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Linear Polyesters Derived from Vanillic Acid*

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I. INTRODUCTION

In the long quest for useful products from lignin, very little attention has been paid to the possibility of making synthetic polymers from compounds obtainable from lignin. Vanillic acid is potentially available from lignin and is a likely source of synthetic polymers since it is bifunctional, containing a carboxyl group and a phenolic hydroxyl group. As an initial step in such an investigation, vanillic acid was converted to dibasic acids which were then esterified with ethylene glycol to form linear polyesters. The fiber-forming properties of these linear polyesters were then studied.

II. PREPARATION OF INTERMEDIATES

Dibasic acids were prepared by etherifying the phenolic hydroxyl group in vanillic acid by reaction with alkylene dihalides according to the well-known Williamson synthesis to link two molecules by means of an alkylene bridge. Four such dibasic acids were prepared, as listed in Table I. The first two members of the series were reported to have been obtained by Cahours[1] by the oxidation of biseugenol ethers of the corresponding glycols. Cahours reported that the acids decomposed on heating without melting and evolved an odor of vanillin. The acids obtained in the present work all had definite melting points without decomposition and no vanillin odor was detected.

The dibasic acids were esterified with ethylene glycol to form the bis-hydroxyethyl esters listed in Table I. In the purification of these esters it was difficult to remove the last trace of ethylene glycol, which probably explains the wide melting range observed in some cases.

The preparation of these intermediates are illustrated by the following examples:

1,2-Bis(2-methoxy-4-carboxyphenoxy)ethane. A mixture of 84 g. (0.5 mole) of vanillic acid, 40 g. (1.0 mole) of sodium hydroxide, 500 ml. of water and 47 g. (0.25 mole) of ethylene dibromide was stirred at 73–5°C. for 22 hours. Titration of a sample of the reaction mixture at this time

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indicated that 92% of the sodium hydroxide had reacted. 10 g. of sodium hydroxide (0.25 mole) was then added and the mixture was stirred at reflux for 4 hours. The solution was then cooled and saturated with sulfur dioxide, yielding 63.8 g. of white precipitate (70%). The product was extracted with 500 g. of boiling ethanol to give 54 g. of insoluble white powder, m.p. 278–81°C.

Bishydroxyethyl ester of 1,2-bis(2-methoxy-4-carboxyphenoxy)ethane. A mixture of 87 g. (0.48 mole) of 1,2-bis(2-methoxy-4-carboxyphenoxy)ethane and 201 g. (3.24 moles) of ethylene glycol was refluxed under an air condenser for 48 hours. The reaction mixture was cooled and poured in a thin stream into 1700 ml. of water with stirring. The hydroxyethyl ester separated as a fine white precipitate which was filtered, washed with water, and crystallized from a 25% solution of ethylene glycol in water. The yield was 76 g. (70%), m.p. 159–62°C.

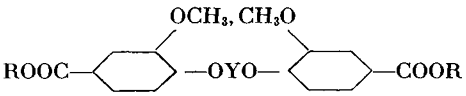
III. FORMATION OF LINEAR POLYESTERS

The purified hydroxyethyl esters were condensed to linear polyesters by heating under vacuum in the conventional manner. Since the esters are easily oxidized at high temperature to give dark colored products, it is essential that all heating be done in the complete absence of oxygen.

The bishydroxyethyl ester was placed in a Pyrex glass tube equipped with a thermocouple well and a tube connected to a vacuum system. The tube was surrounded by an electric heater controlled by a thermostat. The tube was evacuated to a pressure of 0.10 to 0.02 mm. of mercury and heated gradually to a temperature of 275°C. over a period of 3 hours and maintained at 275–80°C. for 12 to 21 hours. The mixture was then allowed to cool and air was admitted to the tube. The product was a hard, colorless, glass-like solid which adhered strongly to glass.

The polymers are very resilient and not easily broken, but when broken with a hammer the pieces tend to fly across the room. The polyesters are quite insoluble in ordinary solvents but can be dissolved in *m*-cresol, which was used as solvent for the intrinsic viscosity measurements listed in Table II.

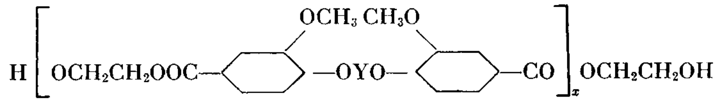
TABLE I



	Dibasic acid (R = H)				Bishydroxyl ester (R = CH_2CH_2OH)			
Y	M.p., °C.	Formula	Neut. equiv. Calc.	Neut. equiv. Found	M.p., °C.	Formula	Sapon. equiv. Calc.	Sapon. equiv. Found
$—CH_2CH_2—$	278–81°	$C_{18}H_{18}O_8$	181	179	159–62°	$C_{22}H_{26}O_{10}$	225	223
$—CH_2CH_2CH_2—$	242–6°	$C_{19}H_{20}O_8$	188	182	141–55°	$C_{23}H_{28}O_{10}$		
$—CH_2CH_2CH_2CH_2—$	236–44°	$C_{20}H_{22}O_8$	195	203	95–115°	$C_{24}H_{30}O_{10}$		
$—CH_2CH_2OCH_2CH_2—$	208–17°	$C_{20}H_{22}O_9$	203	199	112–5°	$C_{24}H_{30}O_{11}$	247	254

TABLE II

Properties of Polyesters



Y	I.V.	M.p., °C.	Softening pt.
$—CH_2CH_2—$	0.61	200–210°	80–85°
$—CH_2CH_2CH_2—$	0.32	95–105°	52–5°
$—CH_2CH_2CH_2CH_2—$	0.36	93–117°	
$—CH_2CH_2OCH_2CH_2—$	0.28	95–118°	

TABLE III

Fiber Properties

$Y = —CH_2CH_2—$

Stretch, %	Stretch temp.	Denier	Tenacity	Elongation, %	Birefringence
0	25°C.	16.2	0.7	14	0.014
25	25°	5.4	2.1	20	—
50	25°	2.7	3.0	50	0.091
40	85°	12.6	1.0	40	—
0	80° [a]	3.0	2.7	100	—
170	80° [a]	1.9	4.2	30	0.120

[a] Stretched in a water bath.

IV. FIBER SPINNING AND FIBER PROPERTIES

Fibers were obtained by placing the polyester in a stainless steel bomb which had an orifice 0.016 inch in diameter in the bottom. The body of the bomb was fitted with a thermocouple well and surrounded by an electric heater which was controlled by a thermostat. The head of the bomb carried a gas inlet tube for the introduction of nitrogen under pressure. The bomb was flushed with nitrogen to remove air and the temperature was raised to slightly above the melting point of the polyester. The molten polymer was forced through the orifice by the application of nitrogen pressure. The fiber was taken one complete turn over a godet wheel and wound on a reel that had a variable speed drive. In this way a stretch could be applied to the fiber. If desired, the fiber could be drawn through a bath as shown in Figure 1.

The fibers were difficult to stretch at room temperature although some increase in tenacity was obtained by giving stretches up to 50%. Stretching in air at 85°C. did not improve the tenacity, but stretching in a water bath at a temperature just below the softening point gave a fiber with a tenacity of 4 g. per denier (Table III). The fiber necked down when stretched and showed birefringence in the stretched area. A comparison of birefringence measurements according to the method of Johannsen[2] is

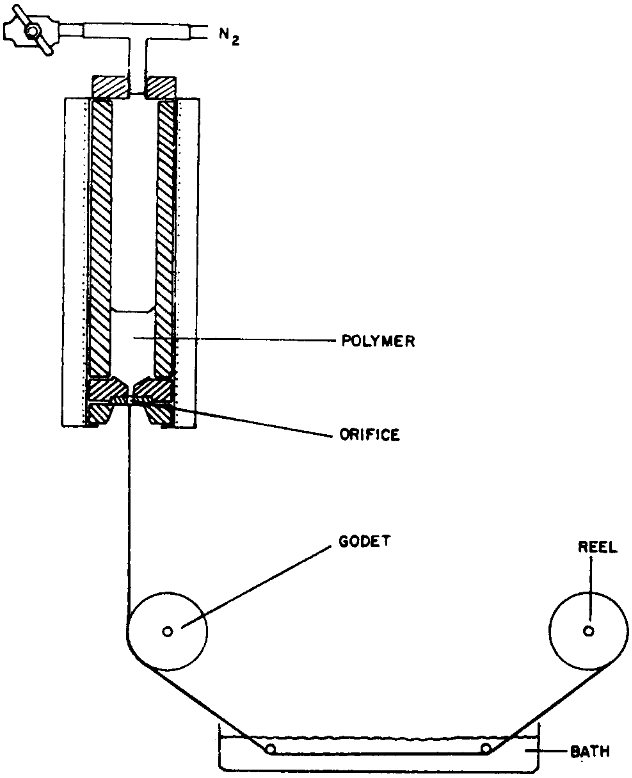


Figure 1

shown in Table III. The increasing birefringence with increased stretch shows that the crystallinity of the fiber is enhanced on stretching. The softening points were not affected by stretching. Although the fiber (Y = $—CH_2CH_2—$) would not melt below 200°C., it shrank when heated to 80°C. This property renders the material unsuitable for textile fibers.

DISCUSSION

It is interesting to compare the polyester (Y = $—CH_2CH_2—$) with a similar polyester made by Dickson[3] from 1,2-bis(4-carboxyphenoxy)ethane, which is identical except for the methoxyl groups. The Dickson polymer is symmetrical and melts at 240°C. and softens at very nearly the same temperature. The methoxyl groups are therefore responsible for the lower melting point and the much lower softening point in the vanillic acid derivative. The methoxyl groups introduce assymetry and interfere with close packing of the molecules and thus prevent the attainment of a high degree of crystallinity as shown by the low softening point.

Side chains in aliphatic linear polymers are known to interfere with crystallinity. Hill and Walker[4] reported that terephthalic acid esters of unsymmetrical glycols were noncrystalline and low melting. In a series of polyurethans prepared by Brewster[5] from ethylene diisocyanates and trimethylene glycols, crystalline polymers were obtained from symmetrical glycols, but 2-methylpropane-1,3-diol gave a liquid polymer. Polyamides made from α,α'-dimethyladipic acid formed weak fibers compared to those from simple adipic acid, and the racemic acid gave weaker fibers than the meso or active acid. The methyl-substituted polyamides formed opaque fibers on extreme stretching. The same phenomenon was observed with ethylenedivanillic acid polyester when given the maximum stretch.

Polyesters of unsymmetrical aromatic acids have been reported including esters of hydroxynapthoic acids,[6] naphthalene dicarboxylic acids,[7] and 2,2'-dimethyl-4,4'-biphenyldicarboxylic acid.[8] In the last case, the polymer was lacking in crystalline properties. As was to be expected, the linear polyesters derived from vanillic acid had a low degree of crystallinity, but still there is definite evidence of crystallinity and the polymers have fiber forming properties.

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(3) J. T. Dickson, U. S. Patent 2,465,150 (1949).

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(5) J. H. Brewster, *J. Am. Chem. Soc.*, **73,** 366 (1951).

(6) F. Linsker, U. S. Patent Application Ser. No. 638,925 (publ. 1950).

(7) J. G. Hill *et al.*, Brit. Patent 604,073 (1948).

(8) E. F. Izard, *J. Polymer Sci.*, **9,** 35 (1952).

Synopsis

Vanillic acid, which is potentially available from lignin, was converted to dibasic acids by etherifying the phenolic hydroxyl group with alkylene dihalides. The dibasic acids were esterified with ethylene glycol and condensed to linear polyesters. The polyesters were converted to fibers by melt spinning. The fibers could be stretched, preferably in a warm water bath, to give fibers with good tenacity and increased crystallinity as shown by birefringence measurements. The polyester obtained from ethylenedivanillic acid melted at 210 °C. but softened and shrank at 80 °C.

Résumé

L'acide vanillique, que l'on peut obtenir au départ de lignine, peut être transformé en acide dibasique par éthérification du groupe hydroxyle phénolique au moyen de dihalogénure d'alcoyle. Les acides dibasiques ont été ensuite estérifiés par l'éthylèneglycol et soumis à polycondensation afin d'obtenir des polyesters. Les polyesters ont été transformés en fibres par filage à l'état fondu. Les fibres peuvent être étirées, de préférence dans un bain d'eau chaude, de façon à obtenir des fibres d'une ténacité suffisante et de cristallinité accrue, ainsi qu'il ressort des measures de biréfringence. Le polyester obtenu au départ d'acide divanillique fond à 210° C mais il se ramollit et se contracte à 80 °C.

Zusammenfassung

Vanillinsäure, die aus Lignin erhalten werden kann, wurde durch Ätherifizierung der phenolischen Hydroxylgruppe mit Alkylen-Dihaliden in dibasische Säuren verwandelt. Die dibasischen Säuren wurden mit Äthylenglycol esterifiziert und zu linearen Polyestern kondensiert. Die Polyester wurden durch Spinnen der Schmelze in Fasern verwandelt. Die Fasern konnten gestreckt werden, was am besten in einem warmen Wasserbad vorgenommen wird, und sie ergaben Fasern von guter Haltbarkeit und erhöhter Kristallini tät. Wie durch Doppelbriechungsmessungen gezeigt wird. Der Polyester, der aus Äthylen-Divanillinsäure erhalten wurde, schmolz bei 210 °C, wurde aber schon bei 80 °C weich und schrumpfte.

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