polymers to the listed intrinsic viscosities given in Table I.

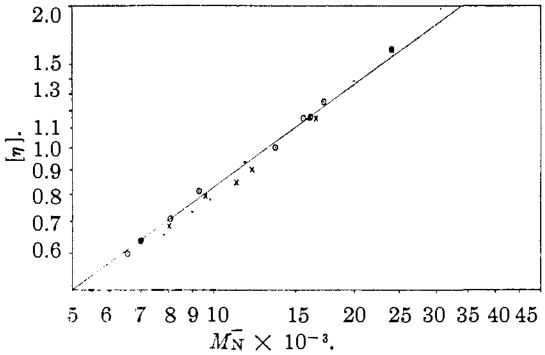

Fig. 2.

Figure 2 is a log–log plot of $[\eta]$ *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.

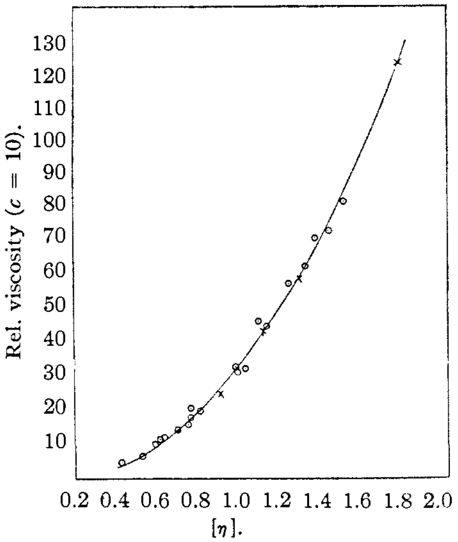

Fig. 3.

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.

WILMINGTON, DELAWARE RECEIVED JUNE 21, 1946

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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 $[\eta] = 4.50 \times 10^{-4} \overline{M}_n^{0.81}$.

[CONTRIBUTION NO. 207 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

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

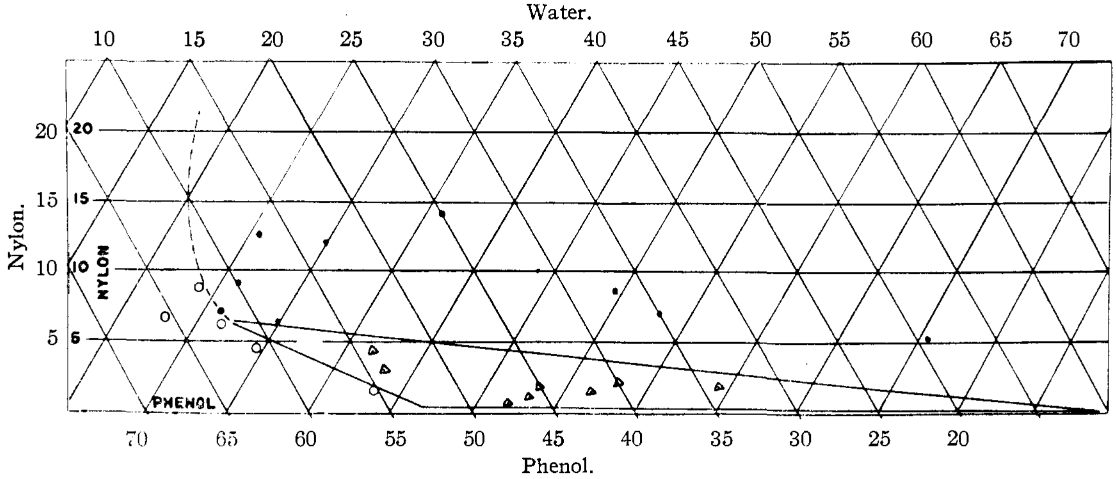

Fig. 1.

cuts and the quantity per cut permitted measurement of a single property only, intrinsic viscosity.

The nylons are linear polyamides formed by the intermolecular reaction of the functional groups, amine and carboxyl. For such polymer formed from bifunctional compounds, Flory[1] has developed theoretical formulas for size-distribution based on the premise that the reactivity of a functional group is independent of the size of the molecule of which it forms a part. The experimental evidence for the validity of this assumption rests largely on kinetic studies of polyester formation and reactions.[2] A recently established relation[3] between the intrinsic viscosities of polyamide solutions and number-average molecular weights supported Flory's thesis. The relation was linear on a logarithmic plot over the range 5–25,000 average molecular weight as determined by residual functional groups and since viscosity is much more nearly a function of weight-average than number-average molecular weights, these results suggested that the ratio between the weight-average and number-average molecular weights is nearly constant as required by Flory's equations. The discovery of a method of fractionation permits an actual experimental check of the distribution deductions at least in the case of one polyamide, "nylon 66," polyhexamethyleneadipamide.

The fractionation method involves separation by selective solubility in the two-phase system,[4] phenol–water. Phenol is one of the few known good solvents for polyhexamethyleneadipamide at room temperature. Flowable solutions up to 33% polymer can be prepared, and mixtures above that figure vary from semi-solids to hard masses. Moderately dilute solutions of the order 10% polymer or less are best made with 85–95% phenol liquefied with water. Further addition of water ultimately results in two liquid phases with close to the same phenol–water ratio in the phases as in non-consolute phenol–water mixtures. The polymer is entirely in the phenol-rich phase at temperatures up to at least 50°. At certain over-all compositions and in the neighborhood of 60° the unusual situation of a three-liquid-phase system occurs. Polyhexamethyleneadipamide (nylon 66) behaves so much like a single molecular species that a phase rule diagram can be constructed. At 70° and higher temperatures, *i. e.*, above the consolute temperature of phenol–water alone (66°), only two phases occur, with polymer in both. As little as 0.01% polymer in the system is sufficient to establish two liquid phases at 70°.

When polymer occurs in two of the phases, material of the higher molecular weight tends to go to the phenol richer phase and this fact serves as the basis for a fractionation procedure.

Figure 1 is the part of the phase diagram of interest for whole polymer with the experimental points indicated for 60°. Any composition represented by a point within the triangle ABC, splits to the three phases represented by the apices of the triangle with approximate compositions 6.5–67, 0.5–58 and 0–16% polymer–phenol. Any point to the right of the dashed line and above the triangle gives two phases with polymer in only one phase. Mixtures represented by points to the left of the line and triangle are consolute. A rough fractionation of nylon was made in 1941 by withdrawing the middle phase and replacement by a suitable mixture of phenol–water so as to make a series of consecutive extractions. This was not satisfactory largely because the low polymer content of this phase made recovery of the solid difficult and because the concentration became lower at each step.

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[1] Flory, THIS JOURNAL, **58**, 1877 (1936) Carothers, *Trans. Faraday Soc.*, **32**, 39 (1936).

[2] Flory, THIS JOURNAL, **61**, 3334 (1939); **62**, 2255, 2261 (1940); **64**, 2205 (1942).

[3] Waltz and Taylor, "Determination of the Molecular Weight of Nylon," to be published, and Taylor, THIS JOURNAL, **69**, 635 (1947).

[4] Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938), has used a two-phase system in fractionating nitrocellulose.

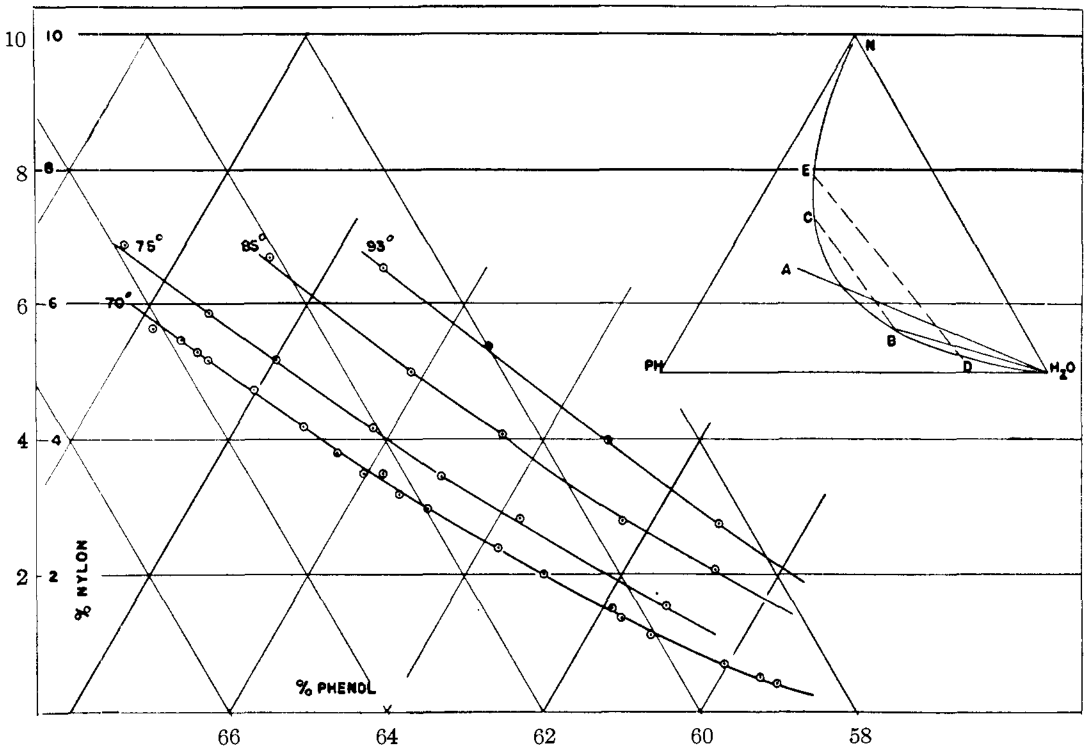

Fig. 2.

Figure 2 is the phase diagram at 70, 75, 85 and 93°. The small triangle is schematic and intended solely to make clear the basis of the procedure. If any consolute mixture, say A, is diluted with water the composition follows along a line headed for the water apex. Upon crossing the curve two phases appear (compositions B and C). If phase C is withdrawn and further dilution made, again the mixture splits along the tie-line to D and E. Each portion withdrawn is higher in polymer content and the phase left is lower; the weights of the phases are inversely proportional to distances along the tie-line from its intersection with the diluting line.

Figure 2 shows the part of the phase diagram experimentally determined by diluting phenol–polymer solutions with water to the cloud point. It will be seen that the curvature of these equilibrium lines is so slight that there is little hope for working in the region above 2% polymer over-all composition and even at 1% the dilution will be extremely critical in the matter of controlling the size of the phases and hence size of the cuts on fractionation. In the actual fractionation work it was found that differences in properties of cuts made above one per cent. polymer were materially less than when made at lower concentrations. No attempt has been made to establish the actual position of tie-lines, first because the polymer is really not a single compound and the lines no doubt would shift as fractions are removed and second, for lack of the precise analytical method required. Qualitatively the phase diagram has been of immense help in orienting the experimental procedures.

A number of fractionations have been made of nylon, taking about ten cuts from each sample. The sharpness of separation when taking so few fractions was not adequate to establish true distribution curves, but the results conclusively established that whole polymers of considerably different average molecular weights had a wide distribution of molecular sizes, all beginning with material estimated as low as 1000, checked both by viscosity and end-group measurements made on the fractions. In the work reported here the number of cuts was increased to 46, which, with the treatment given the data, is believed to furnish a close approximation to the true distribution.

Experimental

Apparatus.—The equipment was made from a 3-necked 5-liter flask by altering the bottom to a wide cone and sealing to its apex, pointing down, heavy-walled glass tubing of 2 mm. bore for withdrawing the lower phase. The flask was provided with a mercury-sealed stirrer, thermometer and opening for introducing water. It was totally immersed in a water-thermostat controlled at 70.0 ± 0.2°. Provision was made for displacing air with oxygen free nitrogen prior to a run and maintaining a pressure of this gas at 10 inches water column during the entire subsequent operation. In air the phenol solution of polymer gradually turns red and the recovered solid is discolored by a resinous impurity.

Materials.—The polymer fractionated was a sample of bright nylon flake with an intrinsic viscosity[3] value of 0.90 residual unreacted functional groups 32 and 97 equivalents of amine and carboxyl respectively per 10^6 g., and 53 acetyl (same units) from acetic acid put in the charge when making the polymer. U. S. P. phenol was redistilled over sodium carbonate and diluted to 87.5% strength. It was sufficiently pure so as not to discolor when stored in clear glass for several weeks. The water for dilution during operation contained 0.5 g. of sodium chloride per liter. Without an electrolyte separation of phases was impractically slow.[5]

Operation.—The procedure was designed to split the sample into two cuts (A and B) of nearly equal weight, followed by separate fractionation of each cut (A_1, A_2, A_3, $\cdots$; and B_1, B_2, B_3, $\cdots$). Most of these cuts were then fractionated again (A_{11}, A_{12}, A_{13}, $\cdots$). In detail, 100 g. of polymer (dry basis) was dissolved in the flask in 3 liters of phenol while heating the bath to 70°. After dilution with 1265 ml. of hot water, 30 minutes of stirring, and several hours for separation, the bottom layer (793 g.) was withdrawn. Further dilution with 25 ml. of water yielded 411 g. more after separating overnight. The total, 1204 g., constituted the A cut. The residue in the flask was the B cut and its fractionation was continued by alternate addition of water and withdrawal of the lower phase. Values of the two are for B_1 25 ml. water and 175 g. withdrawn; B_2 45 and 160; B_3 65 and 105; B_4 150 and 96; B_5 500 and 115; B_6 1830 and 58.

The B_7 fraction was the residue in the flask at very low concentration and to recover its solids, the flask was cooled to room temperature and the phenol-rich phase repeatedly extracted with water till its volume was reduced to 50 ml. or less.

The A-cut was transferred to a duplicate apparatus and after suitable dilution with phenol, fractionation continued by a similar procedure as described for the B-cut. Sub-cuts were handled in the same way. The tables of data give calculated concentrations of the phases and provide information on dilution required with the additional information that over-all concentration of phenol at the first cut of any successive partition is *ca.* 60%. After a dilution made in the morning, separation was usually adequate to draw a fraction in the late afternoon, when another dilution was made for separation overnight.

Polymer Recovery.—The final cuts were made consolute with ethanol and their solids content precipitated by slowly dripping into at least 25 times their volume of distilled water at the boil. The mother liquor was sucked off through a sintered-glass filter stick and the material washed repeatedly by near-boiling water and use of the stick. If the precipitation is done in too small volumes of water or at temperatures below 95° the solid comes down in poor physical form, sticks to glass, and is hard to wash and handle. Samples of lower molecular weight tended to give hazy or cloudy filtrates from the mother liquor but evaporation of these proved that losses were not significantly above those expected from the known solubility of polymer in water.

TABLE I

PRIMARY CUTS

	Phase Concn. % polymer			Av.	Range
Code	Cut	Top	%	$[\eta]$	$[\eta]$
A	4.5	1.30	54.3	1.11	0.20–2.17
B	..	..	44.2	0.69	.10–1.41
A_1	4.80	1.01	18.33	1.40	.25–2.17
A_2	5.65	0.69	12.66	1.27	.20–1.70
A_3	6.50	.46	7.98	1.01	.50–1.35
A_4	7.90	.21	7.90	0.75	.45–0.96
A_5	9.10	.08	4.27	(0.57)[a]	.39– .67
A_6	8.10	.03	1.86	(.38)	....
A_7	..	..	1.36	(.23)	....
B_1	5.30	1.10	9.23	.97	.10–1.41
B_2	5.50	0.85	8.79	.88	.35–1.20
B_3	6.50	.64	6.85	.74	.35–1.00
B_4	7.80	.38	7.49	.59	.31–0.78
B_5	5.90	.15	6.74	.44	.25– .60
B_6	6.10	.03	3.58	(.30)	.22– .37
B_7	..	..	1.46	(.18)	....

[a] Values in parenthesis were measured. All others were calculated from sub-cuts, Tables II and III.

Intrinsic Viscosity.—The sample was dried in a tared bottle for two hours in a vacuum oven at 60°, dissolved in 90% formic acid to give a solution at 0.5–0.6 g./100 ml., and the solution filtered through sintered glass. Viscosity relative to the solvent was measured in Ostwald

TABLE II

FINAL CUTS, A FRACTIONS

	Phase Concn. % polymer			Measured
Code	Cut	Top	%	$[\eta]$
A_{11}	5.10	0.52	3.33	2.02
A_{12}	5.40	.44	2.46	1.80
A_{13}	6.20	.29	4.27	1.55
A_{14}	7.85	.12	4.73	1.17
A_{15}	9.25	.007	3.16	0.71
A_{16}	...	..	0.38	0.30
A_{21}	4.70	.68	0.95	1.67
A_{22}	5.20	.55	2.32	1.61
A_{23}	5.80	.41	2.63	1.45
A_{24}	7.10	.21	3.29	1.30
A_{25}	10.30	.023	2.97	0.85
A_{26}	...	..	0.50	.38
A_{31}	5.40	.59	1.87	1.28
A_{32}	7.45	.21	4.13	1.06
A_{33}	10.00	.007	1.80	0.68
A_{34}	...	..	0.18	.58
A_{41}	5.75	.53	2.92	.90
A_{42}	7.70	.18	3.23	.75
A_{43}	8.80	.016	1.48	.54
A_{44}	..	..	0.27	.46

TABLE III

FINAL CUTS, B FRACTIONS

Code	Cut	Top	%	Measured $[\eta]$
B_{11}	5.40	0.52	1.88	1.37
B_{12}	6.40	.43	1.42	1.24
B_{13}	6.80	.27	2.27	1.04
B_{14}	9.50	.025	3.31	0.65
B_{15}	..	...	0.35	.15
B_{21}	5.85	.47	2.79	1.11
B_{22}	7.25	.20	3.50	0.93
B_{23}	7.10	.011	2.26	.58
B_{24}	..		0.24	.37
B_{31}	5.40	.58	1.63	.94
B_{32}	7.20	.28	2.67	.81
B_{33}	8.90	.047	2.01	.58
B_{34}	..	..	0.54	.36
B_{41}	6.55	.56	2.35	.71
B_{42}	8.65	.24	2.85	.62
B_{43}	8.80	.033	1.81	.46
B_{44}	..		0.48	.36
B_{51}	6.15	.45	1.57	.57
B_{52}	7.00	.30	1.74	.48
B_{53}	11.0	.07	2.47	.40
B_{54}	..	..	0.96	.28

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(5) Howell, *Proc. Roy. Soc.* (London), **137A**, 418 (1932).

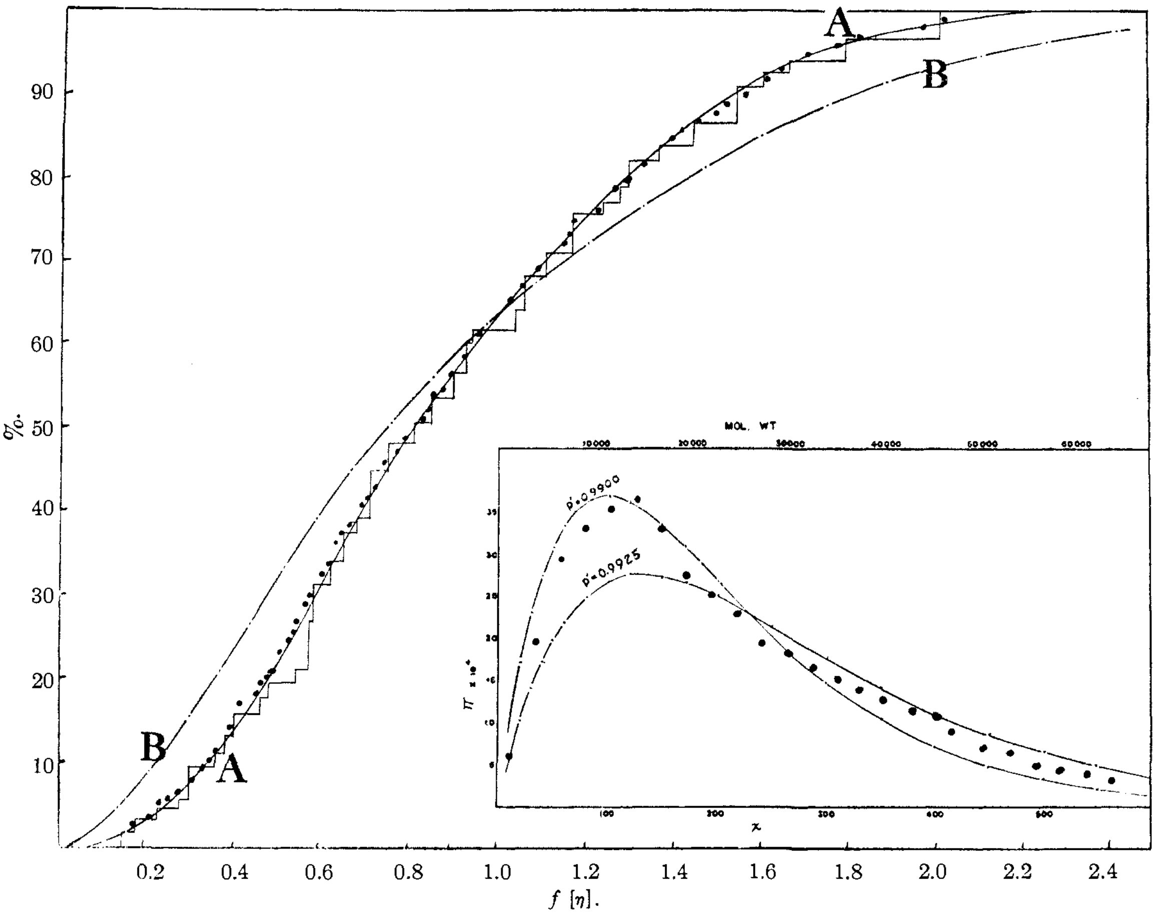

Fig. 3.

viscometers and specific viscosity extrapolated to $c = 0$ from nomographs constructed from the formula.[3]

$$\eta_{sp}/c = [\eta] + 0.11[\eta]^2 c$$

All tests were run in duplicate.

Experimental Results.—In all, 96.24 g. was recovered from 100 g. of flake. Since at least 1.5% of the flake is known to be soluble in water, the recovered values of each fraction were adjusted proportionally to total 98.5 on the basis of mechanical losses during the recovery operation. The experimental data are given in Tables I, II and III. Values for intermediate fractions (*i. e.*, those not recovered) were calculated proportionally from the final fractions.

Treatment of the Data.—The experimental data were assembled in a table of the values of $[\eta]$ in ascending numerical order with adjusted per cent. alongside, and a third column added of cumulative per cent. plus 1.5. The values in the third column were plotted against $[\eta]$ on 50 × 40 cm. cross-section paper and connected step-wise as shown in Fig. 3. Each primary cut (*e. g.*, A_1) was separately plotted stepwise in the same way from its sub-cuts (*e. g.*, A_{11}, A_{12}, $A_{13}\cdots$) and a smooth curve drawn cutting the plateaus. Ranges of $[\eta]$ given in Table I are derived from the curves. From all these curves values of $[\eta]$ were read at 0.5 or 1% intervals and assembled in a table of cumulative total per cent. and $[\eta]$ values. The points shown on Fig. 3 were taken from this table and helped locate the smooth curve A (Fig. 3) drawn through the plateaus.[6]

It is shown in another paper[3] that molecular weight and intrinsic viscosity are related by an equation of the form

$$\overline{M} = K[\eta]^a$$

where $a = 1.39$. Curve B, Fig. 3, is drawn from the 1.39th power of $[\eta]$ values taken from curve A. The values of Δ% in Table IV are read at 0.1 increments of $[\eta]^a$ beginning at 0.05, so that numbers in the first column are averages.

Results and Discussion

Flory's treatment of the case of polymers formed by bifunctional compounds where each specific functional group is contributed by the same compound (in our case $-NH_2$ from hexamethylenediamine and $-CO_2H$ from adipic acid) is complicated by the fact that different formulas are required for even and odd numbers of links in the polymer chain, but he shows that the simpler equation applying when the two groups are contributed by the same monomer applies very closely with a suitable modification to cases of different monomers. For our case it may be written

$$\pi = x(pr^{1/2})^{x-1}(1 - pr^{1/2})^2$$

where π is weight fraction of an x-mer, p is fraction of total amine reacted, r is ratio of amine to

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[6] Methods of constructing distribution curves from fractions are discussed by Mark, "High Polymers," Vol. III, Interscience Press, 1941, pp. 47–63. See, also, Schulz, *Z. physik. Chem.*, **30B**, 379 (1935), and **32B**, 27 (1936).

carboxyl reactants in the system, and x the number of segments in a polymer chain. For our polyamide the mol. wt. is 113 x.

Taking logs of both sides of the above equation and substituting p' for $pr^{1/2}$

$$\log \pi - \log x = x \log p' - \log p' + 2 \log (1 - p')$$

results in an equation for a straight line with slope $\log p'$. To test the form of this equation as to fit,[7] with experimental data, any values proportional to actual π and x values may be used. In Fig. 4 log Δ % minus log $[\eta]^a$ is plotted against $[\eta]^a$ for $a = 1.39$ (circles) and for $a = 1$ (crosses). The straight line is drawn with a slope of -1.005 corresponding to $p' = 0.99$. It is evident at once that unity[8] value for a is inconsistent with the premise of random distribution and for $a = 1.39$ the fit is well within the experimental error. The value 1.39 was established entirely independently of any fractionation results.

In terms of end-groups (equivalents per 10^6 grams) there were 8850 each of amine and carboxyl from hexamethylenediammonium adipate and 53 carboxyl from acetic acid used to make the polymer. By analysis there were 32 amine and 97 carboxyl groups unreacted. Whether the acetic acid is regarded as reducing the amine or increasing the carboxyl in the adipate makes very little difference in calculating r, 8850/(8850 + 53) = 0.9940 or (8850 − 53)/8850 = 0.9941. Strictly on the basis of residual groups measured, r = 8850/(8850 + 97 − 32) = 0.9927. The value of the fraction unreacted, $1 - p$, on basis of amine measured is 32/8850 = 0.0036 while on the basis that excess carboxyl over acetyl measures extent of reaction the value is (97 − 53)/8850 = 0.0050. Calculations from pairs of the above values yield for $pr^{1/2}$ (= p') 0.9934, 0.9934, 0.9920, 0.9927, 0.9914 with an average of 0.9924.

TABLE IV

DATA FROM SMOOTHED INTEGRAL CURVE

$[\eta]^a$ Av.	Δ%	x	$\pi \times 10^4$	(Δ%) × $[\eta]^a$	(Δ%) ÷ $[\eta]^a$	(Δ%) × $[\eta]$
0.03	0.75	12	6.5	0.02	25.0	0.06
.10	4.50	35	19.6	.45	45.0	.86
.20	6.75	58	29.4	1.35	33.7	2.12
.30	7.60	81	33.0	2.28	25.3	3.19
.40	8.15	104	35.4	3.26	20.4	4.21
.50	8.40	127	36.5	4.20	16.8	5.10
.60	7.60	150	33.0	4.56	12.7	5.26
.70	6.35	173	27.6	4.45	9.1	4.91
.80	5.77	196	25.2	4.62	7.2	4.92
.90	5.28	219	22.9	4.75	5.9	4.89
1.00	4.47	242	19.4	4.47	4.5	4.47
1.10	4.26	265	18.5	4.68	3.9	4.56
1.20	3.87	288	16.8	4.64	3.2	4.41
1.30	3.50	311	15.2	4.55	2.7	4.23
1.40	3.25	334	14.1	4.55	2.3	4.09
1.50	3.00	357	13.0	4.50	2.0	4.02
1.60	2.63	380	11.5	4.21	1.6	3.69
1.70	2.53	403	11.0	4.30	1.5	3.72
1.80	2.10	426	9.1	3.77	1.2	3.21
1.90	1.67	449	7.2	3.17	0.9	2.65
2.00	1.50	472	6.5	3.00	.7	2.51
2.10	1.13	495	4.9	2.37	.5	1.93
2.20	1.00	518	4.3	2.20	.5	1.76
2.30	0.90	541	3.9	2.07	.4	1.64
2.40	.77	564	3.3	1.85	.3	1.45
2.75	2.33	...	..	6.40	.8	4.91
	100.0			90.7	228.1	88.8

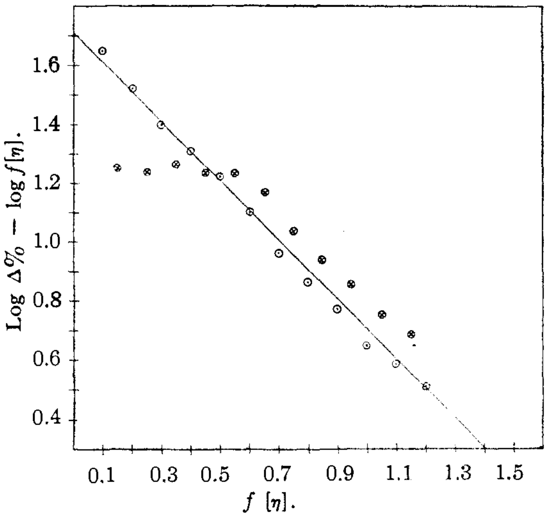

Fig. 4.—⊙, $[\eta]^{1.39}$; ⊗, $[\eta]$.

The number, weight and viscosity[9] molecular weight averages are defined by the equations

$$\overline{M}_n = \Sigma NM/\Sigma N$$
$$\overline{M}_w = \Sigma NM^2/\Sigma NM$$
$$\overline{M}_v = [\Sigma NM^{1+1/a}/\Sigma NM]^a$$

where N is the number of molecules of molecular weight M. To calculate ratios of any pair from fractionation data such as are given in Table IV, where the values increase by small increments, the spread in molecular weight is sufficiently narrow to make all averages for a fraction numerically equal. Then in the units of Table IV $NM \propto \Delta$, $M \propto [\eta]^a$ and $N \propto \Delta/[\eta]^a$. Substitution followed by simplification in the defining equations yields

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{(\Sigma\,\Delta\cdot[\eta]^a)(\Sigma\,\Delta/[\eta]^a)}{(\Sigma\,\Delta)^2} = \frac{(90.7)(228)}{10^4} = 2.07$$

$$\frac{\overline{M}_v}{\overline{M}_w} = \frac{(\Sigma\,\Delta\cdot[\eta]/\Sigma\,\Delta)^a}{\Sigma\,\Delta\cdot[\eta]^a/\Sigma\,\Delta} = \frac{(88.8/100)^{1.39}}{90.7/100} = 0.935$$

It is evident that viscosity and weight averages for whole polymer are not far apart and that the

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(7) This criterion was suggested by Prof. H. Mark of the Brooklyn Polytechnic Institute.

(8) Staudinger, the originator of the idea that molecular weight could best be expressed as a function of $[\eta]$ holds his original position for $a = 1$ in some sketchy work on nylon reported in *Kunstseide*, **24**, 88 (1942). See also Matthes, *J. prakt. Chem.*, **162**, 245 (1943), for work with Perlon, and Staudinger and Jorder, *ibid.*, **160**, 176 (1942), for polyamides in general.

(9) Flory, THIS JOURNAL, **65**, 380 (1943).

ratio of weight to number average[10] is close to 2. Then from the relation $\overline{M}_n = 13{,}000\ [\eta]^a$ established for whole polymer, the molecular weight of a fraction is $26{,}000\ [\eta]^a$.

In the fractional distribution plots of π *vs.* x (Fig. 3), curves are drawn for random distribution for p' values of 0.9900 and 0.9925. The points are taken directly from the data of Table IV calculated from experiment; $x = 26{,}000\ [\eta]^a/113$ and since in effect an area is involved and the coördinate is taken by equal increments, $\pi = \Delta\%\cdot 10^{-2}/\Delta x$ or $\Delta\%\cdot 10^{-2}/23$ for all points except the first. It is evident that random distribution prevails within the limitations within which p' can be known.

Molecular weights discussed throughout this paper are based entirely on functional end-group measurements and they need to be checked by an independent measurement such as osmotic pressure on samples reasonably homogeneous. Attempts at measurements of the required precision have so far been defeated for lack of a suitable solvent–membrane combination but further work is under way. Another point that should be mentioned is that end-groups do not measure molecular weight of abnormal nylon samples. For example, holding molten polymer many hours in sealed tubes results in the disappearance of carboxyl from the polymer and a large increase in amine with no corresponding rational relation to viscosity properties.

Acknowledgments.—The writer is indebted to Miss Gertrude Bemiller of the analytical staff of the Nylon Research Section of the Rayon Department of this Company for most of the test work on the samples and to Mrs. Josephine Pechan of the Chemical Department for assistance in the experimental work. The writer has also profited by similar work on nylon by Mr. C. L. Arcus of the Imperial Chemical Industries, Ltd. of Great Britain.

Summary

Polyhexamethyleneadipamide has been fractionated into 46 cuts in a phenol–water two-liquid-phase system at 70°. The molecular weight distribution has been found to follow that predicted by the Flory equation based on the premise that in bifunctional reactions to form linear polymers, the activity of a functional group is independent of the length of polymer chain to which it is attached.

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(10) The effect of the material of lowest molecular weight on the $\overline{M}_w/\overline{M}_n$ ratio needs some emphasis. It may be noted from the fifth and sixth columns of Table IV that the first two figures contribute a large fraction to the sum of the dividends and practically nothing to the sum of the products. It is estimated that if the 5% of the polymer contributing all below 0.15 were removed, the $\overline{M}_w/\overline{M}_n$ ratio would drop to 1.5 and the osmotic molecular weight increase from 11,000 to 16,000, while a measured $[\eta]$ would only increase from 0.90 to 0.93.

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUIMICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS, UNIVERSIDADE DE SÃO PAULO, BRAZIL]

Mixed Crystals of Sulfoxides, Sulfones, Selenoxides and Selenones

BY HEINRICH RHEINBOLDT AND ERNESTO GIESBRECHT

In a previous paper[1] it was shown that symmetrically substituted sulfoxides give continuous series of mixed crystals with the corresponding sulfones. Furthermore, we have shown that selenoxides and selenones behave in a similar way, and that sulfoxides give mixed crystals in all proportions with selenoxides.[2] From these results it was concluded that we may attribute the same configuration to sulfoxides and selenoxides as to the corresponding sulfones and selenones, and that the selenoxides must have a tetrahedral configuration similar to that of the sulfoxides.

The relationship among these compounds goes so far that continuous series of mixed crystals are also formed by sulfoxides with selenones and by selenoxides with sulfones. Sulfones and selenones are completely isomorphous. This is proved here by the study of the solid–liquid phase diagrams of the four binary systems reported in Table I–IV and Figs. 1–4, all of which were found to form continuous mixed crystals.

Experimental

The study of the solid–liquid phase diagrams of the four binary systems was undertaken with the "thaw-melting method" as described in a previous paper.[1] In the tables "Th. p." means thawing point. All percentages indicated are by weight.

Binary Systems

1. Diphenyl Sulfoxide[3] and Diphenyl Selenone[3]

TABLE I

Selenone, %	Th. p., °C.	M. p., °C.	Selenone, %	Th. p., °C.	M. p., °C.
0.0	70.1	71.0	45.2	68.4	102.1
9.4	60.2	67.3	53.2	73.7	111.4
13.5	59.2	65.1	62.6	81.0	122.0
20.0	58.5	65.3	76.5	96.3	135.5
23.2	59.0	71.2	89.3	116.2	147.1
29.6	61.2	80.3	100.0	153.8	154.9
36.0	63.8	89.5			

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(1) H. Rheinboldt and E. Giesbrecht, THIS JOURNAL, **68**, 973 (1946).

(2) H. Rheinboldt and E. Giesbrecht, *ibid.*, **68**, 2671 (1946).

(3) On the preparation and purification of these compounds see ref. (2).