Effect of Structure on Properties of Aromatic Polyamides

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Synopsis

Polyamides were prepared by reacting 3,5-diamino benzoic acid (DAB) and/or 1,3-bis(3-amino benzamido) benzene (ABB) with terephthaloyl chloride in N,N-dimethylacetamide. Five polymer samples having different contents of pendant carboxyl groups were prepared by changing the molar ratios of DAB : ABB in the initial monomer feed as 1 : 0 (C), 3 : 1 (C_3A), 1 : 1 (CA), 1 : 3 (CA_3), and 0 : 1 (A). The inherent viscosities of the polymers ranged from 0.198 to 0.478 dL/g. DSC and TG studies indicated loss in weight in the temperature range of 80–200°C due to absorbed moisture. The major loss in weight was observed above 400°C. The anaerobic char yield at 800°C depended on the backbone structure and was found to range from 25 to 40%. The resistivities of polyamide film was determined at 110 and 130°C and was found to decrease with an increase in carboxyl content. The dielectric constant of C and C_3A polymer films was determined at frequencies ranging from 100 Hz to 1 MHz and at 110 and 130°C and was found to decrease with an increase in frequency or decrease in COOH content in the backbone.

INTRODUCTION

Aromatic polyamides are both of commercial importance and academic interest. The major application area of fully aromatic polyamide until recently has been restricted to speciality fibers having outstanding mechanical strength and/or high thermal stability. Considerable research efforts have also been expended in the past few years for the development of semipermeable membranes based on aromatic polyamides.[1-5] Such membranes can be used for desalination of sea or brackish water.

In order to overcome some of the shortcomings of wholly aromatic polyamides and to improve processability, solubility, permeability, thermal stability, etc., several structural modifications have been reported in the literature. These include introduction of phenoxaphosphine unit in the backbone[6] disruption of symmetry or introduction of pendant phenyl[7,8] or carboxyl groups.[4,9]

Our research work is mainly directed to the study of effect of pendant carboxyl group on thermal stability and electrical properties of aromatic polyamides. Five polymer samples having different —COOH content were prepared by reacting 3,5-diaminobenzoic acid (DAB) and 1,3-bis(3-amino benzamido) benzene (ABB) with terephthaloyl chloride using the low temperature solution condensation method in dimethyl acetamide according to the following reaction scheme:
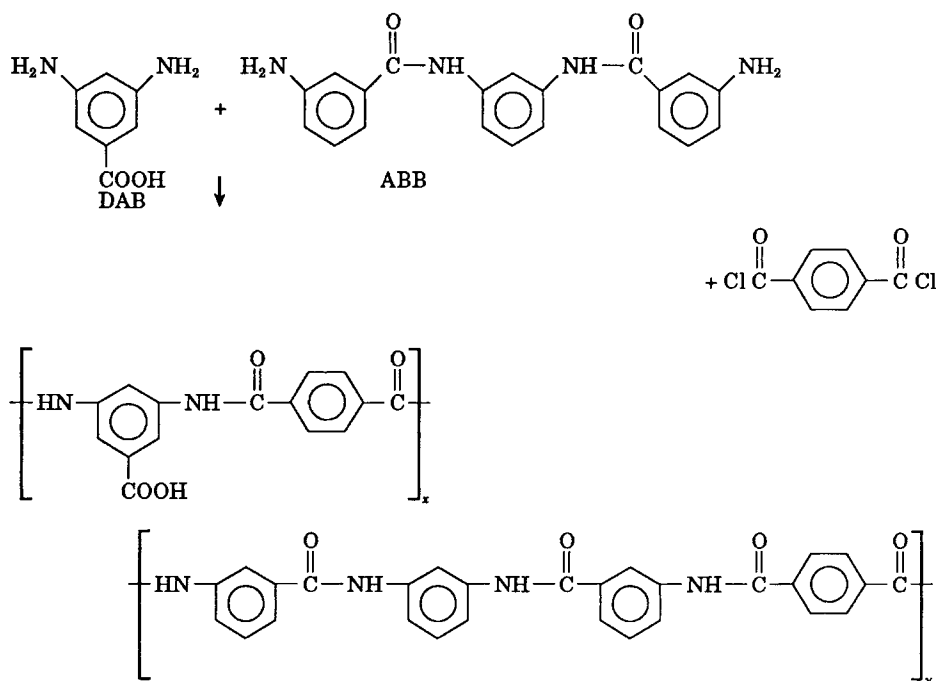
The value of x and y will depend on the molar ratios of diamines taken in the initial feed. The molar ratios of DAB : ABB were varied as 1 : 0 (C), 3 : 1 (C$_3$A), 1 : 1 (CA), 1 : 3 (CA$_3$), and 0 : 1 (A) in the initial feed. The figures in the parentheses indicate the letter designation for these polyamides. No systematic studies have been reported on the effect of pendant —COOH group on properties of such copolyamides, though Preston has earlier reported synthesis and thermal behavior of polymer with structure A.[10]

EXPERIMENTAL

Pyridine was purified by distillation and stored over KOH pellets. 3,5-Diamino benzoic acid was purified by crystallization from water. The mp of pure

TABLE I
Synthesis of Polyamides: Details of Reaction Condition and Inherent Viscosities
of the Polyamides

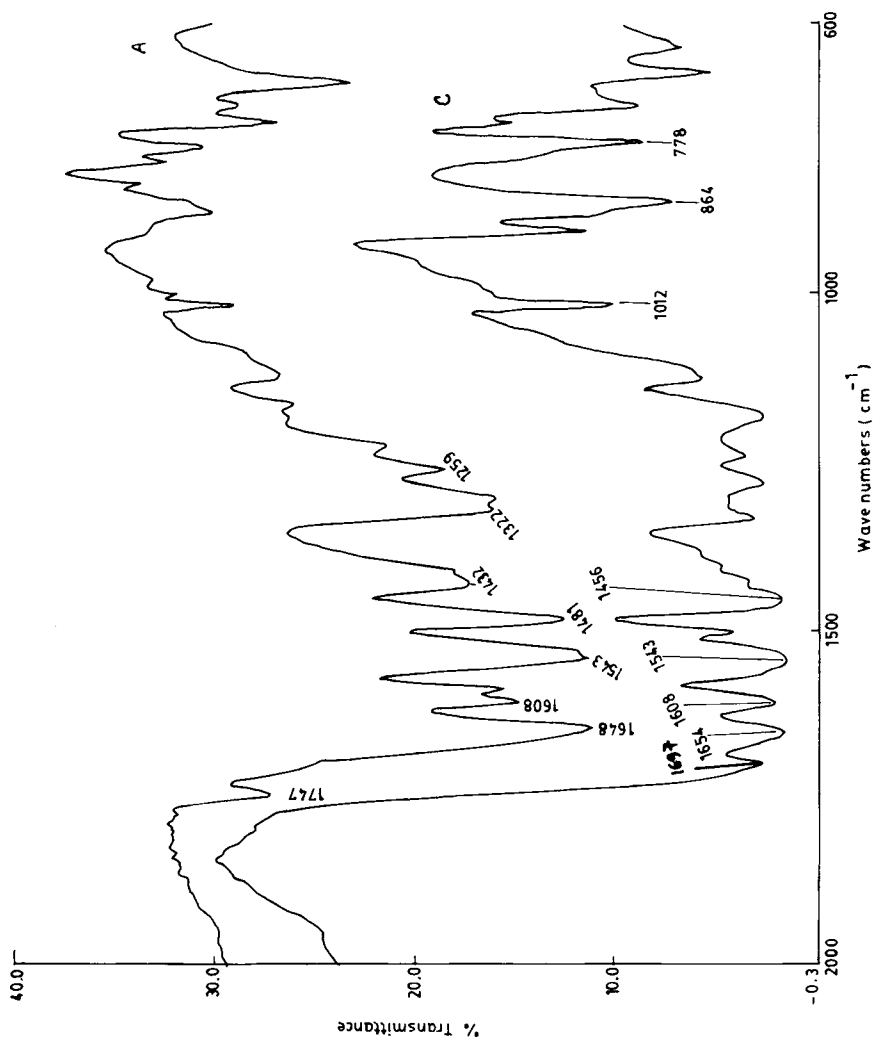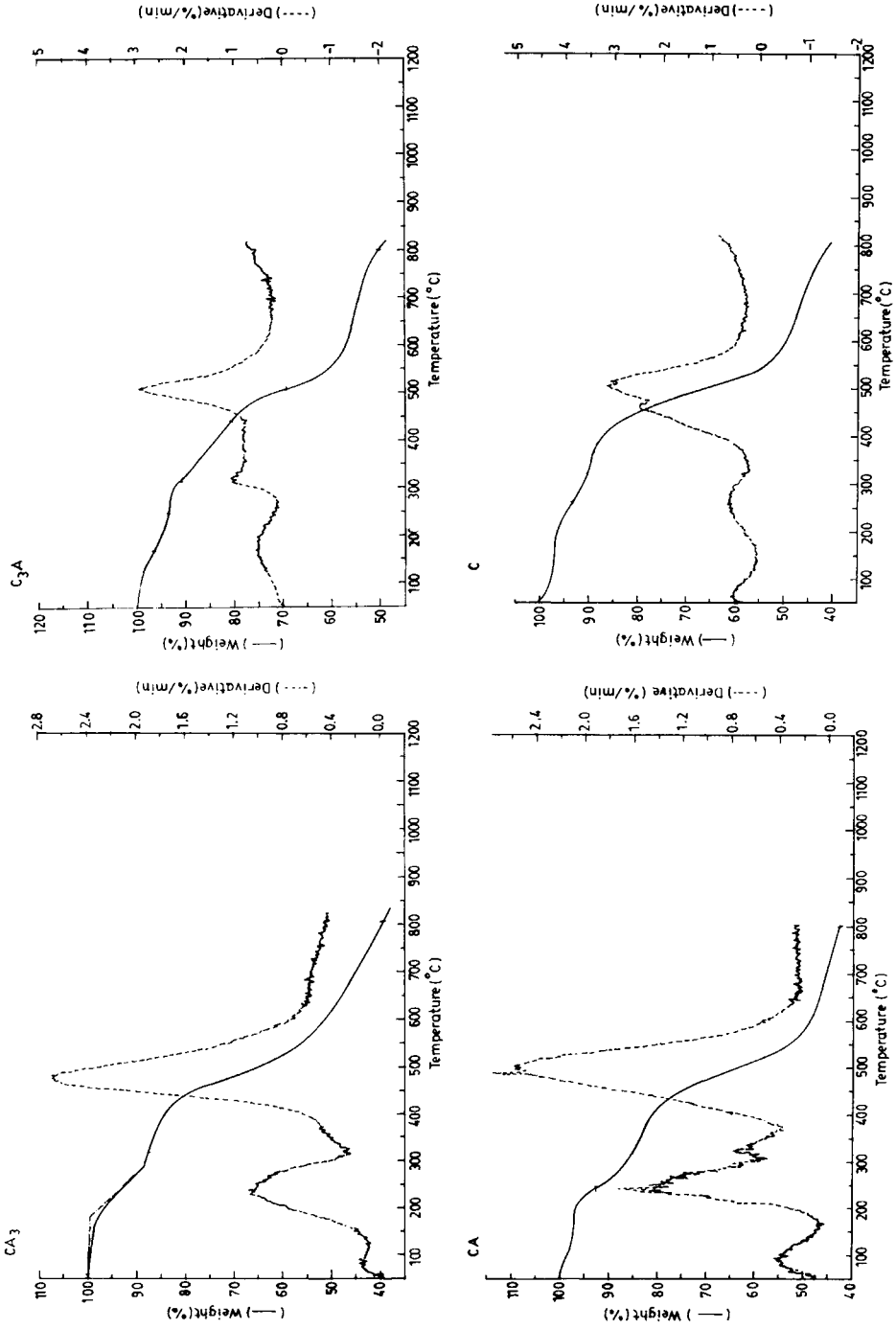| Sample designation	Quantities of the reagents (g)			η_{inh} (dL/g)
	DAB	ABB	TPC	
C	1.52	0	2.1	0.198
C$_3$A	1.14	0.865	2.1	0.268
CA	0.76	1.730	2.1	0.304
CA$_3$	0.38	2.595	2.1	0.478
A	0	3.460	2.1	0.416

Fig. 1. Infrared spectra of polyamides C and A.

Fig. 2.   Thermogravimetric traces of polyamides in nitrogen atmosphere.

TABLE II
Thermal Behavior of Polyamide in Nitrogen Atmosphere[a]

Sample	IDT (°C)	T_{max} (°C)	T_f (°C)	Wt loss (%)	Y_c (%)
C	150	260	330	7.0	41.5
	330	500	650	42.5	
C_3A	110	170	260	3.5	50.5
	270	315	450	13.0	
	450	510	650	25.0	
CA	165	240	370	15.0	43.0
	370	505	670	32.0	
CA_3	125	234	315	11.5	39.5
	315	480	650	32.5	
A	350	465	650	31.0	41.0

[a] IDT = initial decomposition temperature; T_{max} = temperature of maximum rate of weight loss; T_f = final decomposition temperature; Y_c = char yield at 800°C in nitrogen atmosphere.

DAB was 240°C. This amine contained water of crystallization and hence it was dried in a vacuum oven at 80°C for several hours before use. It was stored in a desiccator. Terephthaloyl chloride was recrystallized from dry hexane. Synthesis of ABB was done by preparation of intermediate dinitro compound. To a well-stirred solution of 0.01 mol of m-phenylene diamine in dry DMAc, m-nitrobenzoyl chloride (0.02 mol) was added. The reaction mixture was stirred vigorously and the temperature raised to 100°C. The solution after cooling was
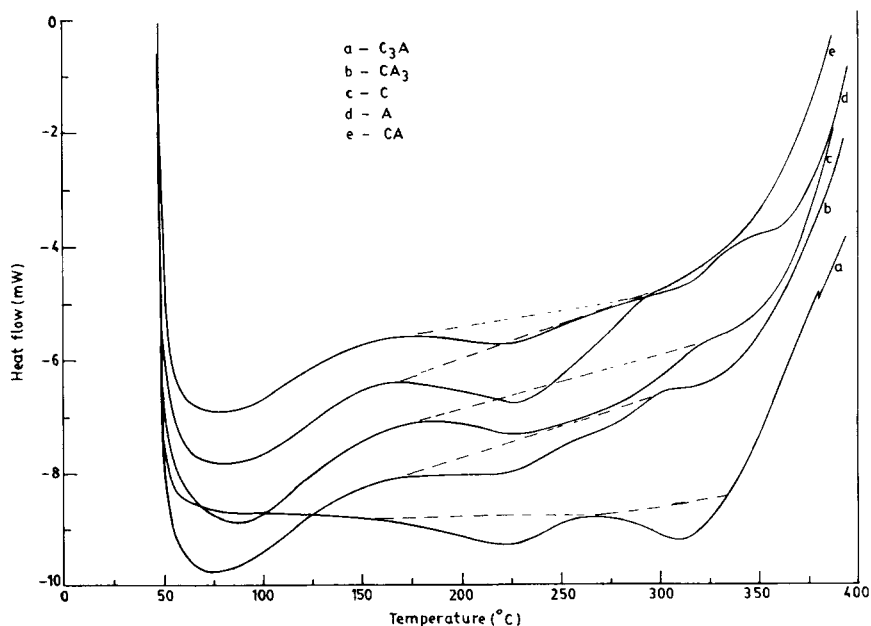

Fig. 3. DSC scans of polyamides in nitrogen atmosphere.

TABLE III
Endothermic Transitions Observed in DSC Traces of Polyamides in Nitrogen Atmosphere[a]

Sample	T_1 (°C)	T_2 (°C)	T_3 (°C)
C	167	250	300
C_3A	160	225	275
	275	312	—
CA	161	234	298
CA_3	150	224	274
A	161	226	284

[a] T_1 = temperature of onset of endotherm; T_2 = peak temperature of endotherm; T_3 = final temperature of endotherm.

poured into ice cold water with rapid stirring. The precipitates thus obtained were washed with hot water, dil $NaHCO_3$ solution and water, and then dried at 60–70°C in an air oven followed by vacuum drying. The dinitro precursor
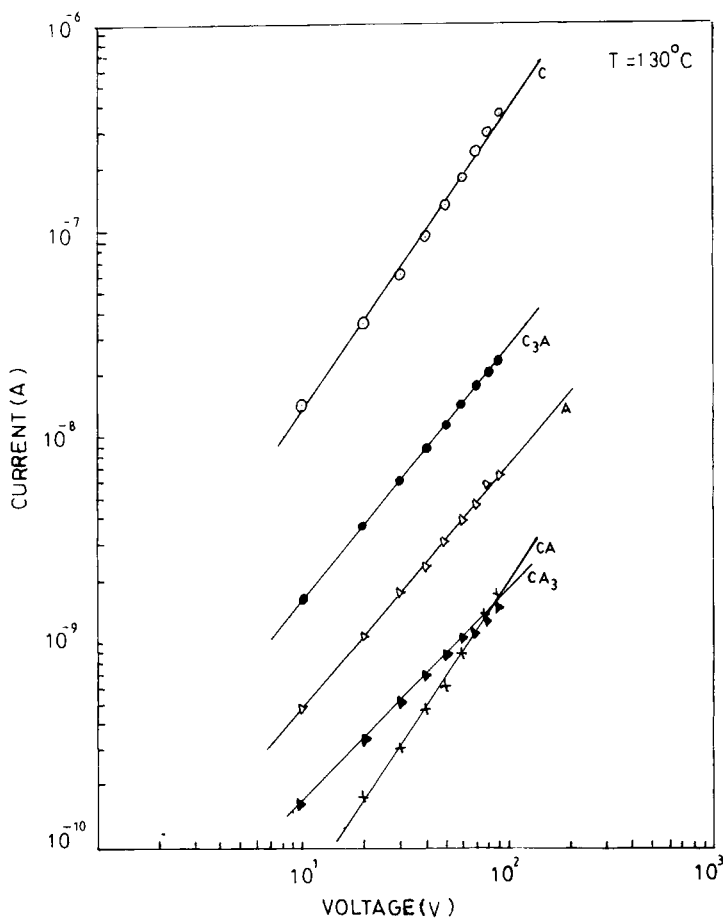

Fig. 4.   Logarithmic plots of current vs. voltage of polyamide films at 130°C.

TABLE IV
Slope Values from log I vs. log V Plot of Polyamide Films

Sample designation	Temperature (°C)	
	110	130
C	1.51	1.42
C_3A	0.78	0.79
CA	1.27	1.39
CA_3	1.19	1.00
A	0.90	0.88

thus prepared was reduced to diamine using Pd/C and hydrazine hydrate. The mp of pure amine was 213–214°C.

Synthesis of Polyamides

Solution polycondensation of diamines and terephthaloyl chloride was done in DMAc at 0°C in nitrogen atmosphere. LiCl was added to enhance the solubility of polyamide. For example synthesis of copolyamide CA_3 was done by dissolving DAB (0.38 g), ABB (2.595 g), and LiCl (0.25 g) in DMAc (36 mL) in a three-necked flask having a nitrogen inlet tube and a stirrer. The temperature was maintained around 0°C. Terephthaloyl chloride (2.19 g) in DMAc (12 mL) was then added dropwise followed by addition of pyridine (1.58 g). The reaction was carried at 0°C for 3 h and then at room temperature for 2 h.

Polymer films of good strength could be obtained by solution casting from DMAc. Alternatively, the polymer could be isolated from DMAc solution by precipitation in water. The details of synthesis and designation of various polymer samples are given in Table I.

Characterization

Inherent viscosity of copolyamides in concn H_2SO_4 (1% soln) was determined at 30°C using a Ubbelohde suspended level viscometer. A DuPont 9900 thermal analyzer having a 910 DSC module was used for evaluation of thermal behavior

TABLE V
Volume Resistivity of Polyamides at 90 V

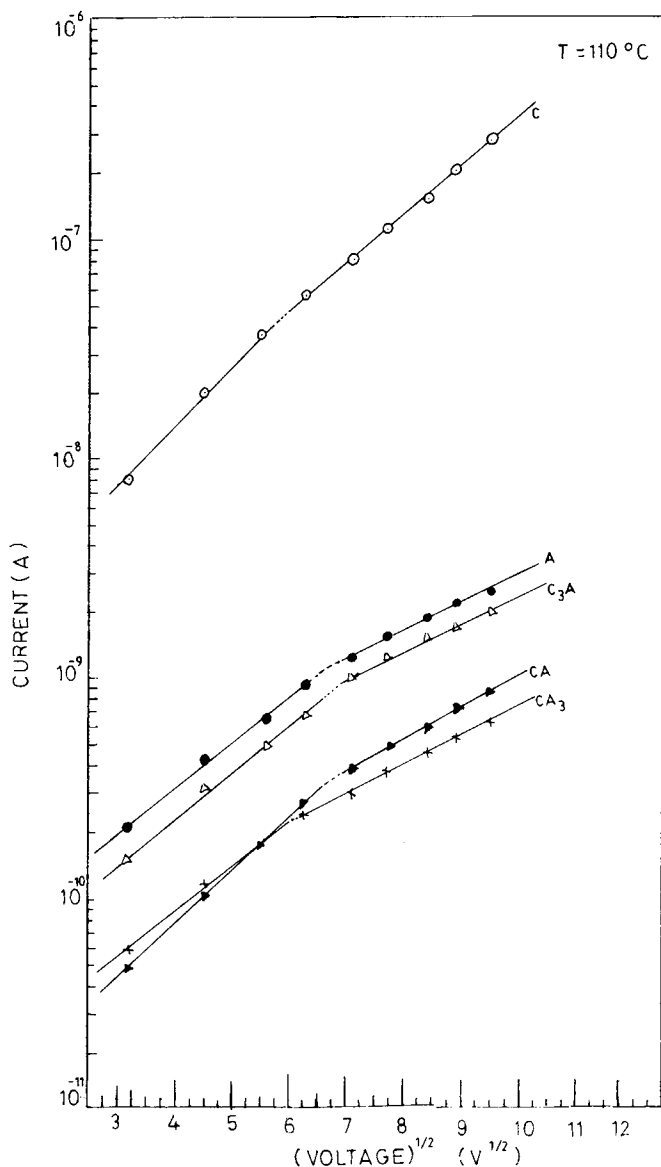| Samples	Resistivity (Ω cm) at	
	$T = 110°C$	$T = 130°C$
C	3.09×10^{10}	2.41×10^{10}
C_3A	4.24×10^{12}	3.77×10^{11}
CA	1.40×10^{13}	7.53×10^{12}
CA_3	2.00×10^{13}	8.93×10^{12}
A	2.80×10^{12}	1.15×10^{12}

Fig. 5.　Dependence of current on square root of voltage of polyamide films at 110°C.

in nitrogen atmosphere. A heating rate of 10°C/min was used. DuPont 1090 thermal analyzer having a 951 TG module was used for assessing relative thermal stability of polymers.

The electrical conductivity measurements were done at 110 and 130°C. The polymer film was coated with silver using the vacuum deposition technique and then sandwiched between two copper electrodes. The whole system was kept in a sample holder for 1 h to attain a constant temperature. An Aplab high voltage regulated power supply (Model 7331) was used for field variation. Current measurements were done on a 610C Keithley electrometer.

TABLE VI

β Values Calculated from log I vs. $\sqrt{V}$ Plots of Polyamide Films

Sample	Temperature (°C)	β (Theoretical)	β Lower field	β Higher field
C	110	0.155	0.585	0.51
	130	0.108	0.61	0.412
C_3A	110	0.098	0.510	0.29
	130	0.069	0.510	0.366
CA	110	—	0.585	0.51
	130		0.61	0.412
CA_3	110	—	0.49	0.28
	130		0.54	0.24
A	110	—	0.46	0.26
	130		0.55	0.277

Dielectric characteristics were evaluated at 110 and 130°C using a Hewlett Packard impedance analyzer (4192A, LF). Frequency was varied from 10^2 to 10^6 Hz. The temperature of the cell was maintained at ± 2°C by using a contact thermometer and an electric relay.
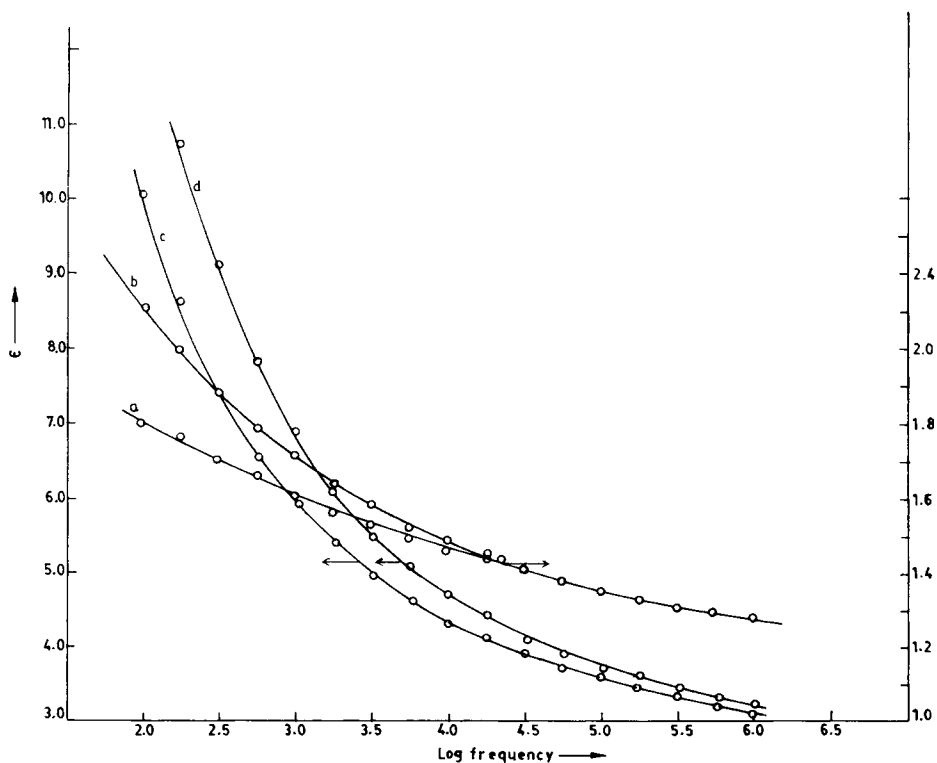

Fig. 6. Dependence of dielectric constant on signal frequency of polyamide films C_3A at 110°C (a) and 130°C (b) and C at 110°C (c) and 130°C (d).
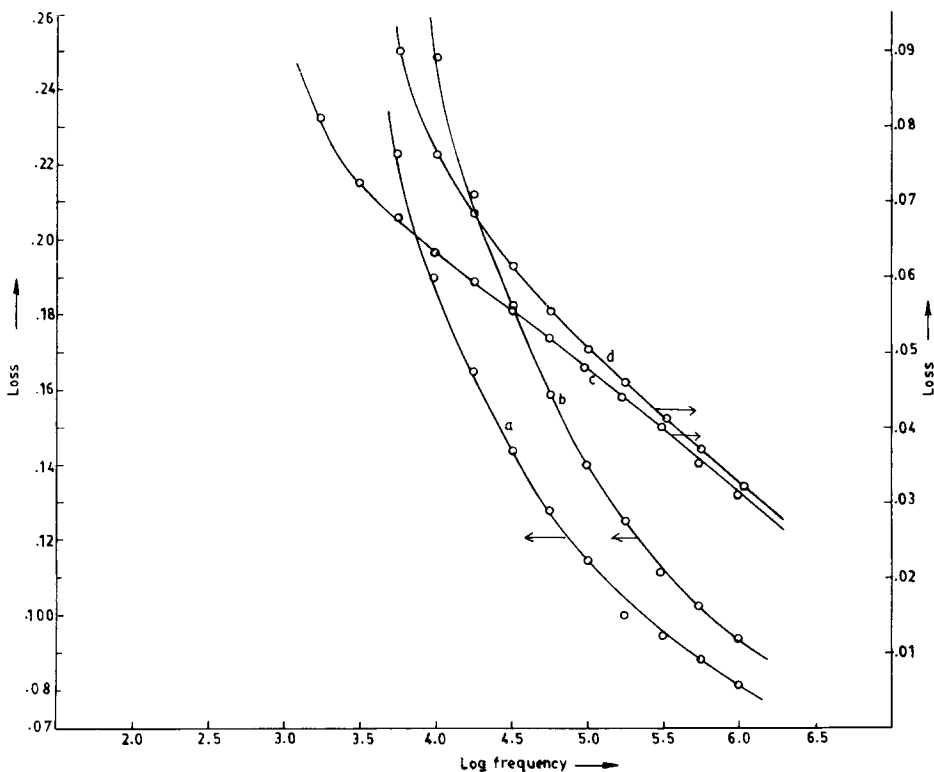
Fig. 7. Plots of tan δ vs. signal frequency of polyamide films C at (a) 110°C and (b) 130°C and C₃A at (c) 110°C and (d) 130°C.

RESULTS AND DISCUSSION

The inherent viscosities of various polyamide samples are given in Table I. The viscosity decreased by increasing the DAB content in the monomer feed. The lowest value was obtained in sample C. The lower (η_{inh}) value in the polymer based on DAB may be attributed to decreased nucleophilicity of the amino group due to the presence of electron withdrawing $-COOH$ group in the monomer.

In the FTIR spectra of polyamide, recorded in KBr pellets using a Digilab FTS 40 spectrophotometer, characteristic bands due to the carboxylic group (1697 cm^{-1}) and the amide group (1655 cm^{-1}) were observed (sample C, Fig. 1). In sample A which did not contain the $-COOH$ group, the absorption band at 1697 cm^{-1} was absent (Fig. 1). In copolyamides, the absorption band at 1697 cm^{-1} gradually increased in intensity as the concentration of DAB monomer increased in the polymer. Heating of the polymer sample at 220°C for 30 min did not influence the position of various IR signals and no additional band due to formation of anhydride group was observed.

In most of the polymer samples a two-step degradation was observed in TG traces recorded in nitrogen atmosphere (Fig. 2). In order to assess the relative thermal stability of polymers, the temperatures of onset and completion of degradation (IDT and T_f) for each step were noted. The temperature of max-

imum rate of weight loss, T_{max}, was recorded from differential thermogravimetric traces. The weight loss observed at T_f was also noted. These results are given in Table II. The loss in weight below 110°C has not been indicated. This loss in weight arises due to loss of absorbed moisture. A weight loss of 7–15% was observed in the temperature range of 125–330°C whereas the major weight loss was observed in the temperature range of 350–800°C. The char yield at 800°C depended on backbone structure and ranged from 39.5 to 50.5%. Weiss et al.[11] have earlier reported a char yield of 50% at 700°C for aromatic polyamide fiber having structure similar to A. This value is similar to the char yield at 700°C in sample A. At 800°C the char yield was lower (41%).

The weight loss observed in the temperature range of 125–330°C may be due to loss of either water or residual solvent (DMAc) or due to decomposition of the polymer backbone. In order to evaluate the weight loss in this temperature range, DSC scans were recorded. Broad endothermic transitions were observed in the DSC traces in the temperature range of 150–300°C (Fig. 3) from which the temperature of onset of endotherm (T_1), extrapolated peak position (T_2), and completion of endotherm (T_3) were noted and are given in Table III.

On increasing the temperature above 350°C, exothermic transitions were observed in DSC traces indicating breakdown of polymer. A good correlation was observed in T_2 values obtained in DSC scans and T_{max} value of TG traces, indicating thereby that the weight loss observed in TG studies is an endothermic process. If the weight loss was due to main chain scission, one would have expected an exothermic process. These studies thus indicate that the weight loss in the temperature range of 120–330°C is due to loss of water and/or DMAc. Water may be strongly associated with the —COOH group or the amide group by hydrogen bonding and, therefore, is lost at elevated temperature.

The electrical properties of polyamide films were evaluated at 110 and 130°C. Variation of current as a function of voltage was determined for various poly-amide films. A linear relationship was observed in log I vs. log V plots in all samples (Fig. 4). The slope of these plots have been calculated at 110 and 130°C and results are given in Table IV. In most of the polyamide films a sublinear behavior was observed.

The resistivity of polyamide film depended on the structure of the polymer, temperature, and field. An increase in —COOH content in the backbone resulted in a decrease in resistivity and lowest resistivity was observed in sample C which contained maximum content of the pendant —COOH group in the backbone (Table V).

A plot of log I vs. $V^{1/2}$ indicated a linear relationship. A voltage-dependent variation in slope was observed in most of the samples. An increase in temperature resulted in a slight increase in the slope Figure 5. The slope values were calculated at low and high fields and results are given in Table VI.

The Schottky coefficient β was also calculated using the equation

$$\beta = \frac{1}{kT} \left(\frac{e^3}{4\pi\epsilon\epsilon_0 d} \right)^{1/2}$$

where k is the Boltzmann constant, T is the temperature in degrees Kelvin, e is the electronic charge, ϵ is the dielectric constant, ϵ_0 is the permittivity of free

space, and d is the thickness of the film. The slopes of log I vs. $V^{1/2}$ at two temperatures have been compared with the theoretical β at 1 MHz for two samples C_3A and C in Table VI. These results show that in C_3A polyamide film at higher temperature and field the observed slope value is more than twice the theoretical β value, indicating the possibility of a Poole–Frenkel type electronic conduction. In the polyamide film C the slope values are four or five times the β theoretical values at high temperature. The mechanism of conduction might be a combination of electronic and ionic types.

A predominantly ionic conduction mechanism has been suggested at higher temperature for aromatic polyamides while at lower temperature electron conduction is predominant.[12] The frequency dependence of dielectric constant and loss (tan δ) for the films C and C_3A are shown in Figures 6 and 7. Increasing the frequency at a given temperature resulted in a decrease in dielectric constant and loss value, showing that lattice vibration is dominating over the applied frequency. The dielectric constant became almost constant above 100 kHz and was in the region of 3.7–3.2 for sample C. These polyamide films were highly lossy materials.

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