

## Synthesis, Characterization and Thermal Properties of Certain New Ether Linkage Azopolyimides

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(Received: 16 August 2011;

Accepted: 22 February 2012)

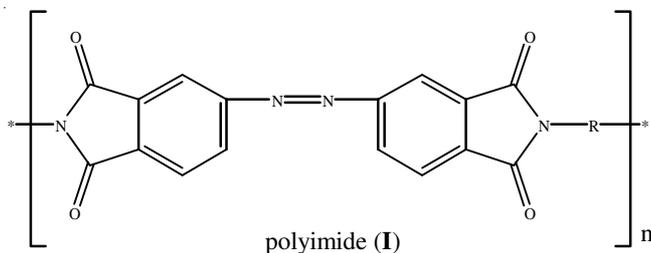
AJC-11100

A ether linkage 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, highly stable, 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, Ether, Synthesis, Characterization, Thermal properties.

### INTRODUCTION

Polyimides have experienced extremely rapid development in recent year<sup>1,2</sup> 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<sup>3,4</sup>. The reaction, illustrated from 3,3',4,4'-azobenzene-tetracarboxylic dianhydride<sup>5,6</sup> (ABTD) condensed with aromatic diamine to form polyamic acid, followed by ring closure to form polyimide(I)<sup>7-11</sup>. The formation of a stable five membered ring is the driving force for forming linear rather than crosslinked polymer.



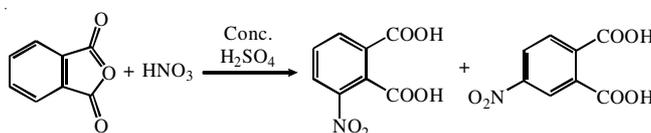
### EXPERIMENTAL

Monomers, 1,4-bis(4-aminophenoxy)benzene (97 %) and 1,4-bis(4-aminophenoxy)-2-methylbenzene (99 %) were obtained from Aldrich and 1,4-bis(4-aminophenoxy)-2-tert-butylbenzene, 1,3-bis(4-aminophenoxy)benzene, 1,2-bis(4-aminophenoxy)benzene and the solvent dimethyl acetamide,

N-methyl pyrrolidone, *o*-dichloro benzene and the reagent acetic anhydride, triethylamine were AR-grade products of fluka chemicals (< 95 %) and 1,2-bis(4-aminophenoxy)-4-tert-butylbenzene, bis-[4-(4-aminophenoxy)]phenylether were obtained from Chriskev (<99 %) and 2,3-bis(4-aminophenoxy)naphthalene (95 %) and 2,3-bis(4-amino-2-trifluoromethyl phenoxy) naphthalene (98 %) were obtained from Ciba.

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

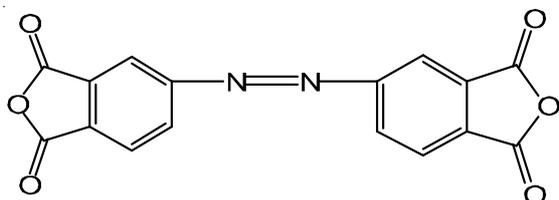
**Preparation of 4-nitrophthalic acid<sup>10</sup>:** A 2 L beaker placed on a piece of board at the bottom of 4 L (1-gallon) crock is fitted with a mechanical stirrer. In the beaker 650 mL of concentrated sulphuric acid (sp.gr. 1.84) is placed and 500 g of technical phthalic anhydride. The mixture is 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 Buchner funnel with 25  $\mu$  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 concentrated 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 % (m.p. 162-164 °C d).

**Preparation of 3,3',4,4'-azobenzenetetracarboxylic dianhydride<sup>5</sup>:** 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 4 h. The resulting dark red solution is cooled, filtered to remove the solids and then acidified with 40 mL of concentrated H<sub>2</sub>SO<sub>4</sub>. The red precipitate resulted is filtered to remove the 3,3',4,4'-azobenzenetetracarboxylic acid formed in the reaction. The acid is washed once with *ca.* 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. 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 acid<sup>19</sup>. 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

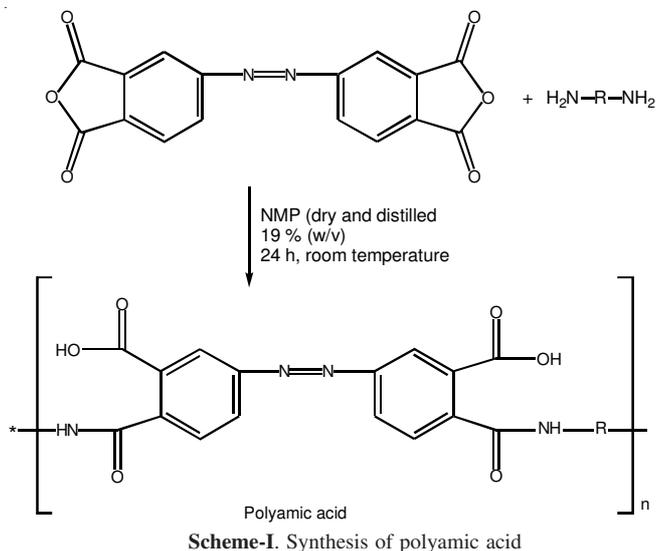


TABLE-1  
DIAMINES (R) USED FOR SYNTHESIS OF POLYIMIDES

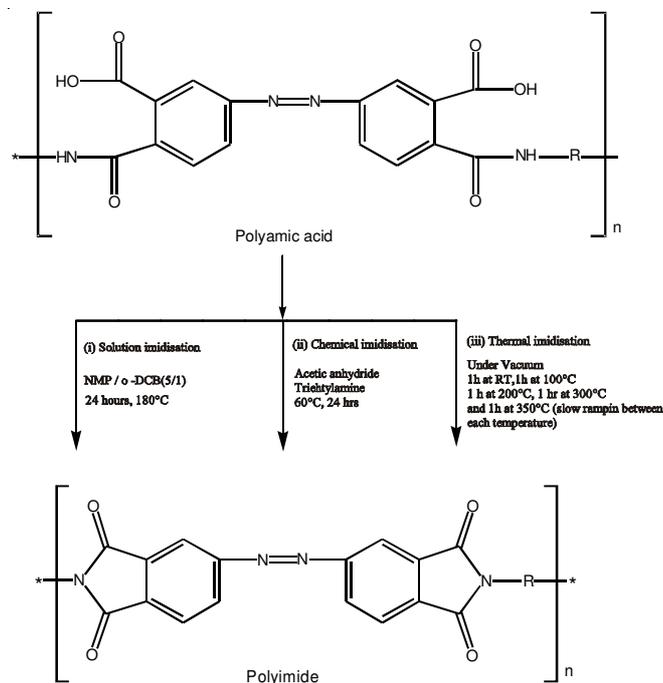
S. No	Diamine (R)	Code
1.	1,4-Bis-(4-aminophenoxy)benzene	PAPB
2.	1,4-Bis-(4-aminophenoxy)-2-methylbenzene	PAPT
3.	1,4-Bis-(4-aminophenoxy)-2- <i>tert</i> -butylbenzene	PAPTb
4.	1,3-Bis-(4-aminophenoxy)benzene	<i>m</i> -BAPB
5.	1,2-Bis-(4-aminophenoxy)benzene	<i>o</i> -BAPB
6.	1,2-Bis-(4-aminophenoxy)-4- <i>tert</i> -butylbenzene	<i>o</i> -APTb
7.	Bis-[4-(4-aminophenoxy)]phenylether,	PAPPE
8.	2,3-Bis-(4-aminophenoxy)naphthalene,	2,3-BAPON
9.	2,3-Bis-(4-amino-2-trifluoromethylphenoxy)naphthalene	2,3-BATF

### Synthesis of polyimides

**Solution imidization method:** The azeotropic solvent, dry and distilled *o*-dichloro benzene (*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 structure 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 30 min 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



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

TABLE-2  
STRUCTURE OF POLYIMIDES SYNTHESIZED

S. No	Polyimides	Code
1.		ABTD-PAPB
2.		ABTD-PAPT
3.		ABTD-PAPTb
4.		ABTD-m-BAPB
5.		ABTD-o-BAPB
6.		ABTD-o-APTb
7.		ABTD-PAPPE

S. No	Polyimides	Code
8.		ABTD-2,3-BAPON
9.		ABTD-2,3-BATF

imidization temperature depended on the  $T_g$  of the resulting polymer. As a general rule, the final imidization 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 retrieved at 200 °C under vacuum for more than 12 h.

## 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 one<sup>9</sup>. 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 ( $CF_3$ ) 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  
YIELD, COLOUR AND VISCOSITY OF POLYIMIDES BY CHEMICAL IMIDIZATION METHOD

S. No.	Code of the polyimides	Yield (%)	$\eta_{inh}^*$	Colour
1	ABTD-PAPB	75	0.90	Yellowish
2	ABTD-PAPT	90	0.92	Yellowish red
3	ABTD-PAPTb	78	0.90	Yellowish red
4	ABTD- <i>m</i> -BAPB	80	0.85	Light brown
5	ABTD- <i>o</i> -BAPB	84	0.76	Light brown
6	ABTD- <i>o</i> -APTb	85	0.75	Pale yellow
7	ABTD-PAPPE	82	0.86	Brown
8	ABTD-2,3-BAPON	92	1.28	Brown
9	ABTD-2,3-BATF	96	1.08	Yellow

\*Conc. = 0.5 g dl<sup>-1</sup> in conc. H<sub>2</sub>SO<sub>4</sub> at 25 °C

Among the polyimides synthesized, ABTD - 2,3-BAPON shows a highest viscosity of 1.28 g dl<sup>-1</sup> where as ABTD-*o*-APTb shows a lowest viscosity of 0.75 g dl<sup>-1</sup>. Interestingly

long chain diamines *viz.* PAPB, PAPT, PAPT<sub>B</sub> and PAPPE exhibit a viscosity of 0.90, 0.92, 0.90 and 0.86, respectively. Though PAPPE is a long chain diamine, because of the bond angle of three oxygen atoms, it is no longer behaves a rigid one. At the same time, substituents like methyl or *tert*-butyl group slightly increase the viscosity. Comparison can be made with *para*, *meta* and *ortho* oriented polyimides. PAPT<sub>B</sub>, *m*-BAPT<sub>B</sub> and *o*-BAPT<sub>B</sub> based polyimides show a viscosity of 0.90, 0.85 and 0.76 g dl<sup>-1</sup>, respectively. Again, this comparison is an evidence to prove that formation of high viscosity polymers are favoured by *para* > *meta* > *ortho*. 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-PAPB	0.85	0.90	0.84
ABTD-PAPT <sub>B</sub>	0.82	0.90	0.82
ABTD-2,3 BAPON	0.98	1.28	0.91

**Solubility properties:** The azo linkage, though structurally rigid appears to aid solubility<sup>12</sup>. The solubility properties of all the polyimides are reported in Table-5. All the polyimides are soluble in conc. H<sub>2</sub>SO<sub>4</sub>. 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. ABTD-2,3-BAPON and ABTD-2,3-BATF polyimides exhibit the solubility nature in most of the solvents because of the molecular asymmetry and the bulky groups inhibit close packing, thus enhancing the chain-chain interactions which leads to more solubility.

**Stability of polyimides in conc. H<sub>2</sub>SO<sub>4</sub>:** 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. H<sub>2</sub>SO<sub>4</sub> for an interval of time results in decrease in viscosity. Stability

of ABTD-PAPB, ABTD-PAPT, ABTD-PAPT<sub>B</sub> and ABTD-APPE has been studied in conc. H<sub>2</sub>SO<sub>4</sub>. The  $\eta_{inh}$  values with respect to various time interval observed for the polyimides in conc. H<sub>2</sub>SO<sub>4</sub> are given in Table-6. The data show that ABTD-PAPPE has the maximum stability towards conc. H<sub>2</sub>SO<sub>4</sub>. The order of stability in conc. H<sub>2</sub>SO<sub>4</sub> among the four polyimides, on the basis of diamine is given as below: PAPT<sub>B</sub> > PAPT > PAPB > PAPPE.

Polyimide	Time (h)	$\eta_{inh}^*$	% Decrease in $\eta_{inh}$
ABTD-PAPB	0	0.90	0.00
	½	0.88	2.22
	1	0.85	5.56
	2	0.82	8.87
	24	0.79	12.22
	48	0.75	16.66
ABTD-PAPT	0	0.92	0.00
	½	0.90	2.17
	1	0.88	4.35
	2	0.87	5.43
	24	0.83	9.78
	48	0.80	13.04
ABTD-PAPT <sub>B</sub>	0	0.90	0.00
	½	0.90	0.00
	1	0.89	1.11
	2	0.87	3.32
	24	0.85	5.54
	48	0.83	7.76
ABTD-PAPPE	0	0.86	0.00
	½	0.83	3.48
	1	0.80	6.97
	2	0.78	9.30
	24	0.70	18.60
	48	0.68	20.93

\*Inherent viscosity in conc. H<sub>2</sub>SO<sub>4</sub> at 25°C; conc = 0.5 g/dl

The flexible three -O- (ether linkage) unit in diamine part of ABTD-PAPPE polymer decreases the stability compare to other rigid polymers. ABTD-PAPT<sub>B</sub> has rigid structure, bonded at *ortho* positions too through -(CH<sub>3</sub>)<sub>3</sub>- linkage, which is responsible for more stability. In addition to this, the high solvolytic stability of ABTD-PAPT<sub>B</sub> may be due to the operation of weak Vander waals forces between the -(CH<sub>3</sub>)<sub>3</sub>-group present in the diamine and the lone pair of electrons on nitrogen of the azo group. ABTD-PAPT<sub>B</sub> shows a decrease of only 7.76 % in  $\eta_{inh}$  even after 48 h and naturally this may be

S. No.	Code of polyimides	Conc. H <sub>2</sub> SO <sub>4</sub>	TFA	MP + 5 % LiCl	DMAc + 5 % LiCl	DMSO	<i>m</i> -cresol	<i>o</i> -DCB	Acetone	THF	CHCl <sub>3</sub>	DMF
1.	ABTD-PAPB	A	A	C	B	B	B	B	B	B	B	B
2.	ABTD-PAPT	A	A	C	C	B	C	B	B	B	B	B
3.	ABTD-PAPT <sub>B</sub>	A	G	G	G	B	B	B	B	B	B	D
4.	ABTD- <i>m</i> -BAPT <sub>B</sub>	A	A	A	A	B	B	B	B	B	B	D
5.	ABTD- <i>o</i> -BAPT <sub>B</sub>	A	A	A	A	A	C	E	C	A	E	B
6.	ABTD- <i>o</i> -APT <sub>B</sub>	A	A	A	A	A	C	E	C	A	E	B
7.	ABTD-PAPPE	A	A	A	A	A	C	E	C	A	B	B
8.	ABTD-2,3-BAPON	A	A	A	A	A	C	E	C	A	E	A
9.	ABTD-2,3-BATF	A	A	A	A	A	C	E	C	A	E	A

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

due to the nature of the diamine part. These data are useful in lamination studies and fibre formation.

**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)<sup>13</sup>. 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 are associated with  $\pi \rightarrow \pi^*$  transition. The polyimides absorb in the range of 200 to 360 nm in the UV region and at 400-728 nm in the visible region<sup>14,15</sup>. The azo group considerably increases conjugation through lone pair of electrons on the nitrogen atom, thus justifying the highest  $\lambda_{\max}$  values observed for these azopolyimides.

Polymer S.No.	Polyamic acid	UV-Visible data (nm)*	
		UV	Visible
1.	ABTD-PAPB	245, 283	455, 680
2.	ABTD-PAPT	260, 295	711
3.	ABTD-PAPTb	205, 220, 258	465, 720
4.	ABTD- <i>m</i> -BAPB	229, 240	660
5.	ABTD- <i>o</i> -BAPB	270, 360	428, 543
6.	ABTD- <i>o</i> -APTb	247, 291	510, 612
7.	ABTD-PAPPE	265, 281	458, 715
8.	ABTD-2,3-BAPON	236, 260	550, 710
9.	ABTD-2,3-BATF	232, 258, 298, 340	568, 670

\* Solvent conc. H<sub>2</sub>SO<sub>4</sub>

**Infrared spectra:** The important absorptions observed in IR spectra for the polyamic acids and polyimides are presented in Tables 8 and 9. 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 poly(amic acid) precursor into polyimide. Imide absorption bands are observed at  $1780 \pm 10 \text{ cm}^{-1}$  and  $1720 \text{ cm}^{-1}$  (Imide I);  $1375 \text{ cm}^{-1}$  (Imide II);  $1120 \text{ cm}^{-1}$  (Imide III) and  $700 \pm 10 \text{ cm}^{-1}$  (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<sup>16</sup>.

**Thermogravimetric analysis and Differential thermal analysis:** Thermal behaviour of the polyimides were determined 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<sup>17-19</sup>. 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 stability<sup>20-24</sup>. The thermal data of azopolyimides obtained in N<sub>2</sub> atmosphere are given in Table-10, which shows the temperatures of 10 to 50 % decomposition of polyimides in N<sub>2</sub> atmosphere. Char yield (%) is also reported in addition to T<sub>g</sub> and T<sub>d</sub> (°C) where T<sub>g</sub> denotes glass transition temperature and T<sub>d</sub> refers to decomposition temperature. The four ranges between room temperature and 800 °C. The ranges room temperature to 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.

Polyamic acid	Frequency (cm <sup>-1</sup> )	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 <sup>-1</sup> )	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

S. No.	Polymer code	Imide I		Imide II	Imide IV	C=C ring stretch	Aromatic C-H stretch	Imide ring deformation	
		C=O asym stretch	C=O sym stretch	C-N stretch				Imide III C-N-C imide	Aromatic attached to imide ring
1.	ABTD-PAPB	1750	1730	1385	680	1600	3090	1120	720
2.	ABTD-PAPT	1770	1720	1385	690	1605	3090	1140	720
3.	ABTD- <i>m</i> -PAPTb	1777	1715	1390	695	1600	3090	1130	725
4.	ABTD- <i>m</i> -BAPB	1780	1715	1390	690	1605	3095	1135	725
5.	ABTD- <i>o</i> -BAPB	1780	1720	1380	690	1605	3090	1130	725
6.	ABTD- <i>o</i> -APTb	1770	1725	1380	690	1605	3095	1140	740
7.	ABTD-PAPPE	1770	1730	1380	690	1605	3085	1145	730
8.	ABTD-2,3-BAPON	1770	1720	1380	690	1605	3090	1140	740
9.	ABTD-2,3-BATF	1778	1720	1379	690	1605	3090	1138	725

TABLE-10  
THERMAL ANALYSIS OF POLYIMIDES IN NITROGEN ATMOSPHERE

S. No.	Polyimide code	Weight loss (%)					T <sub>d</sub> (°C)	No of stages of weight loss	T <sub>g</sub> (°C)	Residue yield (%)	Exothermic temperature
		10	20	30	40	50					
1.	ABTD-PAPB	560	640	675	745	825	550	4	240	47.2	70, 270, 650, 690
2.	ABTD-PAPT	557	591	568	616	645	560	4	238	49.5	85, 120, 290, 510
3.	ABTD-PAPTb	548	588	662	710	730	565	4	-	51.0	111, 210, 230, 595
4.	ABTD- <i>m</i> -BAPB	556	595	668	715	750	602	3	235	50.5	-
5.	ABTD- <i>o</i> -BAPB	540	585	612	660	705	595	3	-	52.0	-
6.	ABTD- <i>o</i> -APTb	525	540	570	601	640	550	3	-	54.4	375, 560, 610
7.	ABTD-PAPPE	555	610	660	703	786	590	4	Lowest 221	53.0	240, 390, 515
8.	ABTD-2,3-BAPON	550	585	609	646	-	565	4	290	62.0	110, 360, 580
9.	ABTD-2,3-BATF	540	580	609	648	-	585	4	300	60.0	120, 590, 620

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