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Processable Heat-Resistant Polymers. XV. Synthesis and Properties of Polyamideimides from N-(p-carboxy Phenyl) Trimellitimide and p,p′-Di(amino Phenyl) Methane

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ABSTRACT

Polyamideimides (PAI) were prepared by the polycondensation reaction of the diacid chloride of N-(p-carboxy phenyl) trimellitimide and p,p'-di(amino phenyl) methane following three different techniques. The solution, thermal, chemical, and electrical properties of the polymer were studied. The polymer was found to be soluble in highly polar solvents. The solubility parameter of the polymer calculated from Small's group contributions agreed well with the experimental value. The polymer was found to be fairly thermostable and only 10% weight loss occurred at 360°C. X-ray diffraction study revealed that the polymer is amorphous. The electrical properties of the polymer at room temperature were also studied.

INTRODUCTION

Copolyimides such as polyesterimides [1-5] and polyamideimides [6-10] are the finest examples of processable heat-resistant polymers. For versatile applications such as adhesives, high temperature coatings, insulators, and laminates, these polymers have secured a significant

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place in modern material development. Compared with other heat-resistant polymers, these polymers are industrially important due to low monomer cost [11] and better solubility in commercially available solvents [12-14].

In our program on processable heat-resistant polymers, we have already reported the synthesis of saturated and unsaturated polyesterimides [15-17] and polyamideimides [18-22]. In our present paper we report the synthesis and properties of polyamideimide from N-(p-carboxy phenyl) trimellitimide and p,p'-di(amino phenyl) methane.

EXPERIMENTAL

Reagents

Trimellitic anhydride (TMA) was obtained from Amoco Chemical Corporation, U.S.A., and used after crystallization from acetic anhydride.

Para-amino benzoic acid (BDH, India) and p,p'-di(amino phenyl) methane (DDM) (BDH, England) were purified after crystallization from ethanol.

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

N,N-Dimethylformamide (DMF) (E. Merck, India) and 1-methyl-2-pyrrolidone (NMP) (Koch Light Lab., England) were dried over phosphorus pentoxide and distilled under reduced pressure (~20 torr). All other solvents used were pure grade.

Polymer Synthesis

The polyamideimide was prepared from the diacid chloride of imidodicarboxylic acid (IDCA-DC) and DDM by three different methods.

Synthesis of Polyamideimide (PAI) by Melt Polymerization (Method A). The acid chloride having cyclic imido groups IDCA-DC was reacted with DDM at high temperature to prepare PAI. A typical procedure is as follows: 1.98 g (10 mmol) of DDM was taken in a 100-mL flask fitted with a stopcock, a stirrer, a thermometer, and a nitrogen purge tube. The amine was heated to 90°C and 3.48 g (10 mmol) of IDCA-DC was added to the mixture. It was heated in an anthracene bath at 250°C for 15 min and 300°C for another 30 min. The solid mass was removed from the flask and washed several times with chloroform and alcohol. It was finally purified by dissolving in DMF and precipitated by methanol.

Synthesis of PAI by Solution Polymerization (Method B). IDCA-DC was reacted with DDM at 30-70°C using polar solvents. A typical run follows: 3.48 g (10 mmol) of IDCA-DC in 25 mL DMF was taken in a three-necked flask fitted with a stirrer, a thermometer, and a nitrogen purge tube. The solution was cooled to 0°C and 1.98 g (10 mmol) of DDM and 1.58 g (20 mmol) of pyridine were added to the mixture. The solution was stirred for 10 h at 30-40°C and then for 5 h at 60-70°C. 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 water and ethanol and finally with chloroform. The polymer was purified by dissolving in DMF and reprecipitated by methanol.

Synthesis of PAI by Interfacial Polymerization (Method C). The polycondensation by interfacial method was carried out by the standard procedure reported elsewhere [23]. A typical example follows: In a 100-mL flask fitted with a high speed stirrer, a thermometer, and a stopcock, 1.98 g (10 mmol) of DDM was taken together with 40 mL of water and 5 mL of THF. The flask was placed in a water bath maintained at 30-35°C. Next, a solution of 2.12 g (20 mmol) of sodium carbonate in 10 mL of water was added to the mixture and stirred to make a homogeneous solution. To the clear solution 3.48 g (10 mmol) of IDCA-DC in 35 mL dichloromethane was added and stirred for 45 min at 30-35°C. The precipitated polymer was isolated by filtration, washed with alcohol and chloroform, and finally purified by dissolving in DMF and precipitated by methanol.

Characterization and Properties of the Polyamideimide

Viscosity Measurement. Viscosity measurements were carried out in a 0.5% (w/v) solution in DMF at 30°C using an Ubbelohde suspended level viscometer.

Density Measurement. The density of the polymers was measured in dry benzene at 30°C by means of a small pychnometer.

IR Spectroscopy. The spectrum of the polymer was recorded with a Perkin-Elmer 237B spectrophotometer using a nujol mull (Fig. 1).

X-Ray Diffraction. The x-ray diffraction diagram of the polymer sample was recorded with a Dorn I (USSR) x-ray diffractometer using Ni-filtered CuKα radiation.

Solubility Characteristics

Polymer 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 the solvent effect such as swelling or dissolution [24]. A solubility map was prepared by plotting the solubility parameter (δ) vs the hydrogen bonding index (γ) for polymers. The midpoint of the solubility map indicates the solubility of the polymer.

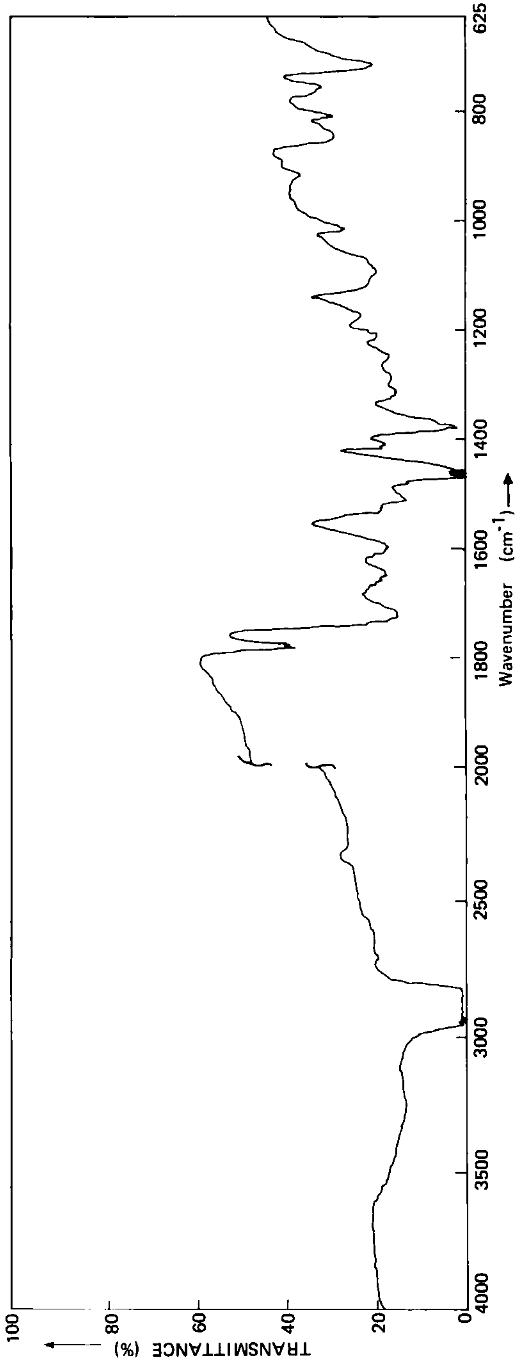


FIG. 1. IR spectrum of the polyamideimide.

Thermal Behavior

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for polymers 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.

Differential scanning calorimetry (DSC) of the polymer sample was made with a Perkin-Elmer DSC-2. The measurement was recorded at a heating rate of 10°C/min.

Electrical Properties

The dielectric constant (ϵ'), dielectric loss, and electrical conductivity of the polymer with frequency f were measured at room temperature (~30°C) with a polymer pellet of 1.253 cm diameter and 0.215 cm thickness by using a Radio Capacitance Bridge (Type-716C) and a Q-Meter (Marcony Circuit Magnification Meter, Type-329G) at 10^3-10^7 Hz.

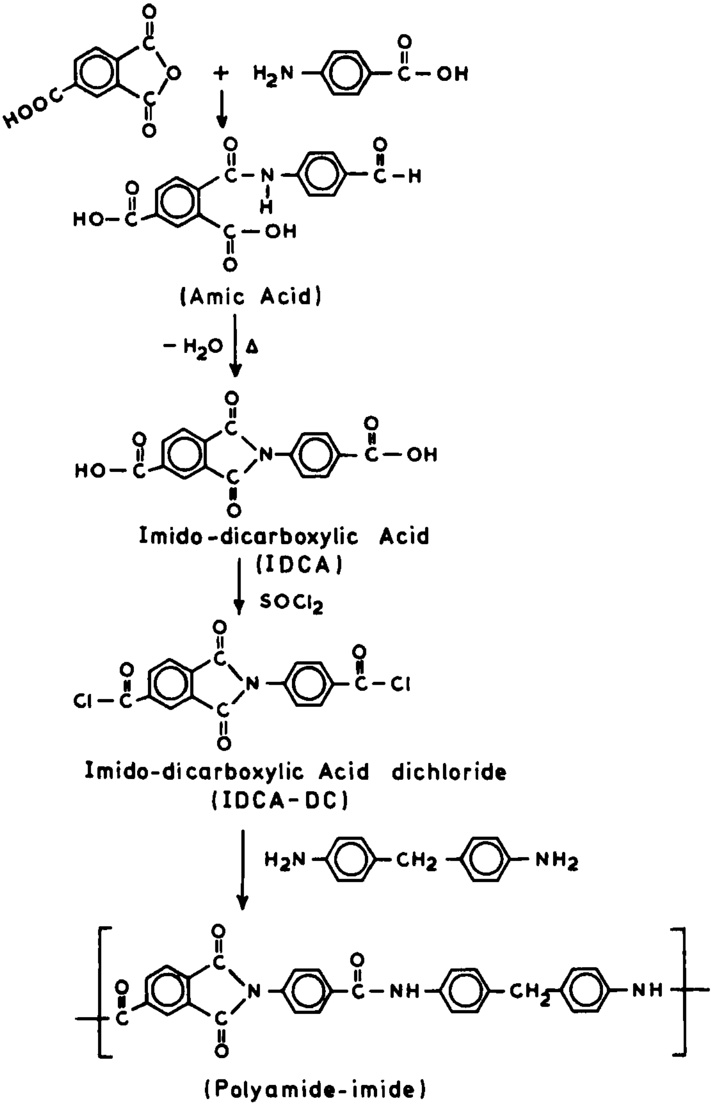
RESULTS AND DISCUSSION

The polycondensation of the diacid chloride of IDCA and p,p'di-(amino phenyl) methane is, in fact, a polyamidization reaction involving a diacid chloride and a diamine. The detailed reaction scheme for the synthesis of polyamideimide is shown in Scheme 1.

The physical properties of the polyamideimide are shown in Table 1. It is observed that the yield is the highest in the case of Method A. However, the inherent viscosity is the highest by Method B. The yield of the polymer is found to depend on the nature of the solvent as well as on the type of acid acceptor used (Table 2). TEA seems to be marginally better as an acid acceptor. The inherent viscosity is practically unaffected by a change of solvent or acid acceptor (Table 2).

Polymer Characterization

The structure of the repeat unit may be represented fairly satisfactorily from nitrogen analysis and IR spectroscopy. The characteristic IR bands for the polymer are observed near 1780 and 1725 cm^{-1} due to asymmetrical and symmetrical carbonyl stretching of imides, and near 720 cm^{-1} due to ring carbonyl deformation of imides. The characteristic amide carbonyl stretching bands are observed near 1650 and 1450 cm^{-1}, and the $-CH_2-$ stretching band, which generally comes near 2950 cm^{-1}, unfortunately superimposes with the broad nujol band near 2900 cm^{-1}.


(Amic Acid)
$-H_2O$
Δ
Imido-dicarboxylic Acid
(IDCA)
$SOCl_2$
Imido-dicarboxylic Acid dichloride
(IDCA-DC)
(Polyamide-imide)

SCHEME 1.

TABLE 1. Yields and Physical Properties of the Polyamideimide[a]

Method of polymerization	Yield (%)	Inherent viscosity[b] (dL/g)	Density (g/cm^3)	T_g[c] (°C)	Nitrogen (%) Calc	Nitrogen (%) Found
A	90-93	0.31	1.26	-	8.88	8.62
B	82-86	0.35	1.26	226	8.88	8.97
C	80-84	0.17	1.24	-	8.88	8.72

[a] Polymerization condition: [IDCA] or [IDCADC] = 10 mmol, [p,p'-di(amino phenyl) methane] = 10 mmol, [acid acceptor] = 20 mmol.

[b] Measured in DMF (0.5 wt%) solution at 30°C.

[c] Calculated from DSC curve (Fig. 5).

TABLE 2. Effect of Solvents and Acid Acceptors on the Yield and Inherent Viscosity of the Polyamideimide[a]

Solvent	Acid acceptor	Yield (%)	Inherent viscosity[b] (dL/g)
DMF	Pyridine	84.6	0.34
DMSO	Pyridine	85.0	0.34
DMSO + 10% LiCl	Pyridine	86.0	0.34
DMAC	Pyridine	86.4	0.35
DMF	TEA[c]	92.3	0.34
DMSO	TEA	82.8	0.34
DMSO + 10% LiCl	TEA	89.0	0.34
DMAC	TEA	91.6	0.35

[a] Polymerization was carried out by Method B. Reaction conditions are the same as shown in Table 1.

[b] Inherent viscosity was measured in DMF (0.5 wt%) solution at 30°C.

[c] TEA = triethyl amine.

Solution Viscosity Behavior

The inherent viscosity of the polymer prepared by three different methods is shown in Table 1. It is observed from Table 1 that the inherent viscosity of the polymer is not very high. However, the molecular weights of the polymers prepared by Methods A and B possess higher molecular weights than the polymer prepared by Method C (Table 1). Similar observations have been reported by other workers [25].

The inherent viscosity of the polymer has been found to decrease by about 6.3% during the first 6 days of storage in DMF at room temperature. Unlike polyamic acid, a precurser of polyimide, which generally does not form a stable solution [6, 15], the solution of this polymer is fairly stable. A similar type of solution viscosity behavior has been observed for other polyamideimides [17-20, 26, 27].

The x-ray diffraction data of the polymer are shown in Fig. 2. It is evident from Fig. 2 that the polymer is amorphous in nature. Thus this polymer finds its application in high temperature coatings and cable enamels where low molecular weight amorphous polymers are desired.

Solubility Characteristics and Solubility Parameter of the Polyamideimide

The solubility behavior of the polyamideimide is presented in Table 3. This polymer, like other polyamideimides [17-20, 26, 27], is soluble in highly polar solvents such as DMF, DMAC, NMP, m-cresol, formic acid, and DMSO. The higher solubility of this polymer in highly polar solvents may be explained by considering the theory of copolymerization [28].

The solubility parameter of the polymer has been calculated from the molar attraction constant, G values, of different groups reported by Hoy [29, 30]. It is generally used to indicate the interaction between polymer molecules and solvents, and it is one of the most common ways to measure the effect of polarity in polymer structure upon the polar attraction between polar molecules. The calculated solubility parameter (δ) of the polymer may be obtained by using the relationship

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

where ΣG is the sum of the Small's group contribution [31], M is the formula weight of the polymer repeat unit, and ρ is the density of the polymer. The solubility parameter obtained from the above equation is 11.56 (Table 4). This is in fairly good agreement with the experimental value of δ, 11.4 (Fig. 3).

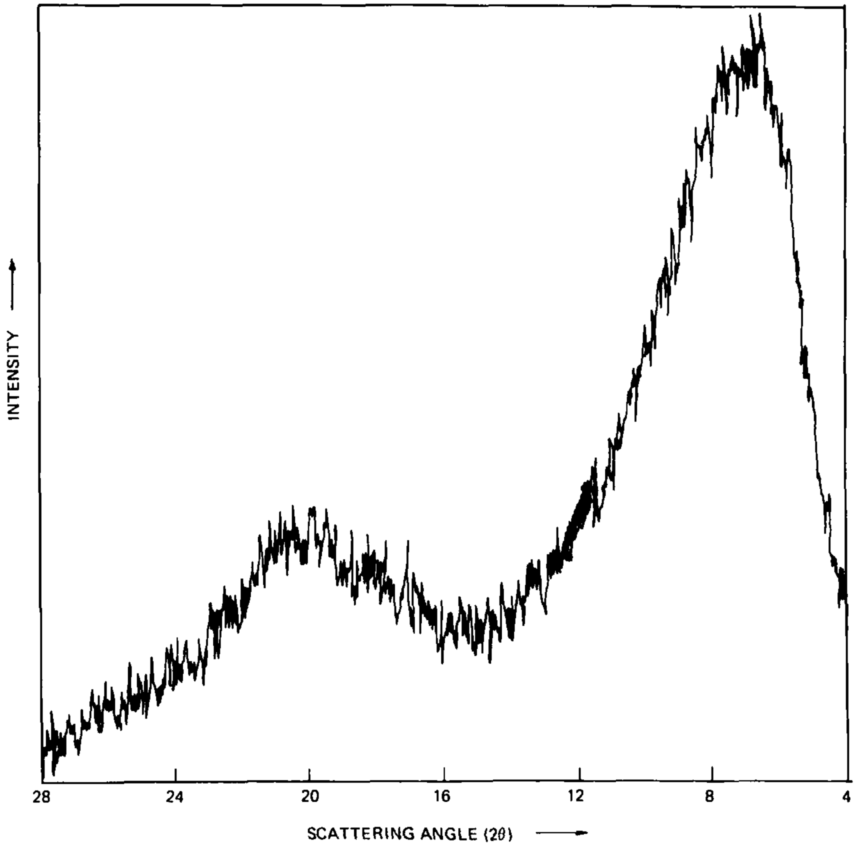


FIG. 2. X-ray diffraction of the polymer.

Thermal Behavior

TGA and DTA of the polymer in air are shown in Fig. 4. TGA data indicates that an initial weight loss of about 9% occurs at 100-110°C. This is due to a loss of moisture or entrapped solvent present in the polymer. There is practically no subsequent weight loss up to 300°C which indicates that the polymer is fairly thermostable. The degradation of the polymer follows a complex process, and the maximum weight loss occurs at 420°C. The overall thermal stability of this polymer is found to be better than that of other polyamideimides reported elsewhere [18-20, 26, 27]. The glass transition temperature of the polymer is found by DSC measurements to be 226°C (Fig. 5).

TABLE 3. Solubility Behavior of the Polyamideimide

Solvent	Solubility parameter (δ)	Hydrogen bonding index (γ)	Solubility[a]
Chloroform	9.16	2.2	-
Carbon tetrachloride	8.55	2.2	-
Cyclohexane	8.19	2.2	-
Benzene	9.16	2.2	-
Toluene	8.93	3.8	-
Cyclopentanone	10.42	6.4	±
Cyclohexanone	10.53	5.2	±
Acetone	9.62	5.7	-
Dioxane	10.13	5.7	-
Ethyl acetate	8.91	5.2	-
Hexane	7.27	2.2	-
Ethylene dichloride	9.86	2.7	-
Chlorobenzene	9.67	2.7	-
Decane	7.74	2.2	-
Dimethylsulfoxide	13.00	5.0	+
Dimethylformamide	11.79	6.4	+
Diacetone alcohol	9.77	6.9	±
Ethyl methyl ketone	9.45	5.0	-
Methyl isobutyl ketone	8.40	5.0	-
Nitrobenzene	10.00	3.2	-
Pentane	7.02	2.2	-
Tetrahydrofuran	9.10	5.3	-
Formic acid	12.1	-	±
m-Cresol	10.2	-	+
Conc H_2SO_4	-	-	+
Dimethyl acetamide	10.8	-	+
N-Methyl-2-pyrrolidone	11.00	5.6	+
Methyl acetate	9.46	5.2	-
Methylene dichloride	9.88	2.7	-

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

TABLE 4. Solubility Parameter (δ) of the Polyamideimide

Functional groups	G values $(cal/cm^3)^{1/2}$	Number of functional groups/substitutions in the polymer chain	Total G values $(cal/cm^3)^{1/2}$
$-CH_2-$	131.51	1	131.51
$-CH=$ (aromatic)	117.12	15	1756.80
$=C=$ (aromatic)	98.12	9	883.08
$C=O$	262.96	4	1051.84
$-NH-$	180.03	2	360.06
$-\overset{\vert}{N}-$	61.08	1	61.08
Five-membered ring	20.99	1	20.99
Six-membered ring	-23.44	4	-93.76
m-Substitution	6.60	1	6.60
p-Substitution	40.33	4	161.32
			$\Sigma G = 4339.52$
Solubility parameter, δ = 11.4 (from the solubility map)		Solubility parameter, δ = 11.56 (from Small's group contribution)	

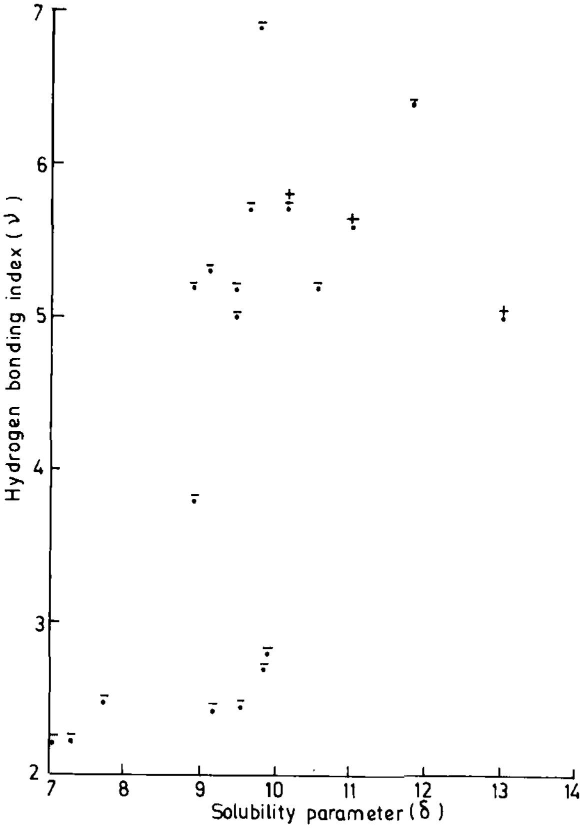


FIG. 3. Solubility map of the polymer.

The low glass transition temperature of the polymer compared with polyimides satisfies the criteria of the melt fabrication technique. The higher T_g of the PAI prepared from p,p'-di(amino cyclohexyl) methane [26] compared with this polymer may be explained on the basis of the fact that at higher temperatures a chair to boat conformational change is possible due to the presence of cyclohexyl ring. This is probably responsible for the higher T_g value of the polymer.

Electrical Properties

The relationships of dielectric constant (ε') and dielectric loss (tan δ) of polymers with frequency, f, at room temperature (~30°C)

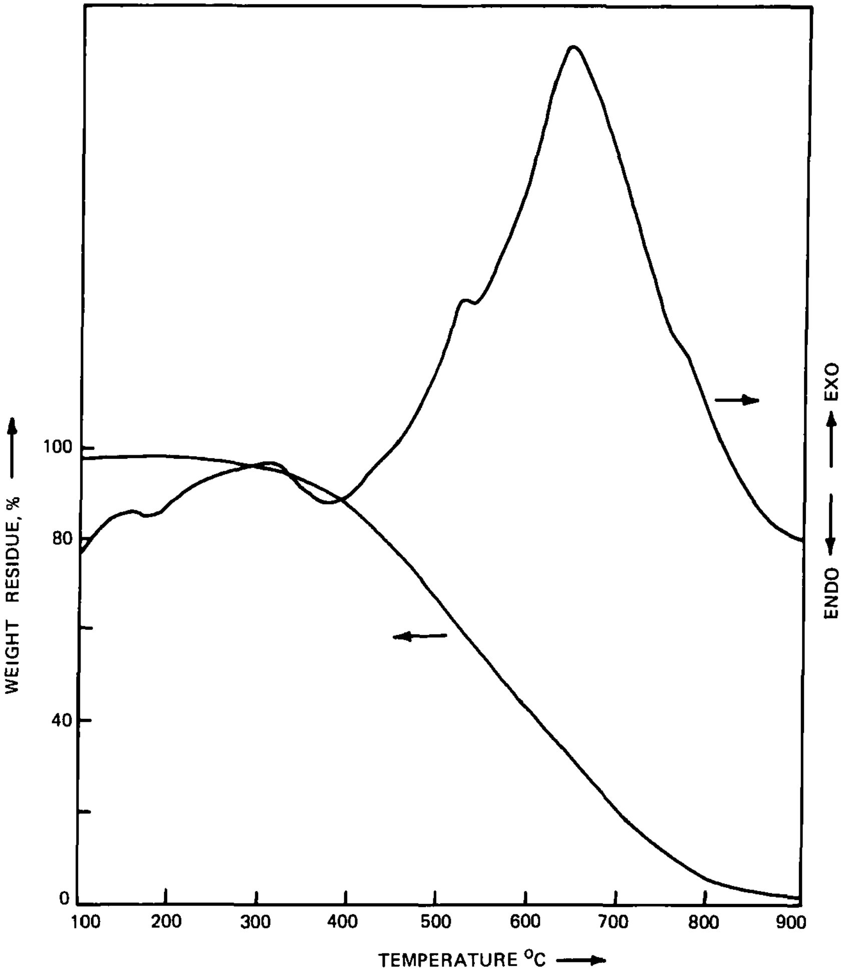


FIG. 4. TGA and DTA of the polymer.

are shown in Fig. 6. From Fig. 6 it is evident that the dielectric constant of the polymer gradually decreases from 4.6 to 3.1 with an increase of frequency. This may be explained on the basis of the fact that when a polar polymer is placed in an alternating electric field, the polar groups in the polymer will tend to orient in the direction of the applied field. Thus, in an alternating electric field the polar groups in the polymer will tend to orient and give a high dielectric constant only when the frequency at alternation is low enough to permit the motion and orientation of the polar groups [32]. At high frequency the

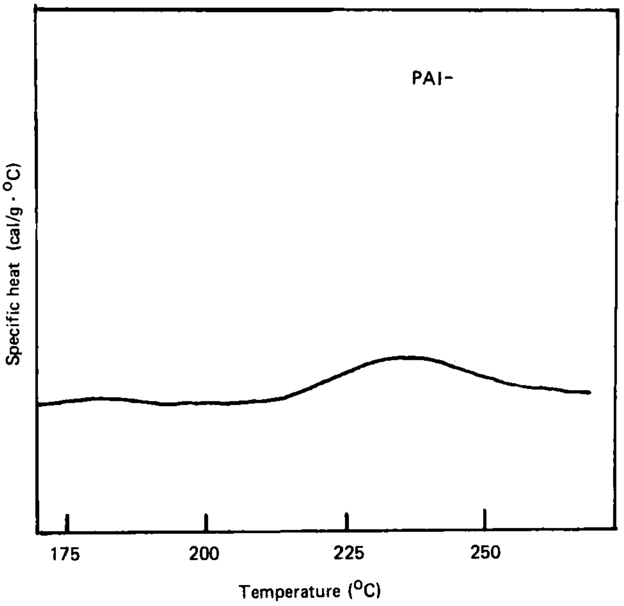


FIG. 5. Differential scanning calorimetry (DSC) of the polymer.

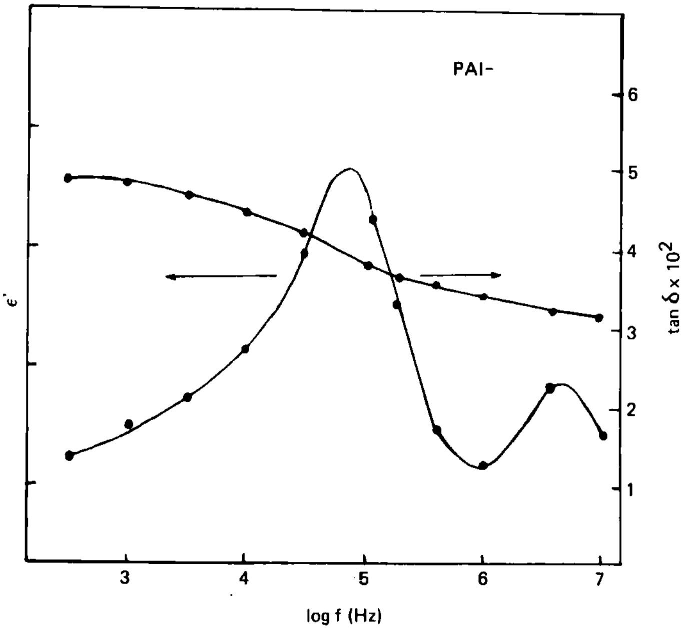


FIG. 6. Variation of dielectric constant (ε'), and dielectric loss (tan δ) with frequency (log f) of the polymer

polar groups will not be able to orient at all, and consequently the dielectric constant of the polymer decreases. The tan δ vs log f plot (Fig. 6) shows a maximum near 4.1×10^3 Hz. This is possibly due to dipole group losses of the polar groups present in the macromolecular chain. The relaxation time (τ) determined at this maximum is found to be 3.88×10^{-5} s. Relaxation time determined by the relationship $2\pi f_{max} = 1$ is the average or the most probable relaxation time, because in every polymer there is a set or spectrum of relaxation times that is determined by a set of structural units of different mobility [33].

The electrical conductivity of the polymer is found to increase with an increase of frequency. The higher value of ac conductivity is possibly due to the heterogenity of the sample, conducting impurities, molecular weight distribution, and crystal defects, and generally exerts its influence in the lower frequency region.

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