hydrochlorides and α-naphthylthioureas. The hydrochlorides were analyzed for chlorine. The data are summarized in Tables II and III. In several cases the secondary amine was prepared from both possible combinations of aldehyde and amine, and the two products shown to be identical by comparison of physical constants and derivatives.

Summary

1. A procedure has been described for the preparation of aldimines from aliphatic aldehydes and amines.

2. The catalytic hydrogenation at low temperatures and pressures of the aldimines has been studied, and several unsymmetrical, secondary aliphatic amines have been prepared, their physical constants determined and certain derivatives made.

NOTRE DAME, INDIANA RECEIVED SEPTEMBER 25, 1943

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1a]]

Linear Superpolyesters from Dilinoleic Acid

BY JOHN C. COWAN AND DONALD H. WHEELER[1b]

Linear superpolymers prepared from saturated dibasic acids with other difunctional molecules have been described by Carothers.[1c] However, the preparation of linear superpolymers from dibasic acid containing non-benzoid unsaturation has not been described despite reported preparation of such α-polyesters[2] and α-polyamides.[2a]

Vorländer[3] reported the preparation of a resinous polyethylene maleate and crystalline polyethylene fumarate. Carothers[4] prepared the same polyesters, reporting that the maleate polymer was crystalline, and the fumarate resinous. In addition, Carothers reported that both polyethylene maleate and fumarate were heat-convertible to insoluble three-dimensional polymers.

Bradley[5] and Vincent[6] showed that these polyesters were oxygen-convertible and confirmed Carothers' observation on their heat-convertibility. Vincent reported that one polyester, the triethylene glycol citraconate, was very difficult to heat-convert. This observation indicated that under controlled conditions certain types of unsaturated dibasic acids might give linear superpolyesters. It was believed that the kind of unsaturation present in the acid, as well as the possible effect of steric hindrance, were important.

Dibasic acids which contain unsaturation not conjugated with the carboxyl groups, or contain unsaturation which does not easily shift to conjugation, have not been readily available until recently. By suitable polymerization,[7] and fractional distillation[8] under reduced pressures, the esters of linoleic acid of semi-drying oils can be converted to esters of dilinoleic acid.[8a] Although the structure of dilinoleic acid is not known with certainty, the following data indicate its properties[8,9]

Unsaturation	Two double bonds
Molecular weight	560
Neutral equivalent	280
Conjugation	Negligible[10]
Conjugation after alkali treatment[11]	Negligible[12]
Melting point	Non-crystalline at −60°

Bradley[8] described the preparation of the polyester of triethylene glycol dilinoleate. He obtained a viscous liquid which had an acid value of 13.1. This description indicates that the polymer was an α-polyester, having a molecular weight of approximately 4,300. No description of an attempt to prepare superpolyesters was reported. As a part of the program of the Oil and Protein Division of the Northern Regional Research Laboratory on the polymerization phenomena of semi-drying oils, an investigation of the polyesters of dilinoleic acid was undertaken.

By use of methods developed by Carothers[13] and Flory[14] superpolyesters were prepared from dilinoleic acid with ethylene, decamethylene, and hydrogenated dilinoleyl glycols.[14a] All superpolyesters were soluble in chloroform and, in

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[1a] The Northern Regional Research Laboratory is one of four Regional Laboratories authorized by Congress in the Agricultural Research Act of 1938 for the purpose of conducting research to develop new uses and outlets for agricultural commodities. These Laboratories are operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

[1b] New address: General Mills, Inc., Minneapolis, Minnesota.

[1c] Carothers and Hill, THIS JOURNAL, **54**, 1559 (1932); **54**, 1566 (1932).

[2] The terminology of Carothers to designate molecular weight ranges of a condensation polymer is used throughout this paper: α-polymers, 800–5,000; ω-polymers, 5,000–10,000; and superpolymers, above 10,000. This terminology is used merely for convenience in referring to the molecular weights of the polyesters.

[2a] Carothers, U. S. Patent 2,174,619 (1939).

[3] Vorländer, *Ann.*, **280**, 167 (1894).

[4] Carothers and Arvin, THIS JOURNAL, **51**, 2560 (1929).

[5] Bradley, Kropa and Johnston, *Ind. Eng. Chem.*, **29**, 1270 (1937).

[6] Vincent, *ibid.*, **29**, 1267 (1937).

[7] Bradley and Johnston, *ibid.*, **32**, 802 (1940).

[8] Bradley and Johnston, *ibid.*, **33**, 86 (1941).

[8a] This terminology is used since the product is apparently a dimer of linoleic acid and its structure is unknown.

[9] Jackson and Cowan, unpublished data.

[10] Bradley and Richardson, *Ind. Eng. Chem.*, **32**, 963 (1940).

[11] Kass and Burr, THIS JOURNAL, **62**, 1796 (1940).

[12] Teeter and Cowan, unpublished data.

[13] Carothers and Hill, THIS JOURNAL, **54**, 1557 (1932).

[14] Flory, *ibid.*, **62**, 1057 (1940).

[14a] Hydrogenated dilinoleyl glycol was prepared from dimethyl dilinoleate esters by high pressure hydrogenation, using Adkins catalyst. The sample used in this investigation was prepared by Organic Chemicals Manufacturers, University of Illinois.

general, exhibited solubilities similar to those reported by Carothers for saturated superpolyesters. The dilinoleate superpolyesters were non-crystalline plastic solids which on continued exposure to oxygen converted to insoluble three-dimensional polymers. Also, by long heating at temperatures as high as 290–300°, conversion to insoluble three-dimensional polymers was effected. However, some doubt remains as to whether this conversion was actually caused by the high temperature or by traces of oxygen which might have come in contact with the polyesters.

Despite indications from end-group determinations, and from the general properties of the polyesters, it was believed that additional proof of the linear nature and high molecular weight of these polyesters was necessary. This proof was established by use of the relationship of the logarithm of viscosity of the molten polyesters to the square root of molecular weight from end-group determination. Flory[14] showed that this relationship is linear for polyesters from saturated dibasic acids, and he obtained molecular weights in excess of 10,000. Polyesters from dilinoleic acid with decamethylene and hydrogenated dilinoleyl glycols were readily converted to superpolyesters having molecular weights of 10,000 with little deviation from the linear viscosity relationship. However, at higher molecular weights of the order of 20,000–30,000, close correlation was not obtained. At a molecular weight of 20,000, a small deficiency or excess of either reactant makes an enormous variation in the molecular weight obtained by end-group titration (see experimental part). Therefore, failure to obtain exact correlation at high molecular weights is not surprising. Such a failure is probably due to the loss or decomposition of either reactant or to impurities present in the reactants.

Superpolyesters from ethylene glycol were obtained by means of glycolysis. In all cases where dilinoleic acid was used with a theoretical or a slight excess over the theoretical amount of ethylene glycol, deviations from the viscosity relationship occurred at molecular weights above 5,000–6,000. It was believed that the difficultly controllable loss of ethylene glycol and its decomposition[15] at temperatures used for polyesterification were responsible for the failure of dilinoleic acid and ethylene glycol to give superpolyesters when molar or approximately molar quantities of the glycol were used. However, when an excess of glycol was used with the dilinoleic acid, and a glycolysis catalyst added, a superpolyester was obtained. Viscosity determinations indicate that superpolyesters having molecular weights as high as 24,000 were obtained by this method.

Direct comparison of preparations of polyesters from dilinoleic acid and hydrogenated dilinoleic acid showed that the unsaturation did not contribute to the viscosity of the final products. This behavior was maintained when an inert atmosphere was kept over the reaction mixture and oxygen excluded from the reaction. This work shows that essentially linear superpolymers can be obtained containing non-conjugated unsaturation, and therefore this type of unsaturation is not functional under proper preparative conditions.

Bradley[5] studied the properties of triethylene glycol maleate and triethylene glycol succinate. He obtained relative viscosities and molecular weights by end-group titration of the polyesters at various stages of reaction up to molecular weights of approximately 3,000. Application of Flory's relationship to Bradley's data indicates that under special conditions, *i. e.*, under an atmosphere of pure nitrogen, linear α-polyesters having molecular weights of 2,500 were obtained with triethylene maleate. This work indicates that superpolyesters from maleic and citraconic anhydride and other unsaturated dibasic acids or anhydrides might be obtained by suitable methods. However, conditions required for the preparation of superpolyesters may cause heat conversion too readily to make possible preparation of such superpolyesters. Investigation of the use of unsaturated dibasic acids other than dilinoleic acid for the preparation of superpolyesters is planned, to determine whether essentially linear superpolymers can be obtained which contain conjugated aliphatic unsaturation. This work will determine if conjugated aliphatic unsaturation is functional under preparative conditions necessary for formation of superpolyesters.

Experimental

Dilinoleic Acid.—The acids used in this investigation were prepared from corn or soybean oil. The method used was essentially that described by Bradley[8] for the preparation of methyl dilinoleate from dehydrated castor oil. Corn or soybean oil was converted by methanolysis to methyl esters. The distilled methyl esters were polymerized at 300° with 0.3% anthraquinone catalyst for sixteen to twenty-four hours. Unpolymerized esters were removed by distillation under reduced pressure of 1–5 mm., and the residual methyl dilinoleate carefully fractionated in a short path pot still (a modified alembic flask)[16] at 2 to 50 microns, or in a cyclic molecular still.

Middle cuts of the main methyl dilinoleate fraction were taken as pure dilinoleate for the preparation described. The presence of about 5% linolenic acid in soybean oil resulted in a dimeric product of slightly higher refractive index and iodine value, but otherwise it was very similar to the methyl dilinoleate from corn and dehydrated castor oil.

Methyl dilinoleate from corn oil had the following analysis: Calcd. for $C_{38}H_{68}O_4$: C, 77.20; H, 11.64. Found: C, 77.46; H, 11.68.

The acid was prepared from the ester by usual methods; neutral equivalent varied slightly with each preparation.

Hydrogenated Dilinoleic Acid.—To 3 liters of anhydrous ethanol was added 346 g. of methyl dilinoleate and approximately 20 g. of Raney nickel catalyst[17] suspended in anhy-

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(15) Gallaugher and Hibbert, THIS JOURNAL, 59, 2514 (1937); 59, 2521 (1937).

(16) Falkenburg, Teeter and Cowan, unpublished work.

(17) Adkins and Covert, THIS JOURNAL, 54, 4116 (1932).

drous ethanol. The material was hydrogenated in a high pressure bomb at 100° and 1,400 pounds for two and one-half hours. Two additional treatments with fresh catalyst were carried out at 150° and 1,000 pounds for three hours each. The final product had an iodine value of 15.6, n^{30}_{D} 1.4705, and d^{30}_{4} 0.9306. It is possible that some alcoholysis occurred, giving a mixed ester. On saponification and neutralization the hydrogenated dilinoleic acid was obtained: neutral equivalent, calculated, 282.4; found, 299, 286.9, on two different preparations.

Hydrogenated Dilinoleyl Glycol.—Methyl dilinoleate from corn oil was hydrogenated, using Adkins catalyst, copper chromium oxide.[5,18]

Anal. Calcd. for $C_{36}H_{66}(OH)_2$: sapon. no., 0.0; OH no., 209.5; I no., 0. Found: sapon. no., 6.8; OH no., 204.1; I no., 11.3.

Original Preparations of Polyesters.—The first preparations of the polyesters from dilinoleic acid were made from the acid and ethylene glycol without catalyst. Several preparations were made with a variation in the amount of reactants used, and all of the polyesters prepared exhibited properties somewhat similar to superpolyesters. However, later work showed that these esters were probably ω-polyesters, although some preparations such as the following may have higher molecular weights.

A mixture of 328 g. of dilinoleic acid (neutral equivalent 288) and 45 g. of ethylene glycol was heated under carbon dioxide ebullition in a Claisen flask for seventy-two hours and for one hundred and forty-six hours in a pot still (Corning 3480). Table I shows the temperatures used and neutral equivalent of the polyester.

TABLE I

PREPARATION OF ETHYLENE GLYCOL DILINOLEIC ACID POLYESTER

Sample	Time, hours	Temp., °C.	Neutral equivalent
1	24	125	817
2	72	150	2200
3	120	240	3620
4	162	240	4240
5	170	250	4700
6	194	250	4900

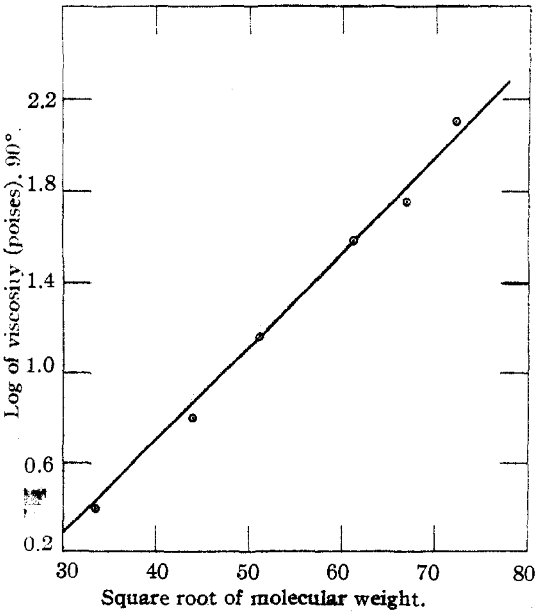

Fig. 1.—Viscosity–molecular weight relationship, polyester from dilinoleic acid with ethylene glycol.

The polyester at the end of one hundred and ninety-four hours dissolved slowly but completely in chloroform. After twenty-four more hours heating at 300 to 320°, the polyester converted to a gel and only a portion of it was soluble in chloroform. The method used to remove samples from the reaction chamber permitted air to enter. Although the increased temperature appeared to be responsible for this gelation, oxygen conversion cannot be ruled out. A film of the soluble polyester having a neutral equivalent of 4,900 was exposed to the atmosphere. After sixty days, the film was only partly soluble in chloroform.

Despite repeated attempts with catalysts to obtain superpolyesters using molar or slightly greater quantities of ethylene glycol, no polyester was obtained which could be classified with certainty as a true superpolyester. Therefore, a study based on Flory's work[14] was undertaken.

Preparation of Superpolyesters and Viscosity Studies.—The esterifications were carried out in a vapor-jacketed vessel fitted with an inlet tube for introducing inert gas (purified nitrogen or carbon dioxide) below the surface of the reaction mixture, and an exit tube sealed with a bubbler to prevent back-diffusion of oxygen. Viscosities were usually measured by the rolling ball method, using 6 mm. i. d. tubes and an $^1/_8$ inch steel ball. The relative kinematic viscosities thus obtained were converted to approximate values in poises by standardizing the viscosimeter with an oil of known viscosity. In several cases, viscosities were measured at reaction temperature with pipets or tubes in the reaction vessel, following the methods described by Flory.[14]

Molecular weights were determined by titrating samples in chloroform with alcoholic sodium hydroxide, using phenolphthalein or brom thymol blue indicator.

1. **Ethylene Dilinoleate.**—An ethylene glycol polyester of approximately 6,000 molecular weight was obtained as follows. A mixture of 50.8 g. (0.1810 equivalent) of dilinoleic acid (neutral equivalent, 286.4) and 5.82 g. (0.1877 equivalent) of ethylene glycol was heated for twenty-four hours at 100°, and then at 155–160° for another twenty-four hours, and then the temperature was raised to 195° for one hundred and fifty hours. Samples taken during the run showed the following neutral equivalents and viscosities.

Sample	Total hours	Molecular weight (neutral equivalent)	30° poises	90° poises
1	30	1142	70.8	2.47
2	42	1960	195	6.15
3	50	2630	514	14.8
4	65	3920	1295	37.7
5	77	4480	2120	56.6
6	140	5190	4650	125.5
7	over 200	5690	12140	....

The relationship of the log of viscosity at 90° to the square root of the equivalent weight is shown in Fig. 1. The values at 30° showed the same degree of agreement with a straight line relationship up to molecular weights of 5,000. Repeated attempts failed to obtain polyesters of much higher molecular weight which correlated with viscosity. Apparently ethylene glycol was lost or decomposed so that the reaction could not proceed above a molecular weight of 5,000 when equivalent amounts of reactants were used.

The experience with the polyesters just described led to the use of excesses of ethylene glycol with the addition of a small amount of alcoholysis catalyst. A mixture of 33.8 g. of dilinoleic acid (0.1205 equivalent), 4.86 of ethylene glycol (0.1567 equivalent, 30.5% excess), and 15 mg. of *p*-toluenesulfonic acid was heated with purified nitrogen passing through the mixture. The reaction was run at 195° with the viscometer pipet in the reaction vessel, and was followed by viscosity values only since acid end-group determinations would be meaningless with such a large excess of glycol. After eighteen days, the viscosity had reached a

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[18] Folkers and Adkins, THIS JOURNAL, 54, 1146 (1932).

value of 4,600 poises at 195°, which corresponds to a molecular weight of approximately 24,000. This value is arrived at by extrapolating to 195° from the viscosities at 30 and 90°, as described in the previous run, making use of the fact that the log of viscosity is a linear function of the reciprocal of absolute temperature (*cf.* Flory, *loc. cit.*). The calculated values for log of viscosity at 195° plotted against the square root of molecular weight showed good agreement with linear relationship. Extension of this curve indicates that a viscosity of 4,600 poises at 195° corresponds to a molecular weight of 24,000. This superpolyester was a soft elastic material which was soluble in chloroform at room temperature.

2. **Polyester of Ethylene Glycol with Hydrogenated Dilinoleic Acid.**—A mixture of 25.48 g. (0.0852 equivalent) of dilinoleic acid (equivalent weight found, 299) and 2.67 g. (0.086 equivalent) of ethylene glycol was heated at 195° under purified nitrogen with the results shown in Fig. 2. The linear relationship was again retained to a molecular weight of approximately 5,000.

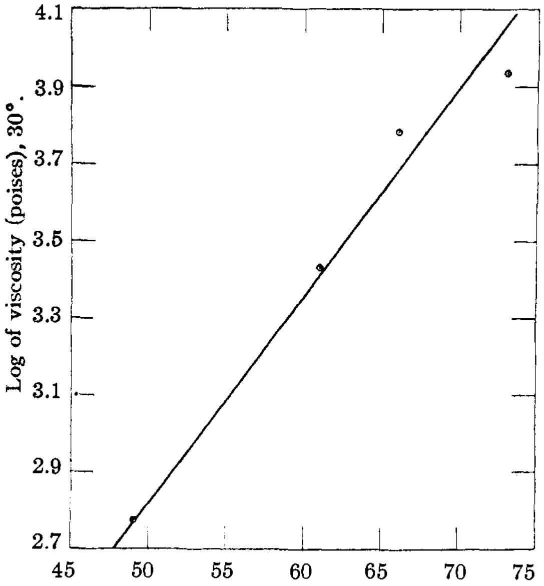

Fig. 2.—Viscosity–molecular weight relationship, polyester from hydrogenated dilinoleic acid with ethylene glycol.

3. **Decamethylene Dilinoleate.**—One method which served to minimize loss of reactants was to use a high molecular weight glycol such as decamethylene glycol with the dilinoleic acid. Although an observable loss of decamethylene glycol occurred, it was much less than when ethylene glycol was used.[18a] A mixture of 31.27 g. (0.115 equivalent) of dilinoleic acid and 9.72 g. of decamethylene glycol (0.116 equivalent) reacted at 195°, and the data obtained on viscosity and molecular weights are shown in Fig. 3. The values up to molecular weights of 10,000 are in excellent agreement with the linear relationship expected. The last two values deviate from an extension of the line for the first four. According to relationships developed by Flory, the deviation of the last two points would correspond to a deficiency of about 0.7% of glycol. Such a deficiency would not appreciably affect the previous points, and is in accord with the qualitative observation of some loss of glycol. The last sample was chloroform soluble, and represents a superpolyester of molecular weight of at least 20,000 or about 28,000, according to viscosity by extrapolation of the first four points.

4. **Polyester from Decamethylene Glycol and Hydrogenated Dilinoleic Acid.**—A mixture of 36.99 g. (0.1289 equivalent) of hydrogenated dimer acid (neutral equivalent found, 286.9) and 11.230 (0.1289 equivalent) of decamethylene glycol was heated at 195° with the results (see Fig. 4) similar to those of the decamethylene dilinoleate run. The deviation of the points beyond the fourth (10,400 molecular weight) corresponds to a loss of 0.8 to 0.9% of glycol. The final sample, with molecular weight of 15,500 by titration, or about 22,000 by vicosity, was also soluble in chloroform.

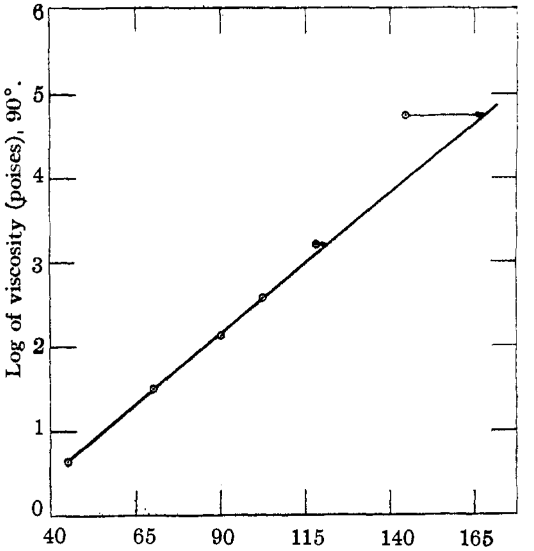

Fig. 3.—Viscosity–molecular weight relationship, polyester from dilinoleic acid with decamethylene glycol.

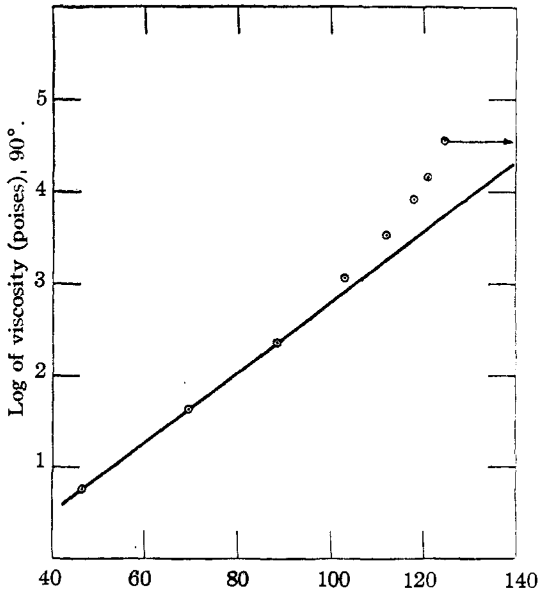

Fig. 4.—Viscosity–molecular weight relationship, polyester from hydrogenated dilinoleic acid with decamethylene glycol.

5. **Polyester from Dilinoleic Acid with Hydrogenated Dilinoleyl Glycol.**—In the first run, an excess of acid was used due to an error in calculations. In the second run, equivalent amounts of glycol and acid were used, assuming

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[18a] Flory[14] reports a similar experience with decamethylene glycol.

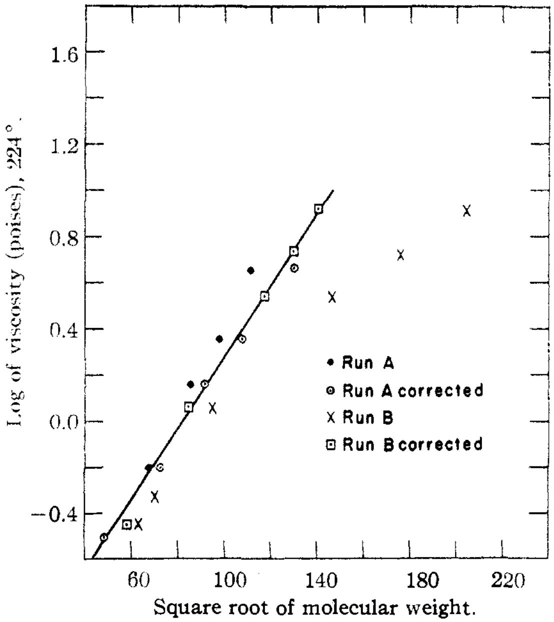

Fig. 5.—Viscosity–molecular weight relationship, polyester from dilinoleic acid with dilinoleyl glycol.

that the ester present in the glycol would be reactive by glycolysis and should be allowed for in calculating the required amount of acid to be used. The viscosity–molecular weight relationships of samples taken during this run indicated that an excess of glycol was present, and since no catalyst was present, it would appear that the ester had not reacted. When the results of both runs were corrected for the excess of acid or glycol present, assuming that the ester is unreactive, the points for both runs showed the same linear relationship of log of viscosity to square root of molecular weight. All corrections were calculated using Flory's equation for approximate percentage error.[14] In the first run, 34.42 g. (0.1214 equivalent) of dilinoleic acid (from soybean oil; neutral equivalent, 283.8) and 32.76 g. (0.1193 equivalent, based on OH no.) of hydrogenated dilinoleyl glycol reacted at 224°. In the second run, 31.14 g. (0.1098 equivalent) of dilinoleic acid and 31.09 g. (0.1131 equivalent) of the same glycol reacted at 224°. The results for viscosity molecular weight relationship are identified as Run A and Run B, respectively, in Fig. 5. The corrected values lie on the same straight line, and again indicate linear superpolyesters of molecular weights up to 20,000. Final samples from both runs were soluble in chloroform.

Summary

Superpolyesters were prepared from an unsaturated dibasic acid, dilinoleic acid, with ethylene, decamethylene and hydrogenated dilinoleyl glycols.

Loss and decomposition of ethylene glycol at reaction temperatures occurred and therefore superpolyesters were not obtained when an equivalent amount of ethylene glycol was used. Superpolyesters from ethylene glycol were obtained when excess of glycol was used and the final stages of the reaction were effected by glycolysis. Superpolyesters having molecular weights of 20,000 or more were obtained by direct esterification when decamethylene and hydrogenated dilinoleyl glycols were used.

A study of the variation of viscosity with molecular weight showed a straight line relationship between log of viscosity and square root of molecular weight up to molecular weights of 10,000 on certain polyesters. Direct comparison of superpolyesters from dilinoleic acid and from hydrogenated dilinoleic acid demonstrated that reaction conditions can be controlled so that non-conjugated unsaturation does not cause crosslinking of chains.

Peoria, Illinois Received September 14, 1943

[Contribution from the Chemical Laboratory of Northwestern University]

Spectroscopic Evidence for Conjugation in Cyclopropane Systems

By Irving M. Klotz

The properties of molecules composed of a cyclopropane ring adjacent to a carbonyl group have been studied for some time, and considerable chemical evidence has been accumulated to show that such structures behave as conjugated systems.[1] Recently similar behavior has been observed in molecules containing a cyclopropane ring adjacent to an olefinic double bond.[2] That these systems are indeed conjugated can be shown also by direct physical evidence, for with recent progress in the theory of absorption spectra[3] it is now possible to interpret ultraviolet spectra in terms of molecular structure.

The intense absorption bands of single ethylenic linkages lie in the region near 1800 Å., and if the carbon atoms are highly substituted, strong absorption may extend somewhat beyond 2000 Å.[4] However, when two double bonds are conjugated to each other a pronounced shift in the absorption toward the red end of the spectrum is observed. Wave-mechanical considerations[3] have shown that high intensity ultraviolet absorption spectra are due to transitions from a neutral ground state of the molecule to an ionic excited state. Conjugation permits the existence of a number of ionic structures which contribute appreciably to the resonance in

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(1) R. C. Fuson, "Organic Chemistry, An Advanced Treatise," Vol. I, second edition, edited by H. Gilman, John Wiley and Sons, Inc., New York, 1943, p. 102.

(2) B. Riegel, M. F. W. Dunker and M. J. Thomas, This Journal, **64**, 2115 (1942).

(3) R. S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939); **7**, 339 (1939).

(4) A. Lüthy, *Z. physik. Chem.*, **107**, 285 (1923).