Polymers from Renewable Resources. Part 5. Synthesis and Properties of a Polyamideimide from Rosin

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ABSTRACT

Polyamideimide was synthesized from rosin-maleic anhydride imidodicarboxylic acid chloride (RMIDC) and bis-(p-aminocyclohexyl) methane (PACM-20). The polymer was characterized by nitrogen analysis and IR spectroscopy. The inherent viscosity value of the polymer was found to be low, indicating its low molecular weight. The polymer was found to be soluble in highly polar solvents. The solubility parameter of the polymer was calculated from Small's group contribution and determined experimentally from solubility map. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) showed that the polymer was fairly thermostable.

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INTRODUCTION

Copolyimides such as polyesterimides and polyamideimides are an important class of processable heat-resistant polymers [1-7]. These polymers combine excellent thermal stability and mechanical properties with better processing characteristics. These are being used in high temperature cable insulation and advanced composites.

The most important raw material for both polyamideimides and polyesterimides is trimellitic anhydride (TMA). This is a petrochemical, and its price is expected to rise further and availability will become uncertain with a deepening of the oil crisis. Crude oil is the basic raw material for most polymers and petrochemicals. The recent energy crisis has started competition between the demand for oil as fuel and oil as feedstock. This has prompted vigorous research activities for the development of alternative and renewable feedstock for polymers and petrochemicals. We have tried to develop a substitute for TMA from gum rosin, an exudate of pine trees [8, 9].

Levopimaric acid of rosin reacts readily with maleic anhydride to form rosin-maleic anhydride adduct (RMA), a Diels-Alder adduct. RMA has been shown to be a substitute for TMA in that the former, like the latter, reacts with aminobenzoic acids to produce dicarboxylic acids containing internal imide groups (RMIDC). We recently reported the synthesis of polyesterimide from RMID and dihydroxy alcohols such as ethylene glycol [6, 8] and diethylene glycol [9]. We have also reported the use of RMA for the synthesis of polyamideimides [10, 11]. We now wish to report the synthesis and properties of a polyamideimide from RMIDC and bis-(p-amino cyclohexyl) methane (PACM-20).

EXPERIMENTAL

Apparatus and Methods of Characterization

Viscosity measurements were made on a 0.5% (g/mL) solution of polymer in N,N-dimethylformamide (DMF) at 30°C using an Ubbelohde viscometer.

The infrared (IR) spectrum was recorded on a Shimadzu (Japan) spectrophotometer on KBr pellets.

Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetry (DTG) were made simultaneously with a Hungarian Mom Derivatograph of the Paulik Paulik-Erdey System at a heating rate of 10°C/min in nitrogen.

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

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

Materials

Thionyl chloride (BDH, India) was freshly distilled before use.
PACM-20 (E. I. du Pont de Nemours Co., U.S.A.) was used as re-
ceived. Rosin, obtained from a commercial source, was used with-
out further purification. Maleic anhydride (Adarsh Chemicals and
Fertilizers Ltd., India) was purified by sublimation. p-Amino benzoic
acid (E. Merck, India) was used as received. All other chemicals
and solvents used were pure grade and further purified by standard
procedures [12].

Monomer Synthesis

Preparation of Rosin-Maleic Anhydride Adduct

Rosin-maleic anhydride adduct (RMA) was prepared by reacting
rosin with maleic anhydride following the method of Ghosh et al. [13]
as modified by Maiti and co-workers [9].

Preparation of Imidodicarboxylic Acid from Rosin-Maleic Anhydride Adduct

Rosin maleic anhydride imidodicarboxylic acid (RMID) was pre-
pared from RMA and p-amino benzoic acid. The details of the pro-
cedure were reported earlier [9].

Preparation of the Diacid Chloride of RMID [10, 11]

RMID acid chloride (RMIDC) was prepared as follows. RMID (0.05
mol) was refluxed for 4 h with distilled and dry excess thionyl chloride
(0.2 mol) in the presence of a small amount of DMF. After the reac-
tion was over, the unreacted thionyl chloride was distilled off under
reduced pressure. The solid residue was extracted with dichloro-
methane, and the diacid chloride of RMID was further purified by
crystallization from chloroform. The product is light-brown, mp
186-187°C.

Polymer Synthesis

Polyamideimide from rosin was synthesized by reacting RMIDC
with PACM-20 in polar solvents in the presence of an acid acceptor.
The addition of the reactants may be carried out by two ways. In the
first method, RMIDC is dissolved in the solvent and the mixture of
PACM-20 and the acid acceptor is added to it (Method A). In Method
B the order of addition of the reactant is reversed, i.e., RMIDC is
added to the amine solution containing the acid acceptor [14].

Method A

2.78 g (0.005 mol) RMIDC was dissolved in 50 mL DMF in a three-necked flask fitted with a stirrer, a condenser, a thermometer, and a nitrogen inlet. The solution was cooled to -5°C and 1.05 g (0.005 mol) PACM-20 and 0.02 mol pyridine were added slowly with constant stirring. The reaction was allowed to continue for 1 h at -5 to 0°C and then at 70°C for 6 h under nitrogen. At the end of the reaction the mixture was cooled to room temperature and the polymer was isolated by precipitation in cold water, filtered, and dried. The polymer was purified by dissolving in DMF and reprecipitation by methanol.

Method B

1.05 g (0.005 mol) PACM-20, 50 mL DMF, and 0.02 mol pyridine were charged in a 500-mL reactor fitted with a stirrer, a drying tube, and a nitrogen purge system. The mixture was cooled to -5°C and 2.78 g (0.005 mol) RMIDC was added with constant stirring so that the reaction temperature was kept below 0°C for 1 h. Next, the temperature was allowed to rise slowly to room temperature. The polymer was isolated by precipitation in methanol. It was purified by dissolving in DMF and reprecipitating in chloroform, dried in air at 100°C, and finally under vacuum at 60°C. The polymer obtained was a brown solid.

RESULTS AND DISCUSSION

Monomer Characterization

Both RMID and RMIDC were characterized by nitrogen analyses and IR spectroscopy as reported earlier [9-11]. The characteristic absorption bands of RMIDC are observed at 1725, 1710, and 720 cm^{-1} due to imide groups and at 1805 cm^{-1} due to the stretching vibration

of $-C\overset{\displaystyle O}{\underset{\displaystyle Cl}{\big\langle}}$.
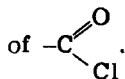
Polymer Characterization

The structure of the repeat unit of the polyamideimide was confirmed by nitrogen analysis (Table 1) and IR spectroscopy (Fig. 1). The characteristic absorption bands of the polymer are observed at 1780 and 1705 cm^{-1} due to imide groups and near 1640 and 1505 cm^{-1} due to carbonyl stretching of amide groups. A band near 1450 cm^{-1} is possibly due to the -CH- bending vibration of the methylene groups

TABLE 1. Yield and Physical Characteristics of the Polyamideimide from Rosin

Method of polymerization	Yield (%)	Color	mp (°C)	Density (g/cm^3)	T_g ^{a} (°C)	Inherent viscosity^b (dL/g)	% Nitrogen^c Calc	% Nitrogen^c Found
A	22	Brown	300	1.06	125	0.09	6.06	5.74
B	66	Brown	300	1.06	125	0.13	6.06	5.80

^{a}Calculated from DTA curve (Fig. 5).
^{b}Inherent viscosity was measured in 0.5% (g/mL) solution in DMF at 30°C.
^{c}Nitrogen content was calculated on the basis of the polymer structure as shown in Fig. 2. Empirical formula of the repeat unit: $C_{44}H_{59}O_4N_3$.
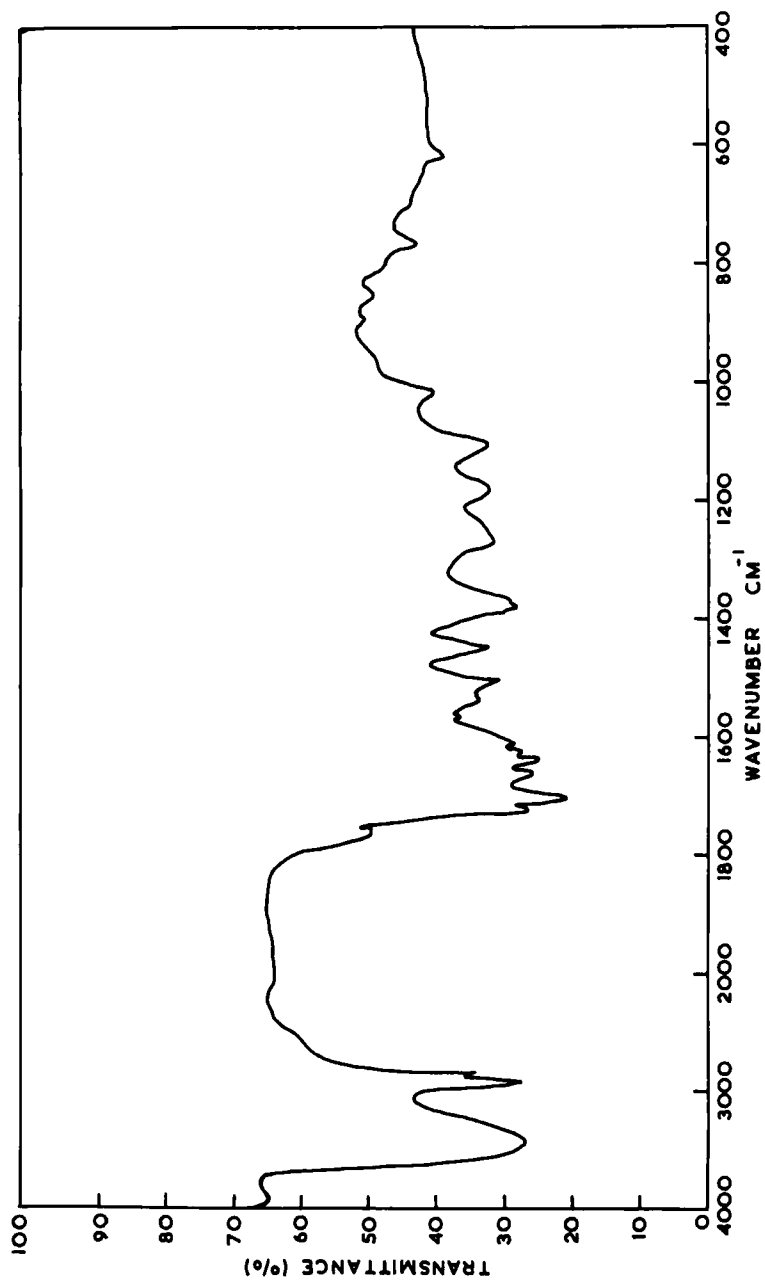
FIG. 1. IR spectrum of the polyamideimide.

of the cyclohexane moiety present in the polymer. The sharp band at 2985 cm^{-1} is probably due to the –NH– group of amide.

The reaction scheme for the synthesis of polyamideimide from rosin and PACM-20 may be represented as in Fig. 2. It is evident from the reaction scheme that RMA reacts like TMA with p-amino benzoic acid
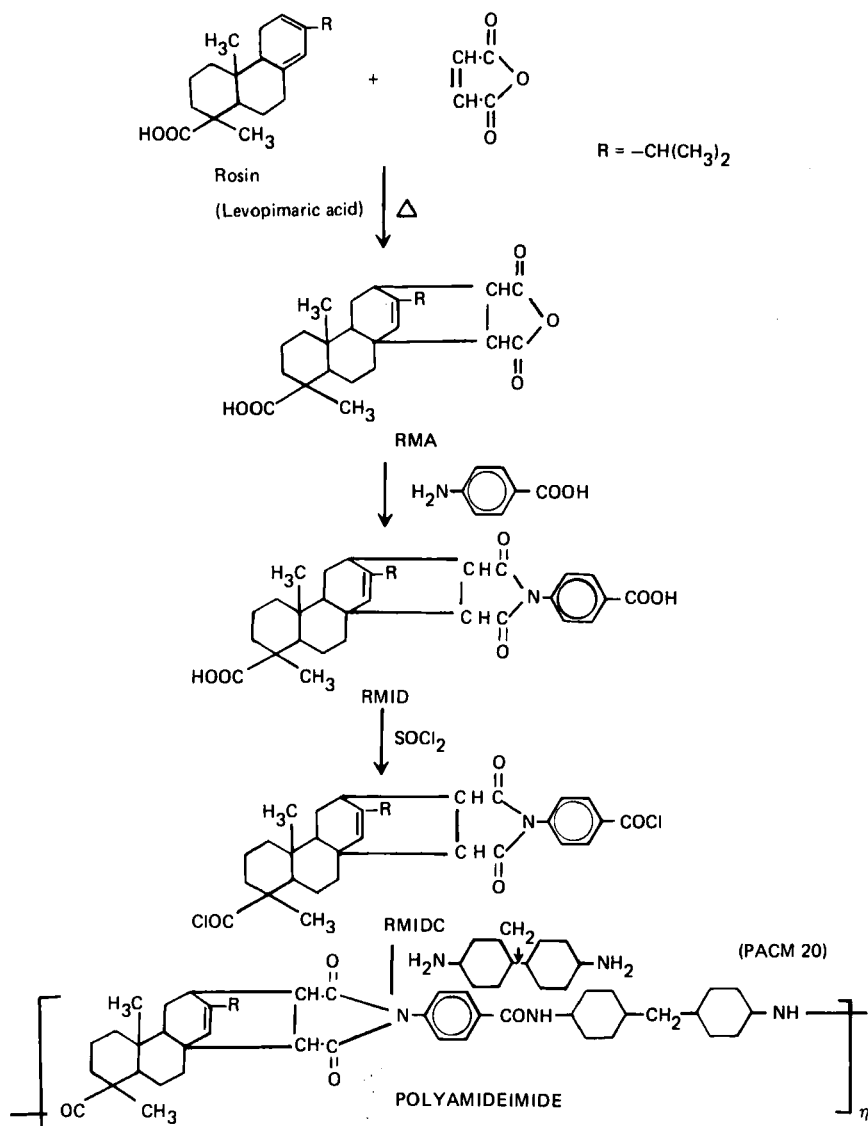

FIG. 2. Reaction scheme.

to form RMID, the substitute for N-(p-carboxyphenyl) trimellitimide.
RMID, like N-(p-carboxyphenyl) trimellitimide, forms an acid chlo-
ride derivative when refluxed with thionyl chloride. RMID or its
acid chloride derivative again, like its TMA-based counterparts, re-
acts with diamines or glycols to form polyamideimides or polyester-
imides. In both the cases the polycondensation reaction proceeds
smoothly in polar solvents.

The properties of polyamideimides and other polymers from rosin
are very similar to those derived from TMA. The polyamideimide
synthesized in the present study, for example, is soluble only in high-
ly polar solvents like DMF, N,N-dimethyl acetamide (DMAC), N,N-
dimethylsulfoxide (DMSO), N-methyl pyrrolidone (NMP), and m-cresol.
The polymer is found to be insoluble in most common organic solvents:
acetone, methanol, ethanol, ethyl acetate, hexane, cyclohexane, cyclo-
hexanone, benzene, toluene, chloroform, carbon tetrachloride, methylene
dichloride, etc.

An x-ray diffraction diagram (Fig. 3) shows that the polymer is
amorphous as there is no sharp peak in the intensity vs scattering
angle (2θ) curve.

Table 1 shows the yield and physical characteristics of the poly-
amideimide. The yield and inherent viscosity of the polymer pre-
pared by Method B are higher than those obtained by Method A. The
very low inherent viscosity values of the polymer indicate that the
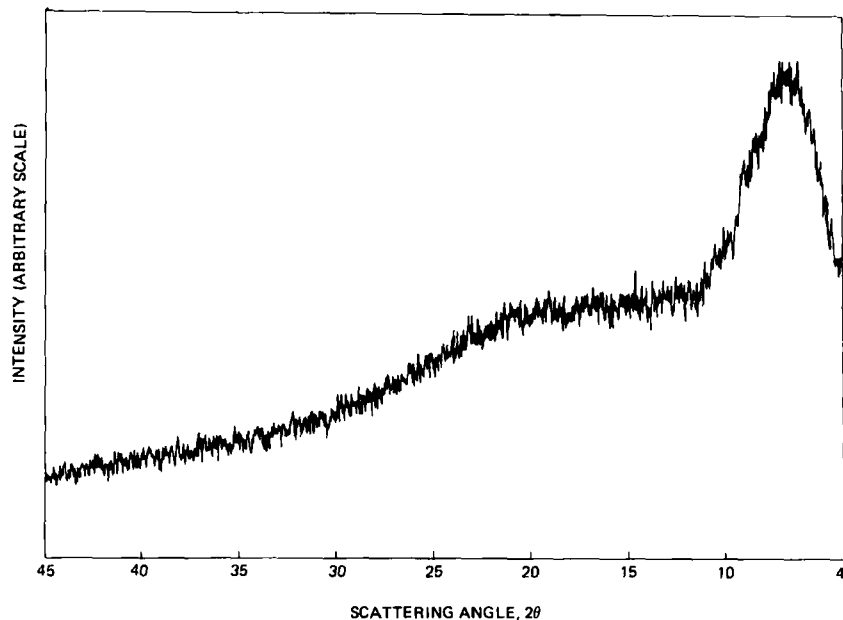polymer has a low molecular weight.

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

Solution Properties

The solubility behavior of the polyamideimide is shown in Table 2. The solubility parameter (δ) and the hydrogen bonding index (γ) of the solvents used are shown in Table 2. It is evident from Table 2 that the polymer is only soluble in solvents having very high values of δ as well as of γ.

A plot of solubility parameter (δ) vs hydrogen bonding index (γ) for the solvents used is illustrated in Fig. 4. The midpoint of the solubility map (Fig. 4) is found to be 10.25, which may be regarded as the experimental value of the solubility parameter of the polymer.

However, the solubility parameter may also be calculated from Small's group contribution, i.e., the molar attraction constant G values

TABLE 2. Solubility Characteristics of the Polyamideimide

Solvent	Solubility parameter, δ $(cal/cm^3)^{1/2}$	Hydrogen bonding index (γ)	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	-
N,N-Dimethylformamide	11.79	6.4	+
n-Hexane	7.27	2.2	-
Nitrobenzene	10.00	3.2	-
Toluene	8.93	3.8	-
Tetrahydrofuran	9.10	5.3	±
Methyl acetate	9.46	5.2	-
1,4-Dioxane	10.13	5.7	±
Dimethylsulfoxide	13.00	5.0	+
Cyclohexanone	10.42	6.4	±
Ethyl methyl ketone	9.45	5.0	-
1-Methyl-2-pyrrolidone	11.00	5.6	+

[a]Solubility keys: +, soluble; ±, partly soluble or swelling; -, insoluble.
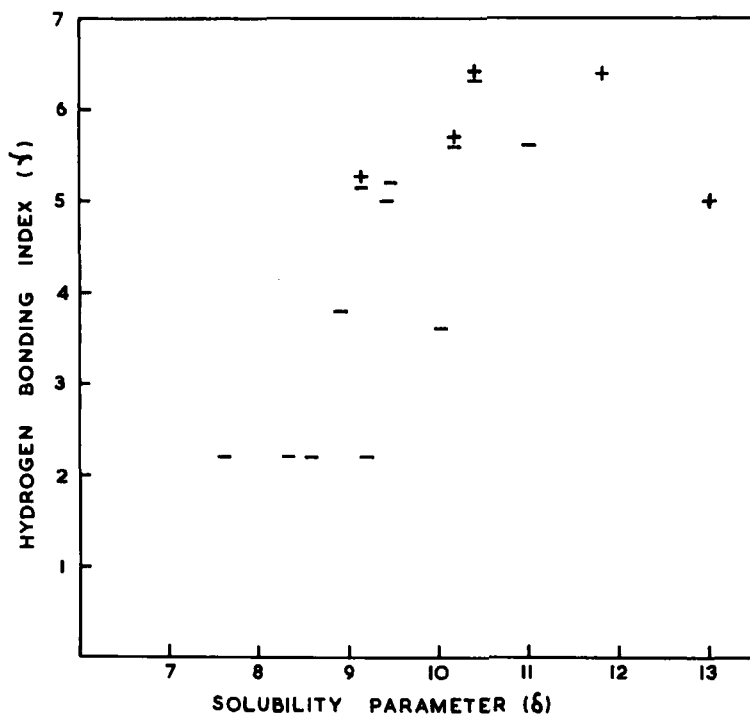
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FIG. 4. Solubility map of the polyamideimide: (+) soluble, (±) swelling or partially soluble, (-) insoluble.

as reported by Hoy [16, 17]. The calculated solubility parameter (δ) of the polymer was calculated by 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 (Table 3). The calculated value of the solubility parameter of the polymer does not agree well with the experimental value. This may be due to the complex structure of the rosin moiety whose values for various group contributions are approximate.

Thermal Behavior

Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential thermogravimetric analysis (DTG) are shown in Fig. 5. TGA indicates that the polymer undergoes about 7% weight

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

Functional group	G value $(cal/cm^3)^{1/2}$	Number of groups in the polymer repeat unit	Total G value $(cal/cm^3)^{1/2}$
6-Membered ring	-23.44	7	-164.08
5-Membered ring	20.99	1	20.99
$>CH-$	85.99	10	859.90
$-CH_3$	147.30	4	589.20
p-Substitution	40.33	4	161.32
$-CH_2-$	131.50	14	1841.00
$>C<$	32.03	3	96.09
$>C=O$	262.96	4	1051.84
$=C-$ (aromatic)	98.12	2	196.24
$>CH$ (aromatic)	117.12	4	468.48
o-Substitution	9.69	4	38.76
$>C=$	84.51	1	84.51
$=CH-$	121.53	1	121.53
$-NH-$	180.03	2	360.06
$>N-$	60.08	1	60.08
		$\Sigma G =$	5950.00
		Solubility parameter $\delta =$	9.09

loss at 200°C and 95% weight loss at 1000°C. It is very likely that a part of the initial weight loss is due to the loss of moisture or entrapped solvent present in the polymer. Viewed in this way, the polyamideimide from rosin appears to be fairly thermostable. The rate of maximum decomposition begins at about 400°C. The rate of decomposition is very fast up to about 500°C when a weight loss of about 60% occurs. Above 500°C the rate of decomposition slows down. This is also corroborated by the DTG curve (Fig. 5). The endothermic peak near 500°C in the DTA curve may be due to some molecular rearrangement in the polyamideimide from rosin. Based on the DTA curve, the T_g of the polymer appears to be 125°C.
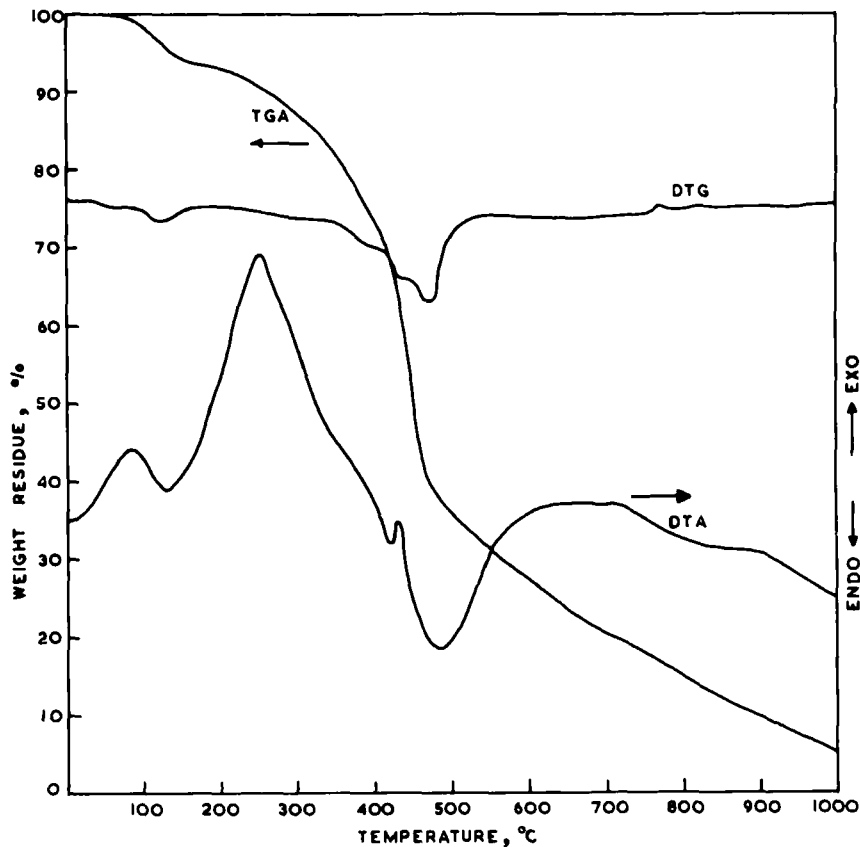
FIG. 5. TGA, DTG, and DTA of the polyamideimide in nitrogen at a heating rate of 10°C/min.

ACKNOWLEDGMENTS

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