



Synthesis, Characterization and Thermal Properties of Some New Azopolyimides

G. LOGESH* and T.V. RAJENDIRAN

Research and Post-Graduate Department of Chemistry, Pachaiyappa's College, Chennai-600 030, India

*Corresponding author: E-mail: g_logesh@yahoo.co.in; dr_v_r@yahoo.co.in

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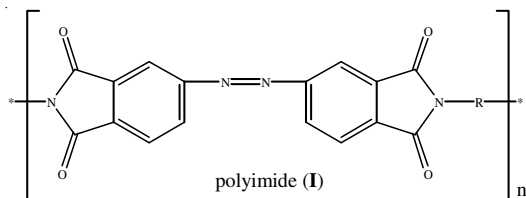
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A new class of aromatic azopolyimides were synthesized from aromatic diamine with 3,3',4,4'-azobenzene tetracarboxylic dianhydride. The synthesis involved the reaction of the dianhydride with respective diamine to yield an intermediate, soluble, open chain precursor polymer of polyamic acid, which on further cyclodehydration by solution, chemical and thermal imidization method yielded the less soluble, high viscosity, high stability, heat resistant or high temperature polyimides. All these polyimides were characterized by UV and IR. Viscosity, solubility, stability and thermal properties of these polymers were also studied.

Key Words: Azopolyimide, Aromatic diamine, Synthesis, Characterization, Thermal properties.

INTRODUCTION

Polyimides have experienced extremely rapid development in recent year^{1,2} the major emphasis being on engineering application. High-strength composite, thermally stable films, moldings compounds and adhesives are numbered among the products. Condensation polyimides were first to be developed^{3,4}. The reaction, illustrated from 3,3',4,4'-azobenzene tetracarboxylic dianhydride^{5,6} (ABTD) condensed with aromatic diamine to form polyamic acid, followed by ring closure to form polyimide(I)⁷⁻¹¹. The formation of a stable five membered ring is the driving force for forming linear rather than cross-linked polymer.



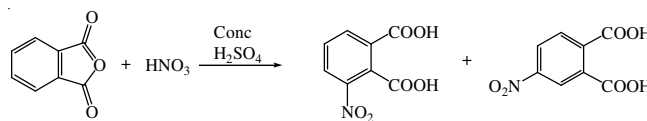
EXPERIMENTAL

Monomers, 2,4-diaminophenol dihydrochloride (98 %) and pyridine-2,6-diamine (99 %) were obtained from fluka and pyridine-2,5-diamine, 2,7-diaminofluorene, phenanthrene-9,10-diamine, 1,8-diamino-4,5-dihydroxy anthraquinone and the solvent dimethyl acetamide, N-methyl pyrrolidone, *o*-dichloro benzene and the reagent acetic anhydride, triethanolamine were AR-grade products of Aldrich chemicals (< 95 %) and 4,4'-diaminobiphenyl-3,3'-diol, 5-(2-(3-amino-4-methylphenyl)-

1,1,1,3,3,3-hexafluoropropan-2-yl)-2-methylaniline, 3,7-diamino-2,8-dimethyldibenzo thiophene-5,5-dioxide were obtained from chriskev (< 99 %) and 5-amino-1-(4-aminophenyl)-1,3,3-trimethyl indane (95 %) from Ciba.

Synthesis of monomers: 3,3',4,4'-Azobenzene tetracarboxylic dianhydride monomer was synthesized by following the procedure given below.

Preparation of 4-nitrophthalic acid¹⁰: A 2 L beaker placed on a piece of board at the bottom of 4 L (1-gallon) crock is fitted with a mechanical stirrer. In the beaker 650 mL of concentrated sulphuric acid (sp.gr. 1.84) is placed and 500 g of technical phthalic anhydride. The mixture is stirred and steam is passed into the crock. When the mixture reaches 80 °C, the steam is shut off and 210 mL of fuming nitric acid (sp.gr. 1.57) is added slowly from a separating funnel at such rate as to maintain the temperature of the stirred mixture at 100-110 °C. The addition takes 1 to 2 h. After fuming nitric acid has been added, 900 mL concentrated nitric acid (sp.gr: 1.42) is added as rapidly as possible without causing the temperature to rise above 110 °C. The mixture is then stirred and heated by passage of steam into the crock for 2 h longer.

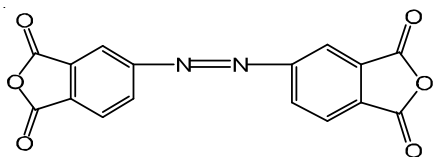


The mixture is allowed to stand overnight and then poured into 1.5 L of water in a 4 L crock. After cooling, the solid mixture of 3- and 4-nitrophthalic acids is filtered by suction through a Buckner funnel with 25 micron nylon filter cloth or

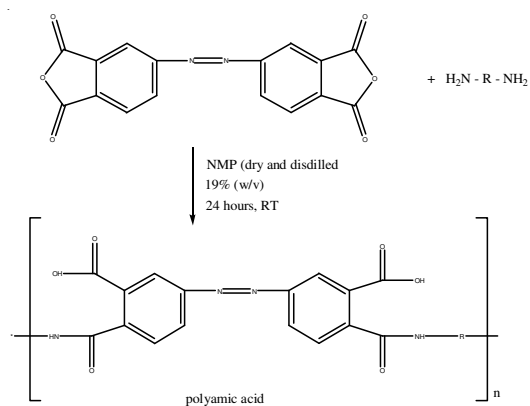
through a filter plate. The wet cake is returned to the crock and stirred thoroughly with 200 mL of water which dissolves a large amount of the 4-nitrophthalic acid. The mixture is again filtered by suction. The mother liquor is concentrate under reduced pressure (1 mm Hg) at low temperature and the obtained solid is dissolved by boiling with 200 mL of water. The solution is filtered hot and stirred mechanically until crystallization occurs. It is then allowed to stand overnight as the crystallization is slow. The crystals are filtered by suction and air dried. Yield of 4-nitrophthalic acid (stage-I) is 80 % obtained. (m.p. 162-164 °C decomposition).

Preparation of 3,3',4,4'-azobenzenetetracarboxylic dianhydride⁵: To a solution of 48 g of NaOH (1.2 mol) in 300 mL of water is added 42.2 g (0.2 mol) of 4-nitrophthalic acid and 28 g of zinc dust. The mixture is stirred while refluxing for about 4 h. The resulting dark red solution is cooled, filtered to remove the solids and then acidified with 40 mL of concentrated H₂SO₄. The red precipitate which resulted is filtered to remove the 3,3',4,4'-azobenzenetetracarboxylic acid formed in the reaction. The acid is washed once with about 100 mL of water is then pressed to dry and finally is dried at 110 °C with 1 mm Hg for 2 h. The dried solid obtained is dissolved in 100 mL of boiling *N,N*-dimethyl acetamide and is filtered hot. To the solution, added 180 mL of acetic anhydride slowly so as to control the endothermic reaction, which takes place. On cooling red crystals of 3,3',4,4'-azobenzenetetracarboxylic dianhydride (ABTD) are formed. These are removed by filtration and dried at 110 °C with 1 mm Hg pressure. Yield of 3,3',4,4'-azobenzenetetracarboxylic dianhydride (stage-II) is 70 % obtained.

Purification of 3,3',4,4'-azobenzenetetracarboxylic dianhydride: The monomer is purified by treating the crude dianhydride with dioxane, then isolating and decomposing the dianhydride-dioxane complex. 500 g of dioxane is added to 100 g of crude dianhydride under nitrogen atmosphere and the mixture is stirred for 2 h the complex is separated, half of which is heated to 120 °C for 2 h to give 49 g of pure dianhydride. The anhydride melts at 329-331 °C.



Synthesis of polyamic acid: 3,3',4,4'-Azobenzenetetracarboxylic dianhydride (ABTD) monomer was condensed with a diamine to form polyamic acid¹². To a flame dried three necked round bottom flask equipped with a mechanical stirrer, nitrogen inlet and a Dean-Stark trap with a condenser, one equivalent of the diamine was added and dissolved in 25 mL of dry and distilled *N*-methyl pyrrolidone (NMP). To this homogeneous solution one equivalent of the dianhydride (monomer) was slowly added along with 32 mL of *N*-methyl pyrrolidone (19 % w/v). After being stirred for 24 h at room temperature, the resulting polyamic acid, which on further cyclodehydration by solution, chemical and thermal imidization method yielded the polyimides. The general route of synthesis of polyamic acid (PAA) is shown in **Scheme-I** and the diamine used for polyimide is shown in Table-1.



Scheme-I: Synthesis of polyamic acid (PAA)

TABLE-1
DIAMINES (R) USED FOR POLYIMIDES SYNTHESIS

S. No.	Diamine (R)	Code
1.	2,4-Diaminophenol	PhOH
2.	Pyridine-2,5-diamine	2,5-Py
3.	Pyridine-2,6-diamine	2,6-Py
4.	2,7-Diaminofluorene	Flu
5.	Phenanthrene-9,10-diamine	Rene
6.	1,8-Diamino-4,5-dihydroxy anthraquinone ¹³	Qui
7.	4,4'-Diaminobiphenyl-3,3'-diol ¹⁴	Diol
8.	5-Amino-1-(4-aminophenyl)-1,3,3-trimethyl indane ¹⁵	Ind
9.	5-(2-(3-amino-4-methylphenyl)-1,1,1,3,3,3-hexafluoroPropan-2-yl)-2-methylaniline ¹⁶	Hexaflu
10.	3,7-Diamio-2,8-dimethylthiophene-5,5-dioxide ¹⁷	m-DDS

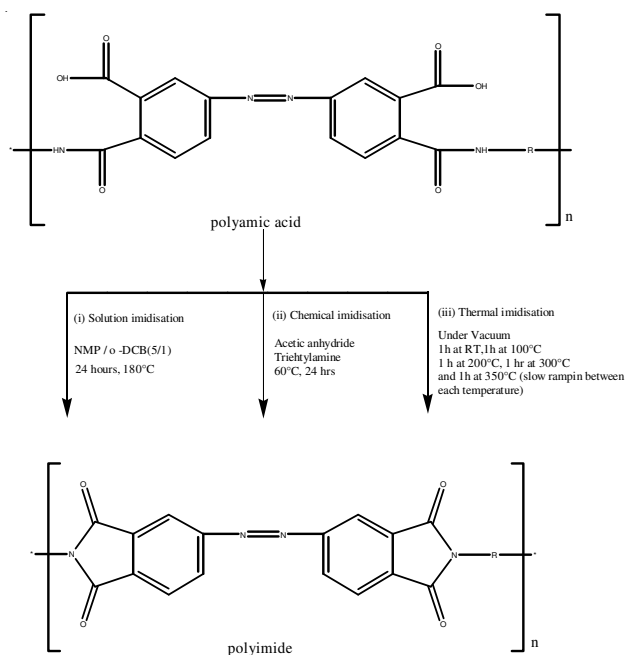
Synthesis of polyimides

Solution imidisation method: The azeotroping solvent, dry and distilled *o*-DCB used to facilitate the removal of water produced during the reaction was used in the following ratio NMP: *o*-DCB/5:1. The *o*-DCB was also used to fill the reverse dean-stark trap to maintain a constant solvent volume inside the flask. The polyamic solution was thermally imidized at 180 °C for 24 h before being cooled and poured into methanol to precipitate the polymer which was subsequently washed with diethyl ether. A general scheme for polyimides synthesized by various methods is shown in **Scheme-II** and the structures of polyimides is shown in Table-2.

Chemical imidization method: Polyamic acid was chemically imidized by the addition of acetic anhydride and triethylamine with a mole ratio of acetic anhydride/triethylamine to polyamic acid of 4:1. The polyamic acid solution with vigorous stirring for 0.5 h at room temperature and then thermally imidized at 60 °C for 24 h. The polyimides were precipitated in methanol and the polymer was washed in methanol and filtered and finally dried at 150 °C under vacuum for 24 h.

Thermal imidization: The following thermal imidization schedule was performed on the polyamic acid cast from solution onto a glass plate: (under vacuum with slow ramping between each hold temperature) 1 h at room temperature, 1 h at 100 °C, 1 h at 200 °C, 1 h at 300 °C and 1 h at 350 °C. The final imidisation temperature depended on the T_g of the resulting polymer. As a general rule, the final imidisation temperature must be > 20 °C above T_g. Following imidization,

the polyimide film was removed from the glass plate with a small addition of water. The film was then redried at 200 °C under vacuum for more than 12 h.



Scheme-II. Various method of synthesis of polyimides; where 'R' = diamine

TABLE-2
STRUCTURE OF POLYIMIDES SYNTHESIZED

S. No	Polyimides	Code
1.		ABTD-PhOH
2.		ABTD-2,5-Py
3.		ABTD-2,6-Py
4.		ABTD-Flu
5.		ABTD-Rene
6.		ABTD-Qui

S. No	Polyimides	Code
7.		ABTD-Diol
8.		ABTD-Ind
9.		ABTD-Hexaflu
10.		ABTD-m-DDS

RESULTS AND DISCUSSION

Viscosity of polyimides: Viscosity of a polymer is a relative measure of its molecular weight. In polymers of comparable rigidity, crystallinity and structure, a polymer with higher rigidity will have higher viscosity than the flexible one⁹. The inherent viscosity of the polyimides synthesized are given in Table-3. In general, viscosities obtained for polyimides depend on : (i) the basicity (pK_b) or ionization potential (IP) of the diamine as an electron donor (ii) electron affinity of the dianhydride as an electron acceptor. (iii) initial solubility of the growing polymer chain in the reaction medium and (iv) on the rigidity of the polyimide back bone. Thus, the polyimides derived from more basic diamines with electron releasing (methyl or *t*-butyl) substituents on the phenylene rings have fairly higher viscosities than those derived from less basic diamines with electron withdrawing (CF_3 , SO_2 , quinone) substituents on the phenylene rings. Polyimides with azodiamines show higher viscosities than that of non-azopolyimides. This may be due to the rigid nature of (high strength/high modulus) azo linkage which is in *trans*-form.

TABLE-3
VISCOSITY OF POLYIMIDES BY CHEMICAL IMIDIZATION METHOD

S. No.	Code of the polyimides	Yield (%)	η_{inh}^*	Colour
1	ABTD-PhOH	90	0.63	Black
2	ABTD-2,5-Py	92	0.74	Shining black
3	ABTD-2,6-Py	94	0.65	Black
4	ABTD-Flu	90	0.75	Brown
5	ABTD-Rene	86	0.55	Reddish brown
6	ABTD-Qui	88	0.62	Light brown
7	ABTD-Diol	82	0.64	Red
8	ABTD-Ind	84	0.70	Light red
9	ABTD-Hexaflu	80	0.62	Dark red
10	ABTD- <i>m</i> -DDS	82	0.64	Yellow

*Conc = 0.5 gdl⁻¹ in conc. H₂SO₄ at 25 °C

Among the polyimides synthesized, ABTD-Flu shows a highest viscosity of 0.75 dl g⁻¹ where as ABTD-Rene shows a

lowest viscosity of 0.55 dl g^{-1} . Structurally grinded polyimides having Flu, Rene, Qui, Ind and *m*-DDS diamines exhibit a viscosity of 0.75, 0.55, 0.62, 0.70 and 0.64 dl g^{-1} , respectively. The CH₂ group present between the two benzene rings of 2,7-diaminofluorene prevents the C-C rotation and makes the polymer a rigid one. Similar observation has been noticed in *m*-DDS due to SO₂ bridging molecule. In Rene and Qui diamines, the two amino groups are on the same side of the molecule, which form almost cyclic imide linkage and hence show low viscosities. Comparing 2,5-Py and 2,6-Py based polyimides, the *para* oriented diamine present in 2,5-positions of pyridine nucleus shows a higher viscosity of 0.74 dl/g whereas *meta* oriented (2,6-Py) polyimide shows 0.65 dl/g. The inherent viscosity of the polyimides synthesized in different methods are given in Table-4.

Code of polyimides (in the form of polyamic acid)	Inherent viscosity by solution imidization	Inherent viscosity by chemical imidization	Inherent viscosity by thermal imidization
ABTD-PhOH	0.61	0.63	0.64
ABTD-Flu	0.70	0.75	0.72
ABTD-Ind	0.62	0.70	0.64

Solubility properties: The azo linkage, though structurally rigid appears to aid solubility¹³. The solubility properties of all the polyimides are reported in Table-5. All the polyimides are soluble in conc. H₂SO₄. They are soluble on long standing in aprotic polar solvents such as *N*-methyl pyrrolidone, dimethyl acetamide and DMSO and some polymers are soluble in less polar solvent like THF. However, these polymers are not soluble in common organic solvents such as chloroform, acetone, *o*-DCB, DMF and THF. They are partially soluble in *m*-cresol and almost soluble in trifluoroacetic acid. This can be explained on the basis of dielectric constant of the solvents which are insufficient to break the bonds of a polymer.

Stability of polyimides in conc. H₂SO₄: Polyimides are more stable towards acid or alkaline hydrolysis since the imide linkage of the polymer backbone is not easily cleaved by the reagents. However, keeping the polyimides in conc. H₂SO₄ for an interval of time results in decrease in viscosity. Stability of ABTD-Rene, ABTD - Diol and ABTD - Hexaflu has been studied in conc. H₂SO₄ since these polyimides were used for

film formation and/or lamination. The η_{inh} values with respect to various time interval observed for the polyimides in conc. H₂SO₄ are given in Table-6. The data show that ABTD-Rene has the maximum stability towards conc. H₂SO₄. The order of stability in conc. H₂SO₄ among the three polyimides, on the basis of diamine is given as below: Rene > Diol > Hexaflu.

ABTD - Rene has rigid structure, bonded at *ortho*-positions too through -CH₂- linkage, which is responsible for more stability. In addition to this, the high solvolytic stability of ABTD-Rene may be due to the operation of weak vander Waals forces between the bridged -CH₂- group present in the diamine and the lone pair of electrons on nitrogen of the azo group. ABTD-Rene shows a decrease of only 12.73 % in η_{inh} even after 48 h and naturally this may be due to the nature of the diamine part. These data are useful in lamination studies and fibre formation.

Polyimide	Time (h)	η_{inh}^*	Decrease in η_{inh} (%)
ABTD-Rene	0	0.55	0.00
	½	0.55	0.00
	1	0.54	1.82
	2	0.52	5.45
	24	0.50	6.36
	48	0.48	12.73
ABTD-Diol	0	0.64	0.00
	½	0.64	0.00
	1	0.62	3.125
	2	0.60	3.75
	24	0.55	14.06
	48	0.54	15.63
ABTD-Hexaflu	0	0.62	0.00
	½	0.60	3.23
	1	0.58	6.45
	2	0.56	9.68
	24	0.51	17.74
	48	0.50	19.35

*Inherent viscosity in conc. H₂SO₄ at 25 °C; conc. = 0.5 g/dl

UV-Visible spectra: The UV-Visible spectra of the polyimides are of interest because of the presence of the azo group and bathochromic shift is shown by the polymers relative to that of *trans*-azobenzene (238.84 nm and 432.9 nm)¹⁴. Typical data are given in Table-7. The absorption in the visible region are due to $n \rightarrow \pi^*$ transition whereas those in the UV region

S. No.	Code of polyimides	Conc. H ₂ SO ₄	TFA	MP + 5 % LiCl	DMAc + 5 % LiCl	DMSO	<i>m</i> -cresol	<i>o</i> -DCB	Acetone	THF	CHCl ₃	DMF
1.	ABTD-PhOH	A	A	C	C	B	E	B	B	B	B	B
2.	ABTD-2,5-Py	A	A	A	A	B	B	B	B	B	B	B
3.	ABTD-2,6-Py	A	A	A	A	B	B	B	B	B	B	B
4.	ABTD-Flu	A	F	F	F	B	B	B	B	B	B	D
5.	ABTD-Rene	A	F	F	F	B	B	B	B	B	B	D
6.	ABTD-Qui	A	F	F	F	B	B	B	B	B	B	B
7.	ABTD-Diol	A	A	F	F	B	B	B	B	B	B	D
8.	ABTD-Ind	A	A	F	F	B	B	B	B	B	B	B
9.	ABTD-Hexaflu	A	A	F	F	B	B	B	B	B	B	E
10.	ABTD- <i>m</i> -DDS	A	A	F	F	B	B	B	B	B	B	D

-A = Soluble, B = Insoluble, C = Soluble on heating, D = Colour change, E = Partially soluble, F = Soluble on long standing

are associated with $\pi \rightarrow \pi^*$ transition. The polyimides absorb in the range of 200 to 273 nm in the UV region and at 400-728 nm in the visible region^{15,16}. The azo group considerably increases conjugation through lone pair of electrons on the nitrogen atom, thus justifying the highest λ_{\max} values observed for these azopolyimides.

TABLE-7
UV-VISIBLE SPECTRAL DATA OF POLYAMIC ACID

Polymer S. No.	Polyamic acid	UV-Visible data (nm)*	
		UV	Visible
1.	ABTD-PhOH	265,280	455
2.	ABTD-2,5-Py	270, 275	740
3.	ABTD-2,6-Py	200, 230, 250	465, 720
4.	ABTD-Flu	310	460
5.	ABTD-Rene	190, 230, 270, 360	420
6.	ABTD-Qui	245	410
7.	ABTD-Diol	370	450, 705
8.	ABTD-Ind	370	460, 730
9.	ABTD-Hexaflu	260	650,710
10.	ABTD-m-DDS	280, 290	690

*Solvent conc. H₂SO₄

Infrared spectra: The important absorptions observed in IR spectra for the polyamic acids and polyimides are presented in Tables 8 and 9. The assignments have been made following the standard values¹⁷. The O-H stretching frequency was observed as a band around $3410 \pm 10 \text{ cm}^{-1}$ for polyamic acid. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the polyamic acid precursor into polyimide. Imide absorption bands are observed at $1780 \pm 10 \text{ cm}^{-1}$ and 1720 cm^{-1} (imide I); 1375 cm^{-1} (imide II); 1120 cm^{-1} (imide III) and $720 \pm 10 \text{ cm}^{-1}$ (imide IV) in the cyclodehydrate samples. All those bands were very strong and were absent in the amic acid. Spectra of imide I band is attributed to the stretching vibrations of weakly coupled carbonyl groups. The imide II, III and IV bands have been assigned to axial, transverse and out-of-plane vibrations of the cyclic imide structures.

Thermal analyses

Thermogravimetric analysis and differential thermal analysis: Thermal behaviour of the polyimides were determined

TABLE-8
IR DIFFERENCE BETWEEN POLYAMIC ACID AND POLYIMIDE

Polyamic acid	Frequency (cm ⁻¹)	Assignment
	3447-3260 (m)	N-H stretch and COOH
	3520-3500 (s)	-OH group of COOH
	1710 (s)	C=O of COOH group
	1660 (s) amide I	C=O (CONH)
	1550 (m) amide II	C-NH
	1411	O-H inplane deformation
	1320	C-O stretching
Polyimide	Frequency (cm ⁻¹)	Assignment
Imide-I	1780 (s)	C=O asymmetric stretching
	1720 (ws)	
Imide-II	1375 (s)	C-N stretch, axial
Imide-III	1120	Transverse
Imide-IV	690 (s)	Aromatic imide C=O bending or out-of-plane

by thermogravimetric analysis and differential thermal analysis in nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. The thermal stability of a polymer depends on the bond energies of the various bonds in the polymer backbone^{12,18-19}. Higher these bond energies between atoms, greater is the thermal stability. Factors such as (i) high chain stiffness (ii) high resonance (iii) high degree of crystallinity (iv) high interchain bonding or interactions are known to enhance the thermal stability. Physical and morphological factors may also influence the polymer stability²⁰⁻²⁴. The thermal data of azopolyimides obtained in N₂ atmosphere are given in Table-10, which shows the temperatures of 10 to 50 % decomposition of polyimides in N₂ atmosphere. Char yield (%) is also reported in addition to T_g and T_d (°C) where T_g denotes glass transition temperature and T_d refers to decomposition temperature. The four ranges between RT (room temperature) and 800 °C. The ranges RT-150 °C and 300-500 °C show little weight loss, but those from 150-300 °C and 500-800 °C show a large weight loss. The weight loss of the range 150-300 °C is due to dehydration and crosslinking reaction during polyimide formation. This is an exothermic reaction. In the range of 300-500 °C, polyamic acid is changed partially into polyimide because of little weight loss. Above 500 °C, a high exothermic peak is in evidence due to thermal decomposition.

TABLE-9
FT-IR FREQUENCIES OBSERVED FOR POLYIMIDES

S. No.	Polymer code	Imide I		Imide II C-N stretch	Imide IV	C=C ring stretch	Aromatic C-H stretch	Imide ring deformation	
		C=O asym stretch	C=O sym stretch					Imide III C-N-C imide	Aromatic attached to imide ring
1.	ABTD-PhOH			1395	690	1603	3090	1145	820
2.	ABTD-2,5-Py	1780	1720	1380	690	1600	3090	1100	725
3.	ABTD-2,6-Py	1780	1720	1380	690	1600	3090	1120	740
4.	ABTD-Flu	1770	1720	1390	690	1600	3090	1120	725
5.	ABTD-Rene	1775	1720	1395	690	1590	3080	1100	740
6.	ABTD-Qui	1780	1720	1390	690	1590	3080	1145	725
7.	ABTD-Diol	1780	1720	1380	690	1595	3085	1145	730
8.	ABTD-Ind	1770	1725	1380	690	1595	3085	1145	735
9.	ABTD-Hexaflu	1765	1730	1380	685	1595	3090	1100	735
10.	ABTD-m-DDS	1760	1725	1385	685	1605	3095	1120	740

TABLE-10
THERMAL ANALYSIS OF POLYIMIDES IN NITROGEN ATMOSPHERE

S. No.	Polyimide code	Weight loss (%)					T _d (°C)	No of stages of weight loss	T _g (°C)	Residue yield (%)	Exothermic temperature (°C)
		10	20	30	40	50					
1.	ABTD – PhOH	490	530	590	602	-	570	3	-	60.4	130, 645
2.	ABTD – 2,5-Py	506	540	595	610	-	565	3	-	60.4	380, 640
3.	ABTD – 2,6-Py	515	545	600	620	-	545	3	-	65.3	390, 690
4.	ABTD – Flu	560	600	630	662	-	410	4	Highest 315	65.0	200, 270, 400, 535, 605
5.	ABTD – Rene	520	545	580	604	-	525	4	-	63.2	-
6.	ABTD – Qui	480	525	565	600	-	490	4	-	60.1	-
7.	ABTD – Diol	550	590	610	645	675	580	3	-	58.8	-
8.	ABTD – Ind	540	580	608	648	695	545	3	-	56.4	-
9.	ABTD – Hexaflu	552	591	606	647	-	560	4	285	61.0	350, 440, 520
10.	ABTD – m – DDS	510	545	602	622	-	520	3	306	60.2	-

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