Azopolyamides-Synthesis and Thermal Studies

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ABSTRACT

Fifteen new azopolyamides have been synthesized from 2,2 [1]- dimethoxy – 4, 4 [1] – diamino azobenzene [(benzenamine – (3,3[1]- dimethoxy – 4,4 [1] – azo) bis] condensed with different diacids / diacid chlorides, following low – temperature solution or phosphorylation or interfacial polycondensation method. These polyamides were characterized interms of viscosity, solubility, UV – Visible, FT – IR and X–ray diffraction studies. Thermal stability of these polyamides was studied using TGA and DTA methods.

Key words: Synthesis, Characterization, Thermal properties.

INTRODUCTION

With the impetus derived from aerospace and military industries for high – modulus and high strength fibres, considerable progress has been made in recent years on the synthesis of heat – resistant polymers for special end uses. Among the various classes of thermally stable polymers, polyamides are of great importance[1]. The azo chromophore in a polymer back bone increases the chain stiffness and imparts colour to the polymer[2]. Such polymers may, therefore, have potential application as high modulus fibres and high grade pigments of good stability towards light and organic solvents[3]. In recent years, extensive work has been done by many authors. Nanjan and co – workers [4-6] from this laboratory reported the synthesis, characterization and fibre and / or film studies of azopolyamides, polyimides, poly hydrazides, polyamide – imides and polyesters.

EXPERIMENTAL

2,2[1]- Dimethoxy – 4,4[1] – diamino azobenzene was synthesized from 2 – methoxy – 4 – nitroaniline (m.p 320ºC), yield was 40% [7].

Terephthaloyl chloride (m.p. 79ºC), isophthaloyl chloride (43ºC), 2,5 – Dichoro terephthalic acid (m.p 306ºC), 4, 4 [1] – azodibenzoyl chloride (m.p. 164ºC), 3,3[1] - azodibenzoyl chloride (m.p 97 – 98ºC), 4,4[1] – azoxy dibenzoyl chloride (m.p. 146º), 3,3[1] azoxy dicarbonyl chloride (120ºC), 4,4[1] – stilbene dicarbonyl chloride (m.p. 228 – 232º C), 3,3 – stilbene dicarbonyl chloride (m.p. 228 –

232° C), pyridine – 2,6 – dicarboxylic acid (m.p. 61°C), biphenyl – 4,4[1] – dicarbonyl chloride (m.p. 184° C), 4,4[1]- dicarboxy diphenyl methane (m.p. 334°C), dibenzyl – 4,4[1] – dicarbonyl chloride (m.p. 119°C), 4,4[1] – oxy dibenzoic acid (290°C) and pyromellitoyl diglycine diacid (koch – light GR) were used for synthesis[4].

Polymerization

Phosphorylation, low – temperature solution and interfacial polycondersation methods were followed.[8-10]

Characterization

Viscosity measurements were carried out in conc. $H_2 SO_4$ (98%) using ubbelhode viscometer.

UV – Visible spectra of the polymers in conc. $H_2 SO_4$ were recorded with a CARL – ZEISS spectrophotometer employing a closed cell. FT – IR spectra of the polymers were recorded using KBr pellets with a Perkin – Elmer 257 or Backman IR 20 spectrometer using KBr pellets.

Non – isothermal studies (TG and DTA) were carried out for all the polymers in nitrogen atmosphere using Stanton – Red craft simultaneous TG – DTA recorder.
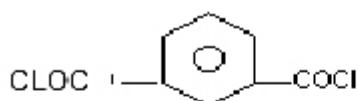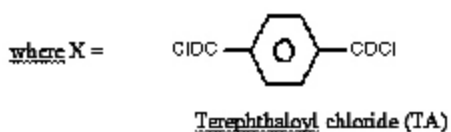
Wide angle X – ray Cu K_a radiation (1.541°A) of power 30 Kv and 10 m A was employed.
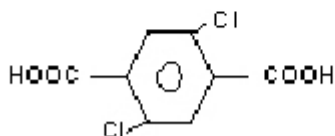
RESULTS AND DISCUSSION

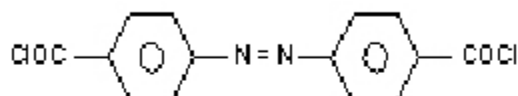The scheme of polymerization reaction can be given as:

CH₃OAZ – X
Polyamide

Scheme – I

where X =
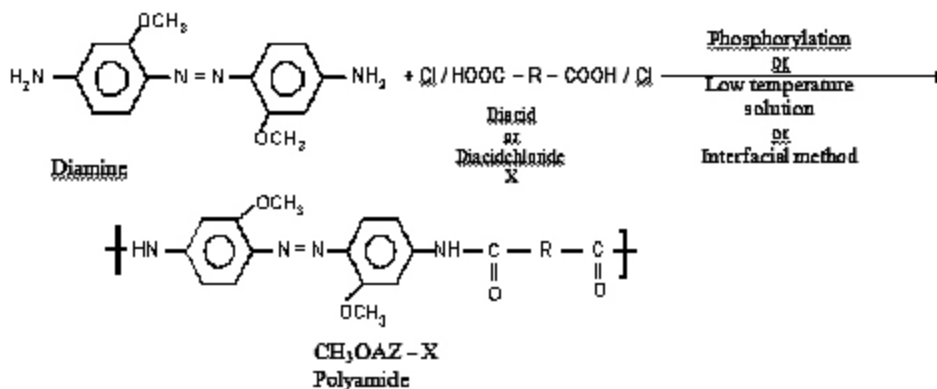
Terephthaloyl chloride (TA)

Isophthaloyl chloride (IT)

2,5 – Dichloroterephthalic acid (Cl TA)

ClOC—⟨O⟩—N = N—⟨O⟩—COCl

4,4' – Azodibenzoyl chloride (Az)

ClOC—⟨O⟩—N = N—⟨O⟩—COCl
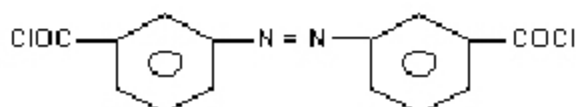
3,3' – Azodibenzoyl chloride (IAz)

ClOC—⟨O⟩—N = N—⟨O⟩—COCl
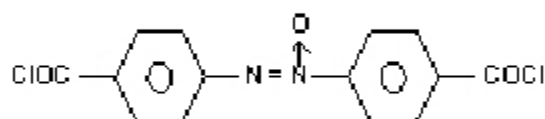
4,4' – Azoxydibenzoyl chloride (Azox)

HOOC—⟨O⟩—N = N—⟨O⟩—COOH
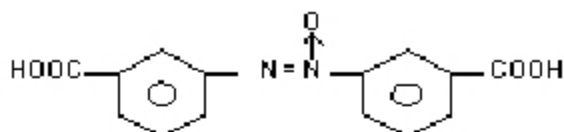
3,3' – Azoxydibenzoic acid (IAzox)
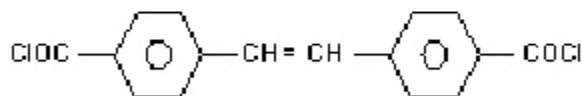
ClOC—⟨O⟩—CH = CH—⟨O⟩—COCl

4,4' – Stilbene dicarbonyl chloride (ST)
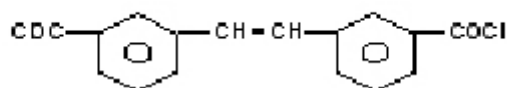
COC—⟨O⟩—CH = CH—⟨O⟩—COCl

3,3' – Stilbene dicarbonyl chloride (IST)

COC—⬡—CH – CH—⬡—COCl

3,3'— Stilbene dicarbonyl chloride (IST)

HOOC—⬡(N)—COOH
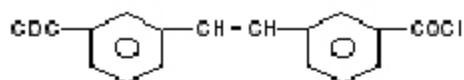
Pyridine – 2,6 – dicarboxylic acid (Py)

COC —⬡—⬡— COCl

Biphenyl – 4,4' – dicarbonyl chloride (Diph)

HOOC—⬡—CH₂—⬡— COOH
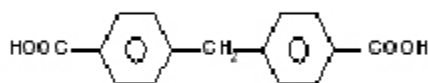
4,4'— Dicarboxy diphenyl methane (Diphme)

COC —⬡— CH₂ —CH₂—⬡— COCl
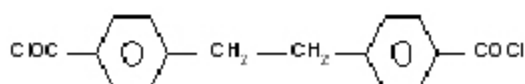
Bibenzyl – 4,4' – dicarbonyl chloride (Dipheth)

HOOC—⬡—O—⬡— COOH
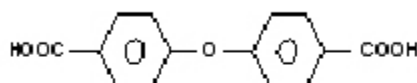
4,4'— oxydibenzoic acid (Dipheoxy)

HOOC—CH₂—N(CO)₂⬡(CO)₂N—CH₂—COOH
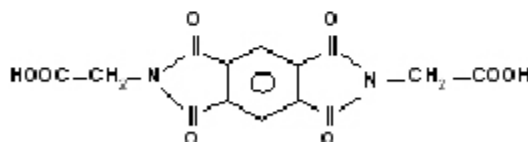
Pyromellitoyl diglycine diacid (Py –MDG)

Scheme I gives the structure and codes of the polyamides. The first four letters of the code refer to the diamine part. The rest of the code refers to the diacid part, based on either the substituent or the rings connecting moiety.

UV – Visible spectral and moisture regain data are presented in Table–1 and appear to depend on (i) the basicity of the diamine (ii) nature of the diacid (iii) initial insolubility of the growing polymer chain in the reaction medium and (iv) on the rigidity of the polyamide.

From Table 1, it is clear that the rigid polymers (para oriented) like CH_3 OAZ – TA , CH_3OAZ – AZ and CH_3O AZ – ST show high viscosity (0.95, 1.20 and 0.80 respectively) since they are structurally rod – like. However, stilbene based polymers show less viscosity on comparison with other two, since during polymerization itself,

Table 1: Properties of Polyamides

S. No	Polymer code	Polymeri--zation method	% Yield	η_{nh}* (dlg⁻¹)	colour	UV – Visible λmax in nm UV	Visible	Moisture regain at RH65%
1	CH_3AZ – TA	LTS	90	0.95	Light brown	211.4 253.8	400 539.4	2.80
2	CH_3OAZ –IT	LTS	80	0.65	Reddish brown	209 248.3	442	2.40
3	CH_3OAZ – Cl TA	LTS,P	70	0.80	Cherry red	212 260	468 -	2.20
4	CH_3OAZ – AZ	LTS,P	85	1.20	Dark brown	202.1 255.2	418 540.6	1.80
5	CH_3OAZ – IAZ	LTS,P	75	0.60	Dark brown	200.9 340.6	395 521.5	1.89
6	CH_3OAZ – AZOX	LTS,P	70	0.65	Brown	210.0 265.2	- -	2.00
7	CH_3OAZ – IAZOX	P	80	0.82	Dark brown	205, 245 327	- 440	1.65
8	CH_3OAZ – ST	LTS, I	75	0.80	Light brown	204	348.2	2.20
9	CH_3OAZ – IST	LTS	65	0.65	Pale yellow	201 240.4	324.0 515.6	2.41
10	CH_3OAZ – Py	LTS,P	60	0.70	Yellowish red	262.4 -	- 490.0	2.35
11	CH_3OAZ – Diph	LTS, I	80	0.80	Light brown	208.9 263.3	428.0 475.2	3.60
12	CH_3OAZ – Dipme	LTS	85	0.76	Light brown	215 270	- 515	3.15
13	CH_3OAZ – Dipheth	LTS,P	75	0.65	Brown	204.0 338.9	375.2 501.4	2.85
14	CH_3OAZ - Diphoxy	LTS,P	70	0.74	yellowish red	212.1 242	- 455	3.40
15	CH_3OAZ – Py MDG	P	75	0.80	Dark brown	230 258.6	- 485.0	2.90

* Inherent viscosities were measured at 0.5 g /dl in conc.H_2SO_4 at 25°C

P = Phosphorylation method; I = Interfacial method, LTS – Low temperature solution method.

partial insolubility has been noticed in DMAc / Licl solvent. Very high viscosity ($\eta = 1.20$) observed for CH_3O AZ – AZ may be due to the fast reaction of amine groups (2 moles) with diacid chloride resulting in high strength / high modulus polymers. Nitrogen atom present in the benzene nucleus of CH_3OAZ – Py polymer has no remarkable change or effect on viscosity. Introduction of ether group, azo group or methylene group at the midst of two benzene rings of diacid moiety leads to viscosities of different low orders. Nevertheless, introduction of $-N=N-$ group between the two phenyl groups (CH_3O AZ – IAZ) enhances the viscosity to 0.82 which is appreciable compare to other linkages like $-CH_2-CH_2-CH_2-$, $-O-$ etc. The reason is attributed to the resonance stabilization and trans - isomerism.

The $-CH_2-$ linkage lower the viscosity in addition to stability which is evidenced from thermal studies whereas oxygen linkage increases the solubility of the polymers which is useful for spinning fibres or casting films.

It is of interest to compare the CH_3, Cl and CH_3O substituents on the benzene ring of the diamine part. It has been reported from this laboratory that the order of substituents that favours chains formation is $CH_3 > O$ $CH_3 > Cl$. In addition to favouring long chain formation, introduction of CH_3 or CH_3O or Cl group in the diamine part increases the viscosity compare to unsubstituted polymer (AZ – AZ). Similar comparison can also be made with aromatic – aliphatic polyamides synthesised in this laboratory. Table 2 shows that polymers derived from aliphatic diacids show lesser viscosities. Conclusions may be drawn that wholly aromatic polyamides yield high viscosities compare to aliphatic or easily soluble diacids / diacid chlorides, whatever be the polymerization method followed.

All the polyamides synthesized are soluble in conc. H_2SO_4 and solubility is slow in CF_3COOH, but insoluble in common organic solvents such as $CHCl_3$, C_2H_5OH and acetone. In other solvents DMAc, DMF, DMSO and NMP, the azopolyamides are soluble to a lesser extent. i.e. partially soluble and in some cases, soluble on heating. Flexible (meta or ortho oriented) polymers are more soluble than rigid (para oriented polymers). This may be due to the higher frequency of incidence of the NHCO groups in the polymers derived from the diacids, which increases the polar nature of the

Table 2: Comparison of viscosity of Azopolyamides [4,5,9]

S. No	Aromatic-aromatic			Aromatic - aliphatic		
	Polymer code	Method	η_{nh}^{*} (dlg^{-1})	Polymer code	Method	η_{nh}^{*} (dlg^{-1})
1.	AZ-AZ	LTS[36]	1.48	AZ-MA	P	0.22
				AZ-SU	P	0.23
				AZ-GL	P	0.34
	AZ-TA	LTS	0.72	AZ-AD	P	0.24
2.	CH_3OAZ-TA	LTS	0.95	CH_3OAZ-SU	P	0.29
	CH_3OAZ-AZ	LTS	1.20		LTS	0.360.51
	CH_3OAZ-AZOX	LTS	0.65	CH_3OAZ-AD	P	
	CH_3OAZ-ST	LTS	0.80		LTS	0.53
3.	CH_3AZ-TA	LTS	0.98	CH_3AZ-MA	P	0.32
	CH_3AZ-AZ	LTS	2.90	CH_3AZ-SU	P	0.34
	CH_3AZ-AZOX	LTS	0.54	CH_3AZ-GL	P	0.44
	CH_3AZ-ST	LTS	0.24	CH_3AZ-AD	P	0.80
4.	ClAZ-TA	LTS	0.52	ClAZ-MA	P	0.24
	ClAZ-AZ	LTS	0.64	ClAZ-SU	P	0.26
	ClAZ-AZOX	LTS	0.37	ClAZ-GL	P	0.38
	ClAZ-ST	LTS	0.24	ClAZ-AD	P	0.30

Table 3: Thermal analysis data of the polyamides (in Nitrogen atm)

| Polymer Code	% Weight loss						T^*_{max} (°C)	AA	DTA	
	10	20	30	40	50	60			Exotherm temperature	Endo
CH₃OAZ–TA	408	480	530	710	800	-	395	2	365, 570	-
CH₃OAZ – IT	280	405	485	580	690	830	420, 565	4	350, 460, 520	315
CH₃OAZ –ClTA	290	430	502	601	695	844	440	4	360, 440, 510	540
CH₃OAZ –AZ	410	490	600	-	-	-	565	3	290, 460	340
CH₃OAZ – IAZ	275	395	472	582	678	620	560	3	260, 510	258, 315, 545
CH₃OAZ – AZOX	330	405	480	625	780	915	475	4	310, 360, 455, 560	310, 400
CH₃OAZ - IAZOX	320	416	492	700	-	-	350	2	365, 570	-
CH₃OAZ – ST	320	400	465	545	760	870	530	4	370, 475, 525, 570	-
CH₃OAZ – IST	300	390	480	520	720	848	520	3	340, 440, 550	-
CH₃OAZ – Py	275	396	475	580	675	810	415, 550	4	260, 350, 470	290
CH₃OAZ – Diph	278	390	474	585	670	770	552	3	290, 495	-
CH₃OAZ – DiphMe	350	420	505	580	695	-	320	3	310, 420	575
CH₃OAZ – Dieth	280	392	476	585	672	750	542	3	260, 300, 510	-
CH₃OAZ - Diphoxy	255	420	500	590	800	-	380	4	365, 370, 405, 470	-
CH₃OAZ - PyMDG	340	410	490	570	680	720	305	3	310, 395, 405	520

Heating rate = 10°C / min

T*max = Temperature at which maximum degradation occurs.

AA = Number of stages of weight loss.

Table 4: Comparison of TGA and DTA data of some polyamides (N$_2$ atm)

Polymer Code	Weight loss %						T_{max}* (°C)	AA	Exotherm (°C)§
	10	20	30	40	50	60			
AZ – AZ**	430	475	-	-	-	-	450	-	400@
CH$_3$OAZ – AZ	410	490	600	-	-	-	565	3	290, 460
ClAZ – AZ	419	468	558	720	-	-	440	2	288, 445
CH$_3$AZ – AZ	420	460	635	-	-	-	370	3	165, 370
PA – TA**	450	-	-	-	-	-	575	-	-
PA – IT**	480	-	-	-	-	-	585	-	-
CH$_3$OAZ – TA	408	480	530	710	800	-	395	2	365, 570
ClAZ – TA	408	470	550	680	820	-	418	2	310, 420
CH$_3$AZ – TA	405	480	508	765	-	-	365	2	365, 570
¨AZ – Adi#	334	361	388	477	550	-	340	-	-
CH$_3$OAZ – ST	340	400	502	545	760	870	530	3	370, 475, 525, 570
ClAZ – ST	280	285	410	546	563	585	300	3	590
CH$_3$AZ – ST	200	440	505	560	800	915	535	3	390, 495, 525, 590
CH$_3$OAZ – AZOX	330	405	480	625	780	915	475	4	310, 360, 455, 560
ClAZ – AZOX	355	415	528	700	-	-	382	2	340, 390, 485, 530
CH$_3$AZ – AZOX	290	400	445	550	780	905	455	4	305, 355, 450, 570

AA - No. of stages of weight loss

PA=
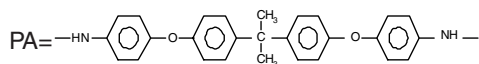
♣ - In air atmosphere, heating rate 10°C/min

** - Ref. 11

♦ - Heating rate 2°C/min;   Adi - Adipic acid;   IT - Isophthaloyl group ;   # - Ref. 10

material and lead to higher magnitude in the hydrogen bonding between the polymer and the solvent. Solubility is an important property which determines the extent of processability and end uses of a polymer. Stirring plays little effect on solubility.

The UV – visible values of trans – azobenzene (238.4, 432.9nm), 4, 4[1] - azodianiline (238, 410 nm), 2,2[1]- dichloro – 4,4[1]- diamino azobenzene (249.6, 457.8nm) and 2,2[1]- dimethyl - 4,4[1]- diamins azohenzene (208.07, 265.5 and 407.83 nm) were reported earlier from this laboratory[11].

In all the derivatives of trans – azo benzene, there is no appreciable change in visible region because the colour of all the organic compounds are almost dark brown. However, appreciable change in UV values are noticed. $\alpha \rightarrow \pi^*$ transition easily taking place in the case of 2,2[1] – dimethoxy – 4,4[1] – diamino azobenzene. The two methoxy groups throw the two benzene rings out – of – plane due to steric hindrance and consequently reduces the resonance effect through amide linkage and results in slow polymerization reaction which reflects in lesser viscosity.

The gradual change in colour from light to dark brown can be explained on the basis of ð electrons transfer from – N = N- towards carbonyl group i.e. conjugation effect is destroyed as evidenced by bathochromic shifts in λ max values. The intensity of the colour varies with pH. In strong bases like 2 M NaOH, the colour of the polymer is intensified. The original colour is, however, restored

on the addition of dil. HCl. This may be due to enolisation of the amide group which results in considerable resonance interactions with the –N = N- linkage. Nevertheless, the colour of the diamine and / or polymer depends on the temperature at which it is derived. If the temperature of the reaction mixture is low, the colour is highly golden yellow and, it is brown / dark brown when the temperature is high.

The amide I and II bands in combination with NH stretching are considered to be important for the identification of polyamides. In all the polyamides synthesized, the presence of characteristic bands due to diamines (NH stretching; two bands in the region 3300 – 3500 cm $^{-1}$) and diacids (C = O stretching 1640 – 1775 cm $^{-1}$) and (C – H stretching 2500 – 2700 cm $^{-1}$) confirm the formation of amide linkages and hence of the polyamides. 3300 – 3400 cm $^{-1}$ frequency shows the presence of NH stretching as broad peaks with medium intensity and indicates that the amides are in trans - form. The broadness of the peaks obtained indicates that the NH groups are involved in hydrogen bonding.

Thermal stability of a polymer depends on the bond energies of the various bonds in the polymer backbone. Higher these bond energies between the atoms, greater is the thermal stability. Further, factors such as high resonance stabilization, high chain stiffness, high degree of crystallinity and high interchain attraction are known to enhance the thermal stability. Physical and morphological factors may also influence the polymer stability.

Table 3 summarises the thermal data of all the polyamides obtained in nitrogen atmosphere. Representative TG and DTA curves are presented in Fig. 1. In general, the TG curves show three stages of weight loss. In the first stage, a weight loss of 1-5 % occurs which is accompanied by a small endotherm in the temperature range 100 – 145°C in the DTA curves; this can be attributed to the removal of water or entrapped solvents. The second stage corresponds to a steep fall in the TG curves. In the temperature range 145 – 290° C, there is also a sharp endotherm observed in most of the cases. These may be due to the change in structural pattern of the polymers. The weight loss

in this portion is about 20% corresponding to major decomposition of the polymers evidenced by derivative curves. In the third stage, weight loss in the TG curve is steady.

The T_{max} values (temperature at which maximum degradation occurs) obtained from DTG (derivative curve of thermogram) correspond to almost 20% weight loss. Greater the molecular weight, greater is the stability and melting point of a polymer. Thus, T_{max} is highest for the polymer CH_3O AZ – AZ which has the highest molecular weight and it is least for the polymer CH_3 OAZ – IST which has the lowest molecular weight. Cross – linking reactions that may occur on heating above 400°C may also contribute to the higher T_{max} values observed. The effect of substituents become significant only after 350°C. The low 10% decomposition temperature of CH_3OAZ – Diphoxy compared with that of CH_3OAZ – Diph may be attributed to the bond nature and the bridging atom present between the two phenyl groups. In this decomposition range, the end groups might react to eliminate water. The poor thermal stability observed for CH_3OAZ – PyMDG among the fexible polymers may be due to the fact that the pyridine ring reduces the interchain hydergen bonding considerably leading to less close packed structures. On the other hand, the pyridine nucleus may also pump its lone pair of electrons into the adjacent phenylene rings making them prone to oxidation.

At this juncture, it is reasonable to compare the thermal data of some azopolyamides reported from this laboratory. From Table 4, the order of thermal stability of the polymers, interms of substituents can be given as,

$$Cl > OCH_3 > CH_3$$

which is in the reverse order of viscosity .

DTA curves do not show any melting or glass transitions. Glass transition either occurs in a wide temperature range or masked by the broad endotherms due to escape of volatile impurities. This behaviour can be attributed to the highly rigid nature of the polymers. For the same reason, these polymers are not expected to show any definite melting points since degradation preceeds melting.
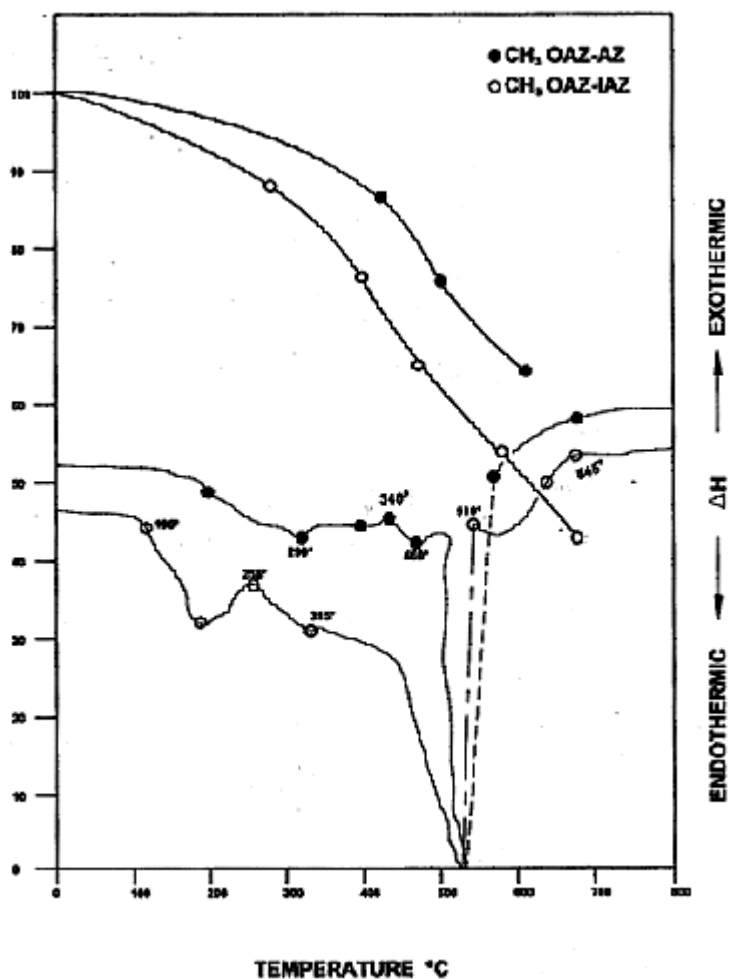
Fig. 1: TGA and DTA curves of CH₃OAZ – AZ and CH₃OAZ – IAZ (DTA curves - Not to scale)

The number of DTA peaks are almost identical to the number of phases in the TG curves. The peak area in DTA corresponds to enthalpy change in the polyamides. The DTA portion corresponds to this show a number of broad exothermic peaks and hence it corresponds to T_{max} in TGA. The exotherms may arise due to decomposition reactions like bond scissions, cyclizations and cross – linking reactions which are quite complex.

Moisture regain

The usage of a fibre is determined by its tensile properties. Moisture absorption creates loss on tensile strength, particularly in elongation at break. From Table 1, it is seen that the moisture regain values are dependent on the following factors: (i) structure, substituent and coil nature or cavities of the polymer (ii) hydrophilic and hydrophobic nature of the polymer (iii) density or closed packed system of the molecule, number of methylene units and aromatic rings present in the polymers.

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