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## Processable Heat-Resistant Polymers

### VIII. Synthesis and Characterization of Polyamideimide from N-(4-Carboxy phenyl) Trimellitimide and Sulfanilamide

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#### SUMMARY:

A novel polyamideimide was synthesized by reacting sulfanilamide and N-(4-carboxy phenyl) trimellitimide or its diacid chloride derivative. The solution, thermal, electrical and a few other properties of the polymer were studied. The polymer was found to be soluble in highly polar solvents. The polymer solution was relatively stable. Thermogravimetric data revealed that the polymer underwent 12% weight loss at 375 °C in air. The dielectric constant of the polymer at 30 °C was found to be 5.45 at 1 kHz. X-ray diffraction data revealed that the polymer is crystalline in nature.

#### ZUSAMMENFASSUNG:

Ein neues Polyamidimid wurde aus Sulfanilamid und N-(4-Carboxy-phenyl)-trimellitimid oder dessen Disäurechlorid hergestellt. Die Lösungseigenschaften, die thermischen, elektrischen und einige andere Eigenschaften des Polymeren wurden untersucht. Die Polymerlösung war verhältnismäßig stabil. Aus thermogravimetrischen Daten ergab sich, daß das Polymere bei 375 °C in Luft 12% Gewichtsverlust erleidet. Seine Dielektrizitätskonstante wurde bei 30 °C und 1 kHz 5,45 bestimmt. Aus Röntgenuntersuchungen ergab sich, daß das Polymere kristallin ist.

#### *Introduction*

Polyimides containing aromatic and heterocyclic rings are among the most promising of the high temperature engineering plastics<sup>1–5</sup>. They possess high

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thermal stability and have already found a secured place in the technology of electrical insulators<sup>6</sup>. However, the major limitations of polyimides as widely used materials are: poor flow characteristics during moulding due to high glass transition temperatures and poor solubility in commercially available solvents<sup>7-10</sup>. To overcome these difficulties copolyimides such as polyesterimides<sup>11-13</sup>, polyamideimides<sup>14-17</sup>, and polybenzimidazoleimides<sup>18</sup> have been developed. Thus copolyimides are a compromise between the high thermal stability and the ease of processability.

Trimellitic acid anhydride is an important petroleum based chemical<sup>19</sup> used for the synthesis of various types of thermostable polymers. The thermal stability of polyamideimides closely resembles to that of polyamides. In this present communication we wish to report a comparative study of a novel polyamideimide prepared by reacting N-(4-carboxy phenyl) trimellitide or its diacid chloride derivative and sulfanilamide.

## *Experimental*

### *Materials*

Trimellitic acid anhydride (TMA) was obtained from Amoco Chemical Corporation (USA) and was used after crystallizing from acetic anhydride<sup>20</sup>. Sulfanilamide (IDPL, India) and 4-amino benzoic acid (E. Merck, India) were used after crystallizing from ethanol. Thionyl chloride (SD, India) was freshly distilled before use. N,N-dimethyl formamide (E. Merck, India) was dried over phosphorus pentoxide and freshly distilled under reduced pressure (20 torr). All other solvents used were pure grade.

### *Characterization and Properties of Polyamideimide*

Viscosity measurements were made on a 0.5% (g/ml) solution of the polymer in DMF at 30°C by using an Ubbelohde suspended level viscometer.

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

Thermogravimetry (TG) and differential thermal analyses (DTA) were made simultaneously with a Hungarian Mom Derivatograph of Paulik Paulik-Erdey system. The measurements were recorded in air at a heating rate of 5°C/min.

The X-ray diffraction diagram was recorded with a Dron I (USSR) X-ray Diffractometer using Ni-filtered CuK<sub>α</sub> radiation.

Dielectric properties and electrical conductivity of the polymer were measured in the form of a pellet (diam. 2.161 cm, thickness 0.163 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<sup>3</sup> to 10<sup>7</sup> Hz.

### *Aging*

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

### *Solubility Characteristics*

The polyamideimide sample was placed in 2 ml of various solvents and was allowed to stand for two weeks<sup>21,22</sup>. The polymer was then observed in order to judge solvent effects such as swelling or dissolution.

### *Density Measurements*

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

### *Synthesis of the Monomers*

N-(4-carboxy phenyl) trimellitimide (IDCA) was prepared by condensing TMA and 4-amino benzoic acid in DMF by following the procedure of Maiti et al.<sup>23</sup>.

### *Synthesis of the Diacid Chloride Derivative of N-(4-Carboxyphenyl) Trimellitimide (IDCA-DC)*

In a three necked 250 ml round bottom flask fitted with a condenser having a calcium chloride tube, a thermometer, and a stopcock, 119.0 g (1.0 mol) of thionyl chloride were taken and 18.66 g (0.06 mol) of IDCA were added slowly with occasional shaking. The mixture was heated in a water bath for 14 h at 70–80°C. At the end of the reaction excess thionyl chloride was removed by distillation under reduced pressure. The solid residue was extracted with chloroform and the crude product was isolated after removal of the solvent. It was further purified by recrystallization from chloroform and dried in vacuum at 80°C. A white powder, yield 68–70%, m.p. 167°C, was obtained. Nitrogen analysis: Calcd. 4.02, found 4.10. Chlorine analysis: Calcd. 20.40, found 20.17.

### *Synthesis of the Polymers*

Polyamideimide was prepared from IDCA or IDCA-DC and sulfanilamide by following two different methods.

## Synthesis of Polyamideimide from IDCA by Low Temperature Polycondensation (Method A)

Polyamideimides (PAI) were generally prepared from IDCA at low temperature in the presence of thionyl chloride in polar solvents<sup>24,25</sup>. A typical run may be described as follows: 3.11 g (10 mmol) of IDCA were dissolved in 30 ml DMF and stirred in a 100 ml three necked round bottom flask containing a thermometer and a calcium chloride drying tube. The solution was cooled to  $-10^{\circ}\text{C}$  and 3.0 g (25 mmol) of thionyl chloride were added. The solution was stirred for 1–2 min, then 1.72 g (10 mmol) of sulfanilamide and 1.97 g (25 mmol) of pyridine were added to the mixture. The mixture was vigorously stirred for 9 h at  $0-5^{\circ}\text{C}$  and finally 1 h at room temperature. At the end of the reaction the mixture was poured into ice/water and the precipitated polymer was isolated by filtration. It was washed several times with cold water and dried. It was further purified by dissolving in DMF and precipitating by methanol.

## Synthesis of Polyamideimide from IDCA-DC (Method B)

The diacid chloride of N-(4-carboxy phenyl) trimellitimide was reacted with sulfanilamide to form polyamideimide. A typical procedure was as follows: 3.48 g (10 mmol) of IDCA-DC were dissolved in 35 ml DMF in a 100 ml three necked flask fitted with a stirrer, a thermometer and a nitrogen purge tube. Next, 1.72 g (10 mmol) of sulfanilamide and 1.58 g (20 mmol) pyridine were added to the solution with stirring. The mixture was further stirred at room temperature for 2 h, at  $40-50^{\circ}\text{C}$  for 5 h and finally at  $60-70^{\circ}\text{C}$  for 3 h. At the end of the reaction the mixture was poured into ice/water. The precipitated polymer was isolated by filtration and dried. It was finally washed with chloroform and further purified by dissolving in DMF and precipitating by methanol.

## *Results and Discussion*

### *Monomer Characterization*

The diacid chloride of N-(4-carboxy phenyl) trimellitimide was characterized by IR spectrum and nitrogen analysis. The characteristic IR bands (Fig. 1) are observed near  $1785$ ,  $1725$  and  $720\text{ cm}^{-1}$  for the imidogroup and near  $1700\text{ cm}^{-1}$  due to the carbonyl stretching of the  $-\text{COCl}$  group which superimposes with the second imide band.

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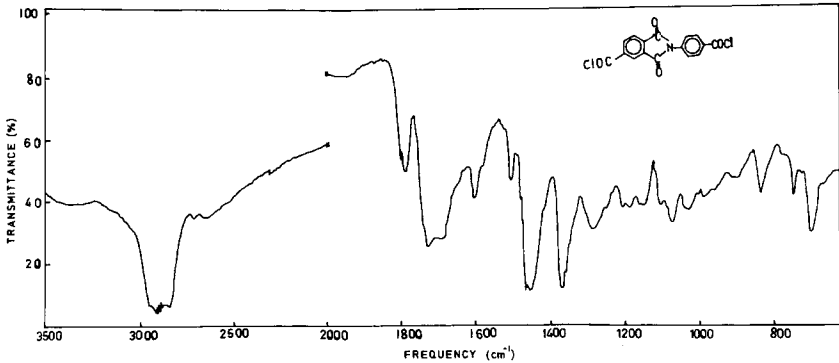
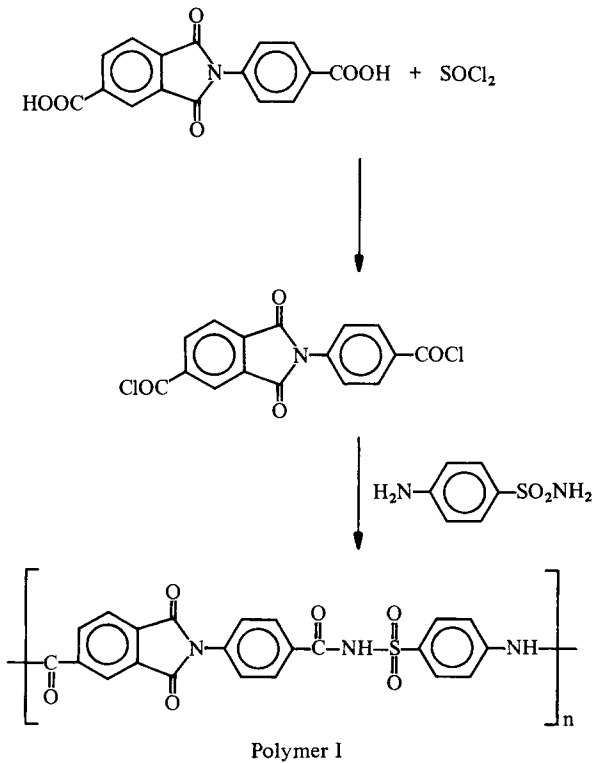


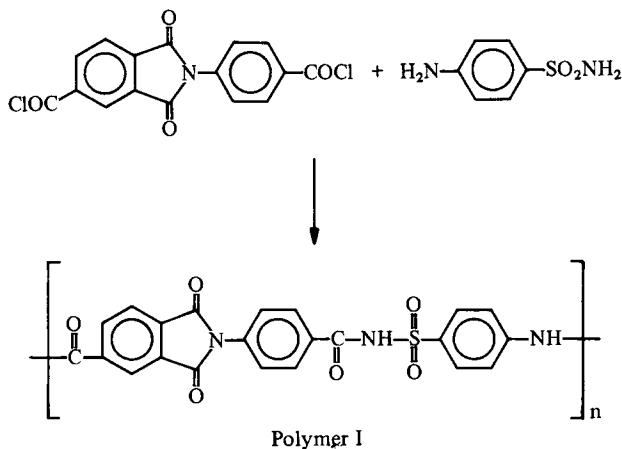
Fig. 1. IR spectrum of the diacid chloride of N-(4-carboxy phenyl) trimellitimide.

### Polymer Characterization

The polyamideimide obtained by low temperature polycondensation (method A) may be schematically represented as follows:



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



No catalyst was used in these polymerization reactions. However, pyridine was used as an acid acceptor to facilitate the polycondensation reaction. The molecular weight of the polymer may be controlled by changing the reaction conditions, solvents, and possibly by using a suitable catalyst. Attempts to achieve a high molecular weight polymer are in progress.

### *Polymer Properties*

The general characteristics of the resulting polyamideimide are shown in Tab. 1. The structure of the repeat unit of the polymer is confirmed by nitrogen analysis and IR spectrum. The characteristic IR bands of the polymer (Fig. 2) are observed near  $1700$  and  $1720\text{ cm}^{-1}$  due to symmetrical and asymmetrical carbonyl stretching of imides, at  $720\text{ cm}^{-1}$  possibly due to ring carbonyl deformation of imides, at  $1650$  and  $1590\text{ cm}^{-1}$  for amides. The  $-\text{S}(=\text{O})_2-$  stretching bands of sulfanilamide are observed near  $1280$  and  $1145\text{ cm}^{-1}$ .

The low inherent viscosity values (Tab. 1) of polyamideimides correspond to their low molecular weight. However, the inherent viscosity value of the polymer prepared by method A is a little lower than that of the polymer obtained by method B, which indicates that the molecular weight of the former is relatively lower than that of the latter.

Tab. 1. Yields and physical properties of polyamideimides\*.

Method of polymerization	Solvent used	Yield (%)	Inherent viscosity <sup>a</sup> (dl/g)	Density (g/cm <sup>3</sup> )	T <sub>g</sub> <sup>b</sup> (°C)	Nitrogen (%)		Sulfur (%)	
						calcd.	found	calcd.	found
A	DMF	66-70	0.14 (0.18) <sup>c</sup>	1.24	220	9.39	9.25	7.16	6.98
	NMP	68-70	(0.19) <sup>c</sup>	1.26	—	9.39	9.11	7.16	6.93
B	DMF	75-76	0.18 (0.22) <sup>d</sup>	1.26	240	9.39	9.05	7.16	7.01
	NMP	79-82	(0.25) <sup>d</sup>	1.27	—	9.39	9.18	7.16	6.88

<sup>a</sup> Measured in 0.5% (w/v) solution in DMF at 30 °C.

<sup>b</sup> Calculated from the DTA curve (Fig. 5).

<sup>c</sup> Inherent viscosity observed after 20 h reaction.

<sup>d</sup> Inherent viscosity observed after 16 h reaction.

\* All polymers have been obtained as white powders.

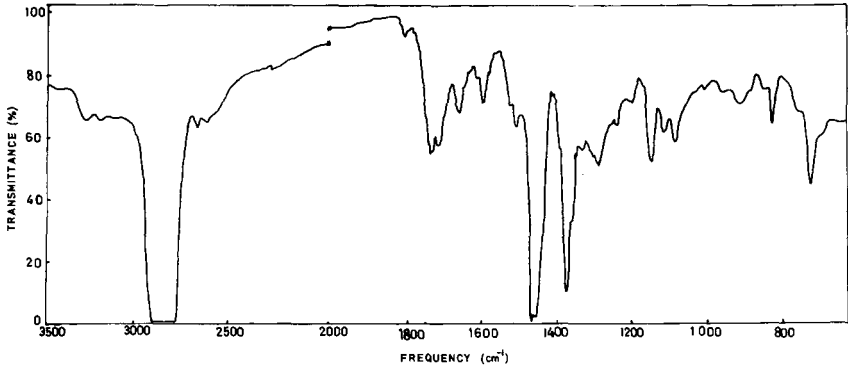


Fig. 2. IR spectrum of the polymer I.

The conventional polyimide precursor, e. g. polyamic acid, does not form a stable solution. The inherent viscosity of polyamic acid on standing decreases<sup>26,27</sup>. But the inherent viscosity of the polymer under investigation in DMF is found to be relatively constant ( $\approx 8\%$  reduction) even after 25 days at room temperature ( $\approx 30^\circ\text{C}$ ), which indicates its better aging properties in highly polar solvents (Fig. 3).

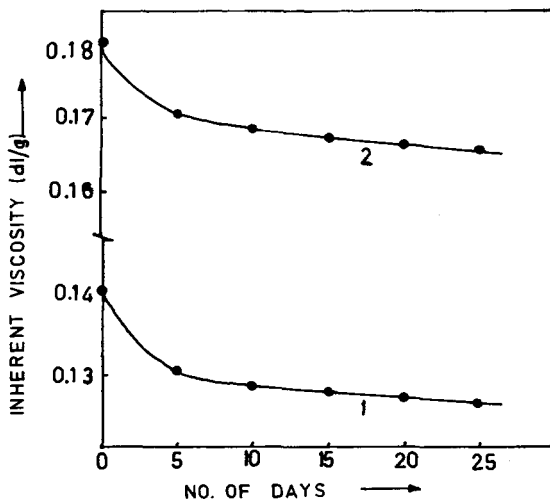


Fig. 3. Plot of inherent viscosity of the polymer I in DMF solution against storage time at room temperature. 1: Polymer by method A, 2: Polymer by method B.



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From X-ray diffraction data (Fig. 4) it is found that there are sharp peaks in the intensity vs. scattering angle ( $2\theta$ ), which shows that the polymer is crystalline in nature.

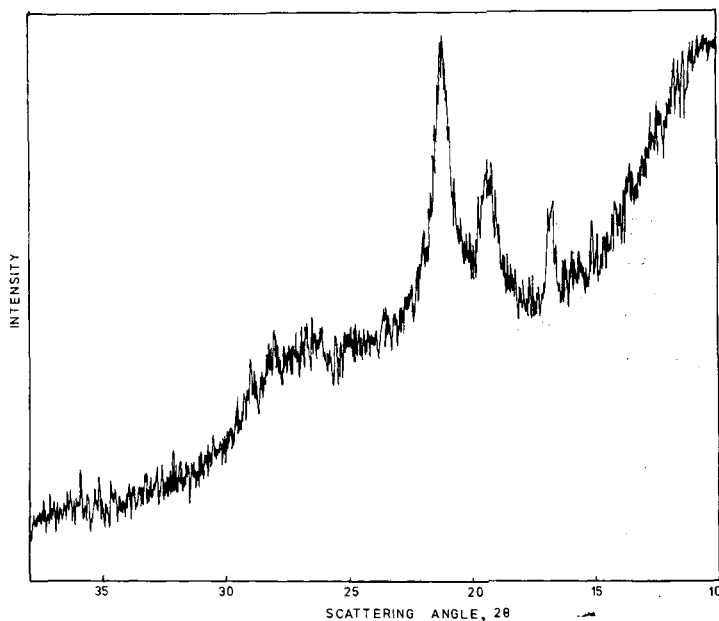


Fig. 4. X-ray diffraction of the polymer I.

Tab. 2. Weight loss of polyamideimide heated at various temperatures.

Weight loss during 1 h heating in air (%)					Total weight loss (%)	Weight loss during 10 h heating in nitrogen atmosphere at 300°C (%)
100°C	200°C	300°C	400°C	500°C		
6.6	4.4	4.8	12.1	28.2	56.1	18.7

At elevated temperature the performance of the polyamideimide polymer appears to be marginally less than that obtained with polyimides<sup>26</sup>. The loss of weight after heating the polymer prepared by method B in air for 1 h at

different temperatures and also in nitrogen atmosphere at 300°C for 10 h (Tab. 2) reveals that the polymer may be safely used at a moderate temperature range ( $\approx 200^\circ\text{C}$ ). Although the higher temperature stability of polyimides may prove superior, the overall properties of this polyamideimide represent a very desirable technological combination.

### Solubility Characteristics

The solubility behaviour of the resulting polyamideimide is listed in Tab. 3. The polymer is found to be soluble in highly polar solvents. It may be explained according to the concept<sup>28-30</sup> that the presence of large polar groups in a macromolecule increases the polymer solubility. This is due to the decrease of the polymer density and consequently better solubility of the polymer in polar solvents.

### Thermal Behaviour

Thermogravimetry and differential thermal analysis data of the polyamideimide in air are presented in Fig. 5. Thermogravimetric analysis indicated that an initial weight loss of about 8% occurs up to 100–110°C

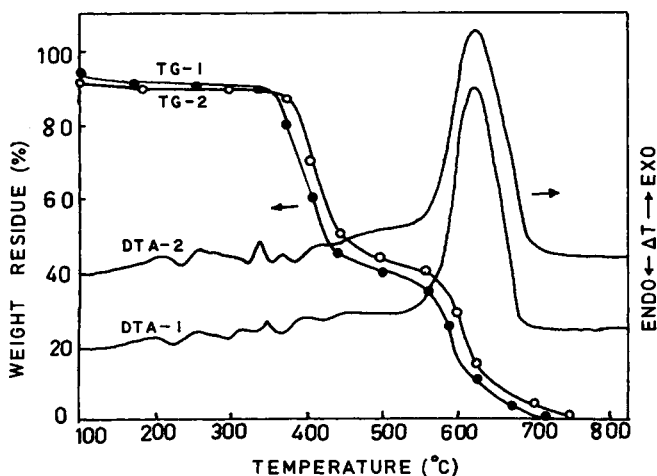


Fig. 5. TG and DTA curves for polyamideimide I. 1 and 2 refer to method A and B, respectively.

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which is due to the loss of moisture or entrapped solvent in the polymer. Subsequently, there is only 4% weight loss up to 350 °C or 375 °C depending on the method of polymerization. The degradation of the polymer is a single stage process and the maximum weight loss occurs around 400 – 600 °C. The glass transition temperature,  $T_g$ , of polymers prepared by method A and

Tab. 3. Solubility characteristics of polyamideimide.

Solvent	Solubility parameter ( $\delta$ )	Hydrogen bonding index ( $\gamma$ )	Solubility <sup>a</sup>
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-Dimethyl formamide	11.79	6.4	+
Dimethyl sulfoxide	13.0	5.0	+
1,4-Dioxan	10.13	5.7	–
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	–
Methyl acetate	9.46	5.2	–
N-Methyl 2-pyrrolidone	11.00	5.6	+
Nitrobenzene	10.00	3.2	–
n-Pentane	7.02	2.2	–
Tetrahydrofuran	9.10	5.3	–
Toluene	8.93	3.8	–
3-Cresol	10.2	—	+
Formic acid	12.1	—	±
N,N-Dimethyl acetamide	10.8	—	+
Conc. H <sub>2</sub> SO <sub>4</sub>	—	—	+
Methylene dichloride	9.88	2.7	–
Methyl isobutyl ketone	8.40	5.0	–

<sup>a</sup> Solubility: + soluble, ± partially soluble or swelling, – insoluble.

method B are found to be 220°C and 240°C, respectively (Fig. 5, DTA curves). The higher  $T_g$  and thermal stability of the polymer prepared by method B compared with those of the polymer prepared by method A may be due to the higher molecular weight of the polymer. The higher inherent viscosity value of the former (Tab. 1) in comparison with the latter also corroborates this fact.

### Electrical Properties

The dielectric properties and electrical conductivity of the polymer at room temperature ( $\approx 30^\circ\text{C}$ ) are presented in Fig. 6 and 7. From Fig. 6 it can be observed that the dielectric constant of the polymer decreases with frequency. The dielectric loss ( $\tan \delta$ ) vs. frequency plot shows a maximum at  $4 \times 10^3$  Hz which is due to the dipole group loss of the polar substituents present in the polymer chain. The relaxation time ( $\tau$ ) value at the maxima was found to be  $3.98 \times 10^{-5}$  s. The higher relaxation time may be explained by the fact that the presence of large polar groups in a macromolecule increases the intra- and intermolecular interactions. The relaxation time determined by following the equation  $2\pi f_{\max} \tau = 1$  is the average, or the most probable, relaxation time, because actually every polymer has a set or spectrum of relaxation times that is determined by a set of structural units of different mobility. The increment of specific conductivity with frequency (Fig. 7) may be due to the low molecular weight impurities<sup>31</sup> or the presence

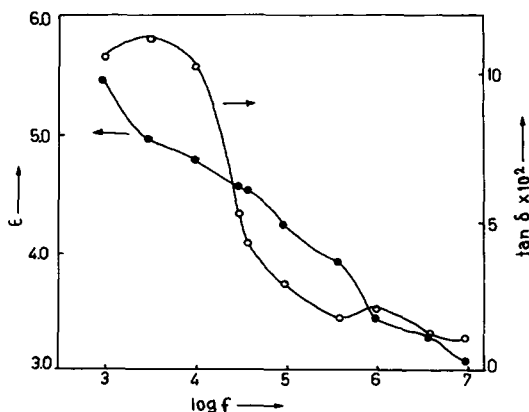


Fig. 6. Variation of dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) of the polymer I with frequency.

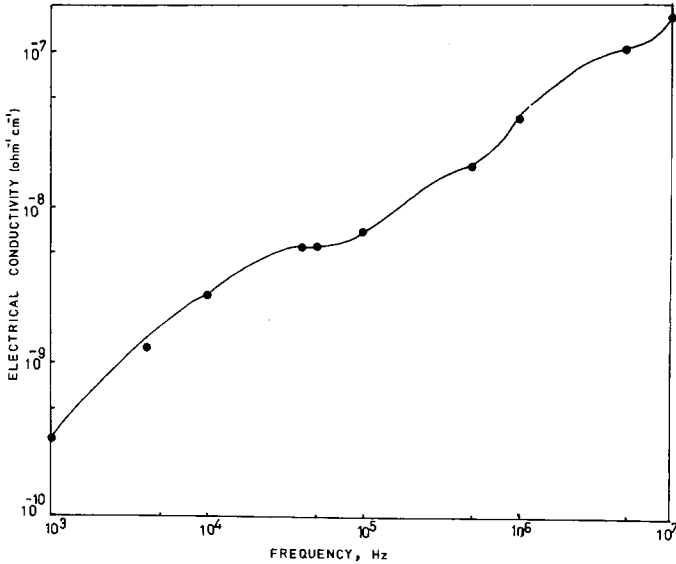


Fig. 7. Variation of specific conductivity of the polymer I with frequency.

of free charges present in the polymer chain. Generally, in the polymer chain the presence of free charges is very low thus the A.C. conductivity of the polymer was found to be low at lower frequency range<sup>31</sup>.

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