at 350°, it is doubtful whether they actually were dealing with a decarboxylation of propionate.[10]

Acknowledgment.—The authors wish to thank Professor Henry Gilman for his assistance in this investigation.

Summary

The reliability of the reactions used to locate carbon dioxide fixed in propionic acid by bacterial fermentations has been investigated.

Alkaline permanganate oxidation is not a reliable method of decarboxylating propionic acid. Dry distillation of barium propionate gives reliable results under proper experimental conditions. The results have been obtained using synthetic propionic acid containing the isotope of carbon (C^{13}) as a tracer of carboxyl carbon.

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(10) After completion of this investigation, Dr. Ruben informed us by private communication that they have been unable to duplicate their previous results[5] and have now found radioactive carbon only in the carboxyl group of the propionic acid.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

Macromolecular Properties of Linear Polyesters: Molecular Weight Determinations on ω-OH-Undecanoic Self-polyesters

BY W. O. BAKER, C. S. FULLER AND J. H. HEISS, JR.

Polymers resulting from the self-esterification of ω-OH acids represent isochemical systems whose number average molecular weights can be unambiguously determined by end group titration. In addition they consist of molecules which are strictly linear and structurally well defined.[1] They are therefore model macromolecular assemblies on which to test the Staudinger viscosity relation,[2,3,4] the connection between polymer size and solubility,[5] and the relation between melt viscosity and average molecular weight.[6] The present investigation attempts to explore and compare these relationships for the ω-OH-undecanoic series of polyesters of high purity and known average size. In addition, it was desired to present further experimental evidence for the chain segment theory of macromolecular properties, which has been found to explain satisfactorily the melting point and solid state behavior[7] of these substances.

Methods

Materials.—The pure ω-hydroxyundecanoic acid was prepared and isolated by Mr. W. S. Bishop of these Laboratories, using largely the method of Walker and Lumsden.[8] Equal weights of the acid were weighed into cylindrical Pyrex reaction tubes fitted with ground-glass stoppers containing a gas inlet tube extending to the bottom of the reactant. The reaction vessels had exhaust tubes near the top. All polymers were prepared in an electric furnace comprising a metal block of high heat capacity whose temperature was kept at 200 ± 1° and was automatically recorded throughout the reaction. Uniformity of temperature all around the reacting mass was established by tests with thermocouples at various points. Pure tank hydrogen was passed through a copper reducing furnace and dried over sulfuric acid. It was then passed through the reaction tubes at a nearly constant rate. The control of gas ebullition through the polymer melt is important not only in water removal during the condensation but also as a stirring agent. The gas flow through each reaction tube could be independently checked at any time by a flowmeter by-pass. There was no reflux in the system.

Equivalent Weights.—Solutions of equal weight concentrations within 0.2% were made by dissolving weighed portions of the dried polyesters in reagent chloroform. These corresponded always to about 1 g. of polymer per 100 cc. of solution, and were exceedingly dilute in terms of normality. They were titrated at room temperature with 0.0096 *N* alcoholic sodium hydroxide standardized with Bureau of Standards potassium acid phthalate. No information on the probable degree of dissociation of the polymer acids or their salts in organic solvents is available. A pronounced effect of non-aqueous solvents on the behavior of organic acids has been widely noted.[9,10] However, the end-points with constant phenolphthalein concentrations as indicators were sharp, and it is felt that the equivalent weights (number average molecular weights) thus obtained are at least equal in accuracy to those of any other size determination on macromolecules.

Solution Viscosity.—The solution viscosities were determined on solutions of the polymer in reagent chloroform. It was found of critical importance for use in the Ostwald

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(1) Carothers and Van Natta, THIS JOURNAL, **55**, 4714 (1933).

(2) Staudinger, *Ber.*, **65**, 267 (1932).

(3) Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932.

(4) Kraemer and Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932).

(5) Schulz, *Z. physik. Chem.*, **A179**, 321 (1937).

(6) Flory, THIS JOURNAL, **62**, 1057 (1940).

(7) Fuller, Baker and Pape, *ibid.*, **62**, 3275 (1940).

(8) Walker and Lumsden, *J. Chem. Ind.*, **79**, 1193 (1902).

(9) Richardson, *Proc. Roy. Soc.* (London), **B115**, 170 (1934).

(10) Parton and Gibbons, *Trans. Faraday Soc.*, **35**, 542 (1939

viscometer to filter through sintered glass not only the pure chloroform but also the solution. The latter operation was done under reduced pressure in such a way that tests showed no change in concentration resulted. The viscometers were thermostated in a water-bath at 25 ± 0.02° and calibrated pipets assured constant volume of solutions, and hence constant fluid heads. General considerations of the capillary viscometer, as discussed, for instance, by Raaschon,[11] were applied to all measurements. Where significant, kinetic energy corrections were used.[12,13] They were never of importance as for efflux times of more than forty seconds the correction for most liquids is ~0.2 second. Efflux times for these solutions were greater than 150 seconds; t_0 for chloroform was 147.7 seconds. Also, for more than 2.5 cc., the drainage error for small capillaries becomes unimportant; a 5-cc. volume was used in these determinations. The correction for the loss of head from the velocity gradient in the capillary[14] was also found unessential. Timing was by a stop watch checked against a split-second precision electric timer, read to ±0.05 second. Some of the time values were read directly with the electric instrument. The included values are averages from repeated checks whose maximum deviation was 0.2 second. Chloroform was a satisfactory solvent; the usual differences were found in other solvents. Association of the polymer molecules was probably negligible, as even that of a homologous monomer was found to be vanishingly small.[15]

Melt Viscosity.—Small steel spheres carefully selected for uniformity were dropped into 7 × 0.8 cm. Pyrex tubes containing liquids of viscosity in the range of the molten polymers, as a viscometer standardization. Their time of fall through a short interval on the scale of a cathetometer was measured when they were midway through the liquid column, to minimize end effects. The calibrating oils were obtained from the Bureau of Standards. The correction of Stokes' law for wall and end effect developed by Ladenburg[16] when computed from the dimensions of the system agreed within 3% with the constant obtained from the calibrating fluids. Thus, satisfactory construction was indicated. The calibrated constant was used, and gave precise absolute viscosities. The tube was completely within a leveled electric furnace consisting of a brass block bored for the tube, a sealed mercury regulator containing hydrogen, and the thermometer. The temperature of the measurements was 90 ± 0.5°. Tests showed that the polyesters did not decompose or change viscosity during three hours at this temperature; they were entirely stable over the measuring period. Melts were freed from gas bubbles by evacuation. Observation with the cathetometer was through insulated windows in the furnace, with strong illumination.

Precipitability.—Solutions of 1.0000 (± 0.0008) g. of the polyester in 50.00 cc. of chloroform were maintained at 25.0° in a thermostat and were slowly titrated, under isothermal conditions, with absolute methyl alcohol from a calibrated buret. Constant strong illumination with a dark background was employed with all samples, and the non-solvent, methyl alcohol, was added until a faint translucent turbidity indicated the end-point. The flask was agitated vigorously during the addition and was covered to avoid solvent evaporation. The end-points were sharp (within a fraction of a drop) and could be reproduced within 1%. Although the solubilities of polystyrenes have been similarly studied,[17] as well as those of many other synthetic and natural high polymers,[18] accurate determinations on the basis of Brönsted's limiting solubility concept[19,20] (strictly applicable only to homogeneous systems) are possible only when a crystalline phase separates. This has been previously attained for a single species in pure form[21] and the present report records results for crystalline polymers containing a distribution of species of known *average* size. X-Ray powder patterns confirmed the expected high crystallinity of the solid contributing the initial cloudiness.

The immediate appearance of turbidity on separation of a new phase has been compared for sensitivity to the abrupt change in viscosity of a polymer solution on the addition of a critical amount of non-solvent[22]; the two methods agreed, so that seemingly invisible aggregates of swollen polymer do not complicate comparative solubility measurements by the turbidity method. A nephelometer was used by the workers cited.

Results

Kinetics.—The kinetics of some polyesterifications involving dibasic acids and glycols have been found by Flory[23] to approximate third-order rates. The self-esterification of ω-OH-undecanoic acid seems also roughly to follow the third-order reaction course, which requires a linear relation between the square of the degree of polymerization $(DP)^2$ and the time.[24] However, as is seen from curve II of Fig. 1, at high molecular weights (and high melt viscosities) there may be some deviation from linearity. This departure is much worse for a plot assuming a second-order reaction, as noted from curve I. The viscous retardation of water removal from the melts of high viscosity may also contribute to the apparent fluctuations in the rate.[24]

Figure 1 is included largely to show that the polymer-homologs were prepared free from any violent kinetic disturbances, and consequently there is implied a comparable molecular distribution function for the various preparations. Kinetic influences on molecular weight averages

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[11] Raaschon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 35 (1938).
[12] Ubbelohde, *Petroleum Z.*, **29**, 23 (1933).
[13] Schulz, *Z. Elektrochem.*, **43**, 479 (1937).
[14] Zeitfuchs, *Natl. Petroleum News*, [7] **29**, 68 (1937).
[15] Davies, *Trans. Faraday Soc.*, **34**, 410 (1938).
[16] Ladenburg, *Ann. Physik*, **23**, 287 (1907); **23**, 9, 447 (1907
[17] Staudinger and Heuer, *Z. physik. Chem.*, **A171**, 129 (1934).
[18] Coltof, *J. Soc. Chem. Ind.*, **56**, 363 (1937).
[19] Brönsted, *Compt. rend. trav. lab. Carlsberg, ser. chim.*, **22** 99 (1938).
[20] Brönsted and Volqvartz, *Trans. Faraday Soc.*, **35**, 576 (1939).
[21] Lovell and Hibbert, THIS JOURNAL, **61**, 1916 (1939).
[22] Sakurada and Saito, *Kolloid-Z.*, **81**, 208 (1937).
[23] Flory, THIS JOURNAL, **61**, 3334 (1939).
[24] Schulz, *Z. physik. Chem.*, **A182**, 127 (1938).

have been recognized,[25] but the randomness of reaction assumption of Flory[26] seems justified in the present materials.

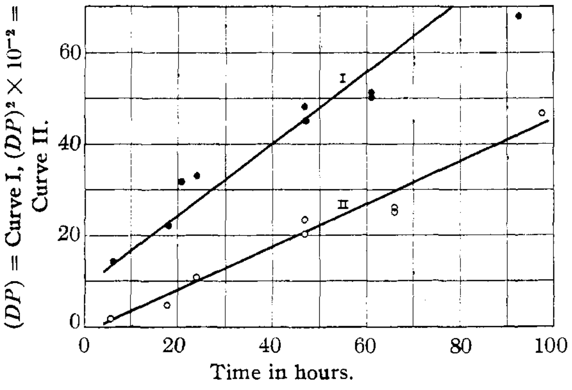

Fig. 1.—Rate of formation of polyundecanoates plotted as a second-order reaction (curve I) and as a third-order reaction (curve II).

Molecular Weights and Solution Viscosity.—Equivalent weight determinations on the polymers $H[O(CH_2)_{10}C_{=O}]_nOH$ yields the number average molecular weight[4]

$$M_n = \Sigma_i \frac{f_i}{M_i} \qquad (1)$$

where f_i is the fractional weight of the constituent of molecular weight M_i. Solution viscosity measurements give a weight average molecular weight, $M_w = \Sigma_i f_i M_i$, where the previous definitions obtain. Table I includes the results of titration and viscosity determinations on the undecanoate series. The viscosities were all at concentrations of 0.4000 ± 0.0020 g. per 100 cc. of solution. Each solution was prepared directly in a volumetric flask. The viscosity of the pure solvent η_0 and that of the solution, η_1 are related to η_{sp} by

$$\eta_{sp} = \eta_r - 1 = \frac{\eta_1}{\eta_0} - 1 \qquad (2)$$

TABLE I

Compd.	Equiv. wt.	$(DP)_N$	η_r	η_{sp}/c	$\ln \eta_r/c$	γ^*	Ml. of precipitant
U14	12,600	68	1.408	1.018	0.854	0.498	49.59
U13	12,500	68	1.409	1.026	.860	.500	49.90
U12	11,100	60	1.368	0.919	.783	.503	50.48
U11	10,950	59	1.358	.894	.764	.503	50.48
U10	9,600	52	1.333	.836	.721	.503	50.55
U9	9,500	51	1.310	.775	.675	.508	51.60
U8	9,200	50	1.311	.775	.675	.508	51.47
U7	8,800	48	1.276	.691	.609	.516	53.25
U6	8,200	45	1.260	.650	.578	.519	53.83
U5	6,000	33	1.190	.473	.434	.540	58.43
U4	5,800	32	1.190	.472	.432	.541	58.87
U3	4,900	27	1.163	.406	.376	.552	61.74
U2	4,000	22	1.134	.335	.314	.574	67.25
U1	2,560	14	1.094	.236	.226	.605	76.63
U0	202	1	1.014	.037	.036	..	...

Figure 2 shows the application of the original Staudinger equation,[2,3] modified by a small additive constant, through a molecular weight range of 202 to greater than 25,000 weight average. The number average molecular weight has been plotted in Fig. 2 since it was obtained directly from the end-group determination, and the ideal distribution[26] of the undecanoate series confers a virtually constant ratio between the number and weight averages. Only this constant ratio permits the use of M_n rather than M_w in Fig. 2. M_w is always involved in viscosity measurements.[27] The computed value of the ratio M_n/M_w for the highest polyundecanoate is 0.51, for the lowest, 0.52, while for the monomer it is, of course, 1, but the monomer falls too close to the origin to be affected by the slopes of the other curves.[28]

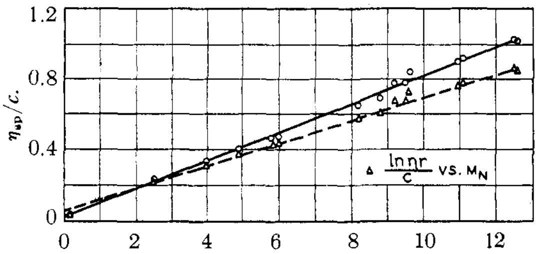

Fig. 2.—Relation between solution viscosity and end group molecular weights of polyundecanoates.

The modified Staudinger equation, for the upper curve on Fig. 2, *for the given concentration and structure*, is

$$\eta_{sp}/c = K'M_w + b \qquad (3)$$

in agreement with other investigations.[4,29,30,31] Staudinger originally proposed no added constant, but has subsequently used one.[32] Unpublished work from these laboratories agrees with recent evidence[33,34] from other compounds that large variations in K' in a given series arise from structural changes, like branching. Further, K'

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[25] Schulz, *Z. physik. Chem.*, **B30**, 379 (1935); **B32**, 27 (1936).

[26] Flory, THIS JOURNAL, **58**, 1877 (1936).

[27] Kraemer and Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

[28] We discuss the solution viscosity results almost entirely elsewhere,[28a] concerning the mechanism of flow, the concentration dependence, its formulation, and the accurate determination of relative molecular weights. Such considerations explain the use of the concentration 0.4 g. per 100 cc. for the molecular weight range, as employed in Table I and Fig. 2. This is, thus, a satisfactory concentration for the present purpose of showing that solution viscosity agrees with three other independent methods of molecular weight determination.

[28a] Baker, Fuller and Heiss, THIS JOURNAL, **63**, in press (1941).

[29] Meyer and van der Wijk, *Helv. Chim. Acta*, **18**, 1067 (1935).

[30] Fordyce and Hibbert, THIS JOURNAL, **61**, 1912 (1939); Lovell and Hibbert, *ibid.*, **62**, 2140 (1940).

[31] Flory and Stickney, *ibid.*, **62**, 3032 (1940).

[32] Staudinger and Daumiller, *Ann.*, **529**, 219 (1937).

[33] Staudinger and Schneiders, *ibid.*, **541**, 151 (1939).

[34] Schulz, *Z. physik. Chem.*, **B44**, 227 (1939).

is really not molecular weight independent but the variation is large only at low molecular weights.[28,35] b is a term perhaps associated with polymer interactions in the flow process.

For the polyundecanoates, a suitable adaptation of the Staudinger equation is

$$\eta_{sp}/c = 0.42 \times 10^{-4} M_w - 0.03, c = 0.4 \text{ g./100 cc.} \quad (4)$$

or

$$\ln \eta_r/c = 0.31 \times 10^{-4} M_w + 0.07 \quad (5)$$

As expected,[36] the two formulations converge at low values of η_r (low concentrations or molecular weights).

Figure 2 demonstrates agreement between the two methods of molecular weight determination, end-group determination and solution viscosity at a given concentration, on unfractionated polymers of chain length and of properties extending well into technical application.

Melt Viscosity.—Flory[6] has reported a linear relation between $\ln \eta$ and $M_w^{1/2}$, where η is melt viscosity at a given temperature, and has applied the method to molecular weight studies. Representative melt viscosity data for the polyundecanoates are included in Table II.

TABLE II

Compd.	η Poise 90.0°C.	$\ln \eta$	M_w	$M_w^{1/2}$	Z_w	$Z_w^{1/2}$
U1	9.8	2.2824	5,000	70.7	326	18.1
U2	36.3	3.5918	8,000	89.4	522	22.8
U5	140.5	4.9440	12,000	109.5	782	28.0
U6	560.0	6.3279	16,400	128.1	1070	32.7
U12	2980	7.9997	22,200	149.0	1443	38.0

Z_w is the number of chain atoms in the molecules of weight average molecular weight M_w. Figure 3 confirms Flory's relation

$$\eta = Ae^{BZ_w^{1/2}} \quad (6)$$

including data for a point of sixfold the viscosity of any previously reported. Figure 3 again contains M_n, the direct titration value, but only because of the constant ratio previously discussed; M_w is the fundamental average in melt viscosity–molecular weight relations.

The molecular weight dependence of viscosity in homologous series has been repeatedly expressed, *e. g.*, by Dunstan[37]

$$\ln \eta = aM + b \quad (7)$$

where a is a general constant and b applies to a given series. A recent formulation[38] is

$$\ln \eta = \frac{A \ln M - B}{T} - 2/3 \ln (CP) \quad (8)$$

where A, B and C are constants, and P is the parachor. Hence, the exponential relation of viscosity to molecular weight of homologs is well known. Batschinski[39,40] expressed the viscosity as inversely proportional to the "free volume," with some variations for substances of high molecular weight. Bingham and Kinney[41] noted that the logarithm of the free volumes is a linear function of the number of carbon atoms in the chain for several short-chain series. In equation (6), η is not very sensitive to the exponent of Z_w. In many cases, an exact evaluation of this exponent may be difficult, but it will not remain $^1/_2$ for short-chain molecules, and this variation suggests that very long chains flow by an alteration of the usual process. Kauzmann and Eyring,[42] as a consequence of Eyring's general theory of viscosity, have proposed that the segment behavior of linear polymers noted for many kinetic processes[43] operates in viscous flow. They have thus derived the factor $BZ_w^{1/2}$ as arising from the coöperation or articulation of the segments as, one or a few at a time, they progress to give eventually a new position to the whole macromolecule. Such a derivation arises from estimating the probability that a segment will remain in its old or "flow" into a new volume.

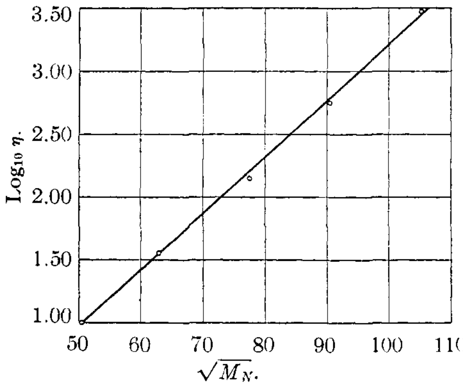

Fig. 3.—Dependence of melt viscosity on molecular weight of polyundecanoates.

The probability that a given segment will occupy a new volume to contribute to the forward motion of the whole molecule is proportional to $(1 - (BZ_w^{1/2}/n))^n$, where n is the number of segments.[42]

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[35] Powell, Clark and Eyring, "Conference on Viscosity," New York Academy of Sciences, February, 1941.

[36] Hess and Sakurada, *Ber.*, **64**, 1183 (1931).

[37] Dunstan, *Z. physik. Chem.*, **56**, 370 (1906).

[38] Lewis, *J. Chem. Soc.*, 1063 (1938).

[39] Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).

[40] Batschinski, *Physik. Z.*, **13**, 1157 (1913).

[41] Bingham and Kinney, *J. Applied Physics*, **11**, 192 (1940).

[42] Kauzmann and Eyring, THIS JOURNAL, **62**, 3113 (1940).

[43] Reference 7 and references therein.

This expression requires, however, certain qualifications, as Eyring and Kauzmann note; for example, n must be much larger than $BZ_w^{1/2}$. We examine briefly below how actually n is related to the expected segment length, for given experiments. For the polyundecanoates, equation (6) may be written

$$\eta = e^{(0.28\, Z_w^{1/2} - 3.47)} \qquad (9)$$

Flory's value of the exponent at a somewhat higher temperature for a dibasic acid–glycol polyester, decamethylene sebacate, is $0.26\ Z_w^{1/2} - 3.29$, in agreement with (9). For polymer U12 of Table II, $BZ_w^{1/2} = 10.64$. Table III shows values of the probability function $e - BZ_w^{1/2}$ observed, and calculated from $(1 - (BZ_w^{1/2}/n))^n$, for various values of n. The probable size of n, then, should not be regarded as set by the approximate probability function; it is an average quantity probably between 12 and 30 chain atoms, and is certainly greater than 1. A more explicit articulation factor may well yield n more exactly. Kauzmann and Eyring[42] have demonstrated an interesting thermodynamic estimation of segment length from the temperature coefficient of the melt viscosity.

TABLE III

Chain atoms per segment	n	$(1 - (BZ_w^{1/2}/)n)^n$ calcd.	$e^{-BZ_w^{1/2}} \approx (1 - (BZ_w^{1/2}/n))^n$ obsd.
1	1400	2.3×10^{-5}	2.4×10^{-5}
12	117	1.4×10^{-5}	2.4×10^{-5}
30	47	5.9×10^{-6}	2.4×10^{-5}
100	14	2.1×10^{-9}	2.4×10^{-5}

The data of Table II and Fig. 3 provide another consistent independent measurement of chain length for the macromolecular undecanoates. The mechanism of the flow apparently involves segment action.

Solubility.—The sharp dependence of solubility on molecular weight for an "isochemical series" noted and interpreted by Brönsted[19,20] had been earlier less consciously explored by non-solvent additions to polymer solutions, for example, by Mardles.[44] The method was formulated quantitatively by Schulz,[5] and applied to some polystyrene systems, in terms of the degree of polymerization as a function of the fraction (of the total volume) of non-solvent addition required to produce the first detectable turbidity. Schulz' approximation may be written

$$\gamma^* = \alpha + (\beta/DP) \qquad (10)$$

where γ^* is fraction of the total volume of non-solvent at end-point, for a given constant initial weight concentration (or base-molar concentration) of polymer; α and β are constants for a given series, and DP is the degree of polymerization. Rigorously, it can be shown that the dependence for a pure crystalline material is

$$\gamma^* \propto \frac{1}{DP} (\ln (DP) - K_1) \qquad (11)$$

where K_1 is a composite constant, but the Schulz equation (10) will be considered here. It has been found to give the expected linearity with four polyoxyethylene glycols of a single species each,[21] but has been tested otherwise only for polystyrene which separates as a non-crystalline swollen substrate.[5,17] The polyundecanoates separate as a highly crystalline phase; even the minute particles causing the initial turbidity give sharp Debye–Scherrer X-ray diffractions with line breadths and background scattering indicating high crystallinity. Also, the high molecular polyundecanoate has a number average chain of 816 atoms or weight average of 1632, whereas the highest crystalline polyoxyethylene glycol has 558 chain atoms,[21] so that the precipitability relation has now been considered for long chains of crystalline polymers containing a "natural" distribution of species, such as would obtain in technical studies.

Figure 4, whose data are also included in Table I, shows regions of validity of equation (10). For low molecular weights, disproportionately smaller amounts of non-solvent are required to effect precipitation than would be expected from the results on longer chain lengths. The point on Fig. 4 for the lowest $(DP)_N$ is from polymer U_1, whose short average chain length implies a large fraction of low species (confirmed by fractionation). Thus, since the precipitabilities were determined at equal weight concentrations for the series, the U_t solution had a notably higher molar concentration than any of the others. It is possible, excluding experimental error, that a relatively higher requisite solvation, without a compensating free energy decrease (as from large kinking entropy in the really long chains), will make the very low polymers appear less soluble than expected from average chain length alone. Too, activities may differ from apparent concentrations. Throughout, of course, the precipitation is a fractionation process. This is shown in Table IV, where η_{sp}/c values for a precipitate

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(44) Mardles, *J. Soc. Chem. Ind.*, **42**, 1277 (1923); *J. Chem. Soc.*, **125**, 2244 (1924).

formed by addition of extra nonsolvent to a given solution are compared to the values for the original polymer. Seemingly complications of liquid phase separation, irreversibility and the like which enter in cellulose acetate and nitrate systems, among others,[45] are absent.

TABLE IV

Polyundecanoate	η_{sp}/c	η_{sp}/c of original
U4′	0.909	0.472
U14′	1.808	1.018
U13′	1.754	1.026

Alternate variables for solubility measurement of macromolecules include concentration and temperature. Schulz's[5] relation proposes both a dependence of the distribution of a polymer between two liquid phases on molecular weight, and a linear dependency of γ^* on ln c, where c is the polymer concentration. Unpublished studies agree generally with the $\gamma^* - \ln c$ form. The slopes of such curves may be developed to reflect somewhat the homogeneity or distribution of the system.

Polymer precipitability frequently exhibits a very strong temperature dependence. Extensive technical use of "cloud points" and turbidity points illustrates recognition of such behavior. These points are Brönsted's "critical temperatures." Schulz[46] observed that the same volume of methyl alcohol was required to precipitate a given polystyrene of *DP* 385 at 0° as for one of *DP* 2200 at 38°. In γ^* determinations like those of the present report, precision in temperature control is essential. Over the range in which α in equation (10) is temperature independent, γ^*, and hence *DP*, is a linear function of *T*. Convenient relative molecular weight determinations may thus be made if the temperature is varied (with agitation to assure equilibrium) on solvent–non-solvent mixtures of constant concentration. The term α involves the change of potential energy of the polymer molecule between the precipitated and dissolved states as a function of solvent–solute and solvent–solvent interaction, and will not be very constant with temperature, for example, in hydrogen bonding solvents. In general, a determination of the turbidity point with temperature in a solvent–non-solvent mixture will excel such a determination in a solution of the solvent alone, for, among other reasons, the swelling stage in the solvent alone makes a poorly defined substrate. Also, the mixtures generally show a steeper temperature coefficient for solution than that of the pure solvent. The occurrence of a well-crystallized substrate, such as occurs in the polyundecanoates, also has been subsequently discussed by Schulz.[47]

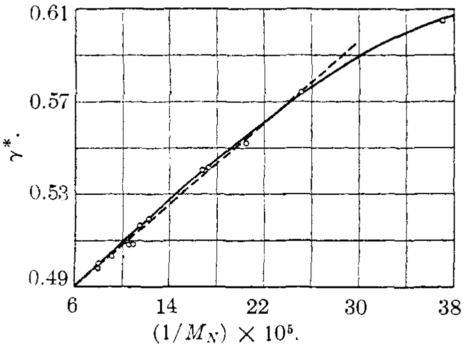

Fig. 4.—Precipitability, γ^*, of polyundecanoates as a function of molecular weight.

The simple precipitability equations will require modification for non-linear macromolecules. Schulz[5] first reported γ^* as independent of the degree of branching. Unpublished studies from these laboratories on controlled branching indicated a somewhat anomalously high solubility for slightly branched molecules, and Schulz has recently recorded similar conclusions.[48]

Branching probably alters the entropy as well as the energy of dissolved polymer molecules, *e. g.*, it reduces the flexibility and hence kinking randomness of the chains. Schulz's theoretical proposals neglect the entropy change on solution, *i. e.*, they treat the potential energy rather than the free energy change accompanying solution. However, the entropy change will also be a function of chain length. For instance, in an ideal solution, the entire free energy change results from the entropy of mixing

$$\overline{\Delta F_1} = -T\overline{\Delta S_1} = RT \ln N_s \qquad (12)$$

where N_s is the mole fraction of the solute. Now, each polymer chain molecule acts as a composite kinetic unit, according to the segment theory.[7,49,50] Hence, segment length (really, the number of segments per molecule) affects the evaluation of N_s, and especially, also, the degree of articulation of the segments. These factors are essential in any complete theory of polymer solubilities.

Entropy effects are especially evident in temperature and structure solubility variations of

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(45) Papkov, Rogovin and Kargin, *Acta Physicochimica U. R. S. S.*, **8**, 647 (1938).

(46) Schulz, *Z. physik. Chem.*, **B46**, 137 (1940).

(47) Schulz and Nordt, *J. prakt. Chem.*, **185**, 103 (1940).

(48) Schulz and Jirgensons, *Z. physik. Chem.*, **B46**, 105 (1940).

(49) Meyer, *ibid.*, **B44**, 583 (1940); Meyer and van der Wijk, *Helv. Chim. Acta*, **23**, 488 (1940).

(50) Powell, Clark and Eyring. *J. Chem. Phys.*, **9** 268 (1941).

polymers. Baker and Smyth have shown that the melting points are increased and the solubilities decreased (at a given temperature) for molecules of such structures (or at such temperatures) that they have gained extra degrees of librational freedom in the solid state[51,52] compared to isomeric or similar, but non-librating, molecules. This concept has been applied to the fusion and solution of polymers by Mark.[53] Polymer chains which are quite cylindrically symmetrical, flexible and weakly interacting may show a surprisingly reduced solubility and temperature coefficient of solution because of their entropy gain (maintenance of a free energy minimum) in the solid which makes a phase change less desirable thermodynamically. Long chain paraffins give some evidence of this behavior. This factor must always be considered in conjunction with the forces between the molecules, which in many cases are predominant in determining solubility. Chain motion has been detected in many solid polymers.[7,54,55,56] Further, as noted before, branched polymers do show different, higher solubilities than unbranched ones of about the same constitution. Also, although an increase in temperature loosens the intermolecular forces holding a given polymer in the solid, it also increases molecular freedom in the solid, and for suitable structures (symmetrical chains, etc.) the temperature coefficient of solubility is reduced compared to the very high value it generally shows.

Finally, one further aspect of polymer solubility as defined by Fig. 4 is whether the fractionation which accompanies the end-point, as shown in Table IV, means that the precipitability method of molecular weight determination, whether by temperature change or nonsolvent addition, is badly sensitive to the form of the high-molecular end of the distribution curve for the given system. The results of Erbring suggest that this is probably not a serious limitation, since he found for a variety of systems[57] that nearly all of the polymer was precipitated by the addition of a few tenths of a cc. of precipitant after the initial turbidity appeared. This would, of course, not occur in a very wide distribution of molecular weights.

The nature of the precipitability relation to molecular weight causes strong suppression of apparent solubility differences at high molecular weights. It also is possible that the convergence of melting point with increasing molecular size noted for crystalline polymers as a consequence of segment action[7] may be paralleled by a solution behavior where the energy and entropy dependence on chain length compensate to leave little variation of solubility with size for very large molecules.

Summary

A definitive study of simple molecular weight determinations has been attempted on a series of strictly isochemical linear self-polyesters from ω-OH-undecanoic acid. The methods of end-group analysis, solution viscosity, melt viscosity and precipitability have been evaluated for fifteen compounds including the average chain length range 13 to 1440 (weight average) chain atoms. Concordant results obtained emphasize the validity of the molecular concept of resins and polymers, since the theoretical principles of each of the four methods apply to molecular assemblies. The polymer molecules have been investigated by chemical reaction (titration), kinetic interaction in dilute solution (solution viscosity), kinetic interaction in a condensed polymer phase (melt viscosity) and by "equilibrium" interaction with a nonsolvent in solution (precipitability). Each measurement yields consistent values for the suitable average molecular weight, and supports the molecular distribution statistics of Flory and Schulz.

All of the solution methods require careful choice of polymer concentration, and this factor is especially critical in application of the Staudinger or somewhat more preferable Arrhenius equation. The strong concentration dependence of the solution viscosity, and its systematic relation to chain length are indicated.

All of the kinetic behavior of chain polymers strongly suggests segment action, *i. e.*, the coupled action of separate sections in a given chain.

The entropy as well as the energy must be regarded in treatments of polymer solubility as a function of chain length, structure or temperature, since kinking randomness in the solution[58] and segment motion in the solid are operating in long-chain thermodynamics.

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[51] Baker and Smyth, THIS JOURNAL, **61**, 1695 (1939).

[52] For solubility data, see Smyth and Lewis, *ibid.*, **62**, 949 (1940).

[53] Mark, *J. Applied Phys.*, **12**, 41 (1941).

[54] Yager, *Trans. Electrochem. Soc.*, **74**, 113 (1938).

[55] Davies, Miller and Busse, THIS JOURNAL, **63**, 361 (1941).

[56] Fuoss, *ibid.*, **63**, 369 (1941).

[57] Erbring, *Kolloid-Z.*, **90**, 17 (1940), and references therein.

[58] See also E. Hückel, *Z. Elektrochem.*, **42**, 753 (1936).