



Synthesis and characterization of novel biodegradable aliphatic copolyesters - poly(ethylene sebacate-co-propylene succinate) and poly(ethylene sebacate-co-propylene adipate)

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ABSTRACT

Synthesis of novel aliphatic biodegradable copolyesters namely Poly(ethylene sebacate-co-propylene succinate) and poly(ethylene sebacate-co-propylene adipate) were carried out using Poly(Propylene Succinate), Poly(Propylene Adipate) and Poly(Ethylene Sebacate) in presence of Poly Phosphoric acid. Synthesis of Poly(Propylene Succinate), Poly(Propylene Adipate) and Poly(Ethylene Sebacate) were carried out using respective diols and diacids in presence of titanium tetrabutoxide as catalyst. Newly synthesized copolyesters were characterized by solubility studies, viscosity measurements, thermal analysis, IR Spectroscopy and Nuclear Magnetic Resonance Spectroscopy (¹H-NMR and ¹³C-NMR). The characteristic peaks present in the homopolyesters were recorded in the copolymers as well. DSC analysis of the copolyesters showed that the introduction of methylene units in the di-acid decreased the T_m and T_g.

Keywords: Aliphatic polyester, polycondensation, Poly(Ethylene Sebacate-co-Propylene Succinate), Poly(Ethylene Sebacate-co-Propylene Adipate), differential scanning calorimetry, spectral analysis.

INTRODUCTION

In recent years, biodegradable polymers have attracted considerable attention as green materials and biomaterials in pharmaceutical, medical and biomedical engineering applications including drug delivery systems, artificial implants and functional materials in tissue engineering. Among synthetic polymers aliphatic polyesters have attracted considerable attention as they combine the features of biodegradability, biocompatibility and physical or chemical properties comparable with many traditional and non-biodegradable polymers such as low density polyethylene (LDPE) and polypropylene (PP). Biodegradable final products made from these polymers find a variety of end uses especially as films for packaging and in agricultural applications.[1-3]

Sebacic acid is an intermediate product of ω-oxidation of long-chain aliphatic acids. Compared with short-chain aliphatic acid, sebacic acid is more suitable for the preparation of polyesters, as short-chain aliphatic acids always conduce to intramolecular condensation. However works on polyesters of sebacic acid are rare.[4,9] Poly(Ethylene Sebacate) is chosen as one homopolymer to copolymerize with other homopolymers, Poly(Propylene Succinate) and Poly(Propylene Adipate).

Synthesis of Poly(Propylene Succinate) has been reported only recently.[10,11] due to attractive processes developed for the production of high quality 1,3 propanediol from renewable resources with low cost. Polyesters based on 1,3 propanediol are most promising in terms of biodegradability due to the presence of odd number of methylenes. Consequently, it is planned to initially synthesise and characterize two homopolymers Poly(Propylene

Succinate) and Poly(Propylene Adipate) and then to carryout copolymerization of these homopolymers with Ethylene Sebacate.

EXPERIMENTAL SECTION

2.1 Materials

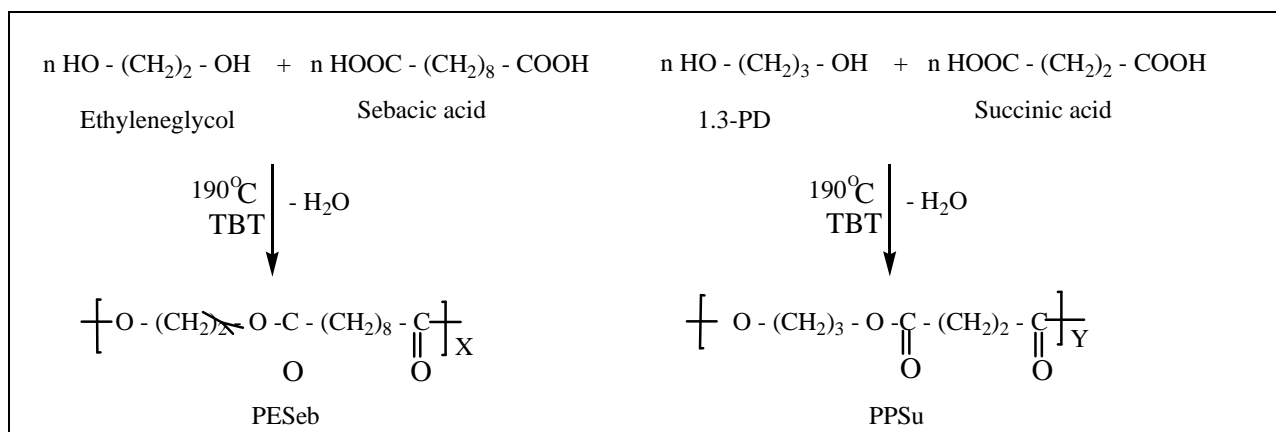
Sebacic acid (99%), Succinic acid (99%), Adipic acid (99%), were purchased from Aldrich Chemical Co. and used as such. Ethylene glycol (purity $\geq 99.7\%$) and 1,3-Propanediol (purity $\geq 99.7\%$) were supplied by Merck Co. and used as such.

2.2 Synthesis of Polyesters

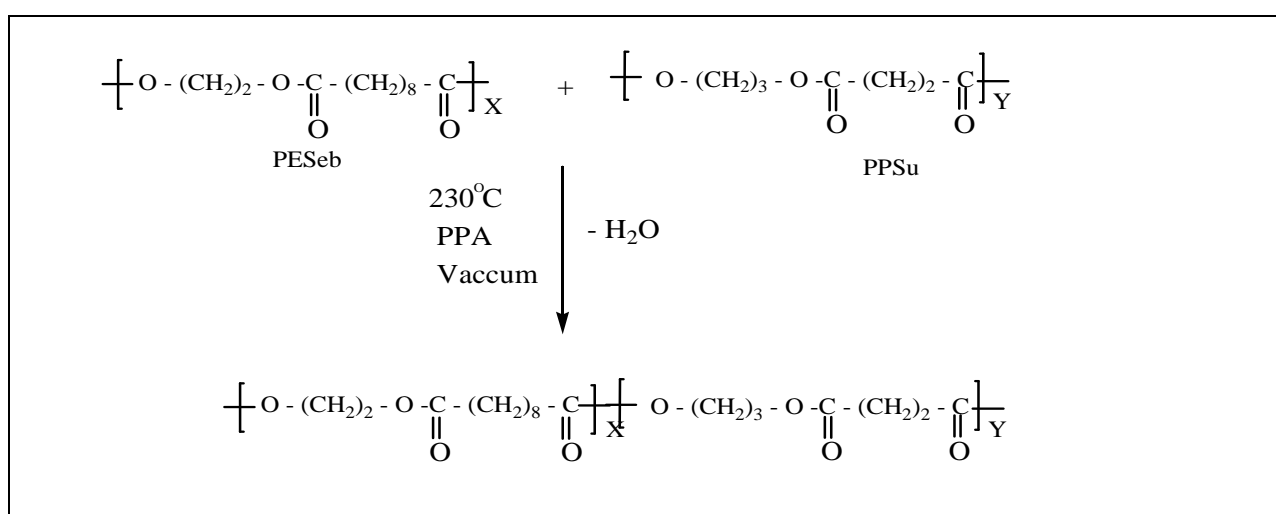
Synthesis of poly(butylene sebacate-co-propylene succinate)

Synthesis of aliphatic copolyesters was carried out by two stage melt polycondensation method in a three necked round bottom flask. At the first stage, the oligomers were prepared using sebacic acid or succinic acid and ethylene glycol or 1,3-propanediol in a molar ratio 1/1.2 and the catalyst titanium tetrabutoxide (3×10^{-4} mol TBT /mol Sebacic acid) was charged into the reaction flask of the polycondensation apparatus. The reaction mixture was heated at 190°C under nitrogen atmosphere and stirred at a constant speed, 500 rpm. The first step, esterification is considered to be complete after the collection of theoretical amount of water, which was removed from the reaction mixture.

First step: Esterification



Second step: Polycondensation



Scheme- I P (ESeb-co-PSu)

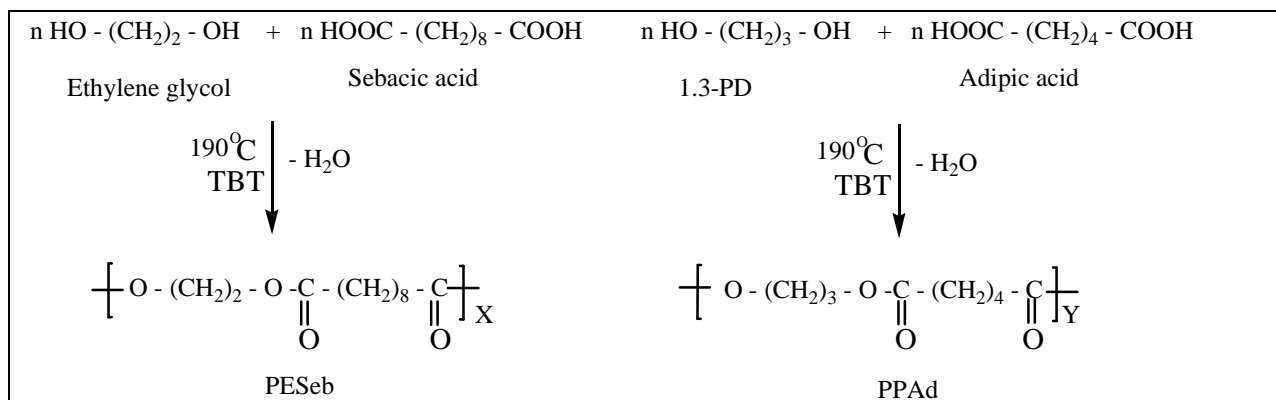
In the second polycondensation step, oligo(ethylene sebacate) and oligo(propylene succinate) were used in 1:1 weight ratio to synthesize P(ESeb-co-PSu) copolymer. In this stage, polyphosphoric acid, PPA, which is believed to prevent side reactions such as etherification and thermal decomposition, was added (5×10^{-4} mol PPA/mol SebA). A

vacuum, 5.0 Pa was applied slowly over a period of about 30 min, to avoid excessive foaming and to minimise oligomer sublimation, a potential problem during the melt polycondensation. The temperature was slowly increased to 230°C, while stirring speed was also increased to 720 rpm. The polycondensation was continued for about 60 min. At the end of polycondensation reaction, the polyester obtained were easily removed, milled and washed with methanol.

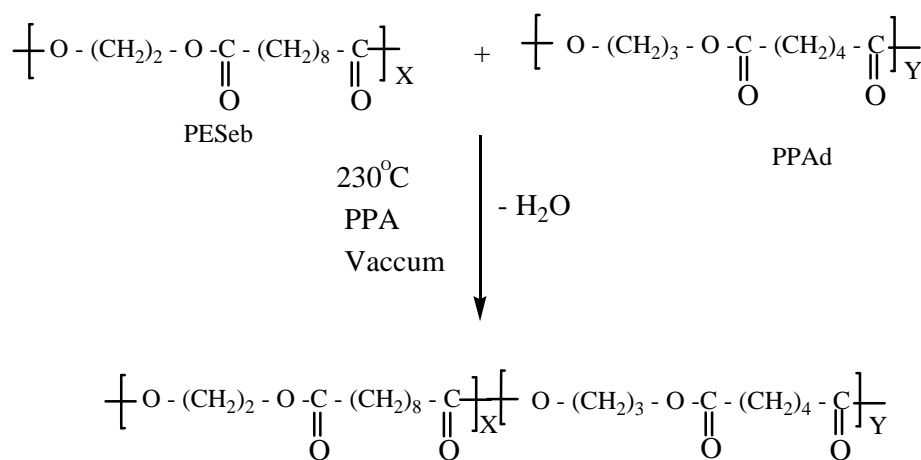
Synthetic route to P(ESeb-co-PSu)copolymers preparation, via the two step polycondensation.

Using the same procedure poly(ethylene sebacate-co-propylene adipate) was also synthesized. Synthetic route to P(ESeb-co-PAd) copolymer preparation, via the two step polycondensation.

First step: Esterification



Second step: Polycondensation



Scheme- II P (ESeb-co-PAd)

2.3 Polymer characterization

2.3.1 Solubility studies Solubility of polymers were determined in various organic solvents. 10mg of the polyester was taken in a small stoppered test tube and 1ml of the solvent was added. The solubility was noted in different solvents.

2.3.2 Viscosity measurements

Inherent viscosity of the copolyesters were measured in chloroform at $30^\circ\text{C} \pm 1^\circ\text{C}$ using Ubbelohde viscometer. For this flow times were determined for the pure solvent and 1% polymer solution by weight at room temperature.

2.3.3 Spectral studies

2.3.4 Infrared spectroscopy

The IR spectra of polymers were recorded using Bruker IFS 66 V – IR spectrophotometer with KBr pellets in the range of $4000\text{-}400\text{cm}^{-1}$ at 25°C .

2.3.5 Nuclear magnetic resonance spectroscopy

^1H and ^{13}C NMR spectra of copolyesters were recorded using JOEL-GSX-400 spectrometer. CDCl_3 was used as solvent and TMS was used as internal standard.

2.3.6 Thermal analysis

DSC thermograms were recorded on a PERKIN ELMER PYRIS-1 differential scanning calorimeter. About 2-4mg of the polymer sample was heated in an aluminium pan with pierced lid under nitrogen atmosphere at a scanning rate of $10^\circ\text{C}/\text{min}$ between a temperature range of -100°C and 500°C .

RESULTS AND DISCUSSION

3.1 Polyester Synthesis

PESeb, PPSu and PPAAd homopolyesters and P(ESeb-co-PSu), P(ESeb-co-PAAd) copolyesters were synthesized by two-step polycondensation reaction.

The polymerisation procedure for the studied polymers involved two different steps according to the well known process used for polyester synthesis.[12,13] In the first stage (esterification), selected diacids reacted with diols and water was eliminated as by-product. At the reaction temperature (190°C) water can be easily removed from the reactor and oligomers were formed. In the second stage (polycondensation) the prepared oligomers condensed at a higher temperature (230°C) with the application of high vacuum. The reactions that took place during these stages and the procedures that were used for the synthesis of the studied polyesters are presented in Scheme I & II.

All the synthesized polyesters were purified by dissolving them in chloroform and precipitated in ice-cold methanol to remove low-molecular part as well as traces of the catalyst.

3.2 Solubility

The copolyesters are freely soluble in chloroform and carbon tetrachloride, soluble in dichloromethane and tetrahydro furan, sparingly soluble in N, N'-DMS and acetone. The prepared copolyesters are insoluble in water, hexane, diethyl ether and methanol.

3.3 Viscosity of the polyesters

The inherent viscosity of the random copolyesters were calculated from the relative viscosity which were obtained from the flow time of the pure solvent and polyester solution using Ubbelohde viscometer in chloroform at 30°C and at the concentration of 0.10g/dL . The η_{inh} of P(ESeb-co-PSu) and P(ESeb-co-PAAd) obtained in the present work is 0.27dL/g and 0.18dL/g respectively. Among polymers of comparable molecular weight, rigid polymers possess a higher viscosity value than flexible one. The viscosity data obtained in the present work is analogous to the above mentioned fact.

3.4 Spectral studies

The IR spectra have been recorded for all the synthesized polyesters and are presented in Fig 1-5.

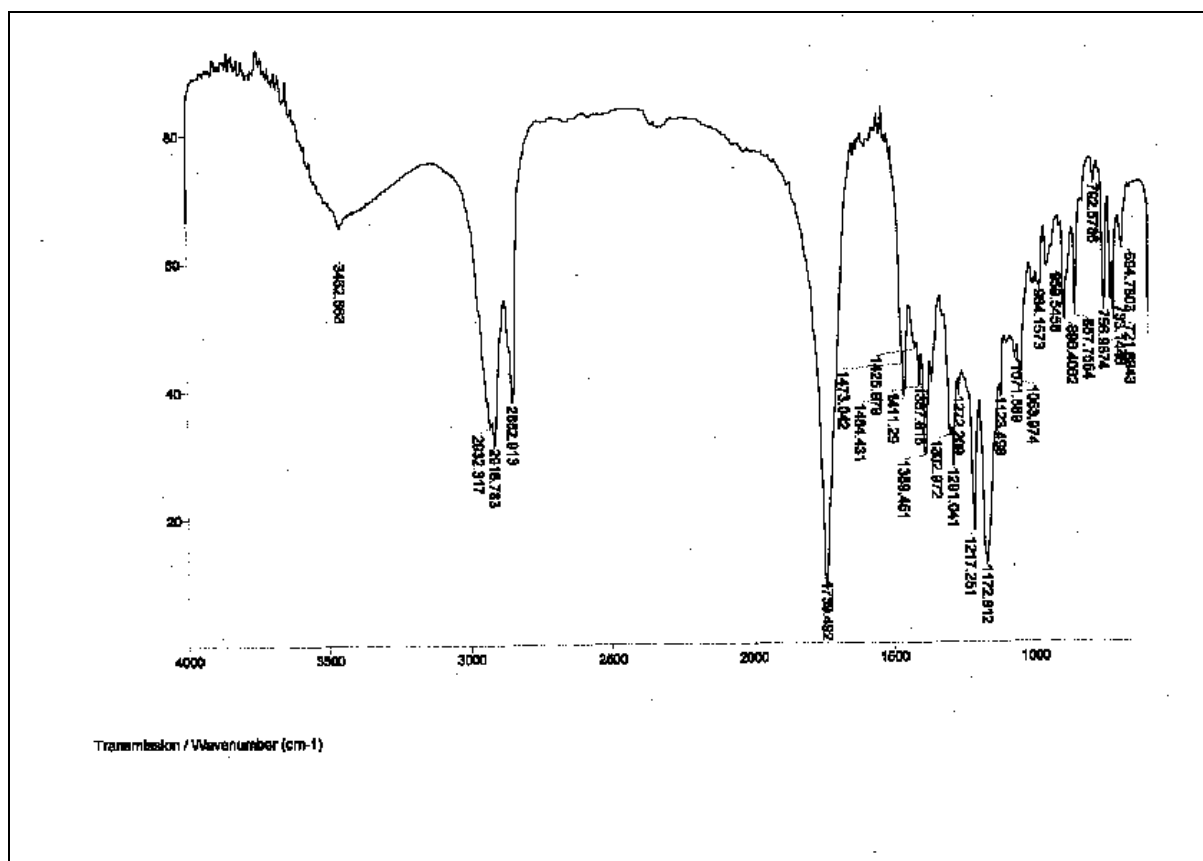


Fig 1. IR Spectrum of PESeb

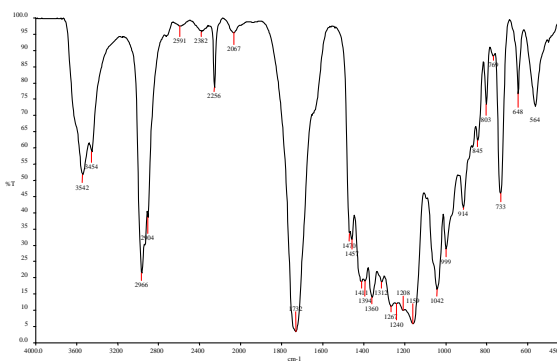


Fig 2 IR Spectrum of PPSu

The prepared polyesters showed characteristic absorption band for ester carbonyl stretching, C-O-C stretching and methylene groups as shown in the table.1

Table 1

Absorption frequency, cm ⁻¹			Assignment
PESeb	PPSu	PPAd	
1739	1732	1732	C=O stretching of ester group
1217,1172	1208,1159	1243, 1172	C-O stretching of ester group
2932	2966	2958	aliphatic C-H stretching
1464	1457	1458	aliphatic C-C stretching

Fig 3. IR Spectrum of PPAd

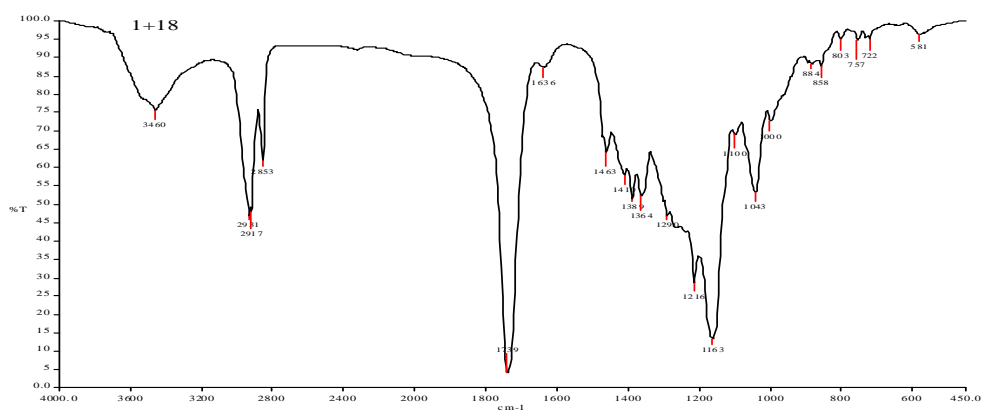
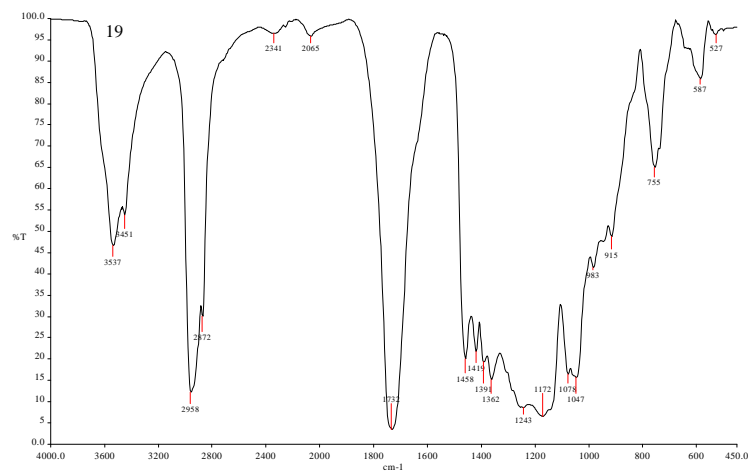


Fig.4. IR Spectrum of P (ESeb-co-PSu)

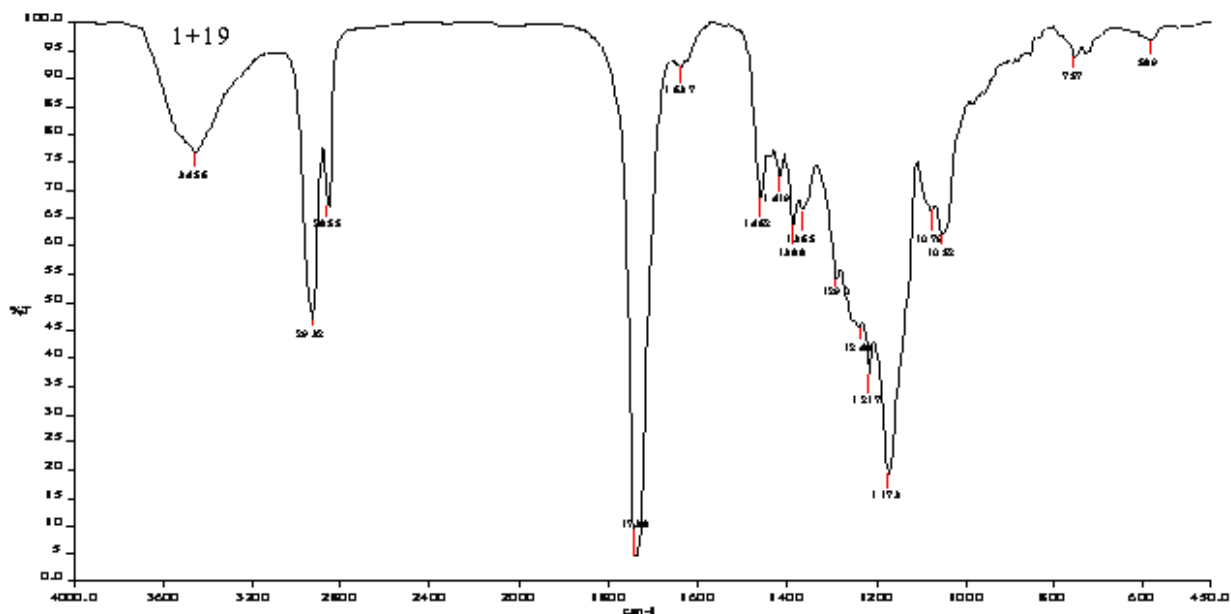


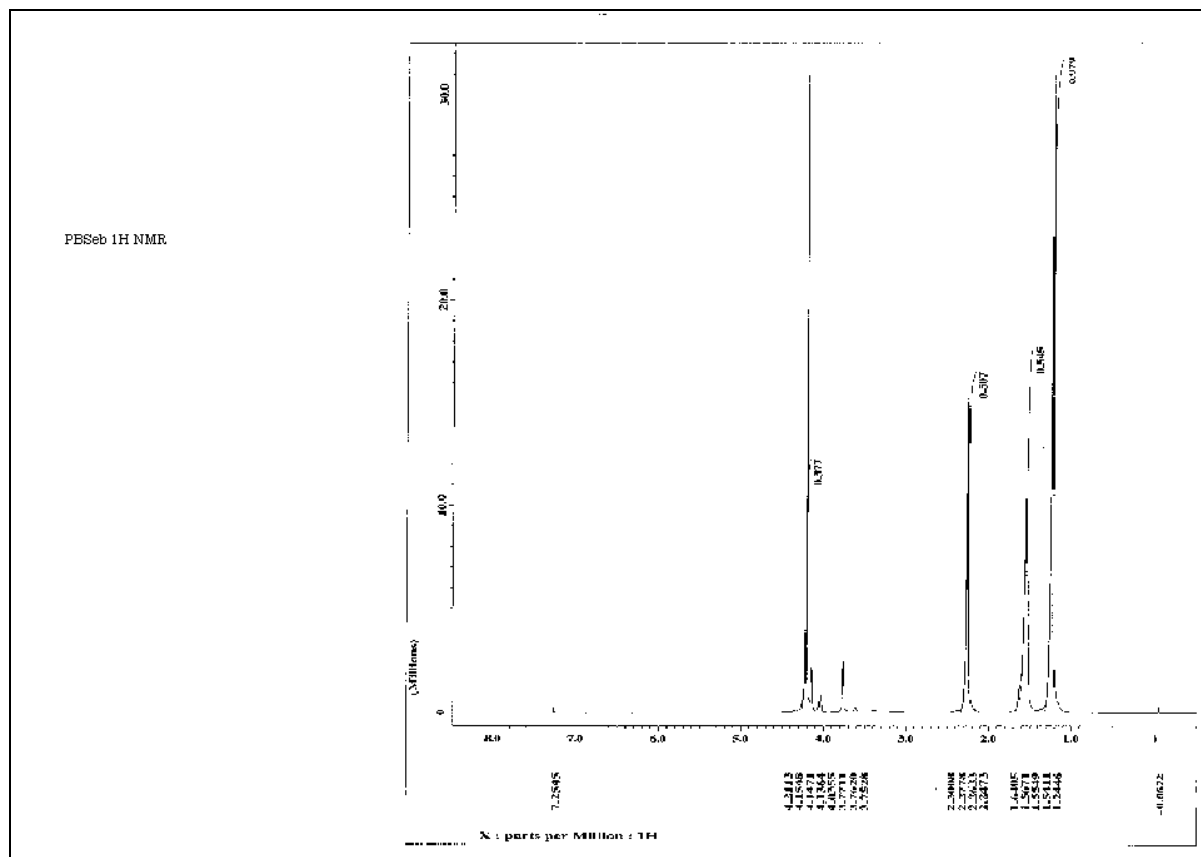
Fig. 5. IR Spectrum of P (ESeb-co-PAAd)

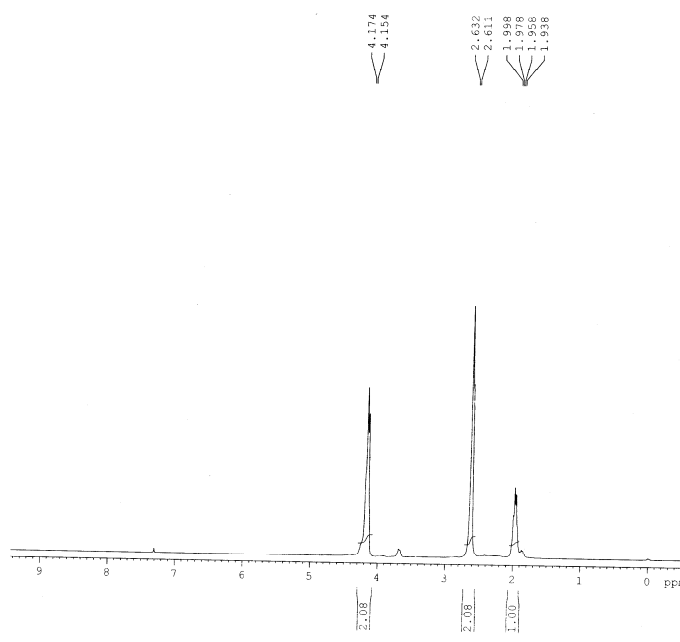
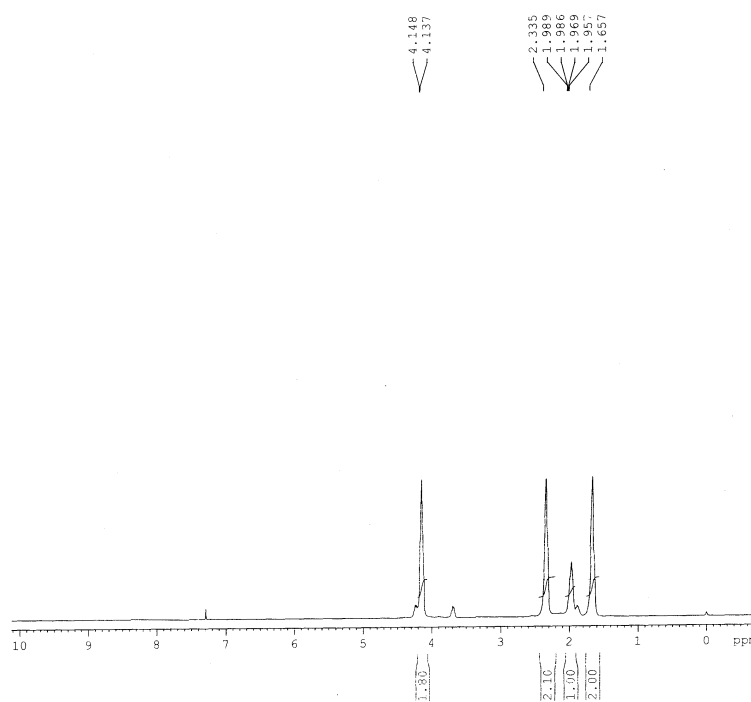
Table 2 IR Spectral data of Copolyesters P (ESeb-co-PSu) & P (ESeb-co-PAd)

Absorption frequency, cm^{-1}		Assignment
P (ESeb-co-PSu)	P (ESeb-co-PAd)	
1739	1738	C=O stretching of ester group
1216, 1163	1217, 1173	C-O stretching of ester group
2931	2932	aliphatic C-H stretching
1463	1462	aliphatic C-C stretching

 ^1H NMR Spectra

The spectra of the polyesters are presented in fig 6-10.

Fig 6 ^1H NMR Spectrum of PESeb

**Fig 7.** ¹H NMR Spectrum of PPSu**Fig 8.** ¹H NMR Spectrum of PPAc

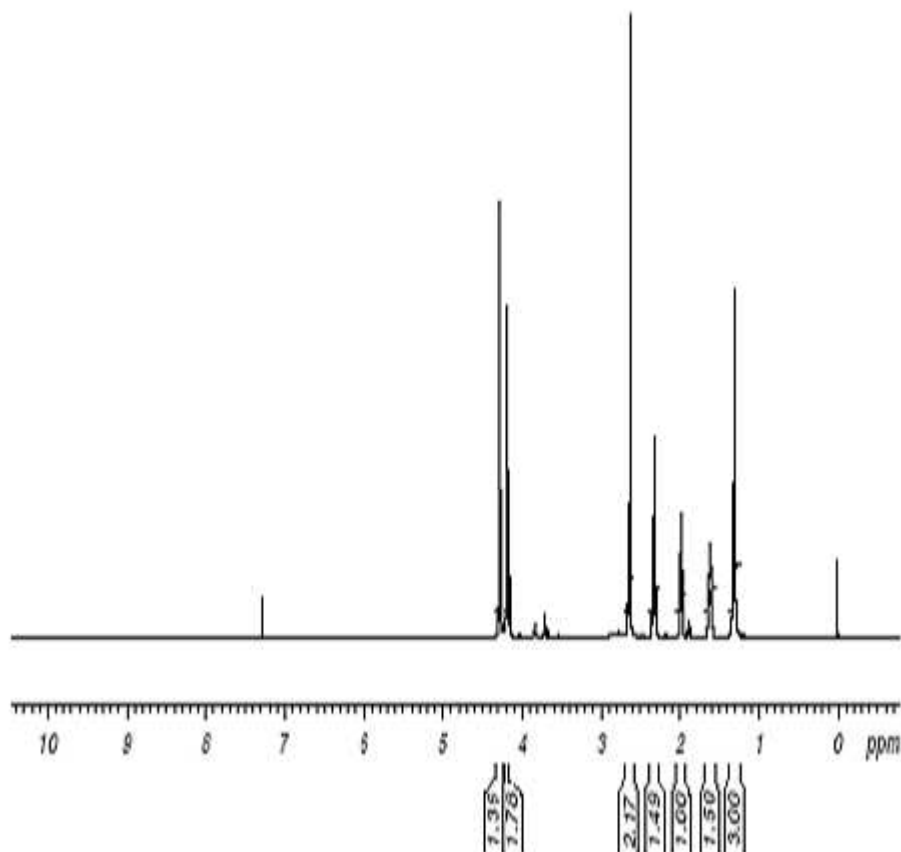


Fig. 9. ¹H NMR Spectrum of P (ESeb-co-PSu)

¹H NMR spectral data of copolyesters, P (ESeb-co-PSu) and P (ESeb-co-PAd)

The ¹H NMR spectrum of P(ESeb) exhibited characteristic peaks at 4.03-4.21, 2.24-2.30 and 1.24-1.64 ppm corresponding to protons of -O-CH₂- of ethanediol, -CO-CH₂- of sebacic acid and -CH₂- of sebacic acid respectively, while the PPSu spectra showed characteristic peaks at 4.15-4.17^[14], 2.61-2.63 and 1.93-1.99^[14] ppm for -O-CH₂- of propanediol, -CO-CH₂- of succinic acid and -CH₂- of propanediol and succinic acid respectively. All these characteristic peaks are found in the spectrum of the copolyester P(ESeb-co-PSu) given in figure (9). The ¹H NMR spectrum of P(PAd) showed characteristic peaks at 4.13-4.14, 2.33 and 1.65-1.98^[15] ppm for -O-CH₂- of propanediol, -CO-CH₂- of adipic acid and -CH₂- of propanediol and adipic acid respectively. All these characteristic peaks are found in the spectrum of the copolyester P(ESeb-co-PAd) given in figure (10). Copolyester prepared by molten state polycondensation has generally been considered to have a random distribution of the structural units because of the almost equal reactivities of the monomers and the random transesterification reaction during the polycondensation process.^[16]

The ¹³C NMR spectra of copolyesters were recorded in CDCl₃ and the relationship between the structure of the monomeric units and the chemical shifts of the carbonyl, -O-CH₂-, -CH₂- signals were established.

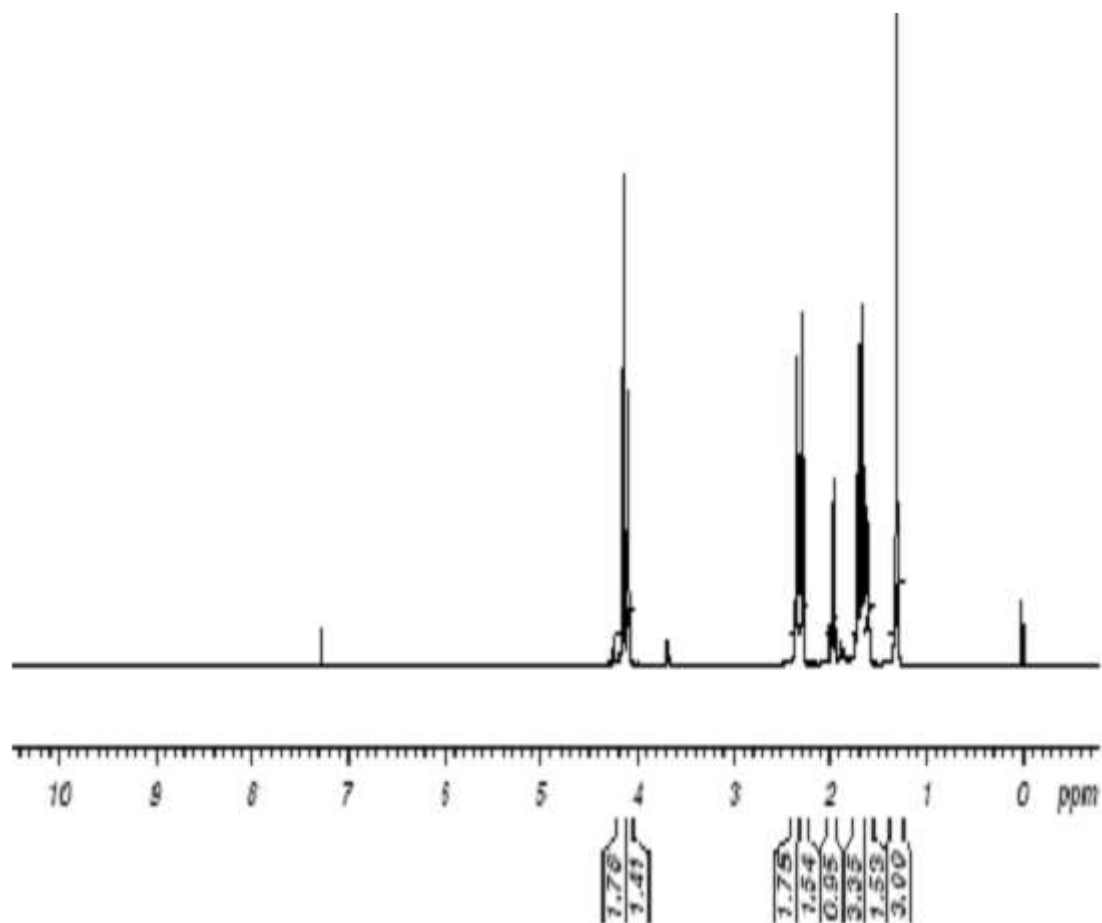


Fig. 10. ^1H NMR Spectrum of P (ESeb-co-PAd)

^{13}C NMR Spectra of Oligomers

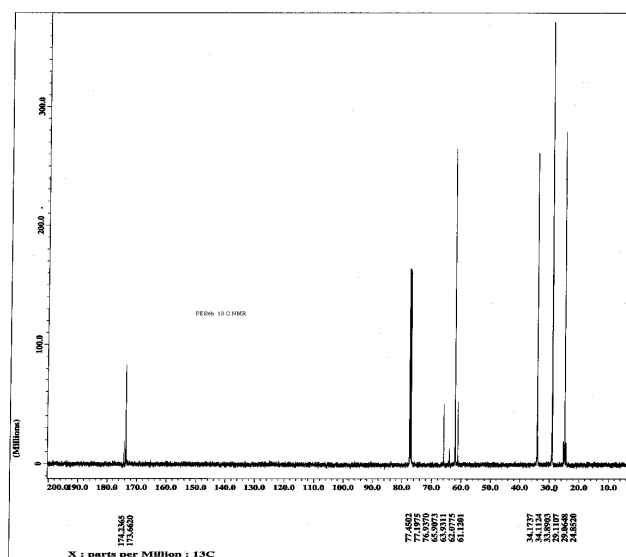
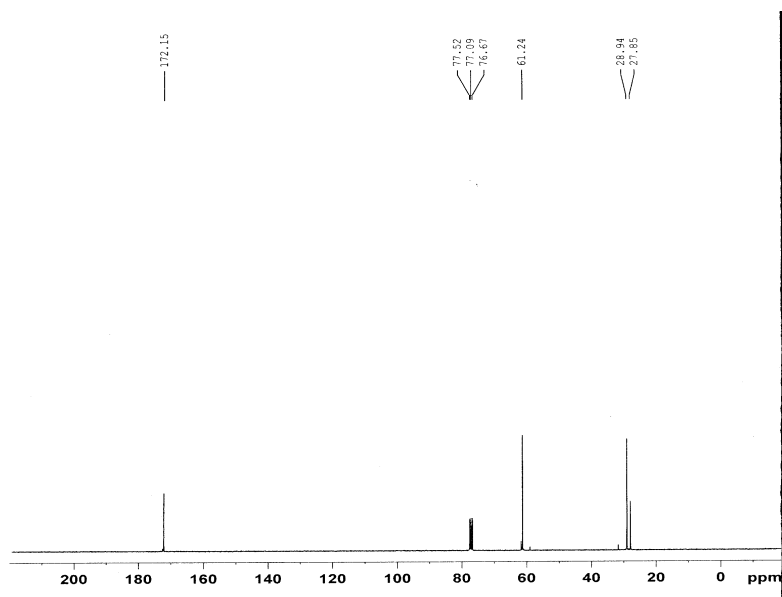
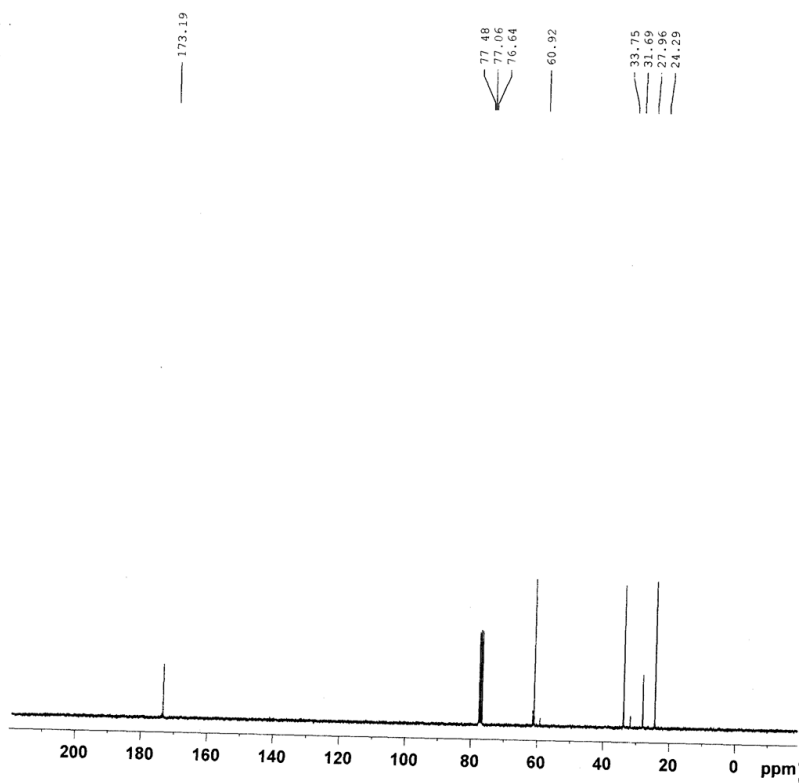


Fig 11. ^{13}C NMR Spectrum of PESeb

Fig 12. ¹³C NMR Spectrum of PPSuFig . 13 ¹³C NMR of PPAAd

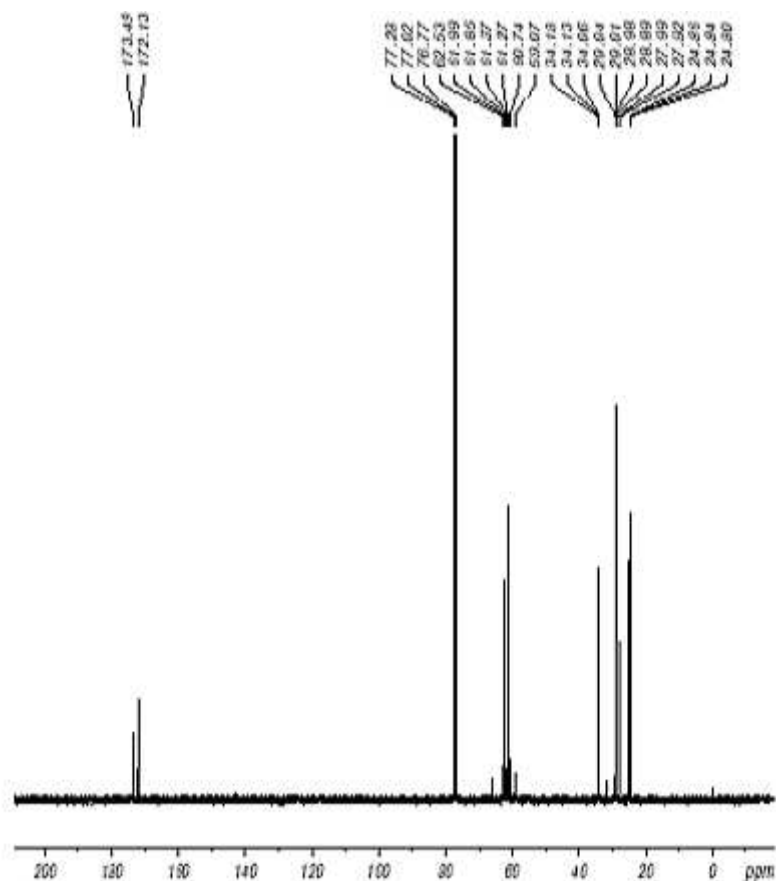
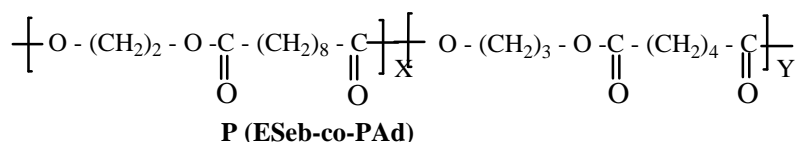
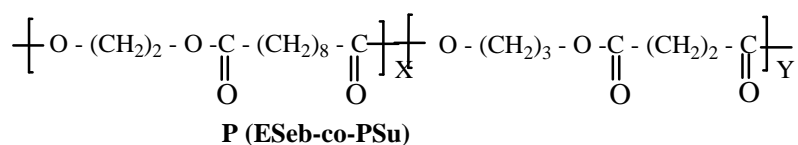
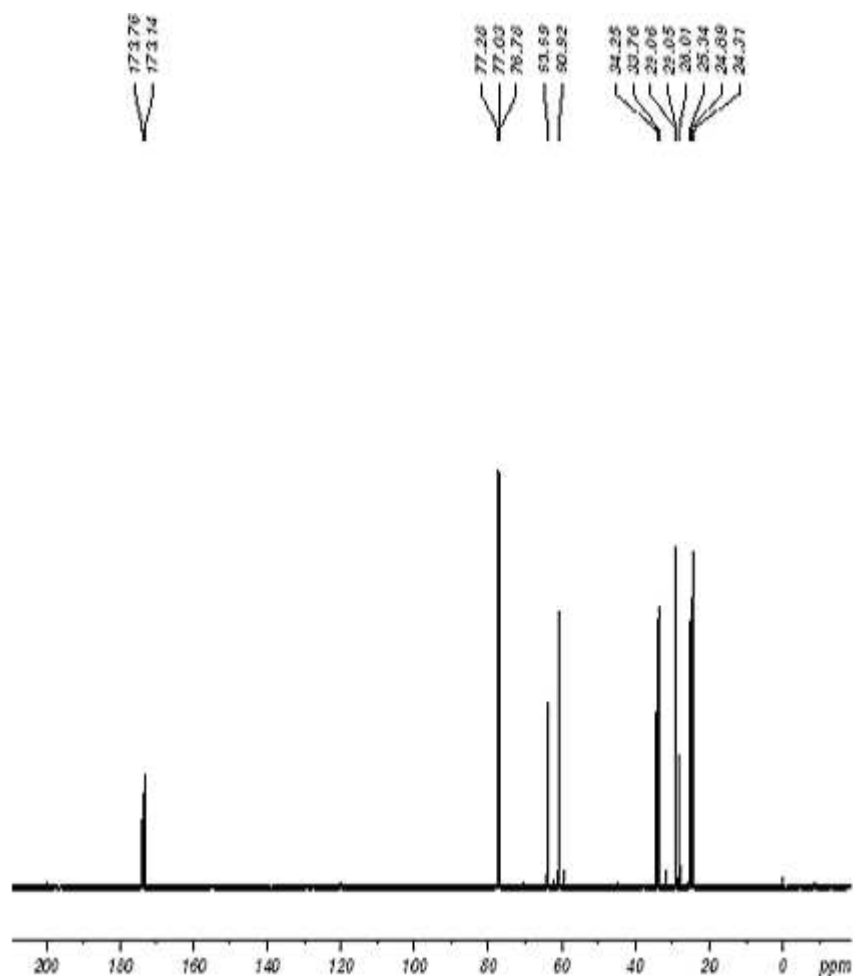


Fig. 14. ^{13}C NMR Spectrum of P (ESeb-co-PSu)

The ^{13}C NMR spectra of PESeb showed signals at 173.66-174.23, 61.12-77.45 and 24.85-34.17 ppm. PPSu spectra showed peaks at 172.15, 64.24-77.52 and 27.85-28.95 ppm. All the characteristic peaks of PESeb and PPSu were also recorded in the copolymer P(BSeb-co-PSu) (fig 14). The ^{13}C NMR spectra of PPAAd at 173.19, 60.92-77.48 and 24.29-33.75^[17] ppm. All the characteristic peaks of PESeb and PPAAd were also found in the copolyester P(ESeb-co-PAAd)(fig 13). Based on these spectral data, it may be concluded that the following structural units are randomly distributed in these copolyesters.



Fig. 15. ¹³C NMR Spectrum of P (ESeb-co-PAD)

Thermal Analysis

The polyesters were further characterised by thermal analysis and the DSC thermograms. The melting temperature T_m and the glass transition temperature T_g were found to be 59.5 and 53.5 °C and -47.0 and -63.8 °C for the copolyesters P(ESeb-co-PSu) and P(ESeb-co-PAD) respectively. It was found that the melting temperatures and the glass transition temperature decreased with increasing number of methylene units.

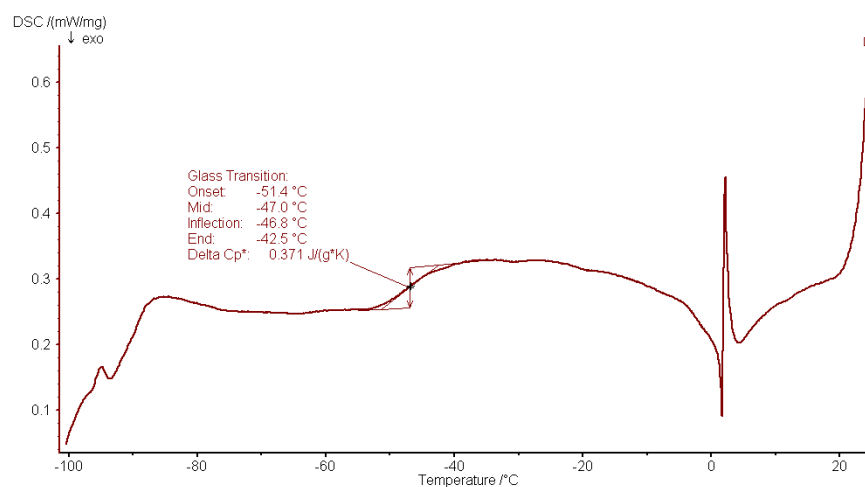
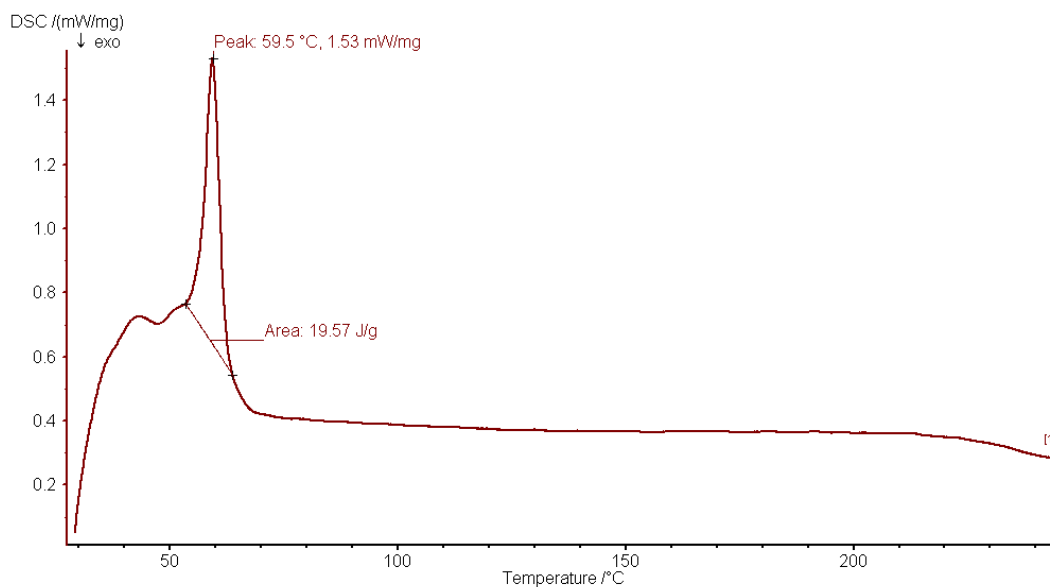
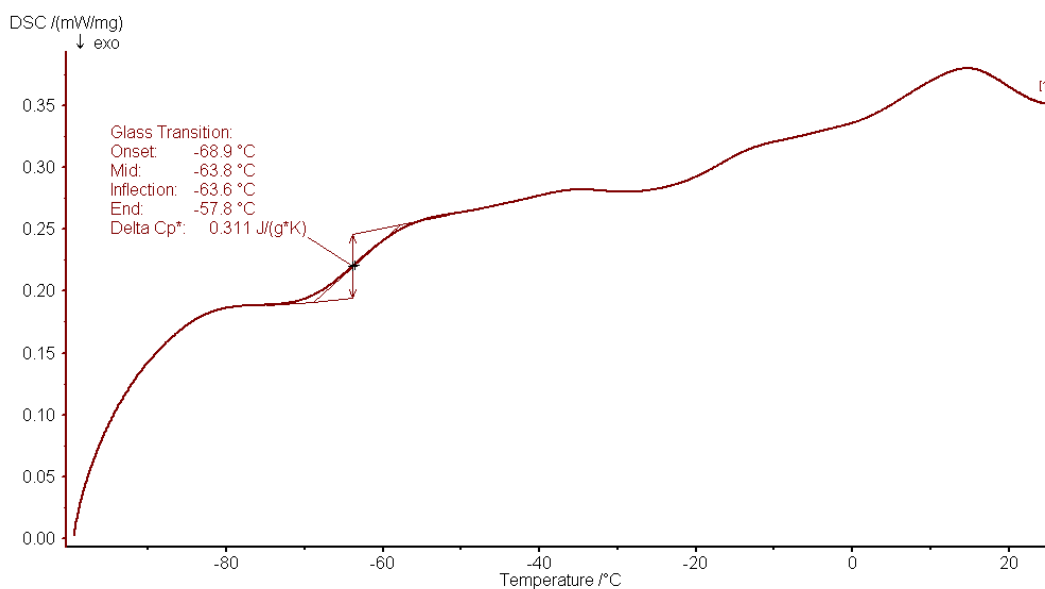


Fig 16. DSC Thermogram of P (E Seb –co- PSu) on cooling

**Fig 17. DSC Thermogram of P (E Seb -co- PSu) on heating****Fig 18. DSC Thermogram of P (E Seb -co- PAd) on cooling**

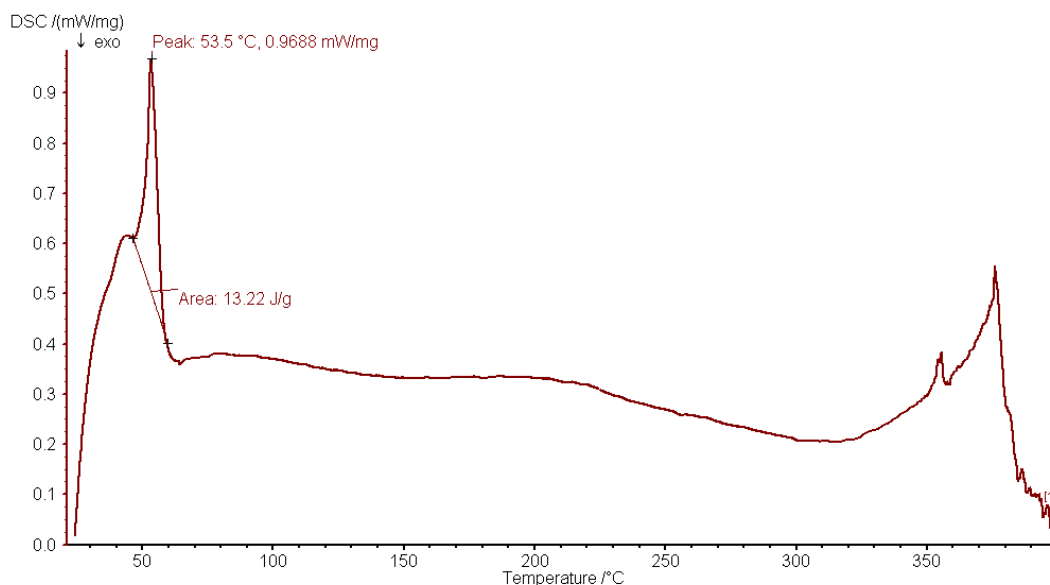


Fig 19. DSC Thermogram of P (E Seb –co- PAd) on heating

CONCLUSION

In this investigation homopolyesters Poly(ethylene sebacate) PESeb, Poly(propylene succinate) PPSu and Poly(propylene adipate) PPAAd and copolyesters Poly(ethylene sebacate-co-propylene succinate) P(ESeb-co-PSu) and Poly(ethylene sebacate-co-propylene adipate) P(ESeb-co-PAd) were synthesised from sebacic acid, succinic acid, adipic acid, ethanediol and 1,3 propanediol by polycondensation in presence of titanium tetrabutoxide as catalyst. The chemical composition of di-acid and diol unit had a 1:1.2 mol ratio. Copolyesters Poly(ethylene sebacate-co-propylene succinate) P(ESeb-co-PSu) and Poly(ethylene sebacate-co-propylene adipate) P(ESeb-co-PAd) were synthesized by a two step reaction of esterification and polycondensation. These copolyesters were synthesised with a view of increasing their solubility and improving their mechanical properties. The two copolyesters were found to be freely soluble in chloroform and carbon tetrachloride. The inherent viscosities of these polyesters showed that the polyester containing succinate units had higher viscosity than the polyester containing adipate unit. The probable structure of the repeating units present in these polyesters were assigned on the basis of NMR spectral data. From the DSC thermograms it was shown that the introduction of methylene units in the di-acid decreased the T_m and T_g .

REFERENCES

- [1] Guillet J.In:Scott G; Gilead D, Degradable Polymers : Principles and Applications, Chapman &Hall, London,1995.
- [2] Albertsson A-C; Ljungquist O.J, *Macromol Sci Chem*, **1986**,A23: 411.
- [3] Ferre T, Fraco L. Rodriguez-Galan A. Puiggali *J. Polymer* **2003**,44:6139.
- [4] Jourdan, N; Deguire, S; Brissae, F, *Macromolecules* **1995**, 28, 8086-8091.
- [5] Papageorgiou, G.Z; Bikiaris, D.N; Achillias, D.S, *Macromol Chem Phys* **2009**, 210, 90-107.
- [6] Tang, J; Zhang, Z; Song, Z; Chen, L; Hou, X; Yao, K, *Eur Polym J*, **2006**, 42, 3360-3366.
- [7] Kolwzan, B; Gryglewicz, S. J, *Synth Lubric*, **2003**, 20, 99-107.
- [8] Berti, C; Celli, A; Marchese, P; Marianucci, E; Barbiroli, G; Di Credico, F, *e-Polymers* **2007**, 057.
- [9] Medellin-Rodriguez, F, J; Phillips, P. J; Lin, J.S, *Macromolecules* **1995**, 28, 7744-7755
- [10] Ranucci E, Liu Y, Soderqvist Lindblad M, Albertsson A.C., *Macromol Rapid Commun* **2000** ; 21:680.
- [11] Liu Y, Ranucci E, Soderqvist Lindblad M, Albertsson A.C, *J. Polym Sci Polym Chem* **2001**, 39-2508.
- [12] Karayannidis G, Roupakias C, Bikiaris D, Achillias D, *Polymer*, **2003**; 44:931.
- [13] Solomon O F, Cuita Z., *J Appl Polym Sci*, **1962**, 6:683.
- [14] Yongxiang Xu, Jun Xu, Dehua Liu, Baohua Guo, Xuming Xie, *Journal of Applied Polymer Science*, **2008**, vol. 109, 1881-1889.
- [15] T. Zorba , K. Chrissafis, K.M. Paraskevopoulos, D.N. Bikiaris, *Polymer Degradation and Stability*, **2007**; 92 ,222-230.
- [16] B.D.Ahn, S.H.Kim, Y.H. Kim, J.S. Yang, *Journal of Applied Polymer Science*, **2001**, vol.82, 2808-2826 .

[17] Dimitrios Bikiaris, Vassilios Karavelidis and Evangelos Karavas, *Molecules*, **2009**, 14, 2410-2430.