Synthesis and Characterization of Certain Biodegradable Thermotropic Liquid Crystalline Random Copolyesters

R.Indira,T.Tamizharuvi and V.Jaisankar[*]

[*] Department of Chemistry, Presidency College, Chennai-600 005.

Abstract:

A series of high molecular weight copolyesters were prepared from isophthalic acid, 1,4-butane diol and sebacic acid/ adipic acid through a two step process of melt polycondensation using titanium tetra butoxide as catalyst. The synthesised random copolyesters were characterised by means of IR, ^{1}H NMR, ^{13}C NMR, gel permeation chromatography (GPC), viscosity measurements, differential scanning calorimetry (DSC), thermogravimetry (TG) and X-ray diffraction (XRD) studies. The effect copolymer composition on the physical and thermal properties, as well as enzymatic degradation was investigated. The enzymatic degradation was performed in a buffer solution with enzyme *Candida cylindracea* lipase. The phase behaviour of the polymers was studied by differential scanning calorimetry and optical polarising microscopy equipped with a heating stage. The copolyesters exhibit thermotropic liquid crystalline behaviour with nematic texture as observed by optical polarising microscopy.

Key words: Liquid crystalline, melt polycondensation, random copolyesters

1.Introduction

In recent years, the amount of plastic wastes has obviously increased all over the world, which brings a serious environmental problem and has drawn more and more concern from the public and scientists. Some measures have been taken to solve this problem, such as reducing the use of plastic products and recycling the plastic wastes. One of the feasible ways to solve the problem is to develop biodegradable plastics.[1] Therefore, a series of biodegradable polymers have been developed in the past decades, most of which are aliphatic polyesters, such as poly(ε-caprolactone) (PCL), poly(lactic acid) (PLA), poly(3-hydroxybutyrate) (PHB), poly(butylene succinate) (PBS), poly(ethylene succinate) (PES), poly(propylene succinate) (PPSu), poly(propylene adipate) (PPAd) and poly(propylene sebacate) (PPSe).[2-7] Aliphatic polyesters are of great importance because of their degradability and have drawn much attention [8,9]. The limitation of these polyesters is due to low thermal and mechanical properties . Copolymerization[10-13] and blend [14,15] with aromatic polyesters are better choices to modify properties of aliphatic polyesters in both mechanical and thermal aspects. Meanwhile, degradability is also expected because some studies have revealed that aromatic polyesters are degradable when they are copolymerised with aliphatic polyesters[16].

The degradation of polyesters by microorganisms is initiated by extracellular hydrolases, which are secreted by the organisms to reduce the molar mass of the polymeric substrate and to make it bioavailable. While for the natural polyhydroxyalkanoates (PHB, etc.) a special group of extracellular hydrolases has been developed by nature[17], it was first demonstrated by Tokiwa and Suzuki that synthetic polyesters also can be attacked by hydrolases (lipases)[18]. A number of other investigations on the degradation of synthetic polyesters by hydrolases have been reported. There is strong evidence that microbial biodegradation of synthetic polyesters in nature is also initially caused by hydrolases secreted from the microorganisms. For PCL, polyester-degrading microorganisms were isolated and the corresponding extracellular enzymes were identified as hydrolases[19- 23] . For aliphatic-aromatic copolyesters a thermophilic actinomycete (Thermobifida fusca) recently could be isolated and the degrading enzyme was characterized to be also a lipase-like hydrolase[24, 25]. Other publications also confirmed that such copolyesters can be attacked by lipases[26-29].

Aromatic polyesters, like poly (ethylene terephthalate) (PET), and poly (butylene terephthalate) (PBT) provide excellent basic material properties but are strongly resistant to microbial attack[30]. Recently, it has been shown that copolyesters containing adipic acid and terephthalic acid as aromatic acid components are also attacked by microorganisms[31]. This group of copolyesters appears to be very promising with regard to widespread commercial applications[32]. Studies have been performed with the particular goal of detecting the fate of the aromatic constituents and proving their biodegradation[33, 34].

In recent years thermotropic liquid crystalline polyesters have received a great deal of attention[35,36].In the 1980s some very interesting attempts were made to synthesize thermotropic random copolymers by introducing

two different lengths of flexible spacers in the main-chain[37,38]. The primary motivation behind such attempts was to decrease anisotropic-isotropic transition temperature(s) and at the same time to broaden the range of temperatures over which a mesophase may reside.

Considering the high commercial potential of aliphatic-aromatic copolyesters and their interesting properties, the present investigation deals with the synthesis and characterisation of certain random aliphatic-aromatic copolyesters. The structure of their repeating units and the effect of copolymer composition on the physical and thermal properties, optical polarising microscopic studies as well as enzymatic degradation are investigated. The enzyme *Candida cylindracea* lipase was used in the degradation studies.

2.Materials and Methods

2.1 Materials

Adipic acid (Lancaster AR grade), Sebacic acid(Merck AR grade) and Isophthalic acid (Lancaster AR grade) were recrystallised from deionised water and used. 1, 4 Butane diol (Lancaster AR grade) was dried with CaO overnight and then distilled under reduced pressure. Titanium tetra butoxide(Ti(OBu)$_4$), used as catalyst, purchased from Lancaster was used as such. *Candida Cylindracea* lipase purchased from Sigma Aldrich was used for degradation studies. All the other materials and solvents used were of analytical grade.

2.2 Synthesis of Copolyesters

The copolyesters were synthesized by two step melt polycondensation method. As an example, the synthesis of poly (butylene adipate–co–butylene isophthalate), PBAIT has been described.   The polycondensation flask was a three neck flask equipped with a nitrogen inlet, a condenser and a thermometer. A magnetic stirrer was used to stir the reaction mixture. The reaction mixture consists of 0.2mol 1, 4 BD, 0.1 mol adipic acid and 0.1 mol isophthalic acid. The reaction mixture is purified with nitrogen and heated in an oil bath. The temperature of the reaction mixture is raised to 150°C in 20min. Then the temperature is gradually raised in 10°C steps every minute to the reaction temperature of 210°C to remove water being the esterification by product. When water ceased to be generated, a predetermined amount of titanium tetra butoxide (Ti(OBu)$_4$) (0.1mmol) catalyst is added to the reaction mixture. Subsequently, the pressure of the reaction system was gradually decreased and polycondensation is continued at 210°C under a final reduced pressure lower than 0.5mmHg. The reaction was terminated when the rotation of the mechanical stirrer is stopped. The resulting crude copolymers were dissolved in chloroform and then poured into excess of dry cold methanol to purify the polyester. The precipitated copolyesters were dried in a dessicator for further characterisation.

2.3 Characterisations

2.3.1 Intrinsic Viscosity and molecular weight

The intrinsic viscosity of polymer solutions in chloroform was measured using Ubbelohde Viscometer. The molecular weights of copolyesters were analysed by gel permeation chromatography using a Shimadzu instrument equipped with a pump and refractive index detector. Tetrahydrofuran was used as mobile phase with a flow rate of 1.0 ml/min. Polystyrene standards from Shapodex were used for calibration.

2.3.1 Fourier- Transform Infrared (FTIR) Spectroscopy

IR Spectra of the copolyesters were recorded using a perkin Elmer IR spectrometer in the range of 700cm-^{1} to 4500cm-^{1}. The samples were embedded in KBr pellets.

2.3.2 ^{1}H NMR measurements

^{1}H NMR spectra were recorded on AV 3500 MHz Spectrometer by using 7% wt of trifluoroacetac acid /CDCl$_3$ mixed solvent.

2.3.3 ^{13}C NMR measurements

^{13}C NMR spectra were recorded at 300-600MHz in deuterated chloroform as solvent.

2.3.4. Differential Scanning Calorimetry (DSC)

The DSC scans were recorded at a heating rate of 10°C/min using a Perkin-Elmer Pyris I analyser. Indium was used as the calibration standard.

2.3.5.Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of copolyesters were carried out using Q50 thermogravimetric analyser system at a heating rate of 10°C/min under a nitrogen atmosphere.

2.3.6.X-Ray diffraction (XRD)

A Siemens D 500 diffractometer with Cu Kα filter radiation was used for assessing crystallinity of the polymers. The samples were scanned over the range of 2θ angle, from 5 ° to 80°.

2.3.7.Enzymatic Degradation

Copolyester films were obtained by hot press method above the melting temperature of the polyesters. The hot pressed films ($10\times10mm^2$ and about 200μm thick) were incubated in duplicate at 30°C in separate petridishes containing 7mL phosphate buffer (pH=7.00 ± 0.01) in the presence of the enzyme lipase from *Candida Cylindracea*. The enzyme concentration was 1mg/mL. The films were removed from the enzymatic solution after selected time intervals, washed with distilled water and dried under vacuum at room temperature to constant weight. This procedure was repeated for every chosen time interval: 9, 24, 48, 72 and 90 h. The extent of biodegradation was quantified using the weight loss and the initial sample weight [38]. A control test without enzyme was also carried out.

2.3.8.Optical polarising microscopy(OPM)

The optical texture of the melts was examined on a hot stage(Mettler FP-5) attached to a polarizing microscope.

3.Results and Discussion

3.1.Intrinsic Viscosity and Molecular weights

The intrinsic viscosity, molecular weight and the polydispersity index of the copolymers are presented in Table1.

Table 1.The inherent viscosity and Molecular Weight of the copolyesters

Copolyesters	Inherent viscosity, η^{inh} (dL/g)	$\overline{M_w}$ g/mol	$\overline{M_n}$ g/mol	Poly dispersity Index $(\overline{M_w}/\overline{M_n})$	Degree of polymerisation
PBAIT	0.78	6598	8994	1.36	15.06
PBSeIT	0.81	7076	9468	0.75	14.32

The extent of polymerization was determined by the molecular weight and the intrinsic viscosity of the polymers. The number average molecular weights ($\overline{M_n}$) of the copolymers PBAIT and PBSeIT were 8994 and 9468 g/mol respectively. The intrinsic viscosities of PBAIT and PBSeIT are 0.78 and 0.81 respectively.

3.2.Fourier- Transform Infrared (FTIR) Spectroscopy

FTIR spectra of copolymers derived from PBAIT and PBSeIT are shown in the Figure (1a&1b). Band characteristics of aromatic esters are observed between 1719.6 cm^{-1} and 1724.9cm^{-1}(C=O stretching) and 728.9 cm^{-1} and 729.2cm^{-1} (ring C–H out of plane bending). The C-H symmetric stretching of aliphatic-CH2- group observed at 2953-2925cm^{-1}.Strong vibrational modes observed at 1168-1164cm^{-1} are associated with C–O stretching modes of esters.(Fig.1a&1b)
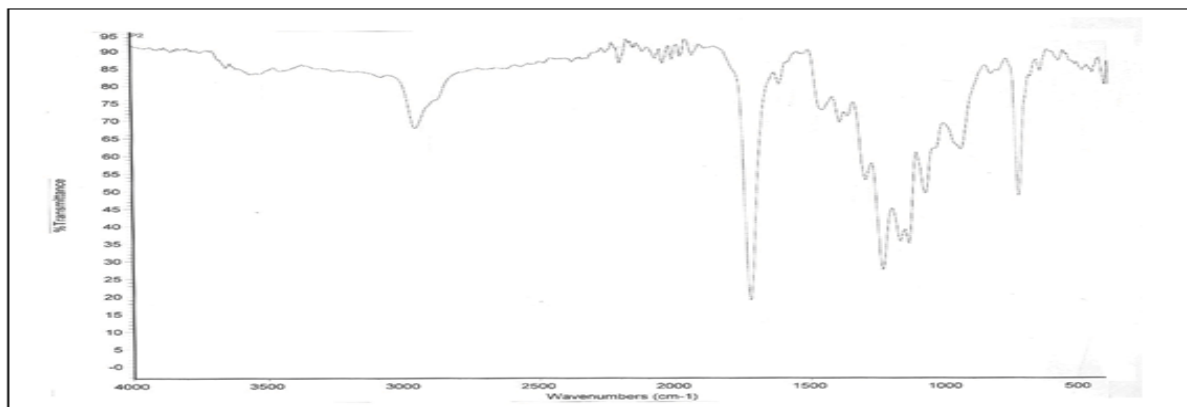
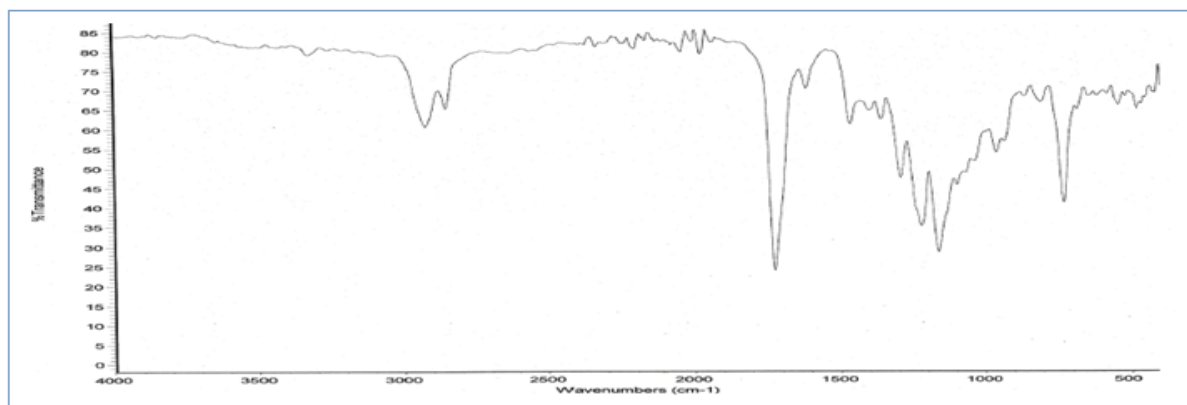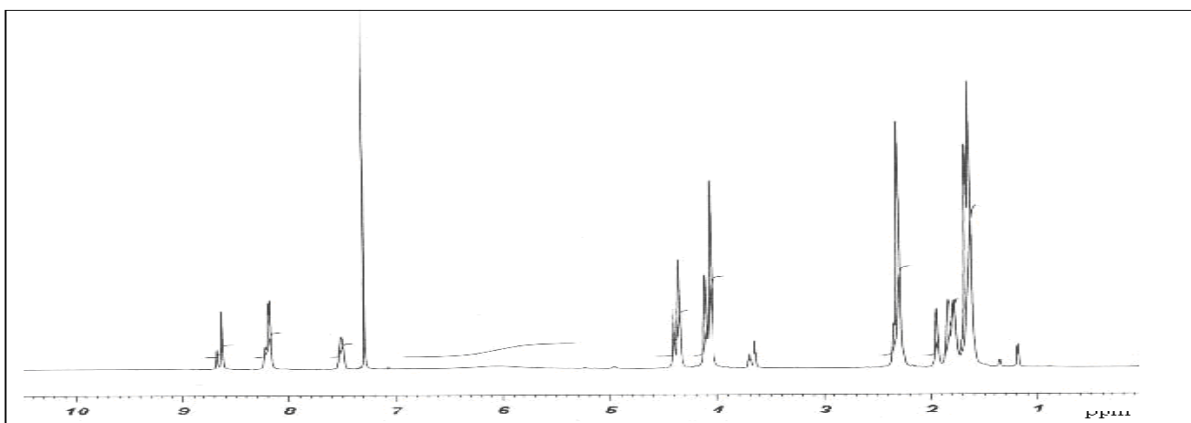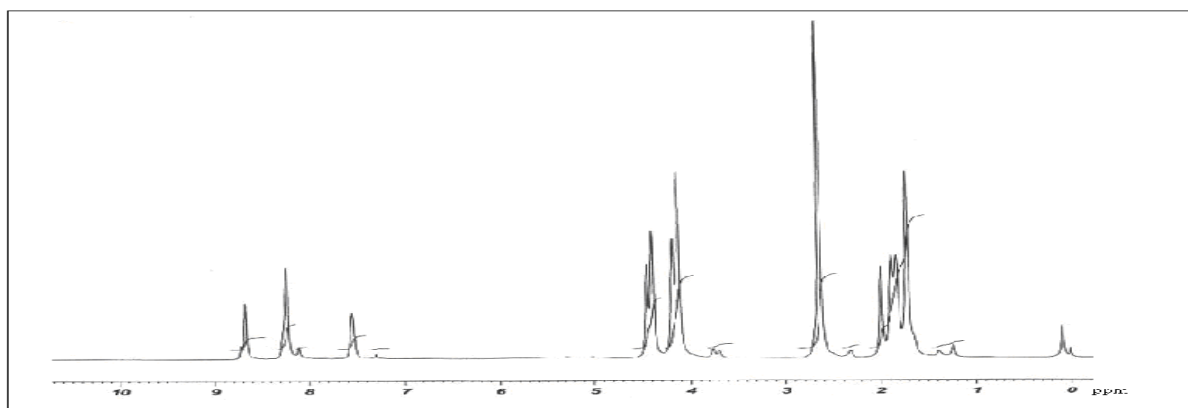Fig.1a. IR spectra of copolyester PBAIT

Fig.1b IR spectra of copolyester PBSeIT

3.3.^{1}H NMR spectral data of random copolyester

The chemical shift values observed from ^{1}H NMR spectra of the copolyesters are as follows.
A singlet at δ = 8.06-8.10 ppm is due to aromatic protons of isophthalic group, multiplet at δ = 4.05-4.12 ppm is due to the protons of –CO-O-CH2- group, multiplet at δ = 1.26-1.29 ppm is due to methylene protons of 1,4 butane diol.(Fig.2a & 2b)

Fig.2a ^{1}H NMR spectra of copolyester PBAIT

Fig.2b ^{1}H NMR spectra of copolyester PBSeIT

3.4.^{13}C NMR spectral data of random copolyester.

The chemical shift values obtained from ^{13}C NMR Spectra of the copolyesters are as follows.
A singlet at δ= 133.70-133.74 ppm is due to quartenary carbon atom of isophthalate. A doublet at δ = 165-173 ppm is due to carbonyl carbon atom of the ester group and multiplet at δ= 63-65 ppm is due to -CH2-CO-group.(Fig.3a&3b)
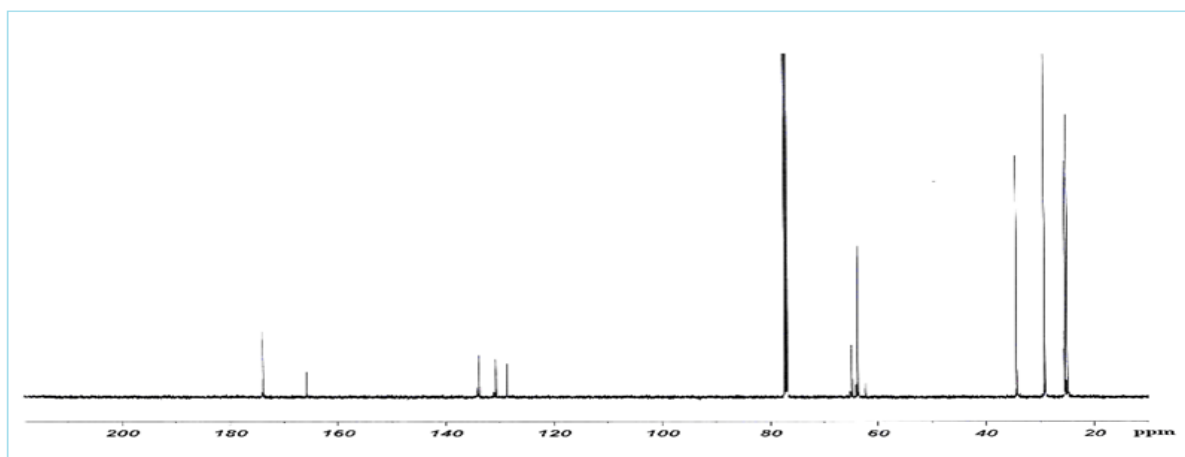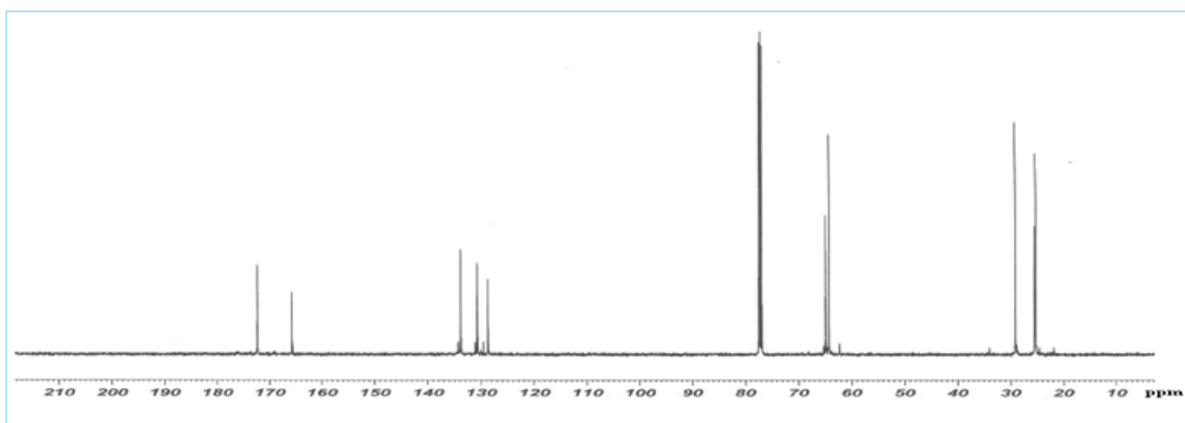

Fig.3a ^{13}C NMR spectra of copolyester PBAIT

Fig.3b ^{13}C NMR spectra of copolyester PBSeIT

3.5.Thermal Properties

The results obtained from DSC analysis are summarised in Table 2. DSC & TGA thermograms of the synthesized copolyesters are shown in Fig4.

Table 2. Thermal properties of the synthesised copolyesters

Copolyesters	Tg (^{o}C)	Tm (^{o}C)	Td (^{o}C)	ΔHm (J/g)
PBAIT	56.3	139.6	402.6	59.6
PBSeIT	54.3	134.3	398.6	58.5

PBAIT is a highly crystalline polymer exhibiting a melting temperature(Tm) of 139.6^{o}C and a heat of fusion of 59.6J/g while for PBSeIT, which is a less crystalline polymer, the corresponding values were 134.3^{o}C and 58.5J/g, respectively. The glass transition temperature (Tg) values of PBAIT and PBSeIT were 56.3^{o}C and 54.3 ^{o}C respectively. The glass transition temperature (Tg) of polymer is closely related to the flexibility of the chains because a high Tg is generally assumed to be connected with relatively high barrier of bone rotations [39]. When the length of the spacer group increases, it is observed on the thermogram that the glass transition temperature (Tg) values decrease. This can be attributed of more number of methylene groups in sebacate unit, which act as soft segments and decrease in Tg value of PBSeT.
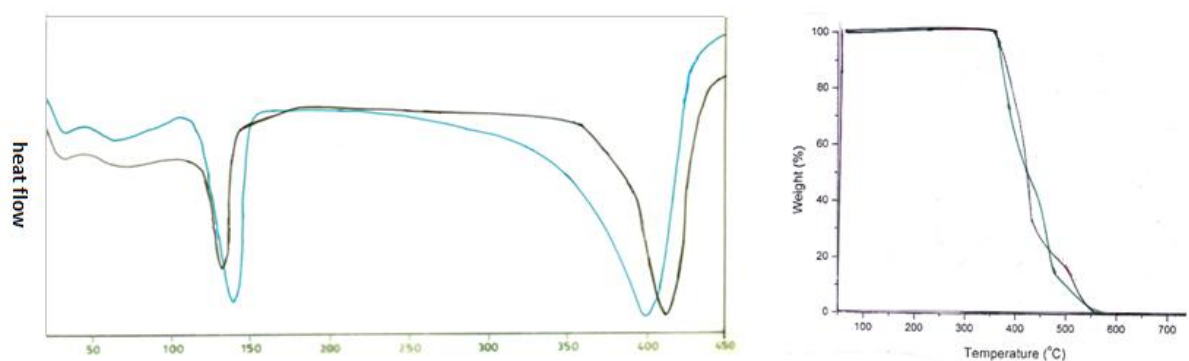

Fig.4 DSC & TGA thermograms of PBAIT & PBSeIT

3.6.X-ray Diffraction Analysis

X-ray diffractogram of the synthesized polymers are shown in Fig 5. Gaussian curves are used to describe the amorphous phase and crystal reflections of a diffractogram[40,41]. The diffractograms reveal that the degree of crystallinity decreases from PBAIT to PBSeIT which is supported by decrease in the melting point obtained from DSC measurements. This indicates that the crystallinity of the polyester decreases with the length of flexible segments.
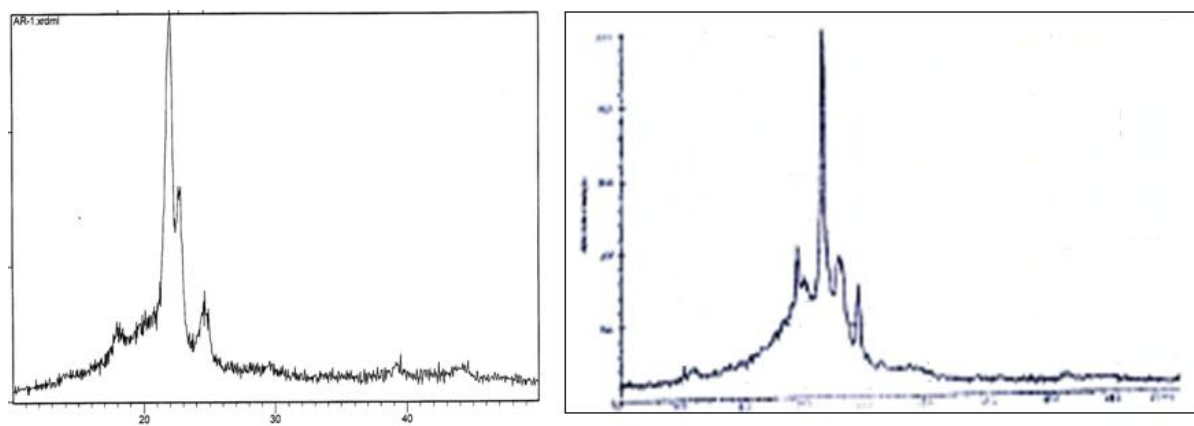

Fig.5. X-ray diffractograms of PBAIT & PBSeIT

3.7.Enzymatic Degradation

In order to examine the biodegradability of the synthesized polyesters, enzymatic hydrolysis was carried out[42]. The enzyme lipase from *Candida Cylindracea* was used for degradation studies. The rate and degree of enzymatic degradation of aliphatic–aromatic polyesters is usually related to their molecular weight, crystallinity, and chemical structure of polyesters. The biodegradability of the copolyesters was determined by monitoring the weight loss or erosion of films with time. The time course of the enzymatic degradation of the polyesters during 90h is shown in Fig6.
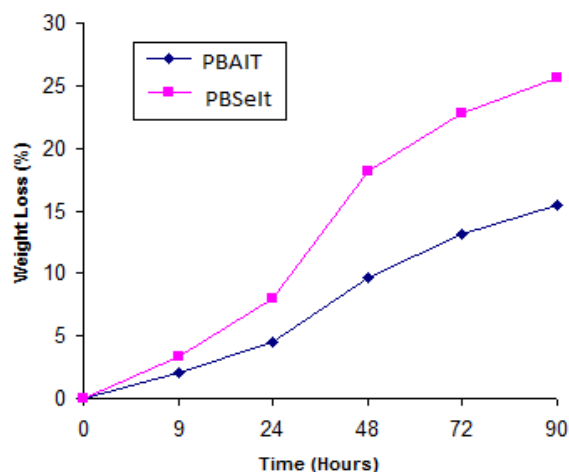

Fig.6 Enzymatic degradation of polyesters, PBAIT and PBSeIT

3.8.Scanning Electron Microscopy

The effect of biodegradation upon the copolyester film surfaces was examined and confirmed by SEM. As seen in the micrograph of Fig.7, the hydrolytic action of the enzyme led to the formation of a rough surface with cavities on the film surface.
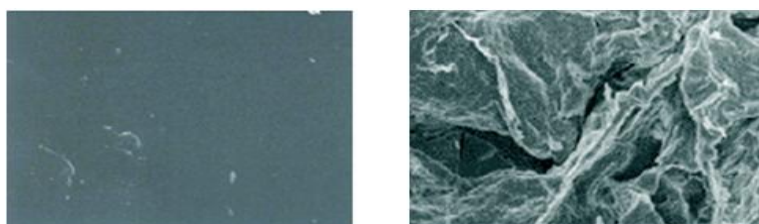

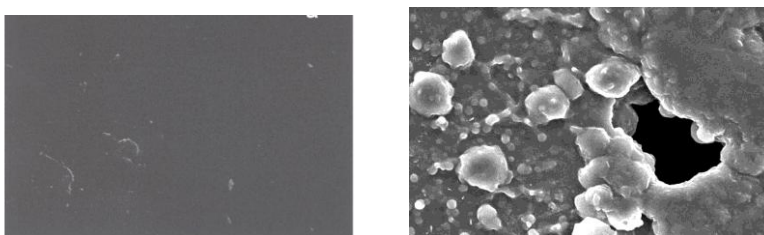Fig7a.SEM Micrographs of PBAIT before and after enzymatic degradation

Fig.7b.SEM Micrographs of PBSeIT before and after enzymatic degradation

3.9.Optical Polarising Microscopic studies (OPM)

The Liquid crystalline morphology was examined by polarizing microscopy. Figure 8 displays the characterization of liquid crystals by polarized light microscopy is the most useful for polymers possessing desired mechanical, thermal and optical properties[43-45]. The synthesized copolyesters exhibit a schlieren texture characteristic of nematics at 120°C, as shown in Fig. 7a & 7b. The isotropic transition temperatures (Ti) for these copolyesters were determined by the polarizing microscope, which are also listed in Table 3. An interesting observation from micrographs reveal that all the exhibiting nematic textures were retained till room temperature during cooling in optical analysis. Therefore, these copolyesters are commonly termed as liquid crystalline glasses.

Table 3.Thermal transition temperatures of the synthesized polyesters

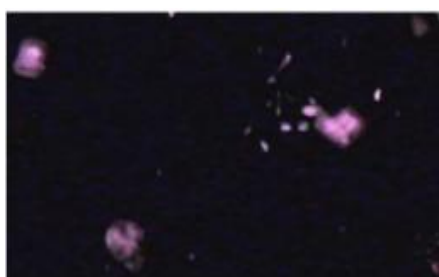| Copolyesters	$T_m(^oC)$	$T_i(^oC)$	$\Delta T(^oC)$	Types of mesophase
PBAIT	136.9	147.0	11.0	Nematic
PBSeIT	134.3	152.0	18.0	Nematic

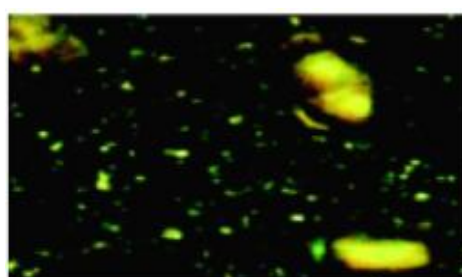

Fig.8a OPM for PBAIT(100X)   **Fig.8b OPM for PBSeIT (100X)**

Conclusion

The Aliphatic-aromatic random Liquid crystalline biodegradable Copolyesters were synthesized from adipic acid/ sebacic acid, isophthalic acid and 1,4-butanediol by   a two-step melt polycondensation, transestrification in the bulk using Titanium tetra butoxide as catalyst at 210°C under reduced pressure. The polymer exhibits good solubility in many common solvents which is an important quality in view of its applications. The synthesized polyesters were characterized by spectral and thermal methods of analysis.

The biodegradation of these polyesters were carried out using the enzyme lipase from *Candida Cylindracea.* The results clearly indicate that the mobility of the polymer chains is the major and general controlling factor on the biodegradability of polyesters. The highest enzymatic degradation rate was observed for PBSeIT, which may be due to its lower crystallinity and melting temperature. Thus, the degradation of polyesters was influenced by the polyester composition, polyester properties such as molecular weight, melting temperature, crystallinity and the glass transition temperature. Thermotropic liquid crystalline copolyesters synthesised in the present study showed nematic texture. Increasing the spacer length of methylene groups a decrease in liquid crystalline temperature and reduction in the clearing, melting transition temperatures along with schlieren texture formation was observed.

Reference:

(1) Rizzarelli P, Puglisi C, Montaudo . Polym. Degrad. Stab, 2004;85: 855.
(2) Anderson J. M et al. Polym. Int. 1998; 46: 163.
(3) Decker C, Bendaikha T. J. Appl. Polym. Sci. 1998;70: 2269.
(4) Umare SS, Chandure AS, Pandey RA. Polym. Degrad. Stab. 2007;92:464.
(5) Bikiaris DN, Papageorgiou GZ. Polymer, 2005;46: 12081.
(6) Kim JK et al. J.Polymer, 2001;42: 7429.
(7) Piao L. H et al.Polymer, 2003;44: 2025.
(8)Plikk P et al. Biomaterials, 2006; 27: 5335
(9)Amass w, Amass A, Tighe B. Polym. Int. 1998; 47: 89
(10)Zagar E et al. Biomacromolecules. 2006; 7: 2210
(11)Deng L.M et al. Acta Mate.2004; 52:5871
(12) Nakayama A et al. Polymer. 1998; 39:1213
(13)Gonasalves KE, Chen X, Cameron JA. Macromolecules. 1992; 25:3309

(14)Yoshie N et al. J. Appl. Polym.Sci.,1995; 56: 17

(15) Lim KY, Kim BC, Yoon KJ. J. Appl.Polym.Sci. 2003;88: 131

(16)Tokiwa Y, Suzoki T. J. Appl. Polym. Sci. 1981; 26: 441

(17) Jendrossek D, Handrick R, Annu Rev. Microbiol. 2002;56:403.

(18) Tokiwa Y, Suzuki T. Nature. 1977; 270:76.

(19) Nishida H, Tokiwa Y. Chem Lett. 1994; 8:1547.

(20) Murphy CA et al. Appl Environ Microbiol. 1996;62(2):456.

(21) Oda Y et al. FEMS Microbiol Lett. 1997; 152(2):339.

(22) Murphy CA et al. Appl Microbiol Biotechnol. 1998; 50(6):692.

(23) Belal E. Investigations on the biodegradation of polyesters by isolated mesophilic microbes. Dissertation, Technical University Braunschweig, Germany; 2003. Available from: http://opus.tu-bs. De/opus/volltexte/2003/501/.

(24) Kleeberg I et al. Appl Environ Polym Degrad. 1998; 64(5):1731.

(25) Kleeberg I et al.Biomacromolecules. 2005; 6(1):262.

(26) Chen Y et al. Biomacromolecules. 2004; 5(1):11.

(27) Herrera R et al. J. Polym Sci Polym Chem. 2002; 40(23):4141.

(28) Nagata M et al. 2001; 57(6):178.

(29) Nagata M et al. Polym J 1997; 33(10):10.

(30)Y.Tokiwa and T.Suzuki. Nature. 1977; 270:76

(31) Witt U, Muller RJ, Deckwer WD. J Environ Polym Degrad. 1995; 3:215-223.

(32) Witt U, Muller RJ, Deckwer WD. J Environ Polym Degrad.1996; 4:9-20.

(33)Witt U, Muller RJ, Deckwer WD. Makromol Chem Phys.1996; 197: 1525-1535.

(34)Witt U, Muller RJ, Deckwer W-D. J Environ Polym Degrad.1997; 5:81.

(35) Cifferi A, Krigbaum WR and Meyer RB. Polymer liquid crystals,Academic press. NY, 1982.

(36)Jin JI et al, Makromol. Chem. Makromol. Symp.1990; 33:97

(37)Watanabe J, Krigbaum WR.. *Macromolecules.* 1984, *17*, 2288.

(38)Percec V, Nava, H, Jonsson, H. *J. Polym. Sci., Part A: Polym. Chem.* 1987, *25*, 1943.

(39)V.Tserki et al. polym Degrad Stab, 2006;9: 367.

(40) Fernandz JP et al. Macromolecules.2004; 34 : 9018.

(41) Wang ZG et al. Polymer. 2000;41(5):1791

(42)Chen. Bor-kuan, Tsay, Sun-Yuan, Chen. Jun-Yuan Polymer. 2005; 46: 8624

(43)S. Li, M. Vert Degradable polymers: principles and applications In: Scott G, Gilead D, editors. London: Chapman & Hall; 1995; P48

(44) Cassidy PE. "Thermally stable polymers" Dekker, New York.1980; p.73.

(45) Liou GS, Kakimoto MA, Imai Y. J. Polym, Sci: Part A. Polym. Chem..1994; 32: 597.

(46) Reiji M et al. J. Oleo Sci. 2006;55(8): 403.

(47) Jaeger K-E et al. Bacterial lipases. 1994; 15:29.