[CONTRIBUTION NO. 206 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

The Relation of the Viscosity of Nylon Solutions in Formic Acid to Molecular Weight as Determined by End-Group Measurements

BY GUY B. TAYLOR

In the high polymer field, interest in relating the molecular weight to some function of the viscosity of a solution of a polymer[1] has persisted since Staudinger[2] proposed his original equation. The present paper is a report of attempts to establish such a relationship for nylon. Intrinsic viscosities derived from measured relative viscosities in formic acid of 25 specially prepared samples are compared with the number–average molecular weight determined by end-group measurements. The viscosity of a polymer solution is more nearly a function of weight–average molecular weight rather than number–average molecular weight, but as will be shown there is probably a constant ratio between the two values for all the samples studied.

Polymeric hexamethyleneadipamide,[3] the compound comprising most currently commercial nylon, is made from pure hexamethylenediammonium adipate ("66" salt).[4] The polymer results from the reaction of amine and carboxyl groups with the elimination of water. The amide links couple hydrocarbon segments end-to-end to form material of high molecular weight. The extent of the reaction is controlled by an equilibrium such that with exact equivalents of carboxyl and amine it is a function of the moisture content at the end of the reaction. With an excess of either amine or carboxyl the coupling of segments can be stopped when the ends of all the chains are one functional group or the other. In actual practice the polymer always contains residual groups of both types and their determination permits an estimate of the number—average molecular weight. Samples with a wide range of both residual amine and carboxyl groups were prepared for our work.

Experimental

Samples.—A series of polymers of various average molecular weights were prepared[5] from specially purified hexamethylenediammonium adipate (salt) with and without small measured excesses of hexamethylenediamine, adipic acid, or acetic acid. The salt (300–500 g.), excess reactant, and water to give 70% salt solution were placed in a 1-liter stainless steel vessel which was then immersed in a fused-nitrate bath at 200°. The temperature of the bath was then raised in the course of two to three hours to 275–280°. During this time steam was constantly released to hold the pressure at 250 lb./sq. in. At the final temperature, the pressure was reduced during about an hour; in most cases the final pressure was atmospheric, in a few cases it was 25 or 50 lb., and in a few others less than atmospheric with a vacuum pump. After holding half to one hour under final conditions, nitrogen pressure was applied to consolidate the melt and keep out air. Then the vessel was removed from the bath and cooled. The solid plug of polymer was broken into small pieces in a cutting machine. A list of the products is given in Table I together with samples of commercial nylon flake, and a high-viscosity fraction prepared from flake.

During preparation the evolved steam was condensed in standard hydrochloric acid and an aliquot back-titrated to determine total nitrogen bases. The residue from a second aliquot evaporated to dryness was heated to 180° to sublime ammonium chloride, and the residual amine hydrochloride was titrated with standard silver nitrate. Another procedure was to add standard alkali to the condensate and boil out ammonia under a reflux condenser. Both methods were found satisfactory with known ammonia–diamine solutions.

In some of the runs of the series the effluent water was caught in excess 0.1 *N* barium hydroxide. A precipitate formed with the first drop of condensed steam and the rate of carbon dioxide evolution appeared to increase as the run proceeded. The supernatant liquor was titrated for alkalinity with both phenolphthalein and methyl red indicators. A second aliquot was boiled under an air-cooled reflux condenser until it lost 20% in volume, after which it was titrated using methyl red as indicator. The difference between the two methyl-red endpoints was taken as ammonia. During the boil-off more precipitate was formed, probably from carbamate, and it was about equivalent to the difference in titer of the first aliquot with the two indicators. The main barium carbonate precipitate was filtered, washed, boiled with standard hydrochloric acid and back-titrated to determine carbon dioxide. There was a small amount of insoluble material that came out with the steam which has not been identified. It is soluble in ether but not in alcohol.

End Groups.—Residual unreacted amine and carboxyl groups were determined by micro-titration methods[5a]; the amine in phenol–ethanol solvent with standard hydrochloric acid using a conductometric end-point; and the carboxyl in benzyl alcohol solvent at 175° with standard alkali, using phenolphthalein as indicator. Acetyl group contents were calculated from the quantity of acetic acid used in making the polymer, since it was found by complete hydrolysis of some of the samples with phosphoric acid that the acetic acid used for making the samples could be recovered quantitatively by distillation.

The titrations were calculated to equivalents per million grams and since there are two ends to every long-chain molecule, the number—average molecular weight is 2×10^6/total end-groups. The reproducibility of either of the methods is scarcely better than ±3 end-groups.

Viscosity.—Data for intrinsic viscosity were obtained with a Ubbelohde[6] viscometer modified with an enlarged receiving reservoir. The 90% formic acid solvent was timed at 112.5 seconds at 25.0 ± 0.03°. Succeeding portions of an accurately known concentration of polymer in the same solvent were then weighed in from a drop-buret to the nearest milligram. This procedure permitted the

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(1) For example see Flory, THIS JOURNAL, **65**, 372 (1943), for polyisobutylenes and Bartovics and Mark, *ibid.*, **65**, 1901 (1943); Sookne and Harris, *Ind. Eng. Chem.*, **37**, 475 (1945), for cellulose acetate.

(2) Staudinger and Heuer, *Ber.*, **63**, 222 (1930); Staudinger and Nodzu, *ibid.*, **63**, 721 (1930).

(3) Carothers, U. S. Patent 2,130,523 (1937); Bolton, *Ind. Eng. Chem.*, **34**, 53 (1942).

(4) Carothers, U. S. Patent 2,130,947 (1938).

(5) Spanagel, U. S. Patent 2,163,638 (1939).

(5a) Waltz and Taylor, "Determination of the Molecular Weight of Nylon," to be published.

(6) Ubbelohde, *Ind. Eng. Chem., Anal. Ed.*, **9**, 85 (1937).

TABLE I

DATA ON END-GROUPS[a]

	Losses		Product			Deficit	Rel. vis.		Mol. wt.
Excess	NH_2	CO_2H	NH_2	CO_2H	Total	CO_2H	$c = 10$	$[\eta]$	$\times 10^{-3}$
0	18	2	126	130	256	12	16.5	0.66	7.8
0	15	2	111	111	222	13	19.1	.75	9.0
0	17	6	104	100	204	..	21.0	.78	9.8
0	..	..	75	95	170	..	29.6	.93	11.7
0	17	..	81	66	147	..	34.5	1.01	13.6
0	18	..	56	44	100	..	61.2	1.39[b]	20.0
0	22	18	47	42	89	9	82.5	1.60	22.5
0	23	14	45	37	82	17	99.0	1.76	24.4
Diamine									
350	58	6	290	13	303	−21	14.0	0.64	6.6
208	26	..	215	31	246	..	18.2	.73	8.1
208	29	..	200	14	214	..	22.6	.81	9.3
69	18	..	96	31	127	..	44.6	1.15	15.7
82	34	10	92	24	116	10	52.6	1.27	17.2
Adipic									
350	10	6	15	320	335	49	12.2	0.60	6.0
285	..	..	15	272	287	..	15.2	.67	7.0
150	13	..	14	133	147	..	34.2	1.01	13.6
150	10	..	15	135	150	..	34.5	1.01	13.3
66	..	..	32	92	124	..	44.4	1.16	16.1
66	18	21	22	62	84	23	83.8	1.61	23.8
Acetic									
177	8	..	21	162	360	..	11.8	0.58	5.6
122	10	..	23	105	250	..	17.3	.71	8.0
75	9	..	40	94	209	..	22.0	.80	9.6
75	11	..	25	77	177	..	27.2	.90	11.3
39	11	15	27	56	122	6	46.3	1.16[b]	16.4
53	(flake)		32	97	182	..	26.0	0.90[b]	11.0
...	(fraction)		...	...	...	..	128.0	2.00[b]	..

[a] Values in first seven columns are in units of equivalents per 10^6 grams. Molecular weight is calculated from total end-groups. [b] Values of $[\eta]$ are direct measurements, others derived from values of "Rel. vis.," Fig. 3.

entire desired concentration range to be explored in one instrument without having to clean it.

Another measurement of more value for plant control than intrinsic viscosity is the relative viscosity of a 10% by volume solution in formic acid. The procedure here is to dissolve 11.00 g. of polymer in 100 ml. of 90% formic acid (sp. gr. 1.20) and to time the flow in a pipet-style viscometer calibrated with glycerol solutions.[7] For small samples one-tenth the above quantities may be used in a Cannon viscometer.[8]

Results and Discussion

In terms of end-groups Table I gives the excess used to make the polymer, losses as measured with the evolved steam while making the polymer, the analysis of the polymer itself, and a materials balance. Since there are 8850 end-group equivalents each of amine and carboxyl in the salt used to make a polymer, it will be seen that the extent of reaction for all samples listed is above 98% of the deficient reactant. Molecular weights given in the table are calculated from total end-groups found by analyses of the polymers and taking no account of the small extent of side-reactions responsible for producing carbon dioxide and ammonia.

In 1938, J. B. Nichols,[9] of this Laboratory made osmotic pressure measurements on several samples of nylon in 90% formic acid at 0.5% concentration of polymer. At that time the only method developed for any end-group was a titration for amine in cresol with an indicator. Three of Nichols' samples were made with the same quantity and character of excess reactant as ours and by the same method. Comparative values of amine end-groups measured are 8-280-22 *vs.* 15-290-25 for the two series and 5600-6800-9700 molecular weight by osmotic pressure *vs.* 6000-6600-10300 molecular weight calculated from our intrinsic viscosity values.

During the course of the present work many attempts were made to measure osmotic pressure by Fuoss[10] dynamic method but nylon was found to contain too much low-molecular weight material that passed through any collodion membrane sufficiently permeable to make the Fuoss technique workable. The Nichols measurements, however, were checked in an experiment utilizing the Fuoss cell as a static instrument with cello-

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[7] Sheely, *Ind. Eng. Chem.*, **24**, 1060 (1932).

[8] Cannon and Fenske, *Oil & Gas*, **33**, 52 (1935); **34**, 45 (1936).

[9] Nichols, J. Alexander's "Colloid Chemistry," chapter on "Colloid Aspects of Nylon," 1946.

[10] Fuoss and Mead, *J. Phys. Chem.*, **47**, 59 (1943).

phane as the diaphragm. A sample of polymer dissolved in *m*-cresol and diluted with three volumes toluene gave 9000 molecular weight at 2.0 g./liter and 9300 at 1.6 g./liter *versus* 11,000 from end-groups. These results are only rough approximations because temperature control was inadequate to control the particularly large liquid thermal expansion error peculiar to the Fuoss cell. In spite of lack of extrapolation to zero concentration[10] and the theoretical objection to the use of mixed solvents[11] in osmometry, it appears safe to conclude that the end-group method does give a fair approximation of the actual molecular weight.

Data for specific viscosity *versus* concentration for five samples are given in Table II and plotted in Fig. 1. The formula chosen[12] to correlate the data is

$$\eta_{sp}/c = [\eta] + k\,[\eta]^2 c$$

with $k = 0.11$. All the lines are drawn with slopes calculated from $k[\eta]^2$ and it will be seen that between c values of 0.2 and 0.7 the data fit the formula very well. Below 0.2 the experimental error is unduly great. Above 0.8 the points for the highest viscosity sample are really below the line, so that the formula's usefulness is restricted to the range stated. Another method[12] employed by some authors for arriving at intrinsic viscosity is to plot $\ln (1 + \eta_{sp})/c$ *vs.* c. On the plot of Fig. 1 this has been done for two samples and gives lower $[\eta]$ values (intersection with vertical axis by straight line extrapolation). If η_{sp} values calculated from the formula are used to draw the $\ln (1 + \eta_{sp})/c$ line over the whole range, a curve will result that slopes away from the straight line to same $[\eta]$ value obtained by the other method. Between 0.2 and 0.6 for c the points fall nearly in a straight line. Any extrapolation method is arbitrary and errors difficult to assess.

TABLE II

DATA ON INTRINSIC VISCOSITY

c	η_{sp}/c	c	η_{sp}/c	c	η_{sp}/c
0.744	0.485	0.672	1.250	0.850	2.33
.527	.477	.580	1.245	.640	2.30
.368	.478	.401	1.212	.464	2.22
.164	.450	.221	1.170	.386	2.18
(0.00)[a]	.48	(0.00)	1.16	.331	2.15
				.259	2.10
				(0.00)	2.00
0.742	0.897	0.614	1.505	0.840	2.31
.640	.892	.520	1.409	.670	2.28
.537	.886	.436	1.475	.558	2.25
.436	.876	.347	1.453	.478	2.21
.332	.864	.253	1.435	.375	2.15
.225	.847	.139	1.380	(0.00)	2.00
.132	.805	(0.00)	1.39		
.058	.778				
(0.00)	.84				

[a] The values opposite (0.00) are straight line extrapolations to give $[\eta]$.

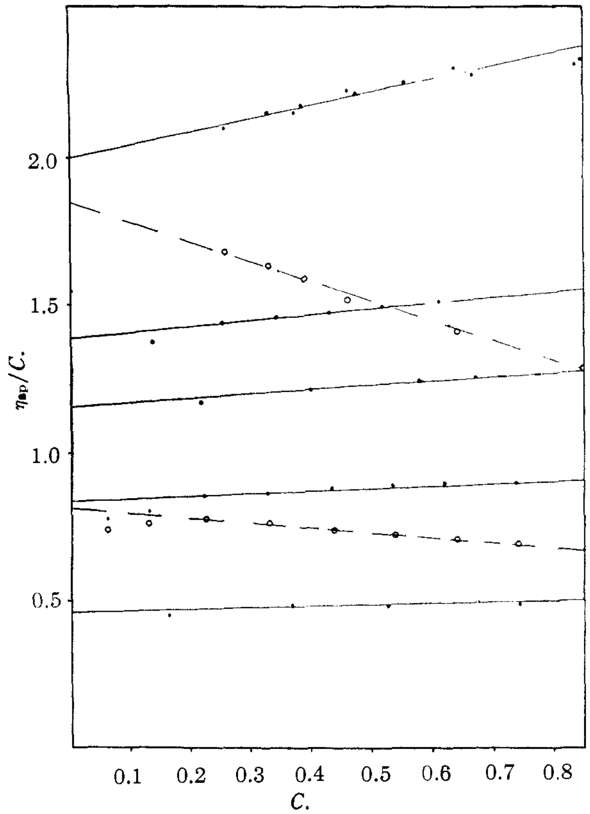

Fig. 1.

Data on the relation between intrinsic viscosity and relative viscosity ($c = 10$) of two samples of nylon together with material fractionated from them are assembled in Table III. The measurements of η_{sp} were made at a single concentration from which $[\eta]$ was calculated. Figure 3 is a plot of data taken from Tables II and III and this plot served to convert measured values of relative viscosities ($c = 10$) of the specially prepared

TABLE III

RELATIVE AND INTRINSIC VISCOSITIES

$\eta_{sp}/0.5$	$[\eta]$	Rel. vis. $c = 10$	$\eta_{sp}/0.5$	$[\eta]$	Rel. vis. $c = 10$
0.28	0.28	5.0	0.53	0.52	12.0
.41	.41	7.9	.67	.65	16.4
.47	.46	10.9	.74	.71	18.5
.55	.54	12.4	.80	.77	20.5
.65	.63	15.1	1.11	1.05	33.6
.74	.71	21.4	1.26	1.18	46.9
1.04	.99	34.4	1.42	1.32	59.9
1.20	1.13	48.5	1.58	1.46	73.8
1.53	1.42	65.0	1.81	1.66	84.9
1.71	1.57	76.1			
1.05[a]	1.00	32.5	1.25[a]	1.17	47.5

[a] Whole polymer, others are fractionated material from that polymer.

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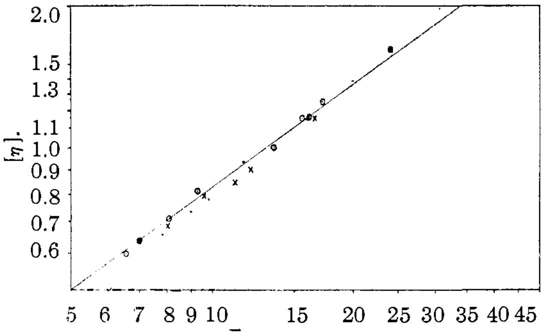
[11] Wall, THIS JOURNAL, **66**, 446 (1944).

[12] Huggins, *Ind. Eng. Chem.*, **35**, 980 (1943), discussed various formulas for extrapolation for $c \rightarrow 0$.

polymers to the listed intrinsic viscosities given in Table I.



$\overline{M}_N \times 10^{-3}$.

Fig. 2.

Figure 2 is a log–log plot of [η] *versus* $\overline{M}_n$' number—average molecular weight.[13]

The line is drawn from the equation[14] whence

$$[\eta] = 11 \times 10^{-4}\,\overline{M}_n^{0.72}$$

$$\overline{M}_n = 13{,}000\,[\eta]^{1.39}.$$

The largest deviation from the line of any single $\overline{M}_n$ value (of the order of 10%) is considered well within the uncertainties of the end-group method of determining number-average molecular weight. The natural inference is that viscosity-average molecular weight is closely proportional to number-average molecular weight for all the samples studied. It will be shown in a subsequent paper that viscosity and weight averages are not very different.

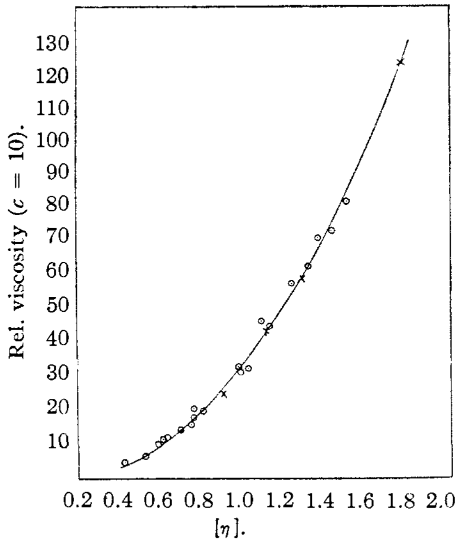


Fig. 3.

Acknowledgments.—The larger part of the test-work on the samples was performed by the analytical staff of the Nylon Research Section of the Rayon Department of this Company.

Summary

Measurements of the intrinsic viscosity and functional end-groups of polymer chains for twenty-five different nylon samples have been made and the relation between the viscosity and molecular weight reduced to the formula $\overline{M}_n = 13{,}000\,[\eta]^{1.39}$. Molecular weights, number averages, ranged from 5 to 25 thousand depending on extent of reaction which was controlled by employing an excess of a functional group and on the conditions of preparation. It is concluded that the ratio of viscosity–average to number–average is nearly a constant for all the samples.

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(13) Matthes, *J. prakt. Chem.*, **162**, 245 (1943), uses the same form of plot to correlate viscosities of a polyamide solution in sulfuric acid. He was the first to show that the molecular weight–intrinsic viscosity relationship required a fractional exponent for $\overline{M}$ in the case of a polyamide.

(14) C. L. Arcus, Imperial Chemical Industries, private communication, proposes for this relation $[\eta] = 4.50 \times 10^{-4}\,\overline{M}_n^{0.81}$.

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The Distribution of the Molecular Weight of Nylon as Determined by Fractionation in a Phenol–Water System

BY GUY B. TAYLOR

It is generally recognized that all synthetic high polymers are heterogeneous as to molecular weight. The distribution of molecular size about an average value may be as important in determining physical properties as that average itself. Not many studies of distribution have been made, principally because of experimental difficulties. At best, all methods are time-consuming which militates against their frequent use. The sedimentation equilibrium method employing the ultracentrifuge, often suggested as the ultimate way to establish a true size-distribution curve, seems to have had little application in the synthetic polymer field. It is doubtful whether this method would be workable with a polymer of the degree of heterogeneity and low molecular weight of nylon. Fractionation, another method for size-distribution studies, has the advantage of supplying samples for examination of properties and in fact is most often utilized solely for the purpose of obtaining material with a narrower range of molecular size than the original material. The present study was designed to secure the true size-distribution by taking a large number of