

# Film Studies of Certain New Aromatic–Aliphatic Polyamides

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**ABSTRACT:** Two new aromatic–aliphatic polyamides containing azo linkage in the main chain based on 2,2'-dimethyl-4,4'-diaminoazobenzene and adipic/2-chloro-5-methyl-1,2-dioic acid ( $\alpha$ -chloro- $\delta$ -methyl adipic acid) were synthesized and analyzed by thermogravimetry and films were cast. Also three polymers obtained from condensation of 4,4'-azodibenzoic acid/adipic acid and 2,2'-bis [4-(*p*-amino phenoxy) phenyl] propane/4,4'-diaminoazobenzene were studied in terms of mechanical and morphological properties. Film studies were carried out in terms of tensile

property, scanning electron microscope, dielectric, microwave, and X-ray diffraction pattern. Thermal studies have been done using thermogravimetric analysis, differential thermal analysis, and pyrolysis-mass spectral data. The results were correlated with structure and orientation of the molecules. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1305–1316, 2004

**Key words:** films; azo polyamides; mechanical properties; tensile properties; dielectric properties

## INTRODUCTION

The commercial Nylon (polyamide film) is well known for its high temperature resistance and good mechanical properties. Nanjan et al.<sup>1,2</sup> studied the mechanical properties of fibers and cast films from substituted dianilines and adipic acid. In recent years attention has been given to the polyamides and polyimides reinforced with glass tubes, which play an important role in transmitting light and electromagnetic considerations.<sup>3</sup> Their main use as dielectric lenses, avionic enclosures, and other devices for aeronautical applications<sup>4</sup> led us to study the dielectric properties of the polyamide films synthesized in this work. Also plasticizers, lubricant, and stabilizers were incorporated during the formation of films to improve the processability and the potential of the materials for applications, especially insulators. The effect of plasticizers are correlated with morphological and mechanical properties. In addition, scanning electron microscope results and mechanical properties of film were evaluated as a function of orientation of molecules (crystalline nature), which were obtained from the X-ray diffraction pattern.

Among the several classes of thermally stable polymers, azo polyamides are of importance. These polymers, which are easily processible, have an excellent balance of mechanical and electrical properties and

good resistance to solvent attack. The presence of an azo group in the main chain of a polymer increases chain rigidity, leading to close packing of the polymer chains and better thermal stability.<sup>2</sup> Hence azo linkage polyamides were synthesized based on azoaromatic diamines and aliphatic diacids.

## EXPERIMENTAL

### Monomers

2,2'-Dimethyl-4, 4'-diaminoazobenzene,<sup>2</sup> 4,4'-diaminoazobenzene,<sup>5</sup> 2,2'-Bis[4-(*p*-amino phenoxy) phenyl] propane, and 4,4'-azodibenzoic acid<sup>5</sup> were prepared. Adipic acid was recrystallized from hot water. 2-Chloro-5-methyl-1,2-dioic acid (Fluka) was used as such.

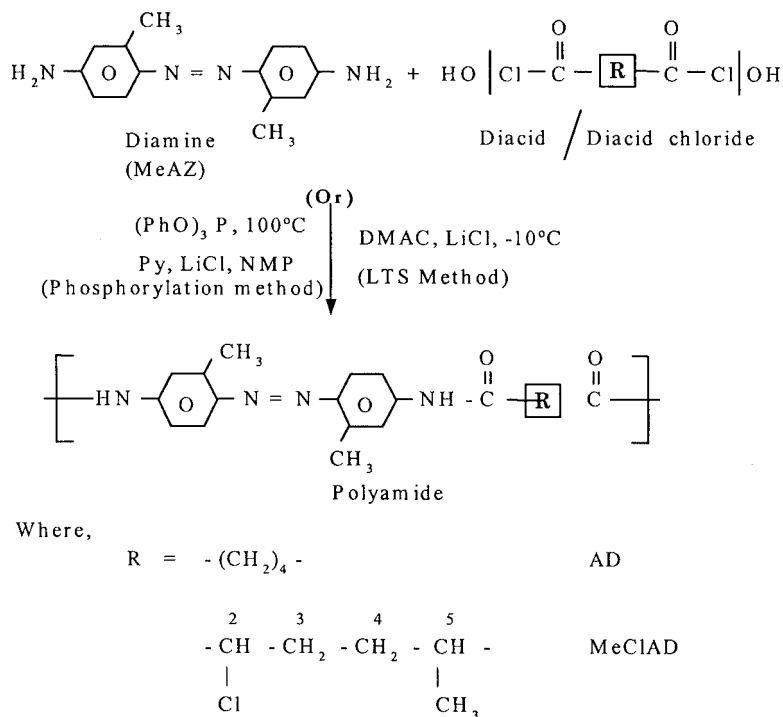
### Polymerization

The polyamides were synthesized by both low temperature solution (LTS) and phosphorylation polycondensation procedures (see Scheme 1).

### Film preparation

The polymer dopes (highly viscous solution) were prepared by dissolving the polymers in a suitable solvent DMAc/NMP/H<sub>2</sub>SO<sub>4</sub>. The dopes were spread using film applicators to ensure films with a fixed length and width (10 mm and 9 mm) and varying thickness (0.006", 0.008", and 0.012"). The films were dried in static air.

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Scheme 1

### Plasticization

The plasticizers such as *p*-toluenesulfonamide (PTS) and *N*-ethyl-*p*-toluene sulfonamide (NEPTS) were found to be effective. An optimum of 0.1 to 0.5% plasticizer concentration was maintained. Films were also cast from plasticized polymer dopes by laboratory wet blending procedure.<sup>6</sup> The use of plasticizers along with stabilizer (stearic acid) and lubricant (calcium stearate) were employed.

### Characterization

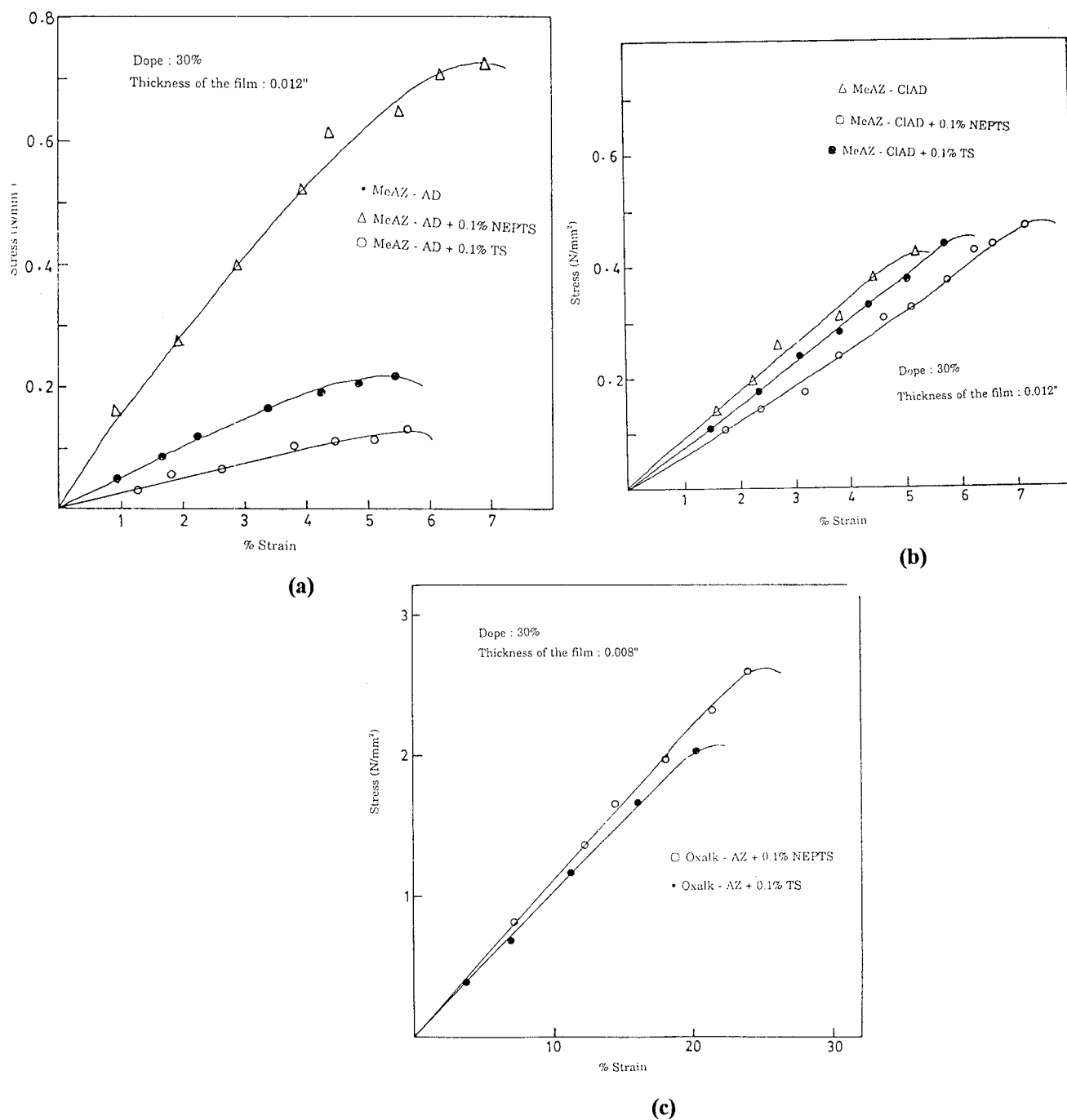
#### Film studies

*Tensile properties of films.* Tensile properties of the films were calculated on an Instron 4501 model tensile strength measuring instrument using pneumatic clamp jaws. The test conditions employed were gauge length, 10 mm; cross head speed, 5 mm/min; and grip distance, 11 mm.

TABLE I  
Tensile Properties of Films<sup>a</sup>

Polymer	Plasticizer	Stress at maximum load (N/mm <sup>2</sup> with respect to thickness of film)			% Strain with respect to thickness of film		
		0.006"	0.008"	0.012"	0.006"	0.008"	0.012"
MeAZ-AD	Without plasticizer	0.637	0.3865	0.2163	3.11	4.23	5.45
	0.1% NEPTS	0.1312	0.4437	0.7326	5.72	6.48	6.92
	0.1% PTS	0.0716	0.121	0.129	4.71	5.32	5.63
MeAZ-MeClAD	Without plasticizer	0.1327	0.3921	0.422	4.11	4.62	5.23
	0.1% NEPTS	0.2231	0.421	0.471	6.023	3.11	7.32
	0.1% PTS	0.099	0.412	0.436	4.82	5.30	5.76
Oxalk-AD	Without plasticizer	0.152	0.43	1.54	6.01	7.46	12.59
	0.1% NEPTS	0.367	0.521	1.43	7.10	7.92	12.94
	0.1% PTS	0.163	0.0637	1.793	6.21	3.11	3.11
Oxalk-AZ	Without plasticizer	2.88	0.1573	0.0637	16.03	19.42	8.35
	0.1% NEPTS	1.04	2.578	0.4425	14.09	23.74	6.47
	0.1% PTS	2.07	2.01	2.231	18.20	20.62	16.27
AZ-AZ (azodiamine- azodiacid)	Without plasticizer	0.2078	0.1325	0.1443	5.45	5.72	5.93
	0.1% NEPTS	0.7437	0.7494	0.0795	7.51	8.37	3.17
	0.1% PTS	0.0761	0.1436	0.2271	4.95	6.72	8.71

<sup>a</sup> Dope concentration = 30%.



**Figure 1** Typical stress—strain curves of polymer films.

*Scanning electron microscope (SEM) studies.* The surface of the film was investigated with a Sterio Scan model 440 SEM. The film was coated with a thin film of gold in the polaron SC 500 sputter coated prior to SEM examination to eliminate local charging and to make them electrically conductive.

*Dielectric studies.* The film samples were measured at 9.1 GHz using the cavity perturbation technique. The cavity used was a TE<sub>105</sub> mode reflection type rectangular cavity. The instrument used was an HP 8720 A Microwave vector Network Analyzer.

*Microwave study.* As a representative case the polymer films (0.006" thickness) obtained from 20% Oxalk-AZ polymers were exposed to microwave for various time intervals (1–16 min) using a 930 W Morphy AC-2000-II Microwave oven. The frequency selected for microwave dielectric heating is 2.45 GHz.

*X-ray diffraction studies.* The surface of the film was investigated with a Sterio Scan Model 440 SEM. The X-ray diffraction patterns were recorded with a Shimadzu XD-D1 X-ray diffractometer. A 35 KV and 25 mA nickel filtered CuK $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation was

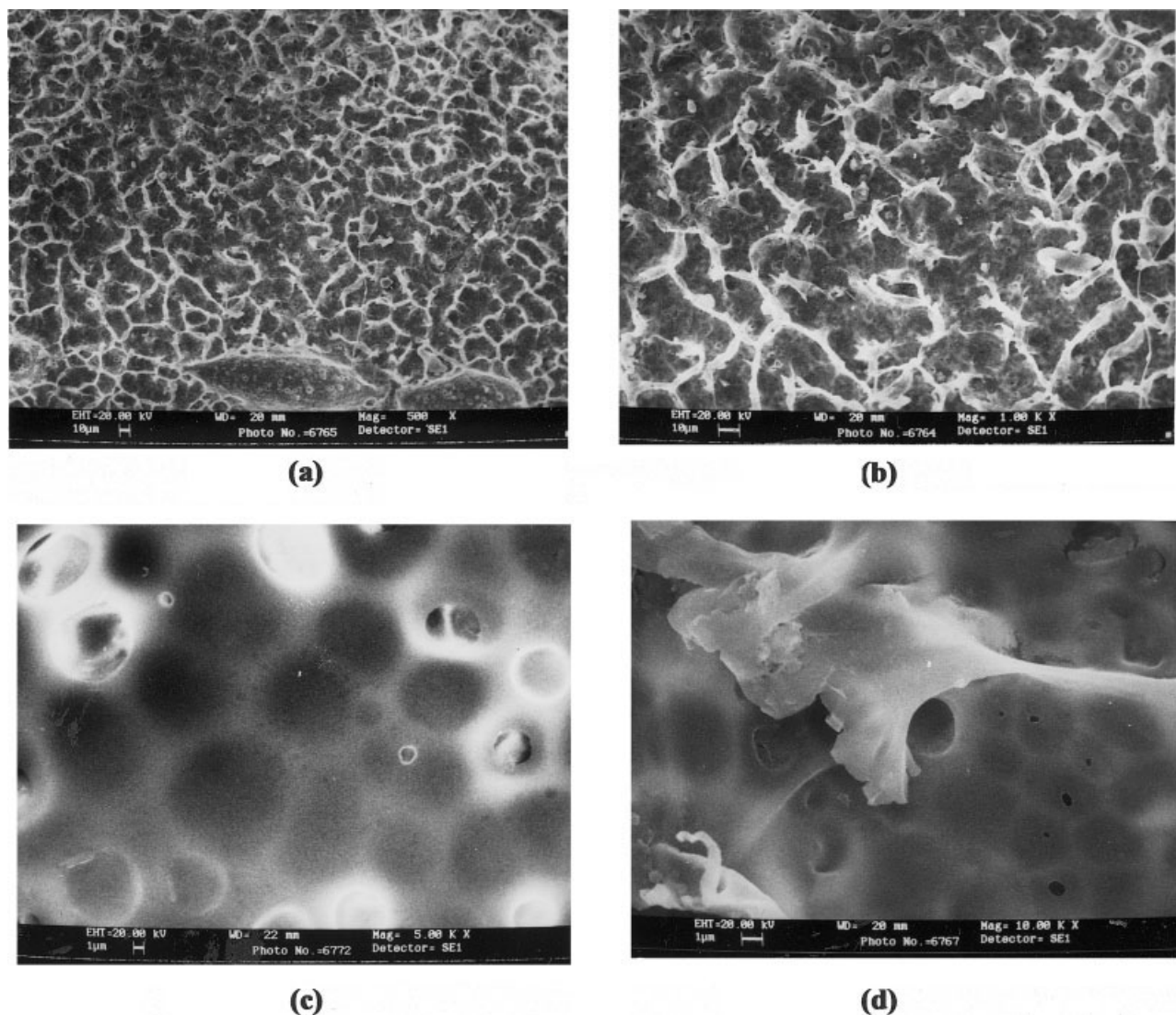


Figure 2 Scanning electron micrographs of Oxalk—AZ film (nonplasticized).

employed. The film was mounted perpendicular to the X-ray beam.

#### Thermal studies

*Thermal studies.* Thermal analyses (TGA and DTA) were recorded in nitrogen for all the polymers using a Stanton-Redcraft simultaneous TG-DTA apparatus or a du Pont 990 thermal analyzer. About 5–10 mg of the sample was heated at the heating rate of 5°C/min for all of the polymers. A thermocouple was used to measure the temperature.

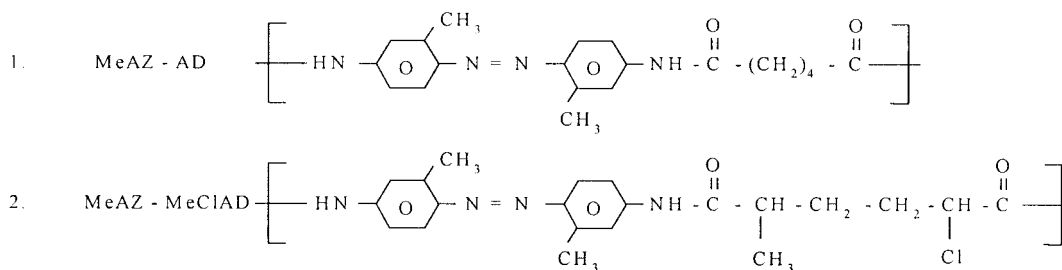
*Mass spectral studies.* The polymer Oxalk-AZ was heated at two different temperatures, i.e., 170 and

250°C for 30 min. The residue obtained was subjected to mass spectral analysis using a QP 2000 Shimadzu Mass Spectrometer by the Direct Inlet Probe Technique.

## RESULTS AND DISCUSSION

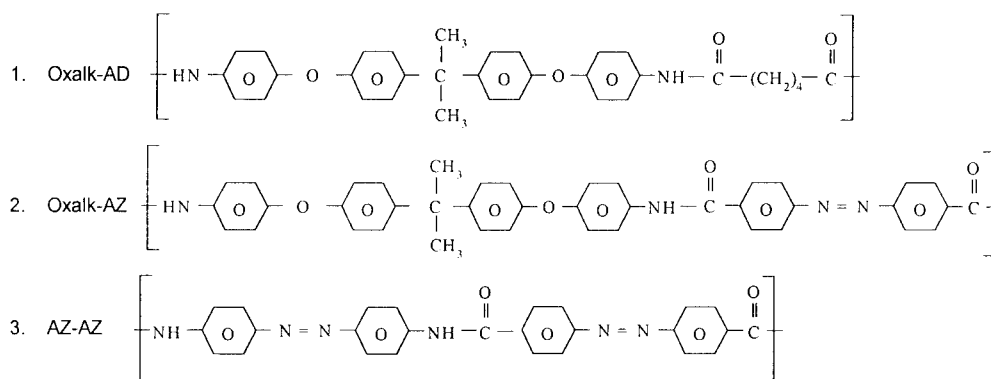
In this article we report the synthesis of two new aromatic-aliphatic polyamides derived from 2,2'-dimethyl-4,4'-diaminoazobenzene and adipic acid/2-chloro-5-methyl-1,2-dioic acid ( $\alpha$ -chloro- $\delta$ -methyl adipic acid) (Scheme 1).

The structures and codes of the polymers synthesized are given below.



Films were also cast from the polymers obtained by the condensation of 4,4'-azo di benzoic acid/adipic acid and 2,2'-bis [4-(p-amino phenoxy) phenyl] pro-

pane/4,4'-diaminoazo benzene by following the LTS and phosphorylation methods. The structures and codes of the polymers synthesized are given below.



**A. FILM STUDIES**

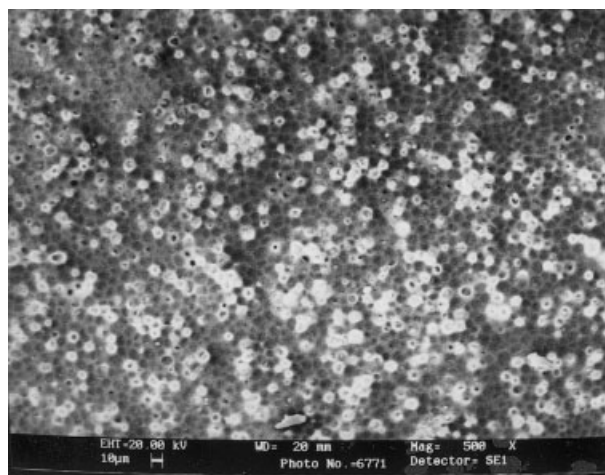
**Film studies**

Film studies

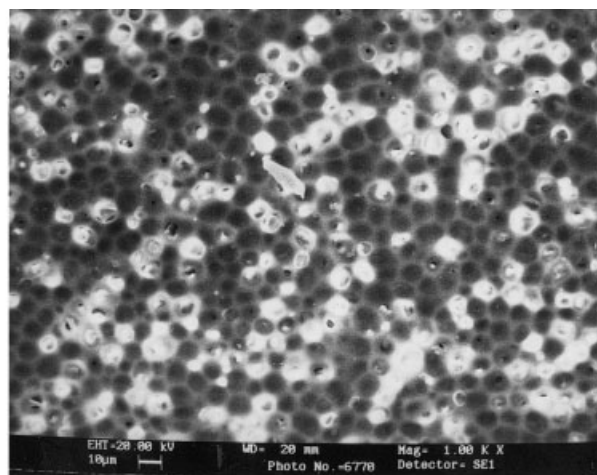
*Tensile properties of films.* Comparison of the % strain and/or stress data (Table I) of the five different poly-

amide films under this study using either 0.1% NEPTS or 0.1% PTS shows that tensile properties of the films are of the following order:

Oxalk-AZ > Oxalk-AD > AZ-AZ > MeAZ-MeClAD > MeAZ-AD



(a)



(b)

**Figure 3** Scanning electron micrographs of plasticized Oxalk—AZ film.

TABLE II  
Dielectric Constant of Films<sup>a</sup>

Sample no.	Sample	$f_1$ (GHz)	Dielectric Study				Microwave study	
			$Q_1$	$\epsilon'$	$\epsilon''$	$\sigma \times 10^{-5}$ (ohm <sup>-1</sup> cm <sup>-1</sup> )	Tan- $\delta$	$D_p$
1	20% Oxalk-AZ	9.14133	1378	2.33	0.09	1.39	25.88	62.06
2	20% Oxalk-AZ + 0.5% NEPTS	9.143441	1316.061	1.45	0.16	2.47	9.06	36.72
3	25% Oxalk-AZ	9.143796	1447.838	1.30	0.03	0.462	43.33	80.31
4	25% Oxalk-AZ + 0.1% NEPTS	9.143851	1407.543	1.28	0.07	1.078	18.29	52.18

<sup>a</sup> Width : Thickness of the film = 0.24 cm : 0.015 cm

The same order is also observed on the basis of molecular weight interms of inherent viscosity ( $\eta_{inh} = 1.89, 1.19, 1.10, 0.80,$  and  $0.80,$  respectively)<sup>5,7</sup>

The superior tensile properties of films obtained from Oxalk-AZ and Oxalk-AD compared to MeAZ-AD (Fig. 1) may be due to linear high strength, high modulus (HS/HM) structure. An increase in the thickness of the film (i.e., from 0.006 to 0.012") generally increases the tensile strength.

Though the AZ-AZ polymer permits a better close packing of the chains, because of the two azo groups, the films cast are weak and thick. This is perhaps due to the high mass transfer in short times leading to large voids in the films during their formation. Films obtained from MeAZ-CIAD and AZ-AZ polymers using plasticizer were inferior in tensile properties. An explanation may be given in terms of larger voids formed during rapid coagulation by the use of concentrated H<sub>2</sub>SO<sub>4</sub> as the solvent in dope preparation. This was also observed by earlier workers for the polyamides synthesized from

unsubstituted diamine and adipic acid<sup>1</sup> and also from 2,2'-dimethyl-4,4'-diaminoazobenzene and 4,4'-azodibenzoyl chloride.<sup>8</sup>

A better tensile property of film obtained from Oxalk-AZ compared to Oxalk-AD ( $\eta_{inh} = 1.89$  and  $1.19,$  respectively) is due to high viscosity of Oxalk-AZ, which is a measure of molecular weight. This also may be due to the benzene moiety of azo diacid. An analysis of Table I shows that the addition of an optimum concentration of plasticizer generally improves the tensile properties and percentage elongation. For example, in the case of Oxalk-AZ polymer (25% dope) the % strain and stress for 0.006" film were 12.9 and 2.131 whereas those for the film obtained from 0.1% NEPTS plasticized polymer were 21.58 and 2.272. The same effect is also observed for 0.1% PTS plasticized polymer film.

Among the different plasticizers the following order is shown in increasing tensile strength when the optimum dope concentration is 0.1%.

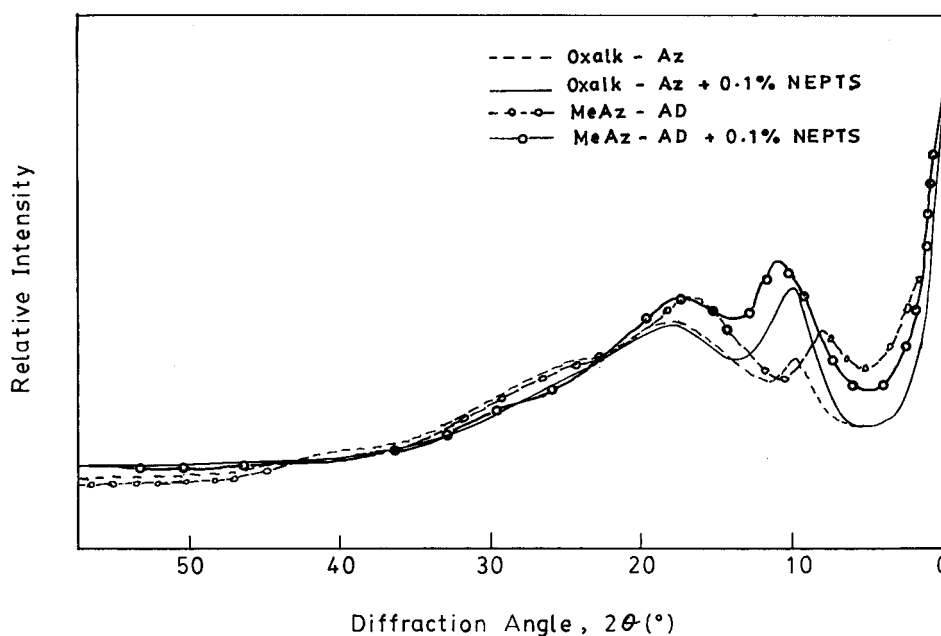


Figure 4 X-ray diffraction curves.

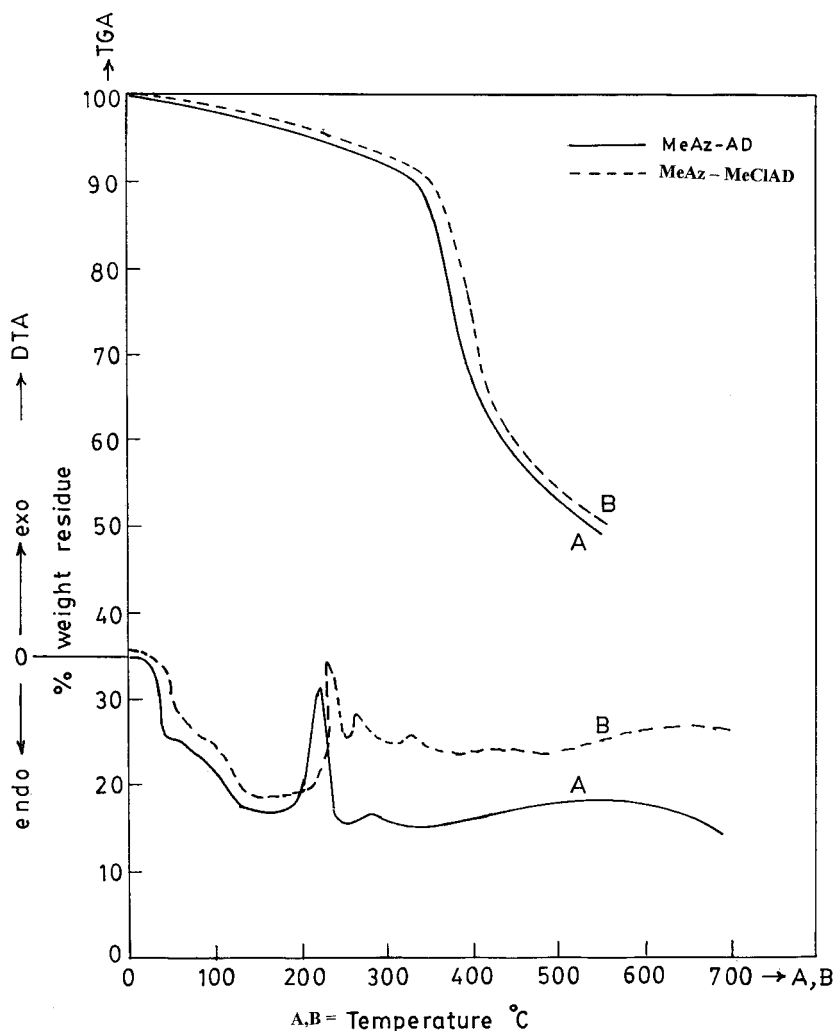


Figure 5 TGA and DTA curves of azopolyamides in  $N_2$  measured at a heating rate of  $5^\circ\text{C}/\text{min}$ .

NEPTS > PTS > unplasticized  
*N*-Ethyl-*o*-toluene sulfonamide and sulfonamide-formaldehyde resins were found to have a retarding effect. The elasticity of the polymeric material, i.e., its ability to undergo large reversible deformations, is increased by the addition of a plasticizer. It is observed that complete compatibility (i.e., mutual miscibility at molecular level) and mobility or diffusibility of the additive is such that any or all the molecules of the system interact with each other. An attempt has been made to use filler (precipitated  $\text{CaCO}_3$ ), stabilizer (stearic acid), and lubricant (calcium stearate) in addition to plasticizer. It has been found that stabilizer and lubricant reduce the viscous nature of the polymer dope and the films obtained were weak, hence, mechanical properties cannot be evaluated. Nevertheless, the use of plasticizer alone confirms the enhancement in mechanical properties.

*Scanning electron microscope studies.* The scanning electron micrographs and in Figures 2(a) and (b)

show the morphologies of the free surface of the manually drawn Oxalk-AZ film. Both of them show a porous fibril structure. The micrographs (c) and (d) show the presence of voids in the film. These voids are smaller in number and size in Oxalk-AZ compared to Oxalk-AD, AZ-AZ, or MeAZ-MeCl AD. The formation of voids may be explained in terms of the events that occur during casting a film, i.e., in polymer-solvent interaction, concentration of polymer dope, and spreading of the fluid. When the voids are larger and random or disordered in their position, then mechanical properties of these films are, no doubt, low. In other words, arrangement of molecules in order or uniformity or crystalline nature leads to high strength/high modular films.

The micrographs [Fig. 3(a) and (b)] of plasticized Oxalk-AZ film reveal a porous structure but with a better orientation of molecules compared to Oxalk-AD, AZ-AZ, or MeAZ-MeCl AD. The nonplasticized polymer films have been reported to be, generally,

TABLE III  
Thermal Stability of polymers<sup>a</sup>

Polymer	Percent weight loss					$T_{\max}$	No. of stages of weight loss	Exotherm temperature
	10	20	30	40	50			
MeAZ-AD	340	365	390	430	540	360	4	360,445
MeAZ-MeCIAD	355	380	410	440	560	370	3	375,360

<sup>a</sup> Heating rate 5°C/ min in N<sub>2</sub> atmosphere.

inferior to those of plasticized polymers. This is attributed to the existence of porosity and lack of orientation in the polymer.<sup>9</sup>

*Dielectric studies: determination of dielectric constant.* The use of polymers as insulating materials is made possible by their high electrical resistance, low permittivity (dielectric constant), small dielectric loss, and resistance to high voltage. The addition of plasticizers lowers all these characteristics and hence insulation property increases. The absolute values of the loss angle and the permittivity depend on the polarity of the plasticizer.

As a representative case, film samples from Oxalk-AZ polymer were measured at 9.1 GHz using the cavity perturbation technique.<sup>10</sup> The dielectric constant ( $\epsilon'$ ) was determined using the formula

$$(\epsilon' - 1) = \frac{V_c}{4V_s} \left\{ \frac{f_0^2}{f_1^2} - 1 \right\} \quad (1)$$

where  $A_c$  = area of cross section of the cavity;  $b$  = breadth of the cavity;  $V_s = A_s \times b$ ;  $A_s$  = area of cross section of the sample;  $f_0$  = resonance frequency of the cavity without sample = 9.14454; and  $f_1$  = resonance frequency of the cavity with sample

$$\begin{aligned} \therefore (\epsilon' - 1) &= \frac{A_c b}{4A_s b} \left\{ \frac{f_0^2}{f_1^2} - 1 \right\} \\ \therefore (\epsilon' - 1) &= \frac{A_c}{4A_s} \left\{ \frac{f_0^2}{f_1^2} - 1 \right\} \end{aligned} \quad (2)$$

where,  $A_c = l b$  = length of the cavity  $\times$  broader dimension;  $A_c = 11.785 \times 2.283$ ; and  $A_s$  = thickness of the sample  $\times$  width of the sample.

Similarly the dielectric loss ( $\epsilon''$ ) can be determined using the formula

$$\epsilon'' = \frac{V_c}{4V_s} \left( \frac{f_0^2}{f_1^2} \right) \left( \frac{1}{Q_1} - \frac{1}{Q_0} \right) \quad (3)$$

where  $Q_0$  = quality factor without sample = 1,480.381 and  $Q_1$  = quality factor with sample.

The conductivity ( $\sigma$ ) is measured using the expression

$$\sigma = \frac{\epsilon'' \cdot \epsilon^0}{2\pi f_1} \quad (4)$$

where  $\epsilon^0$  = permittivity of free space =  $8.854 \times 10^{-12}$

An analysis of Table II shows that the addition of plasticizer lowers the dielectric constant, i.e., for the nonplasticized film the  $\epsilon'$  is 2.33 and for the plasticized film it is 1.45. The reason can be assigned to the increase in crystalline nature as evidenced by the X-ray diffraction studies.

*Microwave study.* Microwave reactions involve selective absorption of MW energy by polar molecules; nonpolar molecules being inert to MW dielectric loss. This study is carried out in terms of 1) polymer curing, 2) effect of rapid heating, 3) hot spots, surface effects, 4) dielectric heating or temperature effect, 5) kinetically and/or thermodynamically controlled reactions, and 6) solvent free organic synthesis, i.e., under dry reaction conditions.

IR spectra were recorded for 20% Oxalk-AZ polymer films (0.006" thickness) each time after exposure to microwave and the results were compared. Interestingly, there was no change in IR spectra. This shows that the film is not affected by microwave. This result has been compared with IR spectral data obtained for this polymer. It has been noted that there is absolutely no change in IR frequencies or peak areas. Also, no physical change was noticed on the films.

The results of microwave experiments can be correlated with the thermogravimetric data. The difference between microwave cured and thermally cured polymer has been rationalized in terms of the temperature profile during the initial stages of the reaction or specific activation. This causes the occurrence of crosslinking reaction or intramolecular reaction.

From the observations the following conclusions are made: 1) The polymer film is transparent to microwave, 2) it acts as an insulator, and 3) there is no indication of ene or isomerization (*cis-trans*) reactions though -N=N- and >C=O groups are present.

*Calculation of  $\tan \delta$  and  $D_p$ .* The extent of heating in a dielectric field in which the polymeric film exposed has been studied in detail. The exact dependence of heating rate in the presence of a dielectric field is given by the following equation

$$\tan \delta = \epsilon'' / \epsilon'$$



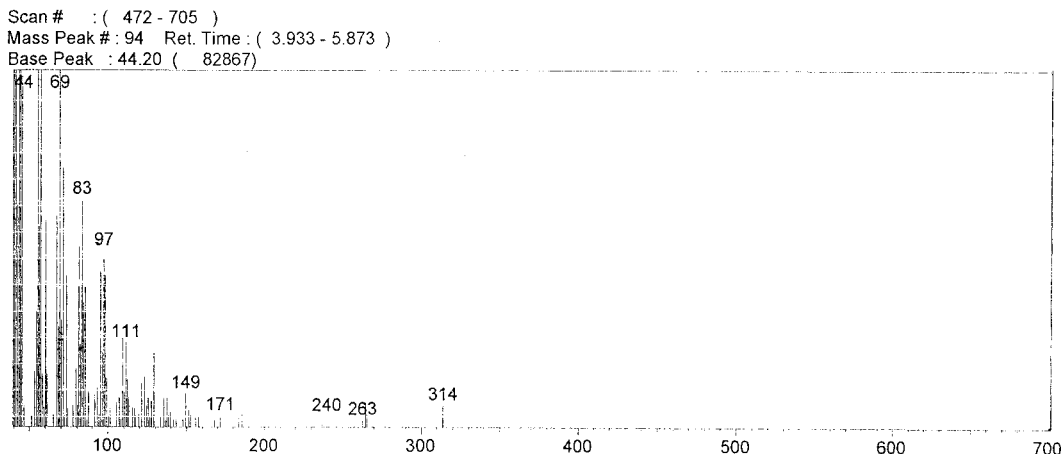


Figure 6 Pyrolysis—mass spectrum of Oxalk—AZ polymer at 170°C.

where  $\epsilon'$  = relative permittivity which is a measure of the ability of a molecule to be polarized by an electric field;  $\epsilon''$  = dielectric loss, which is indicative of the ability of a medium to convert dielectric energy into heat; and  $\tan \delta$  = dielectric loss tangent, which defines the ability of the material to convert electromagnetic energy into heat energy at a given frequency and temperature.

The value of  $\tan \delta$  depends on the following factors: 1) frequency or electromagnetic waves, 2) the temperature, 3) physical state, and 4) composition of the mixture.

The penetration depth on the polymeric film has been studied based on the following equation

$$D_p = \lambda (\epsilon' / \epsilon'')^{1/2}$$

where  $D_p$  = penetration depth and  $\lambda$  = wavelength of the microwave radiation.

The results obtained were given in Table II. An analysis of Table II shows 1) increase in polymer dope

concentration increases the value of both  $\tan \delta$  and  $D_p$ ; 2) plasticized polymer films have lower  $\tan \delta$  and  $D_p$  values compared to nonplasticized films; and 3) the dielectric heating rates depend the value of  $\tan \delta$ , size/quantity of the polymeric film, and heat capacity of the medium.

*X-ray diffraction studies.* Results obtained from the X-ray diffraction pattern were made to correlate the extent of orientation of molecules in terms of crystallinity with the observed mechanical properties.

X-ray diffractograms recorded for the films are 1) Oxalk—AZ polymer film (0.006" thickness) obtained from (a) 20% dope of nonplasticized and (b) 0.5% NEPTS plasticized; and 2) MeAZ—AD film (0.006" thickness) obtained from (a) 20% dope of nonplasticized and (b) 0.5% NEPTS plasticized and are presented in Figure 4. The diffractograms did not indicate sharp and high intensity peaks, indicating very little orientation in these polyamides. However, a comparison of the sharpness of the peaks and their intensity

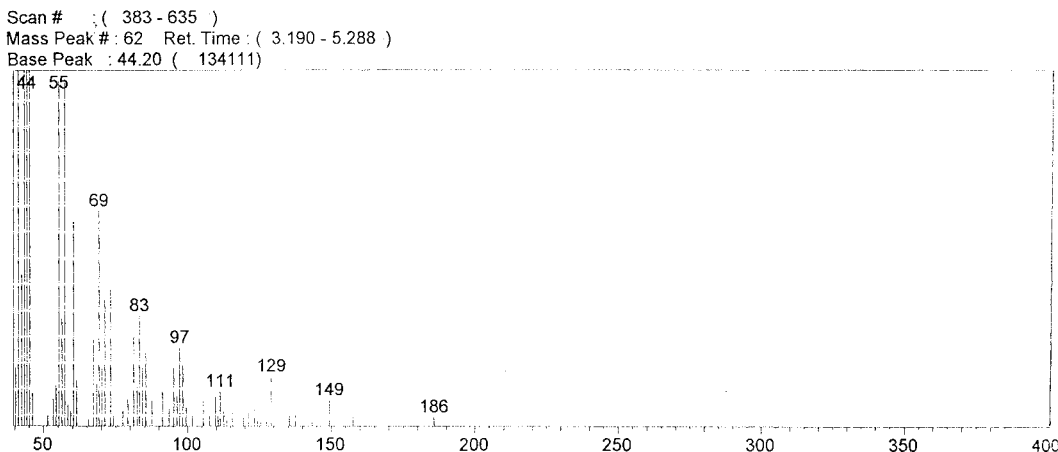
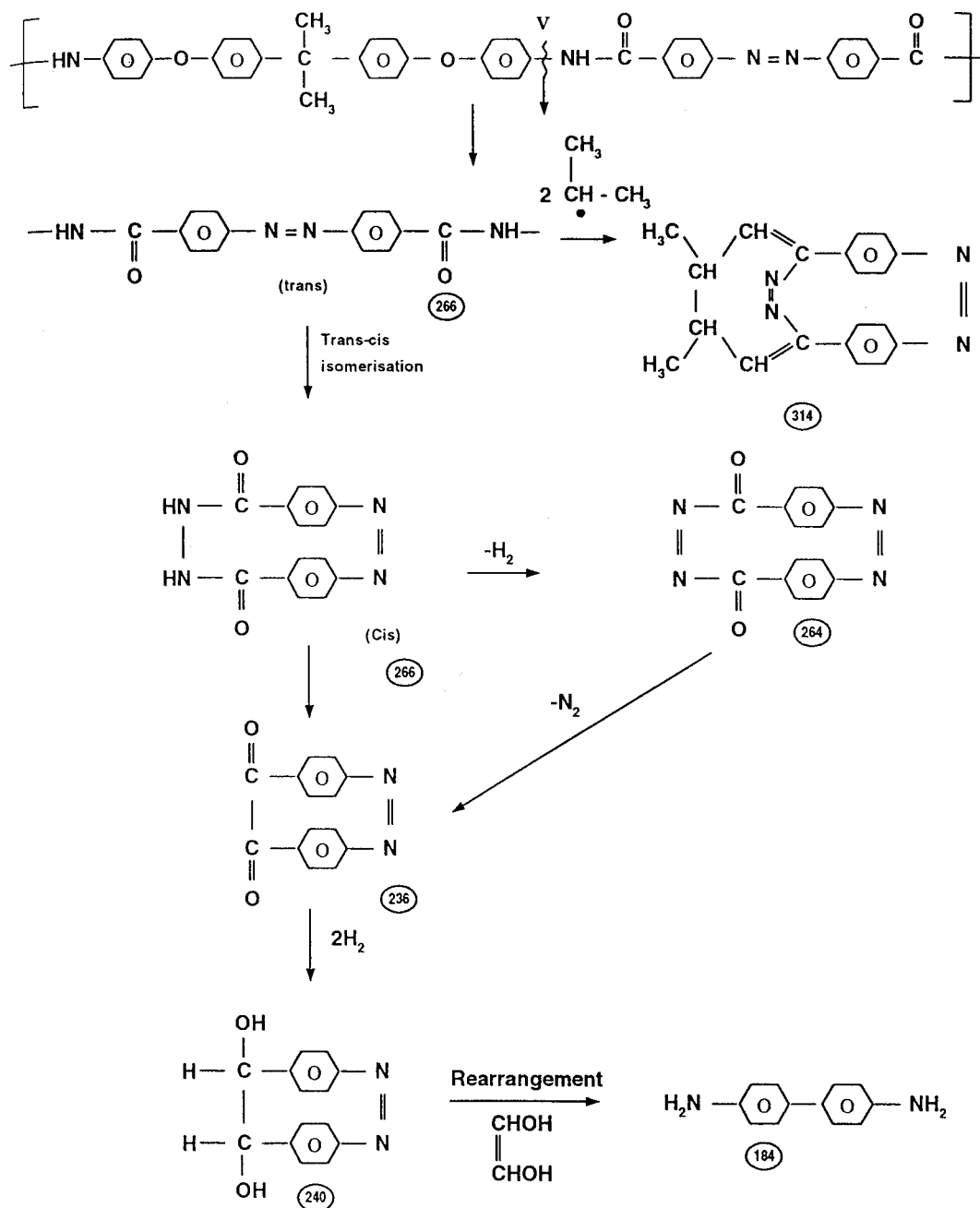


Figure 7 Pyrolysis—mass spectrum of Oxalk—AZ polymer at 250°C.



Scheme 2 Fragmentation pattern of Oxalk-AZ at 170°C.

leads to the following conclusions: both of the films exhibit a crystalline nature and, of the two films, the plasticized film is found to be more crystalline than the nonplasticized film (Fig. 4).

So it may be concluded that the amide group is a polar one and leads to much larger secondary forces in polyamides (due to hydrogen bonding); this is most favorable for crystallization. However, the polyamide chains are not as simple as those of polyethylene and packing requires that chain segments be brought together so that the amide groups are aligned. This restriction leads to somewhat lessened degree of crystallinity in polyamides than expected.

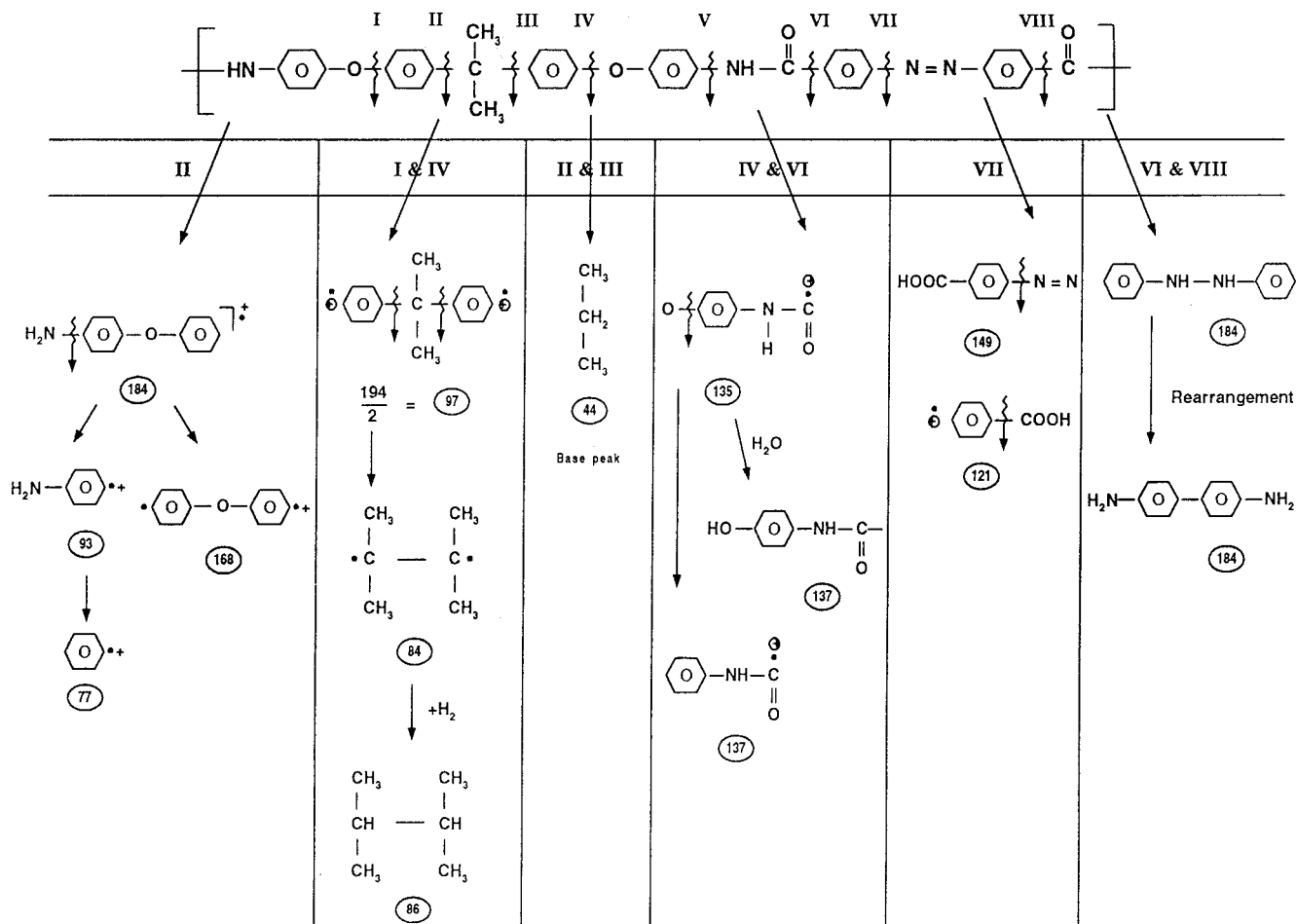
### Thermal studies

Thermogravimetric analysis differential thermal analysis

*Thermogravimetric analysis.* The TGA and DTA curves of the polyamides obtained in  $N_2$  atmosphere are given in Figure 5 and the thermal data are given in Table III.

The TGA curves show three stages of weight loss:

1. In the first stage, an initial weight loss of 1–5% occurs in the temperature range 100–200°C, which may be due to the removal of adsorbed



Scheme 3 Fragmentation pattern of Oxalk—AZ at 250°C.

moisture. Weight loss around 200°C is also likely due to the chain extension that may take place by the condensation of end groups, resulting in the elimination of water.

- The second stage of weight loss (300–500°C) corresponds to a steep fall in the TG curve. The weight loss up to 350°C is about 20%.
- In the third stage, above 430°C, the weight loss in the TG curves is steady. The DTA portion corresponding to this shows a number of broad exothermic peaks. These exotherms may arise due to decomposition reactions like bond scissions, cyclizations, and crosslinking reactions that are quite complex.<sup>11</sup> This type of complex reaction may be due to chlorine substituent in the diacid moiety, which stabilizes by crosslinking reactions. Hence MeAZ–MeCIAD is more stable than MeAZ–AD.

Azo polyamides of our work can be compared with nonazo polyamides synthesized in this laboratory<sup>1</sup>. As a representative case, comparing MeAZ–AD with Oxalk–AD, 20% decom-

position occurs at 365 and 320°C, respectively. Of course, the azo group plays important role in rigidity and close packing in addition to being more heat resistant.

*Differential thermal analysis.* No endotherms, indicating glass transition ( $T_g$ ) or melting ( $T_m$ ) were observed for the polyamides. This behavior is attributed to the highly rigid nature of the polymers and does not show liquid crystalline behavior. They will not have any definite melting points since degradation will precede melting. The first exotherm temperature in DTA corresponds to 20% decomposition and the successive exothermic peaks represent the second, third phase, etc. The exotherms observed in the region  $350 \pm 50^\circ\text{C}$  for all the polyamides are important since they are well defined and have the maximum peak area that is proportional to the enthalpy change in the polyamide. The peak corresponding to  $T_{\text{max}}$  refers to the temperature at which there is a maximum weight loss and the area of the peak corresponds to the activation energy of thermal degradation.

*Mass spectral studies.* The pathways through which a polymer degrades thermally can be investigated by pyrolysis mass spectral studies. In polymers bond scission can, however, take place at any point in the chain. The pathways are, therefore, complex and competitive. The peaks at higher  $m/e$  values that are found to be significant are only considered for arriving at degradation mechanisms. In the polymer Oxalk-AZ studied, the major step is due to hydrolytic scission. Water is probably not a direct product of pyrolysis and its origin could be either due to the adsorbed moisture held by hydrogen bonding in the polymer main chain or due to the reaction between the amino and carboxyl end groups of the polymer chain. Dehydration of primary amides formed during pyrolysis to nitriles may also lead to water formation. The formation of carbon dioxide is suggestive of the hydrolytic type of degradation. Hydrogen abstraction reaction is found to occur normally in the fragmentation patterns. The hydrogen can be abstracted from water or the aromatic rings.

In general, it may be pointed out that, in polyamides, the most facile degradation route is the cleavage of the C-N bond of the amide group, leading to the formation of  $-NH_2$  and  $-COOH$  as the end capped units. The next route is the expulsion of the azo group present in the diamine moiety as nitrogen gas. The azo group present in the diacid part is removed at high temperatures during the course of degradation, ultimately leading to the formation of a number of low-molecular-weight fragments. The major primary process involves loss of  $CO_2$ . Minor competing processes involve losses of H,  $CH_3$ ,  $NH_2$ , and  $C_2H_2$ . The azo group plays a central role in determining the course of degradation of the polymer.

The polymer Oxalk-AZ was heated at two different temperatures, i.e., 170 and 250°C for 30 min. The residue obtained was subjected to mass spectral analysis and the mass spectra are given in Figures 6 and 7. The base peaks at 170 and 250°C correspond to  $m/e = 44$  only. Moreover, the  $m/e$  values from 44 to 184 are common with the same intensity values for 170 and 250°C. The possible fragmentation pattern is shown in Schemes 2 and 3. The bonds that are prone to scission are indicated as I-VIII. In the repeating unit of the polymer ( $m/e = 644$ ), the diamine and the diacid components of the polymer are seen to appear in the mass spectrum recorded. Homolytic cleavage at VII gives  $m/e = 149$ , which on elimination of nitrogen molecule gives  $m/e = 121$ , which confirms the presence of the azo group. All of these steps confirm the

presence and position of the carbonyl and amino groups in the polymer chain.

## CONCLUSION

Investigation of this work reveals the following facts:

1. High-molecular-weight polyamide films have better mechanical properties than the low-molecular-weight films.
2. As the concentration of polymer dope increases, the tensile strength also increases. Better tensile strength is observed if amide type solvent is used for preparing polymer dope.
3. Addition of plasticizer increases the tensile strength but decreases the dielectric constant. Also the type of plasticizer, the thickness of the film, degree of crystallinity, and solvent chosen for dope formation play important roles in determining the tensile strength.
4. The film is not affected by microwave but is transparent and acts as an insulator.
5. It is of interest to note that azo polyamides have more rigidity and thermal stability because of their linear backbone. In addition, electron releasing substituents ( $-CH_3$  group) present in the azo polyamide increases the solubility, which is more useful in film/fiber formation.

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