Asian Journal of Chemistry Vol. 21, No. 2 (2009), 1097-1106

Synthesis and Characterization of New Azopolyimides Derived from Azobenzene Tetracarboxylic Dianhydride

DEVI KANIAKUMARI and T.V. RAJENDIRAN*
Department of Chemistry, Pachaiyappa's College, Chennai-600 030, India
E-mail: dr_v_r@yahoo.co.in

A monomer 3,3′4,4′-azobenzene tetracarboxylic dianhydride (ABTD) was synthesized and polyimides were prepared by polycondensation with aromatic diamines such as 2,2′-dimethoxy benzidine or *ortho*-dianisidine, 4,4′-diamino diphenylmethane, *bis*(*p*-aminocyclohexyl)-methane, 4,4′-diamino diphenyl ether, 4,4′-diamino benzanilide, 2,2-*bis*[4-[*p*-aminophenoxy]phenyl]propane and 4,4′-[1,4-phenylenediisopropylidene]*bis* aniline. The polyimides were prepared through three different methods (i) solution (ii) chemical and (iii) thermal imidization. The polymers were characterized by inherent viscosity, solubility, FT-IR, UV-visible, TGA and DTA studies. Activation energy has been calculated for the thermal degradation of the polyimides.

Key Words: Azopolyimides, Viscosity, Activation energy, Thermal degradation.

INTRODUCTION

As a class of organic resins, the polyimides exhibit outstanding mechanical properties especially their thermal stability. Their introduction in the 1960's made significant contributions to meet the exacting demands in the areas of industry such as aerospace, arament and nuclear development. Du pont led application oriented research in this field culminated in the introduction of a polyimide film under the trade name Kapton in 1961 and varnishes for electrical applications were also made. Polyimides have exceptional heat resistance and most of their mechanical properties remain intact even upto 250 ºC or more. Excellent electrical resistance, solvent resistance, flame retardance, abrasion resistance, oxidative and radiation resistance properties have led to their application in critical areas.

Their solubility can be enhanced to some degree by incorporating flexible linking groups such as -O-, SO_2- (or) -$C(CH_3)_2$ - between the two aromatic rings or by modifying the polyimides by incorporating amide and ester groups to form polyamide-imides and polyester-imides[1]. Lefevere and coworkers[2] and Uneo[3] report the observation in several aromatic azo compounds as characteristic of the azo linkage.

Among the several classes of thermally stable polymers, azopolyimides are of great importance. The azochromophore in polymer backbone increases chain stiffness and imparts colour to the polymer. Such polymer may, therefore, have potential aplications as high modulus/high strength films and high grade pigments of good stability towards light and organic solvents. The synthesis, characterization and fibre/films studies of several wholly aromatic and aromatic-aliphatic azopolyamides were reported earlier from this laboratory[4-9].

EXPERIMENTAL

Lithium chloride was used after drying lithium chloride anhydrous (Lancaster) over P_2O_5 in vacuum drying pistle at 100 ºC. N,N-Dimethyl formamide (LR, BDH, India) was kept over KOH for 24 h and distilled under reduced pressure. Methyl-2-pyrrolidinone (NMP: Fischer Scientific) was dried over sodium hydroxide for at least 12 h prior to distillation under reduced pressure (~torr) (b.p. 205 ºC/760 mm Hg, 82 ºC/10 mm Hg). N,N-Dimethylacetamide (DMAc: Fluka-Puriss) was dried over calcium hydride for at least 12 h prior to distillation under reduced pressure (~torr) (b.p. 163-165 ºC/760 mm Hg. *o*-Dichlorobenzene (*o*-DCB: Fluka-Puriss) was dried over calcium hydride for at least 12 h prior to distillation under reduced pressure (b.p. 180 ºC/760 mm Hg). Diethyl ether (AR, BDH, India) was used (b.p. 34.6 ºC) as such.

2,2′-Dimethoxy benzidine (Aldrich) was recyrstallized from aqueous methanol (m.p. 136-137 ºC). 4,4′-Diamino diphenyl methane m.p. 86-87 ºC (Aldrich, Germany, 97 %) was recrystallized from benzene. *Bis*(*p*-aminocyclohexyl)methane (99.5 % plus) was obtained from du pont (USA) as a gift sample and used as such. 4,4′-Diamino diphenyl ether (Lancaster, England, 98 %) m.p. 191-192 ºC was recrystallized from benzene. 4,4′-Diaminobenzanilide[10] was synthesized and recrystallized from aqueous alcohol m.p. 239 ºC. 2,2-*Bis*[4-(*p*-aminophenoxy)phenyl] propane m.p. 124 ºC was prepared by a slight modification of patent procedure given by Sugano *et al.*[11]. 4,4′-(1,4-Phenylenediisopropylidene)*bis*aniline, purum, fluka (Switzerland) was vacuum distilled.

Synthesis of monomer: 3,3′,4,4′-Azobenzenetetracarboxylic dianhydride (ABTD) monomer was synthesized by known procedure[12,13].

Polymerization method

Solution imidization method: One equivalent of the diamine was dissolved in 25 mL of dry and distilled methyl-2-pyrrolidinone. To this homogeneous solution one equivalent of the dianhydride (monomer) was slowly added along with 32 mL of methyl-2-pyrrolidinone (19 wt. % w/v). After being stirred for 24 h at room temperature, the resulting polyamic acid was thermally imidized in solution. NMP:*o*-DCB/ 5:1. The polyamic solution was thermally imidized at 180 ºC for 24 h before being cooled and poured into methanol to precipitate the polymer. Subsequently it was washed with diethyl ether and dried.

Characterization: The inherent viscosity η of polyimides were obtained from the polymer solution at 25 ºC using DMSO/NMP/DMAc and conc. H_2SO_4 as solvent for all polyimides in an Ubbelhode viscometer. The concentration used was 0.5 g/dl throughout for all the measurements.

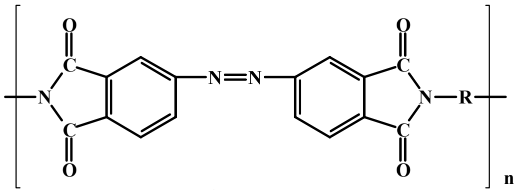
Solubility of the polyimides was determined in various solvents. A solution was prepared and allowed to stand for 24 h. If insoluble in cold, the solution was heated to boiling for few minutes. Whether a polymer was dissolved or swelled in a solvent, was noted.

The UV-visible spectra were recorded for all the polyimides using DMAc, DMSO and NMP as solvent in a closed cell at room temperature, with a CARL ZEISS UV-Vis spectrometer. The samples were incorporated in KBr disc and IR spectra of the polymers were recorded in Bruker Vector 22 spectrometer.

Thermal analysis (TGA and DTA) were recorded in nitrogen for all the polymers using STA-409C model simultaneous TGA-DTA apparatus. About 49 mg of the sample was heated at the heating rate of 10 ºC/min for all the polymers.

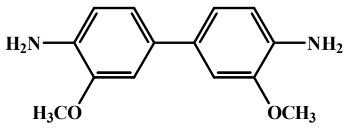
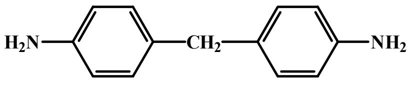
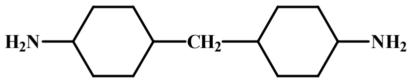
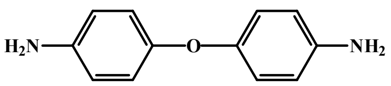
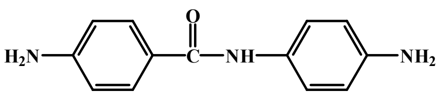
RESULTS AND DISCUSSION

The polyimides were synthesized by adopting three different (solution, chemical and thermal imidization) methods.

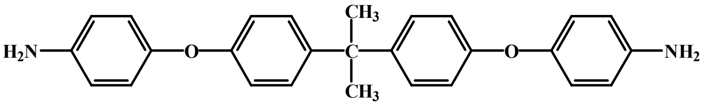


ABTD-R

where the following diamines were used for R

		CODE
1.	 **2,2'-Dimethoxy benzidine or orthodianisidir**	Dimeo
2.	 **4,4'-Diamino diphenylmethane**	DiphyMe
3.	 ***Bis*(*p*-aminocyclohexyl)methane**	CH_2
4.	 **4,4'-Diamino diphenylether**	Diphyeth
5.	 **4,4'-Diamino benzanilide**	BzAni

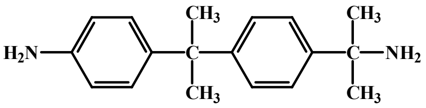
6.



Oxalk

2,2'-*Bis*[4-(*p*-aminophenoxy)phenyl)propane

7.



Bisalk

4,4'-(1,4-Phenylenediisopropylidene)bisaniline

Scheme-I

Scheme-I gives the structures and codes of the polyimides. The first four letters of the code refers to the dianhydride part. The rest of the code refers to the diamine part based on either the substituent or the rings connecting moiety.

The inherent viscosities of azopolyamic acids are listed in Table-1 and comparison between three methods were made in Table-2. In general, polymers of comparable rigidity, crystallinity and structure, a polymer with higher rigidity will have a higher viscosity than the flexible one[14]. A polyimide having η_{inh} below 1.00 is useless because the mechanical properties are not satisfiable in many number of practical applications[15].

TABLE-1
INHERENT VISCOSITIES OF POLYIMIDES

Polyimides	Yield (%)	η_{inh} (dl/g)	η_{inh} in conc. H_2SO_4	Colour	UV-Visible
ABTD-Dimeo	52	0.74	0.74	Reddish brown	404, 728
ABTD-DiphyMe	95	$1.29^{\#}$	1.32	Light brown	406, 680
ABTD-ϕ-CH_2	60	Insoluble	1.02	Dark brown	406, 685
ABTD-Dipheth	95	$0.59^{\#}$	1.18	Yellow	408, 695
ABTD-BzAni	90	$0.62^{\#H}$	1.10	Brown	409, 710
ABTD-Oxalk	50	$1.20^{\$}$	1.28	Brown	456, 728
ABTD-Bisalk	60	1.12^{*}	1.12	Brown	407, 690

Conc. at 25 ºC = 0.50 g/dl.
*DMSO at 25 ºC, $*^{H}$DMSO at 60 ºC, #NMP at 60 ºC, $DMAc at 25 ºC.

TABLE-2
COMPARISON OF VISCOSITY BY DIFFERENT METHODS (dl/g)

Code of polyimides (in the form of poyamic acid)	Inherent viscosity by solution imidization	Inherent viscosity by thermal imidization	Inherent viscosity by chemical imidization
BzAni	1.04	1.01	1.10
Diphyeth	1.12	1.08	1.18
Oxalk	1.14	1.12	1.28

It is evident that ABTD-DiphyMe has very high viscosity of 1.29 in NMP at 60 ºC and 1.32 in concentrated H_2SO_4 at 25 ºC. This difference is mainly due to the polarity of the solvent. At the same time, the diamine is easily soluble in NMP/DMAc when polymerization proceeds. The polyimides derived from benzophenone tetracarboxylic dianhydride (BTDA) with 4,4-diaminodiphenylether (DDE) or 4,4′-diaminodiphenyl methane (DDM) which exhibit the inherent viscosity of 0.86 and 0.85 dl/g, respectively can be compared with present results. It may be concluded that the azo group (present in ABTD-Diphyeth and ABTD-DiphyMe) increase the viscosity to 1.18 and 1.32 dl/g, respectively compare to the carbonyl group present in the main chin of BTDA.

In the present investigation, the polyimides synthesized in the route of chemical imidization can be compared with (i) solution imidization and (ii) thermal imidization methods (Table-2).

Chemical imidization method gives higher viscosity compare to solution and thermal imidization methods. In chemical imidization method, polyamic acid is treated with Ac_2O, pyridine or $(Et)_3N$ at 60 ºC and refluxed for 24 h whereas in solution imidization method, polyamic acid is treated with NMP; *o*-DCB (5:1) and then refluxed for 24 h at 180 ºC. It is evident that Ac_2O and Et_3N play important role in effective polymerization than the solvents NMP and *o*-DCB from where the polyamic acid is derived. The mechanism and other factors are to be studied. The advantage of thermal or bulk imidization gives bubble free films.

The solubility of all the polyimides synthesized in the present investigation are reported in Table-3. Alkl are soluble in concentrated sulphuric acid. They are soluble on long standing in aprotic polar solvents such as NMP, DMAc and DMSO and some polymers are soluble in less polar solvents like THF. However, these polymers are not soluble in common organic solvents such as chloroform, ethanol, acetone, *o*-DCB, DMF and THF. They are partially soluble in *m*-cresol and trifluoro acetic acid. This can be explained on the basis of dielectric constant of the solvents which are insufficient to break the bonds of a polymer. Cross-linking and rigidity

TABLE-3
SOLUBILITY OF POLYIMIDES

Polymers	NMP + LiCl	DMSO	DMAc + LiCl	*m*-Cresol	Acetone	THF	$CHCl_3$	DCB	DMF	TFA	Conc. H_2SO_4
ABTD-Dimeo	E	E	E	E	B	E	B	E	E	E	A
ABTD-DiphyMe	C	E	E	D	B	E	B	B	B	E	A
ABTD-ϕ-CH_2	E	E	E	E	B	E	B	B	B	E	A
ABTD-Diphyeth	C	F	F	E	B	B	B	B	B	B	A
ABTD-BzAni	B	C	B	B	B	A	B	B	B	E	A
ABTD-Oxalk	E	A	A	E	B	C	B	E	B	E	A
ABTD-Bisalk	E	E	E	E	B	E	B	B	B	E	A

A = Soluble, B = Insoluble, C = Soluble on heating, D = Swelling, E = Partially soluble, F = Colour change of the polyimide chains are considered to be the two major factors causing the insolubility of the aromatic polyimides[16]. The azo linkage though structurally rigid, appears to aid solubility[17].

The UV-visible spectra of the polyimides are of interest because of the presence of the azo group and bathochromic shift shown by the polymers relative to that of *trans*-azobenzene[9] (238.84 and 432.90 nm). Typical data are given in Table-1. The absorption in the visible region are due to n-π^* transition whereas those in the UV region are associated with π-π^* transition. The polyimides absorb in the range of 200 to 273 nm in the UV region and at 400 to 728 nm in the visible region.

The wavelength of visible light range from 400 to 750 nm. The azo (N=N) group considerably increases conjugation through the lone pair of electrons on the nitrogen atoms thus justifiying the highest λ_{max} values observed for these azopolyimides. Comparison of these colours reveals that there is a gradual change in colour with respect to change in linkage units due to π-electron transfer from –N=N– towards –C=O– group *i.e.*, conjugation effect as evidenced from bathochromic shift in λ_{max} values.

The IR spectra of polyimides and polyamic acid show bands at 3260, 1411 and 1320 cm^{-1} (due to N–H stretch, O–H in-plane deformation and C–O stretching, respectively). These bands disappeared after cyclodehydration, thus confirming that in polyimides the amido-acid was absent. The O–H stretching frequency was observed as a band around 3550 ± 10 cm^{-1}. A medium absorption band at 330 ± 10 cm^{-1} and a strong band at 610 ± 10 cm^{-1} were observed indicating the stretching mode of vibration of the N–H group. Absorption band observed at 1625 ± 25 cm^{-1} is characteristic of the stretching vibration of the C=O amide group. The C=O (carboxylic) stretching vibrations are observed at 1700 ± 20 cm^{-1}. All the aforementioned infrared absorption bands disappeared after imidization and new bands at (imide I) 1780 ± 10 cm^{-1}, (imide II) 1720 ± 5 cm^{-1}, (imide III) 1390 ± 10 cm^{-1} and (imide IV) 690 ± 10 cm^{-1} are characteristic of imide linkage shows the formation of cyclic imide structure. These frequencies correspond to previouly reported imide ring absorptions.

The N=N stretching vibrations showed a characteristic band at 1400 ± 20 cm^{-1} and 1500 ± 20 cm^{-1}. However, Lefevere *et al.*[2] and Uneo[3] report the observation of frequency at 1500 ± 10 and 1400 cm^{-1} in several aromatic azo compounds as characteristic of the azo linkage. The C-H group showed a medium stretching adsorption band at 3090 ± 20, 1092 and 739 cm^{-1} due to imide ring formation.

Raman spectra are better indicator than IR for C=C, C=O and phenyl groups. A comparison of some of these differences is given in Table-4.

Thermal analysis

Thermogravimetric analysis (TGA): The thermal data of the polyimides obtained in nitrogen atmosphere are given in Table-5 and the thermograms of some of the polyimides are given in Fig. 1.

TABLE-4

ABTD-DiphyMe		ABTD-Diphyeth		ABTD-Oxalk		ABTD-BzAni	
A	B	A	B	A	B	A	B
2935	3778.59	2194	3741.69	2250	3313.65	2439	3380.07
2320	3439.11	2069	3653.13	2194	3011.07	2270	3166.50
2194	3121.77	1333	3535.05	1786	1727.18	2067	838.00
1788	–	1277	3416.97	1469	13.62.00	–	–
1612	–	1237	3321.00	1435	897.26	–	–
1466	–	1081	1660.00	1324	746.54	–	–
1412	–	615	1509.67	1157	–	–	–
632	–	–	857.14	1083	–	–	–
–	–	–	–	617	–	–	–

A = Raman active but IR inactive, B = Raman inactive but IR active.

TABLE-5
THERMAL ANALYSIS OF THE POLYIMIDES

Polyimides	% Weight loss					T_{max} (°C)	AA	T_g (°C)	Exotherm temperature
	10	20	30	40	50				
ABTD-Dimeo	180	315	410	580	690	480.0	3	–	–
ABTD-DiphyMe	100	125	165	180	200	194.6	2	200.0	111.9, 618.7
ABTD-ϕ-CH_2	190	320	420	595	710	485.0	4	–	90.2, 664.8
ABTD-Diphyeth	125	165	185	215	225	547.8	2	228.1	111.7, 207.1, 228, 597.2, 228, 597.2
ABTD-BzAni	100	122	135	152	175	558.3	4	204.0	131.3, 422.2, 591.4, 591.4
ABTD-Oxalk	120	151	226	380	400	403.5	2	407.4	117.6, 377.5, 407.4, 627.7, 407.4, 627.7
ABTD-Bisalk	140	170	240	395	405	395.0	3	–	120

AA = No. of stages of weight loss.

Table-5 shows the temperatures of various per cent weight loss, the temperature at which maximum degradation takes place (T_{max}), glass transition temperature (T_g) and the number of stages of weight loss. Most of the polyimides undergo drastic degradation in the temperature range 200-600 ºC.

In general, TG curves show three stages of weight loss. In the first stage, an initial weight loss 1-5 % occurs in the temperature range 100-200 ºC. It is likely due to the chain extension that may take place by the condensation of end gups resulting in the elimination of water. The second stage of weight loss (300-500 ºC) corresponds to a step fall in the TG curves. The weight loss upto 350 ºC is about 20 %. In the third stage, above 430 ºC the weight loss in the TG curve is steady.

ABTD-Oxalk and ABTD-Bisalk show low thermal stability because of molecular overcrowding though these two polymers are favouring solubility and hence applications oriented. In these polymers interchain hydrogen bonding and steric factor play important role. This ia also evidenced by their infrared data and lower crystallinity due to the presence of substituents in the polymer backbone. However, among these two polymers ABTD-Oxalk shows very high T_g values (474.4 ºC). The amino and substituent groups may also participate in the interaction of polyimide chains and become less vulnerable to thermoxidative reaction.

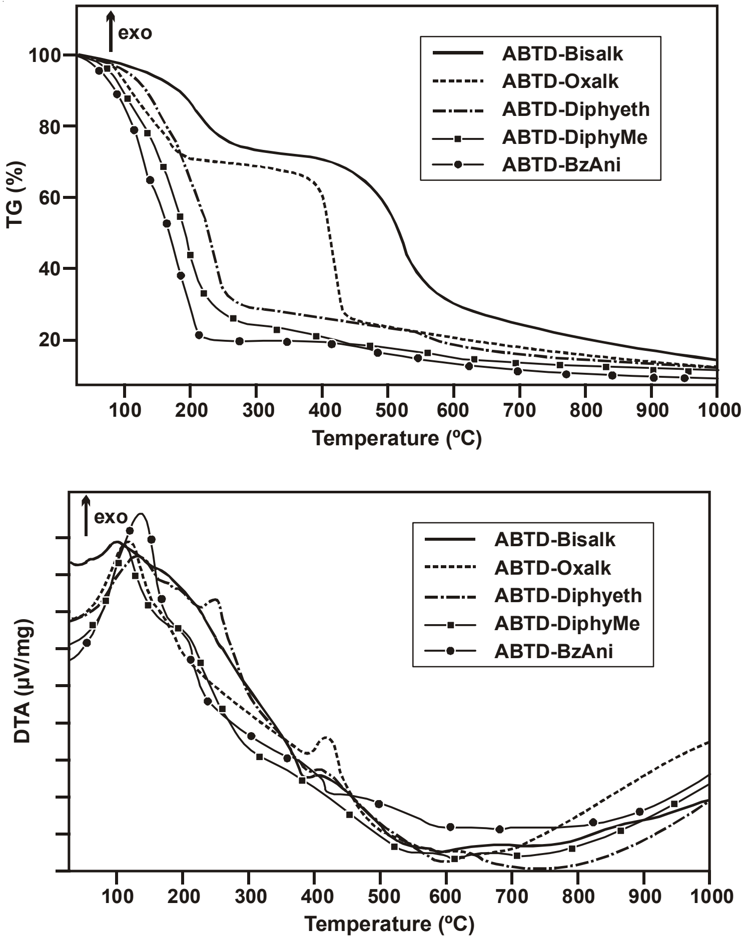


Fig. 1. TGA and DTA curves of polyimides

It is observed that effect of substituent becomes significant only after 300 ºC. This may be due to the fact that at high temperature (> 300 ºC) the phenylene ring might rearrange wherein the substituents play their role more effectively. The derivative curve of TGA shows T_{max} value (*i.e.*, temperature at which maximum degradation occurs). Table-5 shows that most of the polyimides are having T_{max} value in the range 540-600 ºC. Above this temperature, the polyimides show rapid degradation where steep decrease in TG curve is noticed.

Differential thermal analysis (DTA) was carried out in nitrogen atmosphere for all the polyimides. The data are presented in Table-5 and representative curves are shown in Fig. 1.

DTA among any other analytical methods is utilized to probe the T_g of polymers by monitoring the heat capacity as a function of temperature. The glass transition temperature (T_g) is a second order endothermic transition. The glass transition temperature is one at which a polymer undergoes an extensive cooperation segmental motion along the backbone. T_g may also be described as the relaxation point which occurs between the glass and rubbery plateaus. Interestingly, strong endotherm indicating glass transition (T_g) is observed at 407 ºC for the polyimide ABTD-Oxalk. DiphyMe and BzAni based polyimides have also equal T_g (to glass form) due to the flexible linkage, free rotation of benzene nucleus and orientation of molecules in order.

Activation energy from TGA: From the primary thermograms obtained for the azopolyimides, by plotting the per cent weight loss against temperature, activation energy can be calculated[18-21]. The order andenergy of activation for the major decomposition reactions were calculated by various methods (i) Murray and White[18] (ii) Coats and Redfern[19], (iii) Doyle[20] and (iv) Freeman and Carroll's method[21]. The results obtained are given in Table-6.

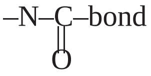
TABLE-6
ACTIVATION ENERGY (kcal/mol) OF POLYIMIDES USING DIFFERENT APPROXIMATE METHODS

Polyimide	(A) Murray and White	(B) Coats and Redfern	(C) Doyle's	Freeman and Carrol
ABTD-BZ$_4$[a]	5.4912	5.4340	5.1729	6.6098
ABTD-Py$_4$[b]	5.9219	5.5566	6.0000	13.7281
ABTD-Biphy[c]	5.5929	5.9840	5.8835	13.3468
ABTD-DiphyMe	7.6260	7.9318	7.7441	17.0562
ABTD-Dipheth	7.1182	7.6267	7.0928	27.4563
ABTD-Oxalk	8.0080	8.3201	8.4295	12.5079

a = *p*-phenylene diamine; b = 2,6-diamino pyridine, c = benzidine.

Table-6 shows the activation energies of some polyimides. The activation energy values are found to be in the range of 7.00 to 27.45 Kcal/mol. The low activation energy values can be attributed to the experimental condition *i.e.* the thermogravimetric analyses were conducted under nitrogen atmosphere which is inert compare to air atmosphere. The kinetics of decomposition is dependent on (i) particle size (ii) thermal stability (iii) orientation of benzene rings in the main chain (iv) substituents present in the polymer backbone and (v) atmosphere in which degradation was carried out which may partially account for the high or low activation energies. On the basis of weight loss occuring during thermal degradation, it is evident that the azo group is cleaved as N_2 which has been supported by mass spectra[8].

It has been found that both heterolytic and homolytic cleavage occur in these polymers. This is also supported by pyrolysis-mass spectral studies. For these polymers distinct reactions are apparent.

(1) Decomposition of one group as N_2 moiety (2) Clevage of  $-N-\underset{\underset{\displaystyle O}{\|}}{C}-$bond

(3) Cleavage of aromatic amine group attached with dianhydrides. All these steps are shown in the thermogram of azo polyimides as number of phases.

The activation energy of decomposition of polyimides are ranging from 7.11 to 8.00 Kcal/mol in Murray and White method[18], 7.62 to 8.32 Kcal/mol in Coats and Redfern method[19] and 7.09 to 8.42 Kcal/mol in Doyle's method[20]. ABTD-Py_4 shows less activation energy than ABTD-Oxalk. Based on the activation energy of thermal degradation of polyimides the following order can be given:

Oxalk > DiphyMe > Diphyeth

The activation energies obtained from Murray and White[18], Coats and Redfern[19] and Doyle's method[20] are all in good agreement with each other with in the experimental error. The large difference in the Freeman and Carroll's method[21] is found to be the determination of the difference differential functions over short temperature intervals[22]. One of these involved is the tangent dw/dt. Therefore, any inaccuracy in determining a single value for dw/dt affects the position of the two points in the plots which are needed to determine the activation energy. Hence, Freeman and Carroll's method is less satisfactory and of limited applicability[23].

ACKNOWLEDGEMENT

The authors wish to thank University Grants Commission, New Delhi, India for financial help under minor project.

REFERENCES

1. D.F. Loncrini, W.L. Wilton and R.B. Hughes, *J. Polym. Sci.*, **A-4**, 4 (1966).
2. R.J.W. Lefevere, M.F.O'Dwyer and R.L. Werner, *Aust. J. Chem.*, **6**, 341 (1953).
3. K. Uneo, *J. Am. Chem. Soc.*, **79**, 3205 (1957).
4. D. Jayaprakash, L. Ravikumar and M.J. Nanjan, *Makromol. Chem. Rapid. Commun.*, **2**, 611 (1981).
5. M. Balasubramanian, M.J. Nanjan and M. Santappa, *Makromol. Chem.*, **180**, 2517 (1979); **182**, 853 (1981).
6. P. Sachindrapal, S.Ramasamy and M.J. Nanjan, *Polym. Bull.*, **5**, 417 (1981).
7. V. Rajendran and M.J. Nanjan, *J. Polym. Sci.*, **25**, 829 (1987).
8. V. Rajendran and M.J. Nanjan, *J. Appl. Polym. Sci.*, **37**, 3281 (1987).
9. V. Rajendran and S.M. Thayumanaswamy, *Iran. Polym. J.*, **11**, 4 (2002).
10. J. Preston and R.W. Smith, *J. Polym. Sci., Poly. Chem. Eds.*, **4**, 1033 (1966).
11. J. Sugano, M. Abe and T. Takenslei, Tap, Pat. 6,723,340 (1967).
12. P.J. Culhane and G.E. Woodword, Organic Synthesis (Collective), Vol. 1, edn. 2, p. 408 (1961).
13. R.L. Hansen and R. Minn, U.S. Pat, 3,476,505 (1969).
14. F.W. Billmeyer Jr., Text Boox of Polymer Science Wiley-Interscience, New York, Ch. 30, edn. 2 (1971).
15. W. Volksen, P. Cotts and D.Y. Yoon, *J. Polym. Sci., B, Polym. Phys.*, **25**, 2487 (1987).
16. R.A. Orwall, T.L. St. Clair and K.D. Dobbs, *J. Polym. Sci. Part B*, **19**, 1385 (1981).
17. C.E. Sroog, *J. Polym. Sci., Macromol. Rev.*, **11**, 161 (1976).
18. P. Murray and J. White, *Transition Br. Ceram. Soc.*, **54**, 151 (1955).
19. A.W. Coats and J.P. Redfern, *Nature*, **201**, 68 (1964).
20. C.D. Doyle, *J. Appl. Polym. Sci.*, **6**, 639 (1962).
21. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
22. R.L. Bohon, Proc. First Toronto Symp. Thermal Anal. H.G. M.C. Adle, Ed. 72 (1965).
23. G.H. Flynn and L.A. Wall, *J. Res. Nat. Bur. Stand*, **70**, 487 (1960).

(*Received*: 27 December 2007; *Accepted*: 19 September 2008) AJC-6879