

## Development of new aliphatic biocompatible polymers from PEG 400 for their applications

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This paper describes about novel aliphatic biocompatible polymers prepared from polyethyleneglycol (PEG 400) moieties by melt condensation of 1,12-decanediol, 1,10-decanediol, 1,8-octanediol and dodecanedioic acid. The structural elucidation and its properties of the polymers obtained were thoroughly investigated by various techniques such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR). The polycondensation reaction was carried by the presence of titanium(IV) isopropoxide as catalyst. Also these polymers were characterized by IR spectroscopy. The inherent viscosities and the solubilities of the synthesized copolymers were analysed with their corresponding results.

Keywords: Polycondensation, PEG 400, solubility, viscosity.

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### Introduction

This paper deals with the investigation on the synthesis, characterisation and preparation of certain random copolyesters containing aliphatic polymer backbone. In this modern world, polymers touch our lives from the daily household materials to complicated artificial heart. In our life we are exposed to huge number of applications in polymers, for instance, food wrapping, drug delivery, surgical sutures, the packaging of various items, protective coating on the surface of materials and so on. This is mainly due to their adaptability as their composition, properties, and forms can be manipulated to readily produce shapes and structures in the form of gels, films, fibers and solids<sup>1,2</sup>.

The objective of the present work is to synthesize the aliphatic copolyesters from dodecanedioic acid, PEG 400 as common monomer with 1,8-octanediol, 1,12-dodecanediol and 1,10-decanediol by melt polycondensation technique in the presence of Ti<sup>IV</sup> isopropoxide as catalyst.

#### Materials and methods:

PEG 400, 1,12-decanediol, 1,10-decanediol, 1,8-octanediol and dodecanedioic acid were purchased from E. Merck. Titanium(IV) isopropoxide purchased from Spectrochem were used as a catalyst.

#### Preparation of copolymers:

The synthesis of aliphatic copolyesters is carried out by two step melt polycondensation process<sup>11</sup>. The obtained copolyester Polyethyleneglycol-co-1, (PEDDDD) 12-dodecane dodecanate, Polyethylene glycol-co-1, (PEDEDD) 10-decane dodecanate, (PEODDD) Polyethylene glycol-co-1,8-octane dodecanate were purified by mixing with smallest quantity of acetone, the mixture is vigorously stirred for 20 min with ice-cold methanol. The obtained slurry is washed with methanol, filtered and dried at room temperature under reduced pressure (760 mm/Hg).

#### Instruments:

The nuclear magnetic (<sup>1</sup>H NMR) spectra were determined by Bruker AVIII 500 MHz with deuterated CDCl<sub>3</sub> as solvent with TMS as the standard. FTIR spectra of the copolyesters were recorded using potassium bromide pellets on a Shimadzu make over the range of 400–4000 cm<sup>-1</sup>. In the Perkin-Elmer DSC-2 instrument, the values are scanned over a range of –50°C to 300°C and heated at a rate of 10°C/min under dry nitrogen atmosphere. Thermal stability was determined by thermo gravimetric analysis (TGA, Perkin-Elmer TGS-2 instrument) over the range of ambient to 800°C at a heating rate of ten degree celsius per minute. The X-ray powder diffraction (WAXD) studies were conducted with a help of GE X-Ray 3003 diffractometer employing Cu K $\alpha$  filtered

radiation to inspect the amorphous/crystallinity of the polymer samples.

### Results and discussion

#### Solubility of random copolyesters:

The random copolyesters are soluble in polar solvents like chloroform, acetone, DMSO and DMF. This may be due to strong interaction of the rigid polymers with the polar solvents. Hence we come to a conclusion that the copolyesters are insoluble in water and alcohols. The results of the solubilities are displayed in Table 1.

#### Inherent viscosity:

The inherent viscosity of the synthesised random copolyesters was determined in chloroform at room temperature using Ubbelohde Viscometer. The values are listed in Table 2. The inherent viscosity values of the aliphatic copolyesters vary from 0.35 to 0.39 dL/g.

From the results, we conclude that on increasing the length of the spacer group in the repeating unit of the poly-

mer backbone, the inherent viscosity value increases. This may probably be due to increase in the degree of polymerisation and hence, the molecular weight.

#### Spectral analysis:

The microstructure of the synthesised copolymer chains are successfully determined by using spectroscopic methods. Commonly employed methods for the analysis and identification of synthesised polymers are FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. In the present investigation, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy methods have been employed to determine the structure of the repeating units for the random copolyesters chosen for the study.

#### FTIR spectroscopy:

An IR spectrum is a common technique for investigating the intermolecular and intramolecular interaction in polymers. The absorption frequencies and their respective graphs are displayed in Table 3 and Fig. 1.

Hence it is observed that the, -C=O stretching frequency

**Table 1.** Solubility of the copolyesters in common organic solvents

Sl. No.	Copolyesters	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	E <sup>e</sup>	F <sup>f</sup>	G <sup>g</sup>	H <sup>h</sup>	i <sup>i</sup>	J <sup>j</sup>
1.	PEDDDDA	+++	+++	++	++	++	+–	--	--	--	--
2.	PEDEDDA	+++	+++	++	++	++	+–	--	--	--	--
3.	PEODDDA	+++	+++	++	++	++	+–	--	--	--	--

<sup>a</sup>A = Chloroform. <sup>b</sup>B = Carbon tetrachloride. <sup>c</sup>C = Dichloromethane. <sup>d</sup>D = Tetrahydrofuran. <sup>e</sup>E = Tri fluoro acetic acid. <sup>f</sup>F = Acetone. <sup>g</sup>G = Water. <sup>h</sup>H = Hexane. <sup>i</sup>i = Diethyl ether. <sup>j</sup>J = Methanol.

(+++) Freely soluble, (++) Soluble, (+–) Sparingly soluble, (-- ) Insoluble.

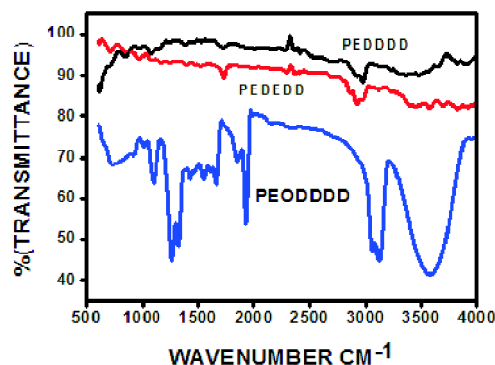
**Table 2.** Inherent viscosity data of random copolyesters

Sl. No.	Copolyester	Inherent viscosity ( $\eta_{inh}$ dL/g)
1.	PEDDDDA	0.3976
2.	PEDEDDA	0.3542
3.	PEODDDA	0.3641

**Table 3.** IR spectral data of random copolyesters

Absorption frequency (cm <sup>-1</sup> )			Assignment
PEDDDDA	PEDEDDA	PEODDDA	
1727	1727	1735	C=O stretching of ester group
1226	1051, 1107	1112, 1180	C-O stretching of ester group
1469	1469	1467	Aliphatic C-C stretching
2853, 2919	2853, 2919	2853	Aliphatic C-H stretching
3440	3440	3447	Broad band assigned to hydroxyl group

for the ester carbonyl group decreases with increase in the length of the spacer groups with respect to the main chain of the polyester.



**Fig. 1.** IR spectra of PEDDDA, PEDEDDA and PEODDDA.

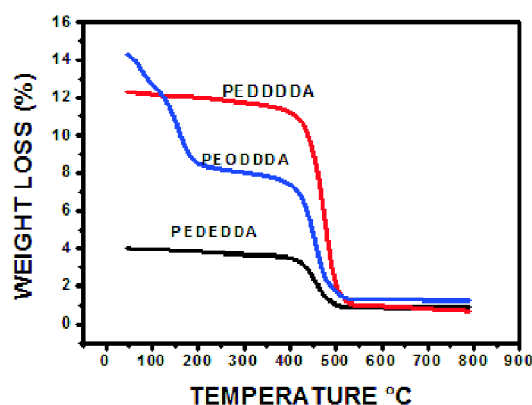




**Table 6.** DSC data of random copolyesters

Sl. No.	Polyester	$T_m$ (°C)	$T_g$ (°C)
1.	PEDDDDA	67.13	-12
2.	PEDEDDA	57.51	-12
3.	PEODDDA	57.84	-24

function of temperature in a controlled atmosphere. The TGA thermograms are presented in Fig. 9 and their corresponding decomposition temperatures ( $T_d$ ) are displayed in Table 7. From the results of TGA analysis, it is proved that all the copolymers could withstand up to 200°C, indicating good thermal stability.



**Fig. 9.** TGA spectrum of PEDDDDA, PEDEDDA and PEODDDA.

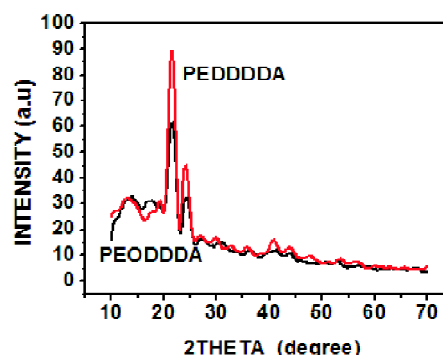
**Table 7.** Thermal decomposition data of random polyesters

Copolymer	PEDDDDA	PEDEDDA	PEODDDA
$T_d$ (°C) (10% weight loss)	210.10	258.62	185.84

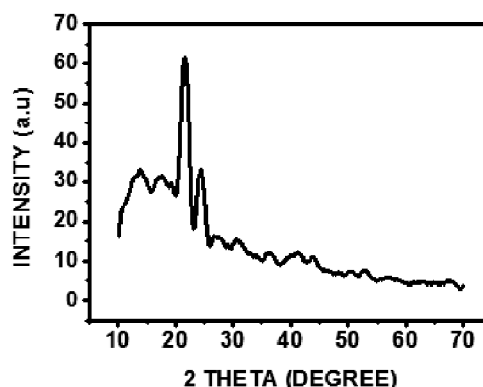
*Wide angle X-ray diffraction analysis:*

Powder X-ray Diffraction (XRD) is one of the primary techniques to examine the physical and chemical characteristics of polymeric materials. It determines the size and the shape of the unit cell for any compound. In the present work, the nature of the random copolyester samples was investigated by X-ray diffraction measurements by continuous scanning at room temperature. X-Ray diffractograms of the copolyesters are highlighted in Figs. 10 and 11 and their corresponding diffraction values are displayed in Table 8. From the results

of XRD analysis, we conclude that the chosen random copolyesters were found to be crystalline.



**Fig. 10.** XRD spectrum of PEDDDDA and PEODDDA.



**Fig. 11.** XRD spectrum of PEDEDDA.

**Table 8.** XRD data of random polyesters

Copolymer	PEDDDDA	PEDEDDA	PEODDDA
$2\theta$ (degree)	21.83, 24.24	21.58, 24.42	21.8, 24.8

**Conclusions**

This work deals with the synthesis and characterisation of PEG 400 based aliphatic random copolyesters. All the copolyesters have been synthesised by direct melt polycondensation of common monomer PEG 400 with diols and di-carboxylic acids using high temperature and high vacuum. Hence we conclude that the structures were elucidated with the help of IR, NMR spectral studies. The copolymers were found to be crystalline and thermally stable with the help of XRD, DSC and TGA studies.

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