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Synthesis, Thermal behavior and antimicrobial activity of Polyester based on 5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

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Abstract

Novel aromatic polyesters have been synthesized with moderate molecular weights by interfacial polymerization of 5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid with different aromatic diols using Tetra butyl ammonium bromide (TBAB) as phase transfer catalyst. The resulted polymers are readily soluble in aprotic polar solvents its show that the presence of bulky group improved the solubility of polyester. Thermogravimetric analysis data showed that these polyesters are thermally stable. The molecular weights of polyesters were measured by gel permeation chromatography. The results show that polyesters could inhibit the growth of the microorganisms to a considerable extent.

Keywords: Thermogravimetric analysis**,** interfacial polymerization, antimicrobial, solubility

Introduction

One of the polymer science specialties that has been known for around 60 years and has a continually expanding range of applications is high temperature or thermally resistant polymers. These polymers fall into the following major categories: polyimide, polyamide, polyarylate, and their copolymers. Polyarylates belong to the class of high-performance engineering plastics and they have good thermal and mechanical properties [1, 2]. Polyester is challenging to process due to its low level of solubility in polar solvent. Recently researchers have introduced bulky and pendent units in backbone of polymer moiety to overcome this drawback [3-6]. Researchers have recently made numerous attempts to develop high-performance polymers with exceptional heat stability and solubility, which has greatly accelerated the development of a wide range of thermostable and processable polymers. Materials called aromatic polyesters have a fantastic array of physical characteristics. They represent a sizable class of technical materials with high performance and strong mechanical qualities, such as good thermal stability, resistance to solvents, and good mechanical properties. As a result, they are used extensively in the

automotive, electrical, and aviation sectors [7, 8]. Aromatic polyesters are also well known as rigid-rod liquid-crystalline polymers [9-11]. Because of their high strength and rigidity, good thermal and dimensional stability, good surface hardness, and good gloss, polyethylene terephthalates are valuable as engineering thermoplastics [12,13].

A convenient way to modify the properties of polymers is copolycondensation. For example, modifying the properties of polyesters by incorporating hydrogen-bonded amide groups, imide moieties, or bulky groups results in copolymers with modified properties [14-21]. Interest in polyamide esters has increased in recent years due to their expected degradability, thermal and mechanical properties. Ester bonds are highly hydrolysable, whereas amide groups have been observed to form intermolecular hydrogen bonds, conferring good fiber-forming properties and increasing the characteristic low melting points of polyarylates. These copolymers typically exhibit intermediate polyester and polyamide properties and offer attractive properties such as high ester bond flexibility, toughness and degradation and good mechanical properties due to hydrogen bond formation between amide groups.

A review of the literature shows that polymers with 5-amino Isophthalic Acid moiety have promising applications in a wide range of domains and several researchers (22–26) published a number of papers on Polymers and Copolymers with 5-amino Isophthalic Acid either in the end group or in the pendent group with the aim of investigating their complexity and biological activity.

Experimental

Materials

9-oxo-Fluorene 4-carboxylic acid, 5-amino isophthalic acid, 4,4’-(propane-2,2-diyl) diphenol, 4,4’-sulphonyl diphenol, 4,4’-dihydroxy biphenyl, hydroquinone, 4,4’-thiodiphenol, 4,4’-(pyridine-2-ylmethylene) bis(2-methylphenol), 4,4’-(pyridine-2-ylmethylene) diphenol were purchased from Aldrich. NaOH, pyridine, thionyl chloride N, N-dimethyl formamide and required solvents were procured from S.D. Fine chem. India. All the chemicals and solvents used for the synthesis purpose were of laboratory grade reagent and used after proper purification whenever it required.

Techniques

Proton nuclear magnetic resonance (1H NMR, 500 MHz) spectra were recorded on a Bruker (Germany) advance 500 instrument. FTIR Spectra were recorded on Jasco-410 spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (cm^{-1}). Inherent viscosities were determined by using Ubbelohde viscometer at 25^0C in Dimethyl formamide. Thermal gravimetric analysis (TGA) data for polymers were obtained by TGA-Perkin Elmer (Pyris 1) in nitrogen atmosphere at a heating rate of 20ºC/min. DSC data for polymers were obtained by DSC- Perkin Elmer (Pyris 1). GPC data were obtained by using GPC instrument PSS win R I –71 detector Shodex equipped with 600E multi solvent delivery system.

Monomer Synthesis: 5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

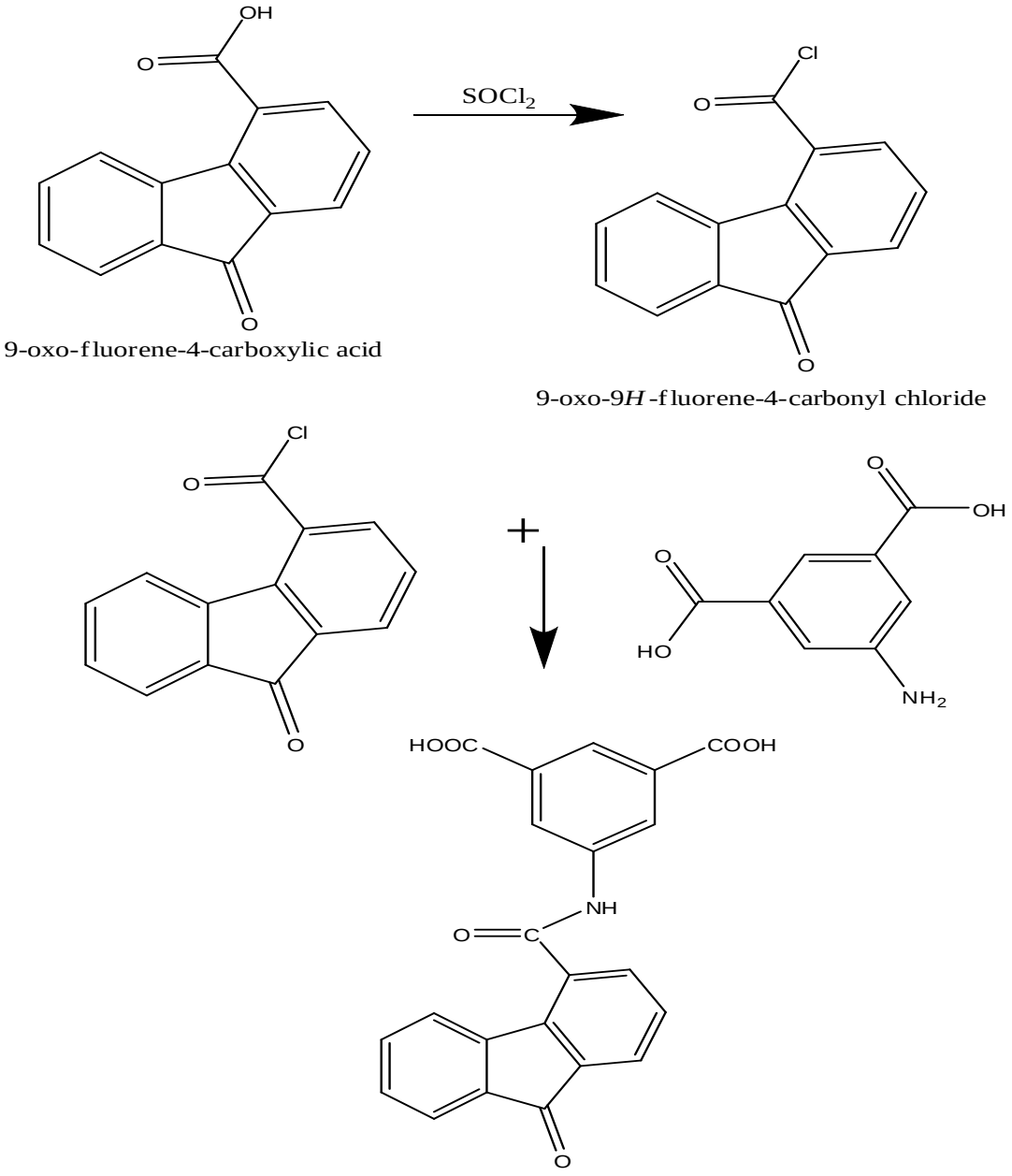
9-oxo-Fluorene 4-carboxylic acid (0.05mole) and thionyl chloride (0.15 mole) were added in round bottom flask. The reaction mixture was refluxed in water bath for 4 hours with frequent shaking. Then distilled out unreacted thionyl chloride by reducing pressure. In residue added 25ml pyridine then cooled up to 0°C. In another flask, solution of 5-amino isophthalic acid (0.051mole) in 40 ml pyridine and cooled to 0°C. The solution was added in to the above prepared solution within the duration of half hour with stirring. The reaction mass was then warmed, and allowed to stand for overnight at room temperature. The reaction mass was quenched in cold HCl-water solution. Obtained precipitates was filtered and washed with water till pH of the filtrate was found neutral. Isolated product was dried at 50°C under vacuum and purified in Toluene. Yield: 86%. M.P > 350°C. The proposed reaction scheme is shown as given in **Scheme 1.**

Synthesis of aromatic polyester with 5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

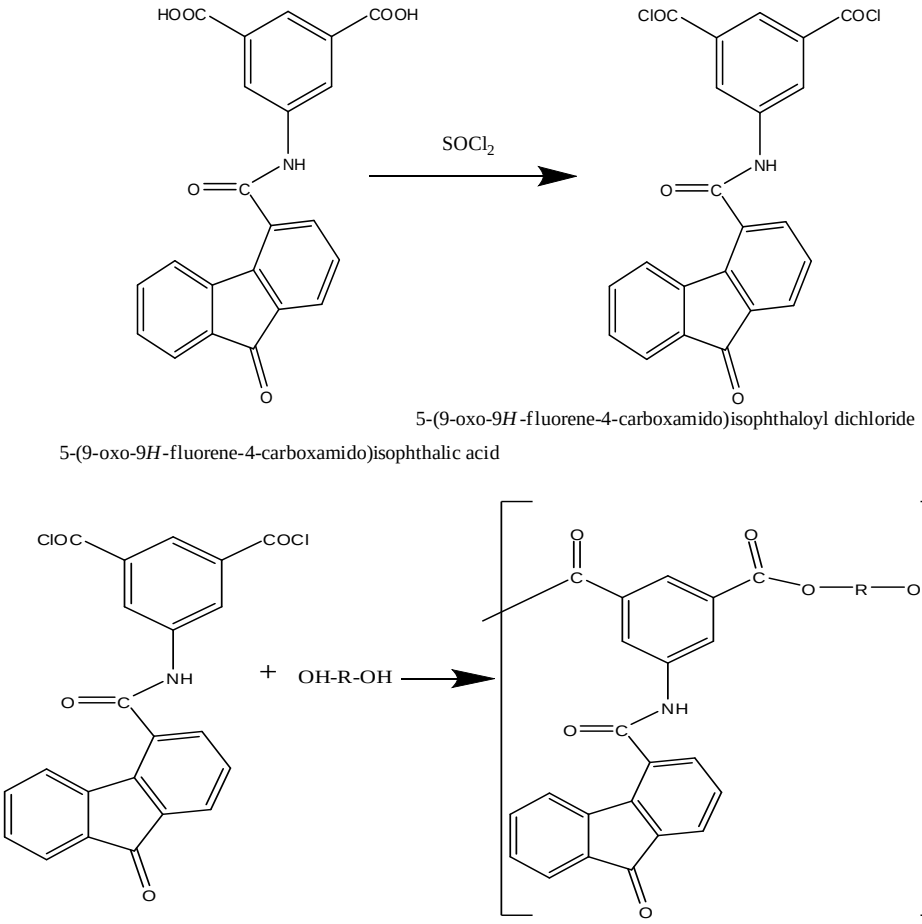
Polyesters were prepared by the procedure reported [27] in the literature**.**

5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid was reacted with thionyl chloride and gives 5-(9-oxo-9H-fluorene 4-carboxamido) isophthalyl chloride. 0.01 mole of acid chloride was dissolved in 40 ml of $CHCl_3$. then added 0.01 mole of diol in appropriate amount of NaOH solution (0.03 mole in 70 ml water). In this reaction mass 0.5 gm of emulsifier Tetra butyl ammonium bromide was added (in 10 ml water). The reaction was stirred for 15 minutes, solid material was obtained and appropriate amount of acetone was added along with demineralized

water. Stirred the reaction mass for more 10 minutes and then filtered, washed with water and finally dried in oven at 50°C. The proposed reaction scheme is shown as given in **Scheme 2.**

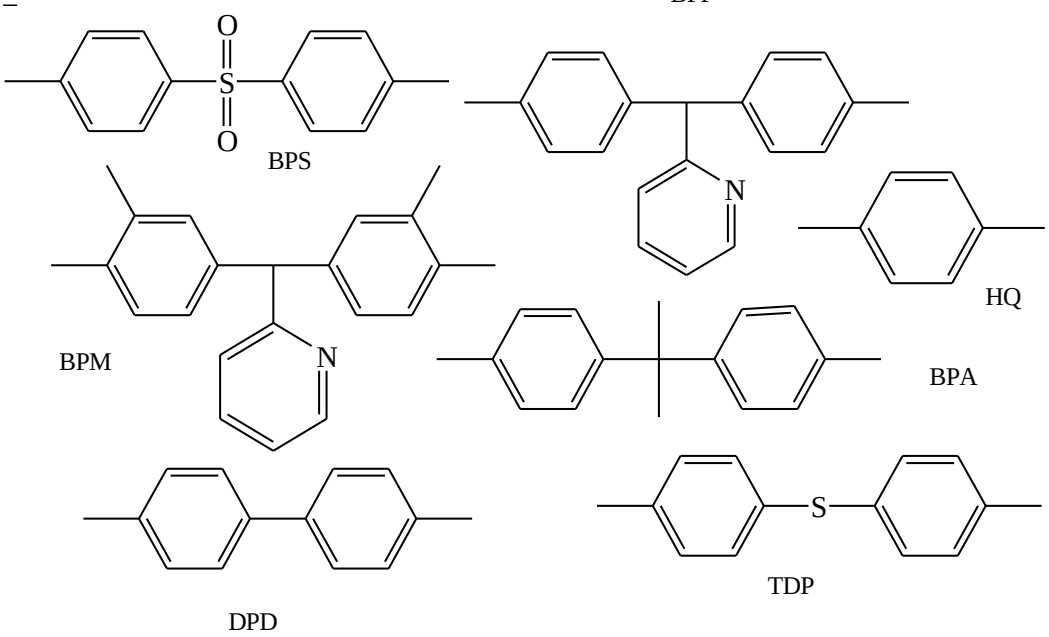


Scheme 1: Synthesis of **5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic ac**



Scheme 2: Synthesis of Polyester

Where R =



Result and Discussion

The solubility of 5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid was studied in different solvents. They were soluble Alcohol, DMF, DMSO and THF. It is summarized in Table- 1, NMR and mass spectra of CPCA shows spectra matched with ideal structure. H^1-

Table 1: Characterization of 5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

Molecular Formula	**Molecular Wt. (g/m)**	**% Yield**	**Color**	**Analysis % Found (Calculated)**		
				C	**H**	**N**
$C_{22}H_{13}NO_6$	387.07	82	Yellow	68.20 (68.22)	3.48 (3.38)	3.58 (3.62)
IR	FTIR Spectra show the characteristic carbonyl absorption peaks for acid at 1738 cm^{-1} due to the carbonyl stretching vibrations and-OH(Stretching) at 2694cm^{-1}					

Characterization of Polyesters by IR Spectra

The formation of aromatic polyesters was confirmed by FTIR spectroscopy analysis. FTIR Spectra of all polymers show the characteristic carbonyl absorption peaks for ester at 1735-1750 due to the carbonyl stretching vibrations. Stretching of amide N-H group appeared around 3100- 3400 cm^{-1}. Banding of amide N-H group appeared around 1500-1600cm^{-1}. Important IR frequencies given in Table-2.

Table 2: Interpretation of IR spectra of polyesters of OFCID

Type	Group vibration mode	PE-OQ	PE-OS	PE-OD	PE-OP	Expected Frequencies (cm^{-1})
Aromatic	=C-H(Str)	2928	2965	3056	3077	3080-2900
	C=C(Str)	1520	1549	1564	1586	1600-1450
			1482	1483	1521	
			1192	1432	1463	540-1400
		733	751	750	765	
	C-H (i-p-d)	1370	1163	1147	1086	1350-1000
		1204	1127	1163	1013	
		1172	1103	1096		
		1052	1068	1002		
		1009	1009	922		
	C-H (o-o-p-d)	894	911	806	856	960-675
		672	833	731	836	
			682	682	679	
-(CH_2)-	C-H (Str)	2851	2850	2858	2949	2960-2850
-C-N-	C-N (Str)	1368	1316	1341	1345	1310-1380
-NHCO-	N-H (Ben.)	1554	1583	1541	1540	1540-1600
	N-H (Str)	3162	3100	3113	3136	3080-3450
-COO-	C=O (Str)	1741	1742	1735	1733	1735-1720
	C-O (Str.)	1294	1294	1212	1220	1260-1225
Sulphone	S=0 (Str)		1293			1300-1160
	S-0 (Str)		633			700-500
	C-S (Str)		583			700-570

Solubility of Aromatic Polyesters

The solubility of polyesters was tested quantitatively in various solvents as listed in Table 3. All the poly-esters are soluble in organic solvents such as DMF, DMAC, sulpholane, pyridine and H_2SO_4 at room temperature, and are insoluble in solvents such as methylene dichloride, methanol, ethyl acetate, acetonitrile and water. The incorporation of the pendant group in the side chain polyesters enhanced their solubility in polar solvents. Solubility data of polyesters given in Table-3.

Tabel-3: Solubility data of polyesters

Polyester	**Ethanol**	**DMF**	**DMAC**	**Sulpholane**	**Pyridine**	**THF**	**H_2SO_4**	**Water**	**Methanol**	**EAC**
PE-OQ	--	++	--	--	++	--	++	--	--	--
PE-OA	--	++	++	++	++	+	++	--	--	--
PE-OM	--	++	++	++	++	+	++	--	--	--
PE-OP	--	++	++	++	++	++	++	--	--	--
PE-OT	--	++	++	++	++	++	++	--	--	--
PE-OD	--	++	++	++	++	+	++	--	--	--
PE-OS	--	++	++	++	++	++	++	--	--	--

++: Soluble at room temp.,

+: Soluble on heating at 50^0C,

--: Insoluble

Physical property

Physical property described in Table-4. Inherent viscosities were determined by using Ubbelohde viscometer at 25^0C in Dimethyl formamide, inherent viscosities in range of 0.35- 0.41dl/g. % of yield in range of 83-91.

Table-4: Physical property of polyester

Polyester	Diphenol	Description	Yield (%)	ηinh (dL/g)[a]
PE-OQ	HQ	Cream powder	88	0.37
PE-OA	BPA	Light cream powder	85	0.40
PE-OM	BPM	Light cream powder	86	0.36
PE-OP	BPP	Light cream powder	83	0.38
PE-OT	TDP	Light cream powder	91	0.35
PE-OD	DPD	Light cream powder	89	0.37
PE-OS	BPS	Light cream powder	86	0.41

Gel permeation chromatography

The molecular weight and Polydispersity value of polyesters are given in Table-5. From the results, it is apparent that the molecular weights of the prepared polyesters were in the range of 14789-19658.

Table-5: GPC data of polyesters

Polyester	Diphenol	Molecular weight[a]		Polydispersity Mw/Mn
		Mn	Mw	
PE-OM	BPM	13823	14789	1.069
PE-OS	BPS	17582	19658	1.118
PE-OD	DPD	14895	16235	1.089

a: Measured by GPC in Dimethyl formamide (DMF), polystyrene was used as a calibration standard.

Thermal Properties

Thermogravimetric Analysis (TGA).

The constant trace of loss in the weight of sample as a function of temperature gave a TG thermogram, which was used further for data analysis. The 10% weight loss were about 210-262^{0}C and the char yield of polyester at 400 ^{o}C were about 38-44%. The data shows that obtained polyester compounds were thermally stable. 5%, 10% weight loss, char yield given in Table-6.

Table-6: Thermal properties of polyesters

Polyester	**Decomposition temperature**		**Char yield[c] (%)**
	T5[a]	**T10[b]**	
PE-OQ	158^{0}C	210^{0}C	38.45%
PE-OM	169^{0}C	214^{0}C	44.78%
PE-OT	232^{0}C	262^{0}C	42.96%

(a) Temperature at which 5% weight loss was recorded by TGA at a heating rate of 20ºC/min in a nitrogen atmosphere.

(b) Temperature at which 10% weight loss was recorded by TGA at a heating rate of 20ºC/min in a nitrogen atmosphere.

(c) Percentage weight of material left undecomposed after TGA analysis at maximum temperature 400ºC in a nitrogen atmosphere.

Differential Scanning Calorimetry of the Polyester.

The thermal properties of all the polyesters have been investigated by DSC measurements. Their phase transition temperatures of first heating scan are listed in Table -7. According to the DSC analysis, glass transition temperature (Tg) in range of 192-222°C.

Table- 7: Transition temperatures of the polyester determined by DSC at scan rate 10°C/min on heating.

Polyester	**Thermal transition from DSC (°C, J/g) Tg°C**
PE-OQ	207.12°C
PE-OM	222.68°C
PE-OP	192.47°C

Antimicrobial Activity

Polyester compounds have been prepared using different monomers. When tested for their response against microorganisms interesting results were obtained. The results indicate that the polyesters inhibit significantly the growth of microorganisms. An antifungal suscepptibility test was used Candila albicans. Bacillus subtillis, Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa and Candila albicans were cultured on Brain Heart Infusion Broth (BHI) for the antibacterial and fungal activity

Each compound was dissolved in Dimethyl formamide (DMF) at a concentration of 200, 400, 600, 800, 1000, 1200 and 1500 µg/mL concentrations. In Table- 8 zone of inhibition in mm is described at concentration of 1500 µg/mL.

Table- 8: Zone of inhibition in mm of polyesters.

Sample	Zones of inhibition in mm				
	B. subtillis	S. aureus	E. coli	P. aeruginosa	C.albicans
PE-OA	25	19	15	13	18
PE-OM	24	20	14	12	17
PE-OS	23	19	13	13	16
PE-OQ	21	16	12	11	18
PE-OT	24	20	15	11	15
DMF	10	10	10	10	10

Conclusion

In this research work, polycondensation was carried out by the reaction of diacid monomer with several aromatic diols using phase transfer catalyst to prepare novel aromatic polyesters. The polycondensation leads to the formation of polymers having inherent viscosity ranging from 0.35 - 0.41 dl/g. By introducing pendent group to the aromatic polyesters, polymers with substantially increased solubility and good thermal stability were obtained. From the results, it is apparent that polyesters can be used for film forming and coating materials.

Symbols and abbreviations

Code **OFCID**: 5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

Code **PE-OQ** : Poly(Hydroquinone)-alt-(5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid)

Code **PE-OA** : Poly(4,4'-(Propane-2,2-diyl)diphenol)-alt-(5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

Code**PE-OM**: Poly(4,4'- (Pyridin-2-ylmethylene) bis (2-methyl phenol))-alt5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

Code **PE-OP** : Poly(4,4'-(Pyridin-2-ylmethylene)diphenol)-alt-5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

Code **PE-OT** : Poly(4,4'-Thiodiphenol)-alt-(5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid)

Code **PE-OD** : Poly(Biphenyl4'4-diol)-alt-5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

Code **PE-OS** : Poly(4,4'- sulphonyl diphenol)-alt-5-(9-oxo-9H-fluorene 4-carboxamido) isophthalic acid

T5: Temperature for 5% weight loss

T10: Temperature for 10% weight loss

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