

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

Viscosities of Linear Polyesters. An Exact Relationship between Viscosity and Chain Length

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Introduction

A number of different equations have been proposed for expressing viscosity as a function of molecular constitution.¹ The fact that nearly all of these contain the molecular weight, or the chain length, explicitly indicates general recognition of the existence of a close relationship between viscosity and the size of the molecule.

One of the best known viscosity-molecular constitution relationships, proposed by Dunstan,^{1a} is

$$\log \eta = aM + b$$

where η is viscosity, M is molecular weight, a is a constant the same for all homologous series, and b is a constitutive factor characteristic of a particular series. Albert^{1e} has shown that the viscosities of homologous esters deviate from Dunstan's equation within the brief molecular weight range 296-352. Members of an homologous series covering a wide range of molecular weights ordinarily are not available. Consequently, it has not been possible to determine with certainty the exact nature of the dependence of viscosity on molecular weight of homologous substances.

Although it is an easy matter to prepare synthetic linear polymers having average molecular weights varying over a wide range, precise molecular weight determination is usually difficult. Correlation of viscosities of molten polymers with their molecular weights does not seem to have been attempted. In fact, very few measurements of viscosities of molten synthetic polymers have been reported,² although much work has been devoted to viscosities of polymers in dilute solutions.

The linear polyesters are exceptionally well suited for investigation of viscosity-molecular

weight relationships. These polymers can be prepared at any desired average molecular weight over a wide range and, when the preparation is carried out under properly defined conditions, their average molecular weights may be determined accurately by titration of the unreacted carboxyl end-group.

The present investigation has disclosed that the viscosities of molten linear polyesters can be represented with astonishing accuracy by the equation

$$\log \eta = A + C'M_w^{1/4} \quad (1)$$

where M_w is the *weight average* molecular weight (*cf. seq.*) and A and C' are constants. Or

$$\log \eta = A + CZ_w^{1/2} \quad (2)$$

where Z_w is the *weight average* chain length (*i. e.*, number of atoms in the chain skeleton) and C is a new constant. Not only does this relationship provide a simple means for determination of average molecular weight, but it also offers a new approach to the relationship between viscosity and chemical constitution.

Experimental Methods

Materials.—Since very small amounts of impurities could affect the experimental results appreciably, the purification of the materials used in this investigation will be described in detail.

Decamethylene glycol, which had been prepared by hydrogenation of diethyl sebacate, was obtained from the University of Illinois. It was stirred vigorously for two hours with boiling 5% aqueous caustic in order to saponify any unreduced ester, then washed with water until all alkalinity had been removed. The glycol was purified further by recrystallization. One batch was recrystallized three times from ethylene dichloride, the hot solution being stirred vigorously while cooling very slowly. Because of the low solubility of decamethylene glycol in ethylene dichloride at room temperature, a second batch was recrystallized twice from an ethylene dichloride-alcohol mixture containing 10% by volume of alcohol. The yield from each recrystallization was 85 to 90%. This glycol was finally recrystallized twice from pure ethylene dichloride. Each batch was dried in air, ground in a mortar to break up aggregates, and then heated at about 65° for two hours in vacuum in order to remove traces of solvent. Both samples gave "flat" cooling curves at the freezing point, 71.9°, with less than 0.05° decrease in temperature when 80% had solidified. On the basis of a freezing point constant calculated from an estimated heat

(1) (a) A. E. Dunstan, *Z. physik. Chem.*, **56**, 370 (1906); (b) E. C. Bingham and C. E. Coombs, *Phys. Rev.*, **47**, 645 (1935); (c) S. Papkov, *Z. physik. Chem.*, **A174**, 445 (1935); (d) M. Souders, *This Journal*, **60**, 154 (1938); (e) O. Albert, *Z. physik. Chem.*, **A182**, 421 (1938); (f) D. J. Lewis and A. R. Morgan, *J. Chem. Soc.*, 1341 (1939).

(2) H. I. Waterman and J. J. Leendertse, *Rec. trav. chim.*, **54**, 139 (1935), have reported the viscosities of a series of low molecular weight polymers of pentene-2 at several temperatures. E. Jenckel and K. Ueberreiter, *Z. physik. Chem.*, **A182**, 361 (1938), studied the viscosities of several polystyrenes near their softening temperatures. J. D. Ferry and G. S. Parkes, *Physics*, **6**, 356 (1935), determined the viscosity of a low molecular weight polyisobutylene at various temperatures.

of fusion (7000 cal./mole), a temperature drop of 0.05° at 80% solidification corresponds to about 0.03 mole % of impurities not soluble in the solid glycol. It must be admitted, however, that some of the most likely impurities (hydroxydecanoic acid, other glycols or possibly decyl alcohol) probably would enter the glycol crystal lattice to some extent. Experimental results obtained with the two batches of glycol are identical (*cf. seq.*).

Diethylene glycol, obtained from the Eastman Kodak Company, was fractionated carefully in a carborundum packed precision column. The boiling point, 129.5 to 130.0° at 10.5 mm., was practically constant throughout the entire distillation. A center cut was retained for use.

Adipic, sebacic, and succinic acids, obtained from the Eastman Kodak Company, were purified by recrystallizing twice from water. Each of these acids melted sharply; adipic acid at 150.6°, sebacic acid at 131.5°, and succinic acid at 187°. Their neutral equivalents were: adipic, 73.1, 73.2, 73.0, calcd. 73.06; sebacic, 101.0, 101.1, 101.3, calcd. 101.12; succinic, 59.0, 59.0, calcd. 59.04.

Viscometric Methods.—The viscometers used to measure viscosities of molten polyesters were similar in design to volumetric pipets. The capacity of the bulb and the diameter of the stem, extending about 4 cm. below the bulb, depended upon the viscosity range for which the viscometer was intended. A bulb volume of 1 cc. and an internal stem diameter of about 0.8 mm. was used for the range 0.1–3 poises. The viscometer designed for 20–300 poises had a 4-cc. bulb and 4-mm. stem.

By means of a three-way stopcock, to which the upper end of the viscometer was connected with rubber tubing, the viscometer could be connected either with nitrogen at a pressure slightly above atmospheric or with a reservoir of air at a pressure from 20 to 200 mm. less than that of the atmosphere. The difference between the atmospheric pressure and the pressure in the reservoir was registered on a mercury manometer. While the viscometer stem was immersed in the molten polymer, the surface of which was at atmospheric pressure, the stopcock was turned toward the reduced pressure reservoir. The time t required for filling the viscometer bulb was measured, after which the stopcock was immediately turned toward the nitrogen supply, causing the viscometer to empty slowly. The viscosity was calculated from

$$\eta = ctP \quad (3)$$

where c is a constant and P is the pressure difference between the atmosphere and the reservoir, corrected for the effect of the mean difference in height between polymer in the viscometer and surrounding polymer.

The calibration constants c were determined by measuring the tP product for liquids of known viscosity. For this purpose mixtures of polymeric ethylene phthalate and *m*-cresol provided liquids having suitable viscosities. The rates of fall of accurately machined steel ball bearings ($1/8$ " in diameter) through columns of these liquids one inch (2.5 cm.) in diameter were measured. The absolute viscosities of the liquids were then calculated from Stokes' law, supplemented with wall corrections as prescribed by Bacon.³

Independent standardizations using glycerol-water

mixture, the viscosity of which was determined from the density using the tables published by Sheely,⁴ yielded c values about 5% lower than those determined by the absolute method described above. This discrepancy is several times the experimental error, and no explanation of its source is suggested. The c 's based on the absolute method have been used here. The viscosity measurements are believed to be accurate (relative to one another) within about $\pm 2\%$, except at viscosities above 100 poises where the error may be about twice this. The possible 5% error in absolute values of the viscosities is of no consequence in any of the results included in this paper.

Above 10 poises it is necessary that the viscometers be allowed to empty very slowly (during five minutes or more) if an accurate subsequent measurement is to be made without cleaning the viscometer. Liquid adhering to the walls of the bulb decreases the effective volume, and hence the time t required for filling the bulb. Above 50 poises it is usually necessary to clean the viscometer between each reading if an error greater than 2% cannot be tolerated.

Several of the viscosities above 100 poises were measured using for viscometers straight glass tubes having 3 to 7 mm. inner diameters. Marks were etched at two points on the tube, usually at 2 and 12 cm., respectively, above the lower end. The time t (in sec.), required for filling the tube from the lower to the upper mark at a mean pressure difference P (in mm.), was recorded. The calibration constants c to be used in equation (3) were deduced from the mean cross sectional area of the tube with the aid of the equation (4) deduced from Poiseuille's law

$$c = 106\sigma/(h_2^2 - h_1^2) \quad (4)$$

where σ is the cross sectional area in sq. cm., and h_1 and h_2 are the distances in cm. of the lower and upper marks, respectively, above the lower end of the tube. Comparison with results obtained with a viscometer of the type described previously confirmed the adequacy of this calibration method.

It should be pointed out that throughout the range investigated the viscous behavior of the polymers is Newtonian; that is, the rate of shear is proportional to the shearing stress. (The shearing stress is proportional to P divided by the length of the stem of the viscometer.) For example, a polymer having a viscosity of about 100 poises at 109° gave the same viscosity within $\pm 2\%$ over a five-fold variation of the shearing stress.

Methods of Polymerization.—Polymers were prepared by heating together precisely equivalent quantities of glycol and dibasic acid in a cylindrical Pyrex bulb sealed to the lower end of a 15-mm. vertical tube about 25 cm. long. Through a stopper in the upper end of this tube the viscometer was inserted. A gentle stream of nitrogen through the viscometer served to stir the mixture and to facilitate removal of water formed in the reaction. The effluent nitrogen and moisture passed through a 12-mm. side arm sealed to the vertical tube near its upper end. The side arm sloped upward for about 15 cm., and then led downward to a small trap for condensing moisture. Loss of a volatile reactant (glycol) was minimized by condensation in the side arm, followed by its return to the re-

(3) J. Bacon, *J. Frank. Inst.*, **221**, 251 (1936).

(4) M. L. Sheely, *Ind. Eng. Chem.*, **24**, 1060 (1932).

action mixture. Provision was made for reducing the pressure of the system by evacuation through the trap. The reaction bulb and several cm. of the vertical tube were heated by a vapor-bath (toluene, 109°; phenetole, 168°; *m*-cresol, 202°), which remained within 0.2° of constant temperature during any one experiment.

Experiments for the purpose of establishing viscosity-molecular weight relationships were carried out at 109° using as catalyst 0.10 to 0.20 equivalent % of *p*-toluenesulfonic acid (*i. e.*, from 1 to 2 mmol. of the catalyst per gram equivalent of dibasic acid). In order to assure rapid removal of water, the pressure was reduced to about 200 mm. After termination of an experiment conducted at this pressure and the above-mentioned temperature, the trap did not contain appreciable amounts of either glycol or acid.

At intervals during the course of the reaction the pressure was brought to atmospheric by introducing nitrogen simultaneously through the viscometer and through the trap. The viscosity was measured and a sample was removed immediately for analysis. The viscometer served as a pipet for removing samples. After having been weighed, samples having molecular weights below about 4000 were dissolved in chloroform; samples having higher molecular weights were dissolved in hot chloroform-chlorobenzene mixture. The solutions were cooled below 25° and titrated with 0.1 *N* alcoholic potassium hydroxide using phenolphthalein as indicator.⁵ The endpoint is very sharp in these solvents. The amounts of sample removed from the reaction bulb were sufficient to require from 4 to 10 cc. of the standard alkali. An accuracy within ± 0.01 cc. was attained easily using a clean 10-cc. buret.

This polymerization method is especially well suited for the study of viscosity-molecular weight relationships. The low temperature, 109°, minimizes possible undesirable side reactions and loss of volatile reactants, which would vitiate molecular weight determination by titration (*cf. seq.*). The acid catalyst not only accelerates the reaction, but it also changes the kinetic order from third to second,⁶ thus causing the molecular weight to increase approximately with the first power of the time. In the "uncatalyzed" third order reaction the molecular weight increases approximately with the square root of the time.

For studies of viscosity-temperature relationships, of viscosities of mixtures of polymers, and of density-temperature relationships, polymers containing catalyst obviously are not suitable because of the changes they will undergo during the course of the measurements. For such studies polymers were prepared by heating together equivalent amounts of glycol and dibasic acid at 202° without catalyst. Except that the pressure was not reduced during polymerization, the procedure described above was followed. Loss of glycol was considerable (about 1%) during the first few minutes, when much of the glycol had not

(5) Definite indication of degradation of high molecular weight polyesters containing catalyst which have been in contact with the atmosphere for a few days has been observed. Apparently, moisture absorbed from the air is capable, in the presence of catalyst, of hydrolyzing some of the ester linkages of the solid polyester. W. H. Carothers and J. A. Arvin, *THIS JOURNAL*, **51**, 2565 (1929), pointed out that polyesters absorb moisture readily. In the present investigation all samples were analyzed within two hours after removal, in order to avoid degradation prior to analysis.

(6) P. J. Flory, *ibid.*, **61**, 3334 (1939).

yet reacted at either terminal OH. Molecular weights of polymers prepared by this method have been deduced from their viscosities using the viscosity-molecular weight relationship established on the basis of experiments carried out using an acid catalyst as described above. The neutral equivalent, determined by titration with alcoholic caustic, did not agree with the molecular weight calculated from the viscosity because OH and COOH groups were not present in equal number. On the basis of the discrepancy between the neutral equivalent and the molecular weight, the deficiency of glycol was calculated (see expression (11')), and this amount was added to the polymer. After about an hour at 202°, the added glycol was completely assimilated by the polymer by means of ester interchange.

Determination of Densities.—The pycnometers used for determining densities of molten polyesters also resembled pipets. The bulb, having a capacity of about 4 cc., consisted of a section of 10-mm. glass tubing. The lower end of the bulb was sealed to a 1.5-cm. length of 5 mm. tubing which was drawn to an abrupt, thin-walled tip having an inside diameter somewhat less than 1 mm. The upper end of the bulb was sealed to a 4-cm. length of 0.5 mm. capillary tubing, which in turn was sealed to a 12-cm. length of 6-mm. tubing. A calibration mark was placed near the middle of the capillary section. The pycnometers were calibrated by weighing the water required to fill them from calibration mark to tip at 25°. The volume of the pycnometer at higher temperatures was corrected for the expansion of the Pyrex glass, using 0.96×10^{-5} per degree for its cubical expansion coefficient.⁷

After allowing sufficient time for polymer and pycnometer to reach the constant temperature of the vapor-bath, the molten polymer was drawn slowly into the pycnometer through the tip, filling it to the calibration mark. The difficulty with which viscous polymer flowed through the small capillary tubing facilitated adjustment to the mark. After permitting the pycnometer to remain briefly with its tip barely in contact with the polymer, it was removed quickly, and polymer on the outside of the tip was wiped away. Polymer in the capillary was frozen in order to prevent subsequent loss by drainage out of the tip. After careful cleaning of its exterior, the pycnometer and its contents were weighed at room temperature. The results are accurate within ± 0.0001 g./cc.

Calculations.—Let a "segment" be defined as one glycol or one dibasic acid residue as contained within a polymer molecule. The extent of reaction *p* will represent the ratio of the number of ester groups to the number of ester plus unreacted carboxyl groups. When COOH and OH are present in equal numbers, $1 - p$ is the ratio of unreacted COOH groups (or OH groups) to the total number of segments, and the number of molecules must equal the number of unreacted carboxyls. Hence

$$1 - p = \frac{\text{number of molecules}}{\text{number of segments}}$$

(7) This value is based on the linear expansion coefficient, 0.32×10^{-5} per degree, reported in the catalog of "Pyrex Laboratory Glassware" (1938). The Corning Glass Works, Corning, N. Y.

and the degree of polymerization DP , defined as the average number of segments per molecule, will be given by

$$DP = 1/(1 - p) \quad (5)$$

Values of DP were calculated from titrations of samples containing *p*-toluenesulfonic acid as follows. Let

- w = weight of sample in g.
- t = titer in moles of potassium hydroxide
- S = mean molecular weight of one segment
(S = half the molecular weight of —ORO—COR'CO—)
- N_0 = number of moles of segments in the sample
- γ = ratio of moles of *p*-toluenesulfonic acid monohydrate (mol. wt. = 190) to moles of segments
- $w = SN_0 + (1 - p)18N_0 + 190\gamma N_0$
- $t = (1 - p)N_0 + \gamma N_0$

Eliminating N_0 from these two equations and solving

$$1/(1 - p) = \frac{w - 18t}{(S + 190\gamma)t - \gamma w} \quad (6)$$

According to (5) this expression is also equal to the degree of polymerization. The average molecular weight M_n is of course $S(DP) + 18$.

The average chain length, *i. e.*, the average number of atoms in the chain skeleton, has been taken to be

$$Z_n = zDP + 1 = z/(1 - p) + 1 \quad (7)$$

where z is the mean number of chain atoms per segment. (For example, z for the decamethylene glycol-adipic acid polyester is 9.) The "1" has been included in (7) to represent the O atom of the terminal OH group.⁸

Discussion of Errors.—The predominant source of error in the results presented in this paper lies in the average molecular weight determination. The method given above assumes that no deleterious side reactions occur, that no appreciable quantities of impurities functionally capable of entering the reaction are present, and that the concentrations of unreacted OH and COOH groups are equal. In defense of the first of these assumptions, it can be pointed out that esterification is known to proceed without appreciable side reactions at moderate temperatures. The latter two assumptions depend upon the purity of the reactants and the quantities of reactants lost by volatilization (see above). The following discussion concerns the effects on the results of a deficiency of one reactant, and of certain impurities conceivably present.

(8) The interpretation of the results presented below would not require any modification if the "1" in (7) had been omitted. This equation must be regarded as a slightly arbitrary definition of Z_n .

Let $N'_0/2$ and $N''_0/2$ be the numbers of dibasic acid and of glycol segments, respectively, in the polymer. Let $r = N'_0/N''_0$. The extent of reaction p will be defined here as the ratio of ester groups to N'_0 , which equals the number of ester groups plus unreacted carboxyl groups. The total number of segments is given by

$$(N'_0 + N''_0)/2 = N'_0(1 + r)/2r$$

The total number of ends of chains, *i. e.*, the total number of unreacted functional groups, is equal to

$$2N'_0(1 - p) + N''_0 - N'_0 = 2N'_0(1 - p) + N'_0(1 - r)/r$$

Since each molecule has two ends

$$DP = \frac{\text{No. of segments}}{(\text{No. of ends})/2} = \frac{1 + r}{2r(1 - p) + (1 - r)} \quad (8)^9$$

When glycol and adipic acid segments are present in exactly equal numbers, $r = 1$, and (8) reduces to (5).

Reexamination of the derivation of (6) shows that when r is not unity, the value of $1 - p$ derived from (6) will differ negligibly from $1 - p$ as defined here. The per cent. error in $1 - p$ calculated from (6) is approximately equal to the percentage difference between the weight of the polymer sample and the weight of another sample containing the same number of dibasic acid residues and having $r = 1$.

The error ΔDP introduced by calculation of DP from (5) when $r \neq 1$ is given by equation (5) minus equation (8).

$$\Delta DP = \frac{p(1 - r)}{(1 - p)(1 - r) + 2r(1 - p)^2} \quad (9)$$

When p is near unity and $(1 - r)$ is small compared with $(1 - p)$, *i. e.*, when the excess of one segment is very small

$$\Delta DP \cong \frac{1 - r}{2(1 - p)^2} \cong (1 - r)(DP)^2/2 \quad (10)$$

When glycol is present in excess $r < 1$ and ΔDP is positive; that is, the DP calculated from (5) is too large. When acid is present in excess, $r > 1$ and the calculated DP 's are too small.

The approximate percentage error is

$$100(1 - r)DP/2 \quad (11)$$

or

$$(\% \text{ excess of one segment}) \times DP/2 \quad (11')$$

The approximate percentage errors in Z_n and in Z_w (the "weight average" chain length, *cf. seq.*),

(9) An equivalent equation has been derived by the author previously by a different method, *THIS JOURNAL*, **58**, 1877 (1936), equation (32). The above notation coincides with that introduced in the paper referred to.

since both are approximately proportional to DP over most of the range investigated, are also given by (11) or (11'). The approximate percentage error in $Z_w^{1/2}$, the abscissa in Figs. 2, 3, 4 and 5, is therefore

$$100(1-r)DP/4 = 100(1-r)Z_n/4z$$

It will be pointed out later that $Z_w \cong 2Z_n$, except at low values of Z_n . Hence, the % error in $Z_w^{1/2}$ is approximately

$$100(1-r)Z_w/8z \quad (12)$$

It follows that for a given value of $(1-r)$ the magnitude of the abscissa error in the above-mentioned figures increases with the cube of the abscissa ($Z_w^{1/2}$) value. If, for example, in the polymerization of decamethylene glycol and adipic acid 0.10% excess of one reactant were present, the magnitudes of the errors in $Z_w^{1/2}$ at $Z_w^{1/2} = 10, 20, 30$ and 40 would be, respectively, 0.014, 0.11, 0.38 and 0.89. At $Z_w^{1/2} = 29$ the error would be about equal to the diameter of one of the experimental points in Fig. 3.

A similar analysis has been applied to the effects of a monofunctional impurity such as decyl alcohol, glycol and dibasic acid being present in equivalent amounts. The same equations, (8) to (12) inclusive, may be used if r is taken as the molar ratio of glycol to glycol plus the monofunctional reactant. Similarly, if a small amount of the glycol were replaced, mole for mole, by an hydroxy acid, these same equations could be used, taking $r = (\text{moles dibasic acid})/(\text{moles dibasic acid plus hydroxy acid})$.

Results

Viscosity and Number Average Chain Length.

—The present investigation was undertaken as a result of the accidental observation that the logarithm of the viscosity η of a linear polyester is approximately a linear function of the square root of the (number) average chain length. Experimental results are shown in Fig. 1 for the polyester formed from decamethylene glycol and sebacic acid. A straight line has been drawn through the points for comparison. Similar graphs of viscosities of the decamethylene glycol-adipic acid and diethylene glycol-adipic acid polyesters showed that in these cases also $\log \eta$ is approximately a linear function of the square root of the (number) average chain length Z_n . In all three cases, however, the experimental points seem to follow curves (concave toward the abscissa) which deviate slightly from straight lines (see Fig. 1).

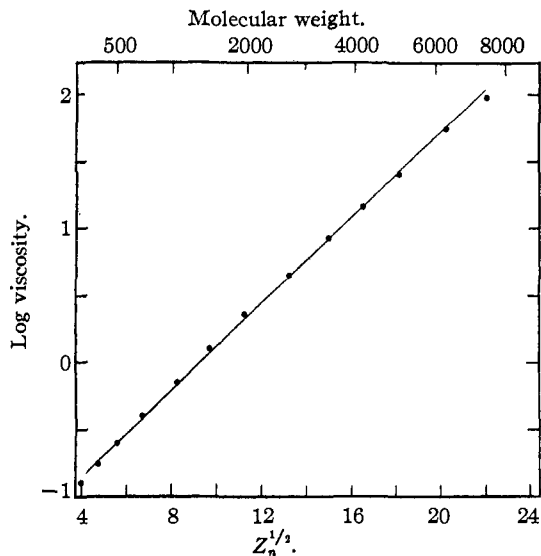


Fig. 1.—Decamethylene sebacate: log viscosity in poises at 109° vs. the square root of the number average chain length. Average molecular weights are included at the top of the figure.

Consideration of Various Averages.—When seeking a relationship between the viscosity and the average chain length of a synthetic polymer, such as a polyester, one must keep clearly in mind that these substances ordinarily are extremely inhomogeneous; some of the molecules of which they are composed are much smaller and some are much larger than the average. It would not seem improbable that the viscosity would depend upon the nature of the distribution of molecular species about the average molecular weight, as well as upon the average molecular weight itself.

Fortunately, the exact nature of the distribution of molecular species in linear polyesters is known from previous work. It has been shown⁹ that the number of molecules possessing x segments is

$$N_x = N_0(1-p)^2 p^{x-1} \quad (13)$$

where p is the extent of reaction as previously defined and N_0 is the total number of segments.¹⁰ Let Z_x ¹¹ refer to the chain length of the species of molecule possessing x segments. In accord with (7)

$$Z_x = zx + 1 \quad (14)$$

or

$$Z_x \cong zx \quad (14')$$

(10) Equation (13) rests entirely upon the postulate that reactivity of terminal functional groups does not depend on the chain length. This postulate has been confirmed by both experiment and theory.⁶

(11) Z_x must not be confused with Z_n . The latter is the number average chain length; the former is the chain length of an individual species.

The number of different average chain lengths which one could deduce for a mixture such as a polyester is unlimited. The common average molecular weight, obtained directly from end-group determinations, osmotic or cryoscopic measurements, is the *number* average.¹² The number average chain length is defined as

$$Z_n = \sum Z_x N_x / \sum N_x \quad (15)$$

These summations, as well as those to follow, are all to be taken from $x = 1$ to ∞ . Substituting (13) and (14) in this equation and evaluating the resulting summations leads to (7), which may be expressed approximately

$$Z_n \cong z/(1-p) \quad (7')$$

Another average, which is less familiar, is the *weight* average.¹² This is defined as

$$Z_w = \sum Z_x W_x / \sum W_x \quad (16)$$

where W_x is the total weight of all molecules having chain length x . To a very slight approximation W_x is proportional to $Z_x N_x$. Hence

$$Z_w = \sum Z_x^2 N_x / \sum Z_x N_x$$

Substituting from (13) and (14'), we have

$$Z_w = z \sum x^2 p^{x-1} / \sum x p^{x-1} \quad (17)$$

Upon evaluating the summations

$$Z_w = z(1+p)/(1-p) \quad (18)$$

By comparison with (7')

$$Z_n - 1/2 Z_w = z/2 \quad (19)$$

a useful formula for calculating Z_w from Z_n .

In similar fashion it can be shown that the root-mean-square chain length is

$$Z_{rms} = (1+p)^{1/2}/(1-p) \quad (20)$$

i. e., it is the geometric mean of the weight and number averages.

From (7'), (18) and (20)

$$Z_n : Z_{rms} : Z_w :: 1 : (1+p)^{1/2} : (1+p) \quad (21)$$

Except when the molecular weight is low, p is near unity. Hence this ratio is approximately $1 : \sqrt{2} : 2$. That is, for linear polyesters *these averages*, as well as many others which could be derived, *are approximately proportional to one another*. It follows, necessarily, that if $\log \eta$ is approximately linear with $Z_n^{1/2}$, it must also be approximately linear with the square root of other

(12) The terms "number average" and "weight average" were introduced by E. O. Kraemer and W. D. Lansing. *J. Phys. Chem.*, **39**, 153 (1935), in order to differentiate the two averages defined by equations (15) and (17), respectively. Wherever the term "average" has been used in this paper without specifying which average, it is the number average which is referred to.

average chain lengths. The deviation from linearity will be slightly greater than, or for some averages perhaps less than, the deviation from linearity in the $\log \eta$ vs. $Z_n^{1/2}$ relationship (Fig. 1), since the various averages are only *approximately* proportional to one another.

Viscosity and Weight Average Chain Length.—Plots of $\log \eta$ vs. $Z_w^{1/2}$ are shown for four polymers, respectively, in Figs. 2, 3, 4 and 5. The complete set of data from one of the experiments with decamethylene adipate is presented in Table I. In all cases $\log \eta$ is more nearly linear with $Z_w^{1/2}$ than with $Z_n^{1/2}$. For decamethylene sebacate and decamethylene adipate there are no deviations from the straight line which are greater than the experimental error, except perhaps below $DP = 2$. In the latter case (Fig. 3) the relationship applies throughout the average molecular weight range 300–10,500, in which the viscosity increases *three thousand-fold*.

TABLE I

DECAMETHYLENE GLYCOL-ADIPIC ACID POLYESTER
Experiment II, 109°, 0.20 equivalent %, *p*-toluenesulfonic acid catalyst.

Time, min-utes	$\frac{DP}{1-p}$	M_n	Z_n	Z_w	$Z_n^{1/2}$	$Z_w^{1/2}$	η in poises
25	2.98	442	27.86	46.7	5.28	6.83	0.230
45	5.21	759	47.91	86.8	6.92	9.32	0.437
67	8.49	1225	77.4	145.8	8.80	12.08	0.927
98	14.13	2027	128.2	247.4	11.32	15.73	2.30
126	18.45	2640	167.0	325.0	12.92	18.03	4.40
163	25.35	3620	229.1	449	15.13	21.19	10.00
190	29.34	4190	265.1	521	16.28	22.83	16.26
223	35.9	5120	324.4	640	18.01	25.29	28.0
265	44.3	6320	400.1	791	20.0	28.1	60.7
308	53.5	7620	482.6	956	22.0	30.9	130
363	63.6	9060	574	1139	23.9	33.7	253
415	73.7	10500	664	1320	25.8	36.3	480

The results from three different experiments on decamethylene adipate are shown as solid circles (Expt. II), open circles (Expt. IV) and squares (Expt. V), respectively, in Fig. 3. In Expt. II the glycol had been purified according to the first procedure described above; in Expts. IV and V glycol purified by the second, and more rigorous, procedure (see above) was used. The amount of catalyst was 0.20 equivalent % in Expts. II and IV, and 0.10 equivalent % in Expt. V. The coincidence of the results from these experiments with the same straight line provides some assurance that the glycol was adequately pure. It also demonstrates that the presence of very small amounts of *p*-toluenesulfonic acid did not affect the viscosities appreciably.

Deviations at moderate molecular weights in the case of decamethylene succinate (Fig. 4) may

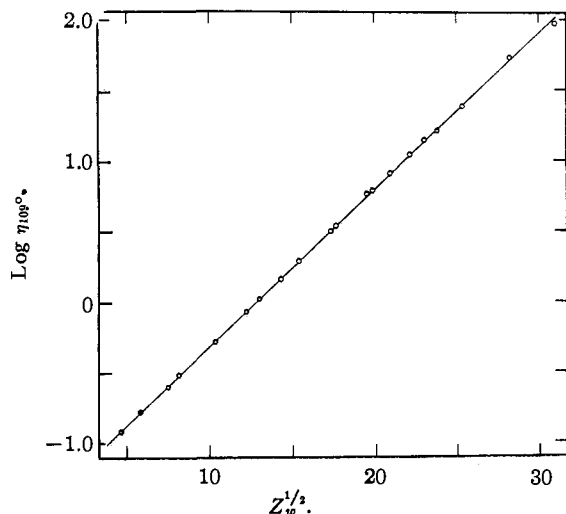


Fig. 2.—Decamethylene sebacate: log viscosity in poises at 109° vs. the square root of the *weight average* chain length.

be due to loss of succinic anhydride. The resulting deficiency in acid would make r (see equations (8) and (10)) become less than unity. Hence, the error in DP , and also in $Z_w^{1/2}$, would be positive, in agreement with the data. In an experiment in which the pressure was maintained somewhat lower than usual, the deviations were greater, and they became appreciable at an earlier stage of the polymerization.

In several experiments with decamethylene sebacate and with the adipate, at molecular weights of 8000 or greater, the $Z_w^{1/2}$ values suddenly

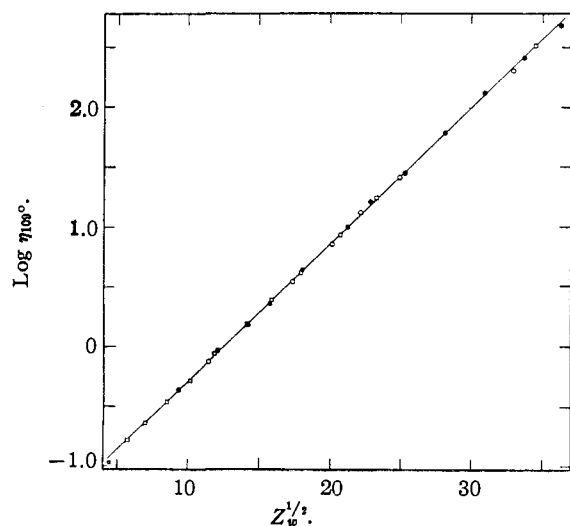


Fig. 3.—Decamethylene adipate: log viscosity in poises at 109° vs. the square root of the *weight average* chain length; \square , 0.10 equiv. % of catalyst; \circ and \bullet , represent separate experiments with 0.20 equiv. % of catalyst.

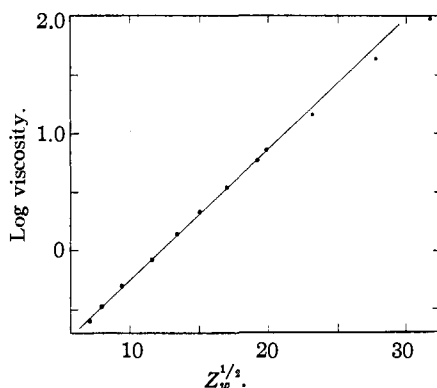


Fig. 4.—Decamethylene succinate: log viscosity in poises at 109° vs. the square root of the *weight average* chain length.

fell to the right of the straight lines in Figs. 2 and 3, respectively. This deviation, once it set in, always persisted at succeeding measurements, sometimes increasing in magnitude. In the experiments in which the deviation was pronounced, the pressure had been reduced below 100 mm. Perhaps these deviations are due, similarly, to volatilization of the less readily formed cyclic anhydrides of sebacic and adipic acid.

The experimental results for diethylene adipate (see Fig. 5, solid and half-filled circles) deviate considerably from the straight line at low chain lengths. In this particular case there is an appreciable change in density with chain length at low average molecular weights (*cf. seq.*). If in the low molecular weight region the viscosities

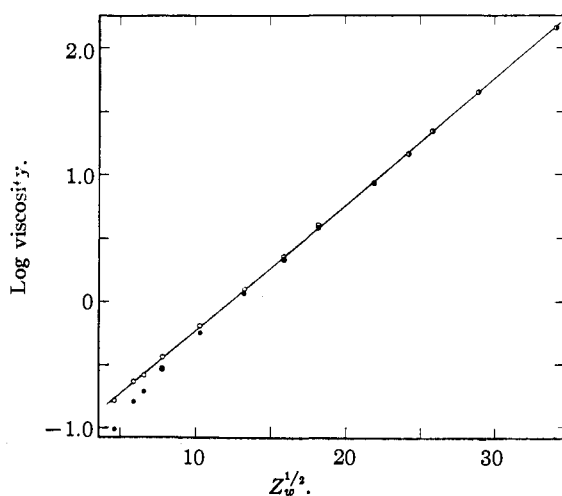


Fig. 5.—Diethylene adipate: log viscosity in poises vs. the square root of the *weight average* chain length; \bullet and \circ represent experimental data at 109°; \circ , viscosities corrected to constant density (1.1240 g./cc.); \bullet , viscosities for which this correction would be negligible.

measured at constant temperature (109°) are converted to viscosities at constant density, *i. e.*, to the limiting density reached at higher chain lengths, a satisfactory linear plot (see open circles) is obtained throughout the range. The propriety of this adjustment will be discussed later.

The equations of the straight lines drawn in Figs. 2, 3, 4 and 5 are as follows

$$\text{For decamethylene sebacate at } 109^\circ \\ \log_{10} \eta = -1.429 + 0.1108Z_w^{1/2} \quad (2.2)$$

$$\text{For decamethylene adipate at } 109^\circ \\ \log_{10} \eta = -1.435 + 0.1144Z_w^{1/2} \quad (2.3)$$

$$\text{For decamethylene succinate at } 109^\circ \\ \log_{10} \eta = -1.37 + 0.112Z_w^{1/2} \quad (2.4)$$

The numerical quantities in (2.4) are less certain for reasons already discussed.

For diethylene adipate at constant density (1.1240 g./cc.)

$$\log_{10} \eta = -1.213 + 0.0992Z_w^{1/2} \quad (2.5)$$

This equation is also satisfactory at constant temperature, 109°, at $Z_w > 100$; *i. e.*, at $M_n > 1700$.

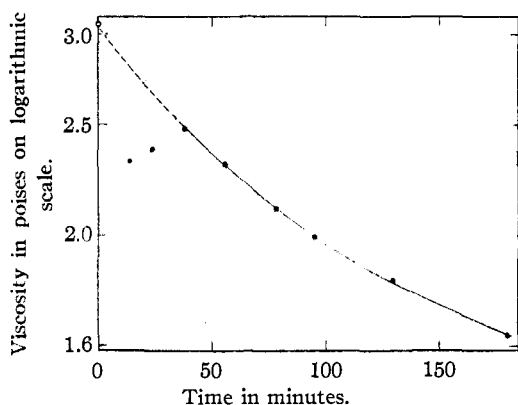


Fig. 6.—Viscosity at 109° of 19.7% mixture of series II (see Table II) as a function of time: ●, experimental points; ○, calculated initial viscosity.

The excellent linear relationships between $\log \eta$ and $Z_w^{1/2}$, obtained in several cases, do not prove that Z_w is necessarily the particular average to which $\log \eta$ should be related. Deviations when other averages are used are too small for a definite decision. Experiments with mixtures of polymers, which will be described next, have shown conclusively that the viscosity is primarily related to the *weight average* chain length.

Viscosities of Mixtures.—A low and a high molecular weight decamethylene adipate polymer were prepared at 202° without catalyst. The viscosities of various mixtures of these were meas-

ured at 109°. In spite of the stirring produced by the stream of nitrogen passing through the viscometer, dispersion of the two polymers into one another was very slow. From fifteen to thirty minutes were required before significant viscosities could be measured. Furthermore, the viscosity decreased continuously with time of heating at 109°. This decrease is believed to be due to ester interchange, which, though it does not affect Z_n , may change the distribution of various species, and in this way bring about a decrease in Z_w .¹³

The initial viscosities of the mixtures were determined by extrapolation of $\log \eta$ as a function of time to zero time, as shown in Fig. 6. The first two points in this figure are low due to incomplete mixing. Succeeding points fall on a smooth curve, which has been extrapolated to $t = 0$. Initial viscosities determined in this way for several mixtures of each of two pairs of decamethylene adipate polymers are given in the second column of Table II. A liberal estimate of the error involved in the extrapolation is included in parentheses.

The Z_w values for the individual polymers from which the mixtures were prepared (see 0 and 100% rows in Table II) were obtained from their viscosities by interpolation in Fig. 3. Their Z_n 's were then calculated from Z_w 's using equation (19). It should be noted that this method for determination of Z_n is equivalent to interpolation from the line (slightly curved) drawn through the experimental points when $\log \eta$ is plotted against $Z_n^{1/2}$.

TABLE II
VISCOSITIES OF MIXTURES OF DECAMETHYLENE ADIPATE POLYMERS

% by weight of higher molecular weight polymer	η_{109° observed	Z_n	Z_w	Calculated η 's From number average	From weight average
Series I					
(0)	0.466 (± 0.002)	50.9	92.5		
16.3	1.75 (± 0.15)	59.5	223.1	0.58	1.88
28.5	4.1 (± 0.3)	68.0	320.6	0.72	4.15
50.4	13.5 (± 0.5)	91.9	496	1.20	13.2
66.4	27.5 (± 1.0)	124	624	2.18	26.9
81.8	53 (± 2)	186	747	5.6	50.0
(100)	97 (± 2)	451	893		
Series II					
(0)	0.532 (± 0.002)	55.7	102.2		
10.1	1.45 (± 0.1)	61.2	194.4	0.61	1.45
19.7	3.03 (± 0.1)	67.6	282.0	0.71	3.06
40.0	11.7 (± 0.7)	86.5	467	1.07	10.9
(100)	164 (± 3)	512	1014		

(13) The decrease in viscosity of a mixture with time of heating is being investigated further, and will be discussed in detail in a later paper.

Z_n 's of mixtures have been obtained by number averaging the Z_n 's of the components.

$$Z_n(\text{mixture}) = \frac{Z_{n,1}N_1 + Z_{n,2}N_2}{N_1 + N_2}$$

where the subscripts 1 and 2 refer to the component polymers, and N_1 and N_2 represent numbers of molecules of each polymer, respectively. Since $Z_{n,1}N_1$ and $Z_{n,2}N_2$ are proportional to the weight fractions w_1 and w_2 , respectively

$$Z_n(\text{mixture}) = \frac{1}{w_1/Z_{n,1} + w_2/Z_{n,2}} \quad (22)$$

Z_w 's of the mixtures have been obtained by weight averaging Z_w 's of components

$$Z_w(\text{mixture}) = w_1Z_{w,1} + w_2Z_{w,2} \quad (23)$$

The viscosity "calculated" from the number average for a given mixture (column five) was obtained by taking the square root of Z_n for the mixture and interpolating to the corresponding η from the $\log \eta$ vs. $Z_n^{1/2}$ plot (not included here). Similarly, the viscosity "calculated" from the weight average (last column) was obtained from Z_w for the mixture using the $\log \eta$ vs. $Z_w^{1/2}$ plot (Fig. 3). The observed viscosities throughout the concentration range are in excellent agreement with those calculated on the weight average basis. The great disparity between the two calculated viscosities given in Table II is indicative of the sensitivity of the calculated viscosity to the method of averaging. Close agreement with a viscosity calculated on the basis of some other average could not be obtained, unless this average is always very nearly equal to the weight average. Not only is $\log \eta$ a linear function of $Z_w^{1/2}$ for a polyester having the "normal" distribution of various sized species obtained by ordinary polymerization, but $\log \eta$ is the *same linear function* of $Z_w^{1/2}$ for the wide variety of distributions obtained by mixing the low and high molecular weight polymers.

Viscosity-Temperature Relationships.—Viscosities of molten polyesters, prepared at 202° without catalyst, were measured at several temperatures from 202° to about 80°, which is a little above their melting points: 73° for decamethylene sebacate, 74° for decamethylene adipate, 69° for decamethylene succinate¹⁴; diethylene adipate polymers never could be induced to solidify even at the temperature of dry-ice. At the highest temperature, usually 202°, for which the viscosity is reported, the polymerization rate was appre-

(14) These are the melting points given by C. S. Fuller and C. J. Froesch, *THIS JOURNAL*, **61**, 2575 (1939).

ciable. The first determination was therefore made at this temperature; successive viscosities were measured at intervals of several minutes, after which the polymer was cooled quickly to the next lower temperature (167°), where the rate of polymerization was much slower. The 202° viscosity was obtained by a slight extrapolation to the time when the temperature was lowered. Two viscosity determinations were carried out quickly at 167°, and the temperature was dropped to 138°. At this temperature and below, further polymerization was negligible during a reasonable length of time. After measuring the viscosity at the lowest temperature, the viscosity at 202° was determined again. After proper correction for the viscosity increase during the additional 202° heating period, the latter 202° viscosity agreed with the first.

TABLE III

VISCOSITY-TEMPERATURE DATA			
Diethylene adipate polymer $M_n = 900$		Decamethylene adipate polymer. $M_n = 4510$	
Temp., °C.	Poises	Temp., °C.	Poises
167.0	0.168	201.5	3.25
137.6	.283	167.0	5.50
116.0	.454	137.9	9.98
99.2	.716	115.9	16.80
79.2	1.36	96.2	30.1
55.3	3.66	82.4	47.5
34.3	11.95		
19.2	38.3		
0.2	280		

Typical data are given in Table III; all results are included in Figs. 7, 8 and 9, where $\log \eta$ is plotted against the reciprocal of the absolute temperature T . The average molecular weight is included with each curve. According to the well-known equation

$$\log \eta = A' + B/T \quad (24)$$

the points in Figs. 7, 8 and 9 should follow straight lines. This is not the case except for a range of about 50° above the melting points of the decamethylene glycol polymers. The straight lines in Figs. 7 and 8 have been drawn through the points in this region. The convex downward curvature which occurs in all cases studied is characteristic of many long chain compounds¹⁵; *e. g.*, *n*-paraffin hydrocarbons, long chain esters, and alkyl halides. The slopes of the diethylene adipate curves became quite large at low temperatures; *i. e.*, the temperature coefficient of viscos-

(15) See M. Souders, *ibid.*, **50**, 1252 (1937).

ity becomes very great. This behavior is characteristic of substances supercooled to the "glassy" region below their melting points.¹⁶

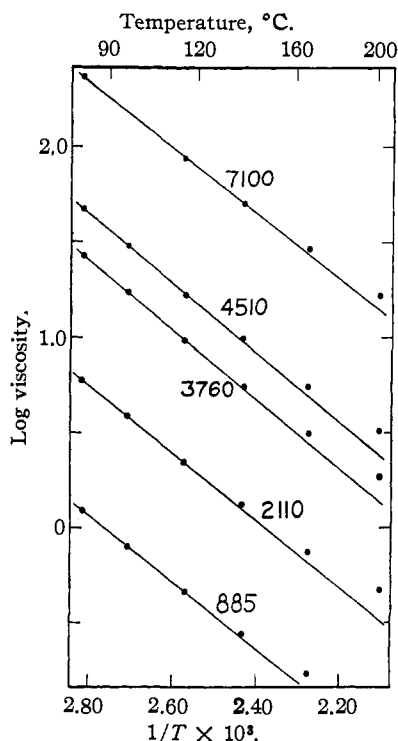


Fig. 7.—Log viscosity (poises) of decamethylene adipate polymers vs. reciprocal absolute temperature. Figures refer to average molecular weights of the five polymers.

The most important feature of these results is the slight dependence of the viscosity-temperature coefficient ($d \ln \eta / dT$) on molecular weight. The slopes of the straight lines for decamethylene adipate (Fig. 7) are the same within 3%, which is within the experimental error. The slopes of the lines in Fig. 8 for the two decamethylene sebacate polymers are in similar agreement. The deviations from the straight lines at higher temperatures are slightly greater at low molecular weights. Careful examination shows that the curves for the three diethylene adipate polymers (Fig. 9) are parallel, except for very slight increases in slope toward higher molecular weights.

To the extent that the temperature coefficient of η is independent of molecular weight, equation (2) must be applicable at any temperature at which the polymer is molten. Furthermore, C in (2) must be independent of temperature. Within a

(16) See, for example, the results of G. S. Parks, L. E. Barton, M. E. Spaght and F. W. Richardson, *Physics*, **5**, 193 (1934), on the viscosity of supercooled glucose as a function of temperature.

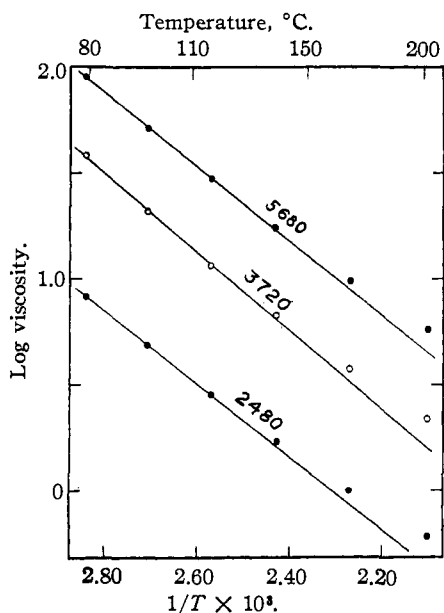


Fig. 8.—Log viscosity (poises) vs. reciprocal absolute temperature: ●, decamethylene sebacate; ○, decamethylene succinate; average molecular weights are included.

temperature interval in which equation (24) is applicable, (2) becomes

$$\log \eta = D + B/T + CZ^{1/2} \quad (25)$$

where η is expressed as a function of chain length and temperature. (D is a new constant and B and C are the same constants used in previous equations.)

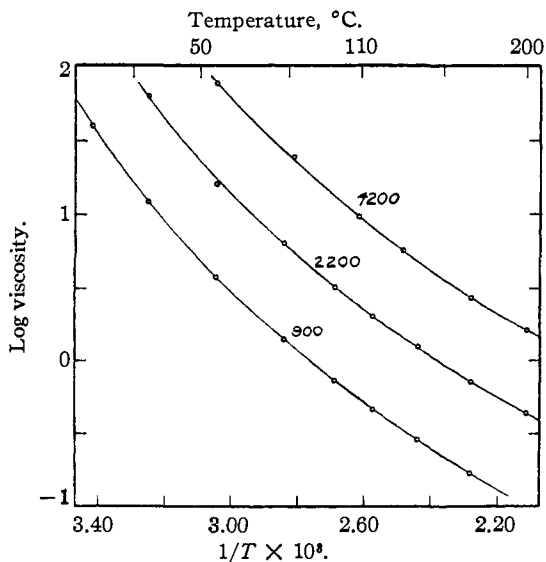


Fig. 9.—Log viscosity (poises) of diethylene adipate polymers vs. reciprocal absolute temperature; average molecular weights are included.

TABLE IV
MEAN SLOPES OF LOG η vs. $1/T$ (80 TO 120°)

Polymer	B	Activation energy for viscous flow in kcal.
Decamethylene sebacate	1760	8.05
Decamethylene adipate	1800	8.23
Decamethylene succinate	1870	8.55
Diethylene adipate	1840	8.40

Values of B for the temperature interval 80–120° are given in Table IV. Activation energies E for viscous flow, which are equal to $(2.3R)B$, are given in the third column of Table IV. This quantity has been interpreted as the energy required for the occurrence of the elementary process which is responsible for viscous flow. Eyring and Ewell¹⁷ have pointed out the analogy of this elementary process to a chemical reaction, and have developed a theory of viscous and plastic flow on this basis. According to their concepts, E consists of two parts: the energy of formation of a hole in the liquid large enough for the entire molecule, or for that part of it which is displaced in the elementary process, to move into; and of the activation energy required for the displacement to occur when a hole is available. For simple molecules E is usually one-fourth to one-third of the heat of vaporization.^{17b} Ewell^{17c} has concluded, on the basis of the magnitudes of the activation energies E for viscous flow in rubber and other polymeric substances, that the hole in these cases must be only a fraction of the size of the entire molecule. Thus, the elementary process must consist either of a displacement of a small portion of the entire molecule, or of a displacement of the entire molecule through a comparatively small distance.

The activation energies for viscous flow in polyesters (Table IV) are not large; they are only two or three times those for simple esters. On the same basis as above, therefore, the elementary process in liquid polyesters must consist of a displacement which is not commensurate with the size of the molecule. Moreover, the present investigation has shown that E does not depend upon molecular size, since the slopes in Figs. 7, 8 and 9 are independent (or very nearly so) of average molecular weight. The conclusion that the elementary processes in low and high molecular weight polyesters are identical is virtually unavoidable.¹⁸

(17) (a) H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936); (b) R. H. Ewell and H. Eyring, *ibid.*, **5**, 726 (1937); (c) R. H. Ewell, *J. App. Physics*, **9**, 252 (1938).

(18) Ewell and Eyring^{17b} have calculated the size of the molecule (probably linear) in liquid sulfur above 190° from the viscosity-temperature coefficient, *i. e.*, from E . In view of the above results with polyesters, such a calculation is probably invalid.

Densities of Polyesters.—The importance of the free volume in relation to viscosity has been emphasized by Eyring and Ewell.¹⁷ Van Wijk and Seeder¹⁹ have shown that the viscosities of a number of simple non-polar molecules depend entirely upon the molar volume V throughout wide variations of both temperature and pressure. Their equation, derived from theory, is

$$\eta = \left(\frac{V}{V-b} \right)^\varphi \quad (26)$$

where b and φ are parameters dependent upon structure alone; b is the actual volume occupied by the molecules, and $V-b$ is the free volume. For other liquids they found that φ is dependent upon temperature to a small degree; in the case of configurational liquids (*e. g.*, water and alcohols) the variation of φ with temperature accounts for a considerable portion of the viscosity-temperature coefficient. In all cases, viscosity appears to vary inversely with the free volume.

These considerations provoked inquiry into the relation of the free volume to the viscosity of long chain substances. If the average actual volume of one chain atom (*i. e.*, b per chain atom) is considered to be constant, then the free volume per cc. must decrease linearly with the density when chain length or temperature is varied. Therefore, density data should offer some insight into the behavior of the free volume.

Densities of decamethylene adipate and diethylene adipate polymers were determined from time to time during polymerization at 109° in the presence of 0.1% *p*-toluenesulfonic acid catalyst. In Fig. 10 the densities are plotted as functions of the average chain lengths Z_n calculated from viscosities. The density of decamethylene adi-

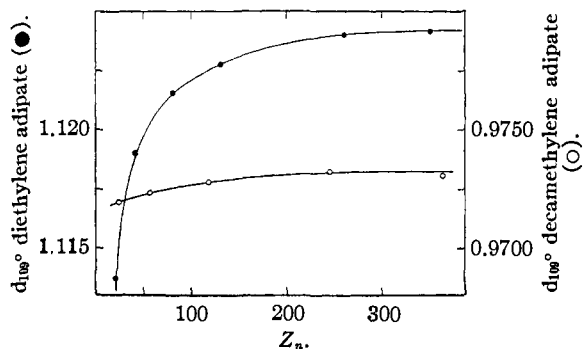


Fig. 10.—Densities (g./cc.) at 109.0° vs. number average chain length: ○, decamethylene adipate; ●, diethylene adipate.

(19) W. R. Van Wijk and W. A. Seeder, *Physica*, **4**, 1073 (1937); *ibid.*, **6**, 129 (1939).

pate, over the range investigated, increases by about 0.0013 density unit. This is no greater than the density change for a 2° temperature rise. Therefore, the free volume must be essentially independent of chain length, and the observed dependence of viscosity on chain length must be situated entirely in φ of (26). In other words, the observed empirical relationship (2) probably represents the direct dependence of viscosity on chain length, unobscured by effects of chain length on other properties of the liquid. If the free volume (per cc.) were not constant with increase in molecular weight, this simple relationship might not have been apparent.

The increase in density of diethylene adipate with chain length is much larger (see Fig. 10). It is tempting, because of the consequences, to attribute this change in density to a decrease in free volume. However, it should be pointed out first that the variation of d with Z_n can also be explained if it is assumed that the average molar volume V is given by

$$V = aZ_n + e \quad (27)$$

where a is the mean volume occupied per chain atom and e is an end-group correction. For the average molecular weight, similarly

$$M_n = \alpha Z_n + \epsilon$$

where α is the mean molecular weight per chain atom of the structural unit, and ϵ is an end-group correction equal to $18 - \alpha$ (see definition of Z_n , equation (7)). Then

$$1/d = V/M_n = g + h/Z_n \quad (28)$$

where d is density in g./cc., and

$$g = a/\alpha \quad h = e/\alpha - \epsilon/\alpha d$$

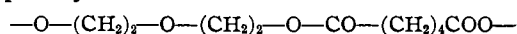
Since the change in d is small, h as well as g may be considered constant. Then, if V is properly expressed by (27), the reciprocal of the density must be linear with $1/Z_n$ according to (28).

TABLE V
DENSITIES OF DIETHYLENE ADIPATE AT 109.0°

Z_n	d , g./cc.	$1/d$	$1/d$ calculated from (27)
21.2	1.1137	0.8979	0.8982
42.1	1.1190	.8936	.8936
81.5	1.1216	.8916	.8914
131	1.1228	.8906	.8906
261	1.1240	.8897	.8898
351	1.1241	.8896	.8896

A comparison of observed reciprocal densities with those calculated from (28), using $g = 0.8891$ and $h = 0.192$, is given in Table V. The agree-

ment is probably within the experimental error. These values of g and h correspond to $a = 14.80$ cc. and $e = 4.43$ cc. ($\alpha = 16.63$ and $\epsilon = 1.38$ for diethylene adipate). The end-group correction, 4.43 cc., indicates that the volume occupied by the end-groups ($-\text{OH}$ and $-\text{COOH}$) is greater by this amount than three times the mean volume per chain atom; *i. e.*, than $3/13$ of the volume occupied by the structural unit



Perhaps this is not unreasonable.

When the specific volumes ($1/d$) of *n*-paraffin hydrocarbons from C_{10} to C_{40} are plotted against $1/Z_n$, approximately a straight line is obtained, but the slope (h) leads to a volume of about 38 cc. for the two terminal H atoms. This value, which is more than twice the volume occupied by one $-\text{CH}_2-$ group, is unreasonable. The author is of the opinion that in this case the increase in density with chain length must be due, principally, to a decrease in free volume per chain atom. The agreement with (28) he regards as fortuitous.

Perhaps the density increase with chain length in the case of diethylene adipate is due likewise to a decrease in free volume, rather than to an excess volume of the end-groups. If this is true, and if (2) should be applied at constant free volume as was suggested above, then the viscosities in Fig. 5 should be corrected for the effect of the change in free volume with chain length. If it be assumed further that the effect of temperature on viscosity is entirely due to change in free volume with temperature, this correction may be introduced by converting each viscosity to the viscosity which would have been observed at the temperature at which the density equals the limiting density at large chain lengths. (Stated briefly, we assume that φ in (26) is entirely responsible for the dependence of η on chain length, and that φ is independent of temperature.)

From the viscosity-temperature coefficient (Table IV) of diethylene adipate we obtain for temperatures in the vicinity of 109°, approximately

$$\Delta \log \eta / \Delta T = 0.0125$$

From the change of density with temperature (Table VII)

$$\Delta d / \Delta T = -0.80 \times 10^{-3}$$

Combining, we obtain for the viscosity correction necessary to convert the viscosity to constant density

$$\Delta \log \eta = -15.6 \Delta d \quad (29)$$

This simple equation is obviously valid only for small corrections.

TABLE VI

CORRECTION OF VISCOSITIES OF DIETHYLENE ADIPATE AT 109° TO VISCOSITIES AT CONSTANT DENSITY (1.1240)

Z_n	η 109° poises	$-\Delta d \times 10^4$ (from Fig. 10)	$\Delta \log \eta$ (calculated from (29))	η at $d =$ 1.1240
14.3	0.098	150	0.223	0.164
21.1	.162	106	.165	.236
25.2	.198	80	.125	.263
33.7	.295	61	.095	.365
56.3	.563	39	.061	.647
90.6	1.16	22	.034	1.25
129	2.16	13	.020	2.26
168	3.88	8	.012	4.00

Open circles in Fig. 5 represent viscosities at the constant density, 1.1240, calculated from (29) taking $-\Delta d = 1.1240 - d$. The calculations are summarized in Table VI. The open circles fall on the same straight line with the points at higher chain lengths (half-filled circles) for which correction is negligible. Viscosities at 109° fall considerably below the straight line at small chain lengths. Thus, the interpretation presented above brings the data for low molecular weight diethylene adipate polymers into agreement with (2). The previously discussed possible explanation for the change of density with chain length of diethylene adipate cannot at present be excluded, however.

In this connection it should be mentioned that at constant temperature $\log \eta$ for *n*-paraffin hydrocarbons from C₁₀ to C₃₆ is definitely not linear with the square root of the number of carbon atoms ($Z_n = Z_w$ for these pure substances). With the aid of viscosity-temperature data and density-temperature data, viscosities of several *n*-paraffins in this range have been corrected to constant density. $\log \eta$ at constant density is approximately linear with $Z^{1/2}$. The range is too brief for a definite conclusion, however. Perhaps further work will show that equation (2) is generally applicable to long chain substances at *constant free volume*.

TABLE VII

DENSITIES AND EXPANSION COEFFICIENTS OF POLYESTERS

Polyester	d at 109.0° g./cc.	$-\frac{dd}{dT} \times 10^4$	Thermal expansion coeff. = $-\frac{d \ln d}{dT}$
Decamethylene sebacate	0.9378	6.6	7.0×10^{-4}
Decamethylene adipate	.9732	6.95	7.15×10^{-4}
Diethylene adipate	1.1247	8.05	7.15×10^{-4}

* These densities are the limiting ones for large chain lengths.

The densities of polyesters prepared without catalyst at 202° were measured at several temperatures from 80 to 167°. Within the experimental error the density is a linear function of temperature in this range. These data are listed in Table VII. The densities are a little greater and the expansion coefficients are somewhat smaller than those for analogous monomeric organic compounds.

Determination of Average Molecular Weights from Viscosities.—By means of equation (1), where $C' = C/\alpha^{1/2}$, weight average molecular weights may be calculated directly from viscosities of the polyesters. If the type of distribution is known, other averages may be computed from M_w . In particular, if the distribution is the "normal" one defined by (13) (*i. e.*, the distribution obtained by all ordinary methods of preparation), then upon taking $Z_n = M_n/\alpha$ and substituting (19) in (2)

$$M_n = (\log \eta - A)^2 \alpha / 2C^2 + \alpha Z / 2 \quad (30)$$

by means of which the number average molecular weight can be calculated from the viscosity. Except for the small second term, $\log \eta$ is linear with M_n . For decamethylene adipate, for example, the viscosity being measured at 109°, equation (30) becomes

$$M_n = 603.6 (\log \eta + 1.435)^2 + 71 \quad (30.3)$$

Since C does not vary with temperature, molecular weights can be calculated from viscosities measured at other temperatures by converting A to the temperature of measurement, using the viscosity-temperature relationships presented above.

Equation (30) provides an unusually simple and precise method for determination of the average molecular weight of these polymers. It is true that its constants are deduced from viscosities of polymers the molecular weights of which have been determined by titration, which in itself is a simple molecular weight determination method. The titration method, however, is only applicable when purity of the reactants and precise stoichiometry of the reaction are assured, as the discussion of errors presented above makes clear. The viscosity method is not limited to such circumstances; it may be applied to polymers prepared from reactants which are not of exceptional purity, and which may not necessarily be present in exactly equivalent amounts.

It should be noted that since the molecular weight depends on the logarithm of η , it is not

necessary that η be determined very accurately. An error of 5% in η produces an error of only about 1.5% in M_n .

Summary

1. The viscosities (η) of molten linear polyesters having average molecular weights in the range 200 to over 10,000 have been measured. Log η has been found to be precisely a linear function of the square root of the weight average chain length throughout this range.

2. The viscosities of mixtures of two polyesters, one of them having a low and the other a high average molecular weight, agree with the same relationship, when the weight average chain length of the mixture is used therein. Thus, the relationship between viscosity and weight average chain length does not seem to depend on the type of distribution of species in the polymer.

3. The viscosity-temperature coefficient ($d \ln \eta / dT$) is independent of the average molecular weight, and its magnitude is not many times greater than that found for similar monomeric substances. It has been concluded that the elementary process responsible for viscous flow must consist of displacement of only a small section of the chain, and that this elementary process is the same for polymers of all sizes.

4. The utility of the viscosity-chain length relationship as a simple and accurate means for determination of molecular weight has been discussed.

5. Densities and thermal expansion coefficients of polyesters have been measured.

6. An analysis of the errors incident to molecular weight determination by end-group titration has been presented.

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Esters of Alginic Acid

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Since alginic acid is a polyuronide,² it would be expected to form two types of esters, *viz.*, alkyl esters and acyl esters, the former because of one carboxyl group per mannuronic residue, the latter because of one or two free hydroxyl groups per mannuronic residue. Of course, the terminal residue will have one additional hydroxyl group. If all of the carboxyl groups are free or are bound as in a salt or in an ester, there would then be two free hydroxyl groups per residue (except for the terminal ones), and dialkyl esters should be possible. However, if the carboxyl groups are bound in lactone formation, then only one hydroxyl group per residue would be free. Therefore the degree of esterification which can be attained presumably would depend, at least in part, upon the extent to which the mannuronic residues of the alginic acid molecule are in the acid or in the lactone form.

Alginic acid might be expected to undergo esterification and etherification of the hydroxyl groups, much as pectin does. The latter can be

formylated, acetylated and nitrated without difficulty.^{3,4} Methylation of pectin fragments or of pectin which has suffered partial degradation has been accomplished by heating the silver salt with methyl iodide under pressure,⁵ by dimethyl sulfate⁶ and by methyl iodide and thallium ethoxide.⁷ Pectin acid has been exhaustively methylated.⁸ Alkylation of the carboxyl group of alginic acid has been effected by heating with methanolic hydrogen chloride.^{9,10}

Acetates of alginic acid have been prepared using acetic anhydride and aqueous hydriodic acid as the acetylating agent.¹¹ A dimethyl ether has been obtained from alginic acid methylglycoside methyl ester (from partially degraded alginic acid and methanolic hydrogen chloride) by the use of methyl iodide and thallium ethoxide.¹⁰

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