

NOTES

Nylon 1313: Synthesis and Polymerization of Monomers

Introduction and Discussion

Interest in *Crambe abyssinica* as an oilseed crop for the United States is based in part on its potential value as a source of polyamide monomers.¹⁻³ *Crambe abyssinica* is one of the richest known sources of erucic (*cis*-13-docosenoic) acid, which makes up 55-60% of the acids of the seed oil glycerides. Erucic acid may be separated from crambe oil by fractional distillation of the free fatty acids obtained by hydrolysis of the glycerides. Alternatively, the oil may be converted to methyl esters, and the methyl erucate fraction from distillation hydrolyzed to the free acid. This paper describes the synthesis of nylon 1313 from erucic acid.

Brassylic acid (1,13-tridecanedioic acid) was made in 60-70% yields by oxidative ozonolysis⁴ of commercial erucic acid (Humko, Memphis, Tenn.). The crude product from the ozonolysis mixture contained about 95% brassylic acid, and the purity was raised to 99%+ by recrystallization. The reaction of brassylic acid with ammonia under conditions described by Sorenson and Campbell⁵ for the preparation of azelanitrile gave brassylic acid dinitrile⁶⁻⁸ (1,11-dicyanoundecane) in better than 90% yield. Catalytic hydrogenation of the dinitrile in the presence of cobalt (Girdler G-67RS catalyst, Chemetron, Louisville, Ky.) and ammonia gave 1,13-diaminotridecane⁹ (99%+ by gas-liquid chromatography, GLC) in better than 90% yield. Brassylic acid and 1,13-diaminotridecane were combined in a 1:1 molar ratio to produce the nylon 1313 salt.

Melt polymerization of nylon 1313 salt containing a calculated¹⁰ amount of the diacetate of 1,13-diaminotridecane as a chain terminator produced a nylon 1313 of about 50,000 molecular weight that had an inherent viscosity (0.5% in *m*-cresol at 25°C.) of 0.95. A detailed account of a study of the physical properties of nylon 1313 will be published later.

Experimental

Brassylic Acid (1,13-Tridecanedioic Acid). A solution of erucic acid of about 85% purity (475 g., 1.40 mole) in acetic acid (630 ml.) and water (70 ml.) was maintained at $26 \pm 2^\circ\text{C}$. by external cooling and vigorous stirring while a stream of oxygen containing ozone (3.05 wt.-%) was passed through it at 5.0 l./min. (The ozone was generated in a Welsbach Corporation Model T-816 laboratory ozonator.) When ozone absorption ceased, the mixture had taken up 100.4% of the theoretical amount of ozone necessary to react with the unsaturation present. Production of ozone in the oxygen stream was terminated, and oxygen was passed through the system at 0.2 l./min. while the reaction mixture was heated externally. When the temperature reached 65°C ., an exothermic reaction began, and the temperature continued to rise spontaneously to 100°C . Cooling was necessary to maintain this temperature while the exothermic reaction took place over about 15 min. Oxygen flow rate was increased to 1.5 l./min., and the system temperature was maintained at 110 - 115°C . for an additional hour before the reaction mixture was allowed to stand overnight at room temperature. The crude brassylic acid which crystallized was filtered off and washed first with water and then with cold benzene before being dried at 70°C . *in vacuo*. The yield of crude brassylic acid was 234 g. (68.5% of theory); m.p. 103 - 107°C .; purity about 96% by GLC. The crude brassylic acid was recrystallized from absolute ethanol (470 ml.) and then from benzene (1000 ml.) to give 188 g. (55% of theory); m.p. 112 - 114°C .; 99.8% pure brassylic

acid by GLC. Fractional distillation of the original filtrate gave pelargonic acid, b.p. 140–143°C./13 mm.; yield 177 g. (80% of theory).

Brassylic Acid Dinitrile (1,11-Dicyanoundecane). Brassylic acid, 96% purity, (500 g., 2.05 mole) and polyphosphoric acid (25 g.) were melted under a slow stream of nitrogen in a three-necked flask equipped with a thermometer, a gas inlet tube, and a simple distilling head, condenser, and receiver. When the melt temperature reached 135°C., the nitrogen was replaced by anhydrous ammonia introduced below the surface of the molten liquid. The temperature rose spontaneously to about 180°C., then was gradually increased to 200°C. and maintained at this point for 2 hr. while ammonia was passed through the system. Water condensed in the receiver without organic material. The flow of ammonia was continued while the reaction temperature was further increased to 300°C. for an additional 7 hr. The small amount of organic matter that condensed in the receiver was returned to the reaction flask. The simple distilling head was replaced by a 15-in. Widmer column, and the reaction product was distilled *in vacuo* to yield brassylic acid dinitrile; 384 g. (91.1% of theory); b.p. 176–180°C./1–2 mm.

ANAL. Calcd. for $C_{13}H_{22}N_2$: C, 75.68%; H, 10.75%; N, 13.58%. Found: C, 75.63%; H, 10.57%; N, 13.38%.

1,13-Diaminotridecane. Brassylic acid dinitrile (52 g., 0.204 mole), *p*-dioxane (160 ml., spectro grade), and Girdler G-67RS cobalt-on-kieselguhr catalyst (10 g.) were placed in a 1170-ml. stainless steel bomb that had been chilled with Dry Ice. The system was flushed with hydrogen, anhydrous ammonia (33 g., 1.94 mole) was added, and the bomb was sealed. The bomb was filled with hydrogen to 1800 psig before shaking and heating were started. The system was heated to 110°C. in 1 hr. and maintained at 110–115°C. for an additional 3 hr. Hydrogen absorption was smooth and rapid, being essentially over after 2 hr. The bomb was cooled, and after the gas was released, the contents of the bomb were removed with the aid of *p*-dioxane. The slurry of products was heated to boiling and filtered to remove the catalyst. Vacuum distillation of the filtrate gave 50 g. (93.5% of theory) of 1,13-diaminotridecane; b.p. 118–119°C./0.4 mm. Purity indicated by GLC was 99.1%.

1,13-Diaminotridecane Diacetic Acid Salt. 1,13-Diaminotridecane (18.19 g., 0.085 mole) was dissolved in absolute ethanol (50 ml.). A solution of acetic acid (0.18 g., 0.170 mole) in absolute ethanol (20 ml.) was added slowly to the diamine solution. There was a slight warming of the mixture, but no crystallization occurred upon prolonged standing. The ethanol was evaporated to leave a clear, viscous oil which crystallized upon cooling *in vacuo* over phosphorus pentoxide. The yield of salt was quantitative, m.p. 79–82°C.

ANAL. Calcd. for $C_{17}H_{38}N_2O_4$: C, 61.04%; H, 11.45%; N, 8.37%. Found: C, 60.95%; H, 11.40%; N, 8.10%.

Nylon 1313 Salt. A solution of 1,13-diaminotridecane (131.2 g., 0.612 mole) in absolute ethanol (225 ml.) was added slowly with vigorous stirring to a solution of brassylic acid (146.5 g., 0.600 mole) in absolute ethanol (1250 ml.). The salt precipitated immediately. Stirring was continued for 0.5 hr. after completion of the addition, and the mixture was allowed to stand overnight. The salt was collected on a filter, washed with two 150-ml. portions of ethanol, and dried in a current of air. The yield was 275 g. (99% of theory); the pH of a saturated aqueous solution of the salt was 7.73 at 25°C.

ANAL. Calcd. for $C_{26}H_{54}N_2O_4$: C, 68.08%; H, 11.87%; N, 6.11%. Found: C, 68.00%; H, 11.95%; N, 6.00%.

Nylon 1313 by Melt Polymerization (Molecular Weight about 50,000). Nylon 1313 salt (500 g., 1.09 mole) and 1,13-diaminotridecane diacetic acid salt (1.540 g.; 0.0046 mole) were placed in a 2-liter round-bottomed flask which had been coated on the inside with a fluorocarbon resin. The system was alternately evacuated and filled with nitrogen three times before it was fitted with a stopper carrying a gas inlet and outlet tube and

a stainless-steel stirrer. A slow stream of nitrogen was passed through the flask as it was heated in an oil bath at $225 \pm 2^\circ\text{C}$. After the melt was stirred for 3 hr., the stirrer was raised above the melt and heating continued for an additional hour. The flask was taken out of the bath and allowed to cool under nitrogen before the block of polymer was removed by breaking the flask. The yield of nylon 1313 was 457 g. (99.3%). Overall yield of nylon 1313 from erucic acid was 50.9%.

ANAL. Calcd. for $-\text{NH}(\text{CH}_2)_{13}-\text{NHCO}(\text{CH}_2)_{11}-\text{CO}-$: C, 73.88%; H, 11.92%; N, 6.63%. Found: C, 73.81%; H, 12.01%; N, 6.46%.

TABLE I

Physical Properties of the Polymer	
Molecular weight (expected from stabilizer employed)	50,000
Molecular weight (light scattering) (in 1M sodium acetate in 80% trifluoroacetic acid) ¹¹⁻¹⁴	47,000
η_{inh} (0.5% in <i>m</i> -cresol at 25°C .)	0.95
$[\eta]$	0.83
Polymer melt temperature, $^\circ\text{C}$.	164-167
T_m (polarizing microscope), $^\circ\text{C}$.	170-172
Specific gravity	1.0245
n_D^{25}	1.536

Physical properties of the polymer are listed in Table I.

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Mention in this article of trade names or firms does not constitute an endorsement by the U.S. Department of Agriculture.

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