

## Synthesis and Characterization of Certain New Azo Polyimides

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Ten new aromatic-aliphatic polyimides containing azo linkage in the main chain, based on 3,3',4,4'-azobenzene tetra carboxylic dianhydride and different aliphatic long chain diamines, were synthesized. The polymers were characterized by viscosity, solubility, spectroscopy, TGA and DTA.

**Key Words:** Aromatic-aliphatic polyimides, Synthesis, Characterization, Thermal properties.

### INTRODUCTION

Polyimides are high performance polymer with wide range of properties including high thermal stability resistance to chemical attack and lower dielectric constant<sup>1</sup>. India is currently engaged in the field of polyimides/composites as dielectric lenses, avionic enclosures and other devices for aeronautical application<sup>2</sup>. Polyimides with trifluoro methyl-substituted benzene in the side chain can enhance the solubility and thermal stability, reduce dielectric constant and moisture absorption and raise the optical transparency<sup>1,3-6</sup>. New fluorinated thermoplastic and elastomeric were studied by Andre *et al.*<sup>7</sup>. Among the several classes of thermally stable polymers, azo polyimides are of importance. These polymers are easily processable, have an excellent balance of mechanical and electrical properties and good resistance to solvent attraction. The presence of an azo group in the main chain of partially aliphatic and aromatic polymer increases chain rigidity, leading to close packing of the polymer chains and better thermal stability. The double bond may be cross-linked to more useful end products. Azo polymers can also be used as high-grade pigments of good fastness to light<sup>8</sup>. Hence azo linkage polyimides show wide applications were synthesized based on azo group containing aromatic dianhydrides with long chain high basic aliphatic diamines.

### EXPERIMENTAL

Concentrated sulphuric acid (AR, BDH India 98 %) was used as such. N-methyl-2-pyrrolidone (NMP; Fisher scientific) was dried over calcium hydride for 12 h prior to distillation under reduced pressure (b.p 205 °C). N,N'-Dimethylacetamide

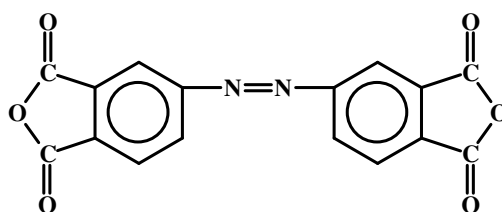
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(DMAc; Fluka-Puriss) was dried over calcium hydride for 12 h prior to distillation under reduced pressure (b.p 163-165 °C). Methanol (AR, BDH, India) was used as such (b.p 78.5 °C). Acetic anhydride (Aldrich) was stored over calcium hydride for at least 12 h prior to distillation under vacuum (b.p 138-140 °C).

Viscosity measurements were made at 25 °C using conc. sulphuric acid as solvent for all polyimides in an Ubbelohde viscometer. The concentration used was 0.5 g/dL throughout for all the measurements. A 10 % solution was prepared and allowed to stand for few hours. If insoluble in cold, the solution was heated. 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 spectrophotometer. IR spectra of the polymers were recorded in Bruker Vector 22 spectrometer. The samples were incorporated in KBr disc. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using JEOL, model GS X 400 BC EXMOD [70,11] SG NON instrument and CDCl<sub>3</sub> solvent. Thermal analyses (TGA and DTA) were recorded in nitrogen for all the polymers in NET Z SCH STA-409 C/CD model simultaneous TGA-DTA apparatus. About 26 mg of the sample was heated at the heating rate of 10 °C/min for all the polymers. Thermocouple was used to measure the temperature.

## RESULTS AND DISCUSSION

Ten polyamic acids were synthesized by low temperature solution method by condensing 3,3',4,4'-azobenzenetetracarboxylic dianhydride (Fig. 1)



with the following different diamines.

S.No.	Structure	Common Name	Code	Symbol
1.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>2</sub> -NH <sub>2</sub>	1,2 - Diamino ethane	DAE	R2
2.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>3</sub> -NH <sub>2</sub>	1,3 - Diamino propane	DAP	R3
3.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>4</sub> -NH <sub>2</sub>	1,4 - Diamino butane (Putrescine)	DAB	R4
4.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>5</sub> -NH <sub>2</sub>	1,5 - Diamino pentane (Cadaverine)	DAPe	R5
5.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>6</sub> -NH <sub>2</sub>	1,6 - Diamino hexane	DAH	R6
6.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>7</sub> -NH <sub>2</sub>	1,7 - Diamino heptane	DAHe	R7
7.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>8</sub> -NH <sub>2</sub>	1,8 - Diamino octane	DAO	R8
8.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>9</sub> -NH <sub>2</sub>	1,9 - Diamino nonane	DAN	R9
9.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>10</sub> -NH <sub>2</sub>	1,10 - Diamino decane	DAD	R10
10.	H <sub>2</sub> N-(CH <sub>2</sub> ) <sub>12</sub> -NH <sub>2</sub>	1,12 - Diamino dodecane	DADo	R12

Synthesis of azo polyimides involves two steps. In the first step aromatic dianhydride condense with aliphatic diamines to give polyamic acid. In the second step, the polyamic acid is converted to polyimide (PI) by following any one of the methods (i) solution imidization (ii) chemical imidization and (iii) thermal imidization methods.

TABLE-1  
VISCOSITY OF POLYIMIDES

No. of methylene units	Code of polyimide	Yield (%)	$\eta_{inh}$ (dl g <sup>-1</sup> ) in conc. H <sub>2</sub> SO <sub>4</sub>		
			Solution imidization	Chemical imidization	Thermal imidization
R <sub>2</sub>	ABTD-DAE	85	0.54	0.58	0.54
R <sub>3</sub>	ABTD-DAP	88	0.61	0.64	0.60
R <sub>4</sub>	ABTD-DAB	90	0.85	0.86	0.84
R <sub>5</sub>	ABTD-DAPe	91	0.91, 0.86*	0.92, 0.88*	0.90, 0.85*
R <sub>6</sub>	ABTD-DAH	92	0.90	0.92	0.90
R <sub>7</sub>	ABTD-DA He	90	0.60	0.61	0.58
R <sub>8</sub>	ABTD-DAO	85	0.58	0.62	0.56
R <sub>9</sub>	ABTD-DAN	78	0.54	0.55	0.48
R <sub>10</sub>	ABTD-DAD	80	0.45	0.56	0.42
R <sub>12</sub>	ABTD-DADo	85	0.48	0.49	0.44

Conc. at 25 °C = 0.50 g/dl; \*DMAc solvent at 40 °C.

Chemical imidisation method gives higher viscosity compare to solution and thermal imidisation methods. It is evident that Ac<sub>2</sub>O and Et<sub>3</sub>N play important role in effective polymerization than the solvents NMP and *o*-DCB from where the polyamic acid is derived. It is evident that ABTD-DAPe shows a high viscosity of 0.91 in conc. H<sub>2</sub>SO<sub>4</sub> at 25 °C and 0.86 in DMAc at 40 °C. This difference is mainly due to the polarity of the solvent and also the solubility in DMAc where the polymer is generated *in situ*. The odd-even number of CH<sub>2</sub> groups in the diamine moiety plays important role in the degree of polymerization in addition to the stereochemistry and basicity. The presence of azo group between the two benzene rings in the dianhydride moiety has increased the viscosity to some extent. The azo group, not only increases the viscosity but also increases the thermal stability of the polyimides. The reason for this enhancement in viscosity may be due to the azo group present in the *trans*-form which favours conjugation effect and rigidity of the polymer chain.

**Solubility:** All polyimides are soluble in concentrated sulphuric acid. They are soluble on long standing in aprotic polar solvents such as NMP, DMAc and DMSO whereas some polymers are soluble in less polar solvents like THF. However, these polymers are not soluble in common organic solvents. The introduction of aliphatic units into the polymer chain (compare to aromatic unit) would facilitate less polymer-polymer interaction and enhance the solubility in 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. Steric factor also

plays important role in solubility. 5 % LiCl composition with the solvents NMP or DMAc favours solubility. In some cases, heating enhances the solubility. Of the several polyimides tested, the common organic solvents like  $\text{CHCl}_3$ , DMF and DMSO give only slight colouration since the polarity of the solvent is insufficient to overcome the strong inter chain hydrogen bonding of the polyimides.

**UV-Visible spectra:** The azo (-N=N-) group considerably increases conjugation through lone pair of electrons on the nitrogen atoms thus justifying the highest  $\lambda_{\text{max}}$  values observed for these azopolyimides. A deepening of colour is observed for the polymers derived from the following diamines.



Comparison of these colours reveals that there is a gradual change in colour with respect to change in linkage units due to  $\pi$  electron transfer from -N=N- towards >C=O group *i.e.*, conjugation effect as evidenced from bathochromic shift in  $\lambda_{\text{max}}$  values. The formation of intermolecular and intramolecular charge-transfer complex (CTC) could be the reason of colouration of aromatic -aliphatic polyimides ranging from pale yellow to deep brown<sup>9</sup>.

TABLE-2  
UV-VISIBLE DATA OF POLYIMIDES

Polyimides	Nature of polymers	UV region	Visible region	Colour
R <sub>2</sub>	Sample(Abs)	360	390	Yellowish brown
	Sample(Trans)	290	400,600	
	Film (Abs)	270		
	Film (Trans)	230		
R <sub>3</sub>	Sample (Abs)	260	380, 460	Reddish brown
R <sub>4</sub>	Sample (full scan)	210, 480, 500	1200,1505,	Light brown
	film (Abs)	260,	1755,1940 500	
	film (Trans)	230	650	
R <sub>5</sub>	Sample (Abs)	240	510, 605	Light brown
R <sub>6</sub>	Sample (Abs)	245	515, 620	Red tinge brown
R <sub>7</sub>	Sample (Abs)	235	500, 595	Pale brown
R <sub>8</sub>	Sample (Full scan) Film	360, 410,	800,1480,1930	Dark brown
	(Abs) Film (Trans)	220 240	390,500 410,610	
R <sub>9</sub>	Sample (Abs)	230	490, 600	Blakish brown
R <sub>10</sub>	Sample (Abs)	240	405, 585	Dark brown
R <sub>12</sub>	Sample (Abs)	240	410, 610	Dark brown

**IR Spectra:** As all polymers have a similar molecular structure, the position of the absorption bands is the same. An increase in the number of methylene groups can be confirmed by a higher intensity of the absorption bands corresponding with the stretching and bending vibrations of the methylene unit. The absorptions at 1706 and 1770  $\text{cm}^{-1}$  are typical imide absorption bands. Polyamic acid bands are observed at 3260, 1411, 1320  $\text{cm}^{-1}$  (due to N-H stretch, O-H in-plane deformation and C=O stretching, respectively). These bands disappeared after cyclodehydration, thus confirming that in polyimide the amino acid was absent. The O-H stretching

frequency was observed as a band around  $3550 \pm 10 \text{ cm}^{-1}$ . A medium absorption band at  $3330 \pm 10 \text{ cm}^{-1}$  and a strong band at  $610 \pm 10 \text{ cm}^{-1}$  were observed indicating the stretching mode of vibration of the N-H group. Absorption band observed at  $1625 \pm 25 \text{ cm}^{-1}$  is characteristic of the stretching vibration of the C=O amide group. The C=O (carboxylic) stretching vibrations are observed at  $1700 \pm 20 \text{ cm}^{-1}$ . The N=N stretching vibrations showed a characteristic band at  $1400 \pm 20 \text{ cm}^{-1}$  and at  $1500 \pm 20 \text{ cm}^{-1}$ . The C-H group showed a medium stretching absorption band at  $3090 \pm 20$ ,  $1092$  and  $739 \text{ cm}^{-1}$  due to imide ring formation. Actually, N=N stretching vibrations are difficult to assign because the absorption is too weak. The very small shifts observed for certain peaks may be due to the electronic effects of the substituents and the +M effects of the lone pair of electrons on the nitrogen atom of the azogroup.

$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra confirm the structure of polyimides. The experimentally observed values were compared with theoretical values. The relative intensity of the aliphatic carbon atoms C11 and C12 (*ca.* 29 and 39 ppm, respectively) cannot be compared<sup>8</sup>. The correctness assignment was verified from the multiplicity of the signals in the proton coupled spectrum.

Thermal behaviour of the polyimides were determined by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) in nitrogen atmosphere at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  (Fig. 1 and 2).

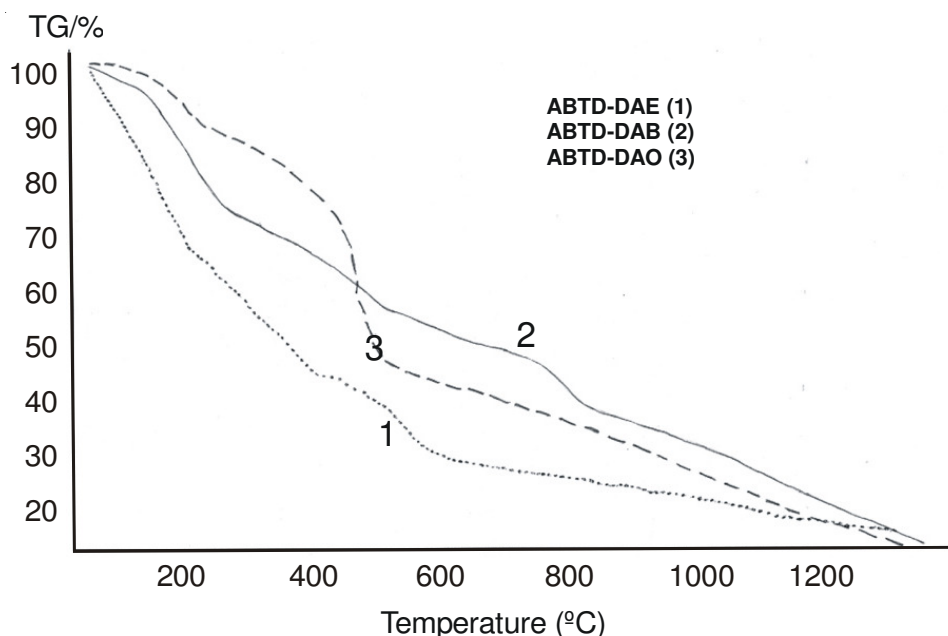


Fig. 1. TGA of polyimide (ABTD-DAE, ABTD-DAB and ABTD-DAO)

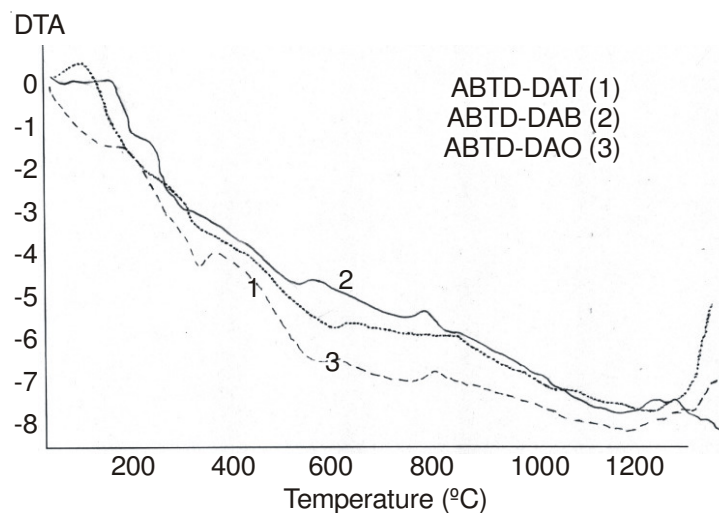


Fig. 2. DTA of polyimide (ABTD-DAE, ABTD-DAB and ABTD-DAO)

TABLE-3  
THERMAL ANALYSIS DATA

Polyimides	Weight loss (%)								$T_{max}$ (°C)	AA	$T_g$ (°C)	DTA Exotherm temperature				BB
	10	20	30	40	50	60	70	80								
R <sub>2</sub>	108	180	220	350	525	750	1400	-	524.2	4	400	91.1	349.9	605.1	-	37
R <sub>3</sub>	120	195	230	410	540	740	1380	-	640.0	4	480	116.0	242.0	510.0	766.0	36
R <sub>4</sub>	180	210	315	420	610	800	1020	1220	784.2	4	284	152.5	234.1	525.0	793.0	31
R <sub>5</sub>	175	206	312	410	602	790	1005	1208	760.0	4	280	140.0	226.0	510.0	786.0	31
R <sub>6</sub>	195	225	340	440	630	825	1040	1225	795.0	4	260	160.0	244.0	540.0	810.0	37
R <sub>7</sub>	174	202	310	406	595	778	1002	1200	770.0	4	245	162.0	230.0	510.0	780.0	34
R <sub>8</sub>	210	395	460	480	525	750	980	1280	477.1	4	240	186.0	340.0	616.7	815.1	31
R <sub>9</sub>	205	390	452	490	515	752	960	1260	460.0	4	235	174.0	320.0	588.0	790.0	27
R <sub>10</sub>	220	397	472	506	535	754	985	1290	480.0	4	238	190.0	315.0	590.0	794.0	26
R <sub>12</sub>	205	385	455	486	512	744	954	1255	470.0	4	230	176.0	320.0	596.0	782.0	18

AA = No. of stages of weight loss; BB = % residue at 1000 °C; Heating rate = 10 °C/min

Table-3 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 to 600 °C. The polyimides DADo and DAN show low thermal stability because of molecular overcrowding formed by long aliphatic chains though these two polymers are favouring solubility and hence applications oriented. In these polymers interchain hydrogen bonding and steric factor plays important role. This is also evidenced by their IR data and lower crystallinity due to the presence of flexible methylene units in the polymer backbone. However, among these polymers ABTD-DAP shows very high  $T_g$  value. (480 °C).

ABTD-DAB show better thermal stability compare to other polyimides based on  $T_{max}$  values. It is a well known fact that extended chain polyimides are more flexible due to highly close packed structure.

The glass transition temperature ( $T_g$ ) is a second order endothermic transition.

$T_g$  of polymers is in the range of 230 to 400 °C.  $T_g$  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 400 and 480 °C for the polyimides ABTD-DAE and ABTD-DAP.DAHe to DADo based polyimides have almost equal  $T_g$  (to glass form) due to the flexible linkage, free rotation of methylene units and orientation of molecules in order. The decreasing order of  $T_g$  generally correlated with that of chain flexibility. For the same reason, other polymers do not show any definite melting point since degradation precedes melting.

The activation energy values (Table-4) are found to be in the range of 3.2 to 6.4 kcal/mol. The kinetics of decomposition is dependent on particle size, thermal stability, orientation of benzene rings in the main chain, substituents present in the polymer backbone and atmosphere in which degradation was carried out which may partially account for the high or low activation energies. On the basis of weight loss occurring during thermal degradation, it is evident that the azo group is cleaved as  $N_2$  which is supported by mass spectra<sup>10</sup>.

TABLE-4  
ACTIVATION ENERGY (K cal/mol) OF POLYMERS USING  
DIFFERENT APPROXIMATE METHODS

Polymide	Murray and White (Fig. 3c)	Coats and Redfern (Fig. 3d)	Doyle's (Fig. 3b)	Freeman and Carroll (Fig. 3a)
ABTD-DAE	3.270	3.407	3,702	10.738
ABTD-DAB	5.076	5.432	5.020	15.970
ABTD-DAO	6.827	6.403	6.423	18.732

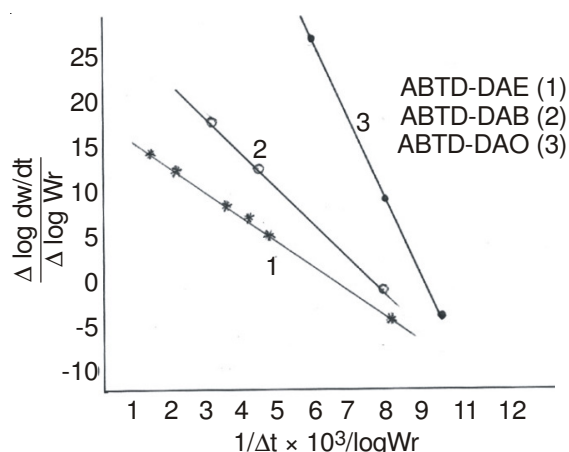


Fig. 3a. Activation energy curve (by Freeman and Carroll method) of polyimide (ABTD-DAE, ABTD-DAB and ABTD-DAO)

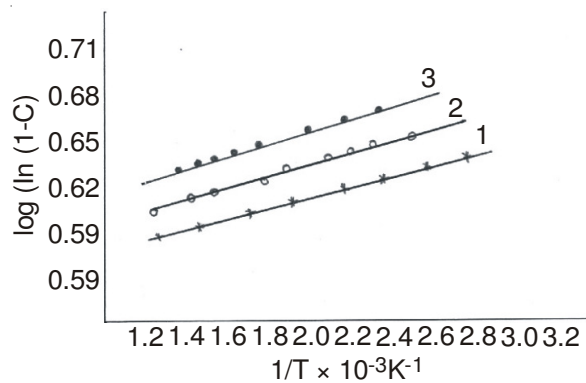


Fig. 3b. Activation energy curve (by Doyle's method) of polyimide (ABTD-DAE, ABTD-DAB and ABTD-DAO)

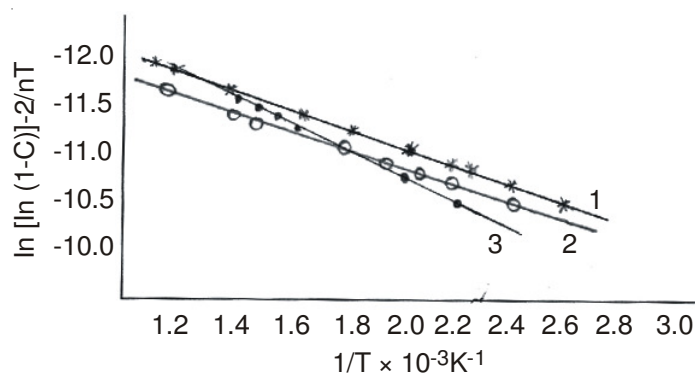


Fig. 3c. Activation energy curve (by Murray and White method) of polyimide (ABTD-DAE, ABTD-DAB and ABTD-DAO)

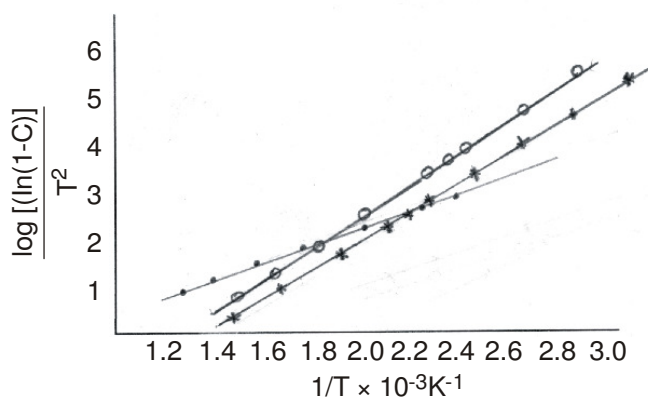


Fig. 3d. Activation energy curve (by Coats and Redfern method) of polyimide (ABTD-DAE, ABTD-DAB and ABTD-DAO)



It has been found out that both hetrolytic 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 azo group as N<sub>2</sub> moiety

(2) Cleavage of  $\text{-N}-\overset{\text{O}}{\parallel}{\text{C}}$  bond

(3) Cleavage of aromatic amine group attached with dianhydrides

Activation energy obtained for polyimides from Murrays and White method, Coats and Redfern method and Doyles methods shows satisfactory results but Freeman's and carroll's method is less satisfactory and of limited applicability<sup>11</sup>.

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