectroscopy:

Infrared spectroscopy has been used extensively in qualitative and quantitative analysis IR spectra of the synthesis polyesters was used for the structural arrangement and confirmation of functional group. The FT-IR spectra of the synthesized polymers were recorded using Bruker IFS 66 VFT – IR spectrophotometer with KBr pellets in the range of 4000-400cm^{-1}.

Nuclear Magnetic Resonance Spectroscopy:

^{1}H and ^{13}C NMR spectra of the three biodegradable copolyesters were recorded using JOEL–GSX–400 spectrometer. DMSO was used as solvent in order to prepare solutions of 5% w/v and TMS was used as internal standard.

Thermal analysis:

DSC Thermograms were recorded for all the three polyesters on differential scanning calorimeter. About 12.9 mg of the polymer sample was heated in an Aluminium seal with pierced lid under nitrogen atmosphere at a scanning rate of 10°C / mts between a temperature range of – 100 °C and 500 °C.

X-Ray diffraction analysis:

A Siemens D 500 diffractometer with Cu Kα filtered radiations was used for assessing the crystallinity of the polymers. The samples were scanned over the range of 2θangle, from 0º-80º.

Test for biodegradability of Polyesters:

The biodegradability of the Polyesters Synthesized was determined by the following method.

Polyester thin films were obtained by hot pressing method. The thin films of area 10 x 10 mm^2 and about 200μm thickness was placed in a Petri dish containing 10ml of phosphate buffer solution (pH 7.00 ± 0.01). After a specific period of incubation, the films were removed from the dish, washed with distilled water and dried weighed till constant weight. This procedure was repeated for every chosen time interval: 9,24,48,72 and 90 hours.

The degree of biodegradation was estimated from the weight loss percentage, D.

$$D = \frac{m_0 - m_t}{m_0} \times 100\%$$

Where m_0 is the weight of original films, m_t is the weight of the residual films after degradation at definite time intervals.

RESULTS AND DISCUSSION:

IR Spectral Studies:

FT-IR spectra of PMMC, PPAC and PSGC are shown in Fig4.1(a), 4.1(b). & 4.1 (c). The synthesized copolyesters showed characteristic absorption band for ester carbonyl stretching at 1716.8,1722 and 1722.1 respectively and between 957.1 to 965.5 cm^{-1} C-H bending, the aliphatic C-H group symmetry stretching obtain at 2965.9, 2941.3 and 2964.4. Strong vibrational modes observed at 1100,1170.2,1722.1 cm^{-1} were associated with C=O stretching vibrations mode

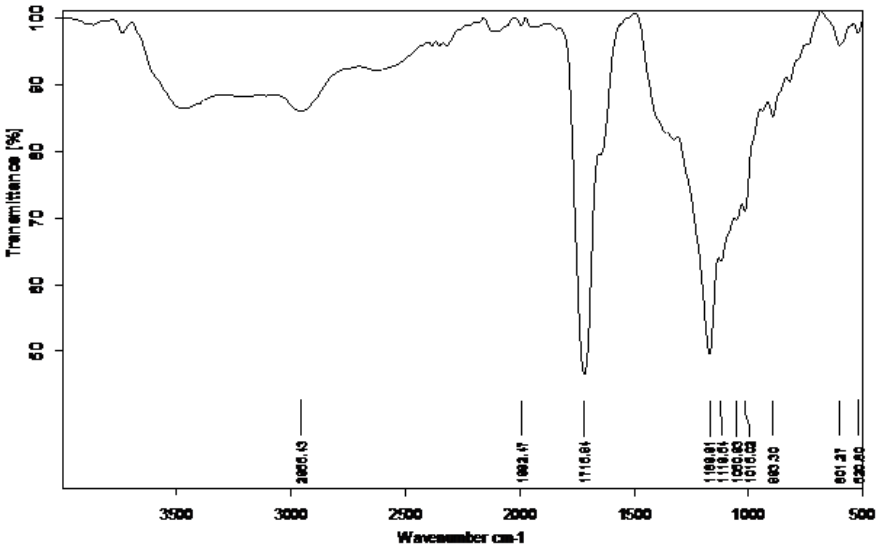


Fig.4.1 (a) IR Spectrum of PMMC

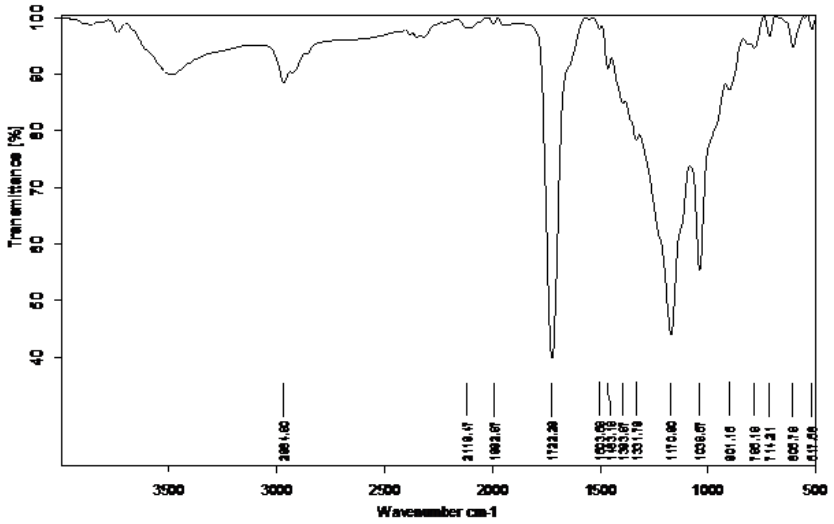


Fig.4.1 (b) IR Spectrum of PPAC

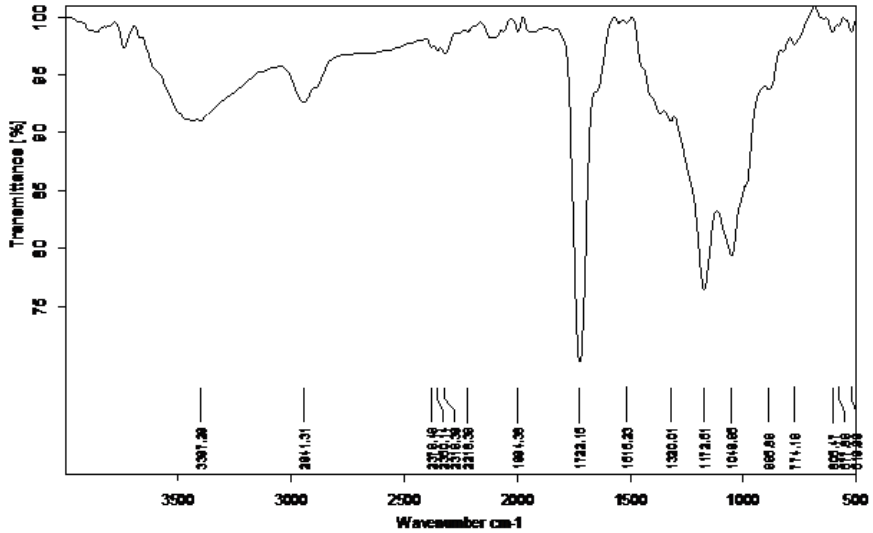


Fig.4.1 (c) IR Spectrum of PSGC

NMR Spectral Studies:

^{1}H NMR is used to study the structure of repeating units and nature of proton present in the polymer chain. ^{1}H NMR spectra of the copolyesters of PMMC, PPAC and PSGC shown in Fig 4.2(a),4.2(b) & 4.2(c) the peak at 3.21,3.25,3.24ppm was attributed to methylene protons of acids at 2.2, 2.0, 2.1ppm was attributed to central methylene proton of diols 1.1, 1.2, 1.3ppm is due to terminal methylene groups of diols.

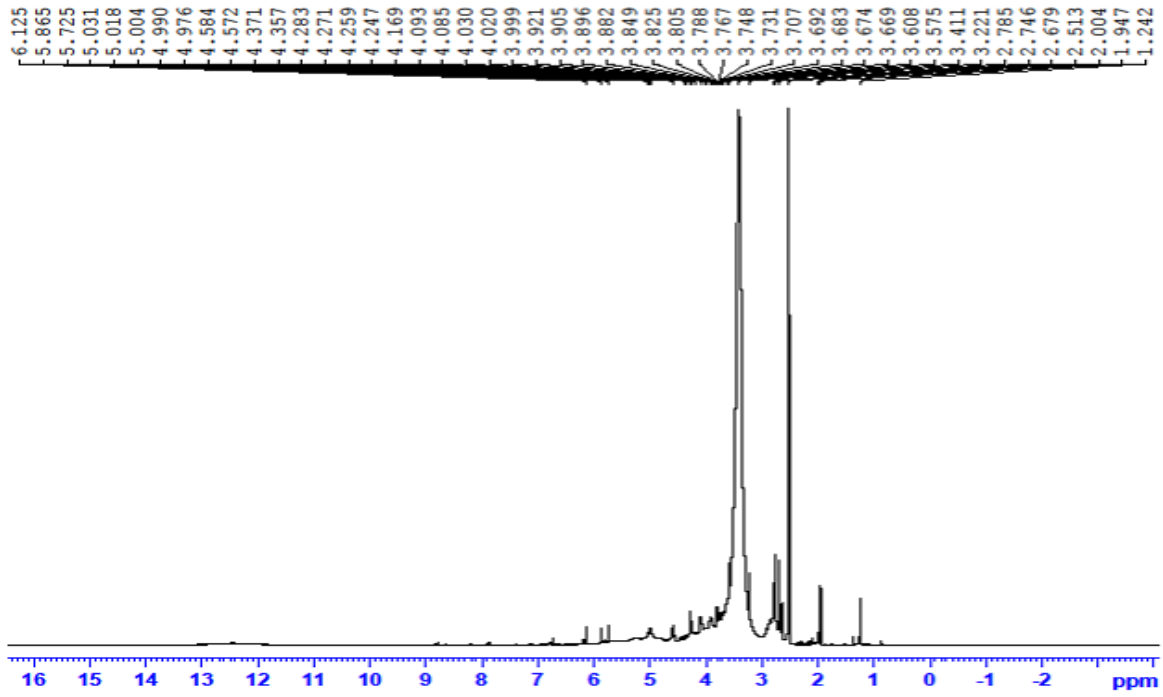


Fig.4.2(a) ^{1}H NMR Spectrum of PMMC

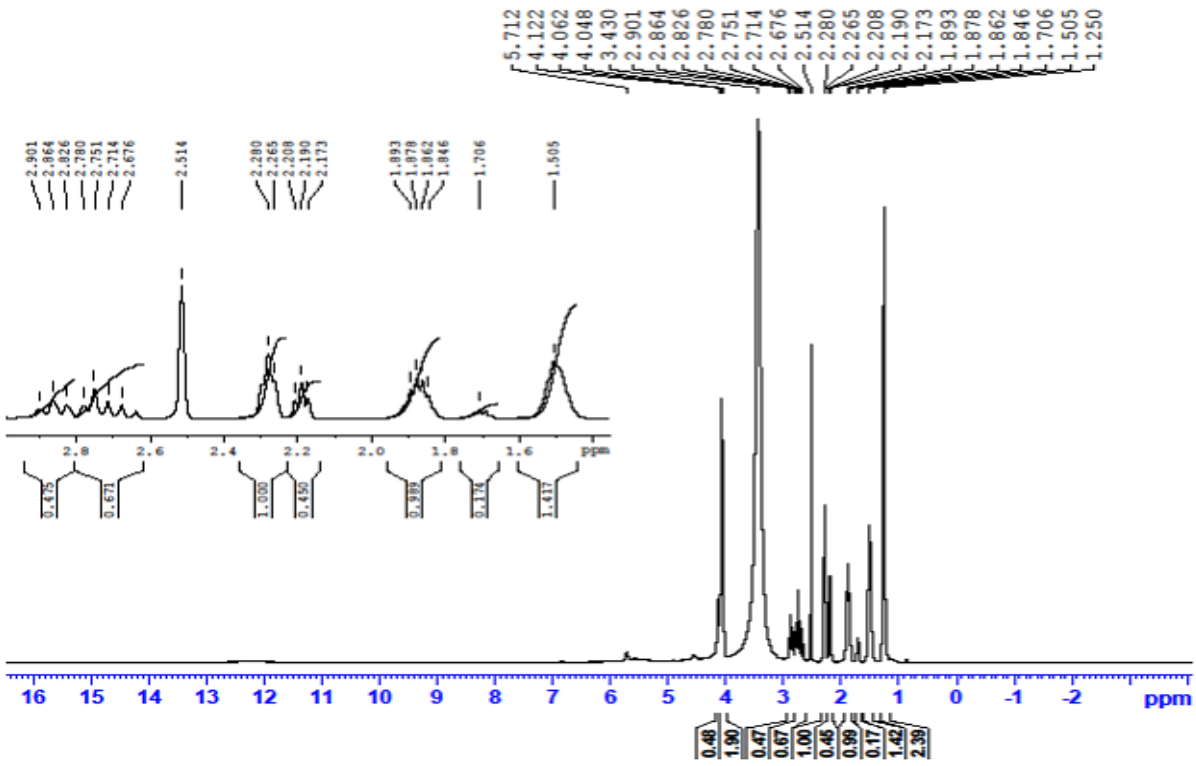


Fig.4.2(b) ^{1}H NMR Spectrum of PPAC

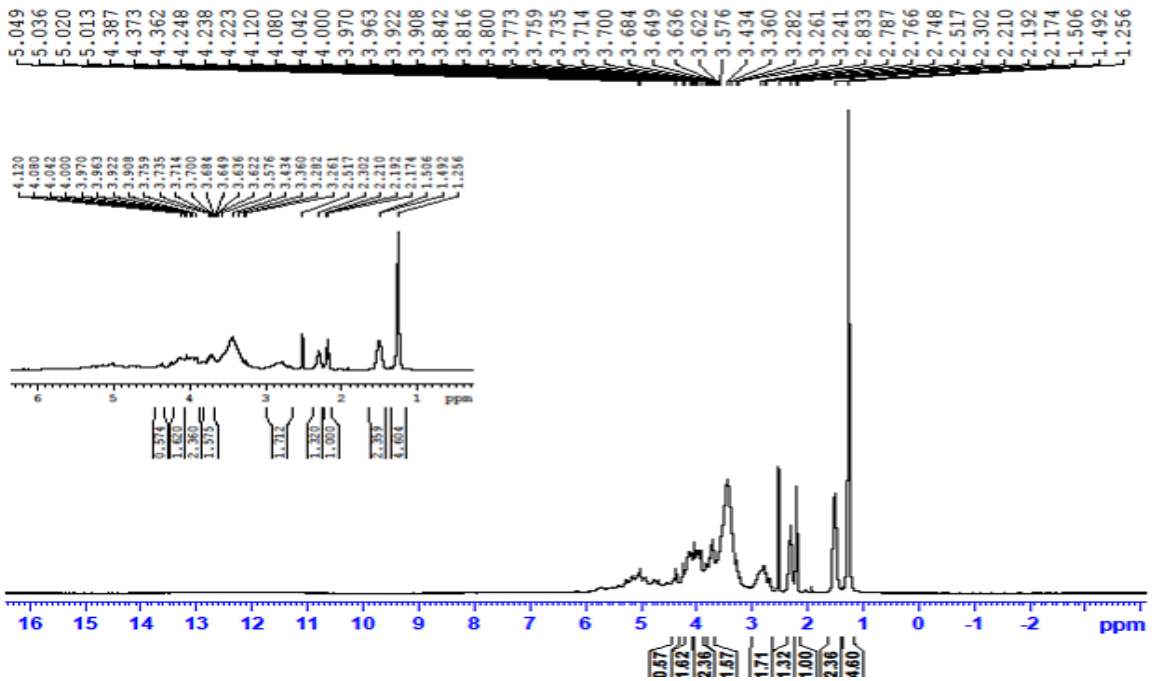


Fig.4.2(c) ^{1}H NMR Spectrum of PSGC

^{13}C NMR Spectra:

The chemical shift value obtained from ^{13}C NMR spectra of the copolymers were recorded. The ^{13}C NMR spectra of the copolyesters are given in Fig. 4.3(a), 4.3(b) & 4.3(c) and the peaks observed in 171.34 to 174,5 was due to carbonayl carbon atom of the ester group and the peaks obtained in 72 was due the CH-C0 group.

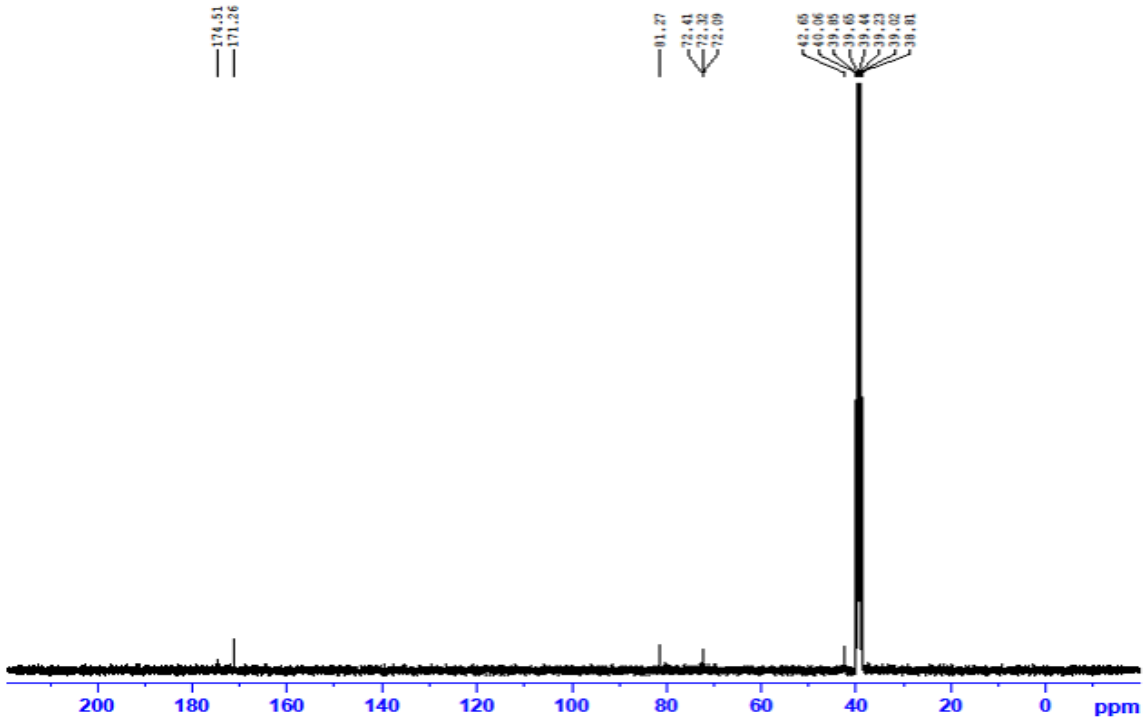


Fig. 4.3(a) ^{13}C NMR Spectrum of PMMC

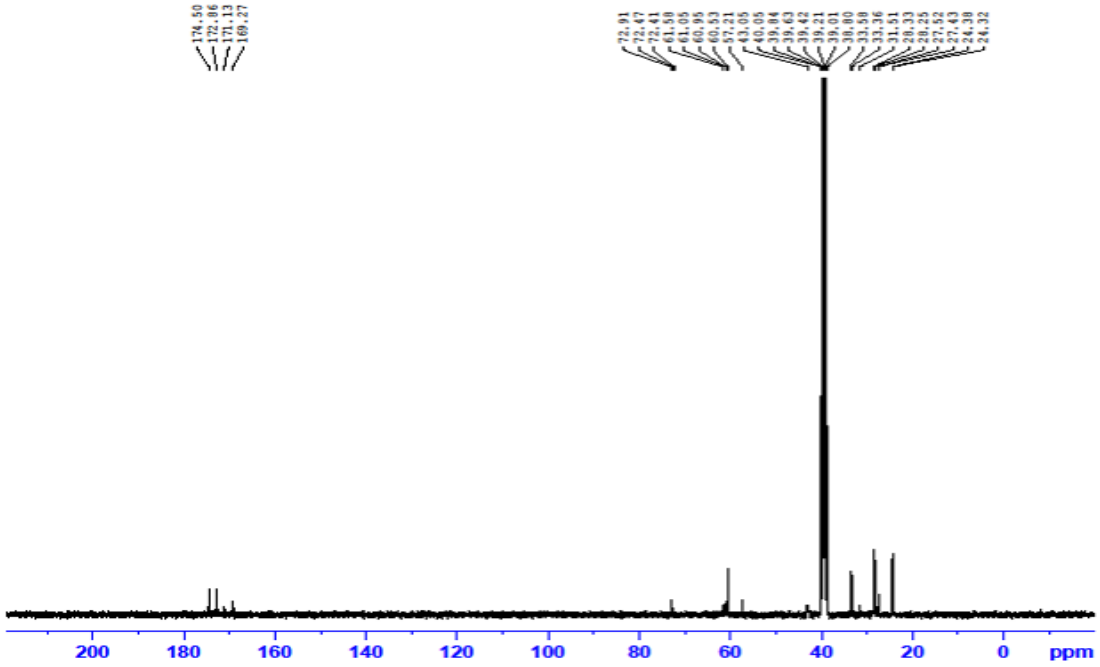


Fig. 4.3(b) ^{13}C NMR Spectrum of PPAC

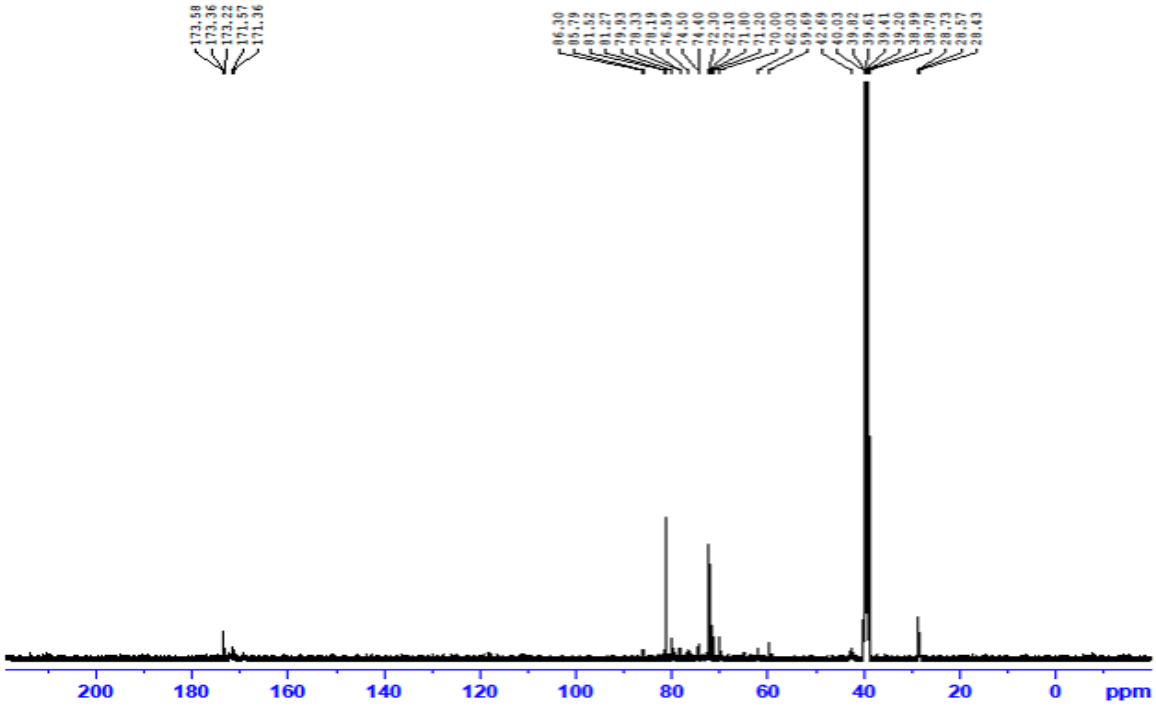


Fig. 4.3(c) ^{13}C NMR Spectrum of PSGC

Thermal Studies:

The DSC thermograms of the three biodegradable copolyesters PMMC, PPAC and PSGC are presented in Fig. 4.4(a), 4.4(b)& 4.4(c) These Thermograms show glass transition temperature (Tg), melting temperature (Tm) decomposition temperature (Td) for the polyesters PMMC, PPAC and PSGC respectively.It is worth nothing that the melting temperature, Tm decreases with increase in the number of methylene group in the repeating unit of the polymer chain.It is observed from DSC data of the copolyesters that polyester PMMC exhibits the lower melting and glass transition temperature while these polyester less crystalline nature.

Polymer	T_g (°C)	T_m (°C)	T_d (°C)
PMMC	-12.6	44.28	312.0
PPAC	-17.0	50.91	358.2
PSGC	-14.5	53.92	374.6

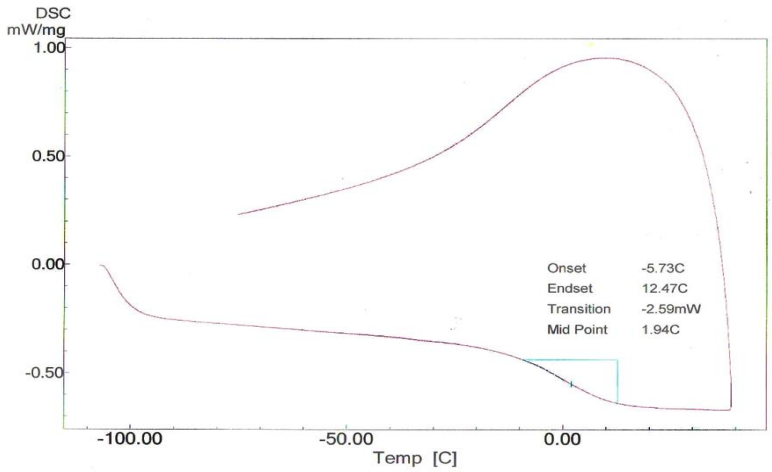


Fig. 4.4(a) DSC Thermograms of polyesters Spectrum of PMMC

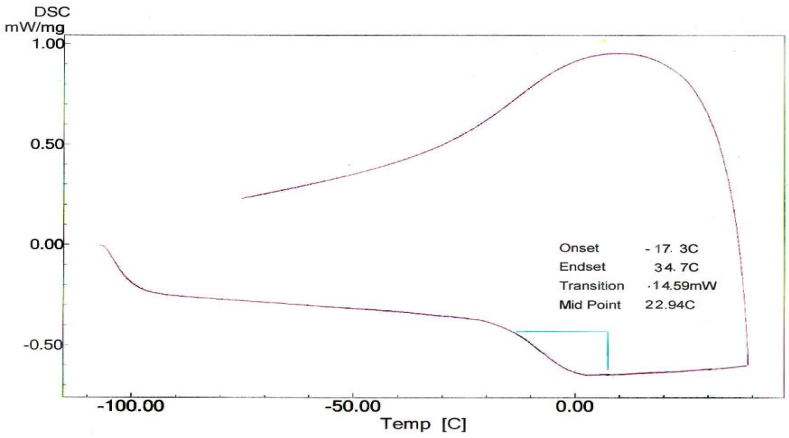


Fig. 4.4(b) DSC Thermograms of polyesters Spectrum of PPAC

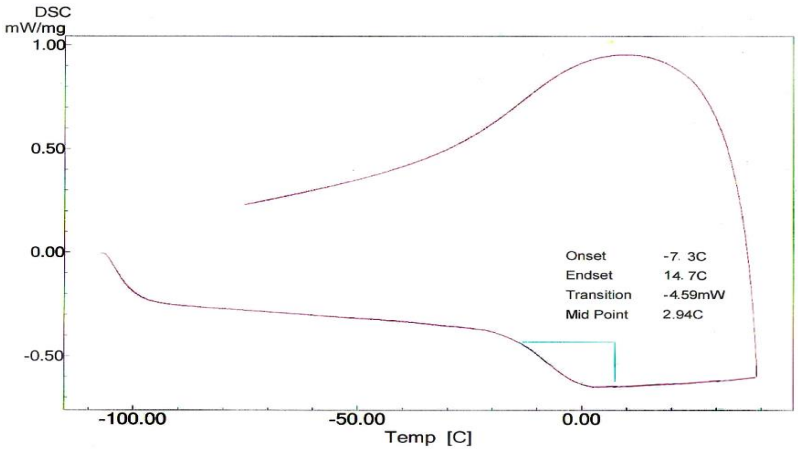


Fig. 4.4(c)DSC Thermograms of polyesters Spectrum of PSGC

Wide Angle X-Ray Diffraction:

Wide Angle X-ray Diffraction Analysis is a primary technique used to determine the degree of crystallinity of the polymers.

The comparison of the diffractograms of three biodegradable copolyesters reveals that the copolyesters, PPAC and PSGC are found to be more crystalline than the copolyester PMMC. The comparison of the diffractograms of the typical copolyesters indicates that the polyester PPAC, PSGC exhibits the highest crystallinity whereas its analogue PMMC shows the lowest. The polyester PMMC having amorphous nature expected to be ready to biodegrade compare with other two polyesters.

X-Ray diffractogram of the synthesized polymers are shown in Fig. 4.5(a), 4.5(b) & 4.5 (c) The crystalline nature of polyesters was determined from X-ray diffractogram. Gaussian curves are used to describe the amorphous phase and all crystal reflections of a diffractogram. In the X-ray diffractogram, the intensity of diffraction peaks increases with the increase in the length of the flexible spacer group. This is in accordance with the study of Chen *et al*. This indicates that the crystallinity of the polymer increases with the length of flexible segments. From the X-ray diffratogram, it is observed that PMMC is highly amorphous in nature than PPAC, PSGC.

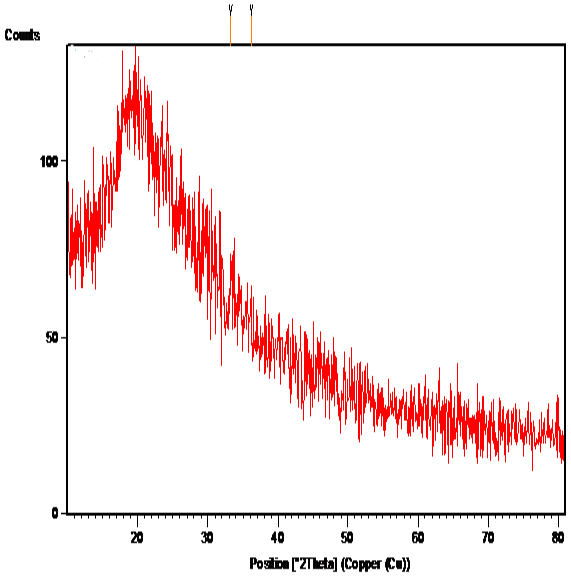


Fig. 4.5(a) WAXD Patterns of Polyesters PMMC

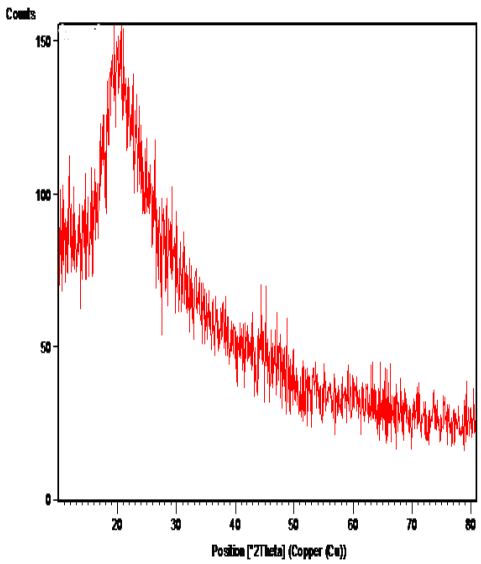


Fig. 4.b(b) WAXD Patterns of Polyesters PPAC

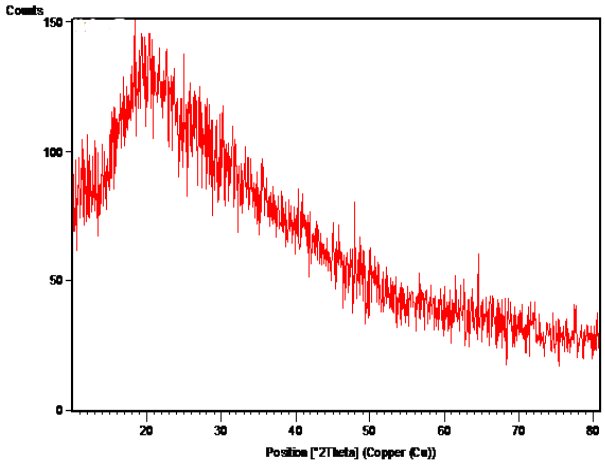


Fig.4.5 (c) WAXD Patterns of Polyesters PSGC

Biodegradation Analysis of Co polyesters PMMC, PPAC and PSGC

The biodegradability of the chemically synthesized polyesters is significantly influenced by the highly ordered chemical structure and physicochemical properties, such as melting temperature and crystallinity of the polymers the rate of degradation decreases with increase in the melting temperature and orientation of the polymer molecules also reduces the rate of degradation.

The weight loss percentage of polyesters, PMMC, PPAC and PSGC during biodegradation using phosphate buffer is determined with specific time interval tabulated and the weight loss percentage of the synthesized polyesters changed with its structural arrangement and crystallinity. Polyester PMMC exhibits higher degradation rate than PPAC and PSGC. The higher bio degradability of these polyester attributed to the less crystalline nature and low melting temperature of this polyester which is correlate with the DSC and XRD data of these polyester.

Table 1: Weight loss Percentage of PMMC, PPAC and PSGC

Time in Hours	Weight loss (%)		
	PMMC	PPAC	PSGC
0	0	0	0
9	4.4	2.2	4.2
24	11,2	8.8	10.8
48	24.2	21.6	23.8
72	38.2	32.5	37.2
90	47.4	42.8	46.2

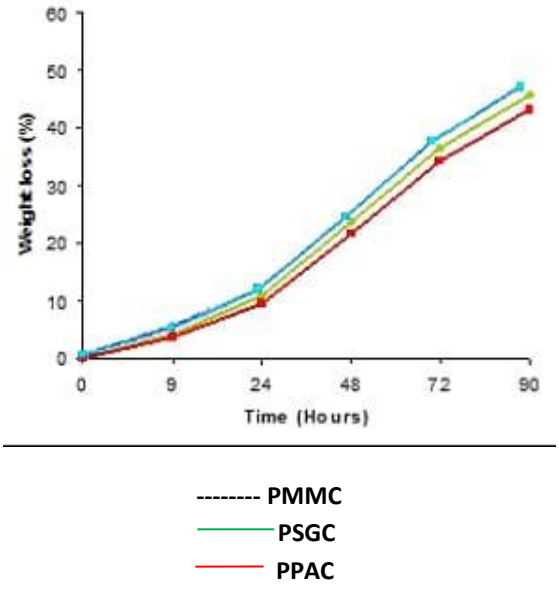


Fig.4.6 Biodegradation Graph of PMMC, PPAC and PSGC

The rate of biodegradation decreases with increase in the number of methylene groups in the repeating unit. This trend is also supported by the thermal data and XRD patterns of the polyesters. PMMC is found to be highly amorphous polymer with low melting temperature, T_m.

CONCLUSION:

The three aliphatic randam biodegradable co polyesters were synthesized from by using direct melt polycondensation reaction in the presence of a highly effective catalyst Titanium tetraisopropoxide at 160˚C-210˚C. The synthesized polymers characterized by FTIR and NMR spectral analysis which confirms the polymers structures and functional groups. Diffrential Scanning Calorimety analysis used to determine the glass transition temperature, melting temperature, and decomposition temperature of the copolyesters. The biodegradability of the Polyesters was determined by weight loss method using phosphate buffers solution. It observed that the copolyester PMMC shows more biodegradable nature than PPAC and PSGC. These synthesized polyesters will be useful in drug delivery and tissue engineering.

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