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An Investigation of the Determination of Molecular Weights of High Polymers by Light Scattering

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The determination of the molecular weights of large molecules by measuring the turbidity of the solution and the change in index of refraction with concentration is discussed. The apparatus, its calibration, and the technique used are treated together with a comparison between molecular weights measured by this method and other methods. The effect of polymolecularity is also presented.

INTRODUCTION

RECENTLY Debye[1] has pointed out that the measurement of light scattering in solutions may be used to determine the molecular weights of high polymers. Since that time we have been interested in examining this method and some data of preliminary experiments have already been published.[2] In the continuation of this investigation a few anomalies have been noted which are as yet incompletely understood. However, in view of the apparent success of this method, we report here in more detail concerning the experimental methods used and some further results obtained. Some limitations and pitfalls as well as an extension of the method to the characterization of molecular weight distributions are discussed.

Before proceeding we review briefly the theoretical background.[3,4] It is common knowledge that some light is always scattered from a beam of light passing through a transparent fluid (Tyndall effect). This, however, would not occur in a medium which was perfectly uniform. Real solutions are never perfectly uniform because of minute thermal fluctuations in density and concentration. These inhomogeneities are the source of the scattered light. The extent of the fluctuations is determined by the free energy change (work) necessary to produce them. On the basis of these considerations, von Smoluchowski[5] and Einstein[6] derived the following expression for the turbidity of a colorless binary mixture.

$$\tau_0 = \frac{32\pi^3 n^2}{3\lambda^4 N_0} \times \left\{ RT\beta \left(\rho \frac{\partial n}{\partial \rho} \right)^2 + \frac{M_1 c}{\rho \left(-\frac{\partial \ln f_1}{\partial c} \right)} \left(\frac{\partial n}{\partial c} \right)^2 \right\}. \quad (1)$$

τ_0, the turbidity of the solution, corresponds to the extinction coefficient in Lambert's law,

[1] P. Debye, J. App. Phys. **15**, 456 (1944).

[2] P. M. Doty, B. H. Zimm, and H. Mark, J. Chem. Phys. **12**, 144 (1944).

[3] S. Bhagavantam, *The Scattering of Light and Raman Effect* (Anhandra University, Waltair, India, 1940); American Edition (Chemical Publishing Company, Brooklyn, New York, 1942).

[4] J. Cabannes, *La Diffusion Moléculaire de la Lumiére* (Les Presses Universitaires de France, Paris, 1929).

[5] M. von Smoluchowski, Ann. d. Physik **25**, 205 (1908).

[6] A. Einstein, Ann. d. Physik **33**, 1275 (1910).

i.e., it is the fractional decrease in the intensity of incident light upon transversing one centimeter of solution, the decrease occurring only from scattering—not absorption. The other symbols are: λ = wave-length in vacuum (cm^{-1}); N_0 = Avogadro's number; R = molar gas constant; T = temperature (°K); β = isothermal compressibility; ρ = density; n = refractive index of solution; M_1 = molecular weight of solvent; f_1 = fugacity of solvent; and c = concentration of solute in grams per cm^3 of solution.

While Eq. (1) has been used successfully in this and previous investigations in this laboratory, and is essentially the one used by Debye,[1] it should be remarked that there is not unanimous agreement on the value of the constant factor before the braces in Eq. (1). Several authors have proposed the introduction of a factor $[(n^2+2)/3]^2$ in this constant. The arguments are well summarized by Cabannes.[4] Since previous experiments[4] designed to decide the question (by measurement of the light scattered by one-component liquids) have apparently been inconclusive, we have not yet attempted to decide the question but have used the formula as originally proposed.

The first term in Eq. (1) represents the turbidity arising from fluctuations of density. This part of τ_0 corresponds essentially to the turbidity of the pure solvent (assuming β to be constant). Thus if the measured turbidity of the solvent is subtracted from τ_0 the remainder, τ, represents the turbidity caused by concentration fluctuations, a quantity directly related to the solute molecular weight.

Substituting in (1) the thermodynamic relation

$$-\partial \ln f_1/\partial c = (\bar{V}_1/RT)(\partial \pi/\partial c), \qquad (2)$$

TABLE I. Comparison of molecular weight measurement.

	Molecular weight	
Material	Osmotic pressure	Light scattering
Polystyrene, No. 1	172,000	178,000*
Polystyrene, No. 2	198,000	182,000
Polystyrene, No. 3	91,000	107,000
Polystyrene, No. 4	—	190,000
Polystyrene, No. 5	—	445,000
Cellulose Acetate, No. 1	(125,000)	123,000
Cellulose Acetate, No. 3	75,000	76,000

* This value was checked independently by two other laboratories.

there is obtained (2)

$$\tau = \frac{32\pi^3 c n^2(\partial n/\partial c)^2}{3\lambda^4 N_0(1/RT)(\partial \pi/\partial c)}, \qquad (3)$$

where π is the osmotic pressure and $\bar{V}_1$ the partial molal volume of the solvent has been replaced by its approximate equivalent M_1/ρ. The osmotic pressure of high-polymer solution of low concentration is given by

$$\pi = (RT/M_2)c + Bc^2 + \cdots, \qquad (4)$$

which, when substituted into (3), gives upon rearrangement

$$\frac{c}{\tau} = \frac{3\lambda^4 N_0}{32\pi^3 n^2(\partial n/\partial c)^2}\left[\frac{1}{M_2} + \frac{2B}{RT}c + \cdots\right]$$

$$= \frac{1}{H}\left[\frac{1}{M_2} + \frac{2B}{RT}c + \cdots\right]. \qquad (5)$$

Thus it appears that a plot of Hc/τ versus c should give at low concentration a straight line whose intercept is the reciprocal of the molecular weight of the solute. Furthermore, the slope of this plot is twice the slope obtained from osmotic pressure measurements when π/cRT is plotted against c. In this way the measurement of the two optical quantities, (1) turbidity as a function of concentration and (2) the change of index of refraction with concentration, gives information similar to that obtained from direct osmotic pressure measurements.

However, it is important to note that whereas osmotic pressure measurements yield a number average molecular weight, turbidity measurements yield a weight average.* In the final section a more exact discussion of this point occurs, but the conclusion can be seen intuitively from a molecular picture of light scattering. In a *very* dilute solution the intensity of the scattered light is equal to the sum of the intensities of the light scattered by the individual molecules.[1] The intensity of the light scattered by a single molecule of a given species is proportional to the square of the molecular weight. Since the number of molecules is equal to the total weight of that

* The number average molecular weight ($\Sigma M_i N_i/\Sigma N_i$) counts each molecule with equal weight, whereas the weight average ($\Sigma M_i^2 N_i/\Sigma M_i N_i$) weights each molecule according to its mass.

FIG. 1. Plot of turbidity data for polystyrene fractions in methyl ethyl ketone.
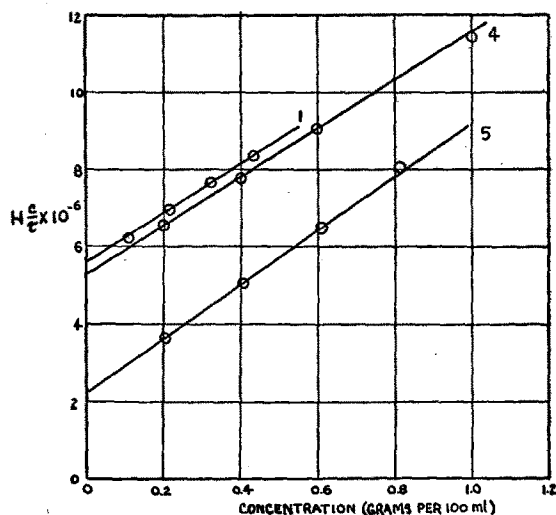

FIG. 2. Plot of turbidity data for polystyrene fractions in methyl ethyl ketone.

species divided by the weight of the individual molecule, the total intensity of light scattered from one species is therefore proportional to the weight of that species multiplied by its molecular weight. Averaging over all molecular weight species yields the weight average molecular weight. This conclusion has been experimentally demonstrated.[7]

EXPERIMENTAL DETAILS

Numerous methods may be adapted to measure the turbidity of high-polymer solutions. One could hope to measure τ directly by measuring the transmission of the solutions. This is usually unsatisfactory, however, because of the small values of τ (10^{-2} to 10^{-4} cm^{-1}) and the frequent presence of absorbing impurities. On the other hand, direct measurement of the intensity of the scattered light conveniently avoids these difficulties and readily lends itself to visual or photoelectric observation. Moreover, it has been our observation that transmission measurements are subject to a number of uncertainties, the absence of which can be assured only by measurements over a rather large spectral range. True absorption, low angle scattering, small amounts of impurities, solute size comparable with wavelength, and other effects still not understood, may

prevent the turbidity as measured by transmission from being the proper value to use in Eq. (5).

Although photoelectric methods are always capable of greater precision, the visual method has certain inherent advantages, such as small aperture, direct view of scattering solution, exact linearity, and freedom from electrical difficulties. We have constructed a turbidimeter attachment** for use with the Zeiss Pulfrich photometer. This turbidimeter was patterned after the Zeiss turbidimeter, except that the light scattered is observed at an angle of 90° to the incident beam, instead of 135°. Light from a mercury bulb (AH-4 100 watt G.E.) is rendered parallel by lens and passes through the solution in a square cell. A small, constant fraction of the incident light is reflected from a glass plate (mounted in the beam) to an opalescent glass which serves as a standard comparison source for the photometer. The dial reading corresponding to matched fields in the photometer is directly proportional to the total turbidity.

It is necessary to calibrate the instrument; that is, to determine the proportionality constant between dial reading and absolute turbidity. One method of calibration is based on measuring the ratio of the intensities of the incident and

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[7] B. H. Zimm and P. M. Doty, J. Chem. Phys. 12, 203 (1944).

** General Gauge and Tool Company, 30 Irving Place, New York.

scattered light, with the help of a white (magnesium carbonate) surface making a 45° angle with the incident beam in place of the solutions. If the solution and the magnesium carbonate are measured successively, the ratio of the photometer readings gives the quantity

$$(ir^2/I)(h\pi/\sin 45°),$$

where i is the intensity of the light scattered from one cubic centimeter of solution at distance r, I is the intensity of the incident beam, and h is the width (in the direction of observation) of the incident beam of homogeneous density. If the scattering of the solutions obeys Rayleigh's law for its angular distribution, i.e., if it varies as $(1+\cos^2 \theta)$ where θ is the angle between incident beam and direction of observation, integration gives

$$\tau_0 = (16\pi/3)(ir^2/I).$$

Correction must be made for the reflectivity of magnesium carbonate (97.5 percent) and for reflection at the glass-air interfaces. Thus the calibration consists of the determination of the ratio of the photometer readings with solution and block in the cell successively together with the measurement of the width of the incident beam in the cell.

Another means of calibration is based on the use of standard opalescent glass prisms furnished by Carl Zeiss and Company. A polymer solution was measured in a Zeiss turbidimeter using two of these standard prisms. The value of the turbidity so obtained checked satisfactorily the turbidity found for the same solution by the previous method.

The measurement of the transmission of a strongly scattering colorless solution offers another method of determining absolute turbidity. Several preliminary attempts yielded inconsistent turbidity values that were also too large, probably indicating absorption. The investigation of this method is continuing.

The sensitivity of our instrument is such that τ_0 values as small as 10^{-4} cm^{-1} may be measured with a reproducibility of 2 percent.

The other optical measurement necessary is the evaluation of $\partial n/\partial c$. Our measurements have confirmed that n varies linearly with c at low concentrations. Consequently one measurement

of the refractive index difference between the solvent and solution determines $\partial n/\partial c$. Since usually the magnitude of the difference for a 1 percent solution is approximately 0.001, a differential method is desirable. We have used a Pulfrich refractometer with a divided cell for this purpose, thus permitting a precision of about 1 percent in this measurement.

Depolarization (ratio of the intensities of the horizontal to vertical components in the scattered light) can easily be measured by the use of a Polaroid or nicol inserted in the solution side of the photometer. Strictly speaking, Eqs. (1) and (5) should contain a factor (Cabannes), depending on the depolarization, which arises from fluctuations in orientation of anisotropic molecules.[1,3,4] In the work reported here the depolarization was so small that this factor was essentially unity.

All solutions and solvents were filtered through fine or medium sintered glass filters. A deep glass cell ($3\times3\times10$ cm) has been used in later work. This permits one to begin measurements with 25 cc of (say) a 1 percent solution. Measured amounts of filtered solvent may be added and stirred; thus all the measurements at different concentrations are made in one continuous operation.

RESULTS

In this section typical examples of the use of this method on some fractionated high polymers are presented together with available osmotic pressure data. The results of the turbidity measurements and osmotic pressure measurements are shown in Table I for the fractions studied.

The most carefully measured fraction (No. 1) was one prepared and measured osmotically by Hanson.[8] The other two polystyrene fractions (Nos. 2 and 3) were prepared and their osmotic pressure determined in this laboratory several years ago. In Figs. 1 and 2 the turbidity data are plotted in such a manner that the intercept is the reciprocal of the molecular weight. The data for two other fractions for which no other molecular weight data are available are also shown in Fig. 1.

The need for extrapolation of $H(c/\tau)$ to infinite

[8] J. Hanson, Thesis, Polytechnic Institute of Brooklyn, 1944.

dilution is clearly shown in the figures. For example, if the molecular weight of sample No. 5 were calculated from the turbidity of its 1 percent solution alone, the value would have been 110,000, instead of the actual value of 445,000. The higher the molecular weight, the larger the error which results from use of data without extrapolation.

The cellulose acetate fractions were prepared by Badgley.[9] The molecular weight in parenthesis is from viscosity measurements. However, the viscosity-molecular weight equation for this series of fractions has been so well established[9] that the value has the validity of an osmotic pressure measurement.

It is interesting to examine the relation between the slope of the $H(c/\tau)$ versus c plot and the π/c versus c plot. As stated previously, if osmotic pressure is represented by

$$\pi = (RT/M_2)c + Bc^2, \qquad (4)$$

the slope of the turbidity graphs should give the value of $2B/RT$.

If one uses Huggins' equation[10]

$$\frac{\pi}{c} = \frac{RT}{M_2} + \frac{RT}{V_1 d_2^2}(\tfrac{1}{2} - \mu_1)c, \qquad (6)$$

where V_1 is the molar volume of solvent, d_2 is the density of solute, μ, the empirical constant of the solvent-solute system, may be used to characterize the slope, B, of the π/c versus c plots. That is:

$$\frac{\Delta(\pi/c)}{\Delta c} = \frac{RT}{V_1 d_2^2}(\tfrac{1}{2} - \mu_1),$$

TABLE II. Comparison of μ values.

	μ (Osmotic pressure)	μ (Light scattering)
Polystyrene-toluene	0.43–0.45[a,b] 0.44[d]	0.43–0.44[c]
Polystyrene—MEK	—	0.47–0.48*
Cellulose acetate-acetone	0.42–0.43[e]	0.44*

* This research.
[a] T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc. 65, 2319 (1943).
[b] Reference 8.
[c] Reference 2.
[d] G. V. Schultz, Zeits. f. physik. Chemie A176, 317 (1936).
[e] Reference 9.

[9] W. Badgley, Thesis, Polytechnic Institute of Brooklyn, 1945.
[10] M. L. Huggins, Ann. N. Y. Acad. Sci. 41, 1 (1942).

and

$$\frac{\Delta[H(c/\tau)]}{\Delta c} = \frac{2}{V_1 d_2^2}(\tfrac{1}{2} - \mu_1). \qquad (7)$$

In other words, it is convenient to compare the slopes of the lines obtained from plots of osmotic pressure and turbidity data by calculating the μ_1, from Eq. (7). In Table II the μ_1 values of the polystyrene-toluene system (previously reported) and cellulose acetate-acetone system obtained from turbidity data are compared with μ_1 calculated from osmotic pressure measurements on the same system.

DISCUSSION

When the particle size of the solute becomes comparable to the wave-length of light, interference between waves from different parts of the same particle occurs and the simple theory outlined above breaks down. The total scattered intensity then falls below that given by Eq. (5). At the same time, instead of the angular distribution of the scattered light being symmetrical about 90° (as is the case with small particles), interference in the case of large particles causes more light to be scattered in the forward than in the backward direction. Measurement of the symmetry of the scattered intensity therefore furnishes a test of the applicability of Eq. (5).

For spherical particles, deviations from Eq. (5) become noticeable when the particle diameter exceeds about one-tenth the wave-length of light. Polymer chain lengths frequently are greater than this by a large margin so that it might be expected that interference would often occur. However, most high-polymer molecules are believed to be loosely convoluted in solution so that the longest dimension of the molecule is on the average much less than the chain length. It is clear that this point is critical, for the average extension of a *randomly* coiled polymer molecule of moderate weight will not exceed one-tenth the wave-length of light, whereas the common interpretation of viscosity measurements, sedimentation constants, and flow birefringence indicate that most polymer molecules are more extended in solution and hence should give rise to a dissymmetry of the angular intensity of the scattered light.

A simple instrument has been constructed to

measure the dissymmetry. A parallel beam of monochromatic light is passed through the solution in a five sided cell. The light scattered at 45° on each side of the normal plane is reflected by the mirrors to the photometer apertures. The relative intensities are then compared by means of the photometer.

Measurements of this type on the solutions of polystyrene in methyl ethyl ketone showed practically no dissymmetry, thus permitting the direct application of Eq. (5). Incidentally the higher molecular weight polystyrene fraction No. 5, dissolved in toluene did exhibit a considerable dissymmetry indicating that the molecule is more extended in the better solvent. On the other hand, all of the cellulose acetates reported here gave noticeable dissymmetries in acetone solution. Corrections based on these measured dissymmetries range upward to 20 percent and have been applied to the results listed in Table II. A detailed discussion of these measurements and corrections will be given later when this study of cellulose acetate fractions is finished.

In most cases, solutions in the concentration range between 1.0 gram and 10.0 grams of polymer per liter have been used both for turbidity and refractive index measurements. The polymer specimens were the result of repeated fractionation of a commercial material or of a sample polymerized under certain controlled conditions. Two types of impurities, which can never be completely eliminated, require special attention and care:

A. Low molecular weight impurities of the solvent or the polymer. All solvents were carefully distilled until their characteristics, such as density, boiling point, and refractive index, did not undergo any changes upon further purification. Some solvents, such as dioxane, formic acid, etc. retain water very tenaciously and have to be kept carefully dry, because even small amounts of water affect the refractive index noticeably. The polymers should be dissolved and reprecipitated before they can be brought into the solution which is finally used for the measurements. It seems advisable to prepare a 2–3 percent solution of the original polymer in the same solvent in which the final measurements are contemplated, and to precipitate it with a volatile precipitant.

The precipitate is filtered off and thoroughly washed with the precipitant. It is then slowly dried at low temperatures in vacuum. Fast drying under more vigorous conditions, such as elevated temperature, leads in certain cases to hornification of the samples, which makes subsequent dissolving difficult and eventually even leads to solutions containing minute gel particles, which may lead to excessive scattering. This process of purification through precipitation should be repeated one or more times; some polymers, e.g., polystyrene, are relatively easily separated from traces of monomer, catalysts, or stabilizers, others e.g., Nylon or rubbery copolymers, retain impurities rather tenaciously. It does not seem easy to prepare any strict prescription at present, and it will be necessary to collect further experience until certain standard procedures can be recommended.

B. Coarse impurities of the solvent and polymer. All solvents and solutions have to be filtered repeatedly until they appear optically clean and until further filtration does not decrease the turbidity any more. All solvents contain a certain amount of dust of mostly inorganic origin, which can be satisfactorily reduced to an insignificant amount by repeated filtration through glass fritters. All polymers contain coarse impurities of various types. Dust of inorganic origin, having large particle sizes (several microns), is comparatively easily removed by precipitation, washing, redissolution, and final filtration through glass fritters. Haze, of organic origin, is frequently owing to chemical and structural heterogeneity of the polymer, such as too highly (or too lowly) acetylated fractions in cellulose acetate or branched (even cross-linked) constituents in vinyl polymers and copolymers. This type of haze, which is chemically closely related to the investigated material and differs from it only slightly in its solubility characteristics, sometimes offers very serious obstacles and eventually can prevent the application of the light scattering method altogether. It seems that a comparatively successful way to reduce this haze is to precipitate the polymer three or four times, using each time *another* solvent and eventually also more than one precipitant. It can be directly observed in such cases that the turbidity of the solution decreases visibly after

each precipitation, but even a solution which appears completely transparent to the eye may still contain enough haze particles to give wrong results. These very large complexes affect the light scattering in about the same way as they affect specific viscosity, because of the fact that they contribute to the total effect according to their weight. Their large size (1000A or more), on the other hand, makes it possible to obtain independent experimental evidence about their presence by measuring the dependence of the turbidity upon the angle between incident and scattered light in the apparatus described previously.

In choosing a solvent for this type of work, one must be mindful of the great importance of the difference in index of refraction between solvent and solute. This difference should be greater than 0.0005 refractive index unit between a 1 percent solution and the solvent. In fact, it is just this difference which determines the lowest molecular weight which can be measured with a given accuracy, for, obviously, the greater the refractive index difference, the lower the molecular weight solute that will give the same scattering. The lowest molecular weights we have measured were near 10,000 where $\partial n/\partial c = 0.07$ for the system investigated. To measure molecular weights lower than this $\partial n/\partial c$ would have to be increased by use of a different solvent or less accuracy would have to be expected. Thus at present the method is limited to molecular weights above 10,000.

Colored solutions offer some difficulty; however, by using light of a wave-length that is outside the absorption band of the solution no trouble is encountered.

At the end of this section it may be reiterated that the few recommendations made are far from being a well worked-out technique. They only represent the limited experience collected during a short period and will have to be considerably improved and expanded in the future.

MOLECULAR WEIGHT DISTRIBUTION

It was shown in a previous letter by Zimm and Doty[7] that Eq. (5) can be generalized to include the case of a solute containing molecules of different degrees of polymerization. By the same methods used to derive Eq. (1), the turbidity of a solution of several different solutes in the same

solvent can be shown to be

$$\tau = \frac{32\pi^3 M_1 n^2}{3 N_0 \lambda^4 \rho} \sum_i \frac{(\partial n/\partial c_i)^2 c_i}{(-\partial \ln f_1/\partial c_i)}, \quad (8)$$

where c_i is the concentration (g/cc) of the ith species of solute.

If all the solute species are homologous polymers of the same monomer, differing only in molecular weight, two important simplifications can be made. In the first place, one might reasonably expect $\partial n/\partial c$ to be independent of the molecular weight so that it can be factored out of the sum. In the second place, it is generally known that the coefficient of the second term in the expansion of the osmotic pressure in terms of concentration (Eq. (1)) is independent of molecular weight in a homologous polymeric series. We might expect, therefore, that this coefficient would be constant in a solution of mixed homologs as in the following equation

$$\pi = \sum \frac{RT}{M_i} c_i + Bc^2 + Cc^3 + \cdots, \quad (9)$$

where B is independent of molecular weight.

Introduction of these assumptions leads[7] to the following expansion for $H(c/\tau)$

$$H\left(\frac{c}{\tau}\right) = \frac{1}{\bar{M}} + \frac{2B}{RT}\left[1 + \left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}\right]c$$
$$+ \left\{\frac{3C}{RT}\left[1 + \left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}\right]\right.$$
$$+ \frac{4B^2\bar{M}}{R^2T^2}\left[\left\{\left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}\right\}^2\right.$$
$$\left.\left. - \left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av} - \left\langle\left(\frac{\Delta M}{\bar{M}}\right)^3\right\rangle_{Av}\right]\right\}c^2 + \cdots, \quad (10)$$

where $\bar{M}$ is the weight average molecular weight and $\langle(\Delta M/\bar{M})^2\rangle_{Av}$ and $\langle(\Delta M/\bar{M})^3\rangle_{Av}$ are the second and third moments of the molecular weight distribution curves about the weight average molecular weight. This reduces to Eq. (5) when the moments are all zero, i.e., when the solute consists of one molecular weight species only.

It can immediately be seen that the plot of $H(c/\tau)$ for solutions of mixed molecular weight may have appreciable (downward) curvature.
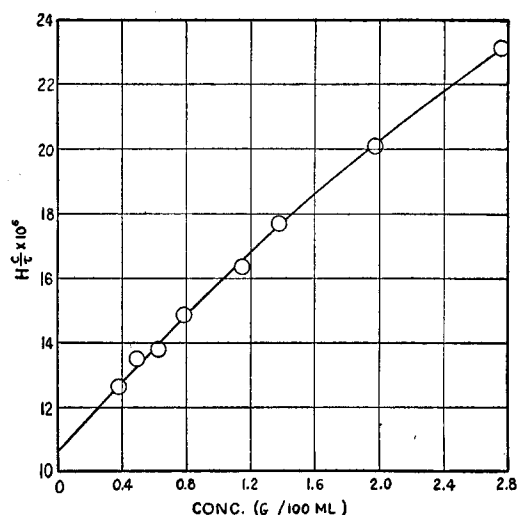
FIG. 3. Turbidity measurements on cellulose acetate in acetone.

Experimental data on a solution of unfractionated cellulose acetate shown in Fig. 3 illustrate this predicted curvature. We see here an observable effect of non-homogeneity of molecular weight which has no counterpart in the case of osmotic pressure. This difference arises from the same reasons that cause osmotic pressure to be related to number average and turbidity to weight average molecular weight.

One way of utilizing this difference would be to plot $H(c/\tau)$ versus c for the unfractionated polymer and draw the best curve through the data. Then either from turbidity measurements on a fraction or from osmotic pressure measurements on the unfractionated polymer one may obtain the slope of the $H(c/\tau)$ versus c plot for a fraction. The difference between this slope and the initial slope of $H(c/\tau)$ versus c for the unfrac-

tionated polymer will give the value of the second moment,

$$\langle(\Delta M/\bar{M})^2\rangle_{Av},$$

which characterizes the "width" of the distribution curve or the dispersion of molecular weights about the average value. By ordinary curve fitting methods the coefficient of the c^2 in Eq. (10) may be determined, from which the third moment,

$$\langle(\Delta M/\bar{M})^3\rangle_{Av},$$

may be evaluated using the previously found value for the second moment. This third moment characterizes the asymmetry of the molecular weight distribution curve. The determination of higher moments would lead to more specific information about the distribution curve but at present this seems impracticable both experimentally and theoretically, for extremely accurate measurements would be required and the compliance of Eq. (10) with the system investigated would have to be rigorously proven. A study of the application of this general method is being continued.

ACKNOWLEDGMENT