[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Comparative Osmotic and Viscosity Measurements with Polystyrene Fractions

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Flory,[2a] Huggins[2b] and Powell, Clark and Eyring[3] have recently very substantially improved the theory of dilute solutions of high polymers and several authors[4] have carried out osmotic, cryoscopic and viscosity measurements with fractionated high polymers, which allow testing the theoretical conclusions. This paper attempts to complement these investigations by a study of the behavior of dilute solutions of three polystyrene samples, which were prepared by polymerization at 60, 120 and 180°, respectively.

Materials

Commercial styrene was purified by washing with a dilute aqueous sodium hydroxide solution and repeated distillation, until it was characterized by the following data: b. p. 146°, *n* 1.5434, *d* 0.907.

Three samples of this material were sealed into glass tubes under nitrogen in the presence of 0.02 weight per cent. benzoyl peroxide and placed in thermostats which were kept at 60, 120 and 180°, respectively. Polymerization was allowed to take place until about 40 weight per cent. of each sample was polymerized. The tubes were then cooled to room temperature, opened and the highly viscous solutions of the polymer in the monomer diluted with a tenfold amount of toluene. The clear solutions, which contained about 4-5% polymer by weight, were then diluted with methanol and the precipitated polymer filtered off. Three specimens were obtained (about 10 g. each), which were repeatedly washed with methanol and finally dried *in vacuo*.

Fractionation

The fractionation was carried out similary to the procedure as first described by Staudinger[5] and as later repeated and not inconsiderably simplified and improved by various authors.[6]

Our procedure was as follows: The material which was to be fractionated was dissolved in methyl ethyl ketone at room temperature at a concentration of 2% by weight. Methanol was then added from a buret until the solution became cloudy.

By slowly warming the system, the cloudiness was completely removed and then the solution was slowly and under gentle stirring cooled to 5°. During this process the gel phase reappears and settles out. It can be separated from the sol phase without difficulty. After the separation the precipitated fraction was redissolved in toluene, completely reprecipitated with an excess of methanol, filtered off and repeatedly washed with methanol. Completely colorless powders were obtained in this way.

The supernatant solution of this (first) fraction was warmed to room temperature again. A small increment of methanol was added, and the above procedure repeated. The whole process was then continued until all of the precipitable polystyrene had been removed. In most cases, this amounted to about 94-95% of the original polymer.

The fractions obtained by the above method were subsequently subjected to two consecutive refractionations of the same type. The production of the gel phase by cooling, rather than by addition of non-solvent at constant temperature, facilitated the establishment of equilibrium between the two phases and therefore affected beneficially the resolving power of the fractionation method.

Some twenty fractions were prepared of each of the three samples and from them four were selected for further investigation. The selection took place in such a way that these four fractions of each sample covered approximately uniformly the whole range of polymerization degree of the material.

Viscosity Measurements

The (four) fractions of the three samples (altogether twelve) were dissolved in toluene and the viscosity of solution up to volume concentrations of about 1.0% was determined in an Ostwald viscosimeter at 30 and 40°. The procedure has been described in a previous paper[7] and need not be repeated; the specific viscosities were calculated in the usual way and finally η_{sp}/c_v was plotted *versus* c_v (compare Fig. 1).

Osmotic Measurements

The solutions of the various fractions in toluene were also used to measure the osmotic pressure with the aid of the instrument described by Fuoss and Mead.[8] The concentrations ranged from 2.0 to 12.0 g. of the fractionated polymer per kilogram of solvent (compare Fig. 2). The temperature was 25°. The procedure has been repeatedly described recently, particularly by Flory[4] and Fuoss and Mead.[8]

Results and Discussion

Figure 1 shows the specific viscosities divided by the volume concentration plotted *versus* the volume concentration in cc. of solute per liter of solvent. Three fractions of the 60 and 120° samples are included and fraction 1 and 3 of the 180° sample. Fraction 2 of this latter sample lies between fractions 1 and 3; it was omitted in order not to overload the lower part of the graph with points and curves. First it can be noticed from Fig. 1 that all observed points (12 for the 60° sample, 12 for the 120° and 8 for the 180° sample) fall with fair approximation on a family of straight lines with the exception of the two last points (c_v around 9.5 of the fraction 60–1 and 60–2.) Apparently these two points show already the influence of higher terms in the equation, which expresses the η_{sp}/c_v values as a function of c_v.

The theory of the viscosity of moderately di-

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[2a] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

[2b] M. L. Huggins, THIS JOURNAL, **64**, 2716 (1942); *Ind. Eng. Chem.*, **35**, 216 (1943). Compare also particularly Chapter IX in E. Ott, "The Chemistry of Cellulose," Interscience Publishing Company, New York, N. Y., 1943, contributions of H. M. Spurlin and M. L. Huggins, on pages 853, 893 and 943.

[3] R. E. Powell, C. R. Clark and H. Eyring, *J. Chem. Phys.*, **9**, 268 (1941).

[4] A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942); D. J. Mead and R. M. Fuoss, THIS JOURNAL, **64**, 277 (1942); P. J. Flory, *ibid.*, **65**, 372 (1943); A. Bartovics and H. Mark, *ibid.*, **65**, 1901 (1943).

[5] H. Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1942.

[6] Comp., *e. g.*, H. M. Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938); A. M. Sookne, H. A. Rutherford, H. Mark and M. Harris; *J. Research Natl. Bur. Standards*, **29**, 123 (1942), and particularly P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

[7] A. Bartovics and H. Mark, *ibid.*, **65**, 1901 (1943).

[8] R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943).

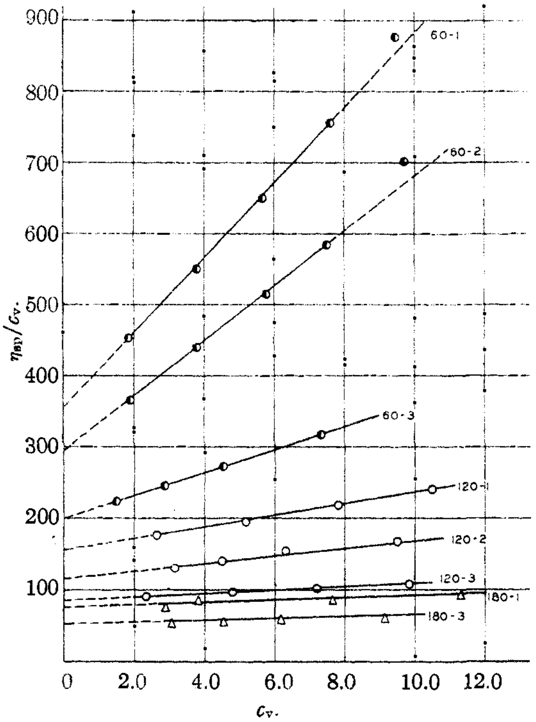

Fig. 1.—Specific viscosities divided by volume concentration plotted against volume concentration in cc. of solute per liter solution.

luted solutions of high polymers was originated by Gold and Guth[9] and Simha[10] and recently extended in several important papers[11] by Huggins. At the best of our present knowledge the specific viscosity divided by the volume concentration is given by

$$\eta_{sp}/c_v = [\eta] + k'[\eta]^2c_v \qquad (1)$$

where $[\eta]$ is the limiting value of η_{sp}/c_v for zero concentration—the so-called intrinsic viscosity of Kraemer[12]—and k' is a constant, characteristic for a given system solvent–solute. Huggins[11] and others[4] have shown that in certain cases—*e. g.* cellulose acetate fractions in acetone—one single constant k' covers the whole family of curves of the type shown in Fig. 1. In the case of the fractions of the three polystyrene samples, this is not possible. Evaluating the data contained in Fig. 1 with equation (1), it becomes apparent that one can fairly well represent the points belonging to the different fractions of one and the same sample by one k'-value but that the three samples need three different k'-constants to represent quantitatively the influence of concentration on η_{sp}/c_v. The values obtained from the data represented in Fig. 1 are

Sample polymerized at 60° $k' = 0.42$
Sample polymerized at 120° $k' = 0.33$
Sample polymerized at 180° $k' = 0.21$

Huggins' theory considers k' to be characteristic for a *certain system* solvent–solute and to describe empirically the way in which during the flow of the liquid around and through the solute particles the molecules of the solvent and the submolecules of the dissolved polymer interact with each other. In this sense Fig. 1 may be interpreted as indicating that the samples, prepared at three different temperatures and dissolved in the same solvent (toluene), must be considered as being *different systems*.

In two previous brief communications[13] it has been shown that the intrinsic viscosity $[\eta]$ of the solution of a high polymer decreases if one adds increasing amounts of a non-solvent to the system and that the k'-value for the system cellulose acetate–acetone drops if one adds methanol to the solution. In these two cases, the system was changed by varying the solvent and it resulted that both $[\eta]$ and k' do not depend upon one partner of the solution, but upon the *interaction of both*.

Figure 2 shows the osmotic pressure divided by the weight concentration plotted against the weight concentration for four fractions of the three polystyrene samples. Although the figure

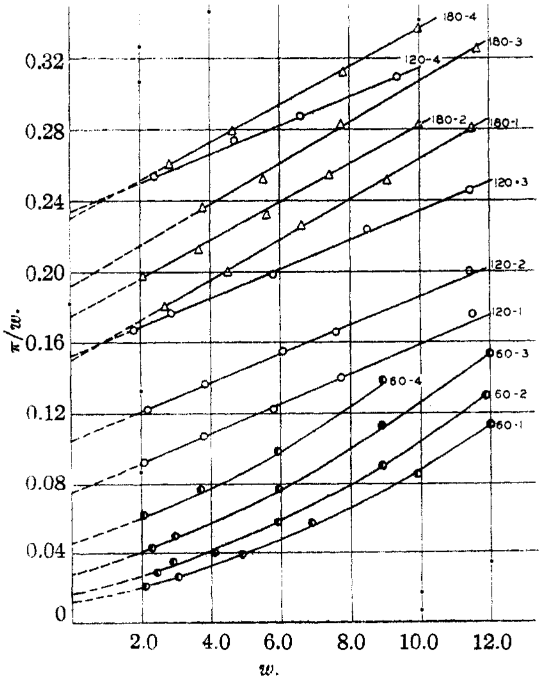

Fig. 2.—Osmotic pressure in cm. of column in capillary divided by weight concentration plotted against weight concentration in grams of solute per kg. of solvent.

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[9] E. Guth and O. Gold, *Phys. Rev.*, **53**, 322 (1938).

[10] R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).

[11] M. L. Huggins, *ibid.*, **42**, 911 (1938); **43**, 439 (1939); This Journal, **64**, 2716 (1942).

[12] It may be pointed out here that Dr. Kraemer has originally defined the intrinsic viscosity to be expressed in reciprocal grams per 100 ccs. units. We have chosen here reciprocal volume fractions, which does not deviate sensibly from Kraemer's definition in this case.

[13] T. Alfrey, A. Bartovics and H. Mark, This Journal, **64**, 1557 (1942); A. Bartovics and H. Mark, *ibid.*, **65**, 1901 (1943).

looks somewhat confusing at first sight, it seems to reveal some interesting information.

Considering first the four fractions of the 60°-sample, it can be seen that the (21) observed points are not arranged on straight, but on slightly upward curved lines. Flory[4] has already observed this fact in his investigation of polyisobutylene fractions and Gee and Treloar[14] have found a similar behavior for solutions of rubber in benzene. According to the theories of Flory[5] and Huggins the π/w *versus* w relationship should be in first approximation a straight line. Huggins[15] has shown, however, that in better approximation one has to expect a certain upward concavity. The third term on the right side of his expression

$$\frac{\pi}{c_2} = \frac{RT}{M_2} + \frac{RT}{V_1 d_2^2}(0.50 - \mu)c_2 + \frac{RT}{3V_1 d_2^2}c_2^2 \qquad (2)$$

π = osmotic pressure
M_2 and d_2 = molecular weight and density of the pure solute
c_2 = concentration in grams of solute per cc. of solution
V_1 = molal volume of solvent
μ = constant, characteristic for the system solvent–solute

provides for an upward curvature of the lines in Fig. 2, but it seems that the observed deviation is larger than equation (2) would predict. We would, however, like to point out that we do not consider our observed points in this part of Fig. 2 (fractions 60–1, 60–2, and 60–3; w below 6 g. of solute per kg. solvent) to be accurate enough to draw any reliable quantitative conclusions as to the curvature of the $\pi/w - w$ curve. More and better measurements will have to be awaited to contribute to this question.

We have attempted to extrapolate the curves for the four fractions of the 60°-sample to the ordinate and obtain the intercepts which, according to equation (2), are reciprocal to the molecular weight of the pure solute. Again, we would like to emphasize that, owing to the curvature, this extrapolation includes a certain degree of arbitrariness, which is a weak spot of this investigation. Using the dotted lines as inserted in Fig. 2, one arrives at the molecular weights as given in Table I. The initial slopes of the dotted parts of the four 60°-sample curves are very nearly identical and lead to a μ-value of 0.48.

Considering the four fractions of the 120°-sample, it can be seen that nearly all (19) points fall fairly well on straight lines. Only the last point of the 120–1 and 120–2 fraction seem still to indicate the tendency of the upward concavity as expressed in the fractions of the 60°-sample. The extrapolation to zero concentration, which we consider to be more reliable than before, leads to the molecular weight given in Table I and shows that the four 120°-sample curves have very similar slopes. The μ-value is 0.45 and expresses that increasing concentration affects the osmotic pressure of these fractions at very low concentrations more than it affects the 60°-fractions.

TABLE I

Fraction	M_2	$[\eta]$	
	SAMPLE POLYMERIZED AT 60°		
60–1	2,050,000	355	$k' = 0.42$
60–2	1,580,000	295	$\mu = 0.48$
60–3	890,000	200	$K = 1.6 \times 10^{-2}$
60–4	550,000	140	$a = 0.70$
	SAMPLE POLYMERIZED AT 120°		
120–1	340,000	155	$k' = 0.33$
120–2	240,000	118	$\mu = 0.45$
120–3	167,000	86	$K = 6.6 \times 10^{-3}$
120–4	108,000	62	$a = 0.80$
	SAMPLE POLYMERIZED AT 180°		
180–1	169,000	73	$k' = 0.21$
180–2	145,000	59	$\mu = 0.43$
180–3	132,000	53	$K = 4.0 \times 10^{-4}$
180–4	110,000	45	$a = 1.10$

Looking finally at the four fractions of the 180°-sample, it can be noticed that the (17) observed points fall on reasonably straight lines, the extrapolation of which leads to the molecular weights of Table I and to a μ-value of 0.43.

It seems, therefore, that, as far as the μ-value is concerned, the toluene solutions of the fractions of the three samples prepared at different temperatures behave like different systems, inasmuch as the activity of the solvent molecules depends in a different way upon the concentration of the solute for each of these samples.

This becomes particularly apparent if one considers the two fractions 180–1 and 120–3 and the two fractions 180–4 and 120–4. In both cases the intercepts of the $\pi/w - w$-lines are within the limits of the experimental error the same, while the slopes between the 120- and 180°-samples differ quite distinctly. Although the molecular weights of each pair of these fractions are very nearly the same, their solubility characteristics appear to be quite different.[16] Applying the ideas of Flory and Huggins one arrives at the conclusion that the submolecules (or segments) in polystyrene prepared at 180° interact in a different way with the solvent molecules than those of a sample polymerized at 120°. This interaction includes the heat of mixing as well as the entropy of mixing.

Considering Fig. 1, we see that fractions 180–1 and 120-3 have different intrinsic viscosities and

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(14) G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942).

(15) M. L. Huggins, *Ind. Eng. Chem.*, **35**, 216 (1943).

(16) Unfortunately, we did not succeed in obtaining such coinciding fractions of the 120- and 60°-samples. This was due to the fact that we could not sufficiently control the fractionation operation in order to predetermine the osmotic molecular weight of the different fractions obtained. Experiments are now being carried out, in order to provide for a larger number of overlapping fractions of samples polymerized at different temperatures.

different k'-values. It appears, therefore, that polystyrene fractions having the same molecular weight M_2 can still differ quite appreciably in their thermodynamical and hydrodynamical interaction with the solvent. If we assume a different internal structure, such as branching or ring formation for the materials prepared at different temperatures, these samples would together with a given solvent represent different systems solvent–solute and hence behave differently. It has been shown, in fact, by Flory[4] and others[15] that if one changes the other component of this system, namely, the solvent, one leaves M_2 constant, but changes $[\eta]$, k' and μ. The nearer the polymer is to precipitation, the smaller are $[\eta]$ and k', and the larger becomes μ.

This situation suggested the following experiment: 0.20 g. of each of the two fractions 180–1 and 120–3 were dissolved in 40 g. of solvent. These solutions showed the viscosity and osmotic pressure behavior as required by the corresponding curves in Figs. 1 and 2 ($c_v = 5.0 \times 10^{-3}$). Then the two solutions were mixed and it was attempted to reseparate the original fractions by precipitation with methanol. If the molecular weight were the essential quantity for the stability of a high polymer solution, the reseparation of the two fractions 180–1 and 120–3 should be impossible, because—according to Fig. 2—their molecular weights are almost identical. If, however $[\eta]$, k' or μ is the quantity which affects preponderantly the precipitability of a high polymer, we should expect that the two fractions 180–1 and 120–3 can be reseparated by adding a non-solvent to the toluene solution of their mixture.

As the fractionation of styrene is more easily performed from methyl ethyl ketone, the experiment was carried out with methyl ethyl ketone solutions of the two fractions 180–1 and 120–3. Methanol was added slowly at room temperature until a cloudiness appeared and then the temperature dropped until about half of the material precipitated. Then the precipitate was separated, refractionated, washed and the behavior of its toluene solutions investigated.

We did not succeed in carrying out this experiment as satisfactorily as it was desired, because of the limited amount of fractionated material at our disposal. However, we believe that its results indicate that the two fractions 180–1 and 120–3 can be refractionated from methyl ethyl ketone with methanol and that 180–1 precipitates first.

In our case, the precipitated material was 35% of the total polymer dissolved. We should have added so much methanol and cooled down the solution so far as to obtain 50% precipitation, but when viewed through the flask in which the fractionation takes place, it is not always easy to estimate correctly the amount of the material precipitated. We underestimated this amount and the precipitate was only 35% of the combined weight of the fractions 180–1 and 120–3.

This precipitate was removed and after washing and drying its toluene solution was investigated. The following figures were obtained:

$M_2 = 175{,}000$ $\quad k' = 0.25$
$[\eta] = 75$ $\quad \mu = 0.44$

First it can be seen that M_2 is somewhat higher than the corresponding values of both 180–1 and 120–3. This seems to be not too unreasonable, because dissolving and reprecipitation of polymer fractions generally increases slightly the osmotic molecular weight owing to the removal of short chain length constituents. We may, therefore, conclude that inside the limits of error of the whole method of operation M_2 has not changed appreciably. The intrinsic viscosity of the fraction $[\eta] = 75$ is much closer to 180–1 than it is to 120–3 and we consider this as an indication that the precipitated material contains mainly polymer of the 180–1 fraction and only little, if any, of the 120–3 fraction. This would mean that in a mixture of macro-molecules which have different chain lengths and different internal architecture such as branching, internal ring formation or regular curling, precipitation takes place according to their $[\eta]$-values rather than according to their molecular weights.[17]

The values of k' and μ (0.25 and 0.44) for the precipitate obtained by refractionation are somewhat nearer to the corresponding values of fraction 180–1 than to those of fraction 120–3. However, considering the possible errors of the fractionation and osmotic pressure measurements, we do not want to lay particular emphasis on this fact. But we think it is fair to say that the values of k' and μ as obtained for the reprecipitated fraction (180–1) do not contradict the conclusion that there exists a correlation between the intrinsic viscosity $[\eta]$ and the precipitability of a high polymer, which are both an expression for the internal structure of the dissolved macromolecules.

The next step of the investigation was to study the relationship between the intercepts of Fig. 1 ($[\eta]$-values) and the reciprocal intercepts of Fig. 2 (M_2-values). Previous investigations[18] have shown that the intrinsic viscosities of the fractions of a polymer in a given solvent can be expressed as a function of the molecular weight by

$$[\eta] = KM_2^a \qquad (3)$$

where K and a are two constants characteristic for a certain *system solvent-solute*. If one plots for our twelve fractions logarithms of M_2 against the logarithms of $[\eta]$, one obtains the graph of Fig. 3. It shows that the points characteristic for the fractions of each sample fall reasonably well on a straight line, but on a different straight line for each sample. This seems to be another in-

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(17) We had the privilege of discussing these results with Dr. P. J. Flory, who told us that he had arrived at a similar conclusion from his own observations.

(18) P. J. Flory, THIS JOURNAL, **65**, 372 (1943); A. Bartovics and H. Mark, *ibid.*, **65**, 1901 (1943); R. Houwink, *J. prakt. Chem.*, **157**, 15 (1940).

dication for the fact that the three samples dissolved in the same solvent have to be considered as being different systems. The three values for K and a are contained in Table I. The 60°-fractions deviate most from the Staudinger rule, while the 180°-fractions have an exponent of almost unity.

Several years ago Staudinger, Schulz[19] and others[20] observed discrepancies between the molecular weights as obtained by osmotic measurements and by the Staudinger rule and have interpreted them as being caused by branching. Meanwhile, this argument has lost much of its weight, because the Staudinger rule has been replaced,[4,15] by the more reliable relation (3). However, it seems that the comparison of osmotic and viscosity measurements as presented in this brief report, which does not use the Staudinger rule at all leads to the conclusion that polystyrene samples polymerized at different temperatures do not only differ in respect to their average molecular weight, but also to their general solubility characteristics. This appears to be an indication for a different internal architecture of the macromolecules. To determine whether branching in the sense of Flory,[21] Schulz,[19] Stockmayer[22] and others[20] is responsible for this behavior will require the analysis of samples which have been polymerized under different experimental conditions such as monomer and catalyst concentration, extent of polymerization, etc.

Summary

1. Three samples of polystyrene, prepared by polymerization of the pure monomer at 60, 120 and 180°, were fractionated.
2. The specific viscosities of these fractions were measured at 30 and 40° in toluene up to volume concentrations of about 1.0%. The intrinsic viscosities and k' constants for all fractions were determined.

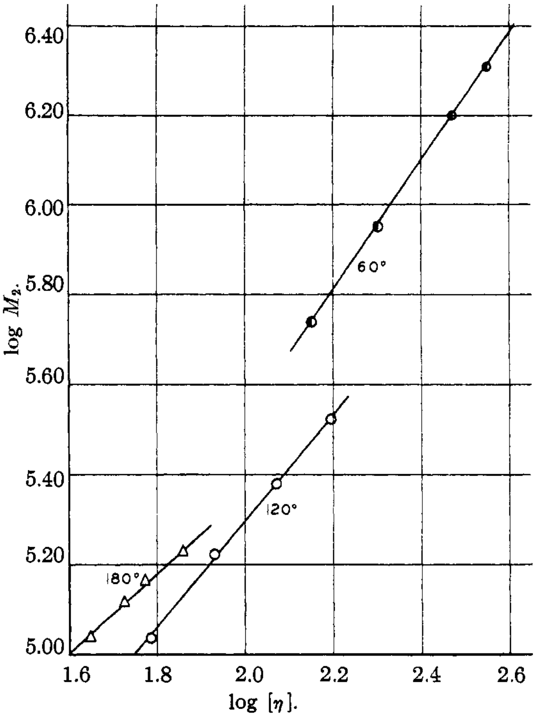

Fig. 3.—Log of the osmotic molecular weight is plotted against the log of the intrinsic viscosity.

3. Osmotic pressures of the fractions were measured and the molecular weights and μ-constants of these determined.
4. The fractions of each individual sample show very closely the same k' and μ values, while there is a definite difference in these constants from sample to sample.
5. The relationship between $[\eta]$ and M_2 is given by the expression $[\eta] = KM_2^a$; the values for K and a were determined for all three samples.

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[19] H. Staudinger and G. V. Schulz, *Ber.*, **68**, 2320 (1935); *Z. physik. Chem.*, **B44**, 227 (1939).

[20] H. Mark and R. Raff, "High Polymeric Reactions," New York, N. Y., 1941, pp. 191, 219.

[21] P. J. Flory, THIS JOURNAL, **63**, 3083 (1941).

[22] N. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943).