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Polymers from Renewable Resources. Part 9. Synthesis and Properties of a Polyamideimide from Rosin

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ABSTRACT

Polyamideimide was synthesized from rosin-maleic anhydride adduct by the reaction of its acid chloride with diaminodiphenylmethane. The same polymer has also been prepared by the self-polycondensation of the amino acid prepared from the adduct and diaminodiphenylmethane in the presence of thionyl chloride at ambient temperature. The amino acid and the polymer were characterized by IR spectra and elemental analysis. The polymer was found to be soluble only in highly polar solvents. The inherent viscosity of the polymer was found to be low, indicating low molecular weight. The x-ray diffraction data indicated that the polymer was amorphous. The solubility parameter calculated from Small's group contribution agrees well with the experimental value. Thermogravimetric analysis, differential thermal analysis, and isothermal aging showed that the polymer was fairly thermostable.

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INTRODUCTION

Recently, due to the oil and feedstock crisis, research and development activities have been increasingly carried out to find suitable alternative, preferably renewable, sources for polymers and petrochemicals [1, 2]. In our program on polymers from renewable resources, we have successfully identified and developed the forest product gum rosin as a feedstock for polymers and polymer chemicals [3-9]. Other workers have also reported the use of rosin derivatives as raw materials for polymers [10-22]. In the present communication we report the synthesis and properties of a polyamideimide from rosin-maleic anhydride adduct (RMA) and diaminodiphenylmethane.

EXPERIMENTAL

Apparatus and Methods of Characterization

Viscosity measurements were made on a 0.5% (g/100 mL) solution of polymer in N,N-dimethylformamide at 30°C by use of an Ubbelohde viscometer.

The infrared (IR) spectra were recorded on a Perkin-Elmer 237B spectrophotometer using Nujol mulls.

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

The solubility characteristics of the polymer were observed after placing the sample (0.02 g) in 2 mL of various solvents for a week to judge the solvent effects such as swelling or dissolution.

The x-ray diffraction diagram was recorded with Dorn I (USSR) x-ray diffractometer with MoK$_\alpha$ radiation.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were done simultaneously with a Du Pont 1090 system in air at a heating rate of 10°C/min. Differential thermal analysis (DTA) was carried out in air at a heating rate of 10°C/min.

Isothermal aging was done in a specially designed oven to measure the weight loss at different time intervals in air at 200 and 300°C.

Materials

Rosin, obtained from commercial source, was used without further purification. Maleic anhydride (Adarsh Chemicals and Fertilizers Ltd., India) was purified by sublimation. Diaminodiphenylmethane (E. Merck, W. Germany) was used after crystallization from benzene. Thionyl chloride (Ranbaxy, India) was freshly distilled before use. All other chemicals and solvents used were "pure" grade and further purified by standard procedures [23].

Monomer Synthesis

Preparation of Rosin-Maleic Anhydride Adduct

Rosin-maleic anhydride adduct (RMA) was synthesized by reacting rosin with maleic anhydride following a method reported earlier [5].

Preparation of Monoacid Chloride of RMA

Monoacid chloride of RMA (RMA-Cl) was synthesized as described earlier [8].

Preparation of Rosin-Imidoamino Acid [RIAA]

RIAA was prepared as follows. In a 150-mL reactor fitted with a stirrer, a thermometer, a water-cooled condenser with a drying tube, and a nitrogen purge tube, 2.97 g (0.015 mol) of diaminodiphenylmethane was dissolved in 10 mL of DMF. 4.0 g (0.01 mol) of RMA was dissolved in 10 mL of DMF separately, and the solution was added to the diamine solution dropwise at 80°C with stirring. During addition, the temperature of the reaction mixture was raised to 135°C and maintained for 1.5 h. DMF and the by-product water formed during the imidization reaction were removed by distillation, while fresh, dry DMF was added to the reaction mixture continuously. This procedure was continued for 2 h. After the reaction was over, the reaction mixture was poured into excess water. The precipitate was filtered, washed thoroughly with water, and then washed with diethyl ether to remove unreacted RMA and diaminodiphenylmethane. It was finally dried at 40°C under vacuum for 10 h. Yield 90%.

Polymer Synthesis

The polyamideimide from rosin was synthesized by two routes.

Method A

A solution of RIAA in N-methylpyrrolidone (NMP) was treated with thionyl chloride in the presence of triethylamine as an acid acceptor. A typical run is as follows. In a reaction flask fitted with a stirrer, a thermometer, and nitrogen inlet and outlet tubes, 5.3 g (0.01 mol) RIAA was dissolved in 60 mL NMP, and 2.52 g (0.025 mol) triethylamine was added to it. The solution was cooled to 0°C, and 1.12 g (0.01 mol) thionyl chloride was added to it. The solution was stirred at 0°C for 1 h, at room temperature (~30°C) for 2 h, at 60°C for 3 h, and finally at 100°C for 2 h. Then the reaction mixture was poured into ice water where the polymer precipitated out. The polymer was isolated by filtration, washed thoroughly with water, and finally purified by repeated precipitation with methanol from DMF solution. The polymer was dried under vacuum at 100°C for 10 h.

Method B

4.17 g (0.01 mol) RMA-Cl was dissolved in 20 mL DMF in a reaction flask fitted with a stirrer, a thermometer, and a nitrogen purge tube. 1.98 g (0.01 mol) diaminodiphenylmethane and 1.26 g (0.012 mol) triethylamine dissolved in 15 mL DMF were added to the RMA-Cl solution with constant stirring. The reaction mixture was stirred at room temperature (~30°C) for 2 h, at 60°C for 2 h, and finally at 135°C for 4 h. The reaction mixture was poured into ice water to precipitate the polymer. The polymer was isolated by filtration, washed with benzene, and finally further purified by dissolving it in DMF and reprecipitating with methanol. It was dried at 100°C under vacuum for 10 h.

RESULTS AND DISCUSSION

The reaction scheme for the synthesis of polyamideimide from RMA is shown in Fig. 1.

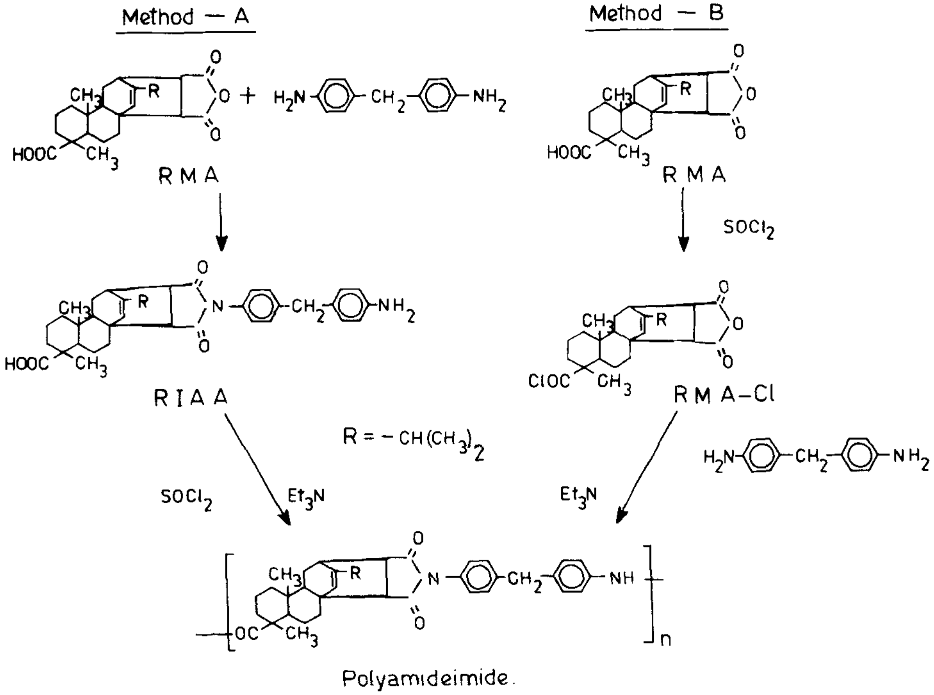

FIG. 1. Reaction scheme for the synthesis of the polyamide-imide from RMA.

TABLE 1. Physical and Chemical Properties of RIAA

Appearance:	Light brown solid
Melting point, °C:	130
Nitrogen analysis:	
Calculated, %:	4.82
Found, %:	4.74
Solvents:	Dimethylformamide, N-methylpyrrolidone, dimethylsulfoxide, dimethylacetamide, methyl ethyl ketone, tetrahydrofuran, cyclohexanone, m-cresol, methanol, ethanol, acetone
Nonsolvents:	n-Hexane, diethyl ether, benzene, toluene, cyclohexane, o-dichlorobenzene, 1,2-dichloroethane, amyl acetate, ethyl acetate

Monomer Characterization

The monoacid chloride (RMA-Cl) was characterized by IR and NMR spectroscopy, as reported earlier [8]. RIAA was characterized by nitrogen analysis (Table 1) and IR spectroscopy (Fig. 2). The characteristic IR bands are observed near 725, 1 725, and 1 785 cm^{-1} for imides. The peak at 1 690 cm^{-1} is due to >C=O of carboxylic acid, and that at 1 625 cm^{-1} is due to >C=C< stretching. The peaks at 3 375 cm^{-1} are due to –OH stretching of –COOH and those at 3 475 cm^{-1} due to NH stretching of the $-NH_2$ group.

Polymer Characterization

The structure of the repeat unit of the polyamideimide was confirmed by nitrogen analysis (Table 2) and IR spectroscopy (Fig. 3). The characteristic IR bands of the polymer are observed near 1 775 and 1 725 cm^{-1} due to symmetrical and asymmetrical carbonyl stretching of imides, at 725 cm^{-1} due to deformational vibration of the cyclic imide, and at 1 640 and 1 550 cm^{-1} due to stretching of the carbonyl group of amide. The broad band at 3 200-3 500 cm^{-1} is due to the stretching vibration of –NH– present in the amide group. The peak for the olefinic double bond appears at 1 635 cm^{-1} and that for aromatic rings at 1 600 cm^{-1} in the IR spectrum of the polymer.

TABLE 2. Yield and Physical Properties of the Polyamideimide

Method of polymerization	Yield, %	Color	Density, g/cm^3	Inherent viscosity,[a] dL/g	% Nitrogen[b]	
					Calculated	Found
A	78	Deep brown	1.36	0.15	4.98	4.72
B	74	Deep brown	1.33	0.14	4.98	4.70

[a] Inherent viscosity was measured in 0.5% (g/100 mL) solution in DMF at 30°C.

[b] Nitrogen content was calculated on the basis of the repeat unit of the polymer shown in Fig. 1. Empirical formula of the repeat unit: $C_{37}H_{42}O_3N_2$.

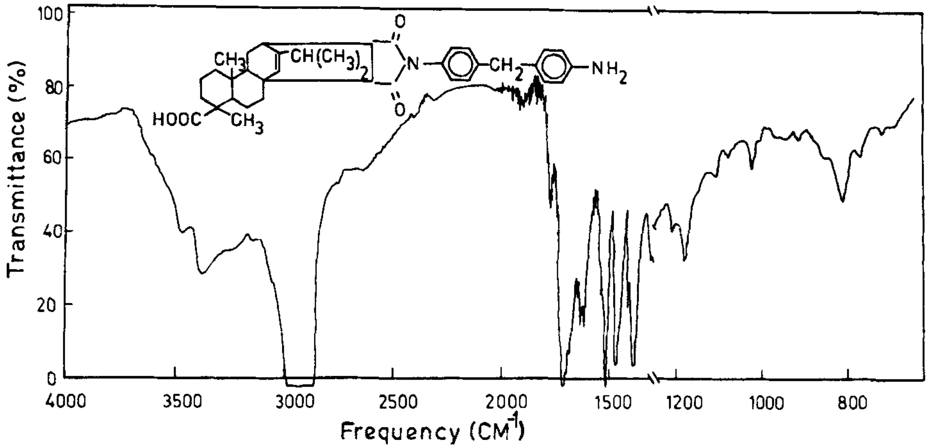

FIG. 2. IR spectrum of RIAA.

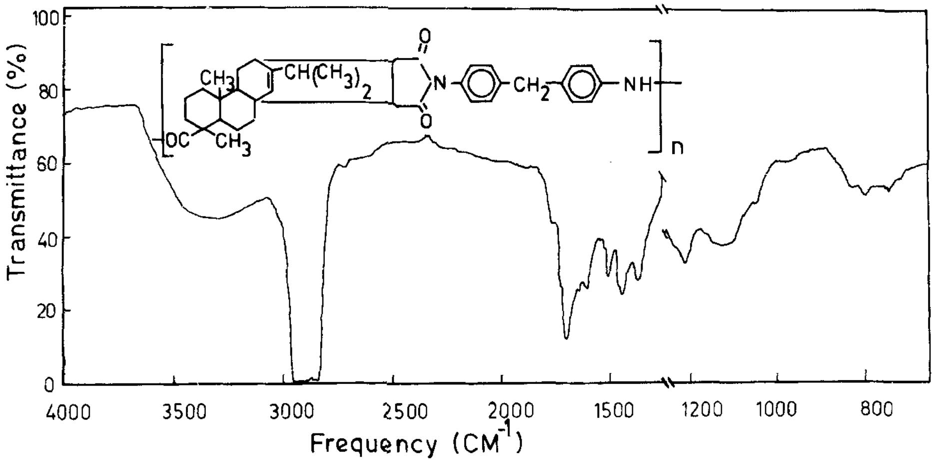

FIG. 3. IR spectrum of the polyamideimide.

Polymer Properties

The yield and physical properties of the polymer are shown in Table 2. The low inherent viscosity which indicates low molecular weight is probably due to steric hindrance and the complex nature of the rosin molecule. That a comparatively low molecular weight product was obtained by Method B may be due to a stoichiometric defect in the monomer feed.

Schuller and co-workers [15] reported a polymer derived from a rosin derivative with the identical repeat unit and a molecular weight of 6 070 corresponding to the inherent viscosity of 0.10 dL/g for a 1.0% solution in DMF at 30°C. Polyamideimide synthesized in our laboratory has an inherent viscosity of 0.13 dL/g for a 1.0% solution in DMF at 30°C, indicating a molecular weight ($\sim$8 000) higher than that reported by Schuller et al. This type of low molecular weight polymer has been used in the preparation of film [11, 15, 18, 20], fiber [11, 15, 20], and ink formulations [19]. Since the polymers from rosin have thermal stability almost comparable with that of conventional polyamideimides [7], they may be recommended for use in coating and cable insulation. However, the molecular weight of such coatings may be increased conveniently by crosslinking through the double bond in the rosin moiety of the polymer. Results of such studies have already been reported [24].

The polymer is soluble only in highly polar solvents and insoluble in common organic solvents (Table 3). The amorphous nature of the polymer was confirmed by the absence of sharp peaks in the intensity vs scattering angle (2θ) curve of the x-ray diffraction diagram (Fig. 4).

Solution Properties

Solubility behavior of the polyamideimide is described in Table 3. That the polymer is soluble only in highly polar solvents is consistent with the behavior of polyamideimides [4, 6, 7, 25].

The solubility parameter can be calculated theoretically from Small's group contribution [26] by the relationship

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

Values of the molar attraction constant, G, for the different groups used here have been reported by Hoy [27, 28]. The solubility parameter of the polymer calculated by this relationship (11.25) was found to be in good agreement with the value (11.4) obtained from the solubility map (i.e., plotting solubility parameter versus hydrogen bonding index of the solvents).

Thermal Behavior

TGA, DTG, and DTA data of the polyamideimide in air are shown in Fig. 5. The TGA curve shows that the polymer undergoes no weight loss up to 200°C, only 1% weight loss up to 250°C, and 3% weight loss up to 300°C. After 300°C, degradation of the polymer

TABLE 3. 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	-
Ethyl methyl ketone	9.45	5.0	-
Methyl alcohol	-	-	-
Ethyl alcohol	-	-	-
Amyl acetate	-	-	-
Chloroform	9.16	2.2	-
Dichloroethane	9.86	2.7	-
n-Hexane	7.27	2.2	-
m-Cresol	10.2	-	+
Cyclohexanone	10.42	6.4	±
1,4-Dioxane	10.13	5.7	-
Tetrahydrofuran	9.10	5.3	±
N,N-Dimethylformamide	11.79	6.4	+
Dimethylsulfoxide	13.0	5.0	+
N,N-Dimethylacetamide	10.80	-	+
1-Methyl-2-pyrrolidone	11.0	5.6	+

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

occurs in two stages, which is also supported by the two peaks in the DTG curve at 350 and 545°C, respectively. The degradation of the polymer is found to be complete at 580°C. Exothermic behavior from the beginning of the DTA curve may be due to a salt-formation reaction between the –COOH and $-NH_2$ group of the low molecular weight polymer or other unknown side reactions which can occur without weight loss or low specific heat or high thermal conductivity of the polymer. This type of exothermic behavior of the polymer was also found for other polyamideimides from rosin [6, 8]. The T_g is not clear from

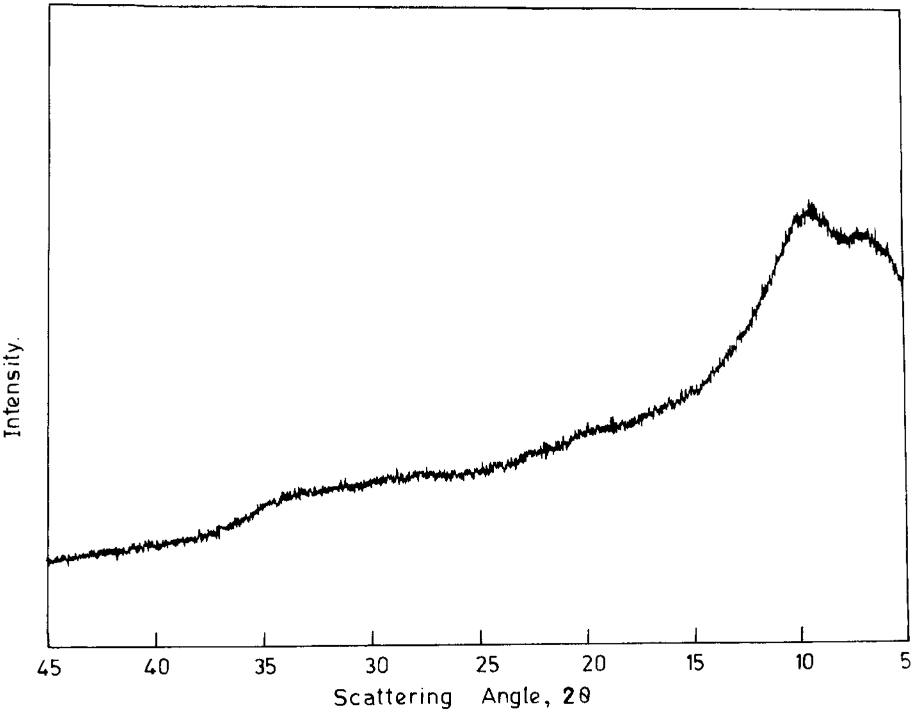

FIG. 4. X-ray diffraction diagram of the polyamideimide.

TABLE 4. Isothermal Aging of the Polyamideimide in Air

Aging time, h:	4	8	12	24
% Weight loss at 300°C[a]	15.1	5.1	4.5	1.8
Cumulative weight loss	-	20.2	24.7	26.5

[a] At 200°C in air there is no weight loss even after 24 h.

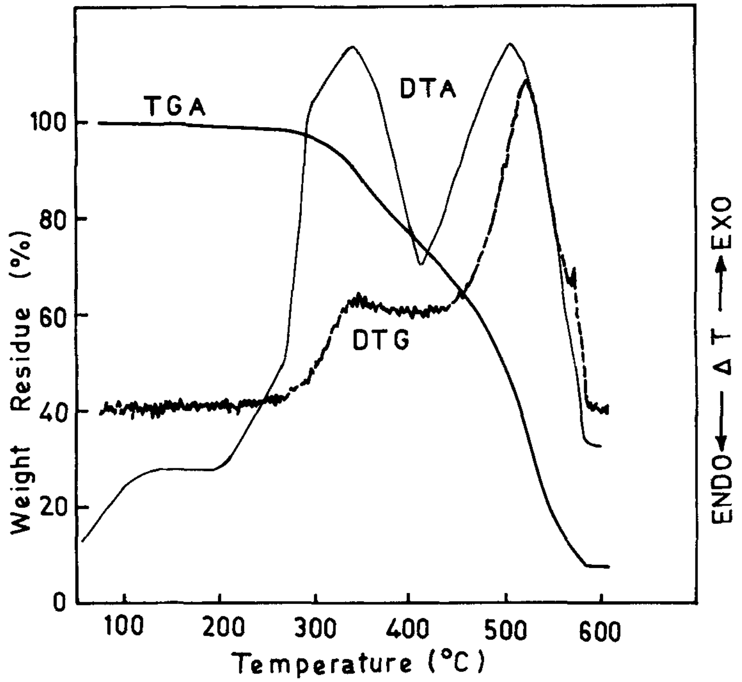

FIG. 5. TGA, DTG, and DTA of the polyamideimide.

the DTA curve. The exothermic peak near 350°C may be due to completion of the polymerization reaction or to a crosslinking reaction in the polymer. After heating the polymer separately at 300°C for 24 h in air, the polymer sample was found to be completely insoluble in DMF, NMP, and even concentrated H_2SO_4. This corroborates the crosslinking taking place during heating at 300°C. The other exothermic peak at 505°C indicates oxidative degradation.

Isothermal aging data at 200 and 300°C in air are shown in Table 4. It was observed that the polymer is stable at 200°C since no weight loss occurs even after 24 h heating at 200°C, but 26.5% weight loss occurs at 300°C. The stability shown at 200°C may be due to the condensed hydrophenanthrene ring and the aromatic ring present in the polymer backbone, and the lower stability at 300°C due to the low molecular weight of the polymer.

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