m. p. 249–250°, uncor., gas evolution. *Anal.* Calcd. for $C_{10}H_8O_2N_2$: C, 63.83; H, 4.28; N, 14.89. Found: C, 63.98; H, 4.08; N, 14.70.

One-half gram of the amino acid was heated in a test-tube just above the melting point until gas evolution ceased. The resulting product, crystallized from water, proved to be 1-aminoisoquinoline (m. p. and mixed m. p. 120–121°).

From 0.01 mole of isoquinoline-4-carboxylic acid and 0.03 mole of potassium amide in a straight reaction tube[9] there was obtained 167.7 cc. of hydrogen, standard conditions (74.8%).

The bulky precipitate formed by treating isoquinoline-4-carboxylic acid with excess potassium amide in a two-legged reaction tube was washed with liquid ammonia and analyzed,[10] after drying *in vacuo* at room temperature. *Anal.* Calcd. for $C_9H_6NO_2K$: K, 19.62. Found: K, 17.0. Calcd. for the diammonate, K, 16.8.

Aminoisoquinoline-carboxylic acid reacts with potassium amide (3 equivalents) in liquid ammonia to form a colorless salt, but no diamino derivative is formed in a one week reaction.

The Action of Sodium Alcoholates on 4-Bromoisoquinoline.—4-Bromoisoquinoline (6.24 g., 0.03 mole) was heated in a glass-lined steel tube autoclave with a solution of 1.15 g. of sodium in 50 cc. of methyl alcohol for seven hours at 235°. Alcohol was evaporated from the reaction product, and the residue steam distilled (some tar remained behind). The water insoluble oil that distilled over was converted to a picrate, m. p. 220–222°, which proved to be identical with isoquinoline picrate, m. p. 222–223.5°; yield 5.80 g. or 0.54 mole per mole of bromoisoquinoline.

Under the same conditions, bromoisoquinoline was heated with a solution of 1.95 g. of potassium in 50 cc. of *t*-butyl alcohol; yield of crude isoquinoline (separated as picrate), 0.43 mole per mole of bromoisoquinoline. Repetitions of this experiment at 190–212° and 180–190° gave 48% and 51% yields of isoquinoline, respectively.

Blau[11] reports the formation of benzene (small yield) and anisole (32.4%) by heating bromobenzene with sodium methylate under pressure at 220–230°.

Summary

1. Isoquinoline-4-carboxylic acid reacts with excess potassium amide in liquid ammonia to form hydrogen and the potassium salt of 1-aminoisoquinoline-4-carboxylic acid.

2. 4-Aminoisoquinoline is prepared in very poor yield by heating 4-bromoisoquinoline with aqueous ammonia, copper and a copper salt in an autoclave.

3. Sodium methylate and potassium *t*-butylate react with 4-bromoisoquinoline when heated under pressure to form isoquinoline in yields approximating 50% of the theoretical.

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[9] Bergstrom, THIS JOURNAL, **56**, 1748 (1934).

[10] Bergstrom, *ibid.*, **46**, 1556 (1924).

[11] Blau, *Monatsh.*, **7**, 622 (1886).

[CONTRIBUTION FROM THE BASIC SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI]

Viscosities of Polyester Solutions and the Staudinger Equation[1a]

BY PAUL J. FLORY[1b] AND PALMER B. STICKNEY[1c]

Introduction

Staudinger and co-workers[2,3] have advanced the following relationship between viscosities of dilute solutions of linear polymers and their molecular weights

$$\eta_{sp}/c = K_mM \qquad (1)$$

where the specific viscosity η_{sp} equals the relative viscosity η_r minus one, c is the concentration in moles of recurring unit per liter and M is the molecular weight. Staudinger has advocated the use of (1) for determining the molecular weights of such substances as polystyrenes, cellulose and its derivatives, polyoxymethylenes and polyethylene oxides. This method has had much appeal because of its exceptional simplicity compared with the few other known methods which are applicable to high molecular weight substances. However, the validity of the Staudinger equation has been the subject of much controversy during the past eight years.[4]

Staudinger originally presented as the basis for (1) viscosities of solutions of monomeric long chain compounds, *e. g.*, *n*-paraffins, esters, and ketones. However, very careful measurements carried out by Meyer and van der Wijk[5] have shown that the viscosities of carbon tetrachloride

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[1a] This paper was presented before the Organic Plastics Section, Paint and Varnish Division, of the American Chemical Society at the Cincinnati meeting, April, 1940.

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[2] H. Staudinger and W. Heuer, *Ber.*, **63**, 222 (1930); H. Staudinger and R. Nodza, *ibid.*, **63**, 721 (1930).

[3] H. Staudinger, "Die hochmolekularen organischen Verbindungen," Verlag von Julius Springer, Berlin, 1932.

[4] See, for example, H. Staudinger, K. H. Meyer and others, *Z. Elektrochem.*, **40**, 434, 446, 449 (1934); I. Sakurada, *Ber.*, **67B**, 1045 (1934); H. Staudinger, *Helv. Chim. Acta*, **19**, 204 (1936); K. H. Meyer and A. van der Wijk, *ibid.*, **19**, 218 (1936).

[5] K. H. Meyer and A. van der Wijk, *Helv. Chim. Acta*, **18**, 1067 (1935).

solutions of *n*-paraffins in the range C_{17} to C_{34} do not agree with (1), but may be accurately fitted to an equation of the form

$$\eta_{sp}/c = KM + I \qquad (2)$$

where I is another constant.[6] Recently Fordyce and Hibbert[7] have found that the specific viscosities of 4.4% solutions of individual species of the polyoxyethylene glycol series in the range $M = 1000$ to 8200 agree with (2), but show large deviations from (1).

Kraemer and Lansing[8] have pointed out that the form of equation (1) requires that the *weight average*[9] molecular weight M_w be used when it is applied to non-homogeneous polymers. Staudinger, and other workers also, have attempted to verify (1) by comparing η_{sp}/c values of a series of unfractionated, or only partially fractionated, polymers with their average molecular weights determined by end-group, osmotic, or cryoscopic methods, all of which yield number average values (M_n). As has been emphasized by Kraemer and Lansing,[8] the use of M_n in place of M_w has been the source of much confusion in the application of Staudinger's equation to non-homogeneous polymers.

In the present investigation viscosities of dilute solutions of decamethylene adipate polyesters in diethyl succinate and in chlorobenzene have been compared with *weight average* molecular weights determined accurately by means of the recently discovered relationship[10]

$$\log \eta = A + C'M_w^{1/2} \qquad (3)$$

where η is the viscosity of the molten polyester, and A and C' are constants evaluated empirically. The relationship between the viscosities of dilute solutions of these non-homogeneous linear polymers and M_w is found to be similar to equation (2) for homogeneous polymers.

Experimental Methods

Materials.—Polymers 1 to 9, inclusive, were prepared from equivalent amounts of pure decamethylene glycol and adipic acid by heating at 202° without catalyst. The method of preparation of the polymers and the procedure for determining their viscosities in the liquid state have been described previously.[10] The amount of glycol lost by volatilization was replaced during the polymerization so that the numbers of hydroxyl and carboxyl end-groups would be approximately equal.[11]

Preparation of higher molecular weight polymers by this method required heating for more than thirty-six hours at 202°. In spite of an oxygen-free nitrogen stream bubbled through the polymer, darkening of the polymer became excessive in some cases, and small amounts of insoluble matter were formed. For this reason, preparation of the high molecular weight polymers, 12 and 13, was carried out at 109° using 0.10 equivalent per cent. of *p*-toluenesulfonic acid catalyst, following the procedure described in a previous communication.[10]

Diethyl succinate was prepared from pure succinic acid and alcohol. It was fractionated carefully at reduced pressure, using a carborundum packed column; b. p. 112.5° (±0.2)(22.5 mm.). The center cut, which was retained for use, contained less than one free acid per 10,000 ester groups.

C. P. chlorobenzene was fractionated before use.

Viscometric Methods.—Ostwald viscometers were used for measuring the viscosities of the solutions. Absolute viscosities were calculated from the following equation, the second term of which introduces a sufficiently accurate kinetic energy correction.[12]

$$\eta = C\rho t - (\rho/8\pi l)\,(V/t) \qquad (4)$$

where C is a calibration constant, ρ is the density of the liquid, l is the length of the capillary and t is the time, measured with a stop watch, for efflux of the volume V. At concentrations below 2%, densities of the solutions were negligibly different from that of the solvent. Hence, the relative viscosities of the solutions could be calculated from the equation

$$\eta_r = (t - u/t)/(t_0 - u/t_0) \qquad (5)$$

where t and t_0 are the efflux times for solution and solvent, respectively, and $u = V/(8\pi lC)$, a constant dependent upon the dimensions of the viscometer.

Three viscometers, designated as "*A*," "*B*" and "*C*," were used. For each of these $V \cong 3.5$ cc. and $l \cong 13$ cm. Their respective capillary diameters were approximately 0.06, 0.08 and 0.16 cm. Viscometers *A* and *B* were calibrated with water at 25.0° ($t = 101.4$ and 26.0 sec., respectively). Viscometer *B* was independently calibrated at 25.0 against a glycerol–water mixture ($t = 621.0$ sec.) the viscosity of which was determined from its density, using the tables of Sheely.[13] The two calibration constants for this viscometer agreed within 0.2%. Viscometer *C* was calibrated with the glycerol–water mixture ($t = 42.7$ sec.).

Viscosities of chlorobenzene solutions were measured with viscometer *A*. Viscosities of dilute diethyl succinate solutions were measured with viscometer *B*; viscometer *C* was used at concentrations above 10%. A summary of data concerning the pure solvents is presented in Table I.

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[6] Staudinger has used equations of the same form (2) for cases in which the molecules possess one or two substituents or groups which are not a part of the recurring unit, *e. g.*, homologous straight chain esters. In such cases I was considered to be a correction for these substituents or groups.

[7] R. Fordyce and H. Hibbert, THIS JOURNAL, **61**, 1912 (1939).

[8] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

[9] The terms "number average" and "weight average" have been defined by Kraemer and Lansing, ref. 8. The weight average molecular weight equals the mean square molecular weight divided by the mean molecular weight, M_n. In general, the greater the non-homogeneity the greater the ratio M_w/M_n; for homogeneous polymers $M_w = M_n$.

[10] P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

[11] See ref. 10, p. 1059.

[12] E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y., 1922, p. 17; see also G. V. Schulz, *Z. Elektrochem.*, **43**, 479 (1937).

[13] M. L. Sheely, *Ind. Eng. Chem.*, **24**, 1060 (1932).

The last column gives the per cent. error in $\eta_r - 1$ (or in $\ln \eta_r$) when $\eta_r = 1.2$, assuming an error of 0.2 sec. in $t - t_0$.

TABLE I

Solvent	Viscometer	t, sec.	Kinetic energy correction, %	Viscosity in poises $\times 10^3$		% error in $\eta_r - 1$ at $\eta_r = 1.2$
				This paper	Lit. val.	
Chlorobenzene, 25.0°	*A*	78.8	1.7	7.61	7.56[a]	1.3
Chlorobenzene, 79.0°	*A*	51.5	3.9	4.60	4.48[a]	1.9
Diethyl succinate, 79.0°	*B*	28.2	3.8	9.58		3.5

[a] These viscosities have been interpolated from the data of J. Meyer and B. Mylius, *Z. physik. Chem.*, **95**, 366 (1920).

Measurements at 25.0° were carried out in a water-bath· A benzene vapor-bath was used for the 79.0° measurements. Since the temperature of the bath varied ±0.6° from day to day depending upon the atmospheric pressure, the measurements were corrected to 79.0° using the relationships $d \ln \eta/dT = -0.80 \times 10^{-2}$ for chlorobenzene, and $d \ln \eta/dT = -1.20 \times 10^{-2}$ for diethyl succinate, which are based on the viscosity–temperature coefficients of the solvents at 79°. (Experiments have shown that viscosity–temperature coefficients of dilute polyester solutions approximate that of the solvent.)

Kraemer and Van Natta[14] observed that the viscosities of tetrachloroethane solutions of polyhydroxydecanoic acids decreased with time, making it necessary for them to measure viscosities immediately after preparation of the solutions. We have observed no decrease in the viscosities of the chlorobenzene solutions after standing at room temperature for several days (without exposure to the atmosphere); at 79° the viscosity did not decrease during one hour. In diethyl succinate it was anticipated that the polymer might be degraded by ester interchange.[15] However, these solutions have maintained constant viscosities for several hours at 79°, when the polymer contained no *p*-toluenesulfonic acid. The viscosities of solutions of polymers 12 and 13, which contained small amounts of this catalyst, remained constant for over one hour at 79°. At 138° the viscosity decreased slowly even in the absence of catalyst.

Ester interchange consists of an acid-catalyzed reaction of hydroxyl with ester groups. The low rate of degradation must be a consequence of low hydroxyl and carboxyl (or sulfonic acid catalyst) concentrations in the diethyl succinate. To be sure, a few hydroxyl and carboxyl groups are furnished by the polymer, but reaction of these with solvent causes no significant change in M_w. Ethyl alcohol formed in this reaction should be capable of degrading the polyester, however.

Results

Polymer Molecular Weights.—The weight average molecular weights M_w (third column of Table III) have been calculated from the melt viscosities η (second column of Table III) of the polymers at 109°, using the empirical relationship[10]

$$M_w = 1207\ (1.435 + \log \eta_{109^\circ})^2 \qquad (6)$$

This equation is founded upon a comparison of viscosities with weight average molecular weights calculated from end-group determinations with the aid of size distribution theory.[10] Therefore, the M_w's used here rest, ultimately, upon end-group determinations. The absolute error resulting from the use of (6) is probably less than 3%; the relative errors resulting from inaccuracies in the viscosities in all cases are less than 1%. Polymers 9 and 13 lie outside the molecular weight range, M_w = 500 to 21,000, for which (6) has been verified experimentally. Considering the accuracy with which (6) applies within the range investigated, we do not believe a comparatively short extrapolation introduces a serious error.

Values of M_n, included for comparison in Table III, have been calculated from the equation

$$M_w = 2M_n - 142 \qquad (7)$$

which is based upon the size distribution theory previously published.[16]

Polymer 2a was prepared by heating decamethylene glycol with a 20% excess of adipic acid at 202° for nine hours. At the end of this time the viscosity had become constant, indicating that all hydroxyl groups had reacted; hence, all of the end-groups were carboxyl. Since (6) has been derived for polymers having hydroxyl and carboxyl end-groups in equal numbers, we have preferred in this case to calculate M_w from M_n determined by end-group titration.

Diethyl Succinate Solutions.—It has been recognized that the value of η_{sp}/c of a linear polymer is not independent of the solvent,[3] although frequently similar values have been observed in different solvents. Staudinger has recommended that "poor" solvents be avoided,[17] otherwise the polymer molecule may be present in a less extended form due to attractions between two parts of the polymer molecule which are stronger than those between polymer and solvent. If, on the other hand, a very good solvent is used, the possibility of distortion of the results due to solvation presents itself. If the solvent is intermediate between "good" and "poor", *i. e.*, if solute–solute attractions and

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[14] E. O. Kraemer and F. J. Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932).

[15] A study of the degradation of polyesters by alcohols will be discussed in another paper. The effects of ester interchange on mixtures of polyesters have been mentioned in ref. (10).

[16] P. J. Flory, THIS JOURNAL, **58**, 1877 (1936). Equation (7) is equivalent to equation (19) of ref. 10.

[17] H. Staudinger and J. Schneiders, *Ann.*, **541**, 151 (1939).

solvent–solute attractions are equal, there will be no solvation effects, and the polymer molecules should assume random configurations.[18]

Similar attractive forces between like and unlike molecules in diethyl succinate-polyester solutions certainly are to be expected. In support of this expectation we have found from density measurements at several concentrations that the volume change on mixing is less than 0.05%.[19,20]

TABLE II

RELATIVE VISCOSITIES OF SOLUTIONS OF POLYESTER 7 IN DIETHYL SUCCINATE

g./1000 cc. solution	η_r at 79°
2.30	1.053
4.13	1.101
7.08	1.185
9.08	1.248
15.52	1.460
24.37	1.796
50.64	3.21
98.7	7.65
195.1	38.3

Relative viscosities of solutions containing up to 20% of polymer 7 in diethyl succinate are given in Table II. Dilute solution data for all of the polymers, including this one, are shown graphically in Fig. 1. The numbers in the figure correspond to the polymer numbers given in Table III. Up to concentrations not greater than 2% and relative viscosities not greater than about 1.5 (*i. e.*, log η_r = 0.175), log η_r is linear with concentration. At higher concentrations, values of log η_r lie below the extrapolation of the straight lines in Fig. 1.

Staudinger[3] and others[8,21] have emphasized that the limiting value of η_{sp}/c for zero concentration should be used in the Staudinger equation (1). Since ln η_r approaches $\eta_r - 1$ asymptotically as η_r approaches unity, *i. e.*, as *c* approaches zero

$$[\eta_{sp}/c]_{c \to 0} \equiv [(\ln \eta_r)/c]_{c \to 0} \qquad (8)$$

Hence, (ln η_r)/*c* may be used as an alternative for η_{sp}/c in (1), as Kraemer and co-workers have pointed out.[8,14] Inasmuch as the identical expressions in (8) are also identical with $(d\eta_r/dc)_{c=0}$, the quantity they represent may be called the "relative viscosity–concentration coefficient at infinite dilution," or, for brevity, merely the "viscosity–concentration coefficient."

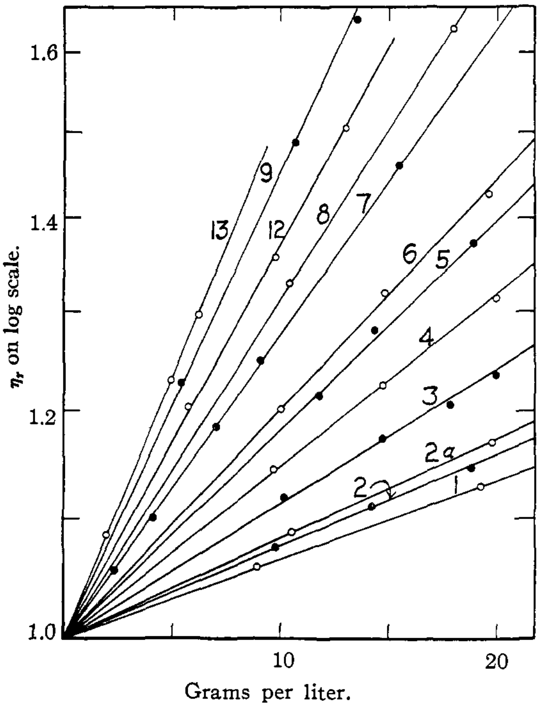

Fig. 1.—Log relative viscosity *vs.* concentration in diethyl succinate at 79.0°. The numbers identify the various polymers (see Table III). Dots and circles are used alternately for the sake of clarity only.

For the polyester solutions which we have studied, log η_r is proportional to the concentration over a considerable range, as already noted. On the other hand, η_{sp} is not linear with concentration above about η_r = 1.1.[22] Hence, it is much easier to evaluate the identical quantities in (8) from a plot of log η_r *vs.* *c* than from a plot of η_{sp} *vs.* *c*, although both methods should yield the same result. The latter method would require measurements at lower concentrations, where greater accuracy in the determination of η_r would be necessary.

Viscosity-concentration coefficients for the polyesters in diethyl succinate have been evaluated from the slopes of the straight lines in Fig. 1.

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[18] The configuration of long chain molecules in solution has been the subject of several recent investigations. See H. Mark, *Chem. Rev.*, **25**, 125 (1939); M. L. Huggins, *J. Phys. Chem.*, **43**, 447 (1939); *J. Chem. Phys.*, **8**, 186 (1940).

[19] J. H. Hildebrand, "Solubility of Non-Electrolytes," second edition, Reinhold Publishing Corp., New York, N. Y., 1936, p. 60.

[20] We hesitate to call these solutions "ideal" in view of the uncertain entropies of mixing in liquids composed of large and small molecules [see E. A. Guggenheim, *Trans. Faraday Soc.*, **33**, 151 (1937); R. H. Fowler and G. S. Rushbrooke, *ibid.*, **33**, 1272 (1937)]. Considering the low solubility of the polymer (<1 g./liter at 25° at $M_w > 20{,}000$), we are inclined to doubt that at low concentrations there are large negative deviations from Raoult's law which are due to abnormally large entropies of mixing (see in particular the results of K. H. Meyer, *Z. physik. Chem.*, **B44**, 383 (1939), on toluene solutions of rubber).

[21] G. V. Schulz, *Z. Elektrochem.*, **43**, 480 (1937).

[22] Likewise for polyoxyethylene glycols E. L. Lovell and H. Hibbert, THE JOURNAL, **62**, 2140 (1940), have shown that log η_r is linear with concentration over a greater range than is η_{sp}.

Expressing c in moles of chain atoms per liter

$$[(\ln \eta_r)/c]_0 = 2.303 \times 15.80 \times (\text{slope})$$

where 15.80 is the mean molecular weight per chain atom of the polyester. Values of $[(\ln \eta_r)/c]_0$ are given in Table III.

Chlorobenzene Solutions.—The decamethylene adipate polyesters are very soluble in chlorobenzene, *i. e.*, chlorobenzene is a "good" solvent.

The results of viscosity measurements in this solvent at 25.0° and at 79.0° are shown in Figs. 2 and 3, respectively. Except for low molecular weight polymers, log η_r is linear with concentration up to η_r = 1.4. The viscosities of the acid end-group polymer 2a are greater than the limiting slope straight line (solid line in Figs. 2 and 3). The data for polymers 2 and 3 suggest similar but smaller deviations. The significance of this behavior will be discussed in a later section of this paper.

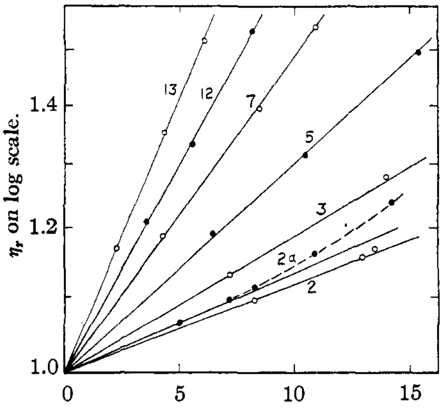

Fig. 2.—Log relative viscosity *vs.* concentration in chlorobenzene at 25.0°. Dots and circles are used alternately for the sake of clarity only.

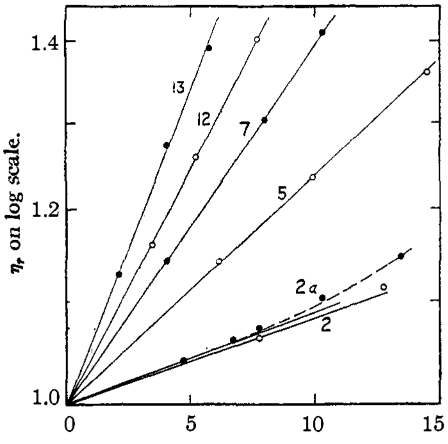

Fig. 3.—Log relative viscosity *vs.* concentration in chlorobenzene at 79.0°. Dots and circles are used alternately for the sake of clarity only.

Viscosity–concentration coefficients, in (moles of chain atoms per liter)$^{-1}$, have been evaluated from the slopes of the straight lines in Figs. 2 and 3, as was described for the diethyl succinate solutions. These, also, are given in Table III.

TABLE III

VISCOSITY–CONCENTRATION COEFFICIENTS AND MOLECULAR WEIGHTS

Polymer	$\eta_{109°}$	M_w	M_n	$[(\ln \eta_r)/c]_0$ Diethyl succinate, 79°	Chlorobenzene, 25°	Chlorobenzene, 79°
1	0.496	1543	842	0.099		
2	1.04	2560	1350	.116	0.174	0.126
2a		2885^a	1513^a	.127	.196	.138
3	4.12	5050	2600	.169	.271	
4	10.8	7360	3750	.216		
5	24.8	9650	4900	.264	.414	.338
6	42.7	11330	5740	.288		
7	164	16030	8080	.384	.630	.524
8	330	18870	9050	.431		
12	590	21400	10770	.496	.828	.687
9	1720	26340	13240	.589		
13	3800	30400	15300	.665	1.094	.912

^{a} Values based on neutral equivalent.

Discussion

Viscosity–Molecular Weight Relationships.—In Fig. 4 the values of $[(\ln \eta_r)/c]_0$ for diethyl succinate and chlorobenzene solution, respectively, are plotted against M_w. In each case the relationship is linear but does not extrapolate through the origin. That is

$$[(\ln \eta_r)/c]_0 = K_w M_w + I \qquad (9)$$

which is similar to (2). Values for the acid end-group polymer 2a, shown as solid circles in Fig. 4, are in good agreement with the results for the other polymers, which have hydroxyl and carboxyl end-groups in approximately equivalent amounts.

The equations for the straight lines are as follows. In diethyl succinate at 79°

$$[(\ln \eta_r)/c]_0 = 1.97 \times 10^{-5} M_w + 0.067$$

In chlorobenzene at 25°

$$[(\ln \eta_r)/c]_0 = 3.35 \times 10^{-5} M_w + 0.094$$

In chlorobenzene at 79°

$$[(\ln \eta_r)/c]_0 = 2.94 \times 10^{-5} M_w + 0.051$$

It is interesting to compare these results with those of other authors.

For polyhydroxydecanoic acids in tetrachloroethane, Kraemer and Van Natta[14] obtained an approximate relationship between $[(\ln \eta_r)/c]_0$

and the *number average* molecular weight, which when converted to the units used above becomes

$$[(\ln \eta_r)/c]_0 = 9.0 \times 10^{-5} M_n + 0.10$$

Since their samples had been recrystallized,[23] the size distribution in their polymers was not that normally found in an unfractionated condensation polymer.[16] M_w cannot be calculated from M_n using equation (7), therefore. In as much as the homogeneity of polyesters is not markedly improved by recrystallization, the ratio of M_w to M_n for Kraemer and Van Natta's samples probably was not much less than two, the approximate value of this ratio for the unfractionated polyester (see (7)). On this basis we conclude that $K_w \cong 5 \times 10^{-5}$.

Results of Fordyce and Hibbert[7] for carbon tetrachloride solutions of pure "single species" polyoxyethylene glycols having molecular weights in the range 800 to 8200 yield

$$[(\ln \eta_r)/c]_0 = 1.22 \times 10^{-5} M + 0.050$$

Probably the most accurate work in this field is that of Meyer and van der Wijk[5] on solutions of n-paraffin hydrocarbons in carbon tetrachloride. Their relative viscosities were sufficiently near unity that one may take their η_{sp}/c values equal to $[(\ln \eta_r)/c]_0$. They have found that the equation

$$\eta_{sp}/c = 14.55 \times 10^{-5} M - 0.01598$$

describes accurately their measurements in the range $M = 240$ to 478 (C_{17} to C_{34}).

From the above summary of viscosity–concentration coefficients of linear polymeric substances of reliably known molecular weights, two features are particularly significant. First, equation (9) appears to be applicable to a variety of polymers, including the polyesters which are extremely heterogeneous. In the second place, the constants K_w and I vary considerably with the solvent, and with the nature of the polymer. In carbon tetrachloride solution, for example, K_w for the n-paraffin hydrocarbons is about twelve times K_w for polyoxyethylene glycols. This is contrary to Staudinger's assertion that his $K_{äqu}$, which is equivalent to our K_w, is approximately the same for different polymers.

Effects of End-Groups on Viscosity.—Kraemer and Van Natta[14] concluded from their results with ω-hydroxydecanoic acid polymers in tetrachloroethane that the Staudinger equation (1) should not be accepted as quantitatively reliable. Staudinger[24] attributed the deviations which Kraemer and Van Natta had observed to the effects of association of carboxyl end-groups. Complete association of the hydroxydecanoic acid polymers (each molecule possessing one carboxyl) would double the effective molecular weight. Staudinger suggested that at low molecular weights association was practically complete, thus doubling the apparent value of K_m. He suggested further that as the molecular weight was increased, association decreased, becoming negligible above $M_n = 10{,}000$; hence, the asymptotic decrease in K_m observed by Kraemer and Van Natta.

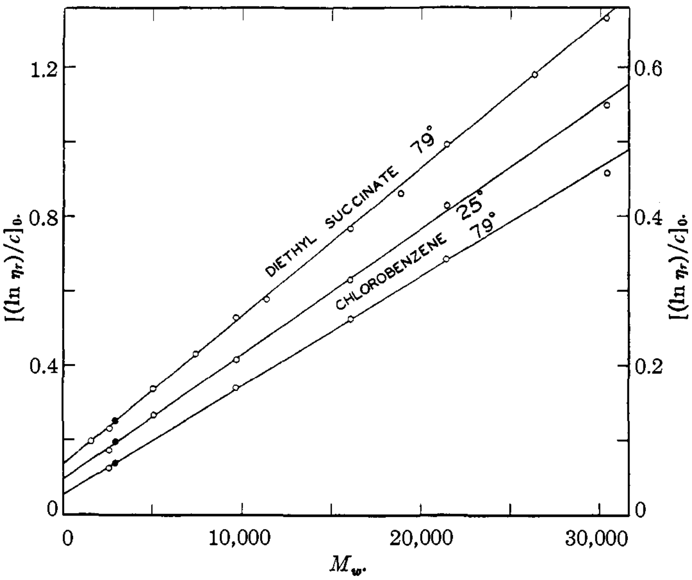

Fig. 4.—Viscosity–concentration coefficient *vs.* weight average molecular weight. Left ordinate scale for chlorobenzene solutions at 25.0° and 79.0°; right ordinate scale for diethyl succinate solutions at 79.0°. Solid circles represent the acid end-group polymer 2a.

For the purpose of subjecting Staudinger's end-group association hypothesis to direct test, the low molecular weight polymer 2a having carboxyl end-groups exclusively was included among the polyesters we have studied. If carboxyl group association were an important factor, the effective molecular weight of this polymer would be abnormally great compared with the other polymers.

Since the degree of association of end-groups must decrease with decrease in concentration,

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[23] See W. H. Carothers and F. J. Van Natta, THIS JOURNAL, 55, 4714 (1933).

[24] H. Staudinger, *Ber.*, 67B, 97 (1934).

in any case $[(\ln \eta_r)/c]_0$ will not be vitiated by the effects of association provided that measurements are extended to concentrations sufficiently low for evaluation of the true limiting value of this quantity. The viscosity–concentration coefficients for polymer 2a in diethyl succinate and in chlorobenzene are in satisfactory agreement with those for the other polymers (see Fig. 4). We conclude that our viscosity–concentration coefficients have not been vitiated by the effects of end-group association. Since Kraemer and Van Natta extended their measurements in tetrachloroethane to low concentrations, it is unlikely that end-group association modified their results appreciably; Staudinger's interpretation of their results certainly is fallacious.

At higher concentrations in chlorobenzene the departure of the relative viscosities for polymer 2a (see Figs. 2 and 3) is probably due to association of the end-groups to a small extent. A similar, but less pronounced, abnormally rapid increase in η_r with concentration has been noted in the case of polymer 2, which possessed carboxyl and hydroxyl end-groups in equal numbers. This behavior also may be due to carboxyl end-group association, which should be more evident at low molecular weights where the end-group concentration is greater. As would be expected, these effects of association are less at 79° than at 25° in chlorobenzene. In diethyl succinate no behavior which could be attributed to association has been observed with any of the polymers.[25]

Viscosity–Molecular Weight Relationship for Very High Polymers.—If it is permissible to extrapolate (9) to much greater molecular weights ($M_n > 100{,}000$) than those included in this investigation, $[(\ln \eta_r)/c]_0$ will become so much greater than I that the latter may be neglected. In this case (9) becomes

$$[(\ln \eta_r)/c]_0 = K_w M_w \qquad (1')$$

which is equivalent to the Staudinger equation (1) except that M has been replaced by M_w. The application of Staudinger's equation at very high molecular weights has been limited to nonhomogeneous substances because no homogeneous high molecular weight linear polymers have been prepared, although in some cases their homogeneity has been improved somewhat by fractionation. Number average molecular weights almost invariably have been used instead of weight averages. The extent of the agreement with (1) which has been obtained in a number of cases[26] probably is due to the fact that M_w/M_n is frequently approximately constant within a given polymer series. At any rate, there appears to be no basis at present for rejecting the modified Staudinger equation (1′) for very high molecular weight linear polymers.

Summary

Viscosities of dilute diethyl succinate and chlorobenzene solutions of twelve decamethylene adipate polyesters having accurately known weight average molecular weights M_w in the range 1500 to 30,000 have been investigated in an effort to establish the relationship between the viscosity–concentration coefficient $[(\ln \eta_r)/c]_0$ and the weight average molecular weight of nonhomogeneous linear polymers. The results do not agree with Staudinger's equation, but are accurately represented by the linear relationship

$$[(\ln \eta_r)/c]_0 = K_w M_w + I \qquad (9)$$

where K_w and I are constants. In view of the results of other investigations, this equation appears to be applicable to linear polymers in general. The implications of these results regarding the applicability of Staudinger's equation at much higher molecular weights have been discussed.

Evidence for slight association of the polymer molecules through their terminal carboxyl groups has been observed in chlorobenzene. By extending the measurements to sufficiently dilute solutions it has been possible to obtain viscosity–concentration coefficients which are not affected by association. Staudinger's conclusion that the departure of Kraemer and Van Natta's results from the Staudinger equation was due to association is erroneous.

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[25] Ebullioscopic determinations of molecular weights of ω-hydroxyundecanoic acid (monomer) in chloroform and in benzene by M. M. Davies, *Trans. Faraday Soc.*, **34**, 410 (1938), are of interest in this connection. At the same concentration, the degree of association was much smaller in the former solvent than in the latter. Association in chloroform appeared to be negligible below 0.05 molar.

[26] See E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938), and G. V. Schulz, *Angew. Chem.*, **49**, 863 (1936).