

Synthesis and Characterization of cyclohexylidene containing novel cardo poly(ester – amide)s

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ABSTRACT: A new aromatic diamine containing ester and a cardo cyclohexylidene moiety, viz; 1, 1-bis (4-aminobenzoyloxy phenyl) cyclohexane; was synthesized through reaction of 1, 1 –bis (4-hydroxy phenyl) cyclohexane and with two equivalents of *p*- nitrobenzoyl chloride followed by catalytic (Pd/C) hydrogenation and was characterized by IR, NMR and mass spectroscopy. A new series of aromatic poly(ester-amide)s was synthesized by low temperature solution condensation of (*p*-BPCDA) with diacid chlorides such as terephthaloyl chloride, (TPC) and isophthoyl chloride (IPC) in DMAc. Co-polyamides were also prepared from diamine (*p*-BPCDA) and TPC and IPC in different mole proportions. These poly(ester – amide)s were characterized by IR spectroscopy, solubility, viscosity, thermal analysis and X- ray diffraction studies. Inherent viscosities of poly (ether -amide)s were in the range of 0.25 to 0.48 dL / g indicating moderate molecular weight built -up. These polymers had better solubility in polar aprotic solvents such as *N,N*- dimethyl acetamide, *N*-methyl-2-pyrrolidone, dimethyl sulphoxide etc. Glass transition temperatures of these poly(ester – amide)s were in the range of 207 to 210 °C when analyzed by DSC under nitrogen atmosphere. Thermogravimetric analysis of these polymers showed no weight loss below 290 °C supporting the fact that these poly(ester – amide)s have excellent thermal stability. X- Ray diffraction pattern of polymers suggested the amorphous nature. The structure - property correlation among these poly(ester – amide)s was studied, in view of their potential applications as processable high temperature resistance materials.

Key Words: 1, 1-Bis (4- aminobenzoyloxy phenyl) cyclohexane, poly(ester – amide)s, low temperature solution polycondensation, solubility, thermal properties, XRD.

I. INTRODUCTION

Worldwide efforts were devoted to the synthesis and evaluation of new thermally stable polymers. The greatest success was achieved with polymers containing aromatic or heterocyclic rings in the main chain backbone and many different hetero-cyclic structures were so incorporated. Because of problems arising through poor availability of starting materials and difficulties in synthesis or processing relatively few of these polymers achieved commercial viability. Of those polyamides and polyimides stand supreme with respect to useful technological properties and processability coupled with heat resistance. Search for new class of thermally stable polymers has diminished quite appreciably and efforts are concentrated on improved methods of synthesis of known structures or on modifications to their structure to improve fabricability with minimum loss of thermal stability. The aero-space and defense applications require high temperature resistance polymers utilization. The thermally stable polymers are insoluble in most of organic solvent, making them difficult to fabricate¹ due to their high softening temperature. Several approaches were made to improve processing characteristics, emphasis was placed on the synthesis of thermally stable polymers by incorporating flexible groups such as, ether, sulphone, oxyethylene, aliphatic linkage, cardo group, bulky pendant group etc. into the polymer backbones, preparation of copolymers and by disturbance of rigid crystalline structure of polymer to improve their solubility in organic solvents without much sacrifice in thermal stability²⁻¹⁰.

Previous studies have reported that incorporation of cardo groups such as cyclododecylidene¹¹⁻¹², *tert*-butylcyclohexylidene¹³ into the backbone of polyamides results in polymers with enhanced solubility retaining high thermal stability¹⁴⁻¹⁸. Wenjeng Guo et al¹⁹ prepared soluble and thermally stable aromatic poly (ester - amide)s and poly(ester-imide)s. In present investigation a new para oriented cardo aromatic diamine containing cyclohexylidene moiety, 1, 1-bis (4- aminobenzoyloxy phenyl) cyclohexane; *p*-BPCDA, (IV) was synthesized and characterized by spectral techniques. A series of poly (ester - amide)s was synthesized from (IV) by low temperature solution polycondensation method with different mol proportion of IPC and TPC. The polymers were characterized by measurement of inherent viscosity, solubility, FT-IR spectra, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and X-ray diffraction so as to study the effect of introduction of cardo cyclohexylidene moiety and ester linkage and structure of aromatic diacid chloride into polymer backbone.

Experimental:**Materials:**

All the solvents / chemicals were purified before use by following the standard procedures²⁰. Pyridine was refluxed with solid potassium hydroxide pellets, fractionally distilled and stored over Linde type 4 Å Molecular sieves. N- Methyl – 2 pyrrolidone (NMP) was dried by azeotropic removal of water with benzene for 6 h, distilled under reduced pressure and stored over Linde type 4 Å Molecular sieves. N-N Dimethylacetamide was refluxed over barium oxide for 4h, the liquid was decanted in a separate round bottom flask and distilled at reduced pressure over calcium hydride and stored over Linde type 4 Å Molecular sieves. Lithium chloride (LiCl) was dried under vacuum at 150 °C for 6h. Isophthalic acid was crystallized from aqueous ethanol. Terephthalic acid was purified via the sodium salt which, after crystallization from water, was recovered to the acid by acidification. 4-Nitrobenzoic acid was crystallized from ethanol.

Phenol, cyclohexanone, glacial acetic acid, conc. hydrochloric acid Pd/C 10% (S. d. Fine Chem Ltd.), isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) were used as received. (S. d. Fine Chem Ltd.) was used as received.

Measurements:

Inherent viscosity measurements were made with 0.5 % (W/V) solution of polymers at 30 ± 0.1 °C using Ubbelohde suspended level viscometer. The solubility of polymers was determined at 3% concentration in various solvents at room temperature or by warming, if needed. Infrared measurements were performed on a Perkin-Elmer Spectrum GX spectrophotometer using KBr pellet technique or in chloroform. NMR spectra were recorded on a Bruker 200, 400 or 500 MHz spectrometer at resonance frequencies of 200, 400 or 500 MHz for ¹H and 50, 100 or 125 MHz for ¹³C measurements using CDCl₃ or DMSO d₆ as the solvent, whereas Mass spectra were recorded on Shimadzu GC-MS, QP-2010 spectrometer. (Column: DP; Length: 30 meters). For DI the instrument programming was: Initial temperature was room temperature and then every 10 °C rise per minute till 350 °C and at the maximum temperature the hold time was 10 minute. The thermogravimetry was performed on Rigaku Thermoflux TG- 8110 at a heating rate of 10 °C / min under the nitrogen atmosphere. DSC analysis was carried out on TA Instruments DSC Q10, at a heating rate of 20 °C / minute in nitrogen atmosphere. X-Ray diffraction patterns of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer powder was used for X-ray measurements.

Monomer synthesis:**a) Synthesis of p- nitrobenzoyl chloride (PNBC):**

In a 100 ml round bottom flask equipped with reflux condenser and calcium chloride guard tube, 20 g (0.12 mol) of p- nitrobenzoic acid (PNBA) and 35 mL (0.48 mol) thionyl chloride were placed. The mixture was stirred with magnetic stirrer, and 4 mL of dimethyl formamide were added. The reaction mixture was heated at 80 °C for 5h to get clear solution. The excess of thionyl chloride was removed by distillation and traces of thionyl chloride were removed azeotropically using dry benzene. The residue was dissolved in dry hexane and filtered rapidly under nitrogen, and filtrate was subjected to distillation to remove hexane. The residual acid chloride (PNBC) was purified by vacuum distillation and distillate was recrystallized from dry hexane. Yield: 81 %, M.P. 73 – 74 °C (Lit. 75 °C).

b) Synthesis of 1, 1-bis (4-hydroxy phenyl) cyclohexane (II) (BHPC):

In a three neck 500 mL round bottom flask equipped with thermowell, condenser and magnetic stirrer were placed 47.0 g (0.5 mol) phenol and 24.5 g (0.25 mol) cyclohexanone. To this solution 100 mL conc. 36 % HCl and 50 mL glacial acetic acid were added. Resulting reaction mixture was stirred for 5 h at 45 °C and over night at room temperature. Then the product was isolated by filtration and washed with hot water and then with benzene. A crude bisphenol, BHPC, was purified by dissolving in minimum quantity of 2 M NaOH at room temperature and the resulting solution was filtered. The filtrate was acidified with conc. HCl to yield the product. The product was filtered, washed with water till acid free, dried and recrystallized from methanol to get white shining crystals of (BHPC). Yield: 79 %, M.P. 189-190 °C (Lit. 190 – 192 °C).

c) Synthesis of 1, 1-bis (4- nitrobenzoyloxy phenyl) cyclohexane (III):

1, 1- Bis (4-hydroxy phenyl) cyclohexane (II) (BHPC) (10.72 g, 0.04 mol) was dissolved in 120 mL dry N, N- dimethyl acetamide (DMAc); and triethyl amine (12 mL, 0.088 mol) were mixed in a 500 mL three neck round bottom flask equipped with a calcium chloride guard tube, a condenser, a thermowell and a magnetic stirrer. The resulting reaction mixture was cooled to 5 °C and a solution of 4 – nitrobenzoyl chloride (15.6 g; 0.084 mol) in DMAc (40 mL) was added dropwise over a period of about 1 h. After complete addition, the reaction mixture was stirred at room temperature for 1 h and at 80 °C for 8 h. The reaction mixture was then poured into 600 mL water. The precipitate was collected by filtration, washed thoroughly with water, methanol and dried. The product was light yellowish in colour. Yield: 71 %, M.P. 185-187 °C.

IR (CHCl₃): 1742 cm⁻¹ (C=O stretching); 1531, 1350 cm⁻¹ (-NO₂ stretching) and 1266, 1170 cm⁻¹ (C-O-C stretching).

d) Synthesis of 1, 1-bis (4- aminobenzoyloxy phenyl) cyclohexane (IV) (p-BPCDA):

A mixture of 14.153 g (0.025 mol) of the bis (ester – nitro) (III) compound and 0.284 g of 10% Pd/C in 150 mL of DMAc was stirred at room temperature under a 4 kg/cm² hydrogen pressure. The progress of reaction was monitored by TLC. The time required for complete conversion of dinitro to diamine was about 30 h. The solution was filtered to remove the catalyst, and the obtained filtrate was poured into 700 mL of stirred water to give a light green product, p-BPCDA. Finally the bis (ester – amine) (p-BPCDA) was recrystallized from methanol. Yield: 80 %, M.P. 260 - 262 °C.

IR (CHCl₃): 3435, 3354 cm⁻¹ (N-H stretching), 1726 cm⁻¹ (C=O stretching), and 1294, 1105 cm⁻¹ (C-O-C stretching).

Synthesis of poly(ester - amide)s:

In a 100 mL three necked round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet, a calcium chloride guard tube, and a thermowell were placed 0.506 g (0.001mol) 1, 1-bis (4- aminobenzoyloxy phenyl) cyclohexane (IV), (p-BPCDA) and 3 mL dry DMAc was added to the flask. The mixture was stirred under nitrogen atmosphere till the dissolution was complete. The reaction flask was cooled to -15 °C with the help of ice – salt mixture. 0.203 g (0.001 mol) Terephthaloyl chloride was added in two lots and stirring was continued for 2 h at 0 °C. Then the mixture was stirred for 12 h at room temperature; and neutralized with 0.075 g (0.00104 mol) lithium carbonate and heated at 80 °C, for 20 min. It was then degassed under vacuum and the polymer was precipitated by adding reaction mixture to excess of rapidly stirred methanol. The precipitated polymer was filtered, washed with water and finally with methanol. It was dried at 80 °C under vacuum for 6 h. The yield of polymer (PCPA – 1) was 90 % and inherent viscosity of polymer was 0.43 dL / g.

The other poly (ester - amide)s PCPA – 2 to PCPA -5 were synthesized by utilizing similar procedure, where in a mixture of different mol % proportion of (TPC) and (IPC) were polycondensed with (IV), (p-BPCDA).

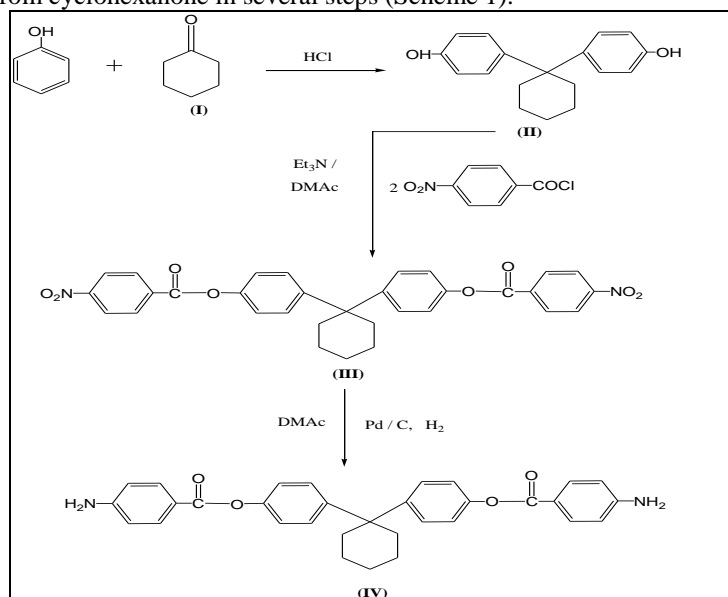
Results and Discussion:

Some aromatic polyamides (aramides) having bulky pendant groups such as phenyl, phenoxy, phenylthio and phenyl carbonyl were characterized by both high glass transition temperature (above 200 °C) and good solubility in organic solvents. Synthesis of cardo polymers, by introduction of bulky loops to polymer backbone was successful to obtain processable or soluble polymers. Soluble and thermally stable polyamides and polyimides were reported¹³⁰⁻¹³¹. These polymers were derived from 1, 1-bis [4-(4- amino phenoxy) phenyl] cyclohexane. However there are no reports on corresponding 1, 1-bis (4- aminobenzoyloxy phenyl) cyclohexane p-BPCDA, (IV) diester - diamine and polymers therefrom. It would be interesting and worth to study the synthesis and characterization of novel new diester – diamine p-BPCDA, containing cyclohexylidene as a pendant group and correlate properties of polymers derived from p-BPCDA.

Hence, in the present work synthesis of novel bis (ester – amine) viz, 1, 1-bis (4- aminobenzoyloxy phenyl) cyclohexane (IV) (p-BPCDA) with preformed diester linkage and the synthesis of poly (ester – amide)s using p-BPCDA and different mol proportion of IPC and TPC is presented.

Synthesis of monomer:

The new bis(ester–amine); 1,1-bis (4-aminobenzoyloxy phenyl) cyclohexane (IV) (p-BPCDA) was synthesized starting from cyclohexanone in several steps (Scheme 1).



Scheme – 1: Synthesis of 1, 1-bis (4- aminobenzoyloxy phenyl) cyclohexane p-BPCDA, (IV).

1, 1-Bis (4-hydroxy phenyl) cyclohexane (II) was synthesized by reacting phenol with cyclohexanone in presence of acid catalyst. The p- nitrobenzoyl chloride (PNBC) was synthesized from p- nitrobenzoic acid (PNBA) and thionyl chloride.

1, 1-Bis (4- nitrobenzoyloxy phenyl) cyclohexane (III) was prepared by condensation of (II) with two moles of p- nitrobenzoyl chloride. Structure of novel (III) was confirmed by IR, NMR and mass spectra. The infrared spectrum of (III) exhibited characteristic absorptions at 1742 carbonyl (C=O) stretching; 1531, 1350 nitro (-NO₂) stretching and 1266, 1170 cm⁻¹ ether (C-O-C) stretching.

¹H NMR spectrum of (III) showed doublet of doublet at 8.36; 8.35 δ corresponding to aromatic protons of phenyl ring with nitro group and at 7.35; 7.18 δ for aromatic proton of phenyl ring attached to cyclohexylidene moiety. NMR signals at 2.32 and 1.57 δ correspond to cyclohexylidene moiety.

¹³C NMR spectrum of (III) showed thirteen NMR signals corresponding to thirteen types of different carbons of which carbonyl carbon appeared at 162.31 δ; whereas tertiary carbons showed signals at 152.58 (C-NO₂); 149.79, 147.17, 145.37 and 44.83 δ. The CH carbons appeared at 130.23, 127.39, 122.68, 120.01 δ, whereas CH₂ carbon gave NMR signals at 36.20, 25.20, and 21.75 δ confirming the formation the structure of compound.

DEPT spectrum of (III) also confirms the structure of bis (ester – nitro) compound, all the quaternary carbons were absent in the spectrum and the peaks of CH carbons appeared as positive signals at up sides at 130.24, 127.39, 122.68, 120.01 δ and CH₂ appeared as negative signals at down side at 36.26, 25.19 and 21.74 δ.

Bis (ester – nitro) compound (III) on catalytic (Pd/C) hydrogenation yielded 1, 1-bis (4-aminobenzoyloxy phenyl) cyclohexane (IV) (p-BPCDA). The structure of bis (ester – amine) (IV) was confirmed by IR, NMR and mass spectra.

Infrared spectrum of bis (ester – amine), p-BPCDA, (IV) exhibited the characteristic absorption band at 1726 cm⁻¹ (C=O stretching); which is about 30 cm⁻¹ lower than that of the bis (ester - nitro) (III). Conjugation of the amino group substituted at the para position and effective delocalization of electron pair from NH₂ to carbonyl caused the absorption shift. Absorption bands at 3451, 3362 cm⁻¹ (N-H stretching) and 1264, 1106 cm⁻¹ (C-O-C stretching) confirms the structure.

¹H NMR spectrum (Fig. 1) of (IV) showed aromatic proton signals at 7.93; 7.88; 7.36; 7.11; 6.90 and 6.64 δ as expected with desired integration and splitting pattern. The amino group signal appeared at 3.36 δ. Peaks at 2.31 and 1.49 δ corresponds to methylene protons of cyclohexylidene moiety.

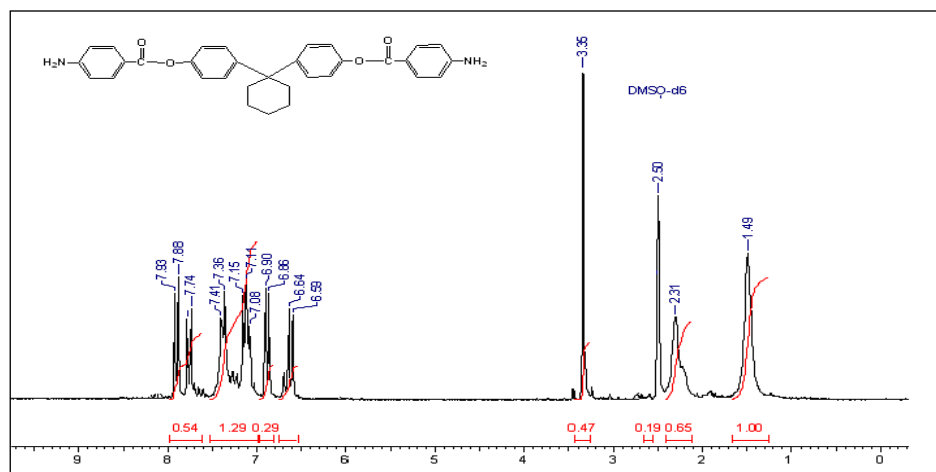


Fig. 1: ¹H- NMR spectrum of bis (ester – amine) (IV)

¹³C NMR spectrum of (IV) bis (ester – amine) showed thirteen NMR signals corresponding thirteen different types of carbons, of which carbonyl carbon appeared at 165.10 δ; whereas tertiary carbons showed signals at 157.07 (C-NH₂); 154.80, 149.08, 132.44, 118.62 and 45.70 δ. The CH carbons appeared at 131.82, 128.33, 122.26, and 113.40 δ, whereas CH₂ carbon gave NMR signals at 36.92, 25.60, and 23.10 δ confirming the formation of bis (ester –amine) compound (IV).

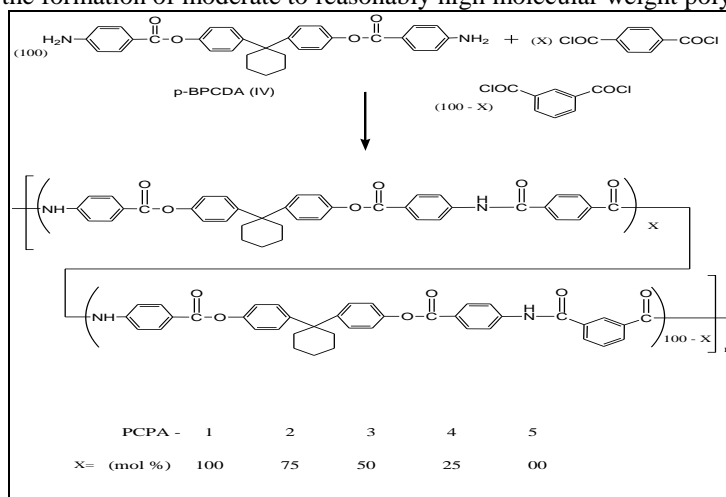
DEPT spectrum of bis (ester – amine) also confirms the structure of (IV), all the quaternary carbons were absent in the spectrum and the peaks of CH carbons appeared as up side (positive signals) at 131.82, 127.71, 121.64, 112.76 δ and CH₂ appeared as down side (negative signals) at 36.28, 25.51 and 22.49 δ.

p- Nitrobenzoyl chloride (PNBC) was synthesized from p-nitro benzoic acid by using thionyl chloride and dimethyl formamide as a catalyst. The observed melting points are same as reported in literature indicating the high purity of PNBC.

Polymerization:
a) Synthesis of poly (ester – amide)s:

Aromatic poly (ester – amide)s were synthesized (Scheme 2) by condensation of p-BPCDA, (IV) with IPC and / or TPC in different mol proportion by low temperature solution polymerization in DMAc. The polymerization proceeded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in methanol.

The data of poly (ester – amide)s from p-BPCDA, (IV) are presented in Table -1. All the polymers were obtained in good yields (80 to 90 %). The inherent viscosities of polymers were in the range of 0.25 to 0.48 dL/g; indicating the formation of moderate to reasonably high molecular weight polymers.

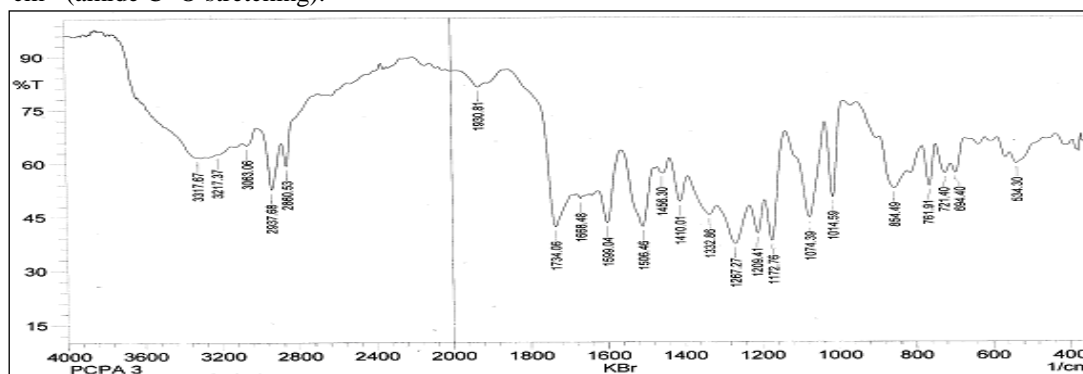

Scheme – 2: Synthesis of poly(ester – amide)s (PCPA -1 to PCPA-5)
Table – 1: Synthesis of poly (ester-amide)s^(a) from p-BPCDA (IV) and (IPC + TPC).

Polymer Code	Diamine	Diacid Chloride		Yield (%)	Viscosity dL/g ^(b)
	mol %				
	(p-BPCDA)	TPC	IPC		
PCPA – 1	100	100	00	90	0.43
PCPA – 2	100	75	25	81	0.48
PCPA – 3	100	50	50	80	0.35
PCPA – 4	100	25	75	82	0.25
PCPA – 5	100	00	100	83	0.34

a) Polymerization was carried out with 1 mmol of p-BPCDA (IV) and 1 mmol of TPC and / or IPC.

b) Measured at concentration of 0.5 g/dL in DMAc containing 2 % LiCl at 30 °C.

The structural features of the poly (ester – amide)s were characterized by FT-IR spectroscopy. The infrared spectrum of polymer PCPA -3 (Fig. 3) showed characteristics absorption at 3317 cm⁻¹ (N-H stretching), 1506 cm⁻¹ (N-H bending), 1668 cm⁻¹ (amide C=O stretching). The polymer PCPA-5 showed similar absorption bands, which are slightly shifted to lower frequency side, viz. at 3325 (N-H stretching), 1506 (N-H bending), 1639 cm⁻¹ (amide C=O stretching).


Fig. 3: Infrared spectrum (KBr) of PCPA-3

All other poly (ester – amide)s PCPA-1, PCPA-2 and PCPA-4 also exhibited strong characteristics absorption bands at around 1734 cm^{-1} (ester C=O stretching) and at 1267 and 1074 cm^{-1} (asymmetrical and symmetrical C – O – C stretching, respectively) due to the ester group.

The absorption band at 3063 cm^{-1} characteristic for aromatic –CH stretching; and absorption band at 2937 cm^{-1} corresponding for aliphatic (–CH stretch) methylene linkage were observed. Disappearance of absorption bands at 3350 cm^{-1} indicated that the amine groups has reacted completely to yield poly (ester – amide)s.

Solubility characteristics of poly (ester – amide)s is tabulated in Table -2. The solubility of polymers was determined in different common organic solvents. It is observed that poly (ester – amide)s synthesized from p-BPCDA, (IV) exhibited better solubility in various polar aprotic solvents such as N-methylpyrrolidone (NMP), N,N-dimethyl sulphoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethyl formamide (DMF). These poly (ester - amide)s also dissolved in pyridine, and Conc. H_2SO_4 etc. whereas in m-cresol they were soluble on heating. These polymers were also partly soluble in THF.

Thus better solubility of these poly (ester – amide)s; as expected; can be attributed to the introduction of cardo cyclohexylidene moiety, flexible ester linkage in the polymer backbone and copolymerization resulted in amorphous nature of polymers.

Thermal behaviour of these polymers was evaluated by means of dynamic thermogravimetry and differential scanning calorimetry. DSC curves (Fig. 4) represent the T_g of poly (ester - amide)s from p-BPCDA, (IV). The glass transition temperatures of the poly(ester-amide)s were in the range of 207 to 210°C . (Table-3).

Table-2: Solubility of poly (ester - amide)s from p-BPCDA (IV) and (IPC + TPC).

Solvent ↓ Polymer →	PCPA-1	PCPA-2	PCPA-3	PCPA-4	PCPA-5
DMAc	++	++	++	++	++
DMSO	++	++	++	++	++
NMP	++	++	++	++	++
DMF	++	+	++	++	++
Pyridine	++	+	++	++	++
m-Cresol	+	+	+	+	+
Conc. H_2SO_4	++	+	++	++	++
THF	+–	+–	+–	+–	+–

++ : Soluble at room temperature

+– : Partly soluble

+ : Soluble on heating

– : Insoluble

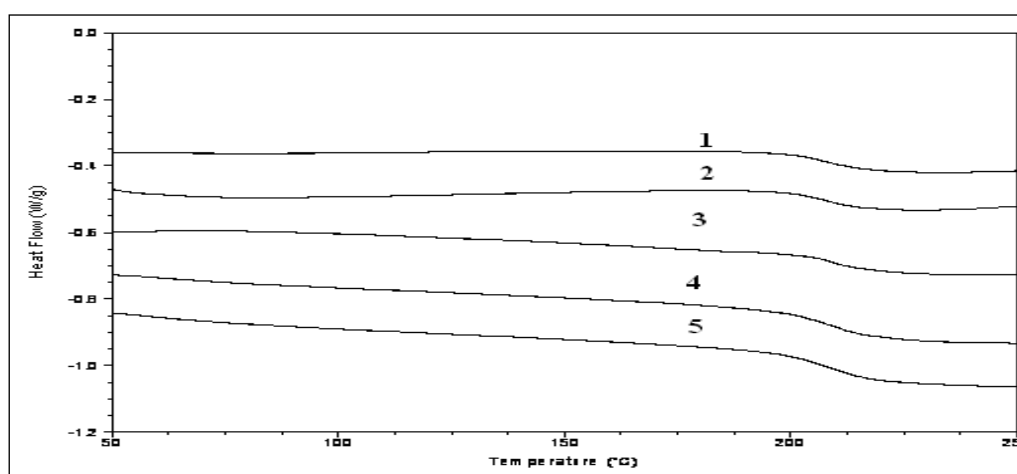


Fig. 4 DSC Curve of PCPA series

Table-3: Thermal analysis^(a) of poly(ester–amide)s from p-BPCDA and (IPC+TPC)

Polymer Code	Decomposition Temperature (°C)		Residual % wt. at 700 °C	T _g (°C) ^d
	T _i ^b	T ₁₀ ^c		
PCPA – 1	325	398	27	208
PCPA – 2	314	388	23	208
PCPA – 3	290	379	21	209
PCPA – 4	300	374	8	207
PCPA – 5	300	376	4	210

- a) Thermogravimetric analysis at heating rate of 10⁰C/min under nitrogen.
- b) Temperature at which initial weight loss observed.
- c) Temperature at which 10% weight loss observed.
- d) Determined by DSC at heating rate 20⁰C/min under nitrogen.

The DSC curves for all the polymers showed similar trend with nearly same values for T_g. The effect of para / meta catenation on T_g is not well pronounced in this series, though poly (ester - amide)s are derived from TPC, (TPC + IPC) and IPC.

The thermal stability of the poly(ester–amide)s was studied by thermogravimetric analysis (Fig. 5) at a heating rate of 10⁰C/min in nitrogen atmosphere. The initial decomposition temperature (T_i), temperature at which 10 % weight loss occurred (T₁₀), and char yields were determined. T_i and T₁₀ values range between 290 to 325⁰C and 374 to 398⁰C respectively. As expected, para - para catenated, TPA based polymer PCPA-1 showed higher values for T_i and T₁₀, and also showed relatively higher char yield. All other polymers had T_i ~ 300 ± 10⁰C and T₁₀ ~ 380 ± 5⁰C.

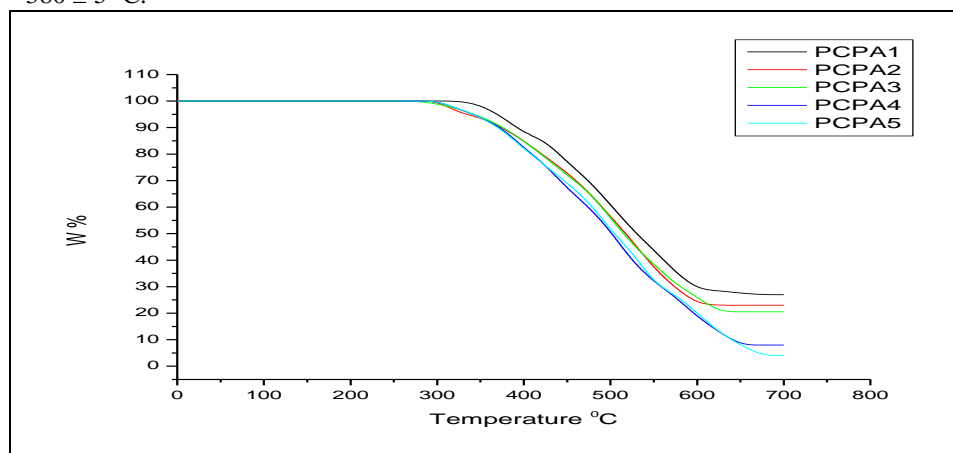


Fig. 5 TGA thermograms of PCPA-1 to PCPA –5

Broad amorphous halos were observed in wide angle X-ray diffractograms of all poly (ester – amide)s. (Fig. 6). It is observed that all the polymers exhibit amorphous nature. Introduction of cyclohexylidene moiety may have disrupted the chain regularity and packing leading to amorphous poly (ester – amide)s. Enhancement in the amorphous nature of the polymers, PCPA-2 to PCPA-4 additionally may be attributed to the random placement of monomers, caused by combination of two monomers (TPC and IPC) in copolymerization, which reduces the orderly arrangement of polymer chains resulting in reduced crystallinity and leading to amorphous nature.

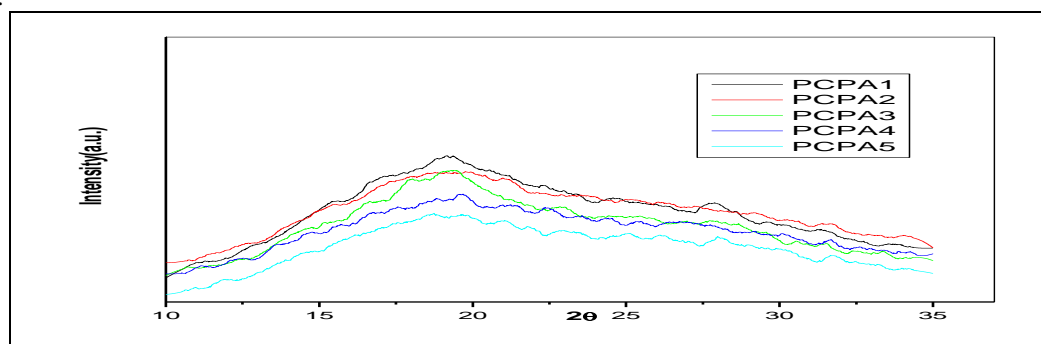


Fig. 6: - XRD curves of PCPA-1 to PCPA-5.

Conclusions:

A new monomer; 1, 1-bis (4- aminobenzoyloxy phenyl) cyclohexane (IV) p-BPCDA, which contained cardo cyclohexylidene moiety with preformed diester linkage was successfully synthesized and characterized by physical constant, IR, NMR and mass spectrometry. A series of new poly(ester-amide)s was synthesized from novel bis (ester – amine); p-BPCDA, (IV) with IPC and / or TPC in different mol proportion by using low temperature solution polymerization method in DMAc solvent. The polymers had inherent viscosities in the range of 0.25 to 0.48 dL/g; and they showed better solubility in organic solvents because of random, nonorder arrangement and less crystalline (i.e. more amorphous) nature; as revealed by XRD. This has been attributed to the flexibility of the system caused by the increased mobility of the molecular segments when amorphous polymers interact with solvent. Incorporation of (IV) increased the solubility remarkably and lowering of Tg. Thermogravimetric analysis showed no appreciable deterioration in thermal stability of these polymers due to introduction of (IV) in poly(ester-amide)s. Thus novel processable poly(ester-amide)s with improved solubility and lower Tg having good thermal stability were successfully synthesized and they could find application as processable high performance polymers.

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