## New Heat-Resistant Polymers. Synthesis and Characterization of Polyamideimides from N-(4-Carboxy Phenyl) Trimellitimide and Benzidine

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# New Heat-Resistant Polymers. Synthesis and Characterization of Polyamideimides from N-(4-Carboxy Phenyl) Trimellitimide and Benzidine

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## ABSTRACT

A new heat-resistant polymer has been synthesized from N-(4-carboxy phenyl) trimellitimide and benzidine. The polymer was characterized by nitrogen analysis, IR spectroscopy, density, viscosity, and x-ray measurements. The polymer was found to be insoluble in all polar organic solvents and only soluble in formic acid and concentrated $H_2SO_4$. The solubility parameter value has been determined. Thermal studies show that the polymer is thermostable up to 300°C. The electrical properties have also been measured.

## INTRODUCTION

It has been established that polyimides possessing an aromatic or a heterocyclic nucleus are promising high temperature plastics [1-5]. However, their poor solubility in commercially available solvents, bad flow characteristics, and high glass transition temperatures offset their applications in many cases [6-8]. The finding of copolyamide-

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imide is a major advancement since they possess high thermal stability along with ease of processibility [9, 10].

As a part of our continuing investigation on the synthesis and evaluation of the properties of various polyamideimides, we have reported the synthesis and properties of various novel polyamideimides in a systematic manner [11-18]. In this present communication we wish to report the synthesis and characterization of a new polyamideimide prepared by reacting N-(4-carboxy phenyl) trimellitimide or its diacid chloride derivative with benzidine.

## EXPERIMENTAL

### Materials

Trimellitic acid anhydride (Chemalog, U.S.A.) was used after recrystallization from acetic anhydride. p-Aminobenzoic acid (E. Merck, India) was used after crystallization from ethanol. Thionyl chloride (Ranbaxy, India) was freshly distilled before use. N,N-Dimethylformamide (E. Merck, India) was dried over phosphorus pentoxide and distilled under reduced pressure (20 torr). N-Methyl pyrrolidone was distilled prior to use. All other solvents used were of pure grade.

### Preparation of Monomer

The dicarboxylic acid, N-(4-carboxyphenyl) trimellitimide (1) was prepared from 4-aminobenzoic acid and trimellitic acid anhydride in N,N-dimethylformamide solution by following the procedure of Maiti et al. [15].

The diacid chloride of (1) was prepared by reacting the acid (1) with excess thionyl chloride in a flask fitted with a condenser and a drying tube for 10 h. The excess unreacted thionyl chloride was removed under vacuum. The solid acid chloride was recrystallized from hot benzene-petroleum ether, mp 167°C.

### Polymerization Procedure

Method A.   3.11 g (10 mmol) of the dicarboxylic acid (1) was dissolved in 20 mL of DMF or NMP and stirred in a 100-mL three-necked flask fitted with a stirrer, a drying tube, and a thermometer. The solution was chilled to about -15°C when 2.40 g (20 mmol) of thionyl chloride was added to the solution and stirred for 5 min in such a way that the temperature remained at -5°C or below. Next, 1.84 g (10 mmol) of benzidine and 2.59 g (25 mmol) of triethylamine were added to the mixture. Immediately after the addition, a solid product began to separate. The mixture was vigorously stirred for

9 h at 0-5°C and finally for 1 h at room temperature. After completion of the reaction the reaction mixture was poured into ice water and the precipitated polymer was isolated by filtration, washed thoroughly with cold water, and dried.

Method B. 3.48 g (10 mmol) of the acid chloride of (1) was dissolved in 30 mL DMF or NMP in a three-necked flask fitted with a stirrer, a thermometer, and a nitrogen purging system. 1.84 g (10 mmol) of benzidine and 2.5 g triethylamine in 10 mL DMF or NMP were added to the solution with stirring. The reaction mixture was stirred at room temperature for 2 h, at 40-60° for 5 h, and finally at 70°C for 3 h. At the end of the reaction the mixture was poured into ice water and filtered immediately.

## Purification of Polymer

Since the polymer is highly insoluble in common organic solvents, the normal reprecipitation technique for the purification cannot be applied with ease. The polymer was dissolved in concentrated $H_2SO_4$ at room temperature and poured into ice water. However, because the process is both hazardous and does not afford sufficiently pure polymer, an alternative method was tried. The polymer was taken up in a Soxhlet apparatus and the low molecular weight impurities were removed by continuous extraction through hot DMF. This method afforded satisfactorily pure polymer.

## Methods of Characterization

Viscosity measurements were carried out in a 0.5% (g/mL) solution of concentrated $H_2SO_4$ at 30°C by using an Ubbelhode suspended level viscometer.

The infrared (IR) spectrum was recorded on a Perkin-Elmer 237B spectrophotometer using a nujol mull.

Thermogravimetric analysis (TGA) was made with a Du Pont 1090 automatic analyzer. The measurements were recorded in air at a heating rate of 10°C/min.

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

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 such solvent effects as dissolution or swelling.

The x-ray diffraction diagram was recorded with a Dron I (USSR) X-ray Diffractometer using Ni-filtered CuKα radiation.

Dielectric properties and electrical conductivity of the polymer were measured in the form of a pellet (diameter 0.985 cm, thickness 0.425 cm) at room temperature (~30°C) 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.

The isothermal aging of the polymer was carried out in a specially designed aging oven in air to measure the weight loss at a fixed temperature after different time periods.

## RESULTS AND DISCUSSION

The polycondensation of dicarboxylic acid (1) and benzidine (2) was carried out at −5°C (Method A) in either DMF or NMP solvent (Scheme 1).

The same polymer (3) was also achieved by the reaction of the acid chloride derivative of (1) with the amine (2) at an elevated temperature (Method B) (Scheme 2).

A catalyst for the polycondensation reaction was found to be unnecessary. Triethylamine was used as an acid acceptor, in both methods, to facilitate the polycondensation reaction.

The general characteristics of the polyamideimide are shown in Table 1.

The structure of the polyamideimide was confirmed by nitrogen analysis and IR spectroscopy (Fig. 1). The characteristic absorption
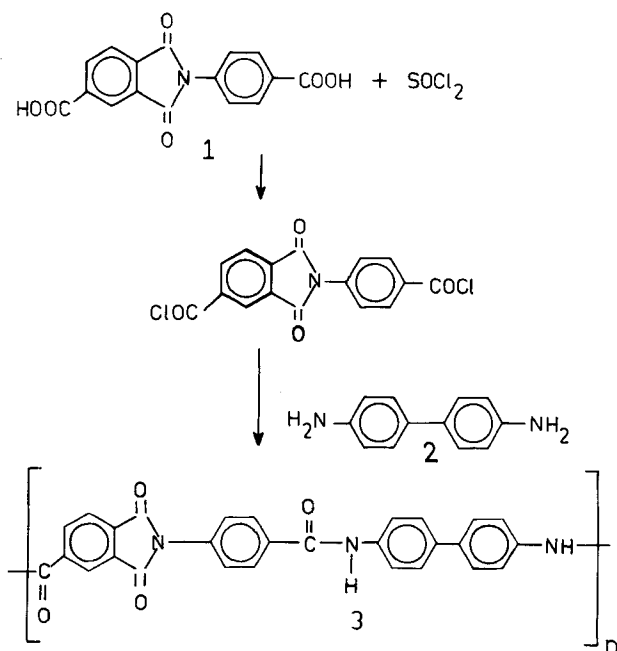
SCHEME 1.
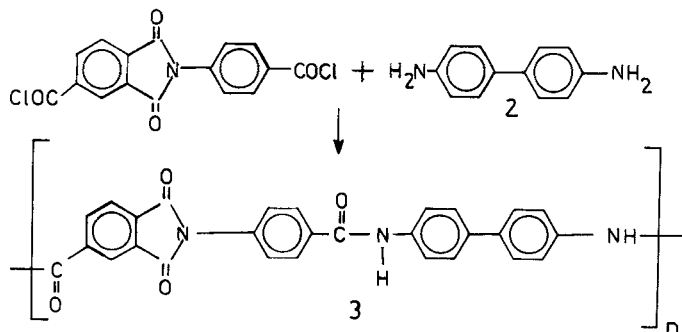
SCHEME 2.
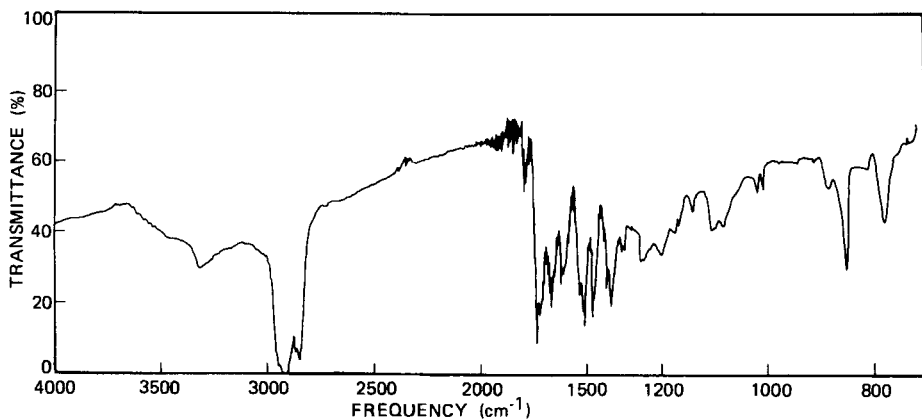


FIG. 1. IR spectrum of the polyamideimide.

bands of the polymer at 1785 and 1725 cm$^{-1}$ are due to symmetrical and asymmetrical carbonyl stretching of imide, and the peak at 720 cm$^{-1}$ is due to ring carbonyl deformation of imides. Peaks at 1660 and 1530 cm$^{-1}$ arise due to the presence of amide functional groups whereas a broad peak at 3320 cm$^{-1}$ arises due to –NH– stretching of amide functionality.

## Solution Properties

The polymer was found to be insoluble in common polar organic solvents; e.g., N,N-dimethylformamide (DMF), dimethylsulfoxide

TABLE 1. Yields and Characteristics of the Polyamideimide

| Method of polymerization | Solvent used | Yield, % | Color | Density, g/cm$^3$ | $T_g$,[a] °C | $T_m$,[a] °C | Inherent viscosity,[b] dL/g | % Nitrogen content[c] Calculated | % Nitrogen content[c] Found |
|---|---|---|---|---|---|---|---|---|---|
| A | NMP | 81 | Yellow | 1.23 | 340 | 550 | 0.32 | 9.15 | 9.07 |
|   | DMF | 76 | Brown | 1.21 | 338 | 550 | 0.30 | 9.15 | 8.98 |
| B | NMP | 85 | Brown | 1.25 | 340 | 540 | 0.33 | 9.15 | 9.01 |
|   | DMF | 72 | Brown | 1.27 | 336 | 540 | 0.39 | 9.15 | 9.11 |

[a]Calculated from the DSC curve.
[b]Inherent viscosity was measured in a 0.5% (g/mL) solution of concentrated $H_2SO_4$ at 30°C.
[c]Nitrogen content was calculated on the basis of the polymer structure 3.

(DMSO), N-methyl pyrrolidone (NMP), N,N-dimethylacetamide (DMAC), hexamethylene phosphoric triamide, m-cresol, and dioxane. Solvents which can dissolve the polymer are formic acid and concentrated sulfuric acid.

The solubility behavior of the polyamideimide is listed in Table 2. The solubility parameter ($\delta$) and the hydrogen bonding index ($\gamma$) of the solvents are shown in Table 2. It is clear from Table 2 that the polymer is only soluble in solvents having very high values of $\delta$ and $\gamma$.

A plot of solubility parameter ($\delta$) vs hydrogen bonding index ($\gamma$) for various solvents shown in Table 2 is illustrated in Fig. 2. The solubility parameter may also be calculated from Small's group contributions [20]. The molar attraction constant G values reported by Hoy [21] were used. The G values for various groups are shown in Table 3.

These were used to calculate the solubility parameter ($\delta$) of the polymer by using the relationship
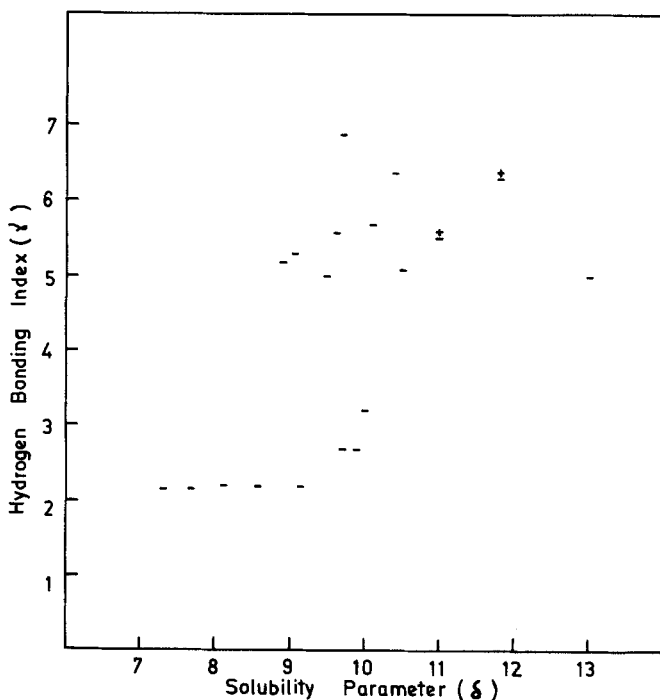
$$\delta = \rho(\Sigma G/M)$$

FIG. 2. Solubility map of the polyamideimide: (+) soluble, (±) swelling or partially soluble, (-) insoluble.

TABLE 2. Solubility Characteristics of the Polyamideimide

| Solvent | Solubility parameter $\delta$, $(cal/cm^3)^{1/2}$ | Hydrogen bonding index $\gamma$ | Solubility[a] of the polymer |
|---|---|---|---|
| Acetone | 9.62 | 5.7 | - |
| Benzene | 9.16 | 2.2 | - |
| Carbon tetrachloride | 8.55 | 2.2 | - |
| Chloroform | 9.16 | 2.2 | - |
| Cyclohexane | 8.19 | 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 | - |
| N,N-Dimethylformamide | 11.79 | 6.4 | ± |
| Dimethylsulfoxide | 13.00 | 5.0 | - |
| 1,4-Dioxane | 10.13 | 5.0 | - |
| Ethyl acetate | 8.91 | 5.2 | - |
| Ethylene dichloride | 9.86 | 2.7 | - |
| Ethyl methyl ketone | 9.45 | 5.0 | - |
| n-Hexane | 7.27 | 2.2 | - |
| N-Methyl-2-pyrrolidone | 11.00 | 5.6 | ± |
| Nitrobenzene | 10.00 | 3.2 | - |
| Tetrahydrofuran | 9.10 | 5.3 | - |
| m-Cresol | 10.20 | - | - |
| Formic acid | 12.10 | - | + |
| N,N-Dimethylacetamide | 10.80 | - | - |
| Concentrated $H_2SO_4$ | - | - | + |
| Methyl isobutyl ketone | 8.40 | 5.0 | - |

[a]Solubility keys: (+) soluble, (±) partly soluble, (-) insoluble.

TABLE 3. Solubility Parameter of the Polyamideimide Calculated from Small's Group Contribution

| Functional group | G value, $(\text{cal}/\text{cm}^3)^{1/2}$ | Number of groups in the polymer repeat unit | Total G value $(\text{cal}/\text{cm}^3)^{1/2}$ |
|---|---|---|---|
| —CH= (aromatic) | 117.12 | 15 | 1756.80 |
| =C= (aromatic) | 98.12 | 9 | 883.08 |
| =C=O | 262.92 | 4 | 1051.84 |
| =N— | 61.08 | 1 | 61.08 |
| —NH— | 180.03 | 2 | 360.06 |
| 5-Membered ring | 20.99 | 1 | 20.99 |
| 6-Membered ring | -23.44 | 4 | -93.76 |
| p-Substitution | 40.33 | 4 | 161.32 |
| m-Substitution | 6.60 | 1 | 6.60 |
| | | | $\Sigma G = 4208.01$ |

where $\rho$ is the density of the polymer, $\Sigma G$ is the sum of Small's group contribution, and M is the formula weight of the polymer repeat unit. The $\delta$ value obtained from the solubility map (Fig. 2) was found to be in agreement with the calculated value of $\delta$, i.e., 11.10 (Table 3).

From the x-ray diffraction data (Fig. 3) it was found that there exist sharp peaks in the intensity vs scattering angle ($2\theta$), which definitely demonstrates that the polymer possesses some amount of crystallinity. The insolubility of polymers in organic solvents, even in highly polar solvents, may be due to the crystalline nature of the polymer. This is again due to the molecular symmetry and rigidity of the benzidine moiety present in the polymer repeat unit.

Thermal Properties

Thermogravimetric studies (TG) of the polymer in air revealed an initial weight loss of about 9% at 100°C due to the loss of moisture or entrapped solvent in the polymer. There was loss of 6% at 450°C. The degradation of the polymer is a single step process, and the maximum weight loss occurs between 500 and 600°C. A complete loss of weight was found at 670°C (Fig. 4). However, when thermogravimetric
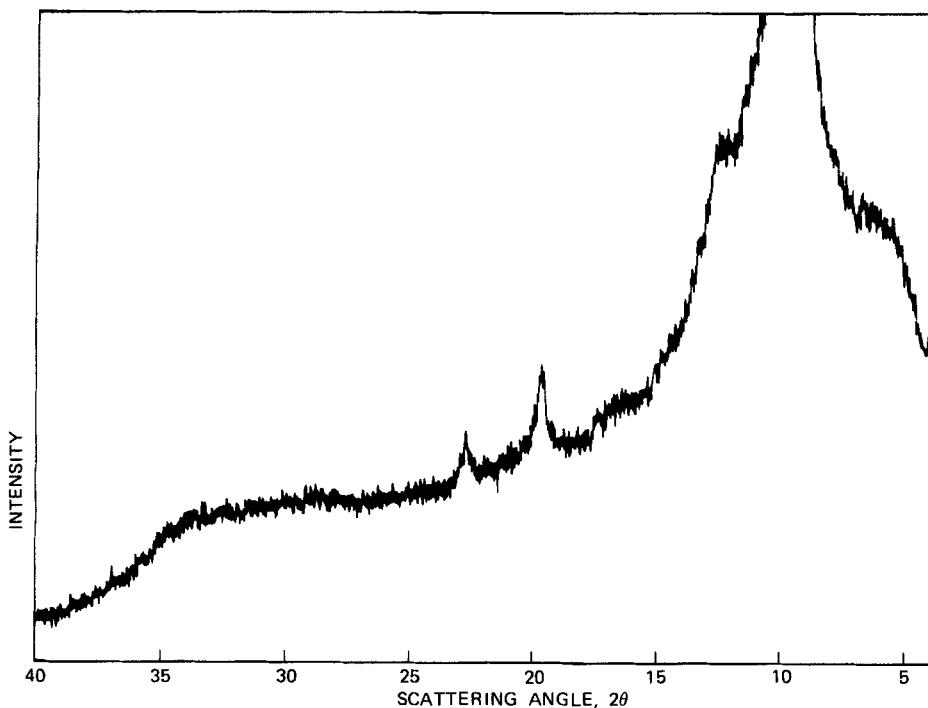
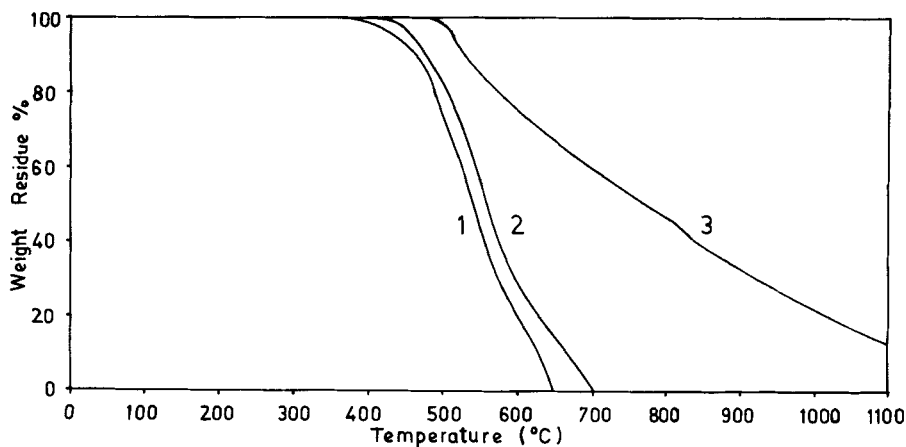FIG. 3. X-ray diffraction diagram of the polyamideimide.



FIG. 4. Thermogravimetric (TG) curves for the polyamideimide.
Curves 1 and 2 refer to polymers prepared by Methods A and B, re-
spectively, when heated in air. Curve 3 refers to polymer prepared
by Method A, heated in an $N_2$ atmosphere. Heating rate: $10°C/min$ in
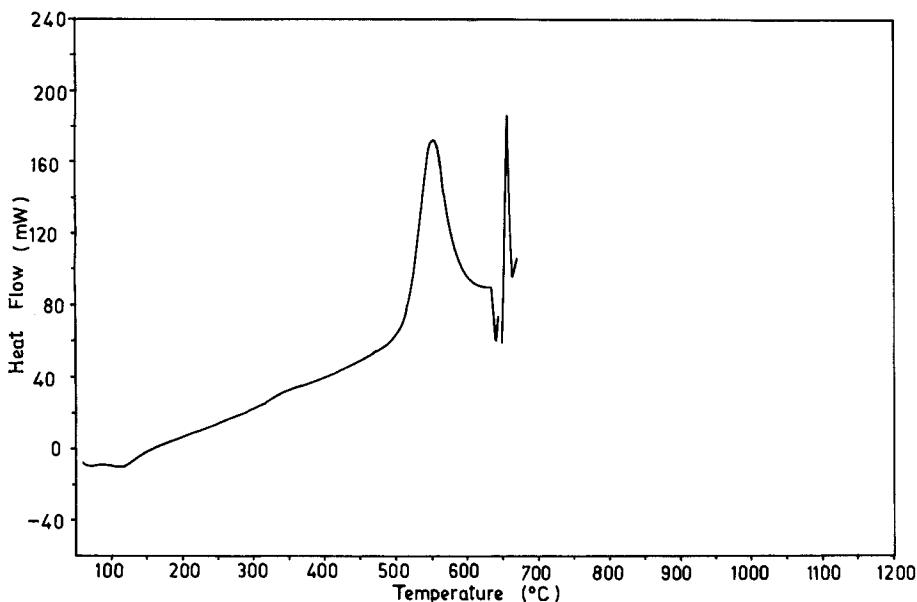both air and $N_2$.

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FIG. 5. DSC curve for the polyamideimide.

analysis was carried out in a nitrogen atmosphere, a weight loss of
only 12.50% at 510°C was observed. Thereafter a slow but continuous
degradation occurred. In this case the degradation was not complete
even at 1000°C where the weight residue was still 18.75% (Fig. 4).
This definitely indicates that the thermal decomposition of the synthe-
sized polyamideimide in nitrogen atmosphere is a much slower process
than in air. From the DSC curve, taken in air (Fig. 5), it was observed
that the glass transition temperature of the polymer is 340°C and the $T_m$
is 550°C.

The performance of the polyamideimide at elevated temperature
(300°C) was found to be reasonably good (Table 4). The cumulative

TABLE 4. Cumulative Weight Loss of the Polyamideimide Heated
at 300°C

| Weight loss in % in air after | | | | | | | |
|------|------|------|------|------|------|-------|-------|
| 1 h | 4 h | 16 h | 24 h | 48 h | 60 h | 100 h | 125 h |
| 0 | 0 | 2.7 | 2.9 | 3.4 | 5.7 | 6.0 | 7.7 |

weight loss at 300°C after 125 h was found to be only 7.7%, which clearly reveals that the polymer can be used at 300°C.

## Electrical Properties

The variation of dielectric constant ($\epsilon'$), dielectric loss (tan δ), and electrical conductivity with frequency at room temperature ($\sim$30°C) are presented in Figs. 6 and 7. The dielectric constant of the polymer decreases with an increase of frequency (Fig. 6). The plot of tan δ vs frequency shows maxima at $10^4$ and $10^6$ Hz. The higher dielectric loss at these two frequency ranges may be due to the dipole group loss of the polar substituents present in the polymeric network. The relaxation time ($\tau$) values, calculated from $2\pi f_{max} \ \tau = 1$, were found to be 1.59 × $10^{-4}$ S and 1.59 × $10^{-6}$ S, respectively, at the maxima. The increment of electrical conductivity with frequency (Fig. 6) may be due to the presence of low molecular weight impurities and the free charges present in the polymeric network [14].
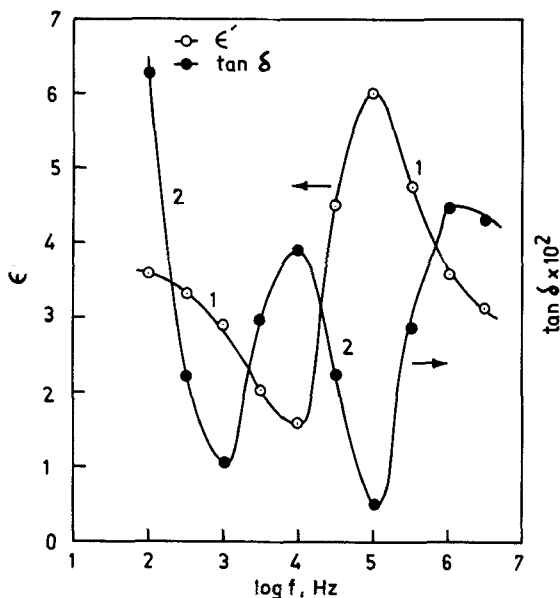


FIG. 6. Variation of dielectric constant ($\epsilon'$) and dielectric loss (tan δ) of the polyamideimide with frequency.
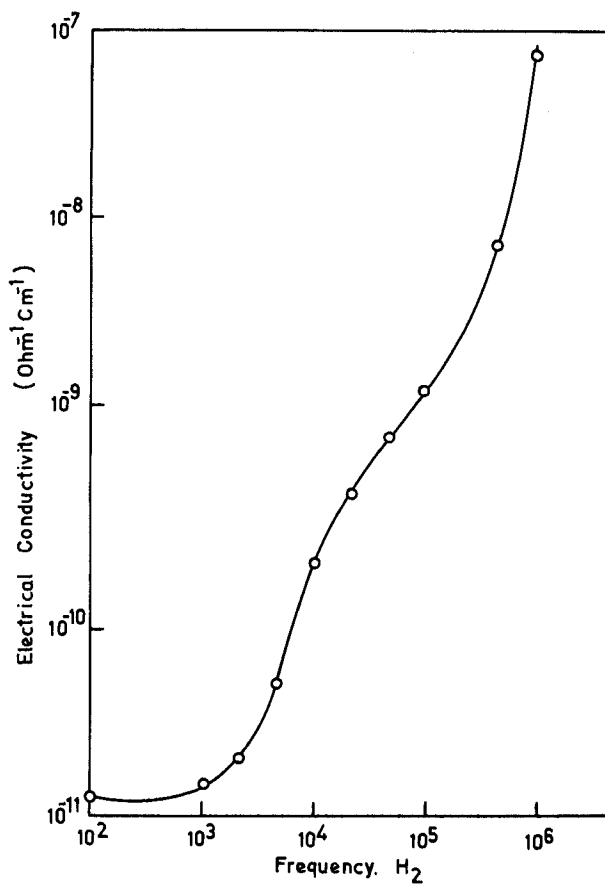
FIG. 7. Variation of electrical conductivity of the polyamideimide with frequency.

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