

# Synthesis and Characterization of Soluble Cardo poly(ester-imide)s derived from 9,9-bis[4-(3,4-dicarboxybenzoyloxy)phenyl]fluorene

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## Abstract

A novel fluorenyl cardo dianhydride-9,9-bis[4-(3,4-dicarboxybenzoyloxy)phenyl] fluorene (BDPF) was synthesized and characterized. A series of fluorenyl cardo poly(ester-imide)s were prepared by polycondensation of BDPF with m-phenylene diamine (m-PDA), 4,4'-oxydianiline (4,4'-ODA), 3,4'-oxydianiline (3,4'-ODA), 2,2-bis[4-(4-amino phenoxy)phenyl]propane (BAPP), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF), 9,9-bis(4-aminophenyl)fluorene (BAFL), 1,6-hexamethylenediamine (HAD). Most of fluorenyl cardo poly(ester-imide)s exhibited excellent solubility in common organic solvents such as 1,2-dichlorobenzene (o-DCB), chloroform (CHCl<sub>3</sub>), tetrahydrofuran (THF), N,N-dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP) etc and intrinsic viscosity in N,N-dimethylacetamide (DMAC) ranged from 0.29-0.52 dL/g. The glass-transition temperatures of these polymers were recorded between 199~283°C by DSC and 5% weight loss temperature of all polymers exceed 400°C in air.

**Keywords:** Cardo; Fluorenyl poly(ester-imide); Solubility; Thermal properties

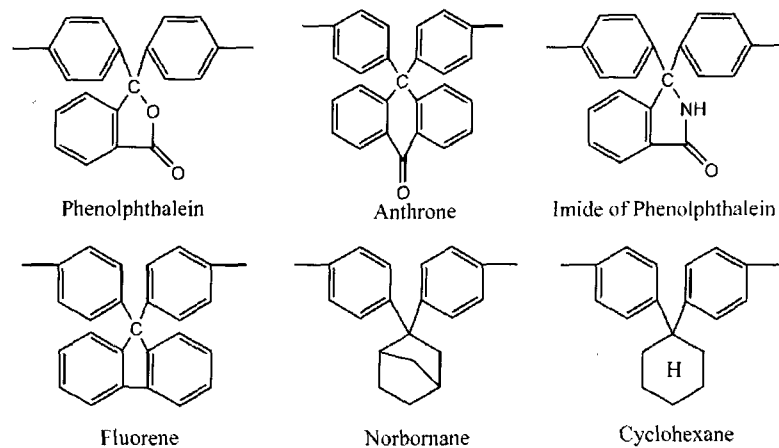
## 1. Introduction

Polyimides are well known as high performance polymers for their excellent heat resistance, electrical insulating properties, and mechanical characteristics, so they are widely used in fields of electrical materials, adhesives, and composite fiber and film materials.<sup>[1-3]</sup> However, they are generally insoluble and infusible in their fully imidized form, leading to processing difficulties; and this process of poly (amic acid) intermediate has several inherent problems such as emission of volatile byproducts (e.g., H<sub>2</sub>O) and storage instability etc. To overcome these problems, much research effort has been focused on synthesis of soluble and processable polyimides in fully imidized form without deterioration of their own excellent properties.<sup>[4-12]</sup>

Poly (ester-imide)s are a class of thermally stable polymers having a wide use mainly in the electrical industry. General poly(ester-imide)s were divided into two species: partly aromatic poly(ester-imide)s and wholly aromatic poly(ester-imide)s. Partly aromatic poly(ester-imide)s have generally property of liquid crystal and low T<sub>g</sub> of about 100-150 °C because of containing aliphatic structure in main chain. Aromatic poly (ester-imide)s have a high T<sub>g</sub> (>200°C), but aromatic poly(ester-imide)s generally insoluble in organic solvents.

Polymers containing at least one element in the repeating unit that is induced in the cyclic side group have become the subject of many investigations. These polymers were termed Cardo polymers from the Latin "Cardo" (a loop), since such groups can be considered as loops at the backbone of the macromolecule<sup>[13]</sup>. The polymer was termed fluorenyl cardo polymer containing fluorenyl structure in the backbone (Scheme 1). The introduction of fluorenyl "cardo" groups into polymers such as

polyimides<sup>[13-19]</sup>, polyamides<sup>[20,21]</sup>, polyquinolines<sup>[22]</sup> etc. can endow with them specific properties: (1)excellent heat resistance; (2)excellent solubility. In our previous study, we successfully prepared a series of polyimides and poly(amide-imide)s containing fluorenyl Cardo structure. The results showed that obtained polymer exhibited excellent solubility in common organic solvents and high thermal stability.



**Scheme 1** Schematic diagram of different Cardo groups

In the present study, our objective is to investigate synthesis and properties of Cardo poly(ester-imide)s derived from 9,9-bis[4-(3,4-dicarboxybenzoyloxy)phenyl]fluorene. A series of fluorenyl cardo poly(ester-imide)s were prepared by polycondensation of BDPF with *m*-phenylene diamine (*m*-PDA), 4,4'-oxydianiline (4,4'-ODA), 3,4'-oxydianiline (3,4'-ODA), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (BDAF), 9,9-bis(4-aminophenyl)fluorene (BAFL), 1,6-hexamethylene diamine (HAD). The solubility and thermal properties of the poly(ester-imide)s were investigated by TGA and DSC etc.

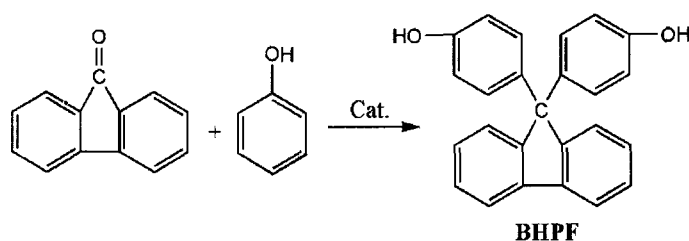
## 2. Experimental section

### 2.1 Materials

Fluorenone (Shanghai coking and chemical corporation), phenol, 1,6-hexamethylene diamine (Shanghai Lingfeng Chemical Reagent Co. Ltd.), trimellitic anhydride (Lancaster). 3,4'-oxydianiline, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane, 9,9-bis(4-aminophenyl)fluorene (Shanghai Research Institute of synthetic resin). DMAc and NMP were dried in  $\text{CaH}_2$  for 2 days and distilled before use.

### 2.2 Monomer synthesis

**9,9-bis(4-hydroxyphenyl)fluorene (BHPF)** In a 250ml four-necked flask fitted with a nitrogen inlet, a thermometer, a condenser and a mechanical stirrer, 37.7g phenol, 0.25g 3-mercapto propionic acid, 36.0g 9-fluorenone and 150ml methylene dichloride was added, and 15ml methanesulfonic acid was dropped in ambient temperature. Then the mixture was refluxed under nitrogen atmosphere for 5 hours, and the warm reaction mixture was cooled, crystallized, filtered and washed with methylene dichloride. The obtained product was dried in vacuum to give a white powder 45.0g. Yield: 65%,  $\text{mp}=225.5\text{-}225.6^\circ\text{C}$  (by WRS-1B digital melting point apparatus). (Scheme 2)



**Scheme 2** Synthesis route of 9,9-bis(4-hydroxyphenyl)fluorene (BHPF)

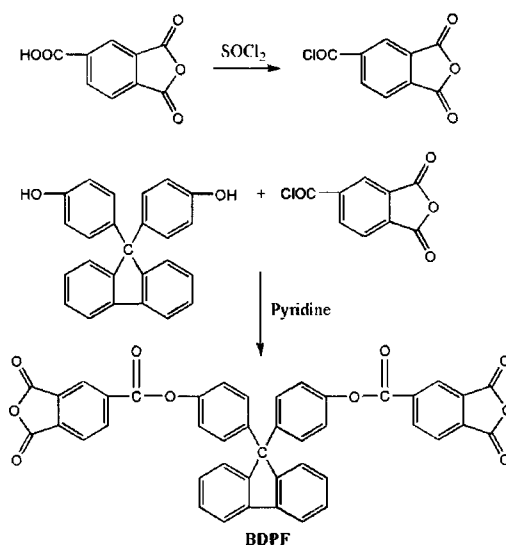
IR (KBr): 3479(OH)cm<sup>-1</sup>.

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) : δ9.32ppm (m, 2H, OH), δ6.64-7.89ppm (m, 16H, aromatic ring) .

<sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) : δ156.54ppm (C11), δ152.37ppm (C1), δ140.02ppm (C6), δ136.70ppm (C8), δ129.38ppm (C9), δ128.33ppm (C3), δ157.96ppm (C4), δ126.62ppm (C2), δ121.00ppm (C5), δ115.54ppm (C10), δ64.32ppm (C7) .

Anal. Calcd for C<sub>25</sub>H<sub>20</sub>O<sub>2</sub>: C,85.69%; H,5.18%. Found: C,85.67%; H,5.30%.

**9,9-bis[4-(3,4-dicarboxybenzoyloxy)phenyl]fluorene (BDPF)** In a 250ml four-necked flask fitted with a nitrogen inlet, a thermometer, a condenser and a mechanical stirrer, 28.8g trimellitic anhydride and excess thionyl chloride was added, the mixture was refluxed under nitrogen atmosphere until the solution was clear and transparent, then the excess thionyl chloride was distilled in vacuum and 20ml anhydrous tetrahydrofuran was added. The solution of 26.3g (0.075mol) BHPF in THF/pyridine (v/v=1:1) was added dropwise then the mixture was refluxed for 2hr. After being cooled, the product was filtered and washed with water, and the yellowish powder was gained and dried in vacuum to afford 50.2g. (Scheme 3)



**Scheme 3** Synthesis route of 9,9-bis[4-(3,4-dicarboxybenzoyloxy)phenyl]fluorene (BDPF)

The aforementioned yellowish solid was dissolved in 160ml acetic anhydride and refluxed for 3 hours, then the solution was cooled, crystallized, filtered and washed with toluene, a off-white solid was obtained and dried in vacuo to afford 29.4g BDPF. Yield: 56.1%, mp=292 °C (by DSC).

FT-IR (KBr): 1846, 1782 cm<sup>-1</sup> (C=O, dianhydride), 1736 cm<sup>-1</sup> (C=O, ester).

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δ7.03-8.57ppm (m, 22H, aromatic ring)

<sup>13</sup>C-NMR (DMSO-d<sub>6</sub>): δ162.68ppm (C12), δ162.33ppm (C20), δ162.23ppm (C19)

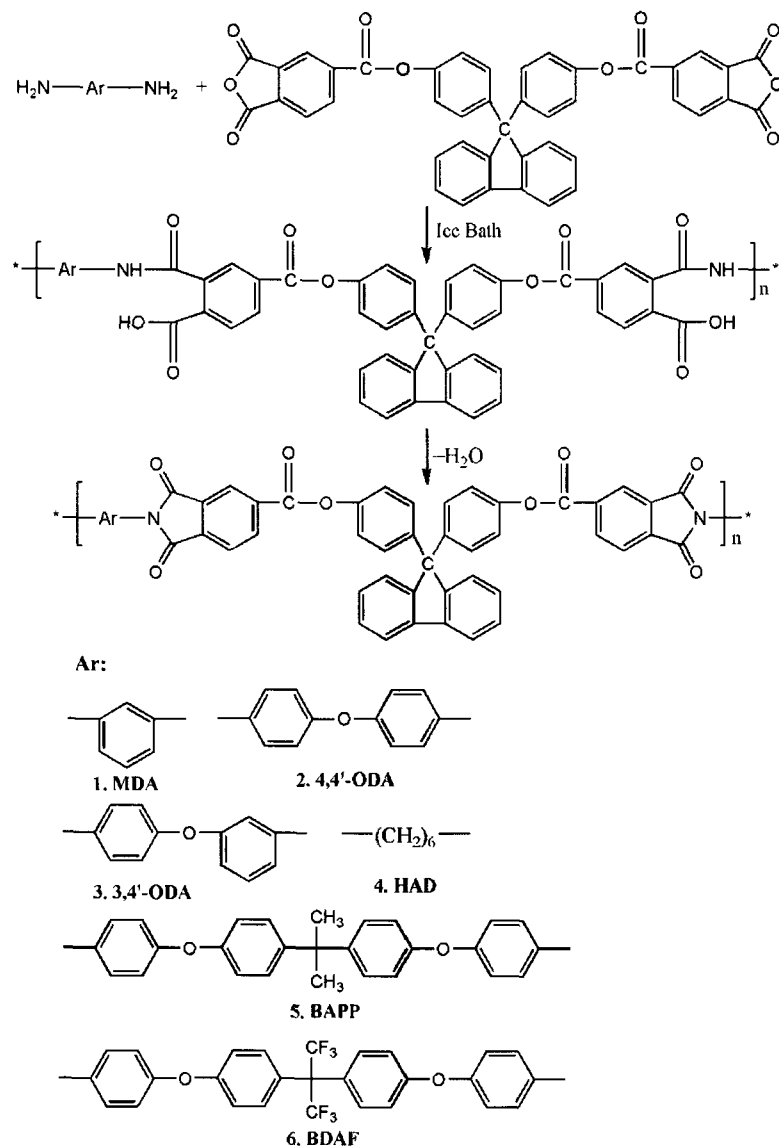
δ150.11ppm

(C11), δ149.10ppm (C8), δ143.46ppm (C1), δ139.47ppm (C6), δ136.89ppm (C18), δ135.68ppm

(C13),  $\delta$ 135.24ppm(C16),  $\delta$ 131.99ppm(C15),  $\delta$ 128.75ppm(C9),  $\delta$ 128.05ppm(C14),  $\delta$ 127.92ppm(C17),  $\delta$ 125.97ppm(C2),  $\delta$ 125.81ppm(C5),  $\delta$ 125.71ppm(C3),  $\delta$ 121.60ppm(C10),  $\delta$ 120.65ppm(C4),  $\delta$ 64.13ppm(C7)

Anal. Calcd for  $C_{43}H_{22}O_{10}$ : C, 73.92%; H, 3.17%. Found: C, 73.62%; H, 3.45%.

### 2.3 Poly (ester-imide)s synthesis



**Scheme 4** Schematic diagram of fluorenyl poly (ester-imide)s

A typical polymerization procedure is as follows (Scheme 4). A diamine was dissolved in dried DMAc, then equivalent molar dianhydride BDPF was added with an ice bath. The reactive mixture was stirred for 8h, then the mixture of acetic anhydride/triethyl amine (v/v=4:1) was added and carried out for 2 hrs at ambient temperature and 80 °C for 1 hr. Then the reaction solution was precipitated in methanol in a high speed blender. The product was filtrated and washed by excess methanol and water, and dried in a vacuum oven at 80°C /2hrs and 200°C /12hrs. The poly (ester-imide) powder was obtained.

### 2.4 Measurements

IR spectra were recorded on a Nicolet 460,  $^1H$ -NMR and  $^{13}C$ -NMR spectra were obtained at 500MHz

using a Bruker Vance DRX-400 in DMSO-d6 with tetramethylsilane as an internal standard. Elemental analysis was performed on a Vario EL III. Inherent viscosity measurements were made with 0.5%(w/v) solution of polymers in NMP at 25±0.1 °C using an Ubbelohde viscometer. The thermogravimetry analyses (TGA) were made with TA TGA-Q50. Experiments were carried out under air and under N<sub>2</sub> atmosphere at a heating rate of 10 °C /min. Differential scanning calorimetry (DSC) was carried out using TA DSC Q10 under N<sub>2</sub> atmosphere at a heating rate of 20 °C /min. Melting point was measured by WRS-1B digital melting point apparatus.

### 3. Result and discussion

#### 3.1 Synthesis of poly(ester-imide)s

All poly(ester-imide)s were prepared by two-step method and chemical imidization. Intrinsic viscosity in NMP of the poly (ester amic acid)s ranged from 0.29 to 0.52 dL/g (Table 1). But it is found that intrinsic viscosity of all poly (ester amic acid)s is low. It could be attributed to the influence of steric hindrance led by a rigid bulky bisphenylfluorene moiety and ester bond of BDPF, so the activity of dianhydride is lower and low molecular weight of poly (ester-imide)s were obtained.

Poly (ester-imide)s were characterized by FT-IR and a FT-IR spectrum of PESI-2, as an example, is presented in Figure 1. As shown in Figure 1, PESI-2 exhibited characteristic absorptions: 1781 cm<sup>-1</sup>, 1720 cm<sup>-1</sup> (C=O, imide carbonyl group), 1375 cm<sup>-1</sup> (C-N, imide group).

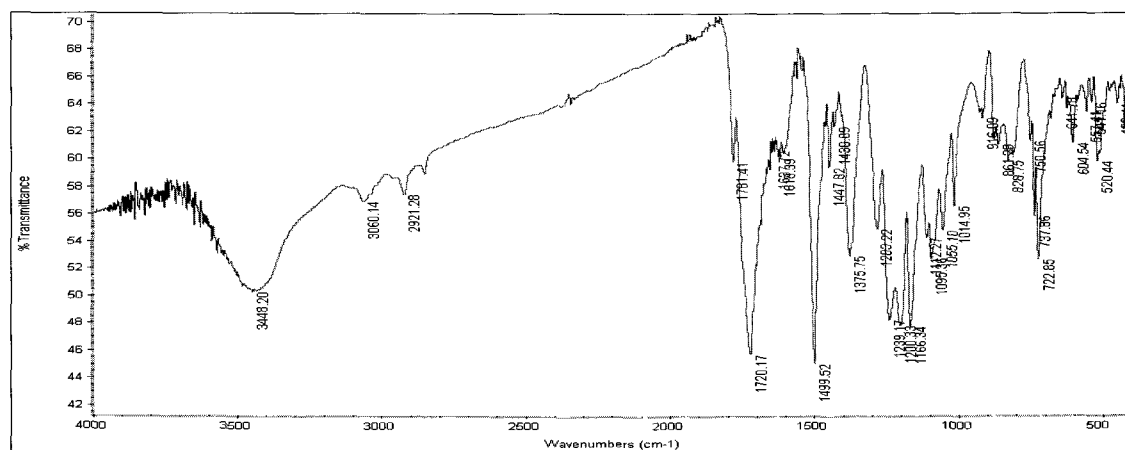


Figure 1 FT-IR spectra of PESI-2 (4,4'-ODA-BDPF)

#### 3.2 Organo-solubility

As shown in Table 1, most of cardo poly(ester-imide)s being prepared from fluorenyl cardo dianhydride and m-PDA, 4,4'-ODA, 3,4'-ODA, BAPP, BDAF, BAFL, HAD exhibited excellent solubility in common organic solvents such as 1,2-dichlorobenzene (o-DCB), chloroform (CHCl<sub>3</sub>), tetrahydrofuran (THF), N,N-dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP) etc. Especially, MDA-BDPF can also dissolve in hot NMP, DMAC, CHCl<sub>3</sub> and DMSO.

It could be attributed to a rigid bulky bisphenylfluorene moiety of BDPF dianhydride leading to the decrease of the intermolecular forces. Moreover, the flexible linkages of diamine such as ether bond (-O-) and isopropyl groups(-C(CH<sub>3</sub>)<sub>2</sub>-) could lead to weaken the conjugation effect of main chain, to increase the conformational entropy of molecule, and to reduce the free energy of

solution, thus, as a result, the solubility of fluorenyl cardo poly(ester-imide)s improve significantly.

**Table 1**

The organo-solubility of poly (ester-imide)s<sup>a</sup>

Code	Poly(ester-imide)s	$\eta$ (dL/g)	o-DCB	DMAc	THF	CHCl <sub>3</sub>	DMSO	NMP
PESI-1	MDA-BDPF	0.29	G	S*	G	S*	S*	S*
PESI-2	4,4'-ODA-BDPF	0.43	G	S	S*	S	S*	S
PESI-3	3,4'-ODA-BDPF	0.44	G	S	S	S	S	S
PESI-4	HAD-BDPF	0.31	S	S	S	S	S	S
PESI-5	BAPP-BDPF	0.49	S*	S	S	S	S*	S
PESI-6	BDAF-BDPF	0.52	S	S	S	S	S	S

a. Solubility: S, soluble at room temperature; Ins, insoluble; S\*, soluble on heating; G, gel.

### 3.3 Tg and thermal stability

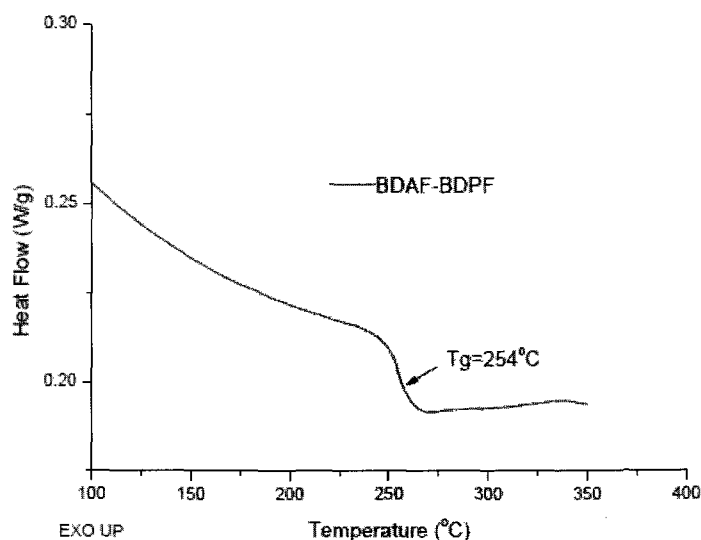
The thermal properties of poly(ester-imide)s were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 2, Figure 2).

**Table 2**

Tg of poly (ester-imide)s

Code	Polymer	Tg (°C)
PESI-1	MDA-BDPF	283
PESI-2	4,4'-ODA-BDPF	257
PESI-3	3,4'-ODA-BDPF	247
PESI-4	HAD-BDPF	199
PESI-6	BAPP-BDPF	237
PESI-7	BDAF-BDPF	254

Tg of poly(ester-imide)s increases with the increase of rigidity of diamines: HAD-BDPF(199°C)<BAPP-BDPF(237°C)<3,4'-ODA-BDPF(247°C)<BDAF-BDPF(254°C)<4,4'-ODA-BDPF(257°C)<MDA-BDPF(283°C). Furthermore, poly (ester-imide) based on fluorinated diamine has a higher Tg, such as BDAF-BDPF(254 °C)> BAPP-BDPF(237 °C). The reason is that the form of hydrogen bond and the steric hindrance induced by the bigger size of -CF<sub>3</sub> than -CH<sub>3</sub> would lead the increase of Tg in fluorinated polyimide.



**Figure 2** DSC traces of poly(ester-imide)s PESI-6 (BDAF-BDPF)

**Table 3**

Thermal stability of Cardo poly(ester-imide)s

Polyesterimide	$T_{max}$ (°C)		TGA wt. loss(°C)						Yc (%)
			5%		10%		15%		
	Air	N <sub>2</sub>	Air	N <sub>2</sub>	Air	N <sub>2</sub>	Air	N <sub>2</sub>	
MDA-BDPF	489,611	536,619	431	429	472	484	494	511	48
4,4'-ODA-BDPF	489,615	509,604	420	429	451	465	471	488	43
3,4'-ODA-BDPF	476,606	497,594	431	425	450	459	463	479	42
HAD-BDPF	475,579	480	416	423	442	444	453	455	19
BAPP-BDPF	486,610	517	424	431	452	472	468	491	35
BDAF-BDPF	489,618	519,568	424	457	459	492	473	509	50

$T_{max}$ =The temperature of maximum rate of decomposition.

Yc=The char yield at 800 °C.

Moreover, to discuss thermal and thermal stability, the onset temperature corresponding to 5%, 10% and 15% weight loss of this system was measured by TGA under air and under nitrogen, respectively (Figure3, Table 3). All poly(ester-imide)s show good thermal stability, powder samples of these poly(ester-imide)s undergo 5% weight loss between 416°C and 431°C in air at a heating rate of 10°C /min and char yields of 19-50% at 800°C under nitrogen atmosphere.

#### 4. Conclusion

In the present work, a novel fluorenyl cardo dianhydride (BDPF) and its poly (ester-imide)s was synthesized and characterized. Most of fluorenyl cardo poly (ester-imide)s exhibited excellent solubility in common organic solvents and good thermal stability.

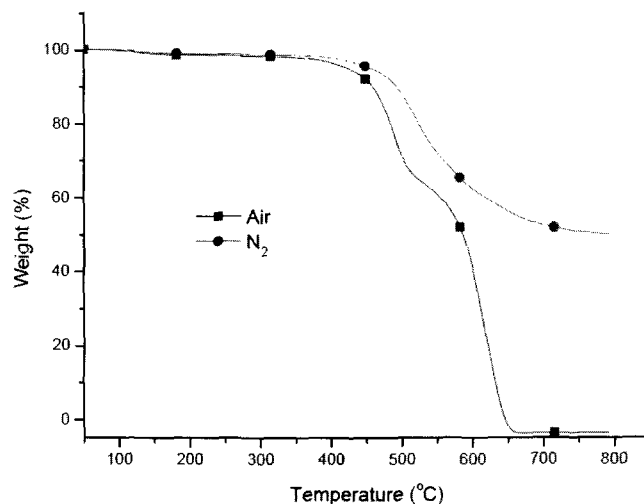


Figure 3 TGA curves of poly (ester-imide) PESI-6 under air and nitrogen atmosphere

## 5. References

- Mittal, K.L.(Ed.)Polyimides: Synthesis, Characterization, and Application, Vols. 1 and 2; Plenum: New York, 1984.
- Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M.(Eds.)Polyimides; Blackie & Son: Glasgow, UK, 1990.
- C.P. Yang, J.A.Chen, J Polym Sci, Polym Chem, 1999; 37:1681-1691.
- Park JW, Lee M, Lee MH, Liu JW, Kim SD, Chang JY, Rhee SB. Macromolecules 1994; 27:3459.
- Imi Y, Malder MM, Kakimito MJ. J Polym Sci, Polym Chem Ed 1989; 22:2198.
- Yang CP, Chen WT. Macromolecules 1993; 26:4865.
- T.L. Grubb et al. Polymer 1999; 40:4279-4288.
- CP Yang, YY Su, FZ Hsiao. Polymer 2004; 45:7529-7538.
- CP Yang, SH Hsiao, KL Wu. Polymer 2003; 44:7067-7078.
- Susanta Banerjee et al. Polymer 2003; 44:613-622.
- DJ Liaw, WH Chen. Polymer 2003; 44:3865-3870.
- ZG Qian et al. Polymer 2002, 43:6057-6063
- Korshak VV, Vinogradova SV, Vygodski YS. J Macromol Sci Rev Macromol Chem 1974; C11:45.
- Reddy TA, Srinivasan M. J Polym Sci: Part A: Polymer Chemistry, 1989; 27:1419-1427.
- Hasio SH, Li CT. J Polym Sci: Part A: Polymer Chemistry, 1999; 37:1403-1412.
- Michinori Nishikawa Poly. Adv. Technol. 2000; 11:404-412.
- Nathakie Biolley, martine Gregoire, Thierry Pascal, Bernard Sillion Polymer 1991; 32:3256-3261.
- E. Said-Galuiev, Ya.Vygodskii etc. J. of Supercritical Fluids 2003;27: 121-130.
- L. Dutruch, T. Pascal etc. Poly. Adv. Technol. 1996; 8:8-16.
- A.D.Sagar, R.D.Shingte, P.P.Wadgaonkar, M.M.Salunkhe. European Polymer Journal 2001; 37:1493-1498.
- P.R.Srinivasan,V.Mahadevan, M.Srinivasan. Journal of Polymer Science: Part A: Polymer Chemistry edition, 1989;19: 2275-2285.
- Stille JK, Harris RM, Padaki SM. Macromolecules 1981; 14:486-493.