[CONTRIBUTION NO. 162 FROM THE GOODYEAR TIRE AND RUBBER CO., RESEARCH LABORATORY]

Polyelectrolyte Behavior of Polyamides. I. Viscosities of Solutions of Linear Polyamides in Formic Acid and in Sulfuric Acid[1]

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It is shown that polyamide solutions in formic acid exhibit typical polyelectrolyte behavior. Thus, solutions of poly-ε-caproamide in anhydrous formic acid show the characteristic steep rise in reduced viscosity as the polymer concentration approaches zero, and small concentrations of added counter ions such as formate ion and bromide ion reduce the dilute solution viscosity. The addition of water to such solutions likewise reduces the viscosity, but a relatively large amount is necessary to completely repress polyelectrolyte behavior. The polyelectrolyte character of these solutions is attributed to partial ionization of the amide groups along the polymer chains, the extent of which was estimated by determining the formate ion concentration using an indicator method. A consideration of amide group ionization and the known small extent of ionization of water in formic acid is sufficient to explain the observed viscosity behavior. In polyamide solutions in 100% sulfuric acid, the polyelectrolyte effect on viscosity is *to a large extent* repressed, even though most of the amide groups probably are ionized, because of the relatively large self-ionization of the solvent; the addition of even a small amount of water, a strong base in 100% sulfuric acid, is sufficient to *totally* repress the polyelectrolyte effect on viscosity.

Introduction

Instead of the expected linear relationship between reduced viscosity and concentration (or inherent viscosity and concentration), such as has been observed for dilute solutions of polyamides in *m*-cresol,[3,4] concentrated sulfuric acid,[3,5] or 90% formic acid,[6] the reduced viscosity of poly-ε-caproamide solutions in anhydrous formic acid rises steeply at low concentrations (see Fig. 1), giving a curve characteristic of the viscosity behavior of solutions of polyelectrolytes.[7] This behavior is interpreted as being due to the basic character of the polymer amide groups in formic acid solution; a considerable number of them react with solvent molecules

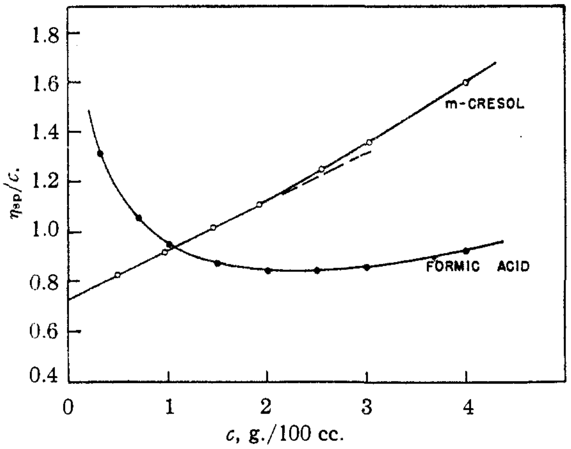

Fig. 1.—The variation of reduced viscosity with polymer concentration for solutions of a polyamide in *m*-cresol and in anhydrous formic acid.

$$-\text{CONH}- + \text{HCOOH} \rightleftarrows -\text{CONH}_2-^{+} + \text{HCOO}^- \quad (1)$$

to produce a polyelectrolyte in solution.

The fact that concentrated sulfuric acid solutions of polyamides exhibit normal (linear) reduced viscosity *vs.* concentration curves prompted the investigation of the behavior of poly-ε-caproamides in *100%* sulfuric acid solution. Presumably, most of the amide groups are ionized in this solvent; consequently, such solutions should also exhibit enhanced viscosities at low polymer concentrations.

Experimental

Poly-ε-caproamides.—Five linear poly-ε-caproamides were synthesized by treating decreasing proportions of sebacic acid with ε-caprolactam to give a series of polyamides with number average molecular weights varying from 4,320 to 26,000 (see Table I). The procedure was essentially that of Schaefgen and Flory.[8] The molecular weights were calculated from the carboxyl and amine end-group titers.

TABLE I

POLY-ε-CAPROAMIDES

Polymer	ε-Caprolactam, g.	Sebacic acid, g.	$\bar{M}_n$	$[\eta]$ H_2SO_4	$[\eta]$ *m*-cresol
A	50.0	2.262	4,320	0.338	0.387
B	40.0	0.878	8,490	.560	.616
C	40.0	.544	12,900	.772	.835
D	40.0	.360	18,200	1.012	1.049
E	40.0	.203	26,000	1.357	1.370

Intrinsic Viscosities.—The intrinsic viscosities of the polymers in concentrated sulfuric acid and in *m*-cresol solution (see Table I) were determined by the method previously described.[8] Average values found for k and β, defined by the equations for viscosity as a function of concentration

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c \qquad (2)^{9}$$

and

$$\ln \eta_r/c = [\eta] - \beta[\eta]^2 c \qquad (3)^{10}$$

were, for sulfuric acid: $k = 0.35$, $\beta = 0.15$; for *m*-cresol: $k = 0.37$, $\beta = 0.13$.

Viscosities in Formic Acid.—Anhydrous formic acid was prepared from Reagent grade 88% aqueous acid by treating it first with anhydrous copper sulfate,[11] and then with anhydrous calcium sulfate[12] ("Drierite"). Titration with standard base showed that the acid treated with and dis-

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(1) Presented before the Division of High Polymer Chemistry at the Chicago Meeting of the American Chemical Society, September, 1950.

(2) Rayon Pioneering Research, E. I. du Pont de Nemours and Co., Wilmington, Del.

(3) J. R. Schaefgen and P. J. Flory, THIS JOURNAL, **70**, 2709 (1948).

(4) H. Staudinger and co-workers also report viscosities of polyamides in *m*-cresol, *e.g.*, see H. Staudinger and H. Schnell, *Makromol. Chem.*, **1**, 44 (1947).

(5) A. Matthes, *J. prakt. Chem.*, **162**, 245 (1943).

(6) G. B. Taylor, THIS JOURNAL, **69**, 637 (1947). However, it is shown in this paper (see Discussion section) that curves in 90% formic acid deviate from linearity.

(7) R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948); R. M. Fuoss and G. I. Cathers, *ibid.*, **4**, 97 (1949); R. M. Fuoss, *ibid.*, **3**, 603 (1948).

(8) J. R. Schaefgen and P. J. Flory, THIS JOURNAL, **72**, 689 (1950).

(9) M. L. Huggins, *ibid.*, **64**, 2716 (1942).

(10) D. Mead and R. M. Fuoss, *ibid.*, **64**, 277 (1942).

(11) V. I. Lyubomilov, *J. Chem. Ind. (U. S. S. R.)*, **18**, No. 6, 34 (1941) [*C. A.*, **38**, 2314 (1944)].

(12) J. W. Stout and L. H. Fisher, *J. Chem. Phys.*, **9**, 163 (1941).

TABLE II

FORMATE ION CONCENTRATION OF FORMIC ACID SOLUTIONS

Compound	*o*-Nitroaniline $M \times 10^2$	Amide group $M \times 10^2$	Added counter ion $M \times 10^2$	B,[a] $M \times 10^4$	H_0	[HCOO⁻]	pK_i	Ionized %
Acetanilide	0.1733	7.94	....	2.44	−0.96	1.05×10^{-3}	2.80	..
ε-Caprolactam	.1138	9.76	....	3.62	− .50	3.72×10^{-2}	1.64	38.1
ε-Caprolactam	.0555	4.76	....	1.33	− .67	2.33×10^{-2}	1.65	49.0
ε-Caprolactam	.0279	2.39	....	0.500	− .83	1.51×10^{-2}	1.59	63.2
Polymer D	.1149	6.98	....	2.22	− .79	1.68×10^{-2}	..	24.1
Polymer D	.0573	3.48	....	0.742	−1.00	9.44×10^{-3}	..	27.1
Polymer D	.0278	1.69	....	.229	−1.22	5.13×10^{-3}	..	30.4
Polymer C	.1226	10.0	....	2.93	−0.67	2.33×10^{-2}	..	23.3
Polymer C	.1187	9.89	1.32[b]	2.93	− .65	2.47×10^{-2}	..	25.0
Polymer C	.0607	4.95	..	0.973	− .89	1.27×10^{-2}	..	25.7
Polymer C	.0595	4.96	1.32[b]	.990	− .87	1.36×10^{-2}	..	27.4
Polymer C	.0607	5.05	0.675[b]	1.02	− .86	1.39×10^{-2}	..	27.5
Polymer C	.0305	2.54	1.32[b]	0.345	−1.06	8.02×10^{-3}	..	31.6
Polymer C	.0286	2.38	0.318[b]	.316	−1.08	7.59×10^{-3}	..	31.9
Polymer C	.1113	8.48	1.55[c]	3.04	−0.59	2.88×10^{-2}	..	15.7
Polymer C	.0535	4.07	0.745[c]	0.942	− .84	1.47×10^{-2}	..	18.3
Polymer C	.0258	1.97	.360[c]	.282	−1.08	7.59×10^{-3}	..	20.2

[a] B = concentration of un-ionized *o*-nitroaniline. [b] Potassium bromide. [c] Butylammonium formate.

tilled from copper sulfate contained 97–98% formic acid by weight, and that the final product obtained by distillation at reduced pressure (50 mm.) from calcium sulfate contained 99.6% formic acid by weight. Aqueous formic acid solutions containing 4.9, 10.3 and 15.1% water by weight were prepared by addition of water to 98% formic acid or to distilled 88% Reagent grade acid. Solutions containing butylammonium formate were prepared by adding distilled butylamine (b.p. 76–77°) to 99.6% formic acid. Exact concentrations of formate ion were determined by titration of a sample (diluted with excess glacial acetic acid) with standard perchloric acid in glacial acetic acid using methyl violet as an indicator. Solutions containing potassium bromide were prepared by adding weighed quantities of Reagent grade potassium bromide to 99.6% formic acid.

The most concentrated polymer solution in each series of viscosity measurements was prepared by agitating the polymer, either in the form of fiber or small pieces, with formic acid (either anhydrous or containing the desired amount of water, butylammonium formate or potassium bromide) until solution had been effected. All solutions were made up by weight. Dilution of the more concentrated solutions with weighed amounts of solvent gave the more dilute solutions. The concentration of polymer (in g./100 cc.) was calculated from the composition by weight and the density. The latter was determined at 30.00° by means of a pycnometer. A density–composition curve for one polymer in a given solvent was assumed to be precise enough to fit other polymers in the same solvent.

Reduced viscosities were calculated from the concentration of polymer in g./100 cc. and solution and solvent flow times in a Ubbelohde No. 1 viscometer. Kinetic energy corrections were made, and relative densities of solution and solvent were taken into account. All viscosities were measured at 30.00 ± 0.02°.

The relative viscosity of a given anhydrous formic acid solution did not change in three days time, indicating that degradation in this solvent was negligible. However, a slow degradation in aqueous formic acid solutions was observed. The magnitude of the degradation is shown by the following data: a solution of 0.993 g. of polymer C in 100 cc. of aqueous 89.7% formic acid decreased 1.06% in relative viscosity (η_r = 1.81) on standing 24 hours (first viscosity measurement made about 24 hours after polymer was first in contact with formic acid). Since all viscosities in a given reduced viscosity *vs.* concentration curve were measured in an interval of about three hours, the shape of the curve is pretty well fixed even though the whole curve may be displaced slightly toward lower values of reduced viscosity due to degradation.

Viscosities in 100% Sulfuric Acid.—Pure 100% sulfuric acid was prepared by mixing appropriate quantities of Reagent grade 96% sulfuric acid and Reagent grade 30% fuming sulfuric acid.[13,14] Acids with freezing points of 10.20° (on sulfur trioxide side), and 10.35° (on water side) were used (literature value 10.5°[13]). Polymer solutions were prepared as before. Reduced viscosities were calculated from the concentration of polymer (in g./100 cc.), and solution and solvent flow times in a Ubbelohde No. 2 viscometer. The value of the reduced viscosity was low due to an appreciable degradation of the polymer, indicated by a continuous diminution in relative viscosity with time. This degradation was much greater for polyamide solutions in the acid slightly on the sulfur trioxide side than in the acid slightly on the water side. For example, the relative viscosity of a solution of polymer A in the former solvent decreased 1.7% in two hours (η_r = 3.10) and 8% in eighteen hours; whereas the relative viscosity (η_r = 1.90) of the same polymer in the latter solvent decreased negligibly in one hour and only 2.9% in eighteen hours. Measurements reported herein were made on solutions using the acid slightly on the water side. Even so, the results are subject to a small error because from three to eight hours elapsed from the time polymer was first in contact with acid until flow times were determined.

Measurement of Formate Ion Concentration.—Formate ion concentration in anhydrous formic acid solutions of poly-ε-caproamide and of selected monomeric amides was measured by the method of Hammett and Deyrup[15] using *o*-nitroaniline as an indicator. The latter compound was purified by recrystallization from mixtures of ethanol and water, m.p. 72.5–73.5° (uncor.). The molecular extinction at 412 mμ in 0.1 *N* sodium hydroxide solution containing 0.4% methanol by volume was determined by means of a Beckman model DU quartz spectrophotometer and checked the literature value of 4500.[16]

Solutions of the amide (either monomer or polymer), *o*-nitroaniline, and in some cases either potassium bromide or butylammonium formate, in anhydrous formic acid (see Table II) were made up by weight. Conversion to concentrations on a volume basis was made using an average density value of 1.209. The extinction at 412 mμ of each solution relative to anhydrous formic acid was determined as soon as possible after addition of the indicator, since the extinction decreased slowly with time. All solutions were prepared, and extinctions measured, at room temperature. Since Hammett and Deyrup[15] showed that solutions of un-

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(13) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **55**, 1900 (1933).

(14) M. S. Newman, H. G. Kuivila and A. B. Garrett, *ibid.*, **67**, 704 (1945).

(15) L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 4239 (1932).

(16) L. Doub and J. M. Vandenbelt, *ibid.*, **71**, 2414 (1949), list 4.5×10^3 as the molecular extinction at 412 mμ, the wave length corresponding to the maximum in the absorption band of *o*-nitroaniline in the visible region of the spectrum.

ionized (colored) *o*-nitroaniline in either formic acid or water had equal specific extinctions, it was possible to calculate the concentration of *o*-nitroaniline from the observed extinction, the cell length, and the known molecular extinction. The acidity function, H_0, of the solution was then determined by use of Hammett's equation.[17]

The logarithm of the formate ion concentration corresponding to the observed H_0 value was then read from a graph similar to that in Fig. 1, ref. 7, p. 4243, using a line drawn through the experimental points. The value of the ionization constant of acetanilide (see Table II) agrees well with the value found by Hammett and Deyrup[15] (pK_i = 2.93), showing that the method employed here is equivalent to the colorimetric method used previously.[15]

Results and Discussion

Viscosities in Formic Acid Solution. Ionization.—The relative viscosity in 99.6% formic acid of each of the five poly-ε-caproamides listed in Table I was measured at polymer concentrations varying from 0.1 to 4 g./100 cc. Graphs of reduced viscosity *vs.* concentration appear in Fig. 2. As the solutions become dilute, *i.e.*, $c < 1$ g./100 cc., the curves swing upward at an accelerating rate giving the steep rise in reduced viscosity characteristic of polyelectrolyte solutions. As the molecular weight rises, the curves at low concentrations become steeper.

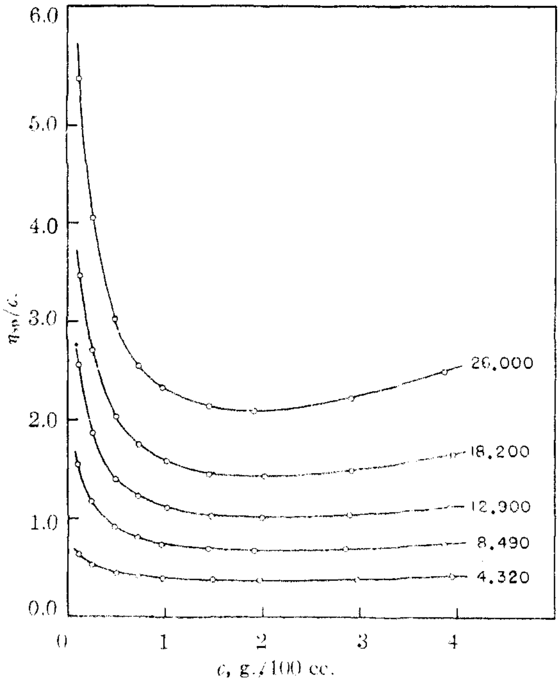

Fig. 2.—The variation of reduced viscosity with polymer concentration for solutions in anhydrous formic acid of poly-ε-caproamides of varying number average molecular weight.

The viscosity behavior of the polyamide solutions in formic acid is attributed to ionization of the polymer amide groups as shown in Equation 1. The extent of this ionization was estimated by measuring the formate ion concentration[15,18] (see Experimental section). The results (see Table II) show, first of all, that an N-substituted amide, *viz.*, ε-caprolactam, is a fairly strong base in formic acid (pK_i = 1.63), and is ionized to a large extent (curve A, Fig. 3). The ionization of polyamides in dilute formic acid solution (curve C, Fig. 3) is less complete[19] than that of ε-caprolactam, but nonetheless considerable. Ionization of the polymers increases with dilution,[18] but not nearly as rapidly as for ε-caprolactam. Small differences in molecular weight (curve C, Fig. 3) make no difference in per cent. of ionization within the precision of the measurements. One can conclude, then, that the poly-ε-caproamides are ionized to the extent of 22 to 32% in the concentration range wherein the measured reduced viscosity rises rapidly with dilution (0.1 to 1 g. per 100 cc. solution). That such partial ionization is sufficient to cause marked polyelectrolyte behavior as far as viscosity

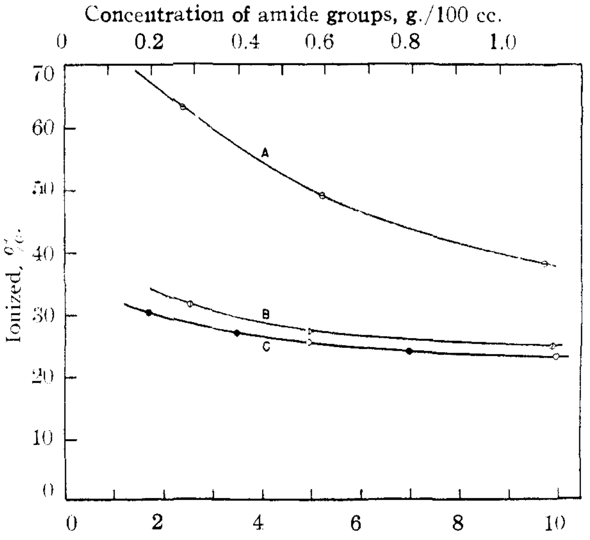

Fig. 3.—Ionization of amides in anhydrous formic acid: curve A, ε-caprolactam; curve B, polymer C, solution 0.0132 *N* in potassium bromide; curve C, ○, polymer C, ●, polymer D.

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[17] $H_0 = pK' + \log([B]/[BH^+])$, where [B] = [*o*-nitroaniline] and $pK' = -0.17$ [see L. P. Hammett and M. A. Paul, THIS JOURNAL, **56**, 827 (1934)].

[18] While this method gives a fairly accurate measure of formate ion concentration in more concentrated polymer solutions where polymer domains overlap extensively, its accuracy is questionable in dilute polymer solutions where we may distinguish between two phases, the polymer phase consisting of polymer domains and the solvent phase. The indicator base (B) will distribute itself uniformly throughout the solution, and the equilibrium constant of the reaction

$$B + HCOOH \rightleftarrows BH^+ + HCOO^-$$

will be about the same in the two phases, since the polymer phase is practically all solvent. The values of the activity coefficients of the ions BH^+ and $HCOO^-$ will be different in the two regions, however, owing to the unequal distribution of charges in the solution. The excess charge of the polycation in the polymer phase will lower the activity coefficient of the anion ($HCOO^-$), but it will raise that of the cation (BH^+) by about the same factor, while exactly the opposite situation will prevail in the solvent phase. The spectrophotometric method measures the total amount of B and hence of BH^+ by difference. The concentration of B will depend not only on total formate ion concentration but also to some extent on the relative volumes of the polymer and solvent phases and on the concentration of formate ions in each. Thus, the determination of total B in solution does not give a direct measure of the degree of ionization, but the results are doubtless approximately valid. Perhaps the observed *variations* in the apparent degree of ionization with concentration and molecular weight are not too significant especially over a wide range in either concentration or molecular weight.

[19] This is due to the increasing difficulty of ionizing successive amide groups along a given polymer chain. See F. T. Wall and E. H. deButts, Jr., *J. Chem. Phys.*, **17**, 1330 (1949).

is concerned has been previously demonstrated.[20] Since degree of ionization is rather insensitive to small changes in molecular weight, in dilute solution the volume of the larger molecules will increase relatively more than the smaller molecules thus giving the steeper rise in reduced viscosity with dilution observed for higher molecular weight polymers. At higher polymer concentrations, $c >$ 1 g./100 cc., the reduced viscosity is less in formic acid solution than in *m*-cresol, and increases only slowly with concentration (Fig. 1). It would seem that in more concentrated polyamide solutions interaction between charged polymer molecules diminishes viscosity.

Addition of Counter Ions.—The effect on reduced viscosity of adding either butylammonium formate or potassium bromide to polyamide solutions in anhydrous formic acid is illustrated by the curves in Fig. 4. Since both butylammonium formate and potassium bromide are strong electrolytes (butylamine is a strong base in formic acid), and the dielectric constant of the solvent is high (*ca.* 58.5[21]), both of these added electrolytes can be assumed to be completely ionized. The addition of formate ions represses the polyelectrolyte effect on viscosity, firstly, by reversal of the equilibrium in Equation 1, and secondly, by association[22] of formate ions with the polyions. Eventually this results in linear η_{sp}/c *vs.* c curves at higher concentrations of formate ion, or at very low polymer concentrations. The curves are similar to those observed by previous workers[23] for polyelectrolytes in solutions containing added counter ions, although the maxima, or let us say points at which the curves become linear, are not as well defined as in previous work.[23] The solutions to which potassium bromide was added decreased in viscosity but failed to yield linear η_{sp}/c *vs.* c graphs, merely giving curves of similar contour at lower values of reduced viscosity. This result was entirely unexpected in view of previous work[23] and it cannot be wholly attributed to an increased ionization or to a more rapid increase in ionization with dilution, since the increase in ionization of polyamides with addition of potassium bromide (curve B, Fig. 3) is small and nearly uniform over the concentration range studied. It would appear that a mere preponderance of counter ions (which are not common ions) is insufficient to totally repress polyelectrolyte behavior in these solutions. This would suggest that perhaps some mass action effect (added counter ions were in most cases common ions) is also partially responsible for the repression of polyelectrolyte behavior observed previously.[23] If one assumes that the formate ion concentration in solutions of polymer D to which butylamine has been added is negligibly different from similar solutions of polymer C,[24] it is seen that the concentration of added formate ion is approximately equivalent to that of the substituted ammonium ion (–CONH$_2$–$^+$) (Table II, second last line) at the point at which the η_{sp}/c *vs.* c curve for solutions to which 8 × 10^{-3} equivalents of butylamine per liter had been added becomes linear (*i.e.*, at 0.49 g. polymer per 100 cc. solution = 0.43 *M*). Such a relationship has been observed previously.[23]

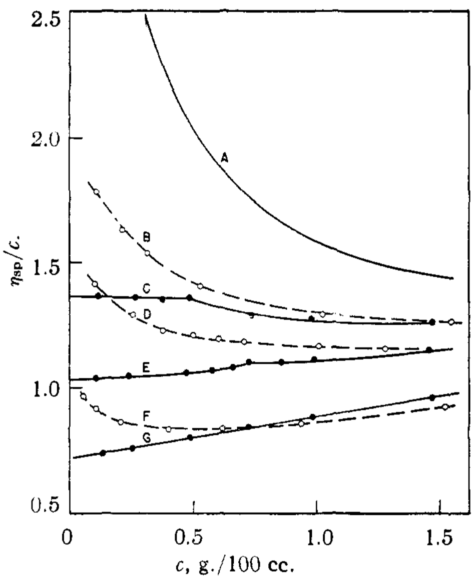

Fig. 4.—The variation of reduced viscosity with polymer concentration for solutions of polymer D in anhydrous formic acid. The effect of added counter ions: curve A, no added counter ions; curves B, D and F, solutions 8.0 × 10^{-3} *N*, 1.6 × 10^{-2} *N* and 6.65 × 10^{-2} *N* in potassium bromide, respectively; curves C, E and G, solutions 8.0 × 10^{-3} *N*, 1.6 × 10^{-2} *N* and 6.55 × 10^{-2} *N* in butylammonium formate, respectively.

Addition of Water.—The viscosity of polymers B and C as a function of concentration was measured in aqueous formic acid containing approximately 5, 10 and 15% water by weight. A slow degradation occurred in the aqueous solutions which was undoubtedly caused by hydrolysis of amide linkages. Its magnitude (see Experimental section) was not great enough to affect the conclusions reached regarding polyelectrolyte behavior, however. Each polymer gave a similar series of curves of η_{sp}/c *vs.* c; the series for polymer C is shown in Fig. 5. These series of curves are typical of polyelectrolyte solutions to which increasing amounts of counter ions have been added. Only in limited concentration ranges do the curves for 90% acid solutions approach linearity. It is not surprising, therefore, that Taylor[6] had difficulty in extrapolating graphs of reduced viscosity *vs.* concentration for polyhexamethylene adipamide ("Nylon") solutions in 90% formic acid to find intrinsic viscosities.

The effect of the addition of water on the viscosity of dilute polyamide solutions, aside from its

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[20] Neutralization of poly-4-vinylpyridine with hydrochloric acid; R. M. Fuoss and W. N. Maclay, *J. Polymer Sci.*, **6**, 305 (1951). Neutralization of polymethacrylic acid with sodium hydroxide; A. Katchalsky, O. Künzle and W. Kuhn, *ibid.*, **5**, 283 (1950).

[21] "International Critical Tables," Vol. 6, p. 83.

[22] J. R. Huizenga, P. F. Grieger and F. T. Wall, THIS JOURNAL, **72**, 2636, 4228 (1950).

[23] U. P. Strauss and R. M. Fuoss, *J. Polymer Sci.*, **3**, 602 (1948). R. M. Fuoss and G. I. Cathers, *ibid.*, **4**, 97 (1949); R. M. Fuoss and U. P. Strauss, *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949); D. T. F. Pals and J. J. Hermans, *J. Polymer Sci.*, **3**, 897 (1948).

[24] Curve C, Fig. 3, would indicate that this is true. Measurements were not made with polymer D in this instance because supplies of it were exhausted.

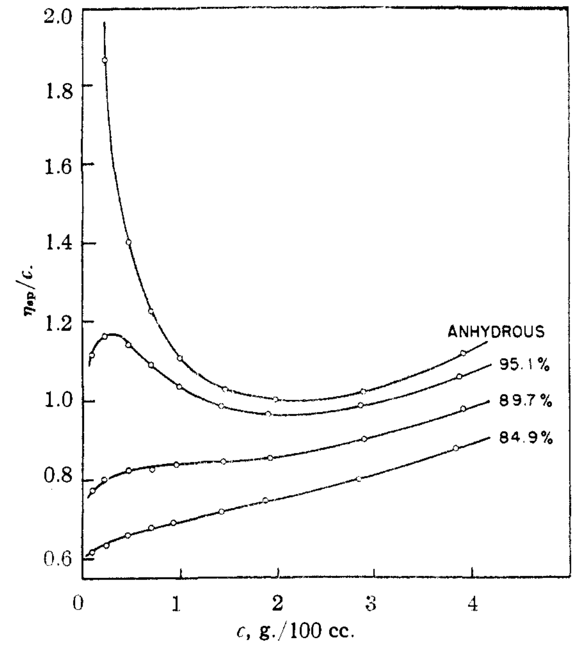

Fig. 5.—The variation of reduced viscosity with polymer concentration for solutions of polymer C in aqueous formic acid.

modification of the solvent medium,[25] arises entirely because of its reaction with the solvent to produce oxonium ions and formate ions. Since the extent of this reaction is small ($pK_{\text{water}} = 4.78$)[15] in comparison with the ionization of the polyamide itself (which represses the ionization of the water), the effect of water is negligible except when its concentration is very high, or the concentration of polymer is very small. Thus the addition of 10 to 15% water has an effect equivalent to that of adding about 10^{-2} mole per liter of butylammonium formate. The formation of a distinct maximum in 95.1% aqueous formic acid is due to the increasing ionization of water as the polymer concentration decreases, which, of course, is due to the fact that the amide group is a considerably stronger base in formic acid than is water. In butylamine solutions the case is reversed and butylamine is completely ionized throughout the concentration range of polymer studied. If one assumes that at the maximum in the reduced viscosity *vs.* concentration curve in 95.1% formic acid (Fig. 5) the concentration of added formate ion due to the ionization of water in formic acid is equal to the concentration of $-CONH_2-^+$ groups, one can calculate (degradation makes the calculation only an approximation) that the added formate ion concentration = ($-CONH_2-^+$) = 5.3×10^{-3} *N*, and that the polymer is 19% ionized. This is about the expected value since the stoichiometric concentration of amide groups is 2.8×10^{-2} *N* and the total formate ion concentration 10.6×10^{-3} *N* (see last two lines in Table II). The maximum in the curve for 95.1% formic acid solutions of polymer B also occurs at an amide group concentration of 2.8×10^{-2} *N*.

Viscosities in Sulfuric Acid Solution.—Graphs of reduced viscosity *vs.* concentration for 100% sulfuric acid solutions of polymers A and C are shown in Fig. 6. The data are subject to qualitative interpretation only because of degradation (see Experimental section). The curves resemble in appearance those given by polyelectrolyte solutions containing a small concentration of added common ion, *i.e.*, bisulfate ion. The rate of increase of reduced viscosity of polymer C at higher concentrations is greater than that observed in anhydrous formic acid solution. The combination of a decreased repulsion between polyions due to an increase in dielectric constant of the solvent and an increased repulsion due to a greater degree of ionization in sulfuric acid can hardly account for the observed difference. Graphs of reduced viscosity *vs.* concentration for these polymers (A and C) in concentrated (96%) sulfuric acid are linear, and the reduced viscosity is lower throughout the range of polymer concentration studied than it is in 100% sulfuric acid solution.

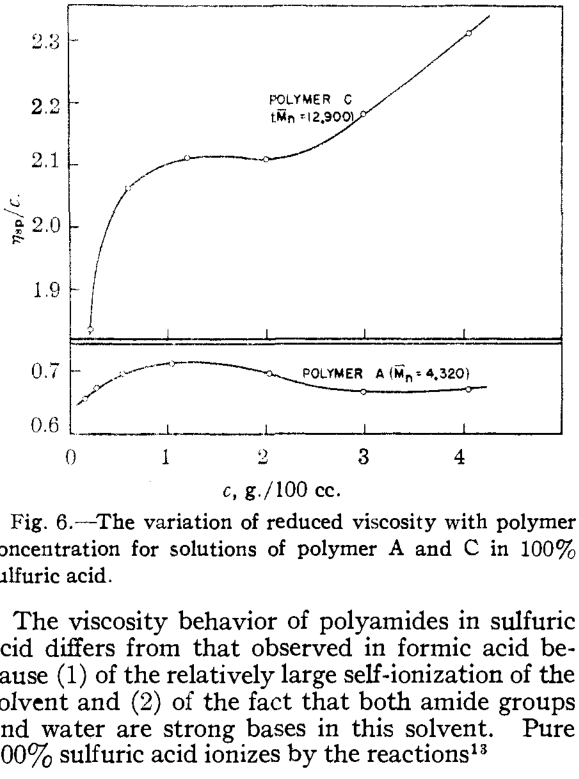

Fig. 6.—The variation of reduced viscosity with polymer concentration for solutions of polymer A and C in 100% sulfuric acid.

The viscosity behavior of polyamides in sulfuric acid differs from that observed in formic acid because (1) of the relatively large self-ionization of the solvent and (2) of the fact that both amide groups and water are strong bases in this solvent. Pure 100% sulfuric acid ionizes by the reactions[13]

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$
$$2H_2SO_4 \rightleftharpoons SO_3 + OH_3^+ + HSO_4^-$$

The sulfur trioxide produced as shown by the latter equation is undoubtedly responsible for the observed slow degradation (see Experimental section) of the polymer in solution. The concentration of bisulfate ions in 100% sulfuric acid was found to be 0.027 *N*[26] by Hammett and Deyrup.[13] Therefore, even though the ionization of a polyamide in 100% sulfuric acid may be large, the presence of a

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[25] For example, it changes the dielectric constant of the solvent. The solubility of the polymer in the new medium is also probably less. Since polyelectrolyte effect on viscosity is so large, however, the change in viscosity due to change in solvent medium is undoubtedly very minor.

[26] Compare this with the concentration of formate ion in anhydrous formic acid, *i.e.*, $(6.4 \times 10^{-7})^{1/2} = 8 \times 10^{-4}$ *N*.

considerable concentration of counter ions formed by the ionization of the solvent itself leads to η_{sp}/c *vs.* c curves (Fig. 6), which are characteristic of polyelectrolyte solutions containing small amounts of added counter ions. The addition of water to a 100% sulfuric acid solution of a polyamide results in the formation of a large concentration of counter ions since water reacts nearly completely with solvent sulfuric acid to produce oxonium ions and bisulfate ions. Even as little as 1% water by weight will yield approximately one mole per liter of bisulfate ions, which is more than sufficient to repress completely the polyelectrolyte effect. This accounts for the linear η_{sp}/c *vs.* c curves obtained for polyamide solutions in concentrated (96%) sulfuric acid. Water also represses the self-ionization of the acid to produce sulfur trioxide, and thereby reduces polymer degradation to the point where it may be disregarded (see next section).

Intrinsic Viscosities.—The intrinsic viscosity, $[\eta]$, of the poly-ϵ-caproamides in concentrated sulfuric acid and in *m*-cresol solution (see Table I) were obtained by extrapolation of linear η_{sp}/c *vs.* c (or inherent viscosity *vs.* concentration) graphs to infinite dilution (see Experimental section). The variation of log $[\eta]$ with log M_n in each solvent is shown in Fig. 7. Like graphs would be obtained using the viscosity average molecular weight since viscosity and number average molecular weight bear a simple ratio to each other.[3] The data for sulfuric acid check the previous results within the experimental error.[3] The intrinsic viscosities in *m*-cresol are somewhat higher than those observed in concentrated sulfuric acid; however, at higher molecular weights the values in the two solvents approach each other. Degradation in sulfuric acid solution is not responsible for this difference; *e.g.*, the relative viscosities of two representative polymer solutions in concentrated sulfuric acid diminished but 0.3% and 0.2%, respectively, on standing for four days.

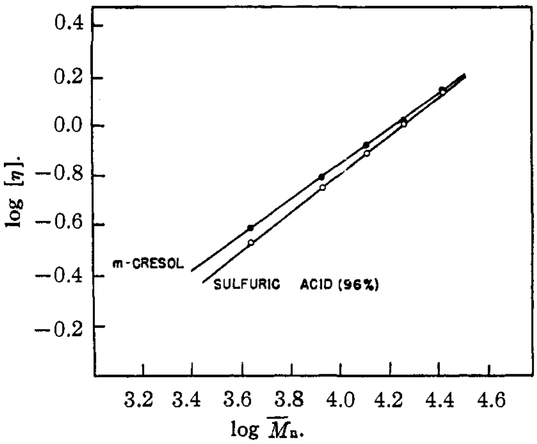

Fig. 7.—Relationships between intrinsic viscosity and number average molecular weight.

The intrinsic viscosity of the polyions in anhydrous formic acid as a function of molecular weight in comparison with tetrachain and octachain polyamides[3] is reported elsewhere.[27]

(27) J. R. Schaefgen and C. F. Trivisonno, forthcoming publication.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Preparation of the Hydrides of Zinc, Cadmium, Beryllium, Magnesium and Lithium by the Use of Lithium Aluminum Hydride[1]

BY GLENN D. BARBARAS, CLYDE DILLARD, A. E. FINHOLT, THOMAS WARTIK, K. E. WILZBACH AND H. I. SCHLESINGER

The preparation of the hydrides of zinc, cadmium, beryllium and magnesium by the interaction of the corresponding metal alkyls with lithium aluminum hydride in ethyl ether solutions is reported. The use of dimethyl aluminum hydride in place of the lithium salt in some instances is also described. The zinc and cadmium hydrides were obtained in pure condition; from beryllium and magnesium hydrides not all of the solvent could be removed. Indications of the existence of alkyl metal hydrides were observed, and zinc borohydride was prepared for the first time. The new substances are described, but detailed discussion of the reactions is deferred to a later paper.

In their paper on the preparation of lithium aluminum hydride, A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger[2] mentioned that treatment of dimethylzinc with this reagent in ether solution produces zinc hydride, but they gave no details of the procedure nor of the properties of the newly discovered hydride. Investigation of the corresponding reactions of the methyl, or occasionally the ethyl, derivatives of cadmium, of mercury, of magnesium, and of beryllium has shown that in each case, except that of mercury, there is obtained a hitherto unknown hydride of a composition in accordance with the valence of the metal (*i.e.*, MH_2).[3] Lithium hydride is obtained by a similar reaction; its inclusion in this paper is, however, not as a preparative method, but as a part of the larger investigation of the reactions of lithium aluminum hydride with metal alkyls.

The new hydrides are non-volatile white powders. Zinc and cadmium hydrides have been obtained ether-free whereas the hydrides of beryllium and of magnesium retained some of the ether used

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(1) Taken from the reports submitted to the U. S. Navy during the period 1945–1948, and from a thesis submitted by Thomas Wartik to the Department of Chemistry, University of Chicago, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. A summary of the subject matter was presented at the national meeting of the American Chemical Society at San Francisco in March, 1949.

(2) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, THIS JOURNAL, 69, 1199 (1947).

(3) Magnesium hydride has recently been prepared by E. Wiberg and R. Bauer (*Z. Naturforsch.*, 5b, 396 (1950)) by thermal decomposition of diethylmagnesium. Although their preliminary article contains no analytical data, it seems likely that their method is simpler and may give purer products than ours.