Loading Procedure.—As previously described.[5,6]

Metering of Boron Fluoride.—A steel cylinder of known capacity was connected to a commercial tank of boron fluoride; the gas was admitted and the pressure created was noted. Next, this loaded steel cylinder was connected to the reaction vessel and the amount of boron fluoride delivered was computed from the observed drop in pressure. For very small additions of boron fluoride, a stream of the gas was passed through weighed liquefied hydrogen fluoride cooled to −70°.

Treatment of Reaction Products.—Gaseous products were released through a washing train and collected in a Dry Ice cooled receiver. Liquids were poured on cracked ice, neutralized, steam distilled, dried and separated by fractional distillation. In the few cases where the olefin and its addition product boiled practically at the same temperature, the composition of the distillate was estimated from the index of refraction, but this procedure was avoided as much as possible by using efficient dephlegmators.

Summary

The addition of hydrogen fluoride to halogenated olefins is accelerated or made possible by using small amounts of boron fluoride as a catalyst. The action is attributed to the formation of a coördinate compound $HF \rightarrow BF_3$, in which the H to F bond is weakened; this favors the supply of protons for the first step of the addition to the double bond. The direction and ease of addition are discussed. Eleven olefins have been tried and the results are tabulated.

COLUMBUS, OHIO RECEIVED SEPTEMBER 22, 1947

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(5) Henne and Haeckl, THIS JOURNAL, **63**, 2692 (1941).

(6) Henne and Whaley, *ibid.*, **64**, 1157 (1942).

[CONTRIBUTION FROM GENERAL MILLS, INC., RESEARCH DEPARTMENT]

Polyamide Resins from Dilinoleic Acid and Ethylenediamine. Molecular Weight–Viscosity Relationships[1a]

BY R. H. ANDERSON AND D. H. WHEELER

Introduction

In 1941, Bradley and Johnston[1b] isolated dilinoleic acid in a pure state as the methyl ester by fractional molecular distillation of the heat-polymerized methyl esters of the acids from dehydrated castor oil. They prepared polyesters of triethylene glycol with molecular weights of about 4300. Cowan and Wheeler[2] prepared polyesters with various glycols having molecular weights up to 20,000 to 30,000.

Polyamides have been prepared by Falkenburg, Teeter, Skell and Cowan[3] from various diamines and the residual polymeric fatty acids or esters (mixtures of dimer and trimers of linoleic and linolenic acids). The polyamide from ethylenediamine and these mixed polymeric fatty acids was proposed as a new synthetic coating material[4] under the name *Norelac*. The molecular weights of these resins were 3,000 to 5,000, determined by the method of end-groups. The same type of polyamide has been commercially prepared on a pilot plant scale,[5] and is apparently finding some use as a coating for heat-sealing and laminating paper.

No description has appeared of polyamides from pure dilinoleic acid and ethylenediamine. The present investigation describes the preparation and some properties of such linear polyamides having molecular weights from 2,000 to 15,000.

Viscosities were determined on solutions in 1:1 butanol-toluene solvent at concentrations from 0.2 to 9.8 g. per 100 cc. and intrinsic viscosities were calculated. The intrinsic viscosity was found to be related to molecular weight by the formula

$$[\eta] = KM^a \qquad (1)$$

Flory and Stickney[6] have pointed out the fact that a relationship such as equation (1) really relates to *viscosity* average (M_v) rather than *number* average (M_n) molecular weights of non-homogeneous polymers, and that M_v is greater than M_n, but less than M_w, the weight average molecular weight.

Now, the molecular weights, as determined by end-group titration in the present study, are actually *number* average molecular weights. The fact that the determined molecular weights and viscosities of these polyamides agree with equation (1) is interpreted to mean that these polymers, as prepared, have essentially a constant ratio of M_v to M_n. Flory[7] has shown on theoretical grounds that for bifunctional condensation polymers, M_w/M_n approaches 2 for higher polymers. Taylor[8] has shown that the ratio is very nearly 2 for 66-nylon polyamide, and that the value of M_v is close to that of M_w. The weight average can therefore be used interchangeably with M_v without introducing serious error.

When mixtures of condensation polyesters or polyamides are considered, the importance of considering a weight average rather than a number average in calculating viscosity is apparent. The viscosity in the molten state of a mixture of polyesters was shown by Flory[7] to agree with the M_w,

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(1a) Paper No. 79, Journal Series, General Mills, Inc., Research Department.

(1b) Bradley and Johnston, *Ind. Eng. Chem.*, **33**, 86 (1941).

(2) Cowan and Wheeler, THIS JOURNAL, **66**, 84 (1944).

(3) Falkenburg, Teeter, Skell and Cowan, *Oil and Soap*, **22**, 143 (1945).

(4) Cowan, Lewis and Falkenburg, *ibid.*, **21**, 101 (1944).

(5) Cowan, Schwab and Falkenburg, *Modern Packaging*, [9] **17**, 103 (1944).

(6) Flory and Stickney, THIS JOURNAL, **65**, 372 (1943).

(7) Flory, *ibid.*, **62**, 1057, 3032 (1940).

(8) Taylor, *ibid.*, **69**, 635, 638 (1947).

but not with the M_n, of the mixture. Similarly, the molecular weight of a mixture of polyamides calculated from its $[\eta]$ is shown in the present study to agree with a weighted average rather than the number average of the mixture.

Experimental

Dilinoleic acid was prepared from a commercial dehydrated castor oil of Z-3 Gardner viscosity by conversion to methyl esters, which were heated for twelve hours at 300° under nitrogen. Unpolymerized methyl esters were removed by ordinary vacuum distillation. The residue of dimer and trimer was fractionally distilled in an alembic flask similar to that used by Cowan, Falkenburg and Teeter.[9] The fractional distillation was repeated three times, taking a middle cut of about 80% on the second and third distillations. On the second and third distillations, the methyl dilinoleate distilled at 20 μ pressure with a vapor temperature of 225–235° and a pot temperature of 255–265°. The pure dimer fraction from the third distillation had a spread in refractive index of 10 units in the fourth place between the first and last small fraction. Continuation of the distillation until the pot temperature was 300° left about 1.2% of undistilled residue having a refractive index only slightly higher than the pure dimer. The pure ester showed the following analytical values: sapn. equiv. 295 (calcd. 294), iodine value 75.2 (calcd. 86.8), mol. wt. (ebul., acetone), 545, 571 (calcd. 588), density 0.943 (25°).

The ester was converted to acid in the usual manner. The acid showed: neutr. equiv., 285; sapn. equiv., 283 (calcd. 280.2). Aqueous ethylenediamine from Carbide and Carbon Co. was redistilled, b. p. 115.5–117.5°, and titrated with standard acid using methyl red indicator. It contained 67.5% ethylenediamine.

Preparations of the polyamides were carried out in a three-necked flask with stirrer, thermometer, dropping funnel and simple side arm take-off for distillate. Dilinoleic acid (70 to 100 g.) was heated to 120° and stirred under vacuum to remove dissolved gases, pure nitrogen was admitted and the calculated amount of ethylenediamine was added over a period of one-quarter hour at a temperature of 120–130°. After addition of the amine, the temperature was raised to 200° at a rate such that the vapor temperature never exceeded 100°. The mixture was then held at 200° for four hours (six hours for polymers no. 8 and 9) under nitrogen and for an additional hour at 200° under vacuum with a Dry Ice trap in the vacuum line to catch any amine. The resin was then cooled to 160°, and poured into containers under inert gas. Samples were stored under nitrogen when not in use.

The distillate plus trap material was titrated for amine lost, which was quite small, −0.1 to 0.2% of original amine.

Carboxylic end-groups were determined by titration of the resin in a 50-50 butanol–toluene mixture with 0.1 N alcoholic potassium hydroxide (phenolphthalein). Amine end-groups were determined by titration with freshly standardized 0.1 N alcoholic hydrochloric acid (brom cresol green). Average molecular weights were calculated from the combined acid and amine end-groups. The molecular weights as determined were in close agreement with those expected on the basis of the excess of acid used. A balance of the free acid and amine groups in the polymer against the amount of acid and amine used as starting materials showed less than 1% discrepancy in every case. This would indicate that not over 1% loss of acid groups occurred by decarboxylation, unless amine were lost in equivalent amounts. Some properties of the resins are given in Table I.

TABLE I

POLYAMIDES OF DILINOLEIC ACID AND ETHYLENEDIAMINE

Poly-mer	Acid no.[a]	Amine no.[a]	Mol. wt.[a]	Soft pt. °C.[b]	Vis-cos-ity[c]	Pene-tra-tion[d]	Gel time[e]
1	51.00	0.00	2,200	94.6	A-3	31.4	1440
2	27.20	.00	4,125	111.0	A-1 to A	6.8	650
3	18.30	.00	6,130	112.5	A	4.1	513
4	16.20	.24	6,800	117.8	B	3.7	465
5	13.23	.43	8,216	118.2	B	3.3	356
6	11.10	.65	9,544	119.2	B to C	2.0	306
7	10.65	.58	10,000	118.4	C	2.8	347
8	3.00	4.91	14,200	122.0	E to F	1.1	70
9	5.51	1.78	15,370	121.5	F	1.9	0

[a] Acid no. and amine no. equal milligrams of KOH equivalent to the acid and amine groups, respectively, in 1 g. of material, whence: Mol. Wt. = 2 × 56,100/acid no. + amine no. [b] Ball and ring. [c] Gardner bubble viscosity at 25° of a 35% solution in 1-1 (wt.) n-butanol-toluene solvent. [d] Tenths of a mm. with A.S.T.M. standard penetrometer needle, 200 g. load, thirty seconds at 25°. [e] Time in seconds for 0.03 inch film to gel in air on a hot-plate at 200°. Gelation is indicated by the drawing of a string upon touching with a pin point.

As shown by the data, with increasing molecular weight, the melting point increases rapidly at first and then levels off somewhat. Viscosity increases regularly and hardness increases (penetration decreases), whereas gel time decreases regularly with increased molecular weight. Gelation is caused by cross-linking induced by oxygen, since the resins are stable at this temperature in the absence of oxygen. The greater the chain length, the fewer cross-links should be necessary to cause gelation, and the shorter the gel time should be.

Solution viscosities of the polyamides were determined at concentrations ranging from 0.2 to 9.8 g. per 100 cc. of solution in 1-1 (wt.) n-butanol–toluene. The viscosities were determined in an Ostwald viscometer of 3.16 cc. volume, 9.5 cm. capillary with a diameter of 0.057 cm. Viscosities were calculated by the following equation which corrects for kinetic energy losses[10]

$$\eta = \rho Ct - (\rho/8\pi l)(v/t) \qquad (2)$$

where C is a calibration constant, ρ is the density and t the time in seconds for efflux of volume v. The viscometer was calibrated with water (t = 82.4) using 0.00894 poise as the value for water at 25°. Most of the measurements were made in a constant temperature bath at 25°, controlled to ±0.02°. Several series were also run at 30°. The values for ηr at 30° were identical with those at 25° within experimental error. The solutions were quite stable, good checks being obtained on samples which had stood for a number of weeks. The solvent had a viscosity of 0.00973 poise at 25° (t = 108.7, ρ = 0.832).

The viscosity data for the polyamides (and for dimer acid) are shown in Fig. 1, where ln $\eta r/c$ is plotted *vs.* concentration. Up to a concentration of 1.5% the values are constant within experimental error, with the values at higher concentrations for the polymers of higher molecular weights showing a progressive tendency to be lower than those obtained up to 1.5% concentration (accentuated in Fig. 1 by the change in scale beyond 2.0).

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[9] Cowan, Falkenburg and Teeter, *Ind. Eng. Chem.*, **16**, 90 (1944).

[10] E. C. Bingham, "Fluidity and Viscosity," McGraw-Hill Book Co., New York, N. Y., 1922, p. 17.

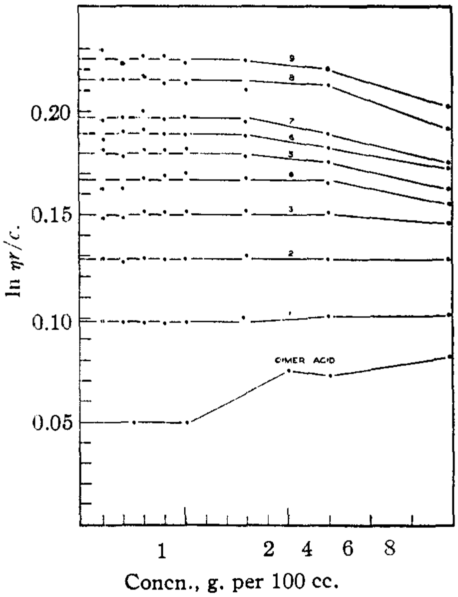

Fig. 1.—ln $\eta r/c$ *vs.* concentration.

The intercepts of the lines with the zero concentration axis, as determined from Fig. 1, are recorded in Table II as $[\eta]$, with the corresponding molecular weights.

Table II

Intrinsic Viscosities and Molecular Weights of Polyamides

Polymer	Mol. wt.	$[\eta]$
1	2,200	0.0986
2	4,125	.129
3	6,130	.150
4	6,800	.167
5	8,220	.180
6	9,640	.190
7	10,000	.197
8	14,200	.215
9	15,370	.225

The relationship of molecular weight to intrinsic viscosity was best represented by a log–log plot of these values, as shown in Fig. 2. The largest deviation, that of no. 4, is 10% while the other samples were within 1 to 6% of the values for the line. The equations for the line in Fig. 2 are

$$[\eta] = 4.06 \times 10^{-3} M_n{}^{0.42} \tag{3}$$

$$M_n = 5.50 \times 10^{5} [\eta]^{2.4} \tag{4}$$

where K of equation 1 is seen to be 4.06×10^{-3} and a is 0.42. Taylor's values on 66 nylon in formic acid were 1.1×10^{-3} and 0.72, respectively.

Intrinsic viscosities of mixtures of high and low molecular weight polymers were determined in the same manner. Mixtures were made of the 2000 mol. wt. polymer with the 10,000 and 15,000 mol. wt. polymers. The mixtures had values for $[\eta]$ which agreed fairly well with the weighted averages of $[\eta]$ and with the $[\eta]$ determined from the weighted number averages ("M_w") by means of Fig. 2, but did not agree with the $[\eta]$ determined from the number average by Fig. 2. The results are shown in Table III.

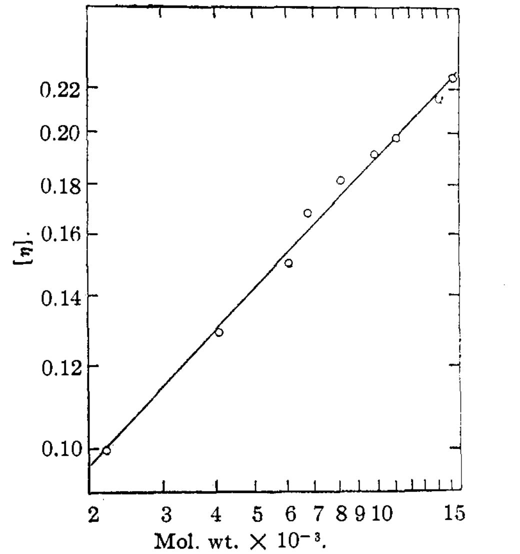

Fig. 2.—Molecular weight *vs.* intrinsic viscosity on log–log scale.

Table III

Intrinsic Viscosities of Mixtures of Polyamides

M. W. 2200 and 10,000

% of 2200	Obs.	Wtd.[a] av.	From "M_w"[b]	From M_n[c]
75	0.131	0.123	0.131	0.109
50	.156	.148	.153	.124
25	.182	.172	.172	.145
M. W. 2200 and 15,370				
50	0.163	0.162	0.179	0.125

[a] $[\eta]$ (weighted av.) = $[\eta]_1 w_1 + [\eta]_2 w_2$. [b] "$M_w$" (Mixt.) = $M_1 w_1 + M_2 w_2$. [c] M_n(Mixt.) = $1/(w_1/M_1 + w_2/M_2)$, where w_1 and w_2 refer to the weight fraction of polymers with determined molecular weights of M_1 and M_2, respectively.

It should be noted that the values for "M_w" referred to in Table III are really weighted number average values rather than true M_w values, since the molecular weights used are the determined number average values. However, the comparisons in Table III are valid if the determined M_n values of the components have a constant ratio to their M_w values, as is believed to be the case. Calculations based on an equation of Flory,[7] relating M_w to M_n for polyesters, indicate that M_w/M_n for the lowest polymer is about 1.86, while for the next higher polymer it is 1.93, with values more nearly approaching 2 for the higher polymers.

Discussion

All of the polyamides except no. 8 had acid end-groups almost exclusively (see Table I). The linear relationship of ln η_r to concentration, up to at least 1.5%, would indicate that association of acid end-groups is not an appreciable factor at these concentrations. Polymer 8, with a more nearly equal number of amino and acid end-groups, also shows no appreciable deviation of ln η_r in Fig. 1, and its general viscosity characteristics are similar to those of no. 9, which is of similar molecular weight, but which has a high ratio of acid to amino end-groups. The dimeric acid did show a slight increase in ln η_r/c with increasing concentration, and the polymer of lowest molecular weight, no. 1, also showed a slight similar increase of this value at concentrations above 1.5%, whereas the higher polymers often showed a slight decrease. These phenomena would indicate some association of acid end-groups at higher concentrations in the cases of polymers with a high concentration of acid end-groups.

Summary

1. Polyamides of dilinoleic acid and ethylenediamine have been prepared with molecular weights from 2,200 to about 15,000.

2. The relationship of molecular weight to intrinsic viscosity can be expressed by the equation

$$[\eta] = 4.06 \times 10^{-3} M^{0.42}$$

3. The nature of this relationship, and the results of a study of the viscosities of mixtures of polymers indicate that the number average molecular weights of the polymers, as prepared, bear a constant ratio to the viscosity and the weight average molecular weights.

4. Except at higher concentrations with polymers of high acid values, association of terminal end-groups is not very significant.

MINNEAPOLIS, MINN. RECEIVED MAY 17, 1947

[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

The Addition of Halogens to an Acetylenic Ketone

BY CHARLES L. BICKEL

Diaryl acetylenic ketones undergo many addition reactions; one of the simplest of these would appear to be the addition of the halogens. The halogenation of a diaryl acetylenic ketone has, however, been investigated in only one case—that of phenylbenzoylacetylene. Nef[1] obtained phenylbenzoylacetylene diiodide by the addition of iodine in ether solution. Later, Dufraisse[2] studied the addition of both bromine and iodine to phenylbenzoylacetylene and obtained phenylbenzoylacetylene dibromide, as well as the diiodide previously described by Nef.

Recent papers from this Laboratory describe the preparation of *o*-chlorophenylbenzoylacetylene,[3,4] a substance which can be obtained in excellent yield from simple starting materials. This acetylenic ketone crystallizes well from oily mixtures and can therefore be isolated more easily than the unsubstituted analogue. These facts suggested the present study of the action of the halogens on *o*-chlorophenylbenzoylacetylene.

Nef stated that an ethereal solution of phenylbenzoylacetylene easily absorbs iodine while Dufraisse stated only that an ethereal solution of the acetylene, treated with an ethereal solution of iodine, gives the iodine addition product. Neither author indicated that the reaction was sluggish. *o*-Chlorophenylbenzoylacetylene, on the other hand, gives no apparent reaction with iodine at room temperature. When a chloroform solution of iodine and the acetylene is heated, there is no evidence of reaction until the solvent has been completely evaporated. Further heating of the residual mixture of iodine and *o*-chlorophenylbenzoylacetylene gives a solid cake from which the iodine addition product can be isolated in good yield.

Although the melting point of phenylbenzoylacetylene diiodide has been variously reported,[1,2] there is no indication in the literature that the melting of this substance is attended by decomposition. *o*-Chlorophenylbenzoylacetylene diiodide, however, decomposes slowly at about 145° and rapidly at 172°, the temperature at which it appears to melt. The decomposition is a clean reaction, iodine and the original acetylenic ketone being the only products. In fact, the thermal decomposition of the diiodide provides the best method of analysis.

o-Chlorophenylbenzoylacetylene, like the unsubstituted analogue, reacts readily with bromine to give a dibromide, a substance which is stable at a temperature one hundred degrees above its melting point. The same dibromide is obtained by treating the diiodide with bromine.

In view of the successful addition of iodine and bromine to *o*-chlorophenylbenzoylacetylene, no difficulty was anticipated in the addition of chlorine. However, attempts to prepare the dichloride have so far met with no success. The acetylenic ketone is recovered unchanged when chlorine is bubbled through its chloroform solution, either at room temperature or at the boiling point of the solution, and even when a trace of iodine is added. When chlorine is bubbled through the molten acetylenic ketone, a red oil is obtained which has as yet given no solid products. Chlorine does not displace bromine from the di-

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[1] Nef, *Ann.*, **308**, 277 (1899).

[2] Dufraisse, *Ann. chim.*, **17**, 133 (1922).

[3] Bickel, THIS JOURNAL, **69**, 73 (1947).

[4] Bickel, *ibid.*, **69**, 2134 (1947).