workers,[7] have shown that methanol lowers the rate of depolymerization but it is not likely that such additions would influence the initial reaction if this is between the urea and the formaldehyde already existing in a dehydrated form.

Data are also given (Table I) for the reaction between N-methylurea and formaldehyde under specified conditions. As in the case of urea[1,3-5] the reaction is shown to be mainly of the slow bimolecular type. The value for the energy of activation ΔE_a is higher than the value for the urea–formaldehyde reaction previously given[1] but is very close to that given by Crowe and Lynch for the reaction between urea and formaldehyde in dilute solution.[5] In addition the value for the bimolecular velocity constant is much reduced by the substitution of one N-methyl group in the urea molecule. Of interest is the fact that no simple methylol compound could be identified in the reaction product after 8–24 hours. Only after allowing the reaction mixture to stand at 20° for one week was methylene bis (methyl urea)[8] m.p. 184° identified in small yield.

Further work with dilute solutions of N-methylurea and other substituted ureas is being carried out and discussion of the reaction between N-methylurea and formaldehyde will be continued in a later paper.

[7] M. Wadano, C. Trogus and K. Hess, *Ber.*, **67**, 174 (1934).

[8] H. Kadowaki, *Bull. Chem. Soc. Japan*, **11**, 248 (1936).

TASMANIA, AUSTRALIA RECEIVED SEPTEMBER 25, 1951

[CONTRIBUTION NO. 189 FROM THE GOODYEAR TIRE AND RUBBER CO. RESEARCH LABORATORY]

Polyelectrolyte Behavior of Polyamides. II. Viscosities of Solutions of Linear and Multichain Polyamides in Formic Acid[1]

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It is shown that dilute solutions of linear, tetrachain, or octachain poly-ϵ-caproamides in anhydrous formic acid exhibit the steep rise in reduced viscosity as the polymer concentration approaches zero characteristic of polyelectrolyte solutions. The data for reduced viscosity as a function of concentration fit the equation $\eta_{sp}/c = A/(1 + Bc) + D$ where A, B and D are constants for a given polymer. The constant D may be identified with the intrinsic viscosity of the uncharged coiled polymer molecule while $A + D$ may be thought of as the intrinsic viscosity of the polyion. Graphs of log $(A + D)$ *vs.* log $\bar{M}_n$ are linear for each series of polymers, and the observed slopes are 1.41, 1.45 and 1.59, respectively, for linear, tetrachain and octachain polymers. Graphs of log $(A + D)$ *vs.* log $\bar{M}_v$ are also linear and show that at the same molecular weight branching decreases the intrinsic viscosity of the polyion, presumably by forming a more compact structure in solution.

It has been shown[3] that linear poly-ϵ-caproamides when dissolved in anhydrous formic acid ionize to produce positively charged substituted ammonium ions along the chains which cause uncoiling of the polymer molecules in dilute solution, thereby resulting in a steep rise in reduced viscosity as the polymer concentration approaches zero. While linear molecules may approach a rod-like structure due to repulsion between ions on the chain in the limit of zero concentration, tetrachain and octachain molecules[4] approach cross-shaped and eight-armed structures, respectively. Solutions containing these latter molecules therefore should exhibit lower viscosities than solutions of the linear molecules because of the restraints placed on expansion of the molecules by the central multifunctional unit. Conversely, the intrinsic viscosity of the polyion should provide a sensitive test for branching in polymer molecules.

Experimental

Polymers (see Table I) were prepared by the method described previously.[3,4] Number average molecular weights were calculated from carboxyl and amine end-group titers,[5] or alternatively, from the intrinsic viscosity in concentrated sulfuric acid.[4] In the case of the multichain polymers the proportion of linear polymer was small (see w_L, Table I). Before use, each polymer was heated at 184° and 1 mm. pressure for four hours to free it of monomeric ϵ-caprolactam.

TABLE I

POLY-ϵ-CAPROAMIDES: VISCOSITIES AND MOLECULAR WEIGHTS

Polymer	$[\eta]$, H_2SO_4 30°	D	A	$(A + D)$	B	$w_L \times 10^2$	$\bar{M}_n$	$\bar{M}_v$
				Linear				
L I	0.338	0.313	0.700	1.013	9.1	0.71	4320	6900
L II	.560	.535	2.19	2.73	10.1	1.5	8490	13500
L III	.772	.760	4.18	4.94	11.5	2.3	12900	20500
L IV	1.060	1.08	7.48	8.56	12.7	5.5	19200[a]	30200
L V	1.357	1.47	11.43	12.9	13.0	7.8	26000	40600
				Tetrachain				
T II	0.421	0.404	1.27	1.67	12.0	1.04	8080	11200
T III	.495	.490	1.92	2.41	10.9	1.26	10100	14000
T IV	.722	.69	3.26	3.95	8.6	1.56	15700	21800
T V	.970	.99	6.72	7.71	10.9	3.5	23700[a]	32500
T VI	1.130	1.25	10.44	11.7	13.8	6.4	29700	40000
				Octachain				
O I	0.286	0.275	0.520	0.759	7.1	0.43	7500	9190
O II	.406	.420	1.35	1.77	7.8	.24	12500	15400
O III	.580	.60	2.58	3.18	6.8	2.0	18400	22300
O IV	.687	.74	4.27	5.01	10.3	0.54	24000	29400
O V	1.032	1.20	8.18	9.38	9.0	3.7	37000	44200
O VI	1.547	1.75	13.1	14.9	8.1	5.2	48500	57200

[a] Estimated from intrinsic viscosity.

Formic acid analyzing 100% by titration and having a freezing point of at least 8.05° was prepared by repeated distillation at reduced pressure of 97–98% by weight formic acid from concentrated sulfuric acid (5 cc. of sulfuric acid to 100 cc. of formic acid). Two successive distillations in which the fraction boiling from 33–34° at 60 mm. was re-

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[1] Presented in the "Symposium on Polyelectrolytes," Division of Polymer Chemistry at the New York Meeting of the American Chemical Society, September, 1951.

[2] Rayon Pioneering Research, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

[3] J. R. Schaefgen and C. F. Trivisonno, THIS JOURNAL, **73**, 4580 (1951).

[4] J. R. Schaefgen and P. J. Flory, *ibid.*, **70**, 2709 (1948).

[5] J. R. Schaefgen and P. J. Flory, *ibid.*, **72**, 689 (1950).

tained gave pure material. The best freezing point obtained was 8.25°.[6]

Viscosities of polymer solutions in 100% formic acid were measured by the method previously described,[3] except that the Ubbelohde viscometer used was modified by enlarging the reservoir portion thereof so that dilutions could be carried out directly in the viscometer. The reduced viscosity of solutions of each polymer was measured at a number of concentrations between zero and 1 g. of polymer per 100 cc. of solution.

Discussion

Reduced Viscosity and Concentration.—All polymers, linear or multichain, exhibited the steep increase in reduced viscosity as concentration of polymer in formic acid decreased characteristic of polyelectrolyte solutions. However, the rate of increase of reduced viscosity became less as the degree of branching increased at a fixed molecular weight (Fig. 1) as predicted.

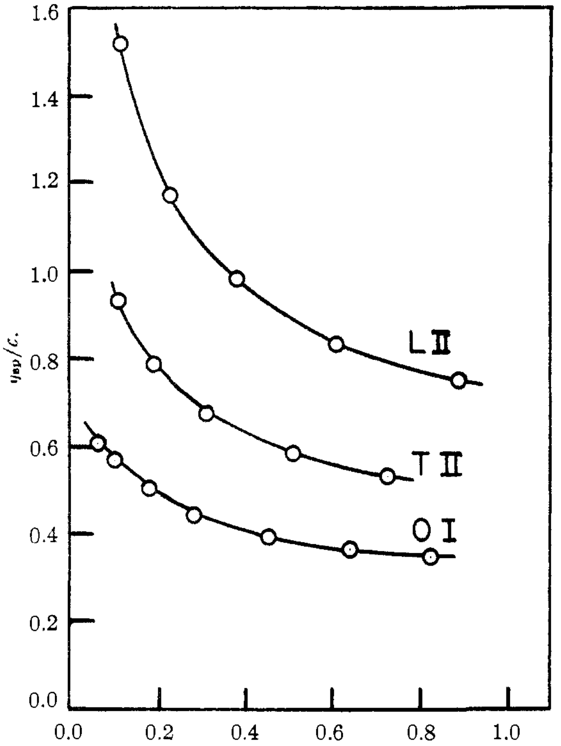

Fig. 1.—Comparison of the reduced viscosity *vs.* concentration behavior of linear and multichain polymers of comparable number average molecular weight.

In order to extrapolate the data for reduced viscosity to zero concentration to find the intrinsic viscosity of the polyion, several empirical relationships between reduced viscosity and concentration were tried. The equation of Fuoss and Strauss[7a]

$$\eta_{sp}/c = Z = A/(1 + Bc^{1/2}) \qquad (1)$$

fits the data fairly well at low concentrations but deviates at higher concentrations ($c > 0.5$ g./100 cc.). Fuoss's modified equation[7b]

$$\eta_{sp}/c = Z = A/(1 + Bc^{1/2}) + D \qquad (2)$$

gives a linear relationship between $1/(Z - D)$ and $c^{1/2}$ if suitable values of D are selected, but the line extrapolates in most cases to negative values of $1/(Z - D)$ at zero concentration, a result not in accord with the facts. The most successful representation of data for all the polymers was obtained by use of the equation

$$\eta_{sp}/c = Z = A/(1 + Bc) + D \qquad (3)$$

Graphs of $1/(Z - D)$ *vs.* c are shown in Fig. 2. Such linear graphs were prepared[8] for each polymer and yielded the values of D, $A + D$, and B shown in Table I.[9]

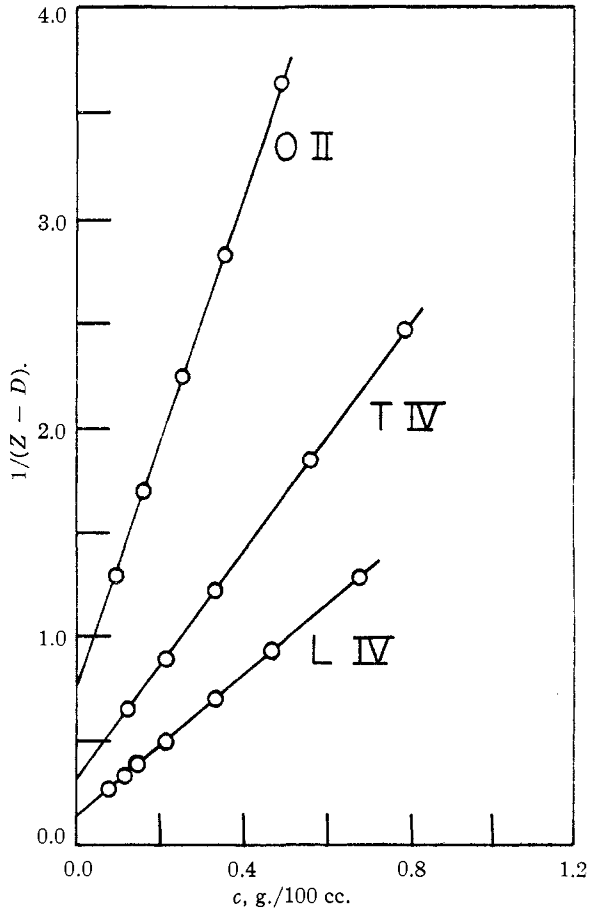

Fig. 2.—Graphs of equation 3 for linear and multichain polymers.

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[6] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 377 *ff.* quotes values of 8.30 to 8.50° for the f.p. of the pure acid.

[7a] R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948).

[7b] R. M. Fuoss and G. I. Cathers, *ibid.*, **4**, 97 (1949).

[8] An alternative method[7b] of evaluating the constants in eq. (3) is to plot $1/[(Z - D)c]$ against $1/c$, the slope and intercept being used to evaluate A and B, respectively. This method gives more weight to data at low concentrations while the reverse is true of the other method. In most cases the values in Table I are averages obtained from the two methods with more reliance being placed on the second method.

[9] A theoretical equation developed by A. Katchalsky and presented in a discussion at the Symposium on Polyelectrolytes in the Polymer Division, New York Meeting of The American Chemical Society, September, 1951, explains the discrepancy observed between eq. 2 which fits aqueous solutions of poly-4-vinyl-N-*n*-butylpyridonium bromides and eq. 3 which fits anhydrous formic acid solutions of polyamides, and gives a theoretical interpretation of the constants in the equations by considering the distances between chain ends as a function of charge density and the nature of the ionic atmosphere. Qualitatively it may be expected that the poly-4-vinyl-N-*n*-butylpyridonium bromides with a charge (or a potential charge) on every second chain atom would differ from a 33% ionized poly-ε-caproamide with a charge on every twenty-first chain atom. Solvent polymer interaction which is very strong in the case of the polyamide formic acid system also must be considered. It may well be that other systems may be investigated which will show dependence on concentration intermediate between one-half and one.

The values selected for D in order to make (3) the equation of a straight line are very nearly the same as the values of the intrinsic viscosity of the polymers in concentrated sulfuric acid, a solution in which polyelectrolyte behavior is repressed by an excess of counter ions.[3] This would seem to identify D with the contribution made to viscosity by the polymer itself and A with the augmentation of viscosity produced by uncoiling of polymer chains due to repulsion between unneutralized (in the sense that counter ions "neutralize" the charge on the polyions and decrease reduced viscosity) charges along the chains. The value of B, which is assumed to be a measure of the electrostatic forces between the polyion and its counter ions, shows the expected trend toward higher values as molecular weight increases *only* in the linear series.

Intrinsic Viscosity and Molecular Weight.—The intrinsic viscosity of the polyions $(A + D)$ is plotted as a function of number average molecular weight in Fig. 3 for each series of polymers. The slope of the lines gives the value of a in the equation

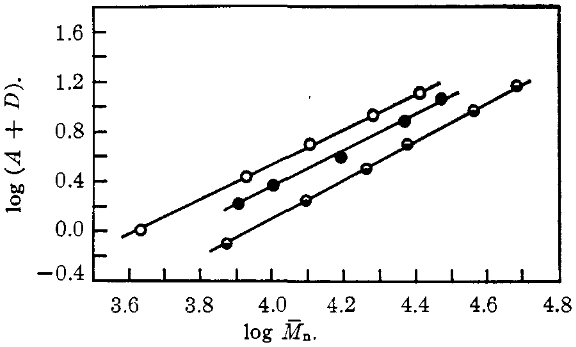

Fig. 3.—The intrinsic viscosity of the polyions as a function of the number average molecular weight: ○, linear polymers, slope = 1.41; ●, tetrachain polymers, slope = 1.45; ⊖, octachain polymers, slope = 1.59.

$$[\eta] = k\bar{M}_n^a \qquad (4)$$

The values obtained for a are intermediate between the value two,[10] that calculated for stiff rods in solution, and the values 0.6 to 0.8 obtained for polyamides in *m*-cresol[3] or concentrated sulfuric acid solution,[4] and indicates a considerable uncoiling of the polymer chains due to the presence of charges along them. The actual values of a are such that although the intrinsic viscosity is *less* numerically at a given number average molecular weight for multichain polymers as compared to linear polymers, the values approach each other at high molecular weights when the effect of branching[11] becomes negligibly small.

Using the values of a from Fig. 3, the ratio $\bar{M}_v/\bar{M}_n$ for each series (including a monochain series using $a = 1.41$) was computed, $\bar{M}_v$ being the viscosity average molecular weight. The equation used[4] is of the form

$$\bar{M}_v/\bar{M}_n = \frac{C}{b}\left[\frac{1}{b!}(a+b)(a+b-1)\cdots(a+1)\Gamma(a+1)\right]^{1/a} \qquad (5)$$

where b is the branching factor and $C \cong 1$ for reactions that are nearly complete.

Monochain	$b = 1$	$\bar{M}_v/\bar{M}_n = 2.19$
Dichain	$b = 2$	1.60
Tetrachain	$b = 4$	1.40
Octachain	$b = 8$	1.23

The viscosity average molecular weight of each polymer was calculated using the equation

$$\bar{M}_v = w_L\bar{M}_{n,L}(\bar{M}_v/\bar{M}_n)_L + (1 - w_L)\,\bar{M}_{n,Q}(\bar{M}_v/\bar{M}_n)_Q \quad (6)$$

where $\bar{M}_{n,L}$ (the number average molecular weight of the linear molecules) $\cong \bar{M}_n/b$; $\bar{M}_{n,Q}$ (the number average molecular weight of the branched molecules) $\cong \bar{M}_n$; and w_L is the weight fraction of linear molecules, *i.e.*, the amine titer/g. polymer divided by the carboxyl titer/g. polymer. A graph of log $(A + D)$ *vs.* log $\bar{M}_v$ is shown in Fig. 4. While the difference in viscosity between branched and linear polymers is noticeable it is not nearly as great as expected, and thus parallels the viscosity behavior (both melt and solution) of the polyamides previously found.[4] Nevertheless, it is significant that the effect of one tetrafunctional branching unit in a polymer of 20,000 number average molecular weight can be detected by determining the viscosity of the polymer solution in an ionizing solvent.

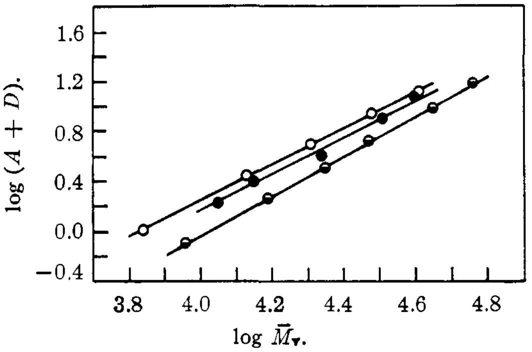

Fig. 4.—The intrinsic viscosity of the polyions as a function of the viscosity average molecular weight: ○, linear polymers; ●, tetrachain polymers; ⊖, octachain polymers.

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[10] M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939).

[11] That is, branching in multichain polymers which is confined to one branching unit, be it tetrafunctional or octafunctional, per molecule regardless of the molecular weight of the polymer molecule.