

absolute alcohol and the resulting solutions quantitatively determined by comparing their ultraviolet absorption at 230 millimicrons with that found for 0.01 *M* solutions of the mixed acyls.

**Determination of Ultraviolet Absorption Curves.**—All ultraviolet absorption data shown in Table V were taken on a Beckmann Ultra Violet Spectrophotometer, Model DU. Hundredth molar solutions of each acyl derivative were made up, and these solutions diluted as became necessary by pipetting a 1-ml. aliquot and diluting to 10 ml. No attempt was made to calibrate the volumetric flasks or pipets used.

In hexane solution, due to the extreme insolubility of the acyl derivatives, it was necessary to determine the spectra of the saturated solutions of the compounds in this solvent. The concentrations of these solutions were found by pipetting a 10-ml. aliquot, evaporating to dryness under vacuum, and taking up the residue in 10 ml. of absolute alcohol. The concentration of this alcohol solution, and hence that of the hexane solution, was then determined by comparing its ultraviolet absorption intensity at 230 millimicrons with that of an alcohol solution of known concentration.

### Summary

1. In the benzylation of *N*-acetyl-*o*-aminophenol and the acetylation of *N*-benzoyl-*o*-amino-

phenol, mixtures of the two possible isomers were obtained showing that a partial rearrangement occurred in each case. These mixtures were quantitatively separated by chromatography, and the identity of the two isomers established by comparison of their ultraviolet absorption spectra with that of the corresponding derivative of *p*-aminophenol.

2. It has been shown that alcohol, pyridine, water and heat cause either pure mixed diacyl derivative to isomerize to yield an equilibrium mixture of the two isomers. In alcohol and in pyridine solutions an equilibrium mixture containing 85 and 77%, respectively, of the *N*-acetyl-*O*-benzoyl form was obtained. It was pointed out that this isomerization in alcohol probably accounts for the conflicting results reported by Raiford and by Bell.

3. In the light of the above facts it seems desirable to reexamine much of the past work in this field.

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## Synthesis of Multichain Polymers and Investigation of their Viscosities<sup>1</sup>

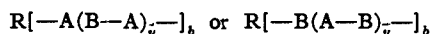
By JOHN R. SCHAEFGEN AND PAUL J. FLORY

Polymerizations in which the structural units are combined in other than strictly linear sequences generally yield gelled, insoluble products owing to the eventual formation of infinite network structures. Established exceptions are so few that thermoplasticity and solubility have sometimes been regarded as exclusive characteristics of linear polymers. On the other hand, non-linear structures have been postulated on various occasions for some of the thermoplastic vinyl polymers,<sup>2,3</sup> and it has been recognized,<sup>4</sup> in principle at least, that monomer units may be assembled in non-linear patterns which do not lead to network formation and the manifestations of gelation resulting therefrom. Chain transfer with previously formed polymer molecules in vinyl polymerizations doubtless leads to some degree of branching without producing network structures.<sup>5-7</sup> However, the extent of such branching, like the cross-linking produced in diene polymers, is not easily measured or controlled.

Effects of departure from linear structure on physical properties of non-gelled polymers have

been the subject of frequent speculation, but little information of a quantitative nature is available as a result of the difficulty of isolating the non-linearity variable. In the first place, the extent of branching or of cross-linking (prior to gelation) in the polymer as a whole usually is difficult to estimate quantitatively. Secondly, such reactions ordinarily occur in a random manner such that the co-existing polymer molecules vary widely in degree of non-linearity, ranging from linear to highly branched structures. Finally, random cross-linking and branching reactions usually broaden the molecular weight distribution, sometimes severely; consequently, alteration of the molecular weight distribution, rather than non-linearity, may be primarily responsible for the effects observed.

In the present investigation a convenient general procedure for synthesizing non-linear condensation polymers of controlled structure has been demonstrated. The principle employed here involves the co-reaction of an A—B type monomer, *e.g.*, an amino acid or hydroxy acid, with a small proportion of a multifunctional reactant of the type RA<sub>*b*</sub> or RB<sub>*b*</sub> where R is a *b*-valent radical and A and B are co-reacting functional groups; such multifunctional reactants may be, for example, a polyamine or a polybasic acid. Polymers so produced can be represented by the formulas



(1) Presented before the High Polymer Forum at the New York Meeting of the American Chemical Society, September, 1947.

(2) G. V. Schulz, *Z. physik. Chem.*, **B44**, 227 (1939); H. Staudinger and G. V. Schulz, *Ber.*, **68**, 2320 (1935); H. Staudinger and J. Schneiders, *Ann.*, **541**, 151 (1939).

(3) H. Mark and R. Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 191, 219, *et seq.*

(4) E. W. Melville, *Trans. Faraday Soc.*, **40**, 217 (1944).

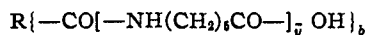
(5) P. J. Flory, *This Journal*, **59**, 241 (1937).

(6) P. J. Flory, *ibid.*, **69**, 2893 (1947).

(7) R. B. Carlin and N. E. Shakespeare, *ibid.*, **68**, 876 (1946).

These "multichain" polymer molecules are therefore composed of  $b$  chains, of average length  $\bar{y}$  units each, radiating from the central radical R. It is to be noted that network formation is precluded so long as the terminal groups A, or B as the case may be, cannot co-react. Also, the degree of branching is fixed according to the functionality of the central unit. The average length,  $\bar{y}$ , of the chains is controlled by the proportion of multifunctional unit employed; it is also dependent on the extent of condensation, which, however, ordinarily is carried very nearly to completion.

The multichain polymers employed in the present investigation were prepared from  $\epsilon$ -caprolactam (instead of the corresponding amino acid) using either a tetrabasic or an octabasic carboxylic acid as the multifunctional reactant. For comparison, monochain and dichain  $\epsilon$ -caproamide polymers (stearic and sebacic acid, respectively, were used as the "multifunctional" reactant) have been prepared as well. Thus, the various polymers for which data are reported herein can be represented by the formula



where  $b = 1, 2, 4, \text{ or } 8$ ,  $\bar{y}$  being varied in each case by manipulating the proportion of the multifunctional reactant. Cyclohexanone-tetrapropionic acid<sup>8</sup> and the analogous octabasic acid, dicyclohexanone-octapropionic acid<sup>9</sup> were used in preparing the tetrachain and octachain polymers, respectively.

### Theoretical

**Stoichiometric Relationships. The Number Average Molecular Weight.**—Let  $Q$  represent the number of equivalents of the multifunctional reactant,  $RA_b$ , that reacts with one mole of A—B monomer. If the reaction were carried to completion, no unreacted B groups remaining, there would be obtained  $Q/b$  moles of polymer molecules, each molecule having  $b$  chains. Since it is never possible to carry the condensation process to absolute completion, a small fraction of the B groups will remain unreacted, and each unreacted B group will subtend a linear chain. Letting  $L$  represent the number of equivalents of unreacted groups per mole of A—B monomer, there will be  $L$  moles of linear molecules and  $Q/b$  moles of multichain molecules in the polymer. The ratio of  $L$  to  $Q/b$  depends on the degree of completion of the reaction and is very small if the reaction is carried reasonably near to completion. (In the examples discussed below,  $A = \text{COOH}$  and  $B = \text{NH}_2$ ; the proportion  $L$  of the latter remaining unreacted in the polymer can be determined by titration of the free amino groups.)

As a consequence of the assumed equal reactivity of the carboxyl groups dealt with here, the average number,  $\bar{y}$ , of monomer units sub-

tended by an A group of a multifunctional unit will equal the number attached to the terminal unit of a linear chain. Therefore  $\bar{y}$  will equal the total number of monomer units excluding those with unreacted B groups, divided by the total number of chains, or

$$\bar{y} = (1 - L)/(Q + L) \quad (1)$$

Letting  $y_L$  represent the average number of units in a linear molecule (including the terminal unit bearing the unreacted B group)

$$\bar{y}_L = \bar{y} + 1 = (Q + 1)/(Q + L) \quad (2)$$

The number average molecular weights of the linear molecules ( $\bar{M}_{n,L}$ ) and of the multichain molecules ( $\bar{M}_{n,Q}$ ) are therefore

$$\bar{M}_{n,L} = m\bar{y}_L = m(Q + 1)/(Q + L) \quad (3)$$

and

$$\bar{M}_{n,Q} = b(m\bar{y} + m_b) = b[m(1 - L)/(Q + L) + m_b] \quad (4)$$

where  $m$  is the molecular weight of an A—B structural unit and  $m_b$  is the molecular weight of the multifunctional unit divided by  $b$ . The number average molecular weight ( $\bar{M}_n$ ) of the entire polymer containing  $L$  moles of linear molecules and  $Q/b$  moles of multichain molecules can now be expressed as

$$\bar{M}_n = \frac{LM_{n,L} + (Q/b)M_{n,Q}}{L + (Q/b)} = \frac{(Qm_b + m)}{(Q/b) + 1} \quad (5)$$

It can be shown further that  $w_L$ , the weight fraction of linear molecules present in the mixture, is given by

$$w_L = L/\left\{L + Q\left[1 + \left(\frac{m_b}{m} - 1\right)\left(\frac{Q + L}{Q + 1}\right)\right]\right\} \quad (6)$$

which reduces to

$$w_L = L/(Q + L) \quad (7)$$

when  $Q$  and  $L$  are both small or when  $m_b$  is similar in magnitude to  $m$ . This relationship will be used in the next section (see equation 25) in deriving the expression for the weight average molecular weight of a mixture of multichain and linear molecules.

**Molecular Size Distribution. The Weight Average Molecular Weight.**—Schulz<sup>10</sup> has derived approximate relationships expressing the molecular weight distribution in polymers composed of a fixed number of chains of random length. His molecular weight distribution relationships were derived for the purpose of treating vinyl polymers believed to be branched. Since branching in vinyl polymers must necessarily be random, his relationships actually are of little value for the purpose intended, except in the  $b = 2$  case representing polymers resulting from diradical chain growth in two directions. Schulz's approximate relationships may be applied to multichain polymers of the present type, provided the chain length is sufficiently great; at low chain lengths the approximations employed by

(8) Bruson and Riener, *THIS JOURNAL* **64**, 2850 (1942).

(9) J. R. Schaeffgen and P. J. Flory, *ibid.*, **70**, 2823 (1948).

(10) G. V. Schulz, *Z. physik. Chem.*, **B43**, 25 (1939).

Schulz became invalid. Instead of these approximate equations, we have preferred to use exact relationships, the derivation of which is set forth below. They are as easily applied as the approximate forms of Schulz.

Let  $p$  represent the fraction of the A groups which have undergone reaction, *i. e.*

$$p = (1 - L)/(1 + Q) \quad (8)$$

If the A groups of the multifunctional units and those of the bifunctional units can be assumed to be equally reactive,  $p$  represents the probability that any given A group has condensed with a B group, since condensation polymerization reactions are known to proceed in a random manner.<sup>11</sup> The probability that a given multichain molecule possesses exactly  $x_1$  bifunctional units in the first chain,  $x_2$  in the second, etc., will be given by

$$P_{x_1 x_2 \dots x_b} = p^{x_1} p^{x_2} \dots p^{x_b} (1 - p)^b \quad (9)$$

Let  $x$  represent the total number of structural units, counting the multifunctional constituent as a single unit. Then

$$x_1 + x_2 + \dots + x_b + 1 = x \quad (10)$$

and

$$P_{x_1 x_2 \dots x_b} = p^{x-1} (1 - p)^b \quad (11)$$

All combinations of the  $x$ 's consistent with equation (10), the individual values of the  $x$ 's ranging from 0 to  $x_b$ , are equally probable. It is to be noted that a given combination is specified by  $b - 1$  of the  $x$ 's, the remaining one being defined by equation (10) above. The number of ways the  $x - 1$  units may be distributed over the  $b$  chains is given, therefore, by the combinatory factor

$$(x + b - 2)! / (b - 1)! (x - 1)!$$

which represents the number of combinations of  $(x - 1) + (b - 1)$  elements (allowing for the permissible zero values) taken  $b - 1$  at a time. Hence, the probability that a given multichain molecule contains  $x - 1$  bifunctional units arranged in any manner is given by

$$P_{x,b} = (1 - p)^b p^{x-1} (x + b - 2)! / (b - 1)! (x - 1)! \quad (12)$$

$P_{x,b}$  represents the mole fraction of  $x$ -mers among the multichain molecules.

In order to obtain the weight fraction distribution and to deduce the weight average degree of polymerization, the summations

$$\sum_{x=1}^{\infty} x P_{x,b} \quad \text{and} \quad \sum_{x=1}^{\infty} x^2 P_{x,b}$$

must be evaluated.

$$\sum_{x=1}^{\infty} x P_{x,b} \equiv \sum_{x=2}^{\infty} (x - 1) P_{x,b} + \sum_{x=1}^{\infty} P_{x,b} \quad (13)$$

Substituting from equation (12)

$$\sum_{x=1}^{\infty} x P_{x,b} = \sum_{x=2}^{\infty} (1 - p)^b p^{x-1} \frac{(x + b - 2)!}{(x - 2)! (b - 1)!} + \sum_{x=1}^{\infty} P_{x,b}$$

(11) P. J. Flory, THIS JOURNAL, 61, 3334 (1939); 64, 2205 (1942).

Shifting limits in the first summation on the right, there is obtained

$$\sum_{x=1}^{\infty} x P_{x,b} = b p / (1 - p) \sum_{x=1}^{\infty} P_{x,b+1} + \sum_{x=1}^{\infty} P_{x,b}$$

Since

$$\sum_{x=1}^{\infty} P_{x,b+1} = \sum_{x=1}^{\infty} P_{x,b} = 1$$

$$\sum_{x=1}^{\infty} x P_{x,b} = (b p + 1 - p) / (1 - p) \quad (14)$$

Replacing  $x^2$  with  $(x - 2)(x - 1) + 3x - 2$  in the summations over  $x^2 P_{x,b}$  and proceeding similarly, there is obtained

$$\sum_{x=1}^{\infty} x^2 P_{x,b} = \frac{p^2 (b - 1)^2 + (3b - 2)p + 1}{(1 - p)^2} \quad (15)$$

The weight fraction distribution is given by

$$w_x = x P_{x,b} / \sum_{x=1}^{\infty} x P_{x,b}$$

which on substituting from equation (14) reduces to

$$w_x = \left[ \frac{(1 - p)^{b+1}}{(b p + 1 - p)} \right] (p^{x-1}) \frac{x(x + b - 2)!}{(b - 1)! (x - 1)!} \quad (16)$$

The corresponding weight fraction distribution expression derived by Schulz,<sup>10</sup> when expressed in the present symbols, is

$$w_x = (-\ln p)^{b+1} p^x (x^b / b!) \quad (17)$$

which approximates equation (16) when  $p$  is near unity (high average molecular weight) except for small values of  $x$ , since

$$\begin{aligned} -\ln p &\cong (1 - p) \\ p^x &\cong p^{x-1} \\ x^b / b! &\cong \frac{x(x + b - 2)!}{(b p + 1 - p)(b - 1)! (x - 1)!} \end{aligned}$$

The molecular weight distribution is narrower the greater the number  $b$  of chains. The dependence of the molecular weight distribution on  $b$  is illustrated in the curves published by Schulz,<sup>10</sup> which are qualitatively similar to the corresponding curves calculated from our equation (16).

The number and weight average degrees of polymerization, respectively, derived from the mole fraction size distribution as given by equation (12) are

$$\bar{x}_n = \sum_{x=1}^{\infty} x P_{x,b} / \sum_{x=1}^{\infty} P_{x,b} = (b p + 1 - p) / (1 - p) \quad (18)$$

and

$$\begin{aligned} \bar{x}_w &= \sum_{x=1}^{\infty} x^2 P_{x,b} / \sum_{x=1}^{\infty} x P_{x,b} \\ &= \frac{(b - 1)^2 p^2 + (3b - 2)p + 1}{(b p + 1 - p)(1 - p)} \quad (19) \end{aligned}$$

Substituting for  $p$  from equation (8) reduces the expression for the number average to

$$\bar{x}_n = 1 + \frac{b(1 - L)}{Q + L} \quad (20)$$

The ratio of the weight to number average degree of polymerization is

$$\frac{\bar{x}_w}{\bar{x}_n} = \frac{(b-1)^2 p^2 + (3b-2)p + 1}{(bp+1-p)^2} \quad (21)$$

Substituting from Equation (8) for  $p$

$$\bar{x}_w/\bar{x}_n = 1 + \frac{b(1-L)(1+Q)}{[b(1-L) + (Q+L)]^2} \quad (22)$$

For small values of  $Q$  and  $L$ , this equation reduces approximately to

$$\bar{x}_w/\bar{x}_n \cong 1 + 1/b \quad (23)$$

which is the result obtained by Schulz. The narrowing of the molecular weight distribution with increase in  $b$  is reflected in the approach of this ratio to unity.

Equation (23) is too coarse an approximation on the one hand and (22) is unnecessarily cumbersome on the other. An intermediate approximation, which can be used with negligible error when  $L \ll 1$  and  $Q^2 \ll (b^2 + 2bQ)$ , is the following

$$\bar{x}_w/\bar{x}_n = 1 + (1+Q)/(b+2Q) \quad (24)$$

For a mixture of  $Q/b$  multichain polymer molecules with  $L$  linear polymer molecules the expression for the weight average molecular weight is<sup>12</sup> (see equations 3, 4, 7, and 24)

$$\bar{M}_w = w_L \bar{M}_{w,L} + w_Q \bar{M}_{w,Q} = w_L \bar{M}_{n,L} (\bar{x}_w/\bar{x}_n)_1 + (1-w_L) \bar{M}_{n,Q} (\bar{x}_w/\bar{x}_n)_b \quad (25a)$$

$$\cong \frac{L}{(Q+L)} \frac{m(1+Q)}{(Q+L)} \left[ 1 + \frac{(1+Q)}{(1+2Q)} \right] + \frac{Qb}{(Q+L)} \left[ \frac{m(1-L)}{(Q+L)} + m_b \right] \left[ 1 + \frac{(1+Q)}{(b+2Q)} \right] \quad (25b)$$

Since the first term in equation (25b) is small,  $(1+Q)$  can be set equal to unity therein. The second term can be simplified since  $L(m_b - m)$  is small in comparison with  $m$ . Then

$$\bar{M}_w \cong 2 mL/(Q+L)^2 + [Qb/(Q+L)^2] (m + mbQ) [1 + (1+Q)/(b+2Q)] \quad (26)$$

**The Viscosity Average Molecular Weight.**— Interpretation of dilute solution viscosities requires evaluation of the viscosity average molecular weight<sup>13</sup> defined as

$$\bar{M}_v = \left[ \sum_{x=1}^{\infty} w_x M_x^a \right]^{1/a} \quad (27)$$

where  $a$  is a constant which usually is in the range of 0.6 to 0.9. Substituting from equation (16) for  $w_x$  and replacing  $M_x$  with  $xm$

$$\bar{M}_v^a = m^a \left\{ \frac{(1-p)^{b+1}}{[p(b-1)+1]p} \right\} \sum_{x=1}^{\infty} \left\{ \left[ (x+b-2)(x+b-3) \cdots (x+1) \right] x^{2+a} p^x / (b-1) \right\}$$

Employing the ratio of  $\bar{M}_v$  to  $\bar{M}_n$ , the latter being the product of  $m$  and  $x_n$  as expressed by equation

(12) The subscript  $b$  on the ratio  $(\bar{x}_w/\bar{x}_n)_b$  in equation (25a) refers to the value of  $b$  for the multichain molecules. The subscript "1" must be used for the co-existing linear species.

(13) P. J. Flory, *THIS JOURNAL*, **68**, 372 (1943).

(18), and expanding the products of the summation

$$\left( \bar{M}_v/\bar{M}_n \right)^a = \left[ \frac{1-p}{p(b-1)+1} \right]^a \left\{ \frac{(1-p)^{b+1}}{p[p(b-1)+1]} \sum_{x=1}^{\infty} \left\{ \left[ x^{b+a} + \frac{1}{2}(b-1)(b-2)x^{b-1+a} + \frac{1}{24}(b-1)(b-2)(3b^2-13b+12)x^{b-2+a} + \cdots \right] p^x / (b-1) \right\} \right\}$$

The summation is made up of terms of the form

$$S_m = \sum_{x=1}^{\infty} p^x x^{m+a}$$

where  $m$  is a positive integer. Replacing the summation by an integral and setting  $y = -x \ln p$

$$S_m = (-1/\ln p)^{m+a+1} \int_0^{\infty} e^{-y} y^{m+a} dy = (-1/\ln p)^{m+a+1} \frac{\Gamma(m+a+1)}{(m+a)(m+a-1) \cdots (1+a) \Gamma(1+a)}$$

Substituting this evaluation of  $S_m$  in the previous equation, the ratio of the viscosity average to the number average may be expressed conveniently as

$$\left( \bar{M}_v/\bar{M}_n \right) = (C/b) [(1/b)(a+b)(a+b-1) \cdots (a+1)\Gamma(a+1)]^{1/a} \quad (28)$$

where

$$C = \left( \frac{1-p}{-\ln p} \right) \left[ \frac{b}{p(b-1)+1} \right] \left\{ \left( \frac{1-p}{-\ln p} \right)^{b+1} \left[ \frac{b}{p^2(b-1)+p} \right] \left[ 1 + \frac{(b-1)(b-2)(-\ln p)}{2(b+a)} \right] + \frac{(b-1)(b-2)(3b^2-13b+12)(-\ln p)^2}{24(b+a)(b+a-1)} + \cdots \right\}^{1/a} \quad (29)$$

The series in brackets converges rapidly when

$$-b \ln p < 1$$

When, in addition to this condition,  $p$  is not less than about 0.8,  $C$  differs inappreciably from unity. To illustrate for  $a = 0.8$ ,  $b = 8$ , and  $p = 0.8$ ,  $C$  as calculated from equation (29) has a value of 1.03 (making a suitable estimation of the values of the unexpanded terms). For all higher values of  $p$  (and/or lower values of  $b$ ),  $C$  is closer to unity. Within the limit of error introduced on replacing summations by integrals,  $C$  may therefore be set equal to unity in equation (28).

### Experimental

**Materials.**— $\epsilon$ -Caprolactam was prepared from cyclohexanoneoxime by a Beckmann rearrangement<sup>14</sup> in 77% yield. The product was distilled at reduced pressure and then crystallized from acetone to a constant freezing point of 68.7–68.8°, determined by a cooling curve.

**Stearic Acid.**—A commercial grade was crystallized once from acetone and then several times from alcohol; m. p. 71–72°<sup>15</sup>; neutral equivalent 284, calcd. 284.5.

**Sebacic Acid.**—An Eastman Kodak Co. product was crystallized several times from distilled water; m. p. 128.5–130°, uncor.; neut. equiv. 101, calcd. 101.1.

(14) P. Schlack, U. S. Patent 2,313,026 (1943).

(15) All melting points are corrected for stem exposure unless marked "uncor."

2,2,6,6-Tetra-( $\beta$ -carboxyethyl)-cyclohexanone (cyclohexanonetetrappropionic acid) was prepared by the method of Bruson.<sup>8</sup> Attempts to convert this acid or its nitrile to cyclohexane-tetrappropionic acid by the Clemmensen method were uniformly unsuccessful. The acid after several crystallizations from water melted at 182.5–184.5°, although one sample prepared by acid hydrolysis of the tetranitrile melted at 195–197°. However, mixed melting points showed that this sample was identical with the lower melting material indicating the existence of allotropic forms. The neutral equivalent was 96.6, calcd. 96.6. A sample of this acid when heated to 253° for three hours in an argon atmosphere turned black and tarry and underwent extensive decomposition with the liberation of gaseous products. When the acid was mixed with three times its weight of  $\epsilon$ -caprolactam and initially polymerized at 200° (see section on Method of Polymerization), little decomposition occurred on further heating at 253° for a period of three hours, thus indicating that the amide is considerably more stable than the free acid.

bis-[3,3,5,5-Tetra-( $\beta$ -carboxyethyl)-4-ketocyclohexyl] (Dicyclohexanonetetracarboxylic Acid).—The preparation of this acid from *p,p'*-diphenol is described elsewhere.<sup>9</sup> Material melting at 274–277° and having a neutral equivalent of 96.6 to 96.8 (calcd. 96.4) was used in making polymers.

**Method of Polymerization.**—The polymerizations were carried out in two steps. In the first step weighed amounts of  $\epsilon$ -caprolactam and the multifunctional co-reactant together with a small amount of distilled water (ca. 17 mole per cent.) were polymerized<sup>16</sup> in a sealed tube at a temperature of about 200° until a low molecular weight polymer was produced (four hours or more). The tube was alternately evacuated and filled with argon or nitrogen (containing in either case less than 0.01% of oxygen) several times before sealing. In the second step the white brittle polymer produced in the first step was heated in an inert gas atmosphere at 253° (diphenyl vapor-bath) alternately at atmospheric pressure and at reduced pressure (down to 15 mm.) until the melt viscosity became constant, or for a period of from six to seven hours (see section on results). The distillate in each polymerization was collected and analyzed for evolved  $\epsilon$ -caprolactam. The amount of  $\epsilon$ -caprolactam used in the calculation of the polymer composition was corrected accordingly.

The apparatus used in the second step was essentially that described previously<sup>17</sup> except that the side-arm attached to the vertical polymerization tube sloped downward. This facilitated the complete removal of the unreacted  $\epsilon$ -caprolactam. The trap in which the distillate was collected was cooled in an ice-bath.

**Melt Viscosity.**—The melt viscosities of the polymers were determined by the method previously described.<sup>17</sup> It was found convenient to use viscometers with two bulbs (or four marks in the case of the straight tube type) using the lower bulb to measure the changing viscosity as the reaction proceeded and saving the clean upper bulb to determine the final viscosity. Melt viscosities were ordinarily taken at the end of a given cycle, a cycle consisting of a fifteen-minute period of heating at reduced pressure followed by a fifteen-minute period at atmospheric pressure during which time the inert gas was bubbled through the molten polymer. When two consecutive viscosity determinations gave values within 5% of each other the reaction was assumed to be substantially complete and a final viscosity was determined. In preparing the higher molecular weight polymers, the heating period at 253° was prolonged to six or seven hours which was several times the length of time required for the lower molecular weight polymers to reach maximum viscosity. After this length of time the reaction was assumed to be complete, and a final viscosity was taken.

**Solution Viscosities.**—Relative viscosities of the polymer solutions in concentrated sulfuric acid were measured

at 25.0 ( $\pm 0.1^\circ$ ) using a Ubbelohde number 2 suspended level viscometer. The efflux time of the solutions was of the order of two minutes or more, making the kinetic energy correction negligible. The density of the solution was equal to that of the solvent within the experimental error.

Solutions were prepared by shaking a suspension of the finely divided polymer in ordinary commercial concentrated sulfuric acid until solution was complete, and making up to volume. To obtain polymer samples in a form which would dissolve readily, the brittle lower molecular weight polymers were ground in a steel mortar, whereas samples of the tough higher molecular weight polymers were drilled out from a solid plug thereof with a one-half inch drill. Concentrations were suitably chosen to obtain relative viscosities in the range 1.15 to 1.25. Values of  $(\ln \eta_r)/c$ , where  $c$  is expressed in g./100 cc. solution, calculated from relative viscosities in this range differed by 3% or less from the infinite dilution values, and were therefore accepted as intrinsic viscosities (*i. e.*,  $(\ln \eta_r)/c$  at  $c = 0$ )<sup>18</sup> without extrapolation. In a few representative cases the change of  $(\ln \eta_r)/c$  with concentration was measured. Solutions for these experiments were made up either individually or by dilution of a more concentrated solution.

The observation of Matthes<sup>19</sup> that degradation of the polymer in concentrated sulfuric acid solution at room temperature is negligible within a twenty-four hour period was confirmed.

**Amine Titer.**—The amino end-group concentration in a polymer was determined by titrating a 50-ml. sample of a 6% by weight solution of the polymer in *m*-cresol with standard 0.1 *N* *p*-toluenesulfonic acid solution using thymolsulfonphthalein as an indicator. The solutions were prepared by shaking and gently warming the finely divided polymer suspension in *m*-cresol until solution was effected. The *m*-cresol (1500 ml.) used for these titrations was distilled at reduced pressure from sulfuric acid (5 ml.) and zinc dust (5 g.), and then redistilled from barium oxide (10 g.) to give a water-white neutral product. The amino group concentration is expressed as equivalents per mole of  $\epsilon$ -caprolactam in the polymer. This value is equal to  $L$ , the equivalents of linear molecules present in the polymer per mole of  $\epsilon$ -caprolactam.

**Melting Points.**—Polymer melting points were measured<sup>20</sup> on the heated stage of a microscope, plane polarized light being used for illumination. One Polaroid film was located between the light source and the sample, and another was placed in the objective of the microscope. With the Polaroids at right angles to each other, the crystalline portions of the sample were seen as light areas against a dark background. As the temperature of the stage was gradually increased, a range of temperature was reached in which the light areas disappeared into the dark background. This range of temperature is recorded as the melting point.

## Results

**Calculations and Errors.**—Viscosity, molecular weight, and melting point data for monochain, dichain, tetrachain, and octachain polymers ( $b = 1, 2, 4,$  and  $8$ ) are recorded in Tables I, II, III, and IV, respectively. The quantities  $Q$  and  $L$ , defined earlier, were calculated in each case from the data in columns 1 and 2, and from the amine titer. The weight fraction of linear molecules,  $w_L$ , was calculated using equation (7). The number average,  $M_n$ , and weight average,  $M_w$ , molecular weights were calculated using equations (5) and (26), respectively. All poly-

(18) E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

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

(20) Unpublished work of H. R. Mighton of this Laboratory. See R. D. Evans, H. R. Mighton and P. J. Flory, *J. Chem. Phys.*, **16**, 685 (1947).

(16) W. E. Hanford, U. S. Patent 2,241,322 (1941).

(17) P. J. Flory, *THIS JOURNAL*, **68**, 1057 (1940).

TABLE I  
 MONOCHAIN POLYMERS

| $\epsilon$ -Caprolactam, g. | Stearic acid, g. | $Q \times 10^3$ | $L \times 10^4$ | $\eta^a$ | $[\eta]^b$ | M. p., °C. | $\bar{M}_n$ | $\bar{M}_w$ |
|-----------------------------|------------------|-----------------|-----------------|----------|------------|------------|-------------|-------------|
| 18.72                       | 3.12             | 6.64            | 6.1             | 1.38     | 0.212      | 213-217    | 1,970       | 3,820       |
| 17.17                       | 2.094            | 4.86            | 3.4             | 2.40     | .248       | 212-216    | 2,600       | 5,090       |
| 18.87                       | 1.445            | 3.05            | 6.0             | 10.0     | .343       | 215-221    | 3,920       | 7,730       |
| 27.72                       | 1.211            | 1.74            | 5.8             | 43.4     | .516       | 219-221    | 6,560       | 13,000      |
| 28.98                       | 0.982            | 1.36            | 5.7             | 103      | .612       | 221-226    | 8,240       | 16,400      |
| 27.34                       | 0.626            | 0.912           | 6.6             | 401      | .804       | 221-225    | 11,860      | 23,600      |
| 28.07                       | 0.498            | 0.707           | 10.0            | 615      | .914       | 220-222    | 14,300      | 28,400      |

<sup>a</sup> Melt viscosity in poises at 253°. <sup>b</sup> Intrinsic viscosity in concentrated sulfuric acid at 25°.

 TABLE II  
 DICHAIN POLYMERS

| $\epsilon$ -Caprolactam, g. | Sebacic acid, g. | $Q \times 10^3$ | $L \times 10^4$ | $\eta^a$ | $[\eta]^b$ | M. p., °C. | $\bar{M}_n$ | $\bar{M}_w$ |
|-----------------------------|------------------|-----------------|-----------------|----------|------------|------------|-------------|-------------|
| 18.57                       | 2.203            | 13.30           | 0.44            | 1.25     | 0.171      | 203-205    | 1,900       | 2,880       |
| 19.04                       | 1.405            | 8.27            | 4.0             | 2.72     | .235       | 211-213    | 2,910       | 4,390       |
| 18.85                       | 1.055            | 6.27            | 3.6             | 5.00     | .281       | 213-215    | 3,770       | 5,690       |
| 18.20                       | 1.010            | 6.22            | 2.5             | 5.82     | .291       | 209-214    | 3,810       | 5,750       |
| 18.44                       | 0.802            | 4.88            | 3.2             | 11.4     | .350       | 214-216    | 4,780       | 7,200       |
| 18.97                       | .699             | 4.13            | 1.6             | 13.7     | .381       | 212-217    | 5,650       | 8,490       |
| 18.73                       | .599             | 3.58            | 7.0             | 23.8     | .427       | 214-218    | 6,280       | 9,550       |
| 18.72                       | .500             | 2.99            | 6.0             | 44.9     | .496       | 214-220    | 7,500       | 11,400      |
| 19.00                       | .488             | 2.88            | 3.7             | 44.5     | .496       | 218-222    | 7,850       | 11,900      |
| 17.00                       | .366             | 2.41            | 5.5             | 143      | .627       | 217-220    | 9,170       | 14,100      |
| 18.08                       | .255             | 1.58            | 5.8             | 460      | .800       | 218-222    | 13,500      | 20,800      |
| 15.72                       | .181             | 1.29            | 6.2             | 735      | .908       | 220-223    | 16,200      | 25,000      |
| 17.56                       | .162             | 1.03            | 4.8             | 1650     | 1.085      | 221-225    | 20,200      | 31,200      |
| 17.73                       | .116             | 0.734           | 13.8            | 3130     | 1.313      | 221-227    | 22,600      | 37,100      |

<sup>a</sup> Melt viscosity in poises at 253°. <sup>b</sup> Intrinsic viscosity in concentrated sulfuric acid at 25°.

 TABLE III  
 TETRACHAIN POLYMERS

| $\epsilon$ -Caprolactam, g. | Tetra-basic acid, g. | $Q \times 10^3$ | $L \times 10^4$ | $\eta^a$ | $[\eta]^b$ | M. p., °C. | $\bar{M}_n$ | $\bar{M}_w$ | $w_L \times 10^3$ |
|-----------------------------|----------------------|-----------------|-----------------|----------|------------|------------|-------------|-------------|-------------------|
| 25.62                       | 4.745                | 21.69           | 18              | 1.84     | 0.177      | 187-188    | 2,390       | 3,110       | 0.82              |
| 26.44                       | 2.754                | 12.20           | 7.2             | 3.75     | .233       | 205-207    | 3,970       | 5,150       | 0.58              |
| 14.39                       | 1.322                | 10.76           | 12              | 5.46     | .289       | 207-209    | 4,400       | 5,720       | 1.1               |
| 28.26                       | 1.968                | 8.15            | 8.6             | 8.20     | .287       | 210-212    | 5,700       | 7,350       | 1.0               |
| 25.54                       | 1.446                | 6.63            | 7.7             | 16.4     | .390       | 214-217    | 6,890       | 8,900       | 1.2               |
| 16.56                       | 0.642                | 4.54            | 8.6             | 39.3     | .459       | 216-218    | 9,620       | 12,600      | 1.8               |
| 28.77                       | 1.089                | 4.43            | 8.8             | 43.5     | .469       | 215-219    | 9,820       | 12,900      | 1.9               |
| 27.03                       | 0.864                | 3.74            | 7.0             | 99.3     | .550       | 219-222    | 11,600      | 15,200      | 1.8               |
| 28.67                       | .598                 | 2.44            | 6.8             | 390      | .649       | 221-225    | 17,000      | 22,800      | 2.7               |
| 28.85                       | .509                 | 2.07            | 8.2             | 589      | .750       | 222-224    | 19,200      | 26,200      | 3.8               |
| 17.28                       | .316                 | 2.14            | 9.2             | 859      | .923       | 220-223    | 18,400      | 25,200      | 4.1               |

<sup>a</sup> Melt viscosity in poises at 253°. <sup>b</sup> Intrinsic viscosity in concentrated sulfuric acid at 25°.

 TABLE IV  
 OCTACHAIN POLYMERS

| $\epsilon$ -Caprolactam, g. | Octa-basic acid, g. | $Q \times 10^3$ | $L \times 10^4$ | $\eta^a$ | $[\eta]^b$ | M. p., °C. | $\bar{M}_n$ | $\bar{M}_w$ | $w_L \times 10^3$ |
|-----------------------------|---------------------|-----------------|-----------------|----------|------------|------------|-------------|-------------|-------------------|
| 4.98                        | 1.0348              | 24.4            | 18              | 2.76     | 0.171      | 183-184    | 4,230       | 5,070       | 0.73              |
| 8.67                        | 0.9913              | 13.4            | 9.3             | 6.00     | .268       | 202-203    | 7,130       | 8,450       | 0.69              |
| 9.21                        | .5750               | 7.32            | 8.4             | 24.2     | .420       | 214-216    | 12,000      | 14,600      | 1.1               |
| 8.93                        | .3313               | 4.35            | 6.1             | 126      | .597       | 219-222    | 19,400      | 23,800      | 1.4               |
| 14.06                       | .3762               | 3.14            | 6.0             | 358      | .806       | 221-222    | 25,700      | 32,400      | 1.9               |

<sup>a</sup> Melt viscosity in poises at 253°. <sup>b</sup> Intrinsic viscosity in concentrated sulfuric acid at 25°.

merizations were carried very nearly to completion, as shown by the low values obtained for  $w_L$  (Tables III and IV), hence the final polymers contained a preponderant number of multichain molecules.

The preceding deductions of structure and the formulas for the computation of molecular weights are based on literal application of stoichiometric considerations. Deviations from these idealized conditions doubtless occur owing to side reactions. These include oxidation, thermal decomposition, anhydride and imide formation.

Oxidation was minimized by carrying out the polymerizations in an argon or nitrogen atmosphere containing, in either case, less than 0.01% of oxygen. However, some oxidation occurred, especially in the higher molecular weight polymers for which the heating period at 253° was prolonged over a six to seven hour period. Small amounts of oxygen were also introduced during the melt viscosity measurements. Such oxidation as occurred presumably lowered the molecular weight by oxidative cleavage of the polymer chain. The magnitude of this effect is difficult to ascertain, but it is believed to have been small compared to the other side reactions mentioned; its effect was therefore neglected.

The most likely reaction to occur in thermal decomposition is decarboxylation. In support of this conclusion, the distillate in some of the polymerizations was found to be slightly acidic. To investigate the magnitude of the decomposition the number of carboxyl end-groups in a given polymer was determined by the method of Waltz and Taylor.<sup>21</sup> The results (Table V) show that loss of carbon dioxide does occur, but that in no case is the magnitude of the deviation between the observed value and that calculated from stoichiometric relationships greater than 9%. The fact that the major part of the octabasic acid used in a polymer could be recovered unchanged by hydrolysis is further proof that decomposition was slight. Loss of carbon dioxide, especially from the multichain molecule, would lower the degree of branching but would leave the molecular weight essentially unchanged since as  $b$  decreases  $\bar{y}$  increases (see equation 4). The molecules which

are formed may, for example, contain an average of 7.5 branches instead of eight.

When the study of octachain polymers was extended to include polymers of higher molecular weight than reported herein, the melt viscosity of a given polymer continued to rise slowly on prolonged heating without seeming to approach a limit, and polymers of very high viscosity gave evidence of being partially gelled. This may have been due to the gradual formation of a small number of anhydride and/or imide linkages. All the polymers reported in this paper, however, were completely soluble and gave no evidence of gelation. It is quite possible, however, that a small number of such anhydride and/or imide linkages (short of gelation) were formed.

Furthermore it was found impossible to remove the last traces of monomeric  $\epsilon$ -caprolactam from the polymer, owing to the occurrence of interchange reactions which constantly evolve small quantities of  $\epsilon$ -caprolactam. This error would tend to make the observed viscosity low. Small amounts (*ca.* 0.15 g. in 16 g. of polymer) of a high melting (*m. p.* > 295°) sublimate which analyzed correctly for  $\epsilon$ -caprolactam were also formed. The material is undoubtedly di- $\epsilon$ -caprolactam, a fourteen-membered ring compound.

Data reported here were obtained under conditions chosen with the object of minimizing errors arising from these various sources. While the results may nevertheless be vitiated by them to some extent, these errors are doubtless inconsequential insofar as the conclusions regarding the effects of branching are concerned.

**Melt Viscosity.**—It has been shown previously<sup>17</sup> that the viscosities of molten polyesters can be represented precisely by the equation

$$\log \eta = A + C\bar{M}_w^{1/2}$$

Graphs of the logarithm of the melt viscosity as a function of the weight average molecular weight for multichain polymers are shown in Fig. 1. The relationships are linear over the range of molecular weight considered just as in the case of polyesters, and the effect of branching is noticeable only in the octachain polymers. The equations for the lines are

$$b = 1, 2 \text{ or } 4 \quad \log_{10} \eta = 2.6 \times 10^{-3} \bar{M}_w^{1/2} - 1.32$$

$$b = 8 \quad \log_{10} \eta = 2.0 \times 10^{-3} \bar{M}_w^{1/2} - 1.00$$

The values of  $C$  are similar to those obtained for polyesters.<sup>17,22</sup> If the logarithm of the melt viscosity is plotted as a function of the square root of the number average molecular weight, individual linear relationships are obtained for each series of polymers.

**Solution Viscosity.**—The change of relative viscosity ( $\eta_r$ ) with concentration for representative linear and multichain polymers was determined in sulfuric acid and in *m*-cresol solution. The function  $(\ln \eta_r)/c$  was plotted against concen-

TABLE V  
CARBOXYL END-GROUP TITRATION OF MULTICHAIN POLYMERS IN BENZYL ALCOHOL AT 155°

| Polymer    | Equiv. COOH/g. polymer<br>Calcd. $\times 10^4$ | Found $\times 10^4$ | %<br>error |
|------------|--|---------------------|------------|
| Tetrachain | 1.87   | 1.85                | 1.1        |
| Tetrachain | 2.34   | 2.17                | 7.8        |
| Tetrachain | 4.04   | 4.10                | 1.5        |
| Octachain  | 18.0   | 16.5                | 8.5        |
| Octachain  | 10.7   | 10.1                | 5.9        |
| Octachain  | 6.15   | 5.65                | 8.9        |
| Octachain  | 3.76   | 3.48                | 8.0        |
| Octachain  | 2.75   | 2.56                | 7.4        |

(21) J. E. Waltz and G. B. Taylor, *Anal. Chem.*, **19**, 448 (1947).

(22) W. O. Baker, C. S. Fuller and J. H. Heiss, *THIS JOURNAL*, **68**, 2142 (1941).

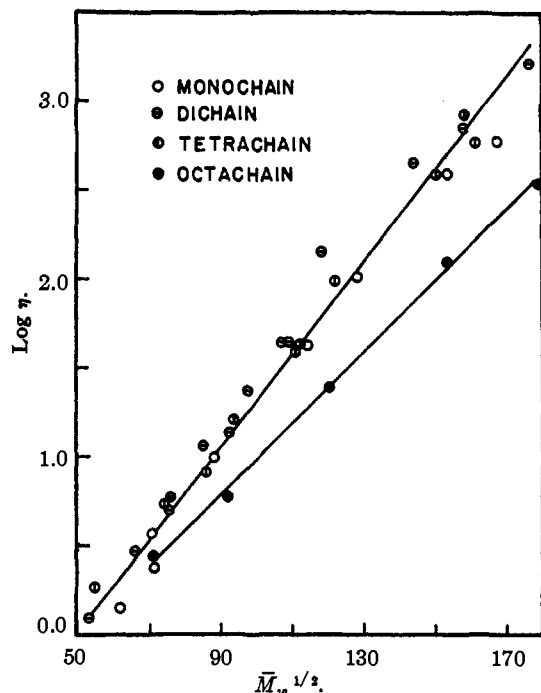


Fig. 1.—Relationships between melt viscosity and weight average molecular weight.

tration and the slope and intercept, corresponding to the intrinsic viscosity,  $[\eta]$ , were determined. Values of the slopes, intrinsic viscosities, and the error involved in calculating the "intrinsic viscosity" from the relative viscosity at  $\eta_r \cong 1.2$  are shown in Table VII. The data fail to show a definite correlation of the slope with the degree of branching.

Intrinsic viscosities of linear polymers generally depend on molecular weight according to a relationship of the form

$$[\eta] = K\bar{M}_v^a \quad (30)$$

where  $\bar{M}_v$  is the viscosity average molecular weight and  $K$  and  $a$  are constants for a given polymeric series. According to equation (28) the ratio  $\bar{M}_v/\bar{M}_n$  is practically independent of molecular weight for a given value of  $b$ . Hence, if equation (30) can be applied to the multichain polymers, plots of  $\log [\eta]$  vs.  $\bar{M}_n$  for polymers having the same  $b$  value should be linear. That this is the case over the molecular weight ranges investigated is shown in Fig. 2. The effect of branching is to lower the intrinsic viscosity at fixed number average molecular weight.

Treatment of the data by the method of least

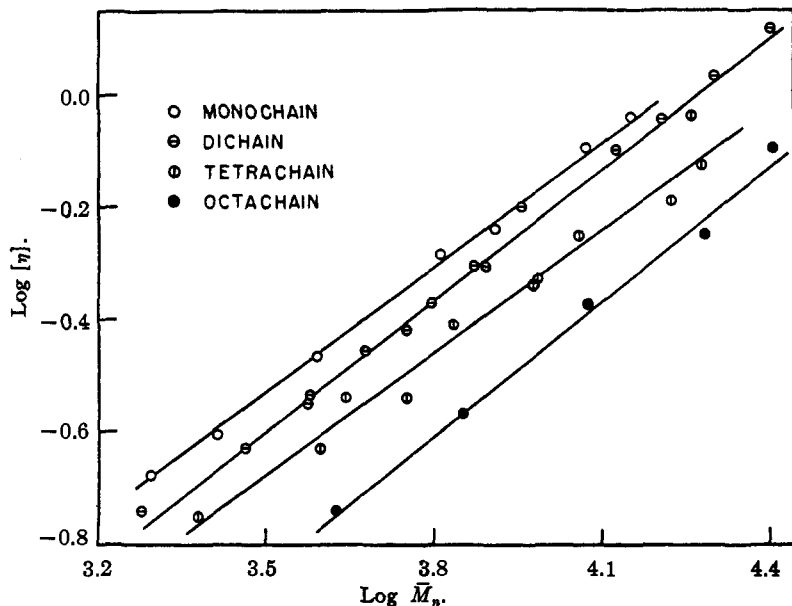


Fig. 2.—Relationships between intrinsic viscosity and number average molecular weight.

TABLE VI  
THE CHANGE OF  $(\ln \eta_r)/c$  WITH CONCENTRATION FOR SELECTED LINEAR AND MULTICHAIN POLYMERS

| Branching                        | $[\eta]$ | $d[(\ln \eta_r)/c]/dc$ | $(\ln \eta_r)/c$<br>at $\eta_r \cong 1.2$ | Error<br>in % |
|----------------------------------|----------|------------------------|---|---------------|
| (1) in sulfuric acid solution    |          |                        |   |               |
| Linear $b = 2$                   | 0.393    | $-29 \times 10^{-3}$   | 0.381                                     | 3.1           |
| Tetrachain                       | .401     | $-26 \times 10^{-3}$   | .390                                      | 2.7           |
| Octachain                        | .428     | $-21 \times 10^{-3}$   | .421                                      | 1.6           |
| Octachain                        | .608     | $-16 \times 10^{-3}$   | .603                                      | 0.8           |
| Octachain                        | .828     | $-102 \times 10^{-3}$  | .809                                      | 2.3           |
| (2) in <i>m</i> -cresol solution |          |                        |   |               |
| Linear $b = 1$                   | .553     | $-31 \times 10^{-3}$   | .542                                      | 2.0           |
| Linear $b = 2$                   | .556     | $-37 \times 10^{-3}$   | .542                                      | 2.5           |
| Tetrachain                       | .541     | $-35 \times 10^{-3}$   | .528                                      | 2.4           |
| Octachain                        | .755     | $-103 \times 10^{-3}$  | .730                                      | 3.3           |

squares yields the following empirical relationships<sup>23</sup> corresponding to equation (30):

$$b = 1 \quad \log_{10} [\eta] = 0.764 (\pm 0.016) \log_{10} \bar{M}_n - 3.20 \quad (31)$$

$$b = 2 \quad \log_{10} [\eta] = 0.794 (\pm 0.018) \log_{10} \bar{M}_n - 3.38 \quad (32)$$

$$b = 4 \quad \log_{10} [\eta] = 0.736 (\pm 0.084) \log_{10} \bar{M}_n - 3.26 \quad (33)$$

$$b = 8 \quad \log_{10} [\eta] = 0.857 (\pm 0.027) \log_{10} \bar{M}_n - 3.87 \quad (34)$$

Within the experimental error, the slopes for the first three cases ( $b = 1, 2, \text{ or } 4$ ) are the same.

Matthes,<sup>19</sup> working with low molecular weight (400 to 5,000) poly- $\epsilon$ -caproamides, obtained values of  $a = 0.67$  and  $K = 12 \times 10^{-4}$  from measurements of molecular weight by end-group analysis and intrinsic viscosities in sulfuric acid. Staudin-

(23) The errors in the slopes shown in parentheses in equations (31) to (34) were estimated as  $2\Delta y/(x_r - x_i)$  where  $x_1, y_1, x_2, y_2, \dots, x_r, y_r$  are experimental points fitted by the equation  $y = ax + b$  and  $\Delta y$  is the standard error in  $y$ .



ger and Schnell<sup>24</sup> carried out similar measurements (viscosities in *m*-cresol) over a wider range of molecular weights (1300 to 20,000), from which they concluded that the exponent  $a$  becomes equal to unity at higher molecular weights. In each case the measurements were carried out on precipitated polymers; consequently, the degree of heterogeneity of their samples cannot be appraised. Within the experimental uncertainties indicated by the scattering of the data, however, their results fit the line drawn through the points for linear polymers in Fig. 2. The values  $a = 0.72$  and  $K = 11 \times 10^{-4}$  obtained by Taylor<sup>25</sup> for poly-hexamethylenedipamide polymers are similar in magnitude to our values for linear poly- $\epsilon$ -caproamide polymers.

A part, at least, of the apparent influence of the degree of branching  $b$  on the intrinsic viscosity-number average molecular weight relationship arises from the dependence of the molecular weight distribution on  $b$ . This effect of molecular weight distribution may be eliminated by converting the molecular weights to viscosity averages, using for this purpose equation (28) and the values of  $a$  obtained from the above empirical equations representing the  $\log [\eta]$  vs.  $\bar{M}_v$  plots. Taking  $a = 0.78$  for  $b = 1, 2$  or  $4$  and  $a = 0.86$  for  $b = 8$ , the ratios of  $\bar{M}_v$  to  $\bar{M}_n$  deduced from equation (28) for  $b = 1, 2, 4$  and  $8$ , respectively, are 1.90, 1.45, 1.22 and 1.12. If the rather trivial allowance which should be made for the small proportions of linear molecules is neglected, the number average molecular weights given in Tables I, II, III and IV may be converted to viscosity averages through the use of these respective factors.

A log-log plot of intrinsic viscosities vs. viscosity average molecular weights is shown in Fig. 3. Within the experimental error the data for polymers in which  $b = 1, 2$ , and  $4$  all fall on the same straight line, while the data for polymers in which  $b = 8$  fall on a somewhat lower line. Thus the effect of branching on dilute solution viscosity becomes noticeable only in the octachain polymer series, a result paralleling the melt viscosity behavior.

**Melting Points.**—An increase in branching at the same molecular weight lowers the melting point (*cf.* Tables I, II, III, IV), and the relative amount of the depression of the melting point by branching depends on the molecular weight, decreasing as the molecular weight increases. In each case the melting points of the high molecular weight polymers ( $\bar{M}_n = 20,000$  or more) approach a constant value of about  $225^\circ$ .

#### Discussion

The results which have been presented demonstrate the feasibility of the scheme outlined in the introduction for preparing polymers with con-

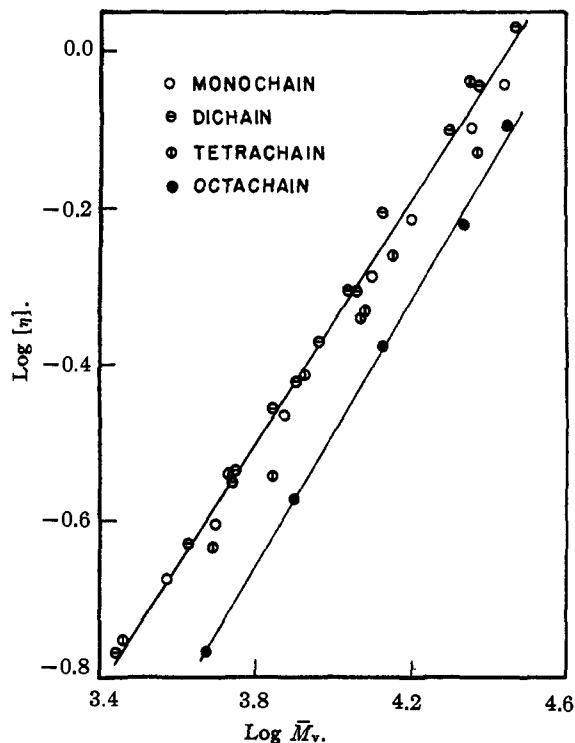


Fig. 3.—Relationships between intrinsic viscosity and viscosity average molecular weight.

trolled degrees of branching. The principle should be capable of numerous extensions. We have found, for example, that polyacrylic acids may be employed as the multifunctional centers. Some of the products obtained in this manner are of much higher molecular weight than those herein reported, and they likewise exhibit the characteristics of ungelled materials. It should be noted that since the degree of polymerization of the polyacrylic acid molecules is non-uniform,  $b$  in this case is not constant.

In place of a polymerizable lactam, an amino acid, N-carboxyamino acid anhydride, hydroxy acid, or lactone may be employed in the preparation of multichain polymers and, similarly, other types of multifunctional reactants can be used (*e. g.*, polyamines or polyhydric alcohols). In any case, it is essential that the reactants be so chosen that all terminal groups of multichain molecules be of such a character that they cannot condense with any terminal groups (or other functional groups) of other multichain molecules.

The essential difference between multichain polymer molecules and the various non-linear polymers, obtained for example by polymerizing polybasic acids and glycols (or polyhydric alcohols and dibasic acids<sup>26</sup>) or by introducing cross linkages subsequent to the polymerization<sup>27</sup> is that

(24) H. Staudinger and H. Schnell, *Die Makromolekulare Chemie*, **1**, 36 (1947).

(25) G. B. Taylor, *THIS JOURNAL*, **69**, 635 (1947).

(26) L. L. Weil, W. H. Stockmayer and C. O. Beckmann, *Abstracts of Papers, Atlantic City Meeting of the American Chemical Society*, April, 1946, p. 38P.

(27) W. O. Baker, *THIS JOURNAL*, **69**, 1125 (1947).

the molecules of the former are uniformly branched whereas those of the latter vary widely in their degree of branching or cross-linking. As a result of this difference, the latter molecules may join together to form infinite networks and gelation may be observed. Multichain polymers are incapable (barring side reactions) of yielding network structures and gelation therefore is not observed. Thus the present observations on multichain polymers lend further support to the hypothesis that gelation is the direct consequence of infinite network formation, that is, non-linearity of polymer molecules does not of itself cause gelation to occur.

The observed effects of branching on both melt and solution viscosities are smaller than might have been expected according to various speculations on this subject. Only in the case of the octachain polymers does the influence of branching (at a given molecular weight) become noticeable within the range and precision of the present experiments. It should be emphasized, however, that the influence of non-linearity may become more pronounced at much higher molecular weights. (This behavior is indicated by the melt viscosity results.)

The intrinsic viscosity probably reflects as a first approximation the effective volume of the polymer particle including the solvent which in effect flows with the particle.<sup>28,29,30</sup> Increase in branching at a fixed molecular weight should therefore be expected to decrease the intrinsic viscosity, in accordance with observation. This decrease, however, is much smaller than would be expected according to the change in effective volume predicted from consideration of random chain configuration.

The present results show that the intrinsic viscosity is not determined, even in rough approximation, by the length of the longest chain of the structure, as Staudinger has contended. Thus, Staudinger's<sup>31</sup> use of the deviation of the intrinsic viscosity from the value normally expected for a linear polymer as a direct measure of the degree of branching is wholly unjustified.

The effect of branching on melting points is small except in the low molecular weight region where the relatively large proportion of the multi-

functional unit is probably primarily responsible for the observed effect because of its inability to enter the crystallites.

**Note Added in Proof.**—Recently Melville and Youngson<sup>32</sup> have reported the synthesis of branched polyesters in which the degree of branching is allegedly the same in all molecules. Their method consists in treating a polyhydric alcohol such as pentaerythritol with polymeric ethylene adipate. Contrary to the contentions of these authors, the ester interchange process whereby these multifunctional reactants are incorporated into the polymer can be counted upon to introduce the polyalcohols at random, giving rise to a statistical array of molecular species in which the number of branching units per molecule is zero, one, two, etc. Evidence that this is so is afforded by the inference that gelation<sup>33</sup> occurs on further polymerization.

The addition of a multifunctional reactant (RA<sub>b</sub>) to a polymerizing system derived from A—A and B—B type bifunctional reactants leads to structural differences in the resultant polymer which must be clearly differentiated from those occurring in a system containing A—B units exclusively. Uniformity of molecular pattern is impossible to achieve in polymerizations of the former type owing to the capacity of the reactants to unite variable numbers of the multifunctional reactant in the same molecule, and owing to the inherent random nature of the reactions involved (including ester or amide interchange). In experiments not reported here<sup>34</sup> we have investigated the influence of our tetrabasic acid on the polymerization of a diamine with a dibasic acid, a system analogous to those investigated by Melville and Youngson. In contrast to the polymerizations reported in this paper, such a system is highly susceptible to gelation. Gel points are in satisfactory agreement with statistical theory,<sup>35</sup> which again substantiates the random nature of these reactions.

### Summary

A general method for the synthesis of branched chain polymers, in which all chains in a given molecule are united at a central multifunctional unit, has been demonstrated. Four series of polymers have been prepared in which the number of chains subtended by the central unit is one, two, four and eight, respectively.

The logarithm of the melt viscosity for a given series of polymers varies linearly with the square root of the weight average molecular weight;  $[\eta]$  is proportional to  $M^a$ .

The effect of branching in the melt viscosity and in the intrinsic viscosity relationships becomes noticeable only when the amount of branching becomes large, that is, when the branching unit functionality is increased to eight.

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