mediately surrounding chains without involving a large zone of activation.

It remains to interpret the diffusion data over the transition region. The heat of solution evidence is that the sorbed gas molecules in this temperature range are surrounded by a region of polymer possessing some freedom for rotation and torsional oscillation while the main bulk of the polymer has not this freedom. The size of these zones will increase with temperature and with the size of the sorbed molecule. The kinetic movements within these zones and their lack of precise boundaries will make them wander in a random manner with low energy of activation through the medium carrying the gas molecule along. This is in qualitative agreement with the data except for hydrogen where the activation energy lies between the values above and below the two transition temperatures. A possible explanation of this and the anomaly in its heats of solution is that the hydrogen molecule is too light to create a zone of disturbance, but it is then difficult to understand why it shows a lower transition temperature.

The author is indebted to Professor R. M. Barrer and to several colleagues for their interest in this work. His especial thanks are due to Dr. J. H. Singleton who made the Pirani gage.

OLD ABERDEEN, SCOTLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polyvinylacetate. A Light Scattering and Viscosity Study[1,2]

BY A. R. SHULTZ

RECEIVED JANUARY 28, 1954

Light scattering measurements on polyvinylacetate fractions in dilute solution confirm the prediction that the extent to which a linear polymer molecule is expanded beyond its random-flight dimensions is a function of its molecular weight. Thus the ratio of the mean-square radius of a linear polymer chain to its molecular weight, R^2/M, increases with increasing molecular weight for a polymer in a thermodynamically good solvent. The Flory–Fox limiting viscosity number theory is found to be valid for high molecular weight polyvinylacetate fractions in methyl ethyl ketone. The value $\Phi = 2.2 \times 10^{21}$ is observed for the universal viscosity constant. The osmotic second virial coefficients, A_2, are empirically correlated with $\overline{M}_w$, $\overline{R^2}_w$ and $[\eta]$ in accord with the qualitative predictions of recent thermodynamic theories.

The effect of solvent media upon the dimensions of polymer molecules in dilute solutions has received considerable attention in recent years. Statistical theories attempting the description of average or most probable polymer coil configurations and the resultant physical dimensions and solution properties have yielded interesting, and upon occasion divergent, predictions. Some discussion of work in this field and further extension of theory has appeared very recently.[3,4]

The dependence of polymer coil dimensions and osmotic second virial coefficients of polymer molecules in dilute solution upon similar contributory factors presents the possibility of correlating these two properties.[3,5,6] Measurements of the concentration dependence and angular dependence of light scattered from dilute polymer solutions permit evaluation of both these quantities for comparison.

Theoretical treatments of limiting viscosity numbers[7,8] have suggested to Flory and Fox[9] the possibility of applying an equivalent hydrodynamic sphere approximation to relate the limiting viscosity numbers of flexible polymer coils to their average dimensions and molecular weights. Subsequent studies[10-14] have shown that this approach possesses considerable merit in describing and predicting viscosities.

The present investigation was conducted to determine experimentally the relationships among the molecular weights, coil dimensions, osmotic second virial coefficients and limiting viscosity numbers of carefully prepared high molecular weight polyvinylacetate fractions in dilute solutions. The data are discussed briefly in terms of recent theories. An attempt has been made to minimize the uncertainty inherent in correlating the various physical observables which depend upon different moments of the molecular weight distributions of the polymer samples.

Experimental

Materials. Solvents.—Reagent grade methyl ethyl ketone, methyl isopropyl ketone and *n*-heptane were dried over $CaSO_4$ and distilled before use. They were stored in the dark at 0°.

Preparation of Polymer.—"Niacet" vinyl acetate was freed of hydroquinone and trace inhibitors by distillation under one atmosphere of nitrogen through a Podbielniak column of 160 theoretical plates. The distilled monomer was stored in the dark at 0°.

The vinyl acetate was bulk polymerized in two sets of two Pyrex glass tubes (A, B and C, D). Azo-bis-isobutyronitrile in the presence of illumination from a medium-pressure mercury lamp was the initiator. Each tube containing monomer and initiator was thoroughly outgassed before

---

[1] This work was supported by the Office of Ordnance Research under Contract DA-19-020-ORD-1545 with the Massachusetts Institute of Technology.

[2] Presented at the 124th National Meeting of the American Chemical Society in Chicago, Ill., Sept., 1953.

[3] B. H. Zimm, W. H. Stockmayer and M. Fixman, *J. Chem. Phys.*, **21**, 1716 (1953).

[4] H. M. James, *ibid.*, **21**, 1628 (1953).

[5] B. H. Zimm, *ibid.*, **14**, 164 (1946).

[6] P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950).

[7] P. Debye and A. M. Bueche, *ibid.*, **16**, 573 (1948).

[8] J. G. Kirkwood and J. Riseman, *ibid.*, **16**, 565 (1948).

[9] P. J. Flory, *ibid.*, **17**, 303 (1949); T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949); P. J. Flory and T. G. Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

[10] T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1909, 1915 (1951).

[11] H. L. Wagner and P. J. Flory, *ibid.*, **74**, 195 (1952).

[12] L. H. Cragg, T. E. Dumitru and J. E. Simkins, *ibid.*, **74**, 1977 (1952).

[13] L. Mandelkern and P. J. Flory, *ibid.*, **74**, 2517 (1952).

[14] P. J. Flory, L. Mandelkern, J. B. Kinsinger and W. B. Shultz, *ibid.*, **74**, 3364 (1952).

polymerization by alternate freezing in liquid nitrogen and thawing under vacuum. The tubes were sealed under vacuum. The polymerization conditions and results are given in Table I.

TABLE I

POLYMERIZATION OF VINYL ACETATE

$T = 2°$; initiator concn. = 0.0146 g./l.; Hg lamp light

Tube	Time, hr.	Conversion, %	$\bar{M}_w \times 10^{-6}$
A	13.67	11.0	1.66
B	13.67	11.2	1.66
C	14.83	13.1	1.51
D	10.50	13.2	1.55

The polymers were isolated by adding acetone and *n*-hexane to each polymerization mixture to yield an approximately 5% polymer solution, then slowly adding this solution to a large excess of *n*-hexane at 20° with rapid stirring. The precipitates were rinsed with hexane and allowed to remain in hexane for 24 hours. The hexane was then decanted and the polymers were dried *in vacuo* at 40° for ten hours and at 60° for 24 hours.

The four polymerizates after isolation were combined and fractionally precipitated at 25° from a dilute solution (initial concentration 3.8 g. polymer/liter) in acetone by successive additions of *n*-hexane to yield fractions 1 to 7. Their limiting viscosity numbers (cc./g. units) in acetone at 25° were, in the order 1 to 7, 566, 495, 432, 348, 244, 155 and 70. Fractions 1 to 5 were each subjected to a refractionation by the same procedure to yield 21 fractions of further decreased molecular weight heterogeneity for the light scattering and viscosity determinations. The initial polymer concentrations in these refractionation solutions were $\leqq 1.3$ g. polymer/liter. Fig. 1 is a schematic representation of the fractionation results.

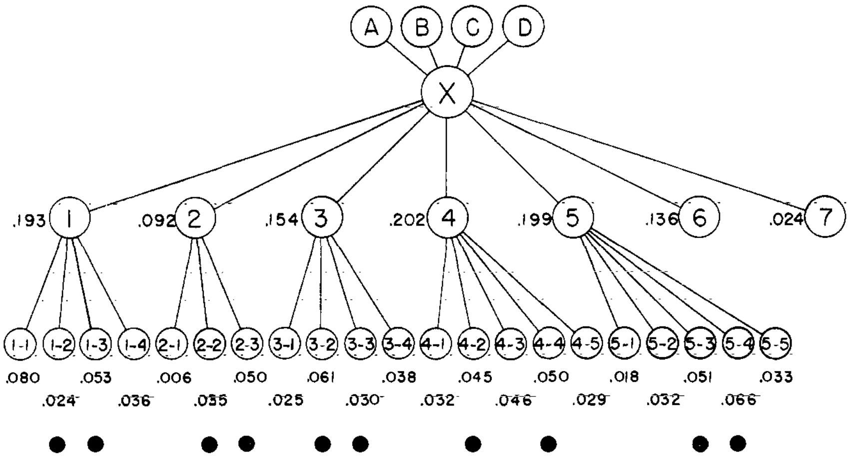

Fig. 1.—Fractionation of combined polyvinylacetate samples A, B, C and D. Designation numbers of fractions are given within the circles. The numbers outside the circles represent the fractional part of the total polymer contained in the respective fractions.

Liquid–Liquid Phase Equilibria Measurements.—System: methyl isopropyl ketone(1)–*n*-heptane(2)–polyvinylacetate(3). The phase separation temperatures, T_p, of solutions of three polyvinylacetate fractions ($\bar{M}_v$ = 500,000, 1,040,000 and 3,700,000) each in three methyl isopropyl ketone–*n*-heptane mixtures (MIPK: C_7H_{16} = 3:1, 4:1 and 6:1 by volume at 25°) at five polymer concentrations (volume fraction of polymer at 25° = 0.009, 0.019, 0.034, 0.055 and 0.080) were determined. From these 45 precipitation temperatures the volume fraction, v_2(CCM), of *n*-heptane in the critical consolute mixture yielding phase separation for the infinite molecular weight polymer species at infinite dilution was obtained as a function of temperature. This required an empirical double extrapolation of the data at arbitrary temperatures, first to the limit of the infinite molecular weight polymer molecule and then to the limit of infinite polymer dilution.

Viscosity Measurements.—The limiting viscosity numbers reported were obtained by measuring solvent and solution flow times in an Ostwald–Fenske viscometer which was calibrated for kinetic energy corrections. A modified Ostwald–Fenske viscometer having a helical capillary was also used for solutions of polyvinylacetate fractions 1-2 and 2-3 in methyl ethyl ketone at 25° to determine approximately the effect of rate of shear upon the limiting viscosity numbers. At 25° the flow times of methyl ethyl ketone in the Ostwald–Fenske and modified Ostwald–Fenske viscometers were 107.1$_2$ and 1640.5 sec., respectively. The corresponding maximum rates of shear were approximately 4000 and 400 sec.$^{-1}$.

Four concentrations of each fraction in the chosen solvent were measured viscometrically and $[\eta]$, the limiting viscosity number, was obtained by simultaneous extrapolation of plots of η_{sp}/c and $(\ln \eta_r)/c$ against c to infinite dilution. Temperature was controlled at 25.0 to ±0.01° during measurements.

Light Scattering Measurements.—Light scattering measurements were made with an instrument constructed by Dr. H. E. Stanley.[15] This instrument resembles in many respects the one described by Zimm.[16] It was operated as a null instrument, *i.e.*, scattered light observed by a photomultiplier detector was balanced by means of an electronic bridge circuit against a portion of the incident beam diverted to a photoelectric tube. An oscilloscope was utilized to observe the balance of the opposed and amplified 120-cycle signals from the scattered light detector and the incident light monitor. The light source was a General Electric AH-4 medium-pressure mercury lamp. The 5461 and 4358 Å. lines were isolated by Corning filter combinations. The light was vertically polarized by neutral filters.

Since the scatterer was operated as a null instrument all absolute intensities of scattered light had to be calculated from comparisons with standards of known turbidity. A 0.5% solution of polystyrene in toluene,[17] possessing an excess turbidity above that of toluene of 0.00125 cm.$^{-1}$ for 5461 Å. light, was used as an operating scattering standard. The primary standard was pure benzene for which the absolute turbidity values[18] $(16\pi/3) \times 16.3 \times 10^{-6}$ cm.$^{-1}$ for 5461 Å. light and $(16\pi/3) \times 48.4 \times 10^{-6}$ cm.$^{-1}$ for 4358 Å. light were employed in all calculations of molecular weights. The comparison of a solution with a standard of known turbidity to determine the absolute intensity of light scattered from the solution requires a scattering volume correction. The calculation of this correction was accomplished in the manner described by Hermans and Levinson.[18b] Thus, at 90° scattering angle using vertically polarized light the absolute intensity of excess scattered light from a solution was obtained from the relation $I_{90,v} = \tau_c(3/8\pi)[n(n + 0.12)/n_c(n_c + 0.12)](I^{\text{obsd.}}/I_c^{\text{obsd.}})$. τ_c is the absolute excess turbidity of the standard and $(I^{\text{obsd.}}/I_c^{\text{obsd.}})$. is the observed ratio of the apparent excess scattering intensities of the solution to that of the standard. n and n_c are the refractive indices of the solution and standard, respectively. The quantity in the square brackets is the scattering volume correction. Its form arises from the scattering geometry involving a conical cell immersed in a cylindrical bath. The constant 0.12 reflects the dimensions of the apparatus.

---

(15) H. E. Stanley, Doctoral thesis, Massachusetts Institute of Technology, 1949.

(16) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

(17) The polystyrene standard was furnished by Professor P. Debye of the Department of Chemistry of Cornell University.

(18) (a) C. I. Carr, Jr., and B. H. Zimm, *J. Chem. Phys.*, **18**, 1616 (1950); (b) J. J. Hermans and S. Levinson, *J. Opt. Sci.*, **41**, 460 (1951).

The refractive index increment, dn/dc, at 25° for polyvinylacetate in methyl ethyl ketone is 0.080 cm.^{3}g.$^{-1}$,[19] and for polyvinylacetate in the methyl isopropyl ketone–n-heptane mixture it is 0.075_3 cm.^{3}g.$^{-1}$.[20] Any change in dn/dc with wave length between 4358 and 5461 Å. was less than the experimental uncertainty which is approximately ±0.5% in dn/dc. The refractive indices of methyl ethyl ketone and the solvent mixture are 1.377 and 1.385, respectively, measured with 5461 Å. light. The difference in refractive indices between methyl isopropyl ketone and n-heptane at 25° was found to be 0.00101 by a differential refractometric measurement with 5461 Å. light. This illustrates the degree to which these liquids constitute an isorefractive index pair.

Scattered light intensities were measured for four concentrations of polymer in the chosen solvent each at thirteen angles in the horizontal plane covering the region 30° to 145° from the direction of the incident beam. The most concentrated solution of each series was prepared by weighing a polymer sample into a 100-ml. flask and diluting to volume with the solvent at 25.0°. Successive dilutions were made from this solution by pipetting 50 ml. of the solvent at 25.0° into 100-ml. flasks and then filling to 100 ml. with the next more concentrated solution. The solutions were filtered under nitrogen pressure through ultrafine sintered glass filters into the light scattering cells to remove dust. With sufficient care in manipulation this procedure proved satisfactory. There was some indication of polyvinylacetate adsorption by the glass filter from the most dilute solutions in the critical consolute mixture. Since the osmotic second virial coefficients were zero in this medium, higher polymer concentrations were used and the effect of the apparent adsorption was rendered negligible.

The temperature of the solutions during the light scattering measurements was 25 ± 0.1°.

Results and Discussion

A precise interpretation of the light scattering and viscosity data of dilute polymer solutions would require complete knowledge of the distribution of molecular weights within the polymer sample studied and the effect of this distribution upon the measured physical quantities. The exact determination of molecular weight distributions is difficult. Various mathematical forms may describe, within the limits of experimental uncertainty, a given actual distribution.[21] In order to avoid as much as possible the troublesome aspects of molecular weight heterogeneity polymers are fractionated to form less disperse systems. The degree of heterogeneity is then assumed to have a negligible effect upon the properties studied, or an attempt is made to approximate the form of the residual heterogeneity and to correct for it.

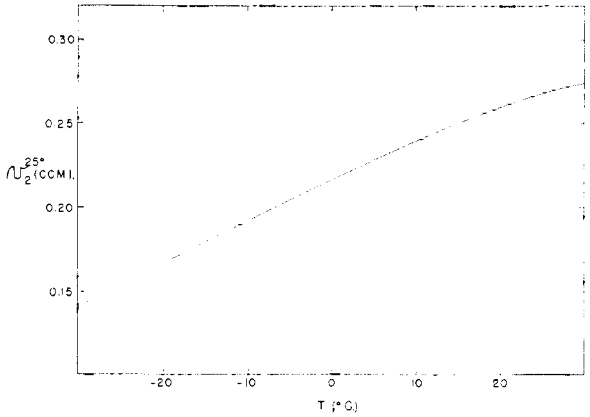

Fig. 2.—Volume fraction of n-heptane (calculated at 25°) in critical consolute mixtures of methyl isopropyl ketone (1) and n-heptane (2) for polyvinylacetate given as a function of temperature, T (° C.).

In the present study the distribution of molecular weights within the polymer samples is assumed to be satisfactorily approximated by the relation[21,16]

$$w(M)\,\mathrm{d}M = \lambda^{z+1}M^{z}e^{-\lambda M}\mathrm{d}M/\Gamma(z+1) \qquad (1)$$

where $w(M)$ is the weight fraction of polymer having a molecular weight in the region of M to M + dM. λ is related to the number-, weight- and z-average molecular weights of the distribution by $\lambda = z/\bar{M}_n = (z+1)/\bar{M}_w = (z+2)/\bar{M}_z$. As is apparent from these latter equalities, z is a measure of the breadth of the distribution.

With the use of equation 1 the light scattering data have been treated in the manner formulated by Zimm.[22,16] His derivation led to the relation

$$Kc/I_\theta = P^{-1}(\theta, z)/\bar{M}_w + 2A_2c + \cdots \qquad (2)$$

K is a constant determined by the optical constants of the system. c is the polymer concentration in g./cm.^{3}. I_θ is the intensity at angle θ of the excess scattered light due to the polymer molecules. $\bar{M}_w$ is the weight-average molecular weight of the polymer and A_2 is the osmotic second virial coefficient. The form of $P^{-1}(\theta, z)$, the reciprocal intensity function of the angle of observation, depends upon the polymer size and heterogeneity.

Application of equation 2 to determine the z-average mean-square radius, $\overline{R^2}_z$, (frequently referred to as the square of the "radius of gyration") and weight-average molecular weight, $\bar{M}_w$, requires an assignment of a value for z for each polymer fraction studied. Every theory of polymer coil configurations in dilute solutions predicts a direct proportionality between the mean-square radius of a linear polymer coil and its molecular weight *if* the coil is immersed in a poor solvent at the plait point temperature, Θ,[23] or in a critical consolute solvent mixture, CCM, corresponding to the plait point for infinite molecular weight polymer in a ternary system.[24] In such media osmotic forces tending to expand or compress the coil are zero and "random flight" prevails. It was therefore deemed desirable to use a "random-flight" medium to obtain an estimate of the relative residual heterogeneities of the polyvinylacetate fractions.

Figure 2 presents the result of the treatment of the three-component phase equilibria for the system methyl isopropyl ketone (1)–n-heptane (2)–polyvinylacetate (3). The volume fraction of n-heptane, v_2(CCM), (calculated at 25°) in mixtures of methyl isopropyl ketone and n-heptane required to produce a critical consolute mixture for polyvinylacetate ($M = \infty$) is plotted as a function of temperature. Thus at 25° the CCM consists of 0.732 part

---

[19] R. O. Howard, Doctoral thesis, Massachusetts Institute of Technology, 1952.

[20] This refractive index increment was measured with a differential refractometer constructed by Dr. M. Fixman; this Laboratory.

[21] F. W. Billmeyer, Jr., and W. H. Stockmayer, *J. Polymer Sci.*, **5**, 121 (1950).

[22] B. H. Zimm, *J. Chem. Phys.*, **16**, 1093 (1948).

[23] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953; Chap. XIII; P. J. Flory and W. R. Krigbaum, "Annual Review of Physical Chemistry," Vol. II, Annual Reviews, Inc., Stanford, Calif., 1951, pp. 383 ff.

[24] A. R. Shultz and P. J. Flory, THIS JOURNAL, **75**, 5681 (1953).

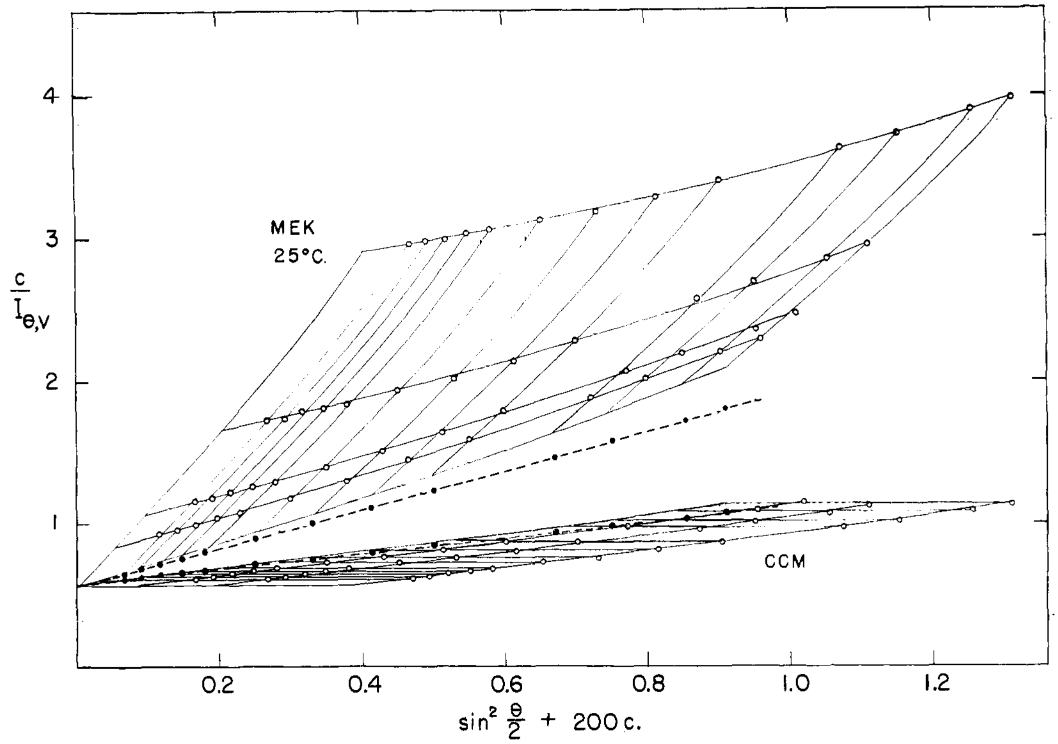

Fig. 3.—Reciprocal excess scattering intensity of polyvinylacetate fraction 2-2 solutions in methyl ethyl ketone (MEK) and a critical consolute solvent mixture (CCM) at 25° given as a function of the scattering angle, θ, and of the polymer concentration, c (g./cm.^{3}). The solid circles are $(c/I)^{\text{cor.}}_{c=0}$ values which lie upon the limiting tangents to the reciprocal intensity curves.

methyl isopropyl ketone and 0.268 part n-heptane by volume.

Scattered light from solutions of fractions 2-2, 2-3, 4-4 and 5-4 in this CCM at 25° was measured as a function of concentration and angle of observation. Figure 3 is a representative Zimm plot for fraction 2-2 in methyl ethyl ketone and in the critical consolute mixture as observed with vertically polarized 5461 Å. light. The arbitrary ordinate scales in the two media have been adjusted by the ratio of the intercepts. The solid circles in Fig. 3 are c/I_θ values at zero polymer concentration corrected to their values on the limiting tangents. The method of calculating these quantities, hereafter referred to as $(c/I)^{\text{cor.}}_{c=0}$, is described by Zimm.[22] Essentially it involves the formation of the plot shown in Fig. 3, extrapolation of the reciprocal excess scattering intensities at each angle to zero polymer concentration and then an approximate extrapolation of the $(c/I)_{c=0}$ against $\sin^2(\theta/2)$ curve to $\sin^2(\theta/2) = 0$. The $(c/I)^{\text{cor.}}_{c=0}$ to values may then be calculated by using the ratio of $(c/I)_{c=0}$ to $(c/I)_{\substack{c=0\\ \theta=0}}$ at each angle, assuming a distribution breadth characterized by z in equation 1. Theoretically only the proper choice of z will lead to $(c/I)^{\text{cor.}}_{c=0}$ which lie on the perfectly straight line representing the limiting tangent to the reciprocal intensity curves. This suggests the possibility of using the limiting tangent calculation to determine the heterogeneity of a polymer sample by ascertaining what z assumption is required to nullify the curvature of the $(c/I)_{c=0}$ against $\sin^2(\theta/2)$ plot. In practice this procedure appears not to possess adequate sensitivity to determine distribution breadths. The limitations of experimental uncertainty in the reciprocal intensities and their extrapolations to zero polymer concentration permit considerable latitude in the choice of z. Thus z values ranging from 10 to ∞ yield $(c/I)^{\text{cor.}}_{c=0}$ values lying upon satisfactory straight lines in $(c/I)^{\text{cor.}}_{c=0}$ against $\sin^2(\theta/2)$ plots for the present series of fractions. However, $z = 4$ was found to be insufficient to eliminate the curvature of the $(c/I)_{c=0}$ vs. $\sin^2(\theta/2)$ plots. The assumptions of Gaussian polymer chains and a particular form for the molecular weight distribution also impose certain theoretical limitations on the physical reality of deductions based upon the exact form of the reciprocal excess scattering curves. Analysis of the scattering data for the four fractions in the CCM revealed that calculation of the limiting tangents to the reciprocal intensity curves upon the assumption that each fraction had a distribution breadth corresponding to $z = 10$ gave a reasonably constant value for $\overline{R^2}_w/\overline{M}_w$. Under random-flight conditions $\overline{R^2}_w = \overline{R^2}_z(z + 1)/(z + 2)$. Assumption of radically different heterogeneities for these fractions in an attempt to bring the $\overline{R^2}_w/\overline{M}_w$ ratios into closer agreement was not deemed justifiable. A ±10% uncertainty in the experimental values of this ratio may exist at these relatively small coil sizes. The limiting tangents of the four chosen fractions in the CCM passing through the $(c/I)^{\text{cor.}}_{c=0}$ calculated[16] from the light scattering data using $z = 10$ are shown in Fig. 4 as observed with 4358 and

TABLE II

LIGHT SCATTERING AND VISCOSITY DATA FOR POLYVINYLACETATE IN METHYL ETHYL KETONE (MEK) AND A CRITICAL CONSOLUTE MIXTURE (CCM) AT 25°

Fraction	$\bar{M}_w \times 10^{-6}$ MEK_{5461}	CCM_{5461}	$\bar{R}^2_z \times 10^{12}$ (cm.^{2}) MEK_{5461}	CCM_{5461}	CCM_{4358}	$[\eta]$(cm.^{3} g.$^{-1}$) MEK	CCM	$A_2 \times 10^4$ (cm.^{3} g.$^{-2}$ mole) MEK_{5461} I	II
1-2	3.46		82			573 (590)		2.43	2.35
2-2	3.02	2.87	73	28.1	28.0	520	149	2.63	2.56
1-3	2.74		66			473		2.85	2.87
3-2[25]	2.15		49			430		2.7	
2-3	1.99	2.07	46	21.2	20.9	412 (421)	127	2.90	2.36
3-3[25]	1.91		45			389		2.77	
4-2	1.74		38			377		2.93	2.82
A[25]	1.67		52			351		2.68	
4-4	1.39	1.37	29.5	14.5	13.3	310	95	3.25	2.90
5-3	1.02		21.0			276		3.47	3.14
5-4	0.87	0.85	16.5	9.0	9.1	231	89	3.51	3.3

5461 Å. light. The arbitrary ordinate scale is based upon comparison of the solutions with the standard polystyrene solution at 90° scattering angle.

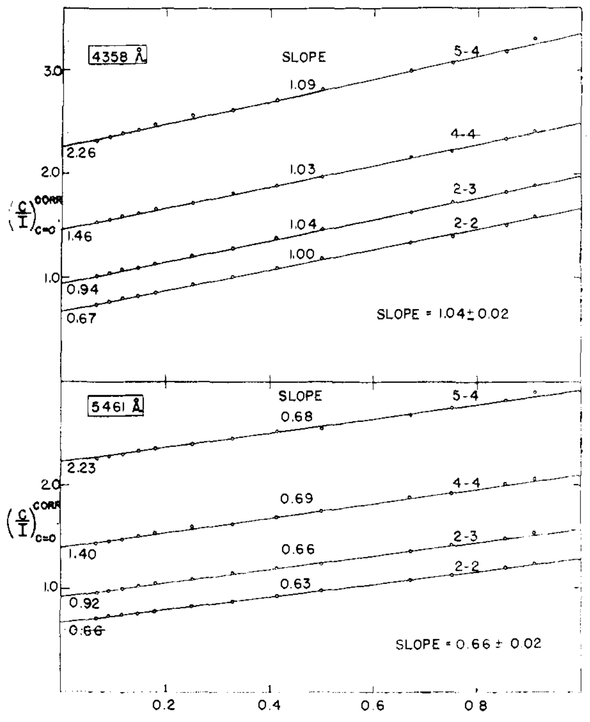

Fig. 4.—$(c/I)^{\text{corr}}_{c=0}$ plotted against the appropriate function of the scattering angle, θ, for polyvinylacetate fractions in the solvent mixture MIPK (0.732)-n-C_7H_{16} (0.268) at 25°. The lines through these points are the limiting tangents to the reciprocal excess scattering intensity curves. The slopes of these tangents are proportional to $\bar{R}^2_z/\bar{M}_w$ for the respective fractions.

Limiting tangents to the reciprocal intensity curves of eight polyvinylacetate fractions in methyl ethyl ketone observed with 5461 Å. light are shown in Fig. 5. All the tangents were calculated assuming $z = 10$.

The light scattering and limiting viscosity number data for ten polyvinylacetate fractions and unfractionated polymer A are summarized in Table II. The $\bar{M}_w$ values were calculated from the intercepts of the reciprocal intensity tangent lines using the optical constants given in the Experimental section. Similarly the $\bar{R}^2_z$ values were calculated from the slope-to-intercept ratios of these lines. The method of determining the osmotic second virial coefficients, A_2, will be discussed in the last section of this article.

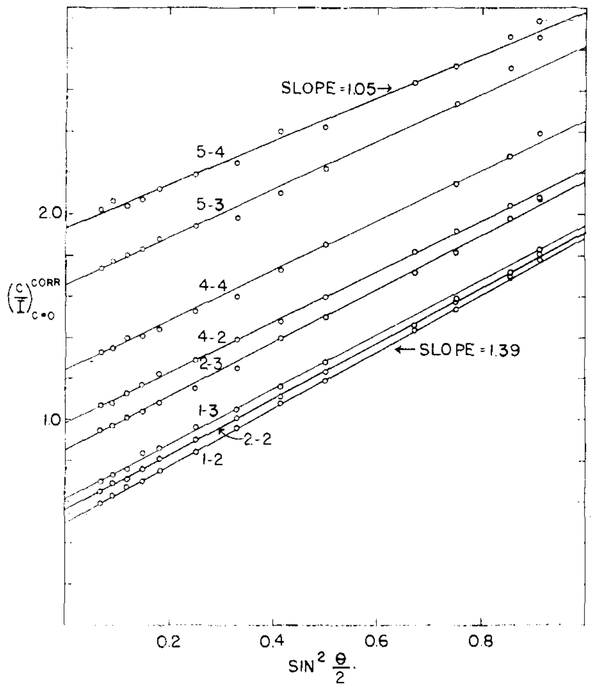

Fig. 5.—$(c/I)^{\text{corr}}_{c=0}$ plotted against the appropriate function of the scattering angle, θ, for polyvinylacetate fractions in methyl ethyl ketone at 25°. The straight lines through these points are the limiting tangents to the reciprocal excess scattering intensity curves for the respective fractions.

Some general comments concerning the quantities presented in Table II may now be made. Very good agreement is observed between the molecular weights of fractions 2-2, 2-3, 4-4 and 5-4 as determined from scattering data in the "good" solvent methyl ethyl ketone and in the critical consolute mixture. The remarkable concordance obtained must be somewhat fortuitous, but it

(25) Data obtained by Mr. Joseph P. Bevak of this Laboratory.

serves to emphasize the general validity of the measurements. The $\overline{M}_w$ values, being functions of the intercepts of the limiting tangents to the reciprocal intensity curves, are very insensitive to the form or breadth of the molecular weight distribution assumed in treating the data. The z-average mean-square radii of these four fractions in the CCM as observed by green light and by blue light are in excellent agreement except for fraction 4-4. In this latter case the 9% disagreement is unexplained, but not excessive.

The unfractionated polyvinylacetate sample was assumed to have the distribution expressed by equation 1 with $z = 1$. This is its theoretical distribution according to the kinetics of the polymerization in which the predominant termination of physical chains was by transfer to monomer. Recent studies[26] on the polymerization kinetics of vinyl acetate dictated the conditions under which the polyvinylacetates used in the present investigation were prepared. In addition to a reasonable knowledge of the molecular weight distribution obtained, the extent of branching in the polymer molecules is known to be negligible. Thus, the difficulty of evaluating physical properties of polymer coils having considerable and unknown degrees of branching was avoided.

In the following sections some of the relationships among the quantities in Table II are presented and discussed briefly in the light of existing theories of dilute polymer solutions.

The Ratio of $\overline{R^2}_w$ to $\overline{M}_w$.—Let us first inspect the dependence of the mean-square radii of the polyvinylacetate molecules upon their molecular weights. In Fig. 6 is shown upon a log–log plot $\overline{R^2}_w/\overline{M}_w$ against $\overline{M}_w$ for four polyvinylacetate fractions in the CCM (observed with 5461 and 4358 Å. light) and for ten polyvinylacetate fractions (open circles) and unfractionated sample A (cross-hatched circle) in methyl ethyl ketone at 25°. The CCM data were used as described above to secure an estimate of the heterogeneities of the fractions. All eight points for the fractions in the CCM lie within ±5% of the horizontal broken line corresponding to the theoretical independence of $\overline{R^2}_w/\overline{M}_w$ with respect to $\overline{M}_w$. The slight apparent decrease in this ratio with increasing molecular weight might indicate that the solvent mixture used was "poorer" than the true critical consolute mixture. This possibility is ruled out, however, since the osmotic second virial coefficients for these solutions were all zero within a small experimental uncertainty. In fact, the disappearance of the virial coefficients was strong corroboration of the effectiveness of the empirical extrapolations of the phase equilibrium data. Any attempt to eliminate this observed slight decrease in $\overline{R^2}_w/\overline{M}_w$ by assignment of differing degrees of heterogeneity would require the postulation that the higher molecular weight fractions are much less disperse than the lower molecular weight fractions. This would be at variance with all present theories of fractionation. It is most logical to assume that the slight deviation of $\overline{R^2}_w/\overline{M}_w$ from a constant value in the CCM is merely a manifestation of experimental limitations.

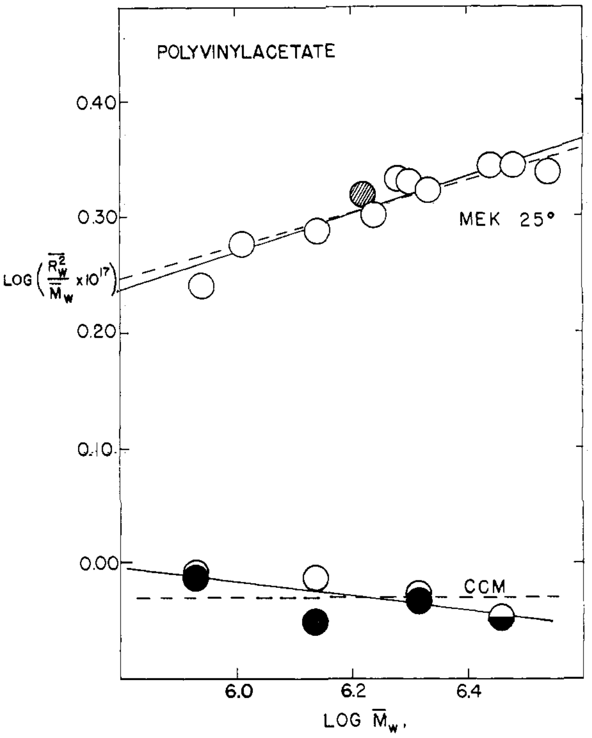

Fig. 6.—A log–log plot of the ratios of the weight-average mean-square radii, $\overline{R^2}_w$, to the weight-average molecular weights, $\overline{M}_w$, against $\overline{M}_w$ for polyvinylacetate fractions in methyl ethyl ketone and in a critical consolute mixture at 25°. The cross-hatched circle represents unfractionated polymer A. Solid circles represent data obtained with 4358 Å. light.

$\overline{R^2}_w$ values for the polyvinylacetate fractions (and for polymer A) in methyl ethyl ketone were calculated according to the relation $\overline{R^2}_w = \overline{R^2}_z(z + 1)/(z + 2)$. In a strict sense this conversion is valid only for distributions of molecules whose chains obey random-flight statistics, but it is nevertheless a good approximation for distributions of molecules which exhibit excluded volumes. The agreement of $\overline{R^2}_w/\overline{M}_w$ of the unfractionated polymer A (cross-hatched circle) with the ratios for the fractions is further evidence that $z = 10$ is a satisfactory assignment for the molecular weight distributions of the fractions. This should not, however, be viewed as a sensitive test for relative degrees of heterogeneity among fractions.

The important conclusion to be drawn from Fig. 6 is that $\overline{R^2}_w$ is proportional to a power of $\overline{M}_w$ which is greater than unity for polyvinylacetate in methyl ethyl ketone. Thus the excluded volume effect[3,4] for this system is a function of the molecular weight as has been predicted by several theoretical treatments.[3,4,9,27,28] The increase in $\overline{R^2}_w/\overline{M}_w$ with increasing $\overline{M}_w$ in the molecular weight region studied exceeds possible experimental error. In this respect the results of the present study are in agree-

---

(26) L. H. Peebles, Doctoral thesis, Massachusetts Institute of Technology, 1953.

(27) W. Kuhn, *Kolloid-Zt.*, **68**, 2 (1934).

(28) M. Yamamoto, *Busseiron Kenkyû*, **44**, 36 (1951); *C. A.*, **46**, 1844 (1952).

ment with recent investigations[29,30] on polymethylmethacrylate solutions in good solvents indicating an increase in $\overline{R^2}_z/\overline{M}_w$ with increasing $\overline{M}_w$. Some authors[31,32] have emphasized the difficulty in obtaining valid experimental evidence concerning the constancy or variability of $\overline{R^2}/M$ occasioned by the unknown molecular weight heterogeneities of polymer samples. The present experimental approach hurdles this obstacle. The measurement of $\overline{R^2}_w/\overline{M}_w$ on the same polymer fractions in the good solvent, methyl ethyl ketone, and in the critical consolute mixture eliminates the possibility that the observed influence of molecular weight upon the expansion of the coils can be attributed to molecular weight heterogeneity or to a systematic instrument error. The vertical separation of the plots for the two systems (Fig. 6) demonstrates the effect of solvent media upon the coil dimensions. The divergence of the plots with increasing molecular weight shows that coupled with the solvent effect there also exists a molecular weight dependent contribution to the expansion of the polymer coils.

The relations represented in Fig. 6 may be expressed as

(Least-square fit)

$$\text{MEK} \quad \log_{10}(\overline{R^2}_w/\overline{M}_w) = -17.707 + 0.163 \log_{10}\overline{M}_w \quad (3)$$

$$\text{CCM} \quad \log_{10}(\overline{R^2}_w/\overline{M}_w) = -16.651 - 0.061 \log_{10}\overline{M}_w \quad (4)$$

(Broken-line approximation)

$$\text{MEK} \quad \log_{10}(\overline{R^2}_w/\overline{M}_w) = -17.565 + 0.140 \log_{10}\overline{M}_w \quad (3a)$$

$$\text{CCM} \quad \log_{10}(\overline{R^2}_w/\overline{M}_w) = -17.030 \quad (4a)$$

$\overline{R^2}_w$ is expressed in cm.^{2} units.

The approximate relations 3a and 4a satisfy the data within experimental uncertainty. Equation 4a is formulated to agree with the theoretically predicted random-flight conditions in the CCM.

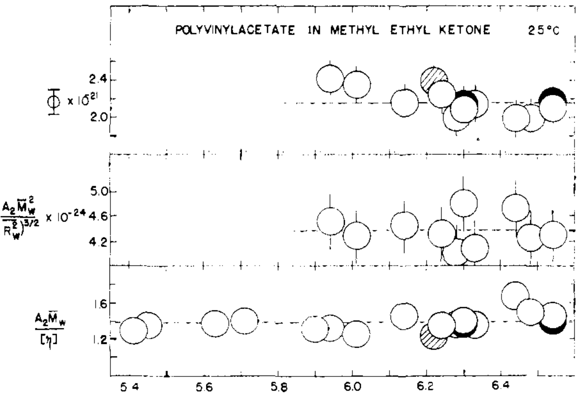

Fig. 7.—A composite graph of thermodynamic and hydrodynamic quantities which are predicted to be essentially independent of molecular weight for solutions of polyvinylacetate fractions in methyl ethyl ketone at 25°.

Equation 3a will be discussed with reference to the molecular-weight and coil-dimension dependence of the limiting viscosity numbers.

Limiting Viscosity Numbers and Coil Dimensions.—Flory and Fox[9] have treated the relation of limiting viscosity numbers, $[\eta]$, to molecular weights and mean-square radii, $\overline{R^2}$, by an equivalent hydrodynamic sphere approach and have obtained the expressions[33]

$$[\eta] = (100 \times 6^{3/2})\Phi(\overline{R^2})^{3/2}/M \quad (5)$$

$$= (100 \times 6^{3/2})\Phi(\overline{R_0^2}/M)^{3/2}M^{1/2}\alpha^3 \quad (5a)$$

Under the conditions specified by these authors Φ should be the same constant for all flexible linear polymers independent of solvent and temperature. $\overline{R_0^2}$ is the unperturbed (random-flight) mean-square radius of a molecule of molecular weight M at a given temperature. $\overline{R^2} = \overline{R_0^2}\alpha^2$ is the mean-square radius of the molecule in any other solvent medium at the same temperature.

Applying equation 5 to a polymer having a molecular weight distribution given by equation 1 Stockmayer[34] has shown that, to the approximation $\overline{R_i^2} \propto M_i^{1+2\epsilon}$

$$[\eta] = (100 \times 6^{3/2})\Phi\gamma(\overline{R^2}_z)^{3/2}/\overline{M}_w \quad (6)$$

$$\gamma = (z+1)\Gamma(z+1.5+3\epsilon)[\Gamma(z+2)/\Gamma(z+3+2\epsilon)]^{3/2}/\Gamma(z+1)$$

Newman has approached this problem of harmonizing the various physical averages by developing the ratio of moments of the molecular weight distribution involved, and the result was applied to a random-flight (*i.e.*, $\epsilon = 0$) situation.[35]

Combination of the limiting viscosity number data of Table II for polyvinylacetate in methyl ethyl ketone at 25° with previous data of Howard[19] yields the empirical relation

$$\log_{10}[\eta] = \log K' + (0.50 + 3\epsilon)\log_{10}\overline{M}_w = -1.871 + 0.71 \log_{10}\overline{M}_w \quad (7)$$

for good fractions in the molecular weight range 246,000 to 3,460,000. Thus in this region $\epsilon \simeq 0.07$. It was this value of ϵ which prompted the approximation (equation 3a) $\overline{R^2}_w/\overline{M}_w = \text{const.} \times \overline{M}_w^{0.14}$

Using equation 6, the data of Table II, $\epsilon = 0.07$ and $z = 10$ for the fractions ($z = 1$ for polymer A) Φ was calculated for polyvinylacetate in methyl ethyl ketone at 25°. The results are presented in the upper graph of Fig. 7. All but one of the polymer fractions yielded values within 10% of $\Phi = 2.18 \times 10^{21}$. The solid circles represent viscosity measurements at low rates of shear. The unfractionated polymer (cross-hatched circle) exhibited a Φ of 2.4×10^{21} which is in good agreement with the Φ values calculated for the fractions.

It is therefore found that the Flory–Fox viscosity concept satisfactorily describes the observed viscosities of high molecular weight linear polyvinylacetates in methyl ethyl ketone at 25°. $\Phi = 2.2 \times$

---

[29] J. Bischoff and V. Desreux, *Bull. soc. chim. Belg.*, **61**, 10 (1952); *J. Polymer Sci.*, **10**, 437 (1953).

[30] G. V. Schulz, H.-J. Cantow and G. Meyerhoff, *ibid.*, **10**, 79 (1953).

[31] T. B. Grimley, *Proc. Roy. Soc.* (*London*), **A212**, 339 (1952).

[32] J. J. Hermans, M. S. Klamkin and R. Ullman, *J. Chem. Phys.*, **20**, 1360 (1952).

[33] The factor $(100 \times 6^{3/2})$ is inserted to preserve the value of Φ as originally formulated by Flory and Fox. The factor 100 converts the units of $[\eta]$ to cm.^{3} g.$^{-1}$ and $6^{3/2}$ transforms $(\overline{R^2})^{3/2}$ to the cube of the root-mean-square end-to-end distance for a random-flight linear polymer coil.

[34] Private communication.

[35] S. Newman, paper presented at the Fall Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

10^{21} for polyvinylacetate indicates that the hydrodynamic behavior of its coils resembles that of other flexible polymer molecules.[10–14] The question of the proper assignment of heterogeneity functions and subsequent correction for such heterogeneity might conceivably produce from 10 to 20% disagreement among the value of Φ reported in the literature. Fortunately the effect of heterogeneity assumptions upon the calculation of the limiting tangent to the light-scattering reciprocal intensity curves and upon the calculation of γ are somewhat compensatory in the determination of Φ. Consequently, Φ is not as sensitive to the heterogeneity assumptions as one might at first believe.

The results of the present light scattering and viscosity study indicate that the deviation from 0.50 of a in the relation $[\eta] = K'M^a$ may be completely attributed to the molecular weight dependence of the expansion of the polymer coils.

The Osmotic Second Virial Coefficient, A_2.—The use of light scattering measurements to determine A_2 requires some careful consideration. The most important question to resolve is the effect of angular dissymmetry in the light scattering upon the initial slope and the curvature of Kc/I_θ against c plots. Treatment of osmotic pressure data is free of this theoretical complication. Thus the osmotic pressure to concentration ratio, π/c, can be expanded in terms of the polymer concentration as follows

$$\pi/c \cong (RT/M)(1 + \Gamma_2 c + \Gamma_3 c^2) \qquad (8)$$

where M is the number-average molecular weight of the polymer and the Γ_n's are virial coefficients ($A_2 = \Gamma_2/M$). Γ_2 may be calculated from properties of the system assuming a statistical model and the third virial coefficient may be semi-empirically related to the second by $\Gamma_3 = g\Gamma_2^2$.[6] In the "hard sphere" approximation $g = 5/8$ and for "soft" molecules $g < 5/8$.[36] For light scattering measurements an expansion of the concentration to excess scattering intensity ratio in powers of the concentration yields

$$Kc/I_0 \cong (1/M)(1 + 2\Gamma_2 c + 3\Gamma_3 c^2) \qquad (9)$$

where I_0 is the excess scattering intensity in the limit of zero scattering angle of a solution of concentration c. M is here the weight-average molecular weight of the solute and the Γ_n's differ slightly from those in the osmotic pressure expansion due to the different molecular weight average. Equations 8 and 9 have been applied to osmotic pressure and light scattering (90°) data with considerable success using $g \leq 5/8$.[11,14,36–38]

Stockmayer and Casassa[36] have discussed in some detail the theoretical difficulties in applying equation 9 to light scattering data at angles other than zero when appreciable angular dissymmetry exists. According to the "single contact" approximation of polymer chain interaction equation 2 is valid and the initial slopes of Kc/I_θ against c plots are equal to $2A_2$ for all angles of observation.[22] However, even to this approximation, the curvature terms of these plots are somewhat complicated functions of the second and third virial coefficients and the angular dissymmetry of the scattered light.

The concentration dependence of Kc/I_θ for the polyvinylacetate fractions in methyl ethyl ketone was treated in two different ways to determine the effect of treatment of data upon the A_2 values observed. Method I consisted of a straightforward plot of the 90° scattering data Kc/I_{90} against c to produce curves exhibiting considerable positive curvature. What appeared to be the best limiting tangents to these curves were drawn and A_2's were obtained from the slopes of these tangents. Method II involved the superposition of log (Kc/I_0) against log c plots (*i.e.*, plots of data extrapolated to zero scattering angle at each polymer concentration) upon a master plot of $\log\,[1 + 2(\Gamma_2 c) + 3g(\Gamma_2 c)^2]$ against $\log\,(\Gamma_2 c)$ in the manner proposed by Fox, Flory and Bueche.[37] It was found that a master plot with $g = {}^1/_6$ gave a ratio between Γ_3 and Γ_2^2 which fitted the extrapolated data at zero scattering angle very satisfactorily.

The virial coefficients obtained by the two methods just described are listed in Table II under the Roman numerals I and II. The agreement is good except for fraction 2-3 in which the value obtained by method II appears to be in error. Although the general agreement is pleasing certain reservations must be made concerning the factors contributing to this agreement. Careful analysis of the concentration dependence of Kc/I_θ at scattering angles ranging from 30 to 145° for polymer solutions yielding considerable angular dissymmetry in the scattered light reveals two tendencies. First, the initial slopes of Kc/I_θ against c plots decrease slightly with increasing angle of observation. Secondly, there is a pronounced increase in the curvature of these plots with increasing angle of observation. The first-mentioned factor should cause the A_2 values obtained by method I to be lower than those secured by the treatment of data in the limit of zero scattering angle. The fact that this is not observed indicates that the estimation of curvature of the Kc/I_θ against c plots may have been low in drawing the limiting tangents at 90°. Such underestimation of curvature is a common fault in the customary treatment of osmotic pressure and light scattering data of polymers in thermodynamically good solvents. Method II is a theoretically more satisfactory approach for obtaining virial coefficients. Its major drawback lies in the necessity of careful measurements of scattered light intensities over a large range of angles and extrapolation of these measurements to zero scattering angle. Admitting the difficulties just discussed we report the values of A_2 obtained by method I as having a probable accuracy of approximately ±10%.

Let us finally examine briefly the relation of A_2 to $\overline{R}^2_{\mathrm{w}}$, $\overline{M}_{\mathrm{w}}$ and $[\eta]$. Although the present stage of excluded volume theory development is not sufficient to give explicit numerical relations among the above quantities, an interesting empirical deduction can be made from the form of the theoretical expressions. Casassa[39] has pointed out that ac-

---

[36] W. H. Stockmayer and E. F. Casassa, *J. Chem. Phys.*, **20**, 1560 (1952).

[37] T. G. Fox, Jr., P. J. Flory and A. M. Bueche, This Journal, **73**, 285 (1951).

[38] W. R. Krigbaum and P. J. Flory, *ibid.*, **75**, 1775 (1953); *J. Polymer Sci.*, **9**, 503 (1952); *ibid.*, **11**, 37 (1953).

[39] E. F. Casassa, Doctoral thesis, Massachusetts Institute of Technology, 1953.

cording to some recent theories of the osmotic second virial coefficient in the limit of large excluded volumes, *i.e.*, for high molecular weight polymer molecules in thermodynamically "good" solvents, the ratio $A_2\overline{M}_w^2/(\overline{R}_w^2)^{3/2}$ should attain an essentially constant value. Qualitatively the constancy of this ratio is an expression of the expectation that the interactions of polymer molecule pairs in such media resemble collisions of spheres whose volumes are proportional to $(\overline{R}^2_w)^{3/2}$. If, then, the volumes of the equivalent hydrodynamic spheres observed viscometrically are also proportional to $(\overline{R}^2_w)^{3/2}$ the ratio $A_2\overline{M}_w/[\eta]$ should be another constant.

The ratio $A_2\overline{M}_w^2/(\overline{R}^2_w)^{3/2}$ is plotted against log $\overline{M}_w$ in the center graph of Fig. 7 for the ten polyvinylacetate fractions in methyl ethyl ketone. Over this molecular weight range the ratio is a constant equal to 4.4×10^{24}.

A plot of $A_2\overline{M}_w/[\eta]$ against log $\overline{M}_w$ for the same system in the lower graph of Fig. 7 reveals a remarkably constant value, 1.39, for this ratio over the molecular weight range 246,000 to 3,460,000. Here again data of Howard[19] have been used to extend the observations to lower molecular weight polymer fractions.

It may therefore be stated empirically that the thermodynamic interaction of a pair of high molecular weight polyvinylacetate molecules in methyl ethyl ketone is similar to the collision of spheres having effective volumes proportional to $(\overline{R}^2_w)^{3/2}$. This observation, coupled with the validity of the equivalent hydrodynamic sphere treatment of limiting viscosity numbers, yields an empirical relation among the quantities A_2, $\overline{M}_w$ and $[\eta]$. It has been found[40] that this relation is valid for several polymers in thermodynamically good solvents, and similar magnitudes for the ratio $A_2\overline{M}_w/[\eta]$ are observed.

Acknowledgment.—The author gratefully acknowledges the encouragement and advice tendered by Professor W. H. Stockmayer during the course of this investigation.

[40] E. F. Casassa, W. H. Stockmayer and R. L. Cleland, unpublished calculations.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C., AND NEW YORK UNIVERSITY, UNIVERSITY HEIGHTS, N. Y.]

The Depolymerization of Polymethylene and Polyethylene

BY L. A. WALL, S. L. MADORSKY, D. W. BROWN, S. STRAUS AND ROBERT SIMHA

RECEIVED FEBRUARY 20, 1954

Depolymerization rates and molecular weight changes of polymethylene have been studied and mass spectrometric analyses of the volatile products obtained. The results are compared with those for commercial and radiation cross-linked polyethylene. Cross linking has little effect on the rate of depolymerization. The behavior of linear polymethylene approaches that predicted by theory for negligible depropagation and pronounced transfer. Provided a single type of intermolecular transfer occurs, the kinetics becomes then equivalent to a random depolymerization and the experimental results are analyzed on this basis. The rate exhibits a characteristic maximum as a function of conversion, which is absent in polyethylene but is predicted by theory. The differences are presumably connected with the branched structure of polyethylene. Current estimates of the amount of long and short branches lead to an increase of the initial rate over that of the linear polymer by a factor not exceeding five. These estimates do not explain the absence of a maximum rate for polyethylene. This seems to require more long branches or longer short branches.

Introduction

The theory of free radical depolymerization previously developed leads to two competing modes of decomposition, namely, scission and rapid zip. Their relative importance determines the three observable quantities usually considered, *viz.*, the rate of conversion to volatiles, dC/dt, the decrease in degree of polymerization, dP_n/dC, and the yield of pure monomer in the volatiles.[1] Methyl methacrylate, and presumably α-methylstyrene, represent one extreme, namely, preponderance of the zip. On the basis of the practically zero yield of pure monomer and the rapid molecular weight decrease, one expects polyethylene to represent the opposite extreme of an almost exclusive scission reaction, proceeding more or less at random. Yet the rate pattern does not conform to this picture. This may be attributed to the fact that the polyethylene molecule is structurally inhomogeneous because of the various types of branches formed during its synthesis.

A study of the linear polymethylene was undertaken with this in mind. It is our purpose to compare the experimental results with those for commercial polyethylene, that is branched polymethylene, and with the prediction of the general theory of chain depolymerization.

The thermal degradation of polyethylene has been the subject of several recent investigations.[2-6] The experimental results are similar in the various studies but no completely satisfactory interpretation has been given, capable of explaining all the features of the decomposition, some of which appear contradictory. The depolymerization produces only negligible amounts of the monomer, ethylene. There is no main product. A broad spectrum of linear hydrocarbons is found, consisting mainly of a wax-like portion of average molecular weight 692.[6] The molecular weight of the residue drops

---

[1] For a review see R. Simha, *Trans. N. Y. Acad. Sci.*, **14**, 151 (1952).

[2] L. A. Wall, *J. Research Natl. Bur. Standards*, **41**, 315 (1948).

[3] W. G. Oakes and R. B. Richards, *J. Chem. Soc.*, 2929 (1949).

[4] S. L. Madorsky, *J. Polymer Sci.*, **9**, 133 (1952).

[5] H. H. G. Jellinek, *ibid.*, **4**, 13 (1949).

[6] S. L. Madorsky, S. Straus, D. Thompson and L. Williamson, *J. Research Natl. Bur. Standards*, **42**, 499 (1949).