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Processable Heat-Resistant Polymers. XII. Polyamideimides from N-(p-Carboxy Phenyl) Trimellitimide

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ABSTRACT

Polyamideimides were prepared by reacting the diacidchloride of N-(p-carboxy phenyl) trimellitimide and ethylene diamine or hexamethylene diamine at 30-70°C. The polymers were characterized by nitrogen analyses and IR spectra. The solution, thermal, electrical, and a few other properties of the polymers were studied. The polymers were found to be soluble in highly polar solvents. The solubility parameter was calculated from Small's group contribution which agrees well with the experimental value. X-ray diffraction data indicated that the polymers are crystalline. T_g of the polymers calculated from DTA curves was found to be above 225°C. Dielectric behavior of the polymers was also studied at room temperature (~30°C).

INTRODUCTION

New linear polymers such as polyimides [1] and polybenzimidazoles [2] are highly thermostable but poorly processable. To achieve workable processability, some amount of thermal stability must be

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sacrificed. Such a compromise between heat resistance and processing ease has led to the development of copolyimides [3-8]. In our present program for the development of processable heat-resistant polymers, we have prepared a group of copolyimides such as polyamideimides [9-14] and polyesterimides [15-18]. We wish to report the synthesis and comparative study of polyamideimides obtained from the diacid chloride of N-(p-carboxy phenyl) trimellitimide and ethylene diamine or hexamethylene diamine.

EXPERIMENTAL

Characterization of Polyamideimides. Viscosity measurements were carried out in a 0.5% (w/v) solution in N,N-dimethylformamide (DMF) at 30°C using an Ubbelhode suspended level viscometer.

The density of the polymer samples was determined by means of a small pycnometer in dry benzene at 30°C.

Infrared spectra were recorded with a Perkin-Elmer 237B spectrophotometer using a nujol mull.

X-ray diffraction diagram was recorded with a Dorn I (USSR) X-ray diffractometer using Ni-filtered CuKα radiation.

Solubility Characteristics. Polyamideimide samples (0.02 g) were placed in 2 mL of various solvents and allowed to stand for 2 weeks [12, 13]. The polymers were then observed in order to judge the solvent effect such as swelling or dissolution. A plot of solubility parameter (δ) vs hydrogen bonding index (γ) of the solvents used was prepared. The midpoint of the solubility parameter range was chosen as the solubility parameter of the polymer.

Thermal Behavior. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were made simultaneously with a Hungarian Mom Derivatograph of the Paulik Paulik Erdey system. The measurements were recorded in air at a heating rate of 10°C/min.

Isothermal Aging. The polymer samples were isothermally heated at 200°C in air in a specially designed aging oven (Thermogravimetric Analyser, Planning and Development Division, Fertiliser Corporation of India) to measure the weight loss at different time intervals.

Electrical Properties. Dielectric constant (ϵ') and dielectric loss (tan δ) of polymers at room temperature (~30°C) were measured with a polymer pellet of 1.253 cm diameter and thicknesses of 0.201 cm (PAI-1) and 0.177 cm (PAI-2) using a General Radio Capacitance Bridge (Type-716C)and a Q-Meter (Mircony Circuit Magnification Meter, Type-329G) at 4×10^2-10^7 Hz.

Materials. Trimellitic anhydride (TMA) was obtained from Tokyo Kasei Industries, Japan, and used after crystallization from acetic anhydride [19].

p-Amino benzoic acid (E. Merck, India) was crystallized from ethanol.

Hexamethylene diamine (Fluka, Switzerland) and ethylene diamine (SD, India) were used after distilling under reduced pressure in a nitrogen atmosphere.

Thionyl chloride (SD, India) was freshly distilled before use.

DMF (E. Merck, India) was dried over phosphorus pentoxide and distilled under reduced pressure (~20 torr). All other solvents used were pure grade.

Monomer Synthesis

Synthesis of N-(p-Carboxy phenyl) Trimellitimide [20].

N-(p-Carboxy phenyl) trimellitimide (CPTM) was prepared by condensing TMA and p-amino benzoic acid in DMF by following the procedure of Maiti et al. [16].

Preparation of Diacid Chloride of CPTM [20].

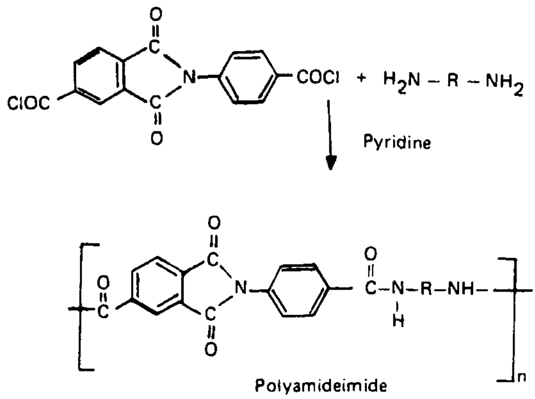
The diacid chloride of CPTM was prepared by reacting CPTM and thionyl chloride for 14 h. The details of the experimental procedure have been reported elsewhere [11].

Polymer Synthesis

The polyamideimide was prepared by reacting the diacid chloride of CPTM with diamine. A typical run is as follows: 3.48 g (10 mmol) of the diacid chloride of CPTM were dissolved in 25 mL DMF in a three-necked flask fitted with a thermometer, a stirrer, and a nitrogen purge tube. 1.16 g (10 mmol) of hexamethylene diamine or 0.60 g (10 mmol) of ethylene diamine and 1.58 g (20 mmol) of pyridine were added to the mixture at low temperature (~5°C) with stirring. The reaction mixture was stirred at room temperature for 2 h, at 40-50°C for 8 h, and finally at 60-70°C for 5 h. At the end of the reaction the mixture was poured into ice water and filtered immediately. It was dried, washed several times with chloroform, and finally purified by dissolving in DMF and precipitated by methanol.

RESULTS AND DISCUSSION

The polymerization of the diacid chloride of CPTM and hexamethylene diamine or ethylene diamine is, in fact, a polyamidization reaction involving a diacid chloride and a diamine. The polyamide-imide obtained by the polycondensation reaction may be schematically represented as follows:



	R
PAI-1	$-(CH_2)_2-$
PAI-2	$-(CH_2)_6-$

Pyridine or triethylamine was used as an acid acceptor to enhance the rate of polymerization reaction. The molecular weight of the polymer may be controlled by changing the reaction conditions, solvents, and preferably by the use of suitable catalysts.

Polymer Characterization

The polyamideimides prepared were characterized by nitrogen analyses and IR spectra. The general characteristics of the resulting polymers are presented in Table 1. The characteristic IR bands of the polymers (Fig. 1) were observed near 1785 and 1720 cm^{-1} due to symmetrical and assymmetrical carbonyl stretching of imides, at 720 cm^{-1} possibly due to the ring carbonyl deformation of imides, and at 1665 and 1530 cm^{-1} due to amide groups. A broad band near 3300-3400 cm^{-1} was due to –NH– stretching of amides and at 1445 cm^{-1} due to the C–H bending vibration of methylene groups present in the macromolecular chain. The C–H stretching band for the methylene groups which were observed near 2900-3000 cm^{-1} unfortunately superimposes with the broad nujol band near 3000 cm^{-1} (Fig. 1).

Solution Viscosity Behavior. The inherent viscosity of the polymers (PAI-1 and PAI-2) is shown in Table 1. Shashoua et al. [21] reported that polyamides prepared from ethylene diamine and hexamethylene diamine possess nearly the same inherent viscosity value. Stephens [22] reported a group of high melting polyamides prepared by interfacial polycondensation of 4,4'-sulfonyl dibenzoyl

TABLE 1. Yields and Physical Properties of the Polyamideimides

Polymer	Solvent used	Yield (%)	Inherent[a] viscosity (dL/g)	Density (g/cm^3)	T_g[b] (°C)	Nitrogen (%) Calc	Nitrogen (%) Found
PAI-1	NMP[c]	76-77	0.317	1.20	235	12.53	12.01
	DMF	69-70	0.263 (0.278)[d]	1.19	-	12.53	12.16
PAI-2	NMP[c]	80-83	0.330	1.17	225	10.74	10.41
	DMF	72-74	0.260 (0.285)[d]	1.16	-	10.74	10.43

[a] Measured in 0.5% (w/v) solution in DMF at 30°C.
[b] Calculated from DTA curve (Fig. 5).
[c] NMP = N-methyl-2-pyrrolidone.
[d] Obtained after 24 h reaction.

dichloride and aliphatic diamines. It was observed that the polyamide having hexamethylene diamine units possesses higher inherent viscosity than the polymer prepared from ethylene diamine. In our case the polyamideimides prepared from ethylene diamine or hexamethylene diamine possess nearly the same inherent viscosity.

The inherent viscosity of the polymers (PAI-1 and PAI-2) in DMF at room temperature (~30°C) decreases to some extent during the initial period of 5 d and thereafter remains practically constant (Fig. 2). The decrease of inherent viscosity during the period of 25 d is about 5.6% for PAI-1 and 4.5% for PAI-2 of the initial value. This is in contrast to the behavior of soluble polyamic acids which do not generally form stable solution. The viscosity of such a solution decreases on standing [15].

Density and Crystallinity. For a polymer to crystallize, the molecules must have sufficient mobility so that successive individual atoms and groups in the polymer molecule can move into precise position in the crystalline lattice which is being formed. The x-ray diffraction data of PAI-1 and PAI-2 (Fig. 3) indicate that PAI-1 is more crystalline than PAI-2. The smaller size of ethylene unit fits into the crystal lattice of the polymer and hence induces a greater degree of crystallinity [23]. The hexamethylene units represent the amorphous zone of the polymer. The presence of this will be reflected in the somewhat higher solubility, lower thermal resistance, and lower density of PAI-2 compared with PAI-1.

Solubility Behavior. Solubilities of polyamideimides are listed in Table 2. The polymers were found to be soluble in highly polar solvents. Similar solubility behavior has been reported by Kurita et al. [24] as well as by Maiti et al. [9-13] for other polyamideimides. The higher solubility of polyamideimides in highly polar solvents compared with polyimides of similar structure may be

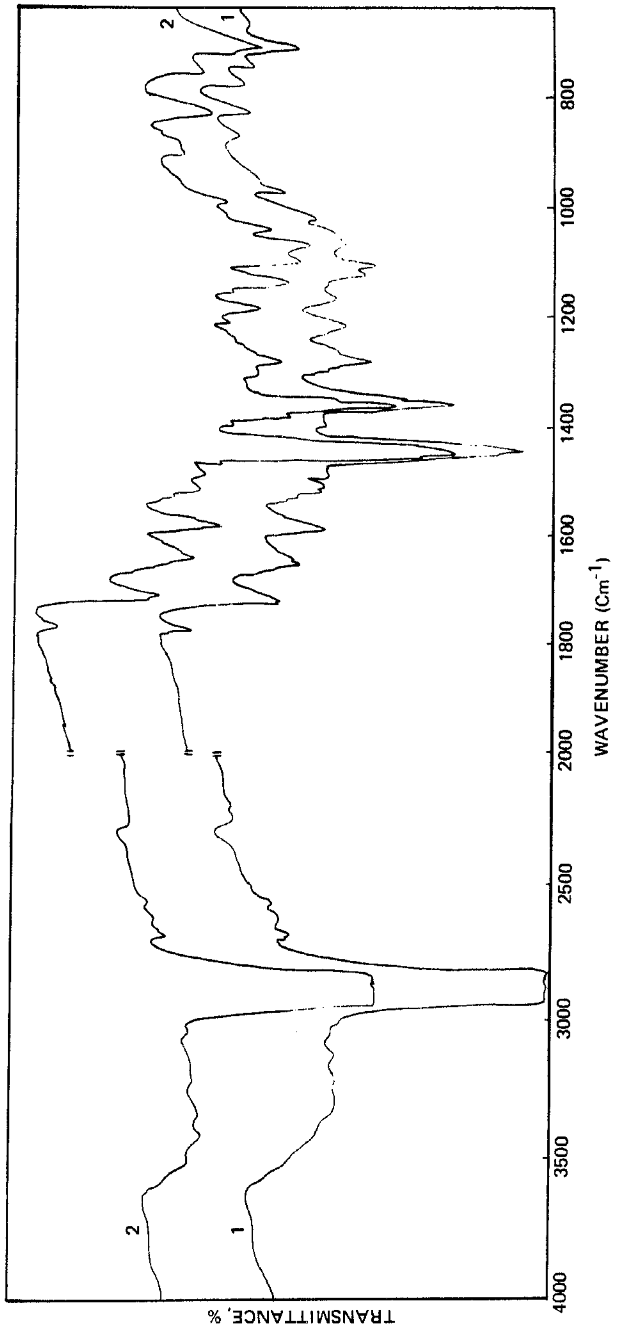


FIG. 1. IR spectra of the polyamideimides PAI-1 (1) and PAI-2 (2).

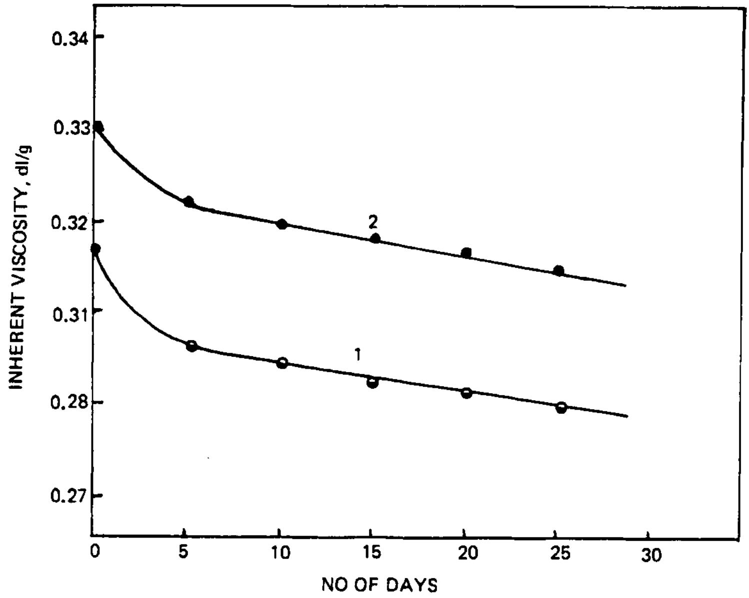


FIG. 2. Aging of the polyamideimide solution in DMF at room temperature: PAI-1 (1) and PAI-2 (2).

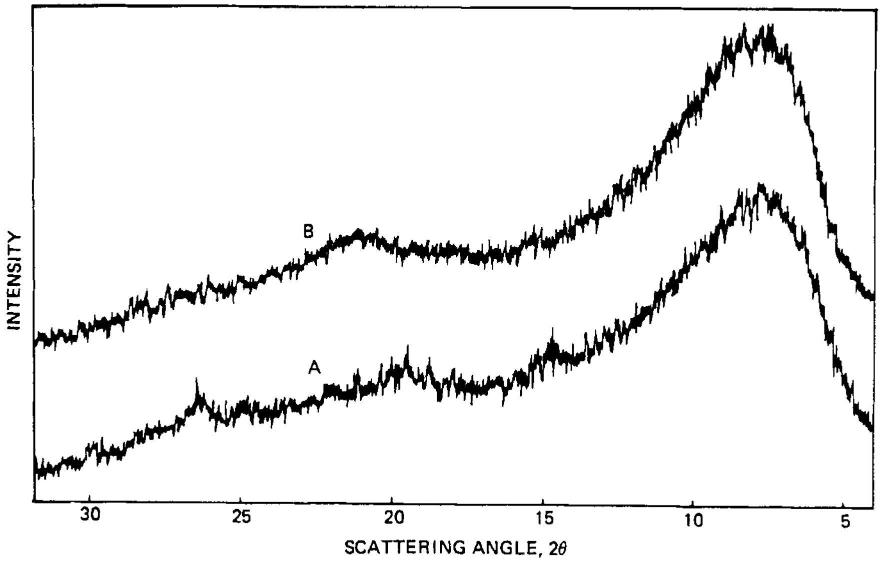


FIG. 3. X-ray diffraction diagram of PAI-1 (A) and PAI-2 (B).

TABLE 2. Solubility Characteristics of the Polyamideimides

Solvents	Solubility parameter (δ)	Hydrogen bonding index (γ)	Solubility[a]	
			PAI-1	PAI-2
Benzene	9.16	2.2	-	-
Carbon tetrachloride	8.55	2.2	-	-
Cyclohexane	8.19	2.2	-	-
Acetone	9.62	5.7	-	-
Cyclohexanone	10.42	6.4	±	±
Chloroform	9.16	2.2	-	-
Cyclopentanone	10.53	5.2	±	±
Decane	7.74	2.2	-	-
N,N-Dimethylformamide	11.79	6.4	+	+
Dimethyl sulfoxide	13.00	5.0	+	+
Chlorobenzene	9.67	2.7	-	-
Ethyl acetate	8.91	5.2	-	-
1,4-Dioxane	10.13	5.7	-	-
Ethylene dichloride	9.86	2.7	-	-
Ethyl methyl ketone	9.45	5.0	-	-
n-Hexane	7.27	2.2	-	-
Methyl acetate	9.46	5.2	-	-
Nitrobenzene	10.00	3.2	-	-
n-Pentane	77-02	2.2	-	-
Toluene	8.93	3.8	-	-
Tetrahydrofuran	9.10	5.3	±	±
N-Methyl-2-pyrrolidone	11.00	5.6	+	+
Diacetone alcohol	9.77	6.9	-	-
m-Cresol	10.20	-	+	+
Formic acid	12.10	-	+	+
N,N-Dimethylacetamide	10.80	-	+	+

(continued)

TABLE 1 (continued)

Solvents	Solubility parameter (δ)	Hydrogen bonding index (γ)	Solubility[a]	
			PAI-1	PAI-2
Conc H_2SO_4	-	-	+	+
Methylene dichloride	9.88	2.7	-	-
Methyl isobutyl ketone	8.40	5.0	-	-

[a] Solubility keys: + soluble, ± partially soluble or swelling, - insoluble.

explained on the basis of the general properties of copolymers [25]. Copolymers, in general, decrease the chain symmetry and consequently the degree of crystallinity in polymers, which in turn increases the solubility.

Solubility Parameter. A plot of solubility parameter (δ) vs hydrogen bonding index (γ) for the solvents shown in Table 2 is illustrated in Fig. 4. The solubility parameter for polymers is calculated from Small's group contributions [26]. The molar attraction constant, G, values for different groups used here have been reported by Hoy [27, 28]. These are used to calculate the solubility parameter (δ) of the polymers using the relationship

$$\delta = \rho(\Sigma G/M)$$

where ΣG is the sum of Small's group contribution, M is the formula weight of the polymer repeat unit, and ρ is the density of the polymer. The δ values (11.13 for PAI-1 and 10.87 for PAI-2) calculated from the above equation are in good agreement with the value of δ, i.e. 10.95, obtained from the solubility map as discussed earlier (Table 3).

Thermal Behavior. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) data of polyamideimides in air are presented in Fig. 5. Thermogravimetric analysis indicates that an initial loss of about 4-5% occurs for both the polymers at 100-105°C which is due to the loss of moisture or entrapped solvent present in the polymer. Subsequently there is only 6% weight loss for PAI-1 and 7% weight loss for PAI-2 at 400°C. The glass transition temperature, T_g, of the polymers (DTA curves, Fig. 5) was found to be 235°C for PAI-1 and 225°C for PAI-2. The degradation of the polymers follows a complex process in which the maximum weight loss occurs at 410-525°C for PAI-2 and at 500-620°C for PAI-1.

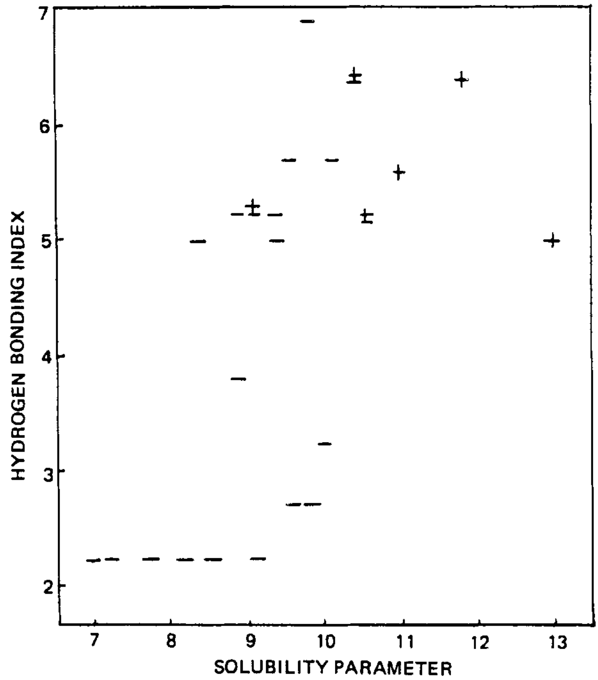


FIG. 4. Solubility map of the polyamideimides.

The higher thermal stability and T_g of PAI-1 compared with that of PAI-2 may be due to the greater rigidity of PAI-1 and also to the higher degree of crystallinity (Table 1). Similar thermal behavior has been observed in different polyamides having ethylene or hexamethylene units in the main chain [29]. In crystalline polymer, intermolecular bonding increases the attractive force between adjacent polymer chains and increases the thermal energy required to separate these chains from each other and hence produce higher T_g and T_m values [30]. Similar thermal behavior has also been observed for other polyamides prepared from aliphatic diamines [22].

Isothermal Aging. The weight losses of the polymers heated at 200°C for 12 h are shown in Table 4. It has been observed that initially a 4.6% weight loss for PAI-1 and a 5.3% weight loss for PAI-2 occurs within 1 h which are possibly due to the loss of moisture or entrapped solvent. Subsequently there are only a 5.3% weight loss for PAI-1 and a 6.5% weight loss for PAI-2 after 12 h heating. However, the polyamideimides prepared from aliphatic diamines (PAI-1 and PAI-2) possess lower thermal stability compared with the polyamideimides prepared from aromatic diamines [22].

TABLE 3. Calculated Solubility Parameter of the Polyamideimides

Functional group	G value (cal· cm^3)$^{1/2}$	Number of functional groups/ substitution in the polymer repeat unit	Total G values for polymers (cal·cm^3)$^{1/2}$ PAI-1	Total G values for polymers (cal·cm^3)$^{1/2}$ PAI-2
$-CH=$ (aromatic)	117.12	7	819.84	819.84
$=C=$ (aromatic)	98.12	5	490.60	490.60
$-CH_2-$	131.50	2	263.00	
		6		789.00
$>C=O$	262.96	4	1051.84	1051.84
$-\overset{\vert}{N}-$	61.08	1	61.08	61.08
$-NH-$	180.03	2	360.06	360.06
Five-membered ring	20.99	4	20.99	20.99
Six-membered ring	-23.44	2	46.88	-46.88
Meta-substitution	6.60	1	6.60	6.60
Para-substitution	40.33	2	80.66	80.66
		ΣG	3107.79	3633.79
Solubility parameter, δ			11.13	10.87

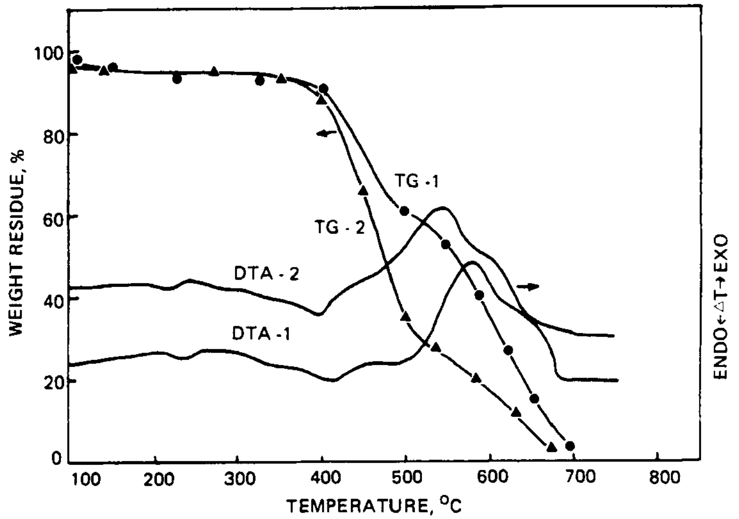


FIG. 5. Thermogravimetric and differential thermal analysis of PAI-1 (DTA-1, TG-1) and PAI-2 (DTA-2, TG-2).

TABLE 4. Isothermal Aging of the Polyamideimides

		% Weight loss at 200°C in air after						
	Polymer	1 h	2 h	4 h	6 h	8 h	10 h	12 h
	PAI-1	4.6	1.0	0.7	0.7	0.8	1.0	1.1
Cumulative weight loss		-	5.6	6.3	7.0	7.8	8.8	9.9
	PAI-2	5.3	1.2	0.8	0.9	1.1	1.1	1.4
Cumulative weight loss		-	6.5	7.3	8.2	9.3	10.4	11.8

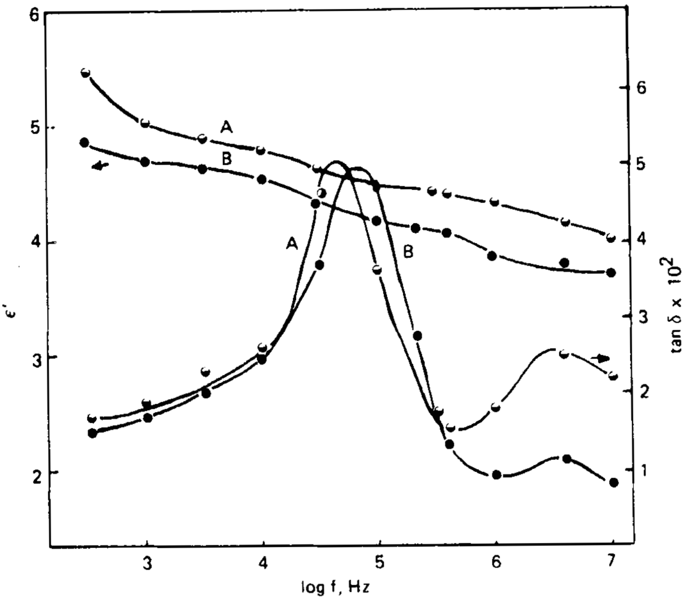


FIG. 6. Variation of dielectric constant (ε') and dielectric loss (tan δ) of PAI-1 (A) and PAI-2 (B).

Electrical Properties. Variation of dielectric constant (ϵ') and dielectric loss ($\tan \delta$) for polymers (PAI-1 and PAI-2) with frequency, f, at room temperature (~30°C) is presented in Fig. 6. The dielectric constant for the polymers gradually decreases with an increase of frequency. This trend has also been observed in other polyamideimides [11-13]. This may be explained on the basis of the fact that in the applied electric field, polar groups in the macromolecule tend to orient in the direction of the applied field. In an alternating electric field, a particular polar group will be flexible enough to respond at low frequency but not flexible enough to respond at high frequency and consequently the dielectric constant decreases at higher frequency values [31]. The plot of $\tan \delta$ vs log f shows two maxima at 4.63×10^4 and 3.16×10^6 Hz for PAI-1, at 7.35×10^4 and 3.39×10^6 Hz for PAI-2. The high dielectric loss of these polymers at these frequency ranges may be due to the dipole group losses of the polar groups present in the polymer chain. It may also be due to the orientational polarization of the polar groups in the macromolecular chain in the direction of the applied field. The relaxation time (τ) values calculated at these maxima were found to be 3.44×10^{-6} and 5.04×10^{-8} s for PAI-1 and 2.16×10^{-6} and 4.69×10^{-8} s for PAI-2. τ, determined by the equation $2\pi f_{\max} \tau = 1$, is the average or most probable relaxation time that is determined by a set of structural units of different mobility [32].

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