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Synthesis and Properties of a New Polyesterimide from a Forest Product

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Synthesis and Properties of a New Polyesterimide from a Forest Product

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ABSTRACT

Polyesterimide offers a class of resin which combines the advantage of high temperature stability with ease of processability. Gum rosin, the exudate of pine trees, has been developed as the raw material for preparation of polyesterimide. Abietic acid of rosin reacts readily with maleic anhydride to form the Diels-Alder adduct, which reacts with p-amino benzoic acid to produce a dicarboxylic acid containing an internal imide group. The dicarboxylic acid reacts with diethylene glycol under melt polycondensation at higher temperature (260-300°C) to produce polyesterimide. The polymer is found to be soluble in highly

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polar solvents. The polymer is amorphous and of low molecular weight. Thermal stability of the polymer has been characterized, and the polymer was found to be thermostable.

INTRODUCTION

Aromatic polyimides are well recognized as an important class of engineering plastics [1-5]. These materials possess extremely satisfactory thermal resistance coupled with many other good qualities, which make them very useful as a material for modern technology [6]. However, the major limitation for widespread use of these resins is their difficulty in processing. Due to high glass transition temperatures, polyimides do not readily lead to a molding process [7]. Since these resins are insoluble in most of the commercially available solvents [8-11], solution processing of these resins also becomes difficult. Copolyimides such as polyesterimide [12-17] offer, on the other hand, a compromise between high temperature stability and ease of processability. Besides, these resins are commercially attractive due to their relatively low cost and better outdoor stability.

Trimellitic acid anhydride (TMA) is an important raw material for preparing polyesterimide and allied polymers. Since TMA is a petroleum-based chemical [18], the recent shortage and rise in petroleum price are expected to increase the price of polyesterimide and related polymers based on TMA. In an attempt to find a suitable substitute for TMA as the raw material for polyesterimide and allied polymers, we have developed rosin, an exudate of conifer trees such as pine, as a source of raw material for such a type of resins. Gum rosin reacts with maleic anhydride and readily forms a Diels-Alder adduct [19]. In the present communication we show that rosin-maleic anhydride adduct (RMA) is capable of being a substitute for TMA. Like TMA, it contains in its molecule one cyclic anhydride group required for imide formation and a carboxyl group necessary for ester linkage. Rosin thus appears to offer an alternative dependable and renewable raw material for synthesis of polymers in general and polyesterimides and allied polymers in particular.

EXPERIMENTAL

Apparatus and Methods of Characterization

Viscosity measurements were made on a 0.5% (g/mL) solution of the polymer in cyclohexanone at 35 ± 1°C by using an Ubbelohde viscometer.

Infrared (IR) spectra were recorded on a Perkin-Elmer, Model 257 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. The measurements were recorded in air at a heating rate of 5°C/min.

Density of polymer sample was determined by means of a small pycnometer in benzene at 30°C. X-ray diffraction diagram was recorded with a Dron I (USSR) x-ray diffractometer using Ni-filtered CuKα radiation.

Materials

Rosin, obtained from a commercial source, is used without further purification. It has the following specifications:

Type	N
Acid content	86.65%
Melting point	56°C
Acid number	162.8

Maleic anhydride (BDH, India) was purified by the sublimation technique. p-Aminobenzoic acid (E. Merck, India) was used without further purification. Diethylene glycol (Sarabhai M. Chemical, India) was dried over sodium sulfate and subsequently distilled under vacuum.

Preparation of Rosin-Maleic Anhydride Adduct

Rosin-maleic anhydride adduct (RMA) was prepared from rosin obtained from a commercial source following the method of Ghosh et al. [20].

100 g Rosin and 30 g maleic anhydride were melted together at 150°C in a flask fitted with a mechanical stirrer and a nitrogen flushing system. The reaction was allowed to continue for about 2 h under nitrogen atmosphere. After the reaction was over, the reaction mass was cooled to room temperature under a nitrogen blanket and the solid mass was powdered. The powdered material was made into a clear solution in diethyl ether. The adduct was purified and isolated by precipitation with petroleum ether, and dried in a vacuum oven to give 63% yield. The product obtained is yellowish white in color (mp 205°C) which cannot be improved by further purification.

TABLE 1. Physical and Chemical Properties of Rosin-Maleic Anhydride Imidodicarboxylic Acid (RMID)

Appearance	Yellow
Melting point	285°C
Elemental analysis for:	
Nitrogen:	
Calculated, %	2.62
Found, %	2.69
Acid number, mg KOH/g:	
Calculated	209.8
Found	208
Solvent	Chloroform, ethyl methyl ketone, m-cresol, dichloromethane, DMAC, DMF, NMP
Nonsolvent	Methanol, hexane, chlorobenzene

Preparation of Imidodicarboxylic Acid from Rosin-Maleic Anhydride Adduct

27 g Rosin-maleic anhydride adduct was mixed with 10 g p-aminobenzoic acid and dissolved in 60 mL dimethylformamide (DMF) in a three-necked flask fitted with a mechanical stirrer, a thermometer, and a nitrogen purging system. The mixture was heated for 3 h at 150°C. After the reaction was over, the reaction mass was cooled to room temperature. About 300 mL water was added when a pale-yellow precipitate was obtained, which was filtered, washed with water thoroughly, and dried in vacuum at 90°C. The rosin-maleic anhydride imidodicarboxylic acid thus produced was purified by reprecipitation from DMF solution by water. The yield of the product was 80%. The general characteristics of the product are shown in Table 1.

Polymer Synthesis [21]

The polycondensation reaction was carried out in a cylindrical reaction kettle (1500 mL capacity) fitted with a nitrogen purging tube, a mechanical stirrer, a thermometer, and a vacuum arrangement through the water-cooled condenser. The reaction kettle was heated by means of a vapor bath. Details of the arrangement are shown in Fig. 1. A typical run for polymer synthesis is as follows: 25.95 g

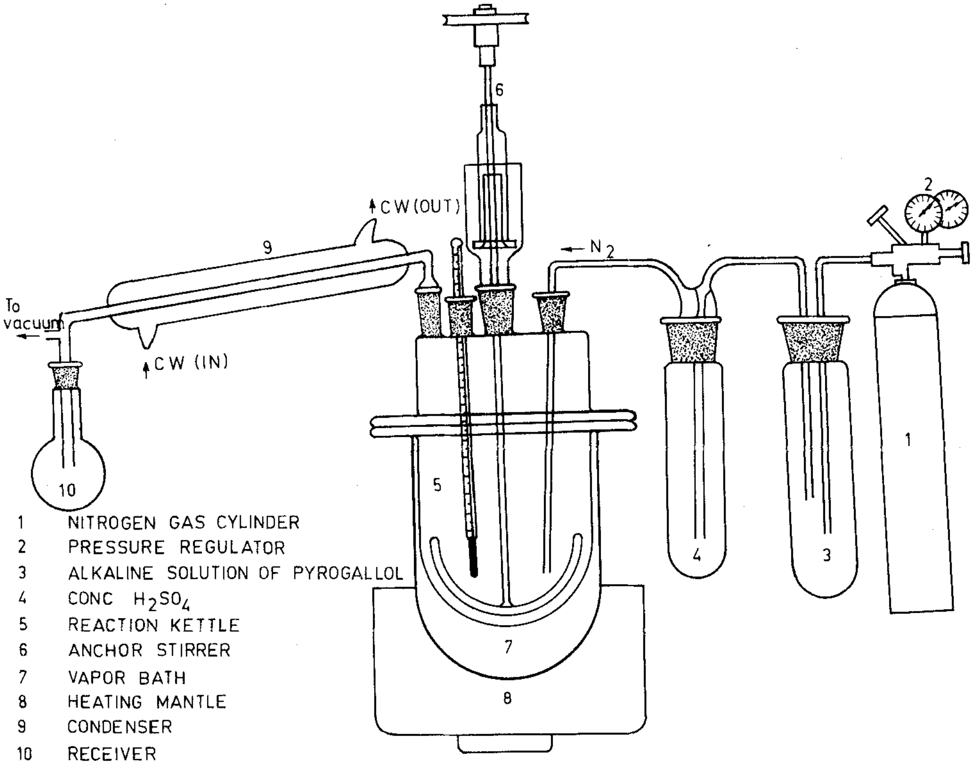


FIG. 1. Experimental set-up of polymer synthesis.

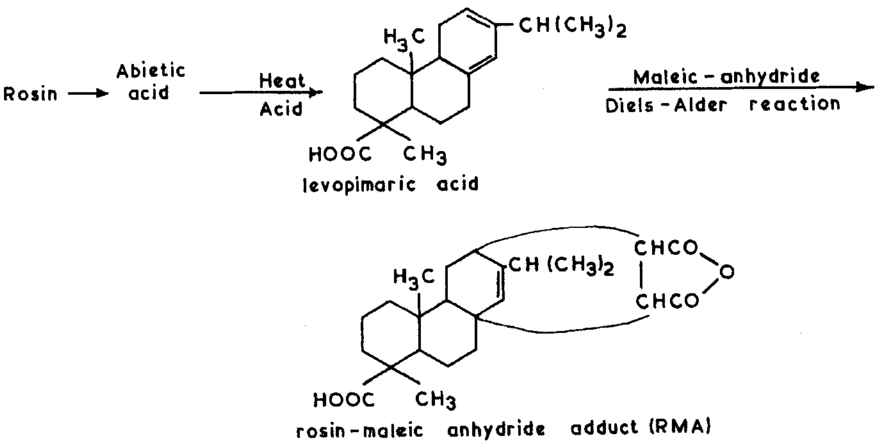
(0.05 mol) of rosin-maleic anhydride imidodicarboxylic acid (RMID) and 20.5 mL diethylene glycol were taken in the reaction kettle. The reaction was carried out in an anthracene vapor bath for 6 h under nitrogen atmosphere. Initially the temperature was kept at 260°C for 3 h. During this period of heating, catalyst (zinc acetate/Sb_2O_3, each 0.1 g) was added. Next the temperature was raised to 280°C and heated for 2 h and finally to 300°C for 1 h. The final 15 min of the reaction was carried out under reduced pressure (~700 mmHg). The molten viscous polymer was poured from the kettle under a flow of nitrogen, which on cooling to room temperature became a solid light brown mass. The yield of polymer is found to be 88%.

Purification of Polymer

Polymer was purified by precipitation several times from a solution in DMF using methanol as the nonsolvent. It was finally washed with diethyl ether and dried in a vacuum oven (~10^{-4} torr) at 100°C for 24 h.

RESULTS AND DISCUSSION

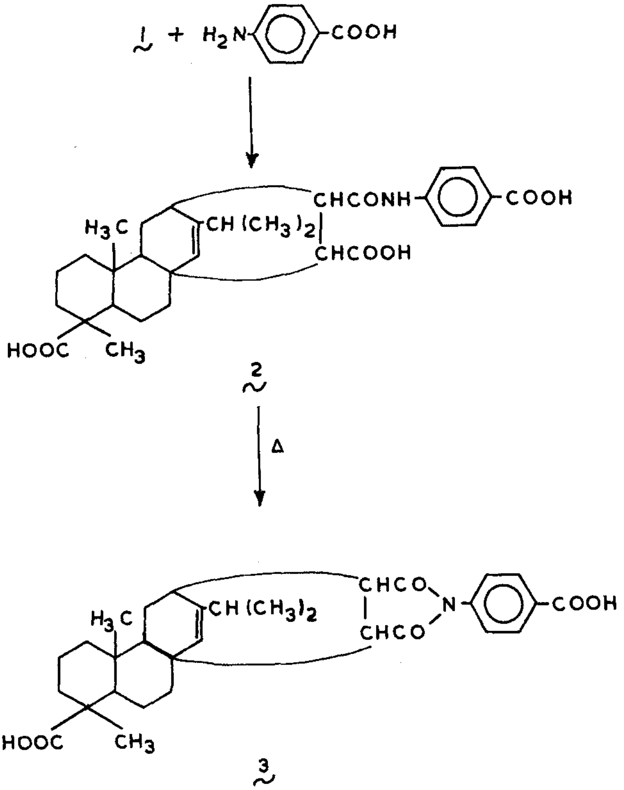
Gum rosin consists of 90% abietic acid. The structure of abietic acid is well known [22, 23]. Mass spectrometric analysis showed that abietic acid contains different isomeric acids [24], one of which is levopimaric acid. Under the influence of heat or strong acid, abietic acid is converted to levopimaric acid [25]. Maleic anhydride actually forms the adduct with levopimaric acid by the Diels-Alder reaction [19, 26]:



1

The reaction scheme for the synthesis of imidodicarboxylic acid from rosin maleic-anhydride adduct (RMID) is as shown on the following page. The reaction scheme is similar to the preparation of N-(p-carboxyphenyl) trimellitimide [27]. Formation of the internal imide group in the RMID acid monomer proceeds most likely through the formation of amic acid (2). The formation of such a type of amic acid was also reported in the case of polyimide synthesis from amine and dianhydride in DMF solution at room temperature [28, 29].

Besides DMF, other solvents such as N,N-dimethyl acetamide and tetrahydrofuran can also be employed. However, highly polar solvents are necessary to dissolve the dicarboxylic acid monomer (3). These solvents associate strongly with both the reactants and the product. This association probably accelerates the reaction for the synthesis of the monomer [10].

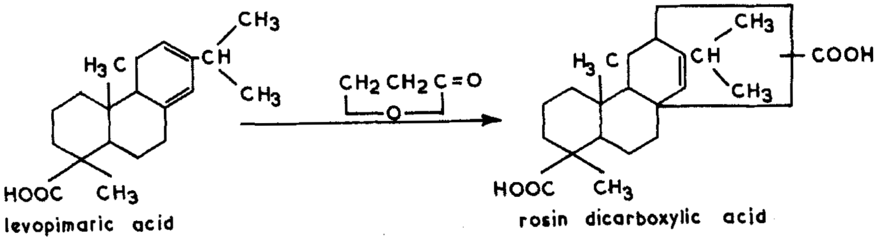


Rosin-maleic anhydride imidodicarboxylic acid (RMID)

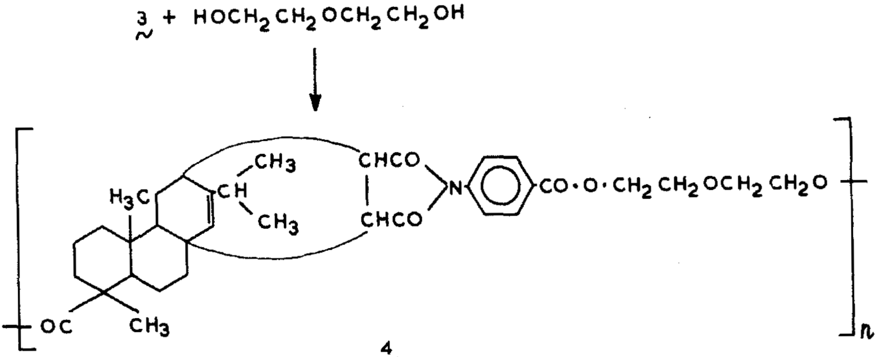
The IR spectrum of RMID is shown in Fig. 2. The absence of an absorption doublet at 1773 and 1850 cm^{-1}, which is characteristic of cyclic acid anhydride [30], indicates that the anhydride group of RMA reacts with the amino group of p-aminobenzoic acid to form an imide group. The presence of an imide group is confirmed by the presence of the absorption band at 1785 cm^{-1}. The band at 1680 cm^{-1} is due to stretching of the carbonyl group.

Halbrook and Lawrence [31] prepared a polyester from modified rosin (dicarboxylic acid) with diethylene glycol. They used β-propiolactone for modification of gum-rosin to form a dicarboxylic acid as shown on the following page. The modified rosin dicarboxylic acid thus obtained was reacted with diethylene glycol to form the polyester.

We have recently reported the preparation of polyesterimide by the single stage process using ethylene glycol as the esterifying agent [32]. Since the carboxyl group of RMA is sterically hindered



by the methyl group, relatively severe reaction conditions are required for making this carboxyl group available for polyesterification reaction. It is therefore desirable that higher boiling glycols should be used for this synthesis. The imidodicarboxylic acid derived from the rosin-maleic anhydride adduct was condensed with diethylene glycol (bp 240°C) at higher polymerization temperatures. The reaction scheme is



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The general characteristics of the polyesterimide are shown in Table 2. The polymer is characterized by elemental analysis and IR spectrum (Fig. 3). The absorption bands at 1780 cm^{-1} and 720 cm^{-1} are due to the imide group. The broad strong peak near 1710 cm^{-1} is due to the overlap of carbonyl stretching of both the imide and ester groups.

Polymer Properties

For coating applications such as cable enamel, low molecular weight amorphous resins are suitable. The x-ray diffraction diagram (Fig. 4) shows that there is no sharp peak in the intensity vs scattering

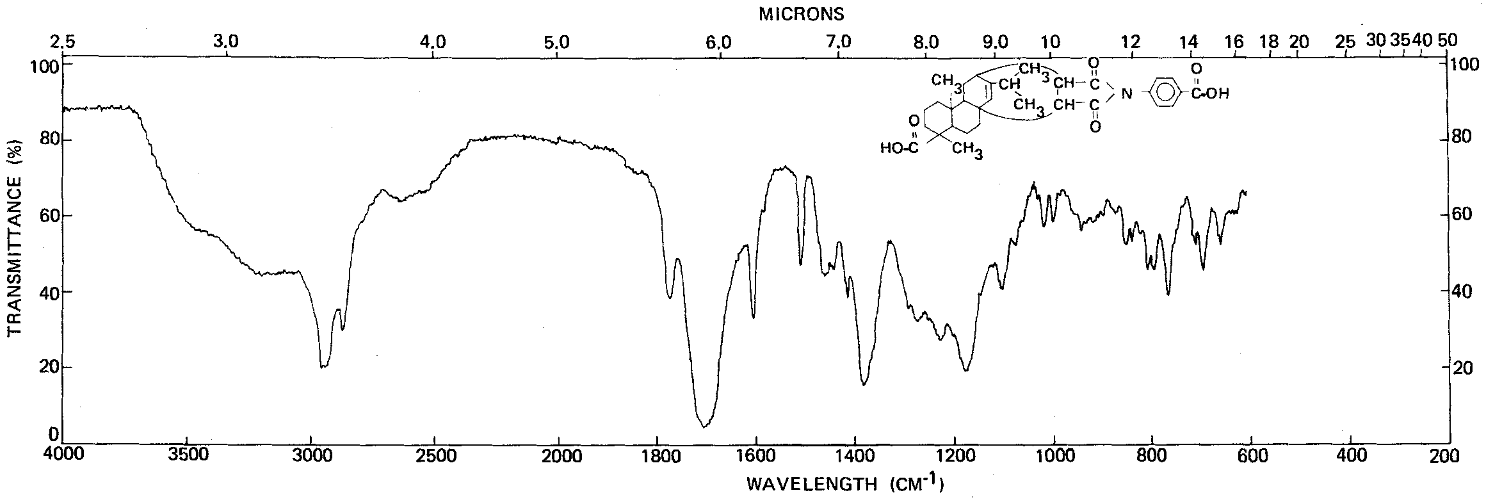

FIG. 2. IR spectrum of RMID.

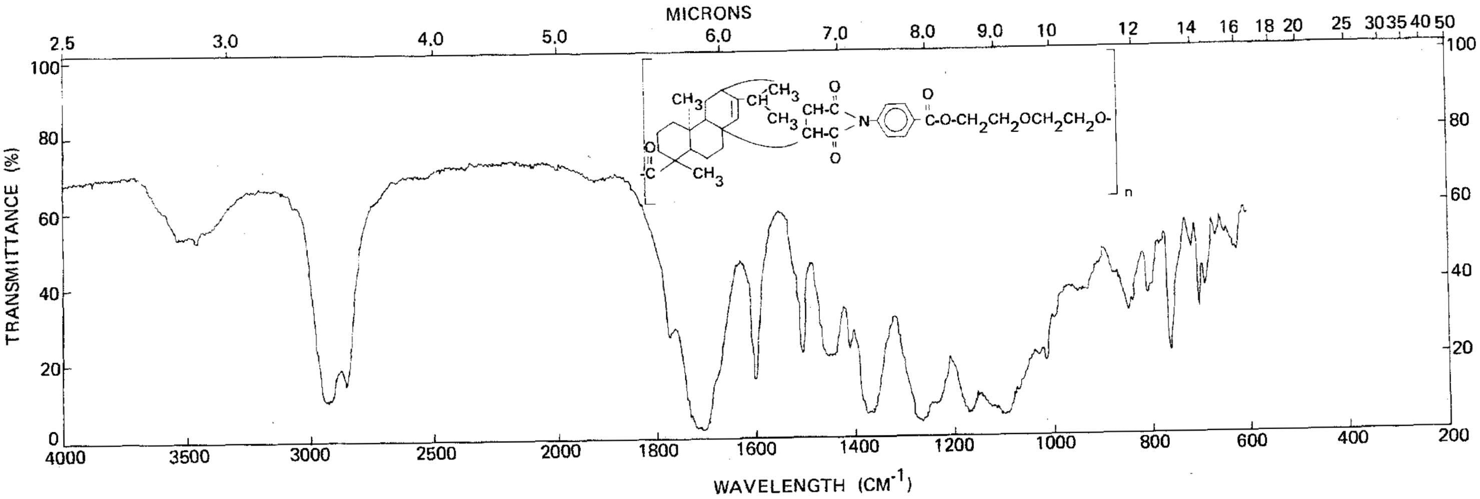

FIG. 3. IR spectrum of polyesterimide [4].

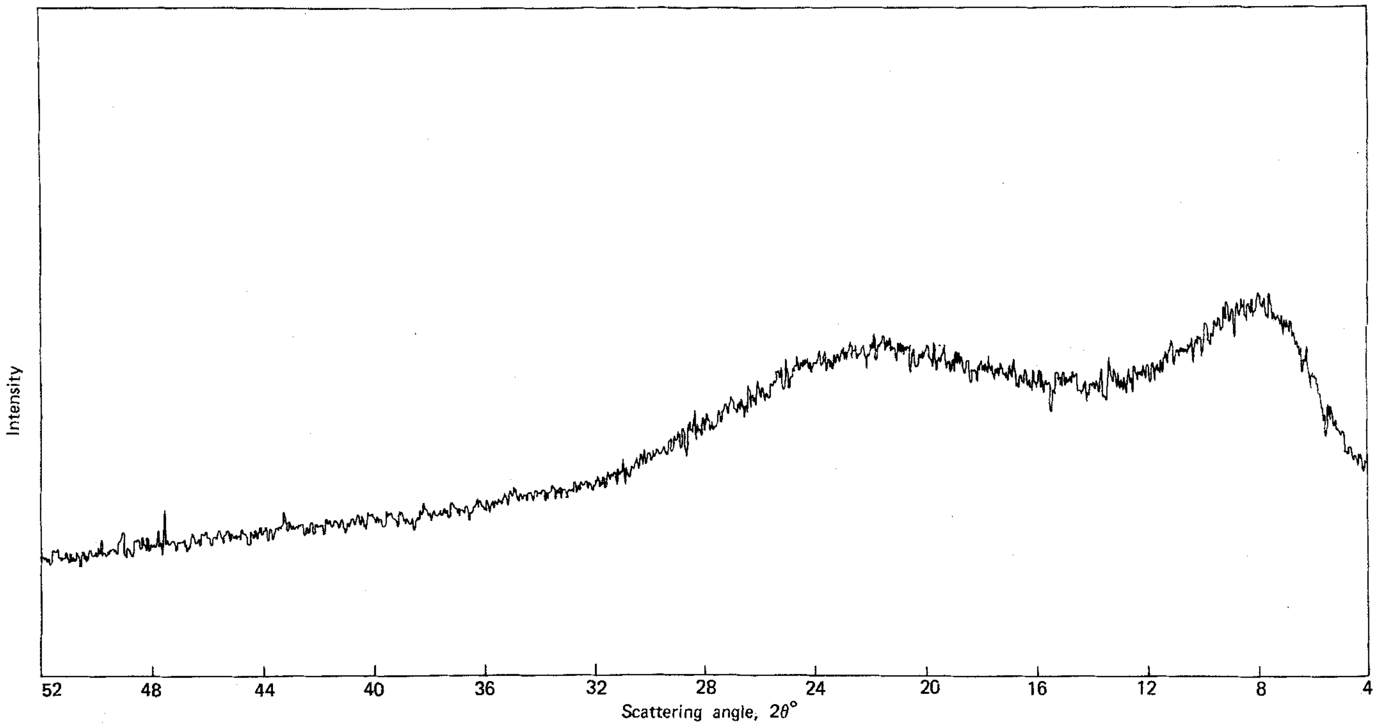

FIG. 4. X-ray diffraction diagram of polyesterimide [4].

TABLE 2. Physical Characteristics of Polyesterimide (4)

Color	Yield[a] (%)	Inherent viscosity[b] (dL/g)	Density (g/cm^3)	T_g[d] (°C)	% nitrogen Calculated	% nitrogen Found
Light yellow	88	0.21	1.16	180	2.41	2.36

[a] Yield was calculated on the basis of total RMID reacted.

[b] Inherent viscosity was measured in 0.5% solution in cyclohexanone at 35°C.

[c] Nitrogen content was calculated on the basis of polymer structure 4.

[d] Calculated from DTA curve (Fig. 4).

TABLE 3. Solution Properties of Polyesterimide (4)

Solvent	Solubility parameter, δ (cal/cm^3)$^{1/2}$	Hydrogen bonding index (γ)	Solubility[a] of polyesterimide (4)
Nitrobenzene	10.00	3.2	-
Methylene chloride	9.88	2.7	-
Ethylene dichloride	9.86	2.7	-
Chlorobenzene	9.67	2.7	-
Carbon tetrachloride	8.55	2.2	-
Benzene	9.12	2.2	-
n-Hexane	7.27	2.2	-
Cyclohexanone	10.42	6.4	-
Acetone	9.62	5.7	-
Decane	7.74	2.2	-
Methyl acetate	9.46	5.2	-
m-Cresol	10.20		+
Formic acid	12.10		+
Concentrated H_2SO_4			+
Dimethylsulfoxide	13.00	5.0	+
N,N-Dimethylacetamide	10.80		+

(continued)

TABLE 3 (continued)

Solvent	Solubility parameter, δ $(cal/cm^3)^{1/2}$	Hydrogen bonding index (γ)	Solubility[a] of polyesterimide (4)
N,N-Dimethylformamide	11.79	6.4	+
N-Methylpyrrolidone	11.0	5.6	+
Toluene	8.93	3.8	-

[a] Solubility keys: +, soluble; -, insoluble.

angle (2θ), which indicates that the polymer is amorphous. The inherent viscosity value (Table 2) indicates that the molecular weight of the polymer is low.

Solution Properties

Table 3 shows the solubility behavior of polyesterimide (4). The polymer is found to be soluble in polar solvents. The solubility of the polymer is found to be better than that of other polyesterimides [13, 14, 27] prepared in our laboratory. The better solubility of 4 may be explained according to the concept [33-35] that the presence of large polar groups in macromolecules increases polymer solubility due to the decrease of the polymer chain density and better polymer solvation with polar solvents.

Thermal Stability

TGA, DTG, and DTA data of the polymer in air are presented in Fig. 5. TGA data have shown that 4 undergoes only 5% weight loss at 350°C, but complete weight loss occurs at 600°C. The maximum rate of weight loss, as is evident from the DTG curve, occurs at 400°C. The degradation of polymer in air appears to be a two-stage process. From the DTA curve, T_g is found to be 180°C, and the onset of oxidative degradation is represented by the exothermic peak at 560°C. It appears from the TGA and DTA study that 4 is a thermostable polymer. The condensed phenanthrene ring-type structure of the rosin is probably responsible for the thermal stability of the rosin-based polymer.

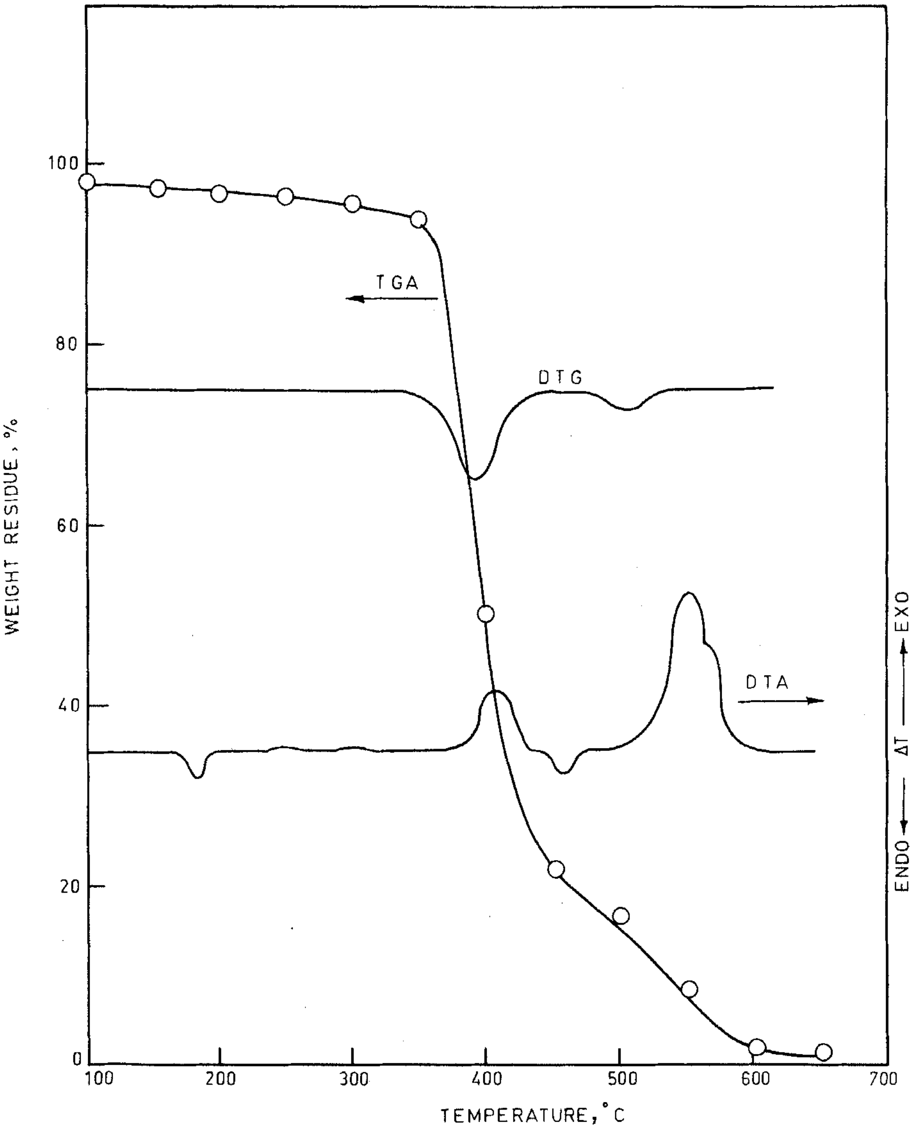

FIG. 5. TGA, DTG, and DTA of polyesterimide [4] in air at a heating rate of 5°C/min.

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