

PHYSICAL CHEMISTRY OF POLYMERS IN DILUTE SOLUTION

G. C. Berry, E. F. Casassa, R. E. Kerwin,
H. Nakayasu, T. A. Orofino, D. J. Plazek
Mellon Institute
Pittsburgh, Pennsylvania

Research at Mellon Institute on the dilute solution properties of high polymers is reviewed. Of concern in theoretical studies have been: the dimensions of branched chain molecules in poor solvents; the effect of heterogeneity in molecular weight on the second virial coefficient for linear polymers; and the effect of intermolecular correlations on Rayleigh scattering when both molecular dimensions and thermodynamic interactions are large. In experimental investigations, polystyrene has been studied to explore the properties of a particular branched structure and the nature of specific solvent effects on configurational and thermodynamic properties. The intrinsic viscosity-molecular weight relation for poly-(vinyl acetate) in butanone has been confirmed for molecular weights lower than have been studied previously. A precision light scattering photometer has been designed and built to meet the exacting requirements of projects now getting under way.

Introduction

Since 1960, research in polymer science at Mellon Institute has been aided by contracts with the Wright Air Development Division. In this paper we present a review of activities in one major division of this effort: that of dilute solution properties of synthetic polymers. Investigations have been both theoretical and experimental in character and have been pursued by a number of investigators individually and collaboratively as indicated by the following subdivision, which will be adopted for the ensuing discussion.

- (a) Conformation of branched-chain structures (G. C. Berry, T. A. Orofino)
- (b) Properties of branched polystyrene (T. A. Orofino)
- (c) Dimensions of polymers: specific solvent effects (T. A. Orofino)
- (d) The second virial coefficient for heterogeneous polymers in good solvents (E. F. Casassa)
- (e) Theory of Rayleigh scattering: effect of intermolecular correlations (E. F. Casassa)
- (f) Viscosity-molecular weight relationship for poly-(vinyl acetate) (R. E. Kerwin, H. Nakayasu)
- (g) Light scattering photometer (G. C. Berry, E. F. Casassa, D. J. Plazek)

Detailed discussions of some of these topics will be found in a Technical Report¹ entitled "Polymer Structures and Properties."

(a) Conformation of Branched Chain Structures

Except at the Flory temperature, the configuration of a polymer chain is not described by the average magnitudes arising straightforwardly from random-flight statistics since the existence of net interaction forces between remotely connected chain segments weights the probability of occurrence of many configurations. The effect may be regarded as the manifestation of a volume which the presence of one segment denies to occupancy by another, and thus the determination of chain properties as a function of this parameter is referred to as the now-famous problem of the "excluded volume."

In very good solvents the large volume effect has so far defied truly rigorous analysis, but for sufficiently small excluded volume, perturbation treatments have been carried out as far as the linear or quadratic approximation to the expansion in terms of a variable

$$z = \left(\frac{3}{2\pi b_0^2} \right)^{3/2} \beta N^{1/2}$$

where b_0 is the equivalent segment length, N is the number of statistically effective segments in the chain and β is the mutually excluded volume for a pair of segments. For the mean square radius of gyration $\langle R^2 \rangle$ of a linear chain the result is well known.²

$$\alpha^2 = \langle R^2 \rangle / \langle R^2 \rangle_0 = 134z/105 + \dots \quad (1)$$

where $\langle R^2 \rangle_0 = Nb_0^2/6$ represents the mean square radius for a true random flight. In the present investigation it has been found possible to generalize this result to the case of the star molecule with f branches radiating from a single point. Aside from being an abstraction amenable to mathematical treatment, this model is of genuine interest in that useful procedures for synthesis of such molecules have now been developed in this laboratory (cf. below). The basis of the calculation is the general relation

$$\langle R^2 \rangle = \frac{1}{2N^2} \sum_i \sum_j \langle L_{ij}^2 \rangle$$

together with the expression from the perturbation treatment²

$$\begin{aligned} \langle L_{ij}^2 \rangle = & \langle L_{ij}^2 \rangle_0 - \beta \int \sum_k \sum_l L_{ij}^2 \left[P(L_{ij}, O_{kl}) \right. \\ & \left. - P(L_{ij})P(O_{kl}) \right] dL_{ij} + \dots \end{aligned} \quad (2)$$

Contrails

Here, N is the total number of segments in the molecule, whatever may be its structure and $\langle L_{ij}^2 \rangle$ is the mean square of the vector distance L_{ij} separating segments i and j . The probability densities $P(L_{ij})$ for the occurrence of L_{ij} , $P(O_{kl})$ for the existence of a contact ($L_{kl} \rightarrow 0$) between segments k and l , and $P(L_{ij}, O_{kl})$ for both events simultaneously, are given by random flight statistics, and are thus readily formulated.² The integration over space assumes a standard form and one is left with the laborious summations (integrations) with respect to i, j, k, l . It is clear that to obtain a result correct through the second term in equation 2 configurations must be considered in which the separation L_{ij} and the contact O_{kl} are specified. The pertinent configurations occur in three groups (a) segments i, j, k, l all in one of the f branches, (b) the segments distributed within two branches, (c) the four segments distributed among three branches. The first two types are equivalent and relate simply to results already known (cf. equation 1) for linear chains having respectively (for the case of equal branches of n segments) n and $2n$ segments. Since configurations with i, j, k, l distributed simultaneously among four branches contribute nothing to the second term of equation 2, only the third category of configurations introduces anything new in the calculation for the f -functional star.

The final result for the star molecule with equal arms of length $n = N/f$ is

$$\alpha^2 = 1 + C_f z + \dots$$

where

$$C_f = \frac{2}{f^{1/2}(3f-2)} \left[(f-1) \frac{268\sqrt{2}}{105} - (f-2) \frac{67}{105} + (f-1)(f-2) \left(\frac{202\sqrt{2}}{15} - \frac{92}{5} \right) \right]$$

Numerical results for a few cases are given in Table I.

It is evident from the tabulation, first that the requirement of identical results for $f = 1$ and $f = 2$ is met, and second that the effect of increasing branching at fixed molecular weight (fixed N) is to increase the expansion factor. The latter finding is consistent with the intuitive notion that the volume exclusion effect should become more marked as the segment density is increased. Every test indicates the correctness of the foregoing results: however, it must be remarked that they are at variance with $C_4 = 1.12$ reported by Fixman.² We have confirmed that Fixman's somewhat different method does give his numerical result (and find also that it gives C_2 incorrectly); but we have so far not been able to discover the origin of the discrepancy.

In current studies the same methods are being applied in elucidating the initial effect of volume exclusion on the dimensions of regular-comb molecules--the branched structures formed by attaching uniform chains at equal distances along a backbone chain.

TABLE I

Expansion of the Mean-square Radius for Star Molecules

f	C_f	
1	$\frac{134}{105}$	= 1.276
2	$\frac{134}{105}$	
3	$\sqrt{3} \left(\frac{6728}{2205} \sqrt{2} - \frac{7862}{2205} \right)$	= 1.298
4	$\frac{1548\sqrt{2}}{175} - \frac{5863}{525}$	= 1.342
8	$\frac{30632}{1155} - \frac{13591\sqrt{2}}{770}$	= 1.559
∞	$f^{1/2} \left(\frac{404\sqrt{2}}{45} - \frac{184}{15} \right)$	

(b) Properties of Branched Polystyrene

Two polystyrene samples closely approximating the idealized uniform three-branched star were employed in a preliminary experimental investigation. These materials were two fractions (of molecular weight about 3×10^5) isolated from an already narrowly distributed mixture of trifunctionally branched molecules prepared (by Dr. F. Wenger of this laboratory) by coupling nearly monodisperse polystyryl lithium with an aromatic compound containing three chloromethyl groups. The synthesis is described in detail elsewhere.³ From fractionation data the weight to number average molecular weight ratio of the parent linear polymer was found to be 1.03; and for one of the branched fractions the same ratio was unity within the error inherent in the comparison of molecular weights from osmotic pressure and light scattering.

The results of the measurements may be summarized as follows:

The Flory temperature⁴ θ , at which the second virial coefficient A_2 vanishes, is $34.3 \pm 0.5^\circ\text{C}$ in cyclohexane irrespective of branching.

The Huggins constant k' in good solvents (benzene at 25° , toluene at 30°) is 0.38 ± 0.02 and unaffected by branching; but there are indications that in a theta solvent k' is slightly larger than that found for the linear polymer.

The intrinsic viscosity ratio $g' = [\eta]_{\text{branched}}/[\eta]_{\text{linear}}$ in cyclohexane at θ is 0.90 in good agreement with the theoretical value predicted by Zimm and Kilb. Results indicate, however, that in good solvents, the Zimm-Kilb relation is not applicable.

Near θ , the second virial coefficient is about one-third smaller (in absolute magnitude) than that found for the linear polymer of the same molecular weight. To put it another way: the entropy parameter⁴ ψ_1 is reduced from 0.33 to 0.21. In the good solvent toluene, however, the virial coefficients are indistinguishable.

The unperturbed mean square radius of the trifunctionally branched chain calculated from intrinsic viscosity and virial coefficient data is in good agreement with the random-flight relation

$$\frac{\langle R^2 \rangle_0}{M} = \frac{3f - 2}{6f^2} \times \text{constant}$$

and the constant established for linear polystyrene either directly⁵ by light scattering or by the combination of viscosities and virial coefficients.⁶

(c) Dimensions of Polymers: Specific Solvent Effects

According to the familiar theory developed by Flory and Fox,⁷ the intrinsic viscosity of a polymer solution may be expressed by the relation

$$[\eta] = KM^{1/2}\alpha^3$$

where the constant K is given by

$$K = \Phi' (\langle R^2 \rangle_0 / M)^{3/2}$$

and Φ' is a universal numerical constant. Viscosity measurements at the Flory

temperature, where α is unity, can thus be used to determine K . If the unperturbed chain size $\langle R^2 \rangle_0$ is a characteristic of the polymer chain at a given temperature without regard to the nature of the solvent, K must similarly be dependent only on temperature and the polymer. Many experimental studies indicate this view to be correct as a first approximation; but it is only reasonable to expect that specific interactions between solvent and polymer may modify $\langle R^2 \rangle_0$ to some degree, and there does exist some experimental evidence supporting the idea that variations of K with solvent may occur.^{8,9}

In order to study solvent effects it is necessary to eliminate the possibly predominant effect of temperature per se. Evidently, this can be done if a polymer is found to exhibit sufficiently similar values of θ in two different solvents. In a preliminary screening, polystyrene with the solvents cyclohexane and diethyl malonate proved to be one combination with the requisite properties. In order that unambiguous results might be obtained it was considered that the polymer used should be relatively homogeneous, to eliminate possible complications from a dispersion of molecular weights; and that it should be of such molecular weight that accurate osmotic pressure, light scattering, and viscosity measurements could be made without difficulties from leakage through osmotic membranes, from high dissymmetry in light scattering, from shear corrections in viscosity, or from phase separation too near θ . Further, enough material should be available to permit all measurements to be made on the same sample. A thirty gram sample of anionically polymerized polystyrene of molecular weight about 4×10^5 (prepared by Dr. F. Wenger) was considered to meet these criteria and was used in the measurements.

The second virial coefficient A_2 was measured by light scattering for both systems over a range of temperatures including θ . Interpolation to $A_2 = 0$, yielded $\theta = 34.8 \pm 0.3^\circ\text{C}$ in cyclohexane and $\theta = 35.9 \pm 1.0^\circ$ in diethylmalonate, the reduced precision in the latter figure arising from the relatively small temperature dependence of A_2 in this system. The value of θ was confirmed for the cyclohexane system by osmotic pressure, which gave $\theta = 34.6 \pm 0.2^\circ$, in good agreement also with published results.¹⁰ Since $\langle R^2 \rangle_0$ does not vary rapidly with temperature, comparison of the intrinsic viscosities at the respective values of θ will indicate whether there exist differences in specific solvent effects in these two systems. From viscosity measurements at θ and two degrees above and below it was concluded that for polystyrene-cyclohexane $[\eta]_\theta$ is 0.555, but for polystyrene-diethylmalonate $[\eta]_\theta = 0.491$. The difference is small but well beyond the limits of experimental uncertainty.

The significance of this effect and its relevance in other systems is of continuing interest. The comparisons made here will be supplemented by data on polystyrene in 1-chloro-*n*-undecane which also exhibits θ near 35° . Direct determinations of $\langle R^2 \rangle$ for a high molecular weight polymer in all three solvents are also planned.

(d) The Second Virial Coefficient for Heterogeneous Polymers in Good Solvents

Available theoretical treatments of the second virial coefficient in the equation of state for polymers in good solvents give results in complicated forms

which it has not been found possible to apply to the general case of solutes heterogeneous in molecular weight. Mathematically, the task involved generally is a double integration over a molecular weight distribution, of a function that cannot itself be expressed analytically.¹¹⁻¹³

In a new approach to the problem we abandon all pretense of a sophisticated model and simply assume that the virial coefficient for a homogeneous polymer is proportional to a negative power of molecular weight. This assumption is quite without theoretical justification, but empirically it conforms to virtually all experimental data on well-fractionated polymers to within the limits of experimental accuracy. Hence we regard it merely as a convenient representation of empirical results, but one which is a vital factor in the avoidance of mathematical difficulty. Thus we write for a homogeneous polymer of degree of polymerization \underline{n} (which need not be identified with the number n of chain segments discussed earlier)

$$A_2 = B_0 n^{-a} \quad (3)$$

where B_0 and \underline{a} depend on the nature of the polymer-solvent pair and the temperature, but not on molecular weight. The virial coefficient A_2 is defined in the usual way as the coefficient of the linear term in the equation of state: e.g., for the osmotic pressure Π

$$\frac{\Pi}{RTc} = \frac{1}{M} + A_2 c + \dots$$

with c the concentration in units of mass/volume.

Since equation 1 still implies little about the virial coefficient for heterogeneous polymers an additional condition is required; that is, we require some relation among the coefficients B_{ij} in the two general expressions

$$A_2^{(\pi)} = \sum_i \sum_j B_{ij} w_i w_j \quad (4)$$

for the osmotic pressure, and

$$A_2^{(R)} = \sum_i \sum_j B_{ij} n_i w_i n_j w_j / \left(\sum_i n_i w_i \right)^2 \quad (5)$$

for light scattering, in which w_i is the weight fraction of component i in the solute. Probably the simplest assumption with some physical basis is that the unlike molecules interact as hard spheres of equivalent radii defined by the B_{ij} from equation 3. An elementary calculation in statistical mechanics gives the appropriate result:

$$2(B_{ij} n_i n_j)^{1/3} = (B_{ii} n_i^2)^{1/3} + (B_{jj} n_j^2)^{1/3} \quad (6)$$

Contrails

As a test of the averaging assumed in equation 4, we can examine the special case of a solute consisting of a mixture of two sharp fractions^{11,14,15} of the same polymer. The very simple theory derived here indicates, interestingly, that there are physically reasonable conditions, determined by the value of \underline{a} and the molecular weight ratio of the two solutes, for which $A_2^{(\pi)}$ and $A_2^{(R)}$ both pass through a maximum as a function of the relative amounts of the two polymers in the solute. At least qualitatively, this result is in agreement with more sophisticated theory¹¹ and with some experimental results.^{14,15}

In dealing with continuous molecular weight distributions we adopt the Schulz distribution function¹⁶

$$f(n) = y^{Z+1} \frac{n^Z}{\Gamma(Z+1)} e^{-yn} \quad (7)$$

$$y = (Z+1)/n$$

where $f(n)dn$ is the weight fraction of polymer with n lying between n and $n + dn$. The parameters of the distribution are $\langle n \rangle$ the weight average value of n and the parameter Z , which increases with decreasing heterogeneity: the limit of infinite sharpness corresponds to $Z = \infty$ while $Z = 1$ denotes the "most probable" or "polyester" distribution.

Substitution of equations 3, 6, and 7 in the integral forms equivalent to equations 4 and 5, yields integrals involving only a single standard form, the Γ function. We obtain for the second virial coefficient from osmotic pressure

$$A_2^{(\pi)} = B_0 y^a \phi^{(\pi)} / 4 [\Gamma(Z+1)]^2$$

$$\phi^{(\pi)} = \Gamma(Z+2-a)\Gamma(Z) + 3\Gamma[3Z+4-2a]/3 \Gamma[(3Z+2-a)/3]$$

and for light scattering

$$A_2^{(R)} = B_0 y^a \phi^{(R)} / 4 [\Gamma(Z+2)]^2$$

$$\phi^{(R)} = \Gamma(Z+3-a)\Gamma(Z+1) + 3\Gamma[3Z+7-2a]/3 \Gamma[(3Z+5-a)/3]$$

These results are such that the form of relation between the virial coefficient and average molecular weight is still that of equation 3 for a single species: hence for a given Z , plots of $\log A_2$ versus $\log \underline{n}$ for a sharp fraction, and of $\log A_2^{(\pi)}$ versus the logarithm of the number average \underline{n} or of $\log A_2^{(R)}$ versus $\log \langle n \rangle$ are all predicted to be straight lines of the same slope $-\underline{a}$. If the three functions (for empirically meaningful values of \underline{a}) are superimposed on a single graph, the plots for a heterogeneous system lie above that for the homogeneous case

with the $A_2^{(\pi)}$ plot uppermost; and the difference increases as heterogeneity increases.² In this definite sense, A_2 is predicted to be increased by heterogeneity, and more strongly for osmotic pressure than for light scattering. In the case of the polyester distribution with $a = 1/4$ (a typical value for systems in good solvents) $A_2^{(\pi)}/A_2^{(R)}$ for a given polymer exhibits, according to this theory, a value equal to 1.26, and thus a difference from unity sufficiently great to be detected by careful measurements. However, in the same instance, the ordinates of $A_2^{(\pi)}$ versus number average \bar{n} and of $A_2^{(R)}$ versus $\langle n \rangle$ should be in the ratio 1.26;² and thus it appears that these two functions may not show experimentally significant differences.

It is possible to apply the theory outlined here to more complicated distributions made up from several Schulz distributions, each determined by a certain Z and $\langle n \rangle$. The results can become cumbersome indeed, but the necessary integrations are as elementary as before. Perhaps the most interesting prediction is that the maximum in A_2 obtained for some mixtures of two homogeneous polymers should in fact be enhanced by heterogeneity if both fractions have the same Z .

(e) Theory of Rayleigh Scattering: Effect of Intermolecular Correlations

A statistical model developed earlier¹³ in deducing approximately the osmotic properties of solutions of polymers in thermodynamically good solvents has been applied to the problem of the scattering of light for the general case in which solutions do not obey van't Hoff's law and the polymeric solute molecules are so large that intramolecular optical interferences cannot be ignored.

In our molecular model a bimolecular cluster (two solute molecules in contact) is represented as a spherically symmetrical distribution of chain segments centered about an arbitrarily chosen "initial contact." With this model it was found that the series expansion for the second virial coefficient in powers of the excluded volume β (or of z), as derived by Zimm,¹⁷ could be summed in closed form prior to a final summation (integration) required for averaging over all intermolecular segment-segment pairs as initial contacts. Although this final step could not be performed analytically, it was possible to show that a simple approximation yielded a result very close to the exact integral. Comparison of this result with that of Flory and Krigbaum,¹¹ (based on the representation of the bimolecular cluster as the interpenetration of two spherically symmetrical distributions of polymer segments centered at the positions of the respective molecular centers of mass) showed a more rapid decrease in A_2 with increasing molecular weight. In some cases, at least, this behavior appeared in better accord with experiment.¹³

In brief, the present study constitutes an attempt to calculate from theory for a homogeneous solute the function $Q(\theta)$ in

$$\frac{Kc}{R(\theta)} = \frac{1}{MP(\theta)} + 2A_2Q(\theta)c + \dots$$

where $R(\theta)$ is the light intensity scattered through the angle θ ; M is the polymer molecular weight; c is the weight concentration; and $P(\theta)$, $Q(\theta)$, are functions, normalized to unity at $\theta = 0$, that determine the angular distribution of scattered radiation. The theory may be regarded as providing some degree of correction to the well-known treatment of light scattering by Zimm in which $Q(\theta)$ is unity at all angles.¹⁸ Zimm's theory is based on the so-called "single contact" approximation by which, in the enumeration of the configurations of a bimolecular cluster, simultaneous multiple intermolecular contacts are not considered. The electro-magnetic aspects of our derivation include nothing novel and the statistical mechanical treatment follows Zimm's procedure^{17,18} rather closely except for the introduction of the particular properties of the model. In spite of the simplifications involved, the single-contact contributions are accounted for properly. Unlike the case of the virial coefficient,¹³ however, double-contact configurations are not treated rigorously. This means that the expression of A_2 in this theory as a series in powers of z reproduces the first two terms of the exact series while only the first term is correct in the analogous development of $Q(\theta)$. In both cases, higher order terms involve approximations of uncertain effect since, of course, an exact result is not available for comparison.

The final result

$$Q^*(\theta) = \frac{w_0}{w_u} \left[\frac{1 - \exp(-\psi/w_u)}{1 - \exp(-\psi/w_0)} \right] \quad (8)$$

depends on two variables: the thermodynamic parameter

$$\psi = 4z/\alpha^3$$

and a quantity characterizing the optical interference effects (and thus the molecular size)

$$u = \frac{8^2 n_b^2 \alpha^2}{3\lambda^2} \sin^2 \left(\frac{\theta}{2} \right)$$

where λ is the wavelength in the medium. The function w_u is extremely complicated but actually turns out to be nearly constant: it is $w_0 = 1.433$ for $u = 0$, increases with increasing u to about 1.469, and then decreases again to w_0 as u becomes infinite. It must follow that $Q^*(\theta)$ is always close to unity whatever the value of ψ and hence that the single-contact approximation of Zimm should always apply for practical purposes.

This is a rather surprising and perhaps implausible result although there seem to be no completely unequivocal experimental data to cite in comparison. It is, however, very much at variance with the predictions of Flory and Bueche¹⁹ who derived $Q(\theta)$ from the Flory-Krigbaum molecular model¹¹ and found a marked decrease from unity with increasing ψ at sufficiently large, but physically reasonable, values of u . Equation 8 also predicts a decrease in $Q(\theta)$, at first, as either u or ψ increases, but the effect is small as compared both to that found by Flory and Bueche and to the limiting dependence at $\psi/u = 0$ indicated by exact theory. It

seems to us that this behavior is a consequence of the extreme symmetry of our model in which all configurations of a bimolecular cluster are represented as spherically symmetrical. The Flory-Krigbaum model is undoubtedly a much more realistic model for the intermolecular interference effects, although it may perhaps err in the opposite direction of underemphasizing the contributions from highly symmetrical configurations.

In the derivation leading to equation 8, it is assumed that the expansion factor α is the same for a single molecule and for a bimolecular cluster. However a completely consistent treatment of the statistical model we have employed, suggests that the expansion α_1 of a single chain is less than that α_2 of the cluster, according to the relation²⁰

$$\alpha_2^5 - \alpha_2^3 = 1.601(\alpha_1^5 - \alpha_1^3)$$

The scattering function obtained if this modification is adopted is

$$Q^\dagger(\theta) = \frac{w_0 [1 - \exp(-\psi w_{u_2})] [P(\theta, u_2)]^2}{w_{u_2} [1 - \exp(-\psi w_0)] [P(\theta, u_1)]^2}$$

where u_1, u_2 indicate the quantities u determined by the respective expansion factors α_1, α_2 .

With this refinement, values of $Q^\dagger(\theta)$ are found significantly less than unity though the effect is still very much smaller than that predicted by Flory and Bueche. Some numerical values are listed in Table II.

TABLE II
The Scattering Function $Q(\theta)$ in Two Approximations

$u = u_2$	w_u	$Q^*(\theta)$ ($\psi > 7$)	$Q^\dagger(\theta)$		
			$\psi = 1$	$\psi = 2$	$\psi = 10$
0	1.433 = w_0	1	1	1	1
2	1.458	0.983	0.905	0.876	0.841
4	1.467	0.977	0.863	0.822	0.774
8	1.468	0.976	0.836	0.787	0.729
18	1.459	0.982	0.824	0.772	0.710
∞	w_0	1	0.822	0.771	0.707

To gain some sense of the physical meaning of these results it is useful to make an estimate of magnitudes of u and ψ attainable in experiment. Choosing polystyrene in toluene as a typical instance of a polymer in a good solvent and

calculating the desired quantities from intrinsic viscosity parameters we obtain, at four molecular weights the results given in Table III.

TABLE III
Parameters for the System Polystyrene-Toluene

M	ψ	u_1^*	u_2^*	R(45)/R(135)*
10^5	1.4	0.22	0.25	1.05
10^6	2.7	3.0	3.5	1.9
5×10^6	4.1	19.1	22.3	1.9
10^7	4.9	42.8	50.2	5.2

* For blue light (436 m μ)

(f) Viscosity-Molecular Weight Relationship for Poly-(vinyl acetate)

The intrinsic viscosity-molecular weight relationship for linear poly-(vinyl acetate) in methyl ethyl ketone has been studied previously,²¹⁻²⁴ but most of the investigations have dealt principally with polymers of molecular weights in excess of 100,000. In connection with other work under way in this laboratory it has become important to know the relationship accurately in a lower weight range. Accordingly, intrinsic viscosity and light scattering measurements on this system have been carried out with nine fractionated polymers of molecular weights from 6,000 to 30,000.

Viscosity measurements were made at 25°C in a Cannon-Ubbelohde viscometer such that kinetic energy corrections were negligible. Light scattering measurements were made at four solute concentrations and at least seven scattering angles and the data were analyzed according to the familiar method of Zimm. Molecular weight calculations were based on a refractive index increment of 0.089 cm³/g, as reported by Shultz,²¹ and Matsumoto and Ohyanagi.²⁴

The new data are well fitted by the equation

$$\log [\eta] = -1.871 + 0.71 \log M_w \quad (9)$$

which also describes the results of Schultz and Howard²² covering the high molecular weight range 240,000 to 3,460,000.

Combining molecular weights from both light scattering and sedimentation diffusion data, Elias and Patat²³ obtained an equation which differs by about 25 per cent from the lowest molecular weight data of this study. However, if their light scattering data alone are considered and one point for a poorly fractionated sample is rejected, the agreement with the present data and those of Shultz is much

improved. Matsumoto and Ohyanagi obtained intrinsic viscosities about 15 per cent lower than given by equation 9 but showing the same molecular weight dependence. However, their polymers were not fractionated and it is perhaps possible that their method of sample preparation leads to some hydrolysis of acetate groups.

We can conclude therefore that Shultz's equation is valid over the entire molecular weight range so far studied 6×10^3 to 3.5×10^6 . From theoretical considerations an abrupt change in slope of the $\log [\eta]$ versus $\log M_w$ relation is expected at some rather low molecular weight, hence further experiments are planned at still lower molecular weights to determine if possible the lower limit of validity of the relation.

(g) Light Scattering Photometer

A precision light scattering photometer has been designed and built with a view to its use in studies of configurational and thermodynamic properties of polymers in dilute solutions. Since a comprehensive description will be found in an ASD Technical Report¹ we offer here only an outline of the main characteristics of the instrument. Most elements of the design are fairly conventional and individually nearly all may be found in instruments constructed previously: a mercury arc light source, glass filters to isolate either the strong blue or green line of the spectrum; a rotating sector to modulate the light source; optical elements to concentrate, collimate and define the incident beam; photomultiplier tubes to detect both scattered radiation and a reference intensity deducted from the incident beam; a tuned bridge circuit for balancing the two photocurrents; a sensitive amplifier-voltmeter as the null detector, a goniometer permitting accurate measurement of scattering angle, and a thermostat for control of sample temperature. While there is thus nothing exceptional in the conception, the abiding goal has been to achieve the utmost of which such apparatus ought reasonably to be capable in precision and reproducibility of measurements. To this end much effort has been put into the finer details of design and in tracking down and eliminating effects that might be characterized as of a second order in regard to influencing accuracy. For example, it is expected that the optical system will prove of such quality that in comparison to commercial instruments there can be attained more accurate measurements of depolarization and better angular resolution of scattered light over a wider range of scattering angles. Also, by a rather simple but effective thermostat design, the precise temperature control needed for meaningful thermodynamic studies over an extended temperature range can be achieved.

References

1. ASD Technical Report 61-22 "Polymer Structures and Properties."
2. M. Fixman, J. Chem. Phys. 23, 1656 (1955).
3. F. Wenger and S.-P. S. Yen, "Synthesis of Branched Polymers. Polystyrene Trifunctional Molecules," Polymer Division Abstracts, 141st meeting of the American Chemical Society, Washington D. C., March, 1962.
4. P. J. Flory, "Principles of Polymer Chemistry" (Cornell University Press, Ithaca, 1953) Chapter 12.

Contrails

5. W. R. Krigbaum and D. K. Carpenter, J. Phys. Chem. 59, 1166 (1955).
6. T. A. Orofino, Polymer Division Abstracts, 2, 161, 140th meeting of the American Chemical Society, Chicago, September, 1961.
7. P. J. Flory and T. G. Fox, J. Am. Chem. Soc. 73, 1904 (1951).
8. T. G. Fox and P. J. Flory, J. Am. Chem. Soc. 73, 1909 (1951).
9. P. J. Flory, O. K. Spurr, and D. K. Carpenter, J. Polymer Sci. 27, 231 (1958).
10. W. R. Krigbaum and P. J. Flory, J. Am. Chem. Soc. 76, 3758 (1954).
11. P. J. Flory and W. R. Krigbaum, J. Chem. Phys. 18, 1086 (1950).
12. A. Isihara and R. Koyama, J. Chem. Phys. 25, 712 (1956).
13. E. F. Casassa and H. Markovitz, J. Chem. Phys. 29, 493 (1958).
14. W. R. Krigbaum and P. J. Flory, J. Am. Chem. Soc. 75, 1775 (1953).
15. E. F. Casassa, Polymer 1, 169 (1960).
16. G. V. Schulz, Z. phys. Chem. B43, 25 (1939).
17. B. H. Zimm, J. Chem. Phys. 16, 1093 (1948).
18. B. H. Zimm, J. Chem. Phys. 14, 164 (1946).
19. P. J. Flory and A. M. Bueche, J. Polymer Sci. 27, 219 (1957).
20. E. F. Casassa, J. Chem. Phys. 31, 800 (1959).
21. A. R. Shultz, J. Am. Chem. Soc. 76, 3422 (1954).
22. R. O. Howard, Thesis, Massachusetts Institute of Technology (1952).
23. H. G. Elias and F. Patat, Makromol. Chem. 25, 13 (1958).
24. M. Matsumoto and Y. Ohyanagi, J. Polymer Sci. 46, 441 (1960).