

# Synthesis And Characterization Of New Aromatic Polyesteramides By Using Phosphorus Oxychloride As A Catalyst

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*Abstract: New aromatic polyesteramide was synthesized from 4-amino benzoic acid and 4-hydroxybenzoic acid. These monomers were carried out by the direct polycondensation reaction with phosphorus oxychloride as a catalyst, pyridine as an activating agent in dimethylformamide solvent system. This method produces polyesteramide of different morphology with fairly high average molecular weight, glass transition temperature and degradation temperature. This polymer has unique characteristics due to different functional group such as ester, amide and aromatic groups present in the polymer matrix which further helps in enhancing thermal and mechanical properties. The obtained polymer was characterized by the different methods such as Fourier transformed infrared spectroscopy, X-ray scattering, differential scanning calorimeter, thermo gravimetric analysis, solution viscosity method, and nuclear magnetic resonance.*

*Keywords: Poly (Ester Amide), 4-Amino Benzoic Acid, Hydroxybenzoic acid and Glass transition Temperature.*

## I. INTRODUCTION

Development of Polyesteramide (PEA) in high performance application with high glass transition temperature and good thermal properties has become very important in mechanical polymeric field. For synthesis of aromatic, aliphatic and combination of aromatic/aliphatic Polyesteramide many synthesis methods has been reported. The Polyesteramide have special structure due to the regular enhancement of ester and amide groups in the same polymer chain, which gave them the properties intermediate between the polyester and the polyamide [1]. Polyesteramide has been developed as promising biodegradable character caused by the existence of hydrolysable ester group in their backbone with good thermal as well as mechanical properties affordable by strong intermolecular hydrogen bonding interaction established between their amide groups.

Liquid crystals were observed in 1888 by Austrian botanist reinitzer who observed that cholesteryl benzoate exhibits two melting points [2]. Onsager in 1933 [3] and Flory in 1956 [4] predicted that rigid rod-like macromolecules should display liquid crystallinity. However, the first main chain thermotropic liquid crystalline polymer was reported in

open literature only in 1975 [5]. Liquid crystalline polymers has classified into main chain, side chain and combined. The mesogen used in the construction of the liquid crystalline polymer can be rod-like, disc-like or amphiphilic. In addition to linear polymer structures, cyclic, branched and crosslinked architectures have also been synthesized. Therefore, liquid crystalline polymers display thermotropic and lyotropic mesophases which was similar to those exhibited by thermotropic and lyotropic low molar mass liquid crystals. In addition, rigid rod like main chain non-amphiphilic polymers like poly(phenyleneterephthalamide), poly(p-phenylene-2,6-benzobisthiazole) and poly(p-phenylene-2,6-benzobisoxazole) exhibited lyotropic nematic mesophases [6].

In this research paper we have tried to synthesize the Polyesteramide by direct polycondensation method. The principle of direct polycondensation method is to form amide, ester linkage from amino acid, hydroxyl acid, diacid, diamine or diol with the help of condensing or activating agent under mild condition in solvent system. Structure was confirmed by Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance (NMR), thermal properties studied by Differential scanning calorimeter (DSC) and Thermo gravimetric analysis (TGA) and crystallinity analysis carried

out by X-Ray diffraction (XRD). Solubility and solution viscosity was studied by viscometry method.

## II. EXPERIMENTAL

### MATERIALS

4-Hydroxybenzoic acid (4HBA), p-aminobenzoic acid (PABA), Dimethylformamide, Pyridine and Phosphorus oxychloride were obtained commercially from S. D. Fine Chemical, Mumbai.

### SYNTHESIS OF POLYESTERAMIDE

Polyesteramide was synthesized according to previously reported method [7]. 250ml three necked jacketed round bottom flask was equipped with reflux condenser, mechanical stirrer and thermometer. 4-aminobenzoic acid and 4-hydroxybenzoic acid was dissolved in dimethylformamide (10 ml). The mixture was kept for stirring at 120°C temperature under nitrogen atmosphere for 10 minutes. Meantime a complex of phosphorus oxychloride in pyridine and solution of bisphenol-A was prepared in another beaker. After 10 minutes complex of phosphorus oxychloride with pyridine was added drop wise to the reaction mixture at 120°C temperature gave exothermic reaction, which formed white precipitate in dimethylformamide solution. This reaction mixture stirred for 3 hours and washed with methanol to separate out the precipitate of polymer. The obtained polymer was filtered using whatman filter paper followed by drying at 120°C which leads to formation of polymer in the powder form. After analysis of thermal properties of polymeric powder, it was formed into film by compression moulding at 250°C under pressure in 10 min processing time.

The reaction scheme of reaction is presented in Figure 1. The variation in composition of monomer with phosphorus oxychloride (POC) catalyst is mentioned in table 1.

Polymer	Mol of 4-HBA	Mol of PABA	Ester & amide ratio	Mol of POC
PEA-1	10 mmol (1.380gm)	0 mmol	100% & 0%	2.5mmol (0.23ml)
PEA-2	7.5 mmol (1.035gm)	2.5 mmol (0.342gm)	75% & 25%	2.5mmol (0.23ml)
PEA-3	5.0 mmol (0.69gm)	5.0 mmol (0.685gm)	50% & 50%	2.5mmol (0.23ml)
PEA-4	2.5 mmol (0.345gm)	7.5 mmol (1.027gm)	25% & 75%	2.5mmol (0.23ml)
PEA-5	0 mmol	10 mmol (1.370gm)	0% & 100%	2.5mmol (0.23ml)

Table 1: Different composition for polyesteramide

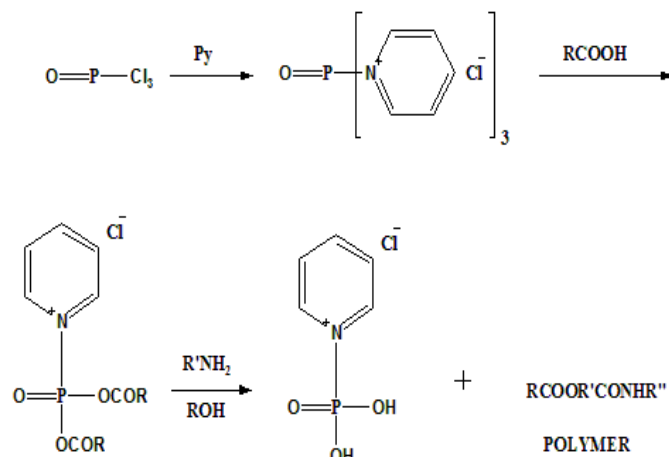


Figure: 1 Mechanism of polyesteramide synthesis

### METHOD OF CHARACTERIZATION

Solubility of polyesteramide was determined for powdery samples in excess of solvent. Viscosity measurements of the polymer solutions were carried out with Oswald viscometer at 30°C using appropriate set up of the thermostate. Fourier transformed infrared spectroscopy of the all polymer was analyzed by using a BRUKER Spectrum One spectrometer in between 4500 cm<sup>-1</sup> to 500 cm<sup>-1</sup>. 1H NMR Spectra was taken with dimethyl sulfoxide-d<sub>6</sub> as a solvent on Bruker DPX-200 spectrometer at 200 MHz (RSIC, CDRI). Differential scanning calorimetry (DSC Q 100 V9.9 Build 303, TA instruments) characterization was done to investigate the glass transition (T<sub>g</sub>) behavior of the polymers under scanning rate of 10°C/min which was maintained for both heating and cooling cycle; whereas nitrogen gas purge rate maintained at 50 ml/min. Thermogravimetric analysis (Simultaneous Thermal Analyzer STA 6000/8000) was done; which has balance range up to 1500mg, accuracy <math>\pm 0.5^\circ\text{C}</math> and temperature range from 15°C to 1000°C. Nature of polyesteramide was observed by X-ray diffraction by using Cu filament at 30 kV and 50 mA powers from 2 to 80° (2θ) scan axis with scan speed 2degree/min.

## III. RESULTS AND DISCUSSION

### SOLUBILITY ANALYSIS

The obtained polyesteramide was difficult to dissolve in many solvent. The solubility of polymer with different composition is mentioned in table 2. It states that dimethylsulfoxide (DMSO) and dimethylacetamide (DMAc) was good solvent for polymer. Polyesteramide showed good chemical resistance due to insolubility in many solvent.

++ Easily soluble, + soluble @ high temperature, - Insoluble even high temperature.

	PEA 1	PEA 2	PEA 3	PEA 4	PEA 5
DMSO	-	+	++	++	++
DMAc	-	+	++	++	++
DMF	-	-	+	+	++

THF	-	-	-	-	-
Chloroform	-	-	-	-	-
Methanol	-	-	-	-	-
Xylene	-	-	-	-	-
P-chlorophenol	+	+	-	-	-
Tetrachloroethane	-	-	-	-	-

Table 2: Solubility of Polyesteramide

### VISCOSITY ANALYSIS

Solution viscosity was carried out oswald viscometer in dimethylacetamide solvent at 0.1, 0.2 and 0.3 gm/100ml concentration which gave viscosity in dl/gm. Different inherent viscosity is mentioned in table 3. It state that PEA 3 has inherent viscosity up to 0.67 dl/gm. PEA 1 did not give result due to insolubility of polymer.

	Colour	Yield	$\eta_{inh}$ in dl/gm
PEA 1	White	93%	-
PEA 2	Light Brown	86%	0.65
PEA 3	Light Brown	85%	0.67
PEA 4	Dark Brown	78%	0.62
PEA 5	Dark Brown	75%	0.60

Table: 3 Solution Viscosities and Yield of Polyesteramide

### FOURIER TRANSFORMED INFRARED SPECTROSCOPY (FTIR) ANALYSIS

FTIR graph of poly (ester amide) is mentioned in figure 2. It indicate the presence of ester linkage C=O stretching around 1728, 1739  $cm^{-1}$ , amide linkage C=O stretching [8] 1649, 1656  $cm^{-1}$ , amide linkage N-H bending 3329, 3332  $cm^{-1}$  and N-H stretching [9] 1593, 1598  $cm^{-1}$ , C-O stretching for ester between 100-1300 $cm^{-1}$ . It also showed the presence of aromatic part C-C stretching around 1512, 1407, 1452  $cm^{-1}$  and C-H stretching 823, 847, 844 $cm^{-1}$  [10].

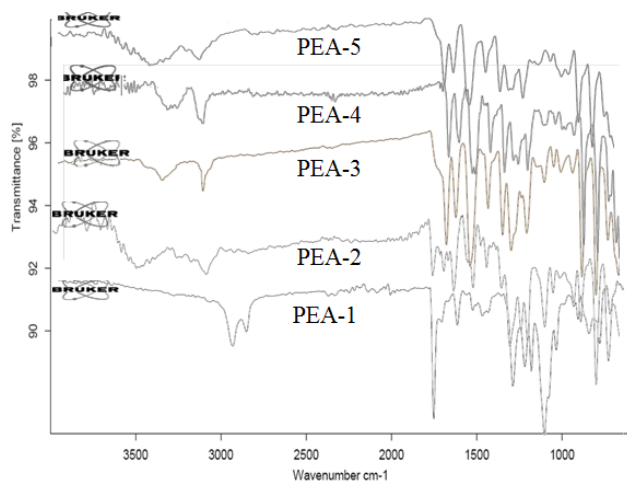


Figure 2: FTIR of Polyesteramide

### <sup>1</sup>H NUCLEAR MAGNETIC RESONANCE (NMR) ANALYSIS

<sup>1</sup>H NMR of PEA 2, PEA 3 and PEA 5 is mentioned in figure 3, 4 and 5 respectively. This gave aromatic C-H 1, 3, 5

positions at 7.98, 7.87 ppm of PEA 2; 7.95, 7.86 ppm of PEA 3 and 7.96, 7.87 ppm of PEA 5. It gave C-H 2, 4, 6 positions at 7.65, 7.67, 7.57 of PEA 2, 3, 5 respectively [11].

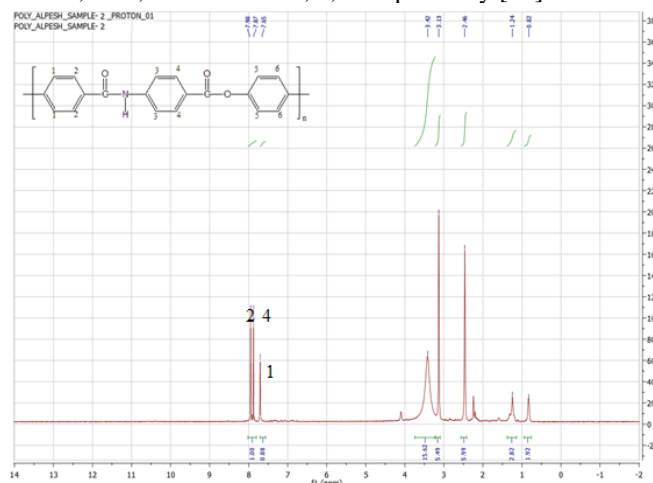


Figure 3: <sup>1</sup>H NMR of PEA 2

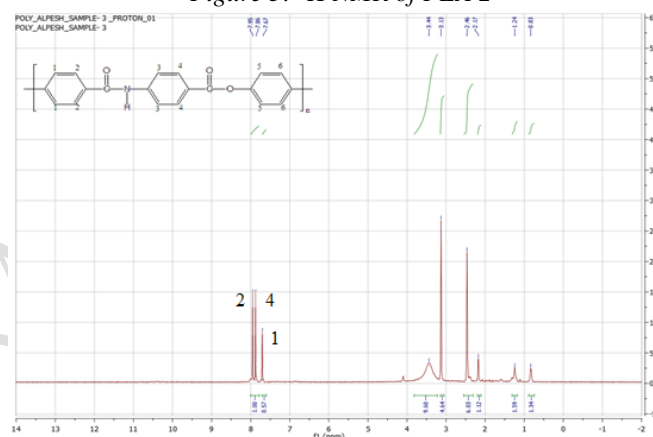


Figure 4: <sup>1</sup>H NMR of PEA 3

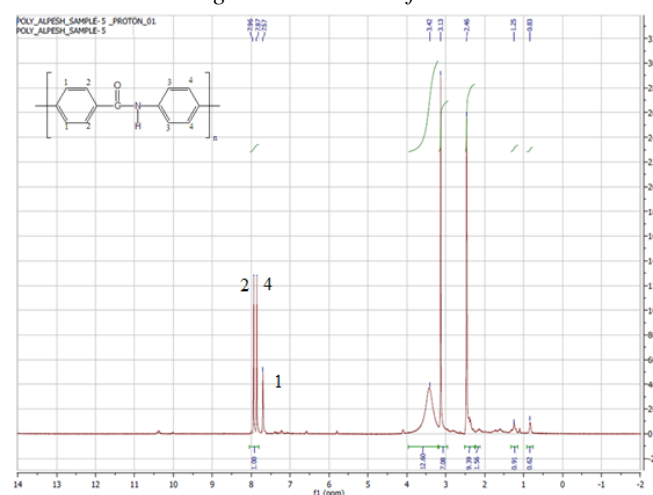


Figure 5: <sup>1</sup>H NMR of PEA 5

### DIFFERENTIAL SCANNING CALORIMETER (DSC) ANALYSIS

Glass transition temperature was studied by DSC which mentioned in figure 6. It showed the glass transition temperature 243°C, 244°C, 246°C, 259°C and 275°C of PEA

1, 2, 3, 4, and 5 respectively [12]. It showed very higher glass transition temperature because of highly aromatic group present in main chain in polymeric chain with ester and amide group. This glass transition temperature was also increased with increased in amide group.

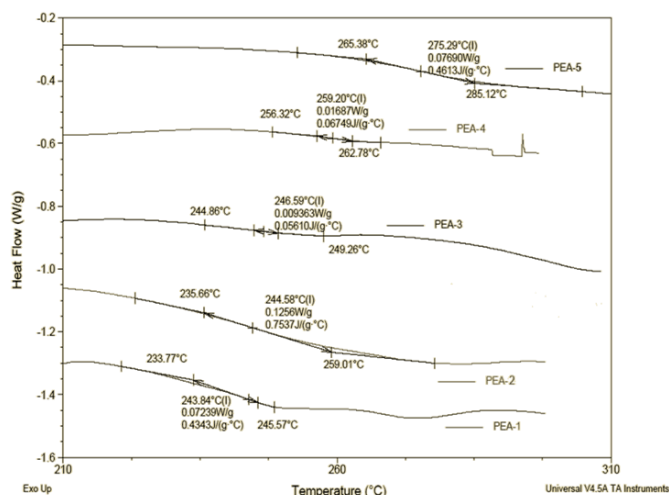


Figure 6: DSC graph of Polyesteramide

THERMO GRAVIMETRIC ANALYSIS (TGA)

Thermal analysis was studied by TGA which mentioned in figure 7 and Table 4. It showed that degradation started from 300°C. It gave 50 to 55 % weight loss up to 600 °C temperature. It showed that degradation completed only up to 60 to 70% even at 900°C temperature. It concluded that due to high level of aromatic group present in polymeric main chain which degraded in to carbon char and it gave high percent of degradation [13].

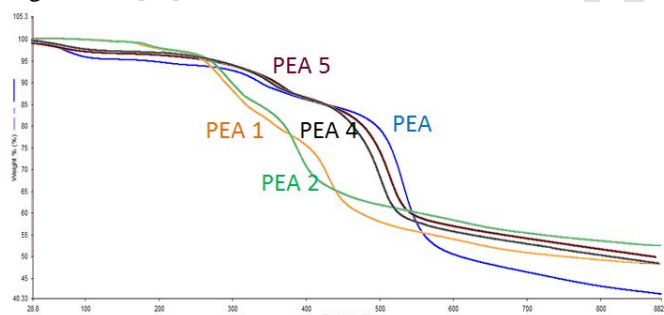


Figure 7: TGA of Polyesteramide

Polymer	PEA 1	PEA 2	PEA 3	PEA 4	PEA 5
10% Degradation	274°C	293°C	339°C	345°C	361°C
50% Degradation	445°C	468°C	609°C	615°C	637°C
Residue Percentage at 900°C	30%	33%	40%	38%	40%

Table 4: TGA chart of Polyesteramide

X-RAY DIFFRACTION (XRD) ANALYSIS

Crystallinity and amorphous nature of Polyesteramide was analyzed by wide angle X-ray diffraction technique which reported in figure 8. It gave 10.84, 8.99, 7.24, 9.05 and 9.33% crystallinity of PEA 1, 2, 3, 4, 5 respectively [14].

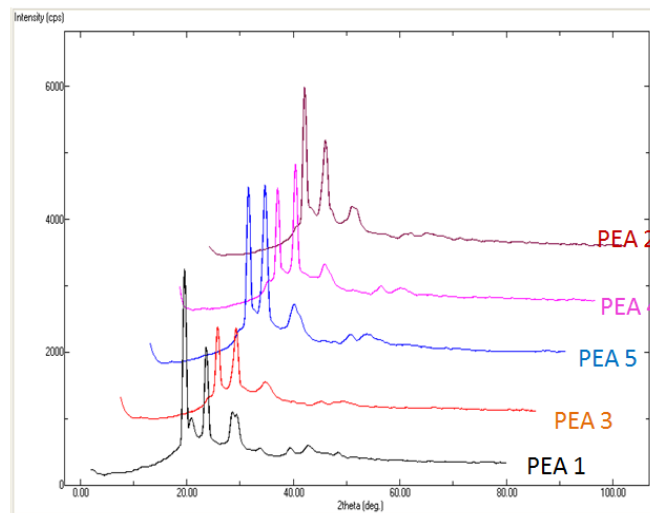


Figure 8: X-ray diffraction of Polyesteramide

IV. CONCLUSION

Polyesteramide was successfully synthesized by using different monomers like 4-hydroxy benzoic acid and P-amino benzoic acid with using phosphorus oxychloride catalyst. Polymer structure was confirmed by FTIR and <sup>1</sup>H NMR. This polymer gave much higher Glass Transition Temperature (Tg) up to 250°C. It gave solution viscosity only up to 0.60 dl/gm because of low molecular weight. It was unable to make film due to very high Tg and unable to melting because of their melting point is higher than its degradation temperature. Polyesteramide gave very good thermal properties because degradation starts from 400°C and 60-70% material degraded even up to 900°C temperature. It showed very good solvent resistance properties. It has come under Lyotropic Liquid crystalline polymer due to their structure and solubility property.

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