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Processable Heat-Resistant Polymers. IX. Synthesis and Properties of Polyamideimide from N-(p-Carboxy Phenyl) Trimellitimide and p,p′-Di-(amino Phenyl) Sulfone

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ABSTRACT

A novel polyamideimide was synthesized by reacting p,p′-di-(amino phenyl) sulfone and N-(p-carboxy phenyl) trimellitimide or its diacid chloride derivative. The polymer was found to be soluble in highly polar solvents. The polymer was characterized by elemental analyses and IR spectrum. It is found to be amorphous and of low molecular weight. The polymer is fairly thermostable, having a T_g of 210-220°C. Thermogravimetric determination revealed that the polymer underwent 17% weight loss at 375°C in air. The dielectric constant of the polymer at 1 kHz was 3.74 at 30°C. The electrical conductivity of the polymer was also measured.

INTRODUCTION

Polyamideimide (PAI) offers a class of resin which combines the advantage of high temperature stability with the ease of processability [1-3]. Like polyesterimide [4-6], PAI is a commercially important processable heat-resistant polymer.

In our present program of development of processable heat-resistant polymers, we have successfully synthesized various types of copolyimides such as polyesterimides [7-9] and polyamideimides [10-14]. In this present communication we wish to report the synthesis and properties of a polyamideimide prepared by reacting p,p'-di-(amino phenyl) sulfone and N-(p-carboxy phenyl) trimellitimide or its diacid chloride derivative.

EXPERIMENTAL

Characterization and Properties of Polyamideimide

Viscosity measurements were carried out in 0.5% (g/mL) solution in DMF at 30°C using a Ubbelhode suspended level viscometer.

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

Infrared spectrum was 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. The polymer was then observed in order to judge solvent effects such as swelling and dissolution.

Aging

The polymer was heated in a specially designed aging oven in air or nitrogen atmosphere to measure the weight loss at different temperatures.

Thermal Properties

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the polymer 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 5°C/min.

Electrical Properties

The dielectric properties and electrical conductivity of the polymer at room temperature (~30°C) were measured with a pellet of 1.253 cm diameter and 0.267 cm thickness by using a General Radio Capacitance Bridge (Type 716C) and a Q-Meter (Mircony Circuit Magnification Meter, Type 329G) at 10^2-10^7 Hz.

Materials

Trimellitic anhydride (TMA) was obtained from Tokyo Kasei Industries, Japan, and was used after crystallization from acetic anhydride [15]. p,p'-Di-(nitro phenyl) sulfone (HOC, India) and p-amino benzoic acid (E. Merck, India) were crystallized from ethanol. Thionyl chloride (SD, India) was freshly distilled before use. N,N-Dimethylformamide was dried over phosphorus pentoxide and distilled under reduced pressure (~ 20 torr). All other solvents used were pure grade.

Monomer Synthesis

Synthesis of p,p'-Di-(amino Phenyl) Sulfone

p,p'-Di-(amino phenyl) sulfone (DAPS) was prepared by reducing p,p'-di-(nitro phenyl) sulfone with stannous chloride and hydrochloric acid in ethyl acetate medium by following the standard method [16].

Synthesis of N-(p-carboxy Phenyl) Trimellitimide

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. [17].

Preparation of Diacid Chloride Derivative of CPTM

The diacid chloride of CPTM was synthesized by reacting CPTM with thionyl chloride for 14 h. The details of the experimental procedure were reported elsewhere [13].

Polymer Synthesis

PAI was prepared by following two different methods.

Synthesis of PAI from CPTM by Low Temperature Polycondensation (Method A)

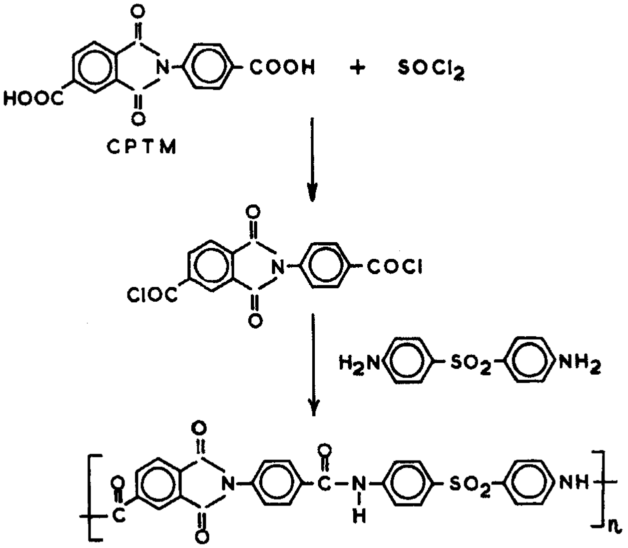
Polyamideimide was generally prepared directly from CPTM by low temperature polycondensation in the presence of thionyl chloride [10, 18, 19]. A typical run may be described as follows: 3.11 g (10 mmol) of CPTM was dissolved in 30 mL DMF in a 100-mL three-necked flask fitted with a thermometer and a calcium chloride drying tube. The solution was cooled to -10°C, 3.0 g (25 mmol) of thionyl chloride was added, and the solution was stirred for 1-2 min. 2.48 g (10 mmol) of DAPS and 1.97 g (25 mmol) of pyridine were added to the mixture. The solution was vigorously stirred for 9 h at 0-0.5°C and then 1 h at room temperature. At the end of the reaction the mixture was poured into ice water. The precipitated polymer was isolated by filtration, washed with chloroform, and finally purified by dissolving in DMF and precipitated by methanol.

Synthesis of PAI via Diacid Chloride of CPTM (Method B)

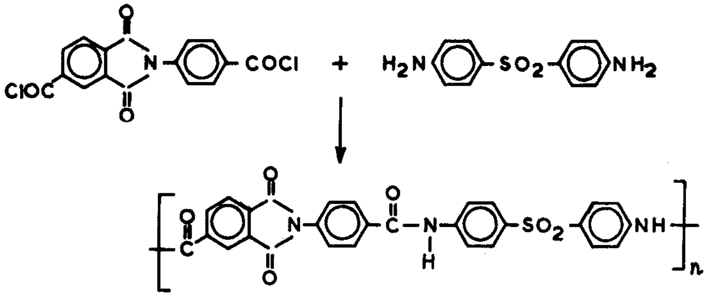
The diacid chloride of CPTM was reacted with DAPS to form polyamideimide. A typical example is as follows: 3.48 g (10 mmol) of diacid chloride of CPTM was dissolved in 35 mL DMF in a three-necked flask fitted with a stirrer, a thermometer, and a nitrogen purge tube. 2.48 g (10 mmol) of DAPS and 1.58 g (20 mmol) of pyridine were added to the mixture with stirring. The solution was stirred at room temperature for 2 h, at 40-50°C for 5 h, and finally at 60-70°C for 3 h. At the end of the reaction the mixture was poured into ice water. The precipitated polymer was filtered, washed several times with chloroform, and finally purified by dissolving in DMF and precipitated by methanol.

RESULTS AND DISCUSSION

The reaction between CPTM or its diacid chloride with DAPS is, in effect, a polyamide formation reaction involving a dicarboxylic acid or its diacid chloride derivative and a diamine. The polymer obtained by the low temperature polycondensation method (Method A) may be schematically represented as follows:



However, the intermediate acid chloride formation as shown in the above-mentioned reaction is evident from the reaction scheme of Method B:



No catalyst was used in these polymerization reactions. Pyridine was used as an acid acceptor to facilitate the polycondensation reaction. The reaction may be successfully controlled by changing reaction conditions, solvents, and by the use of a suitable catalyst.

Polymer Characterization

The polyamideimide prepared was characterized by elemental (nitrogen and sulfur) analyses and IR spectroscopy. The general characteristics of the polymer are shown in Table 1. The characteristic IR bands of the polymer (Fig. 1) were observed near 1780 and 1720 cm^{-1} due to symmetrical and assymmetrical carbonyl stretching of imides; at 1640 and 1535 cm^{-1} due to amide groups. Two sharp bands near 1305 and 1150 cm^{-1} were probably due to the symmetrical and asymmetrical O=S=O stretching of sulfone groups present in the polymer backbone. A broad >NH stretching band of amide was observed near 3300-3400 cm^{-1}.

Solution Viscosity Behavior

The inherent viscosity of the PAI is shown in Table 1. The low inherent viscosity of the polymer corresponds to low molecular weight. However, the inherent viscosity of the polymer prepared by Method A is lower than that of the polymer obtained by Method B.

Polyamic acid, the precursor of polyimides, does not form stable solutions. On standing, the inherent viscosity of the polymer decreases with time [20, 21]. The inherent viscosity of this polymer in DMF decreases slightly ($< 9.0\%$) even after 25 d at room temperature (~ 30°C) (Fig. 2).

TABLE 1. Yields and Physical Properties of Polyamideimide

Method of polymerization	Solvent used	Yield (%)	Inherent viscosity[a] (dL/g)	Density (g/cm^3)	T_g[b] (°C)	Nitrogen content (%)		Sulfur content (%)	
						Calc	Found	Calc	Found
A	DMF	66-67	0.12 (0.15)[c]	1.16	210	8.03	7.76	6.11	5.88
	NMP	70-72	(0.18)[c]	1.18	-	8.03	8.07	6.11	6.01
B	DMF	73-76	0.19 (0.21)[d]	1.18	220	8.03	7.81	6.11	5.83
	NMP	78-80	(0.24)[d]	1.20	-	8.03	7.97	6.11	6.17

[a] Measured in 0.5 wt% solution in DMF at 30° C.
[b] Calculated from DTA curve (Fig. 5).
[c] Measured in DMF at 30° C after 18 h reaction.
[d] Measured in DMF at 30° C after 16 h reaction.

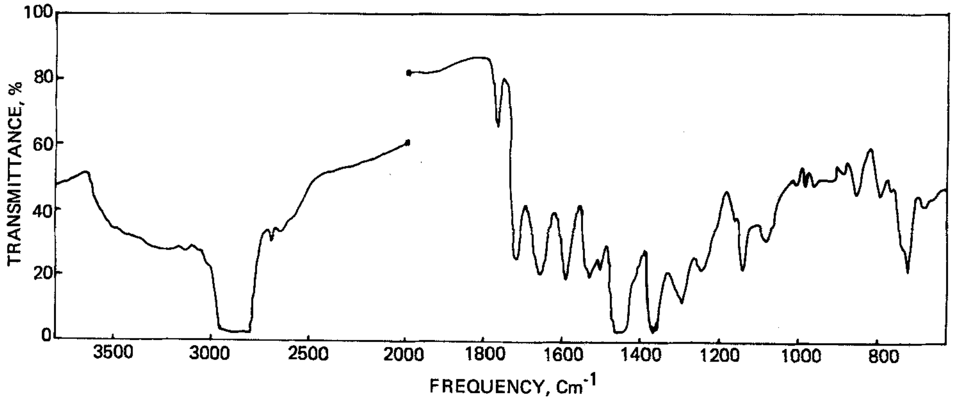


FIG. 1. IR spectrum of polyamideimide.

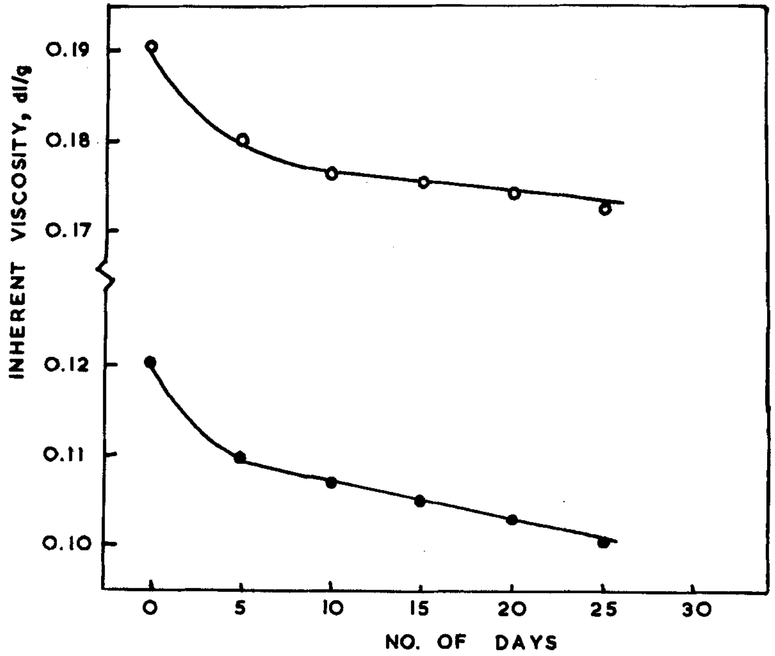


FIG. 2. The plot of the inherent viscosity of the polymer in DMF solution against the storage time at room temperature.

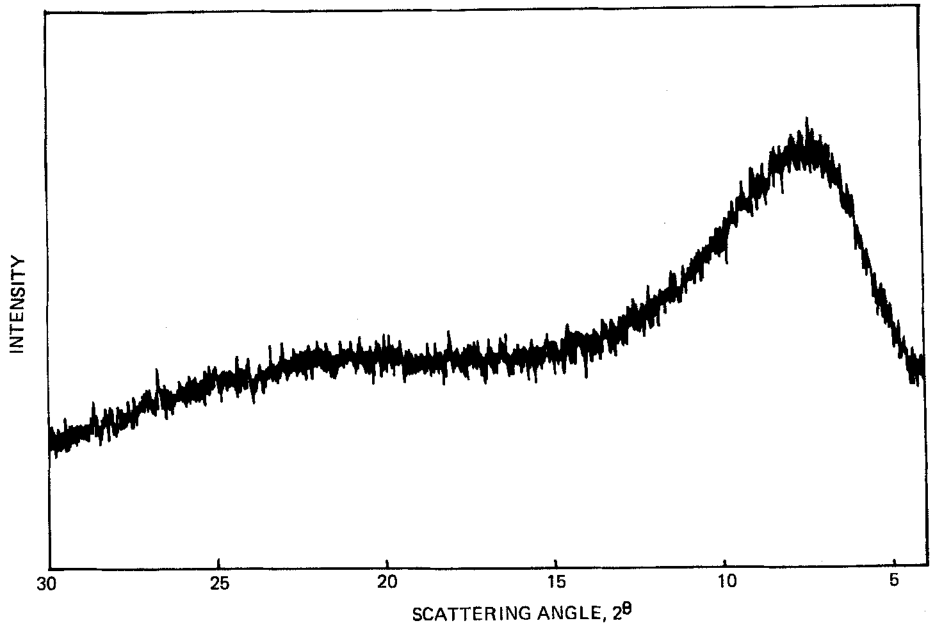


FIG. 3. X-ray diffraction diagram of polyamideimide.

For high temperature coating application such as cable enamels, low molecular weight amorphous materials are desirable. X-ray diffraction data (Fig. 3) show that there are no sharp peaks in the intensity vs scattering angle (2θ), which indicates that the polymer is amorphous.

Aging

At elevated temperature the performance of the PAI appears to be marginally lower than that obtained with polyimides [20]. The loss of weight after heating the polymer obtained by following Method B in air for 1 h at different temperatures and also in nitrogen atmosphere at 350°C for 10 h (Table 2) reveals that the polymer may be safely used in a moderately high temperature range (~ 200°C).

Solubility Characteristics

The solubility of PAI is listed in Table 3. The polymer is found to be soluble only in highly polar solvents. PAI closely resembles polyesterimides in solubility characteristics.

A plot of solubility parameter (δ) vs hydrogen bonding index (γ) for solvents as shown in Table 3 is illustrated in Fig. 4. The value

TABLE 2. Thermal Aging of Polyamideimide[a]

	% weight loss after heating in air for 1 h at					% weight loss after heating the polymer under nitrogen atmosphere at 350°C for 10 h
	100 °C	200 °C	300 °C	400 °C	500 °C	
	7.1	3.1	4.6	11.8	28.2	18.2
Cumulative weight loss	-	10.2	14.8	26.6	54.8	

[a] Prepared by Method B.

TABLE 3. Solubility Characteristics of Polyamideimide

Solvents	Solubility parameter (δ)	Hydrogen bonding index (γ)	Solubility[a]
Acetone	9.62	5.7	-
Benzene	9.16	2.2	-
Carbon tetrachloride	8.55	2.2	-
Cyclohexane	8.19	2.2	-
Chloroform	9.16	2.2	-
Chlorobenzene	9.67	2.7	-
Cyclohexanone	10.42	6.4	±
Cyclopentanone	10.53	5.2	±
Decane	7.74	2.2	-
Diacetone alcohol	9.77	6.9	-
Dimethylsulfoxide	13.00	5.0	+
Dimethylformamide	11.79	6.4	-
Dioxane	10.13	5.7	±
Ethyl acetate	8.91	5.2	-
Ethylene dichloride	9.86	2.7	-

(continued)

TABLE 3 (continued)

Solvents	Solubility parameter (δ)	Hydrogen bonding index (γ)	Solubility[a]
Hexane	7.27	2.2	-
Ethyl methyl ketone	9.45	5.0	-
Methyl acetate	9.46	5.2	-
Methylene chloride	9.88	2.7	-
N-Methyl-2-pyrrolidone	11.00	5.6	+
Methyl isobutyl ketone	8.40	5.0	-
Nitrobenzene	10.00	3.2	-
Pentane	7.02	2.2	-
Toluene	8.93	3.8	-
Tetrahydrofuran	9.10	5.3	±
Formic acid	12.1	-	±
m-Cresol	10.2	-	+
Concentrated H_2SO_4	-	-	+
N,N-Dimethyl acetamide	10.8	-	+

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

obtained from the midpoint of the solubility map (Fig. 4) is found to be 10.90, which may be regarded as the experimental value of the solubility parameter of the polymer.

The solubility parameter may also be calculated from group contributions after Small [22]. The group contributions, i.e., the molar attraction constant G values used here, have been reported by Hoy [23, 24]. The calculated solubility parameter (δ) of the polymer was determined by using the relationship

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

where Σ G 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 (Table 4). This value (10.14) is found to be in fair agreement with the

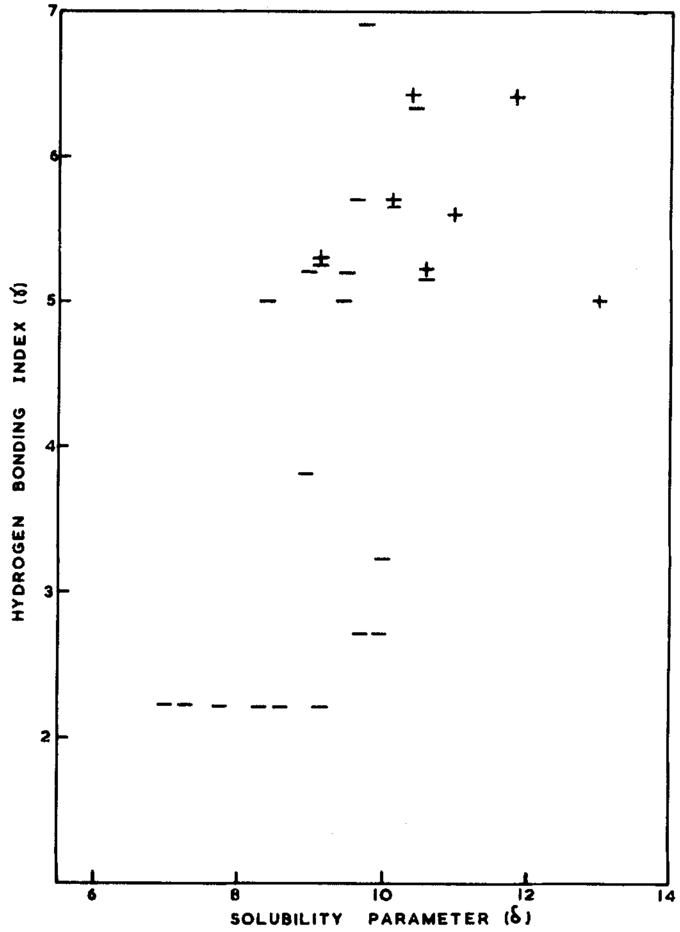


FIG. 4. Solubility map of polyamideimide.

experimental value of δ (10.90) obtained from the solubility map (Fig. 4). However, the exact value for the group contribution of the $-SO_2-$ group was not found in the literature, and we have assumed the value for the $-S-$ group for our calculation (Table 4).

Thermal Behavior

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) data of PAI in air are shown in Fig. 5. Thermogravimetric analysis indicated that an initial weight loss of about 8% occurs up to 100-110°C. This is likely to be the loss of moisture or entrapped

TABLE 4. Calculated Solubility Parameter of Polyamideimide

Functional group	G value $(\mathrm{cal}\cdot\mathrm{cm}^3)^{1/2}$	No. of functional group/substitutions in the polymer unit	Total G values for polymer unit $(\mathrm{cal}\cdot\mathrm{cm}^3)^{1/2}$
$-\overset{\|}{\mathrm{C}}\mathrm{H}$ (aromatic)	117.12	15	1756.80
$=\mathrm{C}=\mathrm{C}$ (aromatic)	98.12	9	883.08
$>\mathrm{C}=\mathrm{O}$	262.96	4	1051.84
$-\overset{\mid}{\mathrm{N}}-$	61.08	1	61.08
$-\mathrm{NH}-$	180.03	2	360.06
Five-membered ring	20.99	1	20.99
Six-membered ring	-23.44	4	-93.76
p-Substitution	40.33	8	161.32
m-Substitution	6.60	1	6.60
$-\mathrm{S}-$[a]	209.42	1	209.42
		$\Sigma G =$	4417.43

∴ Solubility parameter, $\delta = 10.14$

[a]Values of sulfide group, $-\mathrm{S}-$, have been taken for sulfone group $-\mathrm{SO}_2-$.

solvent present in the polymer. Subsequently, there is only 5% weight loss up to 300 or 350°C depending on the method of polymerization. The degradation of the polymer is a single-stage process and maximum weight loss occurs at 400-550°C. From TGA data it is evident that the polymer obtained by Method A is comparatively less thermostable than that obtained by Method B. The glass transition temperature, T_g, of the polymer was found to be 210-220°C depending upon the method of polymerization. The higher T_g and thermal stability of the polymer prepared by Method B may be due to its higher molecular weight. The higher inherent viscosity value (Table 1) also points to the same conclusion.

Electrical Properties

The dielectric constant (ϵ'), dielectric loss (tan δ), and electrical conductivity of the polymer with frequency at room temperature

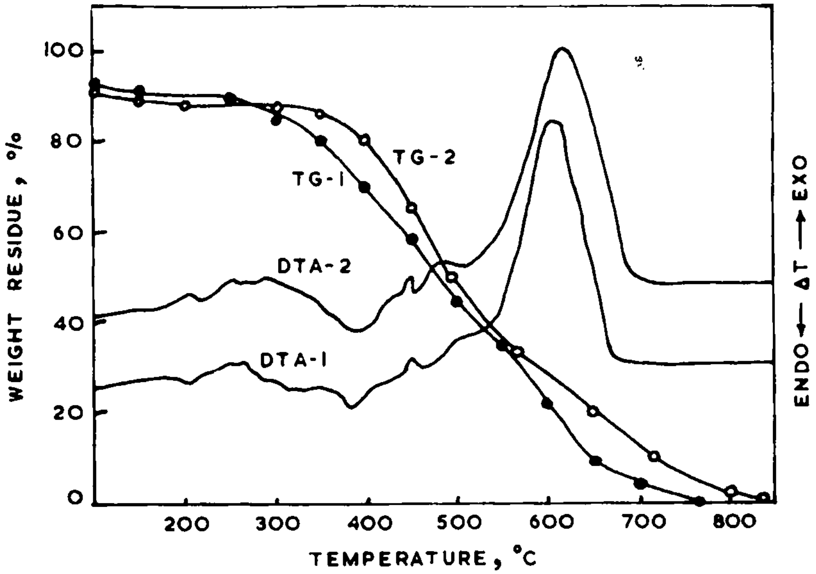


FIG. 5. TGA and DTA curves of polyamideimide. 1 and 2 refer to Methods A and B, respectively.

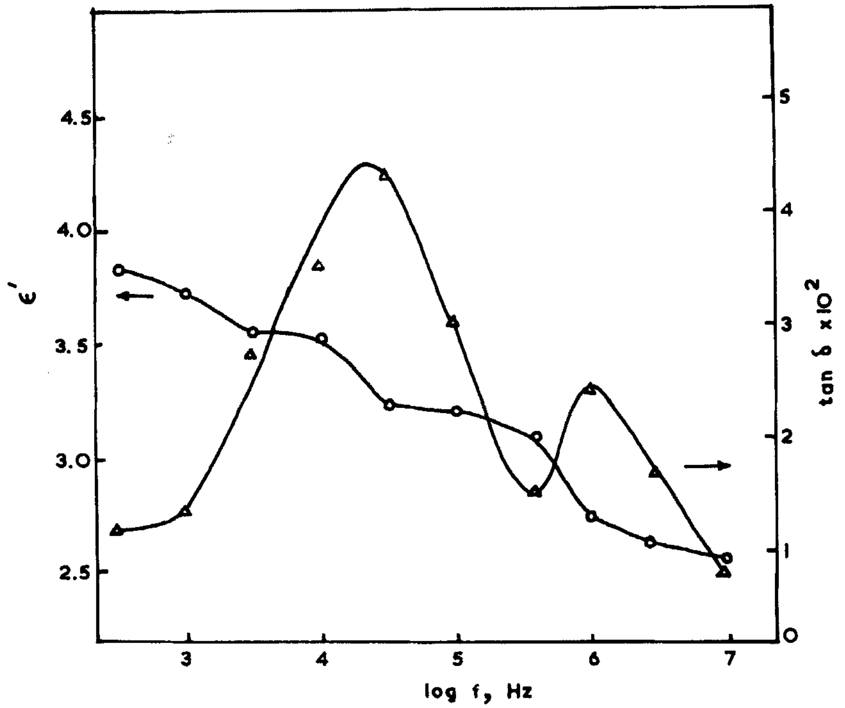


FIG. 6. Variation of dielectric constant (ε') and dielectric loss (tan δ) of the polymer with frequency.

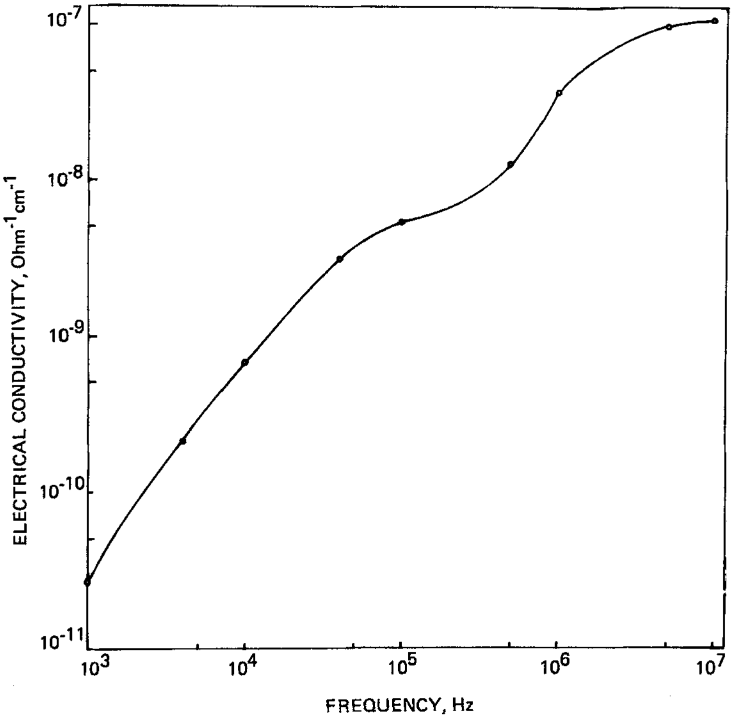


FIG. 7. Variation of specific conductivity of the polymer with frequency.

(~30°C) are represented in Figs. 6 and 7. The dielectric constant of the polymer is very low compared with other polyamideimides [12, 13] and decreases with frequency (Fig. 6). The dielectric loss vs frequency curve shows maxima (Fig. 6) at 2×10^4 and 10^6 Hz. The high dielectric loss at these frequency ranges may be due to the dipole group loss of the polar groups present in the macromolecular chain. Consequently, the relaxation time (τ) value at these two maxima were found to be 7.9×10^{-6} and 1.6×10^{-7} s, respectively. The relaxation time (τ), determined by following the equation $2\pi f_{max}\tau = 1$, is the average or most probable relaxation time because every polymer has a set of relaxation times that is determined by a set of structural units of different mobility.

The electrical conductivity of the polymer gradually rises with frequency (Fig. 7). This may be due to low molecular weight impurities or the presence of free ions present in the polymer [25]. The number of free charges present in the polymer is very small, and hence the electrical conductivity of the polymer was found to be low at lower frequency range [25].

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