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Thermodynamic and Conformational Properties of Polystyrene. I. Light-Scattering Studies on Dilute Solutions of Linear Polystyrenes*

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The results of an extensive study of some dilute solution properties of a series of linear, homogeneous (anionically prepared) polystyrenes ($4.8<10^{-4}M<440$) over a wide temperature interval ($10°<T<110°C$) in decalin and toluene are described. The data are used to obtain detailed comparisons among the second virial coefficient A_2, the mean-square molecular radius $\langle s^2\rangle$, the molecular weight M, and the temperature. The empirical correlations thus obtained are compared to theoretical predictions. In particular, it is found that $A_2M^{\frac{1}{2}}(\langle s^2\rangle/M)_0^{-\frac{3}{2}}$ and $\alpha^2=\langle s^2\rangle/\langle s^2\rangle_0$ are each single-valued functions of the interaction parameter $z=B(\langle s^2\rangle_0/M)_0^{-\frac{3}{2}}M^{\frac{1}{2}}$, when B is assumed to have the temperature dependence $B=B_0[1-(\Theta/T)]$. Certain theoretical predictions for the dependence of $A_2M^{\frac{1}{2}}/\alpha^3$ on z/α^3 are found to adequately describe the form of the observed behavior and can be used as the basis for a satisfactory empirical relation. The observed dependence of α^2 on z is satisfactorily predicted by recent calculations of Flory and Fisk. It is expected that the correlations given among A_2, α^2, and z will be valid for any flexible, nonionic polymer.

I. INTRODUCTION

INVESTIGATION of the properties of dilute polymer solutions has long been of interest, both as a practical means of characterizing polymers and as a means of elucidating the thermodynamic and conformational properties of macromolecules. Indeed, a considerable body of data has been accumulated over the years, and one might suppose that sufficient experimental data are available to test any new or old theory that might be devised to explain the behavior of such properties as the second virial coefficient A_2, the mean-square radius of gyration $\langle s^2\rangle$, or the intrinsic viscosity $[\eta]$, in terms of molecular parameters. Unfortunately, much of the existing data are not useful for this purpose because: (a) The data do not cover a sufficiently wide range of variables—molecular weight, temperature, "solvent goodness," branching, etc.; (b) the data were obtained on poorly characterized materials, possibly exhibiting heterogeneity of molecular weight or chain configuration—e.g., branching; or (c) the data are not of adequate precision. Thus, a need exists for precise and systematic measurements over a wide range of variables on materials of well-defined molecular constitution. Such data will allow as nearly quantitative assessment of theories relating observable properties of dilute solutions to molecular parameters as can now be made.

Recent advances in techniques of anionic polymerization have made it possible to obtain the desired nearly homogeneous materials. Such methods can yield either linear polymers with a very narrow distribution of molecular weights and controlled stereostructure, or branched polymers of controlled and known configuration. We have undertaken solution studies on such materials by measurements that include a wide range of thermodynamic and molecular variables—from a Flory theta solvent to very good solvents, and molecular weights from 4×10^4 to 4×10^6. In all cases, the data have been obtained in such a way that thermodynamic parameters appearing in theoretical relations correlating A_2, $\langle s^2\rangle$, and $[\eta]$ with temperature and molecular weight can be directly adduced.

In this first paper of a series, we deal with light-scattering studies on linear polystyrene in decalin and toluene. It is shown that both A_2 and $\langle s^2\rangle$ can be correlated in terms of a single interaction parameter z, and that certain existing theories can be used to adequately correlate A_2 or $\langle s^2\rangle$ and z.

In later papers, we shall consider viscometric properties of linear chains and studies of branched polymers in dilute solution.

II. EXPERIMENTAL

Materials

Polymers

Linear polystyrene was prepared in these laboratories (by Altares) by anionic polymerization methods described elsewhere.[1] All samples except L-10, S-108, and 705, were prepared *in vacuo* by techniques described elsewhere. The polymers are characterized by a relatively narrow distribution of molecular weights: typically, the ratio of the weight and number average molecular weights M_w/M_n was found to be approximately 1.01 to 1.07 by fractionation studies. Certain samples, designated by the letter F, were separated into three fractions; and the middle fraction was utilized for these studies. All polymers were freed from solvents by freeze drying from benzene solutions followed by evacuation for about one week at 10^{-6} mm Hg at room temperature. Samples 705 and S-108 were

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* Presented in part at the 145th American Chemical Society National Meeting, New York, September 1963.

[1] F. Wenger and S.-P. S. Yen, Makromol. Chem. **37**, 153 (1960).

supplied by the National Bureau of Standards and H. McCormick of the Dow Chemical Company, respectively. Sample L-10 was prepared in a large-scale anionic polymerization in this laboratory.

Solvents

Practical-grade decalin (Eastman Organic Chemicals), a mixture of the *cis* and *trans* isomers, was distilled under nitrogen at reduced pressure. Pure *cis* or *trans* isomers or mixtures thereof could be obtained in this way. Before distillation, the decalin was slightly yellow and fluorescent, but was colorless and free of fluorescence after distillation. Decalin of varying *cis–trans* composition has been utilized. Compositions determined by gas–liquid chromatography are given in Table I. In addition, mixtures of Samples 4 and 5 have been studied.

Similarly, reagent-grade cyclohexane and toluene (Baker Chemical Company) were distilled under nitrogen. Both solvents were colorless and nonfluorescent after this treatment.

All solvents were stored under nitrogen at room temperature in the dark until use and showed no tendency to degrade over the storage period.

Light-Scattering Photometer

The photometer, which was constructed in this laboratory, has been described in detail elsewhere.[2] The optical design is similar in principle to that described by McIntyre and Doderer,[3] and the mechanical construction includes many features utilized by Katz.[4] A highly collimated monochromatic beam is split into two beams, which are then focused in a sample and on a diffuser before a monitoring photomultiplier. The monochromatic light is obtained from a mercury-vapor lamp (Metropolitan-Vickers, 250-W Type ME/D) and interference filters matched to either the 4358-Å or the 5461-Å emission lines of the mercury spectrum. The scattered light is gathered by an optical system which defines the scattering volume viewed as well as the angular acceptance of the detector. An end-on photomultiplier (Dumont K2201) with Cu–Be dynodes having good low-current stability characteristics is used to detect the scattered light. The incident light is chopped mechanically at 450 cps, and the signals from the monitor and detector photomultipliers are balanced in a bridge circuit utilizing a narrow-bandpass voltmeter (Hewlett–Packard Model 302-A). This arrangement provides very stable and reproducible signals.

TABLE I. Decalin compositions.

Sample No.	Percent *cis* isomer
1	51.4
2	61.7
3	66.1
4	99.9+
5	0.0

The apparatus may be adjusted to a variety of optical specifications: for the present work the direction of the extreme rays in the incident beam deviated from that of the principal ray by 27′ and 6′ in the vertical and horizontal directions, respectively, and the angular resolution was 2.7° and 1° in the vertical and horizontal directions, respectively. The detection optical system was adjusted so that its field of view did not exceed the dimensions of the illuminated scattering volume either vertically or horizontally.

The Pyrex scattering cells were constructed in the form of a truncated cone in order to reduce stray-light pickup.[5] These were immersed in a cell bath of the same refractive index as the scattering liquid to eliminate prism effects due to the cell shape.[5] The scattered light was viewed through a cylindrical window in the thermostat surrounding cell and bath.

The sample temperature was held to ±0.02°C over the temperature range 10° to 110°C by circulating thermostat liquid to a heat exchanger surrounding the cell bath.

Calibration of the Photometer

The photometer was calibrated by several methods including the use of Ludox (Ludox HS, E. I. du Pont de Nemours & Company, Wilmington, Delaware), the "Cornell standard polystyrene" (supplied by P. Debye, Cornell University, Ithaca, New York), and polymer samples on which independent measurements of M_n and M_w/M_n had been carried out by osmotic pressure and fractionation studies. Satisfactory agreement was obtained among these methods, and the last one is taken as the final standard for this study since it is the method most readily duplicated elsewhere. Two polystyrene samples were studied in cyclohexane solution; one distributed by the National Bureau of Standards, Washington, D.C. (NBS Standard Sample 705), with $M_n(M_w/M_n)=1.82\times10^5$; the other obtained from T. A. Orofino with $M_n(M_w/M_n)=4.06\times10^5$. Measurements on the standard polymers were carried out with 4358-Å light in cyclohexane at 34.8° and compared with the transverse scattering of a slightly turbid glass used as a working standard. This calibration allowed molecular-weight determinations on other polystyrene samples in cyclohexane and eliminated need for values of the refractive-index increment dn/dc or any refraction corrections; and it is values of M_w so obtained that are taken as most reliable here.

To obtain M_w from further measurements carried out on toluene and decalin solutions, dn/dc and certain

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[2] G. C. Berry, Mellon Institute Quarterly Report, 1966. Copies available on request.

[3] D. McIntyre and M. C. Doderer, J. Res. Natl. Bur. Std. **62,** 153 (1959).

[4] S. Katz (private communication).

[5] E. F. Casassa and S. Katz, J. Polymer Sci. **14,** 385 (1954).

refraction corrections[6] are needed. The corrections appropriate for our instrument are described in detail by McIntyre.[7] In particular, the refraction correction to the angular acceptance is proportional to n^2.[6] Since the incident beam is passed through a dense filter before it meets the glass–air interface at the exit window of the thermostat, no correction is needed for scattering due to a back reflection. Deviations from the expected dependence of the irradiated volume "seen" by the detector upon the sine of the scattering angle were determined from measurements on dilute fluorescein solutions and found to be small, but corrections were applied. Refractive-index-increment measurements were carried out in cyclohexane at 34.5°C, and in *cis*-decalin and toluene at 12°C with a differential refractometer employing a stoppered cell; results for 4358-Å light were 0.181, 0.124, and 0.112, respectively, in satisfactory agreement with literature values.[8,9]

Solution Preparation and Data Analysis

Scattering data were obtained for at least five polymer concentrations for scattering angles θ from 18° to 135°. Solutions were individually prepared to known concentrations for the studies in decalin. Sequential dilutions of the most concentrated solution were made in studies on cyclohexane and toluene solutions with intermediate concentrations being checked by evaporation to dryness. Solutions were clarified by filtration under nitrogen through 0.4-μ-membrane filters, which were inert toward the solvents used (Gelman Instrument Company, Ann Arbor, Michigan).

The data were analyzed according to the well-known equation[10]

$$K_u c/R(u,c)=[MP(u,0)]^{-1}(1+2\Gamma_2 P(u,0)$$
$$\times\{Q(u,c)-[P(u,0)\Gamma_2]^{-1}[\partial P(u,c)/\partial c]\}c+O(c^2)).$$

Here, $u=(4\pi n/\lambda)^2\langle s^2\rangle\sin^2(\theta/2)$; n is the refractive index of the solution and λ is the wavelength of the light *in vacuo*; $P(u,c)$ is the particle scattering factor at concentration c and scattering angle θ; K_u is an optical constant including the depolarization factor; $R(u,c)$ is Rayleigh's ratio; M is the molecular weight; Γ_2 is the second virial coefficient; and $Q(u,c)$ is a scattering factor including multiple interference effects. The quantity in braces, which goes to unity in the limit $c=0$, was found to deviate negligibly from unity at all concentrations for systems encountered here. As usual, the radius of gyration $\langle s^2\rangle$ was extracted from the function $P(u,0)$ at small angles.

Unfortunately, the extrapolations to obtain M, $\langle s^2\rangle$, and Γ_2 are not always simple. It is well known from studies of the concentration dependence of the osmotic pressure Π that plots of $(\Pi/c)^{\frac{1}{2}}$ versus c often exhibit less curvature and yield more reliable estimates of M, and especially of Γ_2, than do plots of Π/c versus c.[11] This presumably occurs because the third virial coefficient Γ_3 is approximated by 0.25 Γ_2^2 and higher virial terms do not appreciably affect Π/RTc at the solute concentrations utilized. Similarly, plots of $[c/R(0,c)]^{\frac{1}{2}}$ versus c, show less curvature than plots of $c/R(0,c)$ versus c, and have been used throughout this investigation to obtain Γ_2 and M. Furthermore, plots of $[c/R(u,0)]^{\frac{1}{2}}$ versus $u'=u\langle s^2\rangle^{-1}$ allow more accurate estimates of $\langle s^2\rangle$ than do plots of $c/R(u,0)$ versus u'. Some basis can be given for this extrapolation by consideration of the particle scattering function $P(u)$ for random-flight polymer chains, even though this theoretical function is not exactly applicable except for theta-solvent conditions. Thus, Fig. 1 shows $P^{-1}(u)$ and $P^{-\frac{1}{2}}(u)$ versus u, together with the initial tangents from which $\langle s^2\rangle$ may be readily calculated. It is evident that empirical linear extrapolation on the square-root plot would yield a much more reliable estimate for the initial tangent than the conventional plot, especially if the data were confined to $u>1$. For example, $u>1$ for $\theta>30°$, for polystyrene of molecular weight 4.4×10^6. Square-root plots of lower-molecular-weight polymers tend to be linear even when the radius

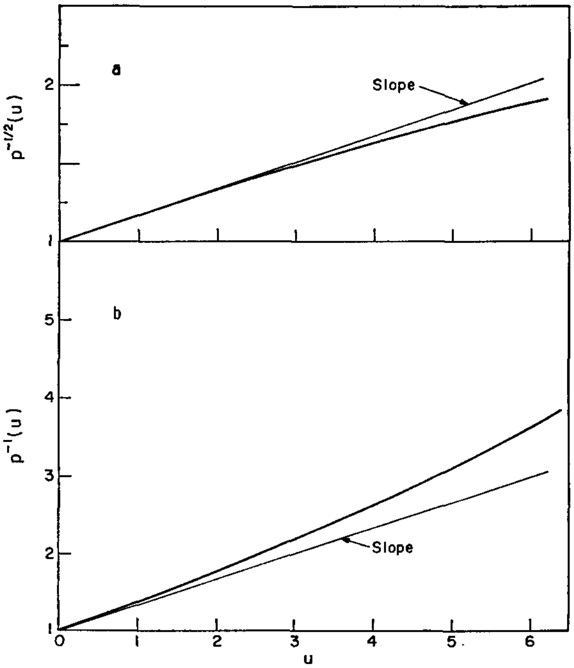

FIG. 1. Theoretical relations for the partial scattering factor $P(u)$ as a function of u, showing the utility of $P^{-\frac{1}{2}}(u)$ plots in determining the initial tangent to $P(u)$.

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[6] J. J. Hermans and S. Levinson, J. Opt. Soc. Am. **41**, 460 (1951).

[7] D. McIntyre, J. Res. Natl. Bur. Std. **68A**, 87 (1964).

[8] J. H. O'Mara and D. McIntyre, J. Phys. Chem. **63**, 1435 (1959).

[9] I. Ehl, C. Loucheux, C. Reiss, and H. Benoit, Makromol. Chem. **75**, 35 (1964).

[10] B. H. Zimm, J. Chem. Phys. **16**, 1093, 1099 (1948).

[11] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, N.Y., 1953), p. 280.

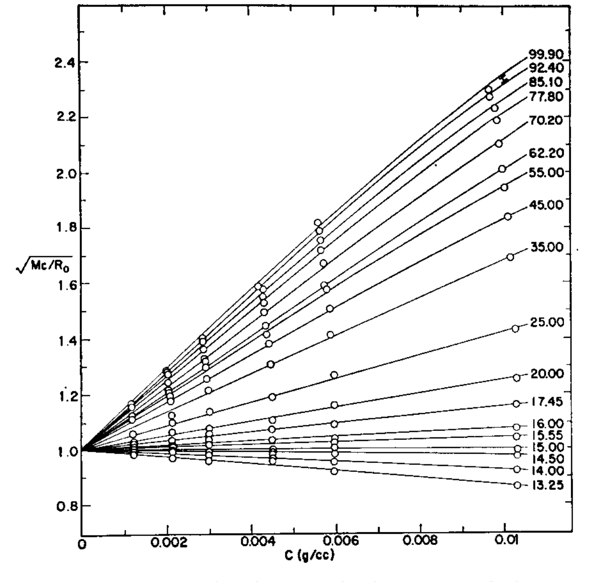

FIG. 2. Representative data obtained by extrapolation to zero angle versus concentration for Sample A-16-F at the indicated temperature.

is sufficiently large to produce noticeable curvature in the conventional plot. Thus, all values of $\langle s^2 \rangle$ obtained here have been derived from the initial tangents of $[c/R(u, 0)]^{\frac{1}{2}}$ versus u'. Figures 2 and 3 show some of the data on Sample A-16-F.

III. RESULTS

Data at the Flory Temperature

The Flory temperature Θ is defined phenomenologically as the temperature at which Γ_2 vanishes.[12]

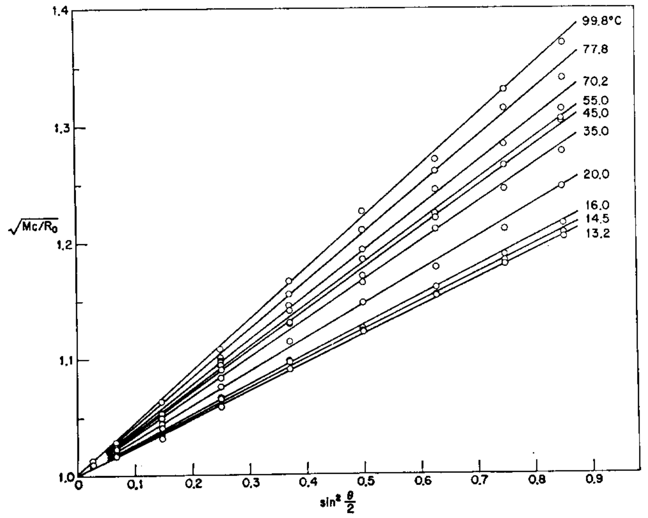

FIG. 3. Representative data obtained by extrapolation to infinite dilution versus $\sin^2\theta/2$ for Sample A-16-F at the indicated temperatures.

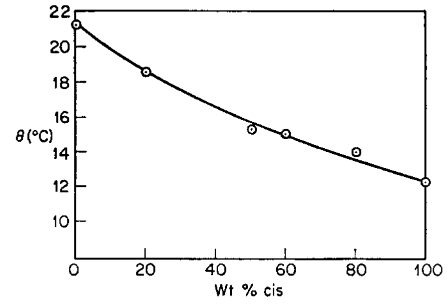

FIG. 4. The Flory temperature of atactic polystyrene in decalin: variation with composition in mixture of *cis*- and *trans*-decalin.

Figure 4 shows Θ for atactic polystyrene in decalin as a function of the fraction of the *cis* isomer in *cis–trans* isomeric mixtures. The value $\Theta = 292.5°\text{K}$ for a *cis* weight fraction of 0.23, found by Okada, Toyoshima, and Fujita[13] is in accord with our data, but the value 304°K reported by Benoit and Reiss[14] for isotactic polystyrene is unexpectedly high. It may be noted that the product $\Theta\rho$, where ρ is the density, is essentially independent of the isomeric composition. This is in accord with the suggestion of Fox[15] that Θ should be related to the cohesive energy density.[16]

Values of the mean-square radius at Θ are listed in Table II for data in decalin and cyclohexane solutions, with Θ taken as 297.8°K for cyclohexane. The expected constancy of the ratio $(\langle s^2 \rangle / M)_\Theta$ is observed, within experimental uncertainty. The extrapolations to obtain

TABLE II. Theta-solvent parameters for polystyrene.

Sample	Solvent[a]	Θ[b]	$10^{-6}M_w$	10^{10} $\langle s^2 \rangle_\Theta$	10^{18} $(\langle s^2 \rangle / M)_\Theta$
Linear polymers					
A-30	2	15.2°C	4.40	0.455	10.35
A-30	CH	···	4.40	0.464	10.60
A-82-F	CH	···	4.04	0.326	8.06
A-5-F	1, 2	15.4	1.56	0.132	8.35
A-5-F	CH	···	1.56	0.121	7.63
A-18	CH	···	1.33	0.0990	7.45
A-17	CH	···	1.20	0.0928	7.85
A-16-F	2	15.2	1.05	0.0820	7.75
A-16-F	CH	···	1.06	0.0770	7.27
A-19	4	12.2	0.622	0.0463	7.27
A-19	CH	···	0.626	0.0484	7.75
L-10	CH	···	0.622	0.0463	7.45
A-48-F	CH	···	0.394	0.0305	7.75
S-108	CH	···	0.247	···	···
A-13	2	15.0	0.186	0.0158	8.47
A-13	CH	···	0.182	···	···
A-3	4	12.0	0.125	···	···
A-3	CH	···	0.123	···	···
A-25-F	3	14.2	0.0482	···	···

[a] See Table I, CH represents cyclohexane.

[b] Θ not determined here, but taken as 34.8°C for cyclohexane. See Ref. 19.

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[12] P. J. Flory and W. R. Krigbaum, J. Chem. Phys. **18**, 1086 (1950).

[13] R. Okada, Y. Toyoshima, and H. Fujita, Makromol. Chem. **59**, 137 (1963).

[14] C. Reiss and H. Benoit, Compt. Rend. **253**, 268 (1962).

[15] T. G. Fox, Polymer **3**, 111 (1962).

[16] J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes* (Reinhold Publ. Corp., New York, 1950).

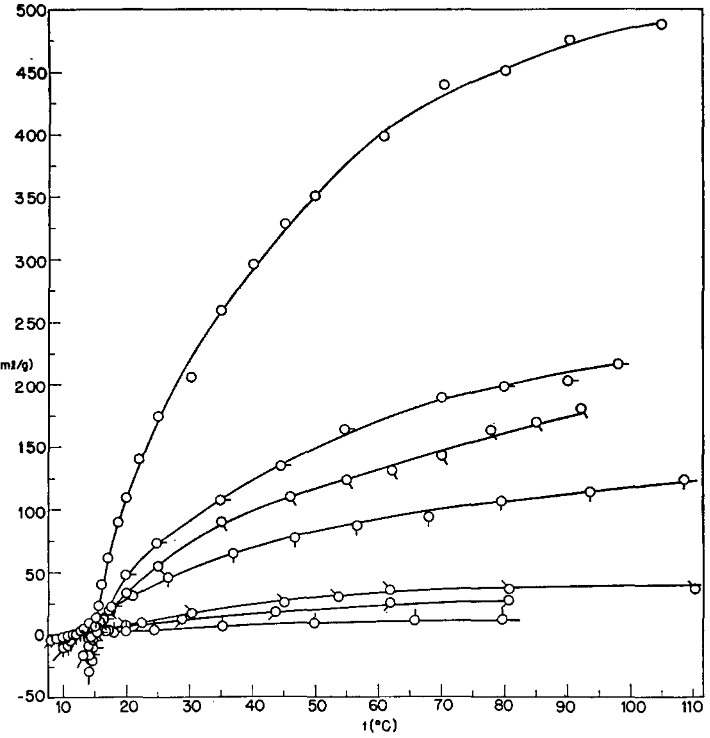

FIG. 5. Dependence of the second virial coefficient Γ_2 (cc/g) on temperature for polystyrene in decalin solutions. The curves are for Samples A-30, A-5, A-15, A-19, A-13, A-3, and A-25 in order from the top to the bottom of the figure at, say, 50°C.

$\langle s^2\rangle$ are most uncertain when $\langle s^2\rangle$ becomes so small $(10^{12}\langle s^2\rangle < \sim 0.2\ \text{cm}^2)$ that the angular dependence of the scattering is too small for accurate measurement, or when $\langle s^2\rangle$ becomes so large $(10^{12}\langle s^2\rangle > \sim 40)$ that the *initial* angular dependence is difficult to ascertain from data confined to angles greater than 18°. In addition, the very-high-molecular-weight unfractionated sample, A-30, is somewhat more polydisperse than the other samples listed in Table II, as shown qualitatively by sedimentation velocity experiments, tending to increase the averaged value observed for $(\langle s^2\rangle/M)_\Theta$. The values for $\langle s^2\rangle/\langle s^2_\Theta\rangle$ are unaffected. Remaining cognizant of these limits, we assign a value of 7.6 to the ratio $10^{18}(\langle s^2\rangle/M)_\Theta$. This is in satisfactory agreement with a value 7.5 obtained by Krigbaum and Carpenter.[17]

Data in Good Solvents

The dependence of Γ_2 and $\langle s^2\rangle/\langle s^2_\Theta\rangle$ on temperature and molecular weight is illustrated in Figs. 5 and 6.[18] (There is no common point of intersection since the data are for solutions with decalins of different compositions, cf. Table II.[19]) The individual values of $\langle s_\Theta^2\rangle$ for each sample were used to construct Fig. 6. The typical increase of Γ_2 and $\langle s^2\rangle$ with both T and M is evident, and it is seen that the rate of increase with increasing T has become small at 100°C, indicating rather "good solvent" conditions at this temperature.

Toluene behaves as a (nearly) athermal solvent for polystyrene in that the value of Θ is so far below the temperature encountered here that Γ_2 and $\langle s^2\rangle$ are essentially independent of temperature. Results obtained from scattering data in toluene at $T = 285$°K (the theta temperature for *cis*-decalin solutions) are given in Table III. These data are in good accord with the values reported by Outer, Carr, and Zimm[20] for

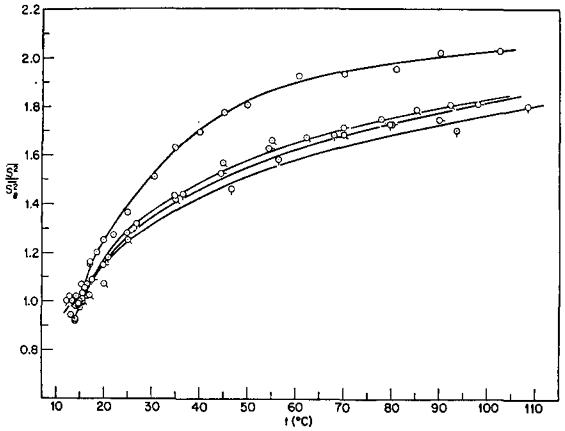

FIG. 6. Dependence of the expansion factor $\alpha^2 = \langle s^2\rangle_{\text{Av}}/\langle s^2\rangle_{\text{Av}\Theta}$ on temperature for various samples in decalin solutions. The polymers are identified in Fig. 5.

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[17] W. R. Krigbaum and D. K. Carpenter, J. Phys. Chem. **59**, 1166 (1955).

[18] Complete tables of the data displayed in Figs. 5 and 6 are available from the author on request.

[19] T. A. Orofino and J. W. Mickey, J. Chem. Phys. **38**, 2512 (1963).

[20] P. Outer, C. J. Carr, and B. H. Zimm, J. Chem. Phys. **18**, 830 (1950).

a polystyrene with $M=1.61\times10^6$ prepared by a free-radical reaction.

IV. DISCUSSION

Second Virial Coefficient

Decalin Solution

The principal objective of this study was to obtain data over a wide range of thermodynamic conditions in a form amenable to a direct comparison of experimental and theoretical calculations. The light-scattering data yield A_2 as a function of M and T, whereas statistical theories are written in the form

$$A_2=4\pi^{\frac{3}{2}}N_aBF'(z),$$
$$B=(1/4\pi)^{\frac{3}{2}}(n/M)^2\beta, \tag{1}$$

in terms of a composite variable z

$$z=BA^{-3}M^{\frac{1}{2}},$$

with

$$A^2=(\langle s^2\rangle/M)_0=\tfrac{1}{6}(n/M)\langle b^2\rangle.$$

Here, the subscript 0 denotes the unperturbed state in which the conformation of the chain molecule is described by random-flight statistics, and n is the number of effective segments (or steps) of mean-square length $\langle b^2\rangle$ in the statistical model. The mutually excluded volume β for any pair of segments is zero at $T=\Theta$ and positive when $T>\Theta$ in the systems of interest here. The function $F'(z)$ decreases monotonically from unity as z increases from zero. Equation (1), with such an $F'(z)$, is the common result of a large body of exact and approximate theories based on a polymer chain obeying random-flight statistics; the function $F'(z)$, of course, depends on the nature of any approximations and receives further comment below. Here we only admit the existence of such a relation and seek to examine our data in the most general way possible to test its validity. Equation (1) is a two-parameter relation, these being, for example, β and $\langle b^2\rangle$ (see Ref. 21 for further general discussion of this relation). The predicted dependence on only two parameters is a consequence of the superposition approximation which intersegmental interactions are taken to be short range and pairwise additive. Presumably the single parameter z will not serve to correlate data on A_2 as a function of M and T if this approximation is inadequate. The procedure to be followed here, then, is to cast our data into the form required by Eq. (1), without regard to the exact nature of $F'(z)$, and to examine it for the completeness of the superposition achieved over a wide span in M and T.

TABLE III. Light-scattering results for polystyrene in toluene ($t=12°$C).

Polymer	Γ_2(ml/g)	$10^{18}(\langle s^2\rangle/M)$
A-30	792	20.6
A-5	344	18.3
A-16	260	16.4
A-19	161	15.0
S-108[a]	97	···
A-13	65	···
A-3	56	···
A-36[b]	30	···

[a] $M_w=2.41\times10^5$.
[b] $M_w=5.4\times10^4$.

It is necessary to know the dependence of B on T explicitly before these equations can be utilized in an analysis of data. This dependence is given formally by the integral

$$\beta=4\pi\int_0^\infty\left\{1-\exp\left[-\frac{u(r)}{kT}\right]\right\}r^2dr,$$

where $u(r)$ is the mean potential of average force between two segments a distance r apart. In general, $u(r)$ depends on both polymer and solvent. Stockmayer has pointed out that attempts to determine the temperature dependence of β over a wide temperature interval by assuming a specific formulation for $u(r)$ are without significance, but that a large class of potentials yield similar results near $T=\Theta$.[21] We can, however, write A_2 in terms of the excess chemical potential of mixing of the solvent $\Delta\mu_1^E$, and the partial molar volume of solvent $\bar{V}_1$ as[22,23]

$$\Delta\mu_1^E/RTc^2\bar{V}_1=-A_2+O(c). \tag{2}$$

Now since $F'(z)$ goes to unity for $z=0$, combination of Eqs. (1) and (2) yields

$$\lim_{z\to0}A_2=4\pi^{\frac{3}{2}}N_aB=(1/R\bar{V}_1c^2)(\Delta s_1^E-\Delta h_1^E/T),$$

where Δs_1^E and Δh_1^E are the excess partial molar entropy and enthalpy of mixing, respectively. Thus, at least in the limit $z\to0$, we can write

$$B=B_0[1-(\Theta/T)], \tag{3}$$

where $B_0\propto\Delta s_1^E$ and $\Theta=\Delta h_1^E/\Delta s_1^E$, Δs_1^E and Δh_1^E being evaluated at $z=0$. This temperature dependence is, in fact, just that suggested by Flory,[12] with B_0 proportional to Flory's entropy of mixing parameter ψ_1. The rigorous statistical theory based on the random-flight model that led to Eq. (1) cannot justify extension of Eq. (3) to $z>0$. We must *assume* that Eq. (3) is valid for the entire temperature interval studied here with the expectation that plots of $A_2M^{\frac{1}{2}}$ as a function of z should not superpose for all temperature and molecular weights if Eq. (3) is inadequate. Equation

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[21] W. H. Stockmayer, Makromol. Chem. **35,** 54 (1960).

[22] H. Tompa, *Polymer Solutions* (Butterworths Scientific Publications, Ltd., London, 1956), pp. 147ff.

[23] Reference 7, pp. 530ff.

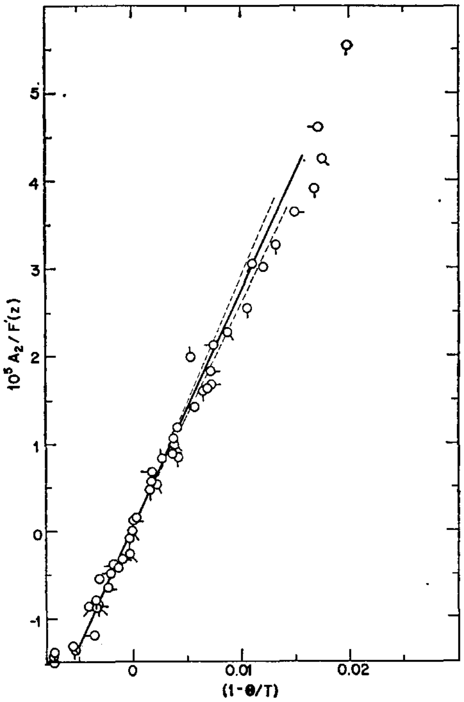

FIG. 7. Determination of the parameter B_0. The dashed lines indicate slopes deviating ±5% from the solid line. The points are identified as in Fig. 5.

(3) permits us to compute z for any T and M, once B_0 and Θ are determined since $(\langle s^2\rangle/M_0)$ is an experimentally determined quantity.

One further preliminary is necessary before we can compare our data with results of statistical calculations. The parameter $\langle s_\Theta^2\rangle$ is the value of $\langle s^2\rangle_0$ at $T=\Theta$, and in general s_0^2 can depend on temperature, with $(\partial\langle s^2\rangle_0/\partial T)$ being either positive or negative, depending on the precise character of the intramoelcular potentials. Thus α^2 at $T>\Theta$ is not necessarily $\langle s^2\rangle/\langle s_\Theta^2\rangle$. However, from data on bulk polymer and solutions, Orofino and Ciferri[24] have shown that $(\partial\langle s^2\rangle_0/\partial T)$ is essentially zero for polystyrene. The complete invariance of $[\eta]$ with T observed for toluene solutions[25] is in accord with their observations. Thus, we have assumed any temperature dependence of $\langle s^2\rangle_0$ to be small enough to be ignored in this study,[26] so that $\langle s_\Theta^2\rangle$ and $\langle s^2\rangle_0$ become synonymous.

We are now able to analyze the data in decalin in accord with the statistical theories. When Γ_2 vanishes, T is equal to Θ, and the derivative

$$\left\{\frac{\partial A_2}{\partial[1-(\Theta/T)]}\right\}_{T=\Theta}$$

is equal to $4(\pi)^{3/2}N_aB_0$. Thus Fig. 7 shows $A_2/F'(z)$ as a function of $[1-(\Theta/T)]$ in the region where a linear relation is observed.[27] The tangent at $T=\theta$ yields the value $10^{27}B_0=0.203$, independent of either molecular weight or the isomeric composition of the decalin solvent.

Equation (1) indicates that $A_2M^{1/2}(\langle s^2\rangle/M)_0^{-3/2}$ is a single-valued function of z for all M and T. Thus,

$$A_2M^{1/2}=4\pi^{3/2}(\langle s^2\rangle/M)_0^{3/2}N_azF'(z), \tag{4}$$

where, for decalin solutions of linear polystyrene,

$$z=0.00975M^{1/2}[1-(\Theta/T)].$$

Since $(\langle s^2\rangle/M)_0$ is independent of M and T for this system, Eq. (4) shows that $A_2M^{1/2}$ should be a function of z only. Accordingly, in Fig. 8, we have plotted $A_2M^{1/2}$ versus z. *We consider the data to support the basic model in its requirement that the single parameter z should suffice to correlate data at different molecular weights and temperatures. The simple temperature dependence given by Eq. (3) appears to be satisfactory for these data.* It may be remarked that, for $z<\sim 1$, the curve deviates only slowly from the initial tangent, as z increases from zero, cf. Fig. 8, permitting reasonably accurate determinations of the initial slope of A_2 versus $[1-(\Theta/T)]$.

The function $F'(z)$ can be expanded in power series in z about $z=0$ to give[28,29]

$$F'(z)=1-2.865z+O(z^2).$$

Figure 9 shows the data for polystyrene in decalin plotted as $F'(z)$ versus z. The light line shows the theoretical slope 2.865 evaluated for the double-contact term in the series expansion. These data indicate that the double-contact approximation becomes inadequate for $z>\sim 0.10$. At higher values of z, the function $F'(z)$ appears to become approximately linear in z with a very small negative slope, indicating that $A_2M^{1/2}(\langle s^2\rangle/M)_0^{3/2}$ would be linear in z in this same interval.

The apparent success in correlating $A_2M^{1/2}$ with z implies that the superposition approximation employed in the statistical-mechanical calculation leading to Eq. (4) is adequate in this case.[28] Data of Krigbaum and Carpenter[17] on polystyrene fractions in cyclohexane, and of Schulz and Kirste[30] on fractions of polymethyl methacrylate in butyl chloride agree satisfactorily with Fig. 8 over the smaller interval in z to which they are restricted. The value of B_0 given by

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[24] T. A. Orofino and A. Ciferri, J. Phys. Chem. **68**, 3136 (1964).

[25] G. C. Berry Part II of this study, (to be published).

[26] Also neglected is a slight temperature dependence predicted or B_0 by some of the lattice theories.[12]

[27] An iterative calculation is used to construct Fig. 7, the first estimate for B_0 being made by setting $F'(z)\equiv 1$. This estimate is then used in conjunction with a theory for $F'(z)$ to obtain an improved estimate for B_0. In actual fact, the first and second estimates for B_0 usually agree satisfactorily. The particular theory used to estimate $F'(z)$ is not of great importance, so long as it is at least correct in the limit $T=\Theta$; we have used Eq. (19) here. This method of determining B_0, as opposed to a straightforward analysis of A_2 versus $1/T$, is most useful for large M since here the function $F'(z)$ rapidly departs from unity as T departs from Θ.

[28] B. H. Zimm, J. Phys. Chem. **14**, 164 (1946).

[29] A. C. Albrecht, J. Chem. Phys. **33**, 151 (1960).

[30] G. V. Schulz and K. Kirste, Z. Physik. Chem. (Frankfurt) **30**, 171 (1961).

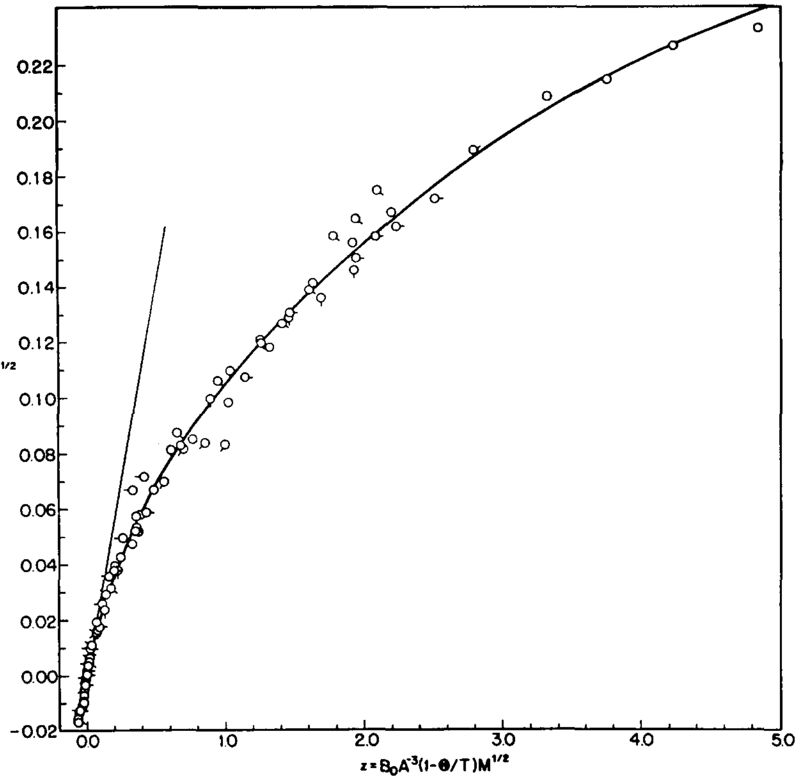

Fig. 8. $A_2M^{\frac{1}{2}}$ as a universal function of the interaction parameter z for polystyrene in decalin. The bold curve is an empirical fit to the data. The light line shows the initial tangent. The polymers are identified in Fig. 5.

Orofino and Mickey[19] is used to compute z for former data; the value given in Ref. 17 is apparently too low because of difficulties associated with determining B_0 for high-molecular-weight polymers (see Footnote 27).

Toluene Solutions

It is convenient at this point to consider a method of extending the empirical correlation shown in Fig. 8 to larger values of z. It is necessary to analyze data in a solvent (toluene, in this study) for which Θ is very low in order to obtain appreciably larger values of z. This, of course, eliminates the possibility of direct determination of Θ and B_0 as described above, since Θ is inaccessible experimentally, but the following procedure based on the information in Fig. 8 can be used instead. It is assumed that (1) the value of $(\langle s^2\rangle/M)_0$ is the same for toluene and decalin solutions of polystyrene and (2) that toluene solutions of polymers sufficiently low in molecular weight that $A_2M^{\frac{1}{2}}$ falls within the range (0 to 0.21) covered by the decalin data obey the same relations as those of higher molecular weight (there is no essential change in the seg-

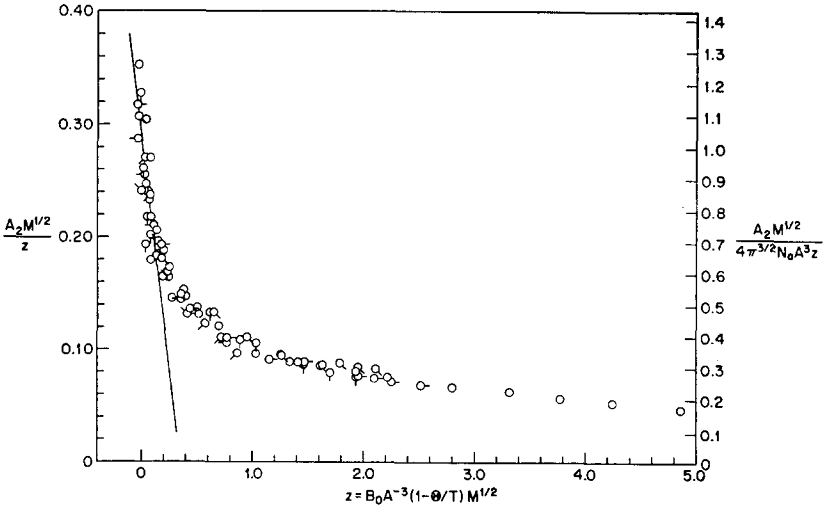

Fig. 9. $A_2M^{\frac{1}{2}}/z$ as a universal function of the interaction parameter z for polystyrene in decalin. The line represents the theoretical initial tangent to this function. The polymers are identified in Fig. 5.

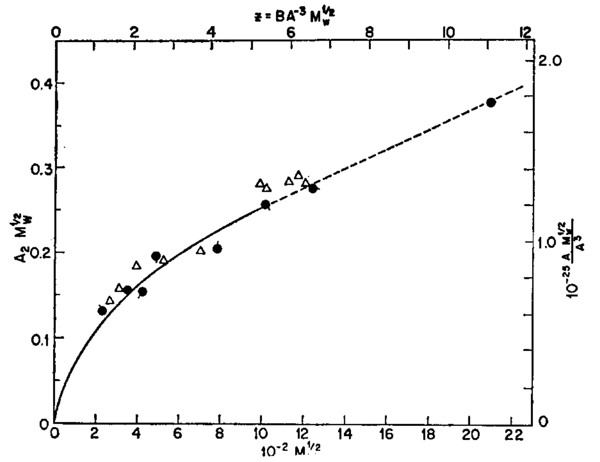

FIG. 10. $A_2M^{\frac{1}{2}}$ as a universal function of the interaction parameter z for polystyrene in toluene and in decalin. The solid curve represents the data in Fig. 8. The points represent data in toluene given in Ref. 30, △, and obtained here, ●; the polymers being identified by the pips as in Fig. 5.

mental density distribution, for example). The second assumption appears to be reasonable, at least for $M>48\,000$ for polystyrene, since data of this molecular weight are seen to correlate well with data for longer chain lengths in Fig. 8. The first assumption implies that specific solvent effects on the unperturbed radius are negligible; it is usually satisfactory in the absence of polar groups. Thus, data for $A_2M^{\frac{1}{2}}$ in toluene as a function of $M^{\frac{1}{2}}$ in the range $A_2M^{\frac{1}{2}}<0.21$ can be used to establish the proportionality factor BA^{-3} between z and $M^{\frac{1}{2}}$. We simply read from Fig. 8 values of z corresponding to the observed $A_2M^{\frac{1}{2}}$ in toluene and then calculate BA^{-3} for toluene as $z/M^{\frac{1}{2}}$. We have done this for five toluene solutions of the polystyrene samples studied previously in decalin, as well as some data of Bawn, Freeman, and Kamaliddin[31,32] to obtain the value $10^3BA^{-3}=5.3$ for the polystyrene–toluene system. Knowing this constant, we can now calculate z from data for toluene solutions of high-molecular-weight polystyrenes, and finally can use this information to extend the empirical curve correlating $A_2M^{\frac{1}{2}}/A^3$ and z, as shown in Fig. 10.

It may be seen immediately from Fig. 10 that if data are confined to systems for which $z>\sim 3$, a useful linear relation can be applied:

$$\frac{A_2M^{\frac{1}{2}}}{(\langle s^2\rangle/M)_0^{\frac{3}{2}}}=10^{24}(6.70+1.04BA^{-3}M^{\frac{1}{2}}),\qquad \text{for } 3<z<12. \tag{5}$$

Equation (5) probably applies to $z>12$ as well, but our data do not extend beyond this limit. This type of relation has been cited previously[33] as a useful extrapolation formula to obtain A^2, and Eq. (5) provides the necessary constants for such an analysis.

Assessment of approximate theories that yield closed expressions for A_2 is made in a later section.

Mean-Square Radius of Gyration

As is well known,[34,35] the ratio α^2 of the mean-square radius $\langle s^2\rangle$ to its unperturbed value $\langle s^2\rangle_0$ can be calculated by a perturbation method in the limit of small z. The result,

$$\alpha^2=1+a_1z+a_2z^2+O(z^3),$$
$$a_1=\tfrac{134}{105}, \tag{6}$$

can be rearranged to give α^2 as a function of the parameter $\zeta\equiv z/\alpha^3$ according to the equation

$$\alpha^2=1+a_1\zeta h(\zeta), \tag{7}$$

where

$$h(\zeta)=1+[\tfrac{3}{2}a_1-(a_2/a_1)]\zeta+O(\zeta^2). \tag{8}$$

The motivation for this rearrangement is that the new variable z/α^3 now defines an interaction parameter in such a way as to include some of the effects of the coil expansion by altering the segment length b by the factor α. This carries the implication that the random-flight distribution function can be satisfactorily modified by simply expanding all dimensions by uniform scale factor α. It is hoped that this procedure may lead to a function $h(\zeta)$ that is practically inde-

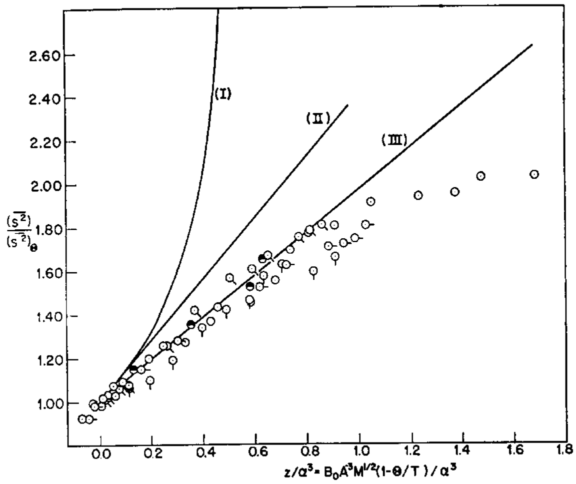

FIG. 11. $\langle s^2\rangle/\langle s^2\rangle_0$ as a function of the universal interaction parameter z/α^3 for polystyrene in decalin, ○, and cyclohexane, ◓. Curve I represents Eq. (14), and Curves II and III represent Eq. (9) with $(a_1h^*)=a_1=1.276$ for the former and treated as an arbitrary constant for the latter. The polymers are identified in Fig. 5, except for the data in cyclohexane taken from Ref. 17.

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[31] C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, Trans. Faraday Soc. **46,** 862 (1950).

[32] We have reanalyzed these data according to the equation $(\Pi/c)^{\frac{1}{2}}=(\Pi/c)_0^{\frac{1}{2}}[1+(\Gamma_2c/2)]$ to obtain slightly different estimate of Γ_2 than those reported in Ref. 30.

[33] H. Sotobayashi and K. Ueberreiter, Z. Electrochem. **66,** 538 (1962).

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

[35] M. Fixman, J. Chem. Phys. **23,** 1656 (1955).

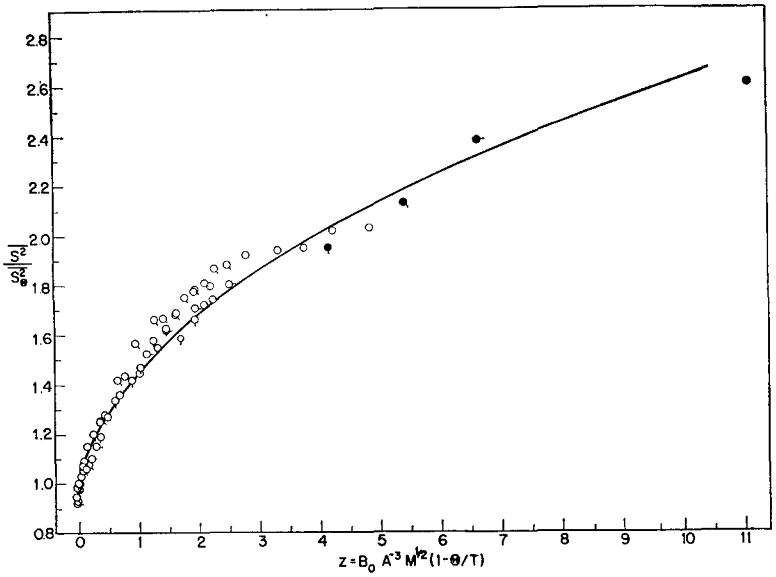

FIG. 12. $\langle s^2\rangle/\langle s^2\rangle_0$ as a function of the universal interaction parameter z for data in decalin, ○, and toluene, ●. The solid curve represents the relation given by Flory and Fisk.[40] The polymers are identified by the pips as in Fig. 5.

pendent of ζ. Consideration of Eq. (7) shows, in fact, that if $h(\zeta)$ is a constant h^*, Eq. (7) becomes simply

$$\alpha^5-\alpha^3=(a_1h^*)z, \qquad (9)$$

the familiar expression derived by Flory[36] and others.[35,37]

Stockmayer[38] has suggested that Flory's numerical constant for the quantity a_1h^* be set equal to a_1 to force Eq. (9) to agree with Eq. (6) in the limit of small z. Consideration of the series expansion, Eq. (8), shows that $h(\zeta)$ is not identically unity or a constant since the coefficient of ζ, for example, is not zero (it approximates $+0.425$ for linear chains[34]). Thus, Eq. (9) can be expected to be adequate only over a limited range of α at best.

The experimental data for decalin and toluene solutions are displayed in Figs. 11 and 12. The interaction parameter z was computed with the known values of B_0 and Θ for decalin solutions, and with the value of B, determined empirically as described above for toluene solutions. In addition, data for polystyrene in cyclohexane[17] are seen to agree well with our results as do data on polymethyl methacrylate in butyl chloride[3] (not shown). It is evident from both figures, especially Fig. 12, which includes data in toluene solutions, that α^2 is not a linear function of z/α^3 over the range of α^2 studied here. Figure 13 shows the empirically derived function $h(\zeta)=(\alpha^2-1)/a_1\zeta$, which may be fitted to within our experimental error by the simple relation $h(\zeta)=(3+\zeta)/3(1+\zeta)$ over the experimental span in ζ achieved here. The function $h(\zeta)$ is seen to become nearly independent of ζ as ζ increases. That is, $\alpha^5-\alpha^3$ seems to become proportional to z for large z according to these results, but exhibits more complicated behavior at small z. This suggests that the calculations given by Flory and others, might be improved by careful consideration of the expansion effects in the region $0<z<5$.

Thus, one can calculate α^2 as

$$\alpha^2=\frac{\displaystyle\int_0^\infty \langle s^2\rangle F(s^2)\exp\left[-\frac{E(s^2)}{kT}\right]ds^2}{\displaystyle\langle s^2\rangle_0\int_0^\infty F(s^2)\exp\left[-\frac{E(s^2)}{kT}\right]ds^2}, \qquad (10)$$

where $\exp(-E/kT)$ is a weight factor for the energy associated with intramolecular interactions of all conformations with radius s^2 and $F(s^2)$ is the random-flight probability distribution for s^2. Neither $F(s^2)$ or $E(s^2)$ is known, but Fixman[39] has recently obtained an explicit expression for the moments of $F(s^2)$, and Flory and Fisk[40] have suggested that these be used to fix the constant ν in an approximation to $F(s^2)$:

$$F(s^2)\propto(s^2)^\nu\exp[-(1+\nu)s^2/\langle s^2\rangle_0]. \qquad (11)$$

Comparison of the moments obtained in these two ways yields $\nu=\frac{5}{2}$. In addition, Fixman[35] showed that $E(s^2)$ will quite generally be given by

$$E(s^2)/kT=Kz\langle s^2\rangle_0^{\frac{3}{2}}/s^3, \qquad (12)$$

given a spherically symmetrical distribution of chain segments. Here K is a constant. Unfortunately, the necessary integration cannot be performed analytically over the entire range of Kz. However, for small Kz, Eq. (10) may be expanded to obtain the result

$$\alpha^2=1+C_1Kz+O(z^2),$$

with $C_1=\langle s^2\rangle_0^{\frac{3}{2}}\langle s^{-3}\rangle_0-\langle s^2\rangle_0^{\frac{1}{2}}\langle s^{-1}\rangle_0$. For $\nu=\frac{5}{2}$, $C_1=0.844$, or $K=1.511$ by comparison with Eq. (9).

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[36] P. J. Flory, J. Chem. Phys. **17**, 303 (1949).
[37] T. B. Grimley, Trans. Faraday Soc. **55**, 681 (1954).
[38] W. H. Stockmayer, J. Polymer Sci. **15**, 595 (1955).
[39] M. Fixman, J. Chem. Phys. **36**, 306 (1962).
[40] P. J. Flory and S. Fisk, J. Chem. Phys. **44**, 2243 (1966).

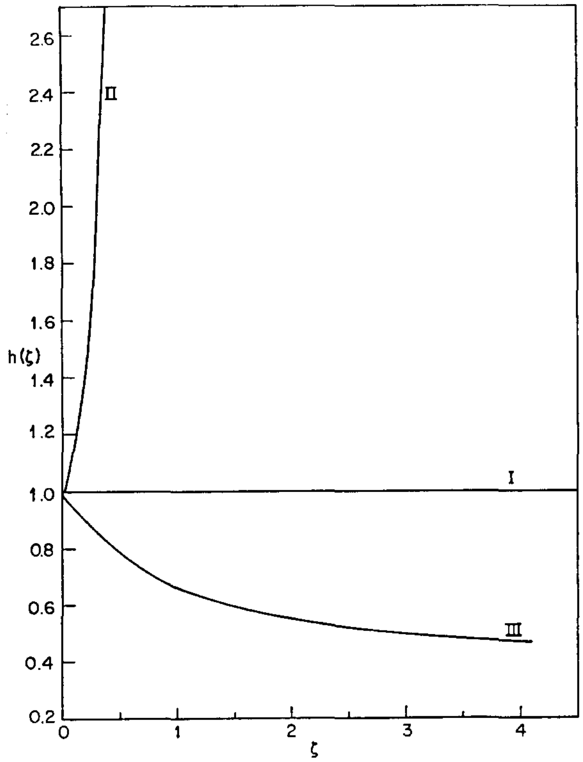

FIG. 13. The function $h(\zeta)$, defined in Eq. (7), versus $\zeta = z/\alpha^3$. Curve II represents Fixman's[42] approximate equation, Eq. (14); Curve I represents Flory's[36] approximate equation, Eq. (9), with $h^* = 1$; Curve III represents the data on polystyrene in decalin and toluene.

Flory and Fisk[40] have numerically integrated Eq. (11) for $\nu = \frac{5}{2}$ with results that are given to within 3% in $\alpha^2 - 1$ by the relation

$$h(\zeta) = 0.508[1 + 0.969(1 + 10\zeta)^{-\frac{2}{3}}], \qquad (13)$$

and $K = 1.511$. An approximate method of integrating Eq. (10) applicable when $Kz > \sim 1$ is given in the Appendix. The results agree satisfactorily with Eq. (13) for $Kz > 1$. In both estimates for $h(\zeta)$, $\alpha^2 - 1$ becomes proportional to ζ for large z. This limiting behavior is in accord with recent theoretical calculations of Edwards.[41]

Equation (13) correlates satisfactorily with our data over the accessible range $0 < z < 12$; the theoretical curve lies only slightly below the data, and the empirical approximation $h(\zeta) = (3 + \zeta)/3(1 + \zeta)$, for most of the range, as may be seen in Fig. 12. This agreement encourages one to believe that Eqs. (7) and (13) provide a resonable correlation between α^2 and z, which can be expected to apply even above the largest z obtained here.

Recently Fixman[42] has discussed an approximate closed-form expression for α that he originally derived earlier[35]

$$\alpha^3 = 1 + \tfrac{3}{2} a_1 z. \qquad (14)$$

An equation obtained by Stockmayer, Kurata, and Roig[43] is essentially numerically equivalent to Eq. (14). It is given by Eq. (14) if the coefficient $\frac{3}{2} a_1$ is replaced by $\frac{3}{2} a_1 \lambda(\alpha)$, where

$$(\tfrac{3}{4})^{\frac{3}{2}} \lambda(\alpha) = [1 + (1/3\alpha^2)]^{-\frac{3}{2}} + (\alpha - 1)(\alpha^3 - 1)^{-1}.$$

The function $\lambda(\alpha) = 1.01 \pm 0.02$ for all $\alpha > 1$. Another relation given by Ptitsyn[44] is also numerically very close to Eq. (14). Figure 13 shows the equivalent theoretical formulation for $h(\zeta)$ obtained by combination of Eqs. (7) and (14); the deviation from the observed $h(\zeta)$ is apparent and very large. In fact, Eq. (14) applies only to a very limited range of data, confined to $0 < z < \sim 0.15$, and application of Eq. (14) to deduce BA^{-3} from data on α^2 versus M would generally lead to erroneously low values. It may also be shown, however, that an expression of the type $\alpha^3 = C_1 + C_2 z$ will conform to the data over limited intervals in z. In particular the constants $C_1 = 2.0$ and $C_2 = 0.325$ will approximate our data over the interval $2 < z < 11$.

Finally, the behavior of α^2 for small z is of some interest, especially in discussions of $[\eta]$ as a function of z to follow in subsequent communications. In principle, data on $\alpha^2 - 1$ versus $[1 - (\Theta/T)]$ could be utilized to obtain B_0 in a way similar to that applied to data on A_2 versus $[1 - (\Theta/T)]$. There are three factors that make this unattractive, however: (1) Data on $\langle s^2 \rangle$ are usually obtained over an appreciably smaller span in M than can be achieved in measurement of A_2; (2) data on $\langle s^2 \rangle$ are usually less precise than data for A_2; (3) the function $\alpha^2 - 1$ versus z exhibits a very narrow region of linearity near $z = 0$, followed by a rapid decrease in $\partial(\alpha^2 - 1)/\partial z$ as z increases, making

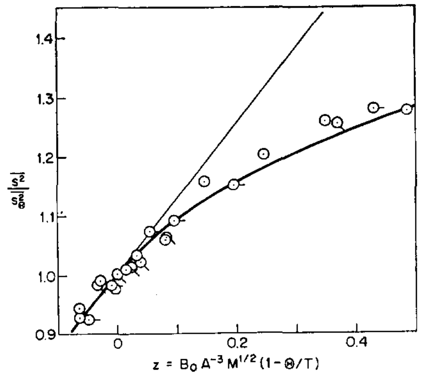

FIG. 14. $\langle s^2 \rangle / \langle s^2 \rangle_0$ as a function of the universal interaction parameter z for small z for polystyrene in decalin. The light line is the theoretical initial tangent, the curve represents the relation given by Flory and Fisk.[40] The polymers are identified by the pips in Fig. 5.

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[41] S. F. Edwards, Proc. Phys. Soc. (London) **85**, 613 (1965).

[42] M. Fixman, J. Chem. Phys. **36**, 3123 (1962).

[43] M. Kurata, W. H. Stockmayer, and A. Roig, J. Chem. Phys. **33**, 151 (1960).

[44] O. B. Ptitsyn, Vysokomolekul. Soedin. **3**, 1673 (1961) [English transl.: Polymer Sci. (USSR) **3**, 1061 (1962)].

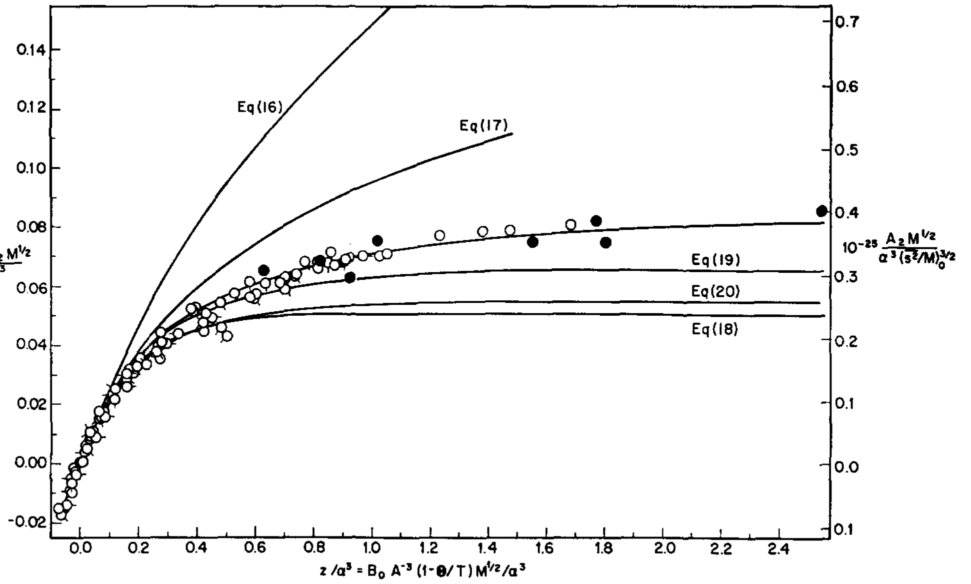

FIG. 15. $A_2M^{\frac{1}{2}}/\alpha^3$ as a function of the universal parameter z/α^3 for data on decalin, ○, and toluene, ●. The curves display theoretical estimates and are labeled according to the corresponding equation they represent, except for the curve through the data which is a modification of either Eqs. (19) or (20), as described in the text. The polymers are identified in Fig. 5.

accurate determination of $[\partial(\alpha^2-1)/\partial z]_{z=0}$ more difficult than the corresponding quantity $(\partial A_2M^{\frac{1}{2}}/\partial z)_{z=0}$ which has been used here. The initial dependence of α^2 on z is shown in Fig. 14, together with the theoretical initial slope $(\partial\alpha^2/\partial z)_{z=0}=\frac{134}{105}$ and the theoretical predicted behavior according to Eqs. (7) and (9). It is evident that the initial linear region is confined to very small z, $z<\sim 0.04$, and that the curve very rapidly falls away from the initial tangent as z increases.

Approximate Treatments of A_2

There have been several attempts to compute the dependence of A_2 on z by methods that yield approximate closed expressions valid for large z, as opposed to the series expansion $F'(z)$, valid only for small z. Naturally, these must contain the parameter α or some factor related to it or must implicitly include some approximate treatment of the dependence of α on z, since the expansion of the coil with increasing z must be considered in the calculation of A_2. One method for approximating the effect of the coil expansion has been to compute A_2 by assuming that the segment length b is independent of z, and then to make the *ad hoc* substitution of an expanded segment length $\alpha_2 b$ for b. The factor α_2 must contain contributions from both intramolecular and intermolecular interactions, and so is not in general equal to the intramolecular expansion factor α discussed above. It has been usual, however, to approximate α_2 to α to obtain the relation

$$A_2M^{\frac{1}{2}}/\alpha^3=4\pi^{\frac{3}{2}}N_a(\langle s^2\rangle/M)_0^{\frac{3}{2}}\zeta F(\zeta), \qquad (15)$$

in which $\zeta\equiv z/\alpha^3$ and, according to various approximate theories,

$$\zeta F(\zeta)=(1/2.303)\ln(1+2.30\zeta), \qquad (16)^{45}$$

$$\zeta F(\zeta)=(1/5.73)\ln(1+5.73\zeta), \qquad (17)^{21}$$

$$\zeta F(\zeta)=(1/5.73)[1-\exp(-5.73\zeta)]. \qquad (18)^{46}$$

These relations are shown together with the experimental data in Fig. 15, where it is seen that, of these relations, the last expression due to Casassa and Markovitz best predicts the shape of the experimental data.

It might be suspected that at least part of the failure of Eq. (18) to predict the correct asymptotic limit to $\zeta F(\zeta)$ is due to the approximation $\alpha_2=\alpha$ since the individual coils in a bimolecular cluster may be expected to expand at a faster rate with increasing z than would be the case for a single chain, so that $\alpha_2>\alpha$ for $z>0$.[47] Unfortunately, it is not clear what function α_2 should be used in conjunction with the calculation of Casassa and Markovitz. In their calculation, the conditional probability for multiple intermolecular contacts given a single intermolecular contact is taken as the product of the conditional probabilities for each additional contact considered individually. This procedure leads to the omission of expansion effects due to intramolecular contacts; thus the replacement of b by αb appears to be a reasonable attempt to include such effects. Casassa[47] later suggested that α be replaced by α_2 calculated for a cruciform molecule, where

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[45] T. A. Orofino and P. J. Flory, J. Chem. Phys. **26**, 1067 (1957).

[46] E. F. Casassa and H. Markovitz, J. Chem. Phys. **29**, 493 (1958).

[47] E. F. Casassa, J. Chem. Phys. **31**, 800 (1959).

$\alpha_2 > \alpha$. This results in the relation

$$\zeta F(\zeta) = \frac{(\alpha_2/\alpha)^3}{5.73}\left\{1 - \exp\left[-5.73\zeta\left(\frac{\alpha}{\alpha_2}\right)^3\right]\right\}, \tag{19}$$

with

$$\alpha^5 - \alpha^3 = (\alpha_2{}^5 - \alpha_2{}^3)a_1/k_1,$$

and with $k_1 = \sim 1.86$ to 2.04. This modification improves the fit to the asymptotic value of $\zeta F(\zeta)$ as shown in Fig. 15, but it appears, in effect, to include some intermolecular contacts more than once. In any case, Eq. (19) with $k_1 = 3.10$, shown by the solid line through the data, provides a satisfactory empirical representation of our data for both decalin and toluene solutions.

Kurata, Fukatsu, Sotobayashi, and Yamakawa[48] have developed another method based on approximate integration of partial differential equations derived from the rigorous theory for the random-flight chain. This method has the advantage of clearly stating the nature of the expansion factor α_2 employed, which in this case is factored into two terms $\bar{\alpha}$ and α^*. The latter refers to expansions resulting from intermolecular contacts *only*, whereas $\bar{\alpha}$ refers to coil expansion involving any kind of intramolecular contacts in the bimolecular cluster. The authors have explicitly included $\bar{\alpha}$ in the final result, whereas α^* is included implicitly through the assumption that $\alpha^{*3} = 1 + k_2 z/\bar{\alpha}^3$. With $\zeta \equiv z/\alpha^3$, there results

$$\zeta F(\zeta) = \left[\frac{(\bar{\alpha}/\alpha)^3}{5.73 - k_2}\right]$$
$$\times\left(1 - \exp\left\{-\left(\frac{5.73 - k_2}{k_2}\right)\ln\left[1 + k_2\zeta\left(\frac{\alpha}{\bar{\alpha}}\right)^3\right]\right\}\right). \tag{20}$$

The coefficient k_2, relating to expansion due to intermolecular contacts, is estimated to be 0.615 by Kurata, Fukatsu, Sotobayashi, and Yamakawa, but is not easily obtained from theory. Comparison of the rigorous expansion for $F'(z)$ to order z^2 with the expansion[29] for $F(z/\bar{\alpha}^3)$ to order $(z/\bar{\alpha}^3)^2$ suggests that the ratio $\alpha^2/\bar{\alpha}^2$ is given by the series expansion

$$\alpha^2/\bar{\alpha}^2 = 1 + 0.090z + \cdots,$$

or that $\bar{\alpha}^2$ is slightly smaller than α^2 for $z > 0$. Approximating the dependence of both α and $\bar{\alpha}$ by an $\alpha^5 - \alpha^3$ relationship at large z suggests that $(\alpha^5 - \alpha^3)/(\bar{\alpha}^5 - \bar{\alpha}^3) = 1.076$, or that $\alpha^3/\bar{\alpha}^3$ is always less than 1.045. Therefore, we set $\bar{\alpha} = \alpha$. Equation (20) then contains only measurable quantities given a value for k_2. The result with $k_2 = 0.615$ compared with the data in Fig. 15 shows that Eq. (20) reproduces the general shape of the observed curve, rapidly attaining an asymptotic limit as ζ increases, but that this limit is lower than that observed by a factor 1.5, being intermediate to the values corresponding to Eqs. (18) and (19), obtained by the methods of Casassa and Markovitz. Alternatively, we can treat k_2 as an adjustable parameter to force agreement between Eq. (20) and our data, such a curve being shown in Fig. 15 by the solid line through the data for $k_2 = 2.37$. This estimate of k_2 is readily derived from the asymptotic behavior of Eq. (20). Thus, if $k_2 < 2.865$, then Eq. (20) yields the expression

$$\lim_{\zeta\to\infty}\frac{A_2M^{\frac{1}{2}}}{\alpha^3(\langle s^2\rangle/M)_0^{\frac{3}{2}}} = \Psi = \frac{4\pi^{\frac{3}{2}}N_a}{5.73 - k_2}. \tag{21}$$

Substitution of the observed apparent limiting value $\Psi = 4.0 \times 10^{24}$ in Eq. (21) yields $k_2 = 2.37$, and finally

$$\alpha_2{}^2 = (\bar{\alpha}\alpha^*)^2 = 1 + (1.186 + \tfrac{2}{3} \times 2.37)z + \cdots$$
$$= 1 + 2.77z + \cdots$$

for the bimolecular expansion factor. Similar values for the limit Ψ have been obtained previously.[49] The corresponding limit calculated with the aid of Eq. (19) is

$$\Psi = \frac{4\pi^{\frac{3}{2}}N_a(\alpha_2/\alpha)^3}{5.73}, \tag{22}$$

which leads to the result for k_1 cited above,

$$\alpha_2{}^2 = 1 + 3.10z + \cdots.$$

In either case, $\alpha_2 > \alpha$, as one expects intuitively.

It is evident from the shape of the experimental curve in Fig. 15 that the function

$$\frac{A_2M^{\frac{1}{2}}}{(\langle s^2\rangle/M)^{\frac{3}{2}}}$$

that can be obtained from data confined to good solvents with $\zeta > 1$ contains no information concerning either the unperturbed mean-square dimension A^2 or the thermodynamic parameter B. The same statement holds for the ratio $A_2M/[\eta]$, of course. Thus, these functions can provide estimates of A^2 and B only at low M, or in relatively poor solvents. This requires that the quantities $A_2M^{\frac{1}{2}}$ and $(\langle s^2\rangle/M)$ must be examined separately as functions of molecular weight by means of empirical correlations in order to deduce $(\langle s^2\rangle/M)_0$ or B from data in good solvents.

Finally, it has been observed that plots of $A_2M^{\frac{1}{2}}$ versus $(\alpha^2 - 1)$ often obey the first-order theory obtained by elimination of z between Eqs. (4) and (6) further from theta conditions than do either of these equations by themselves.[34] Thus, elimination of z yields the result

$$A_2M^{\frac{1}{2}} = \frac{4N_a\pi^{\frac{3}{2}}(\langle s^2\rangle/M)_0^{\frac{3}{2}}}{a_1}(\alpha^2 - 1) + \cdots. \tag{23}$$

Figure 16 shows $A_2M^{\frac{1}{2}}$ versus $(\alpha^2 - 1)$ for our data.

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[49] G. C. Berry, V. C. Long, and L. M. Hobbs, Polymer **5**, 31 (1964).

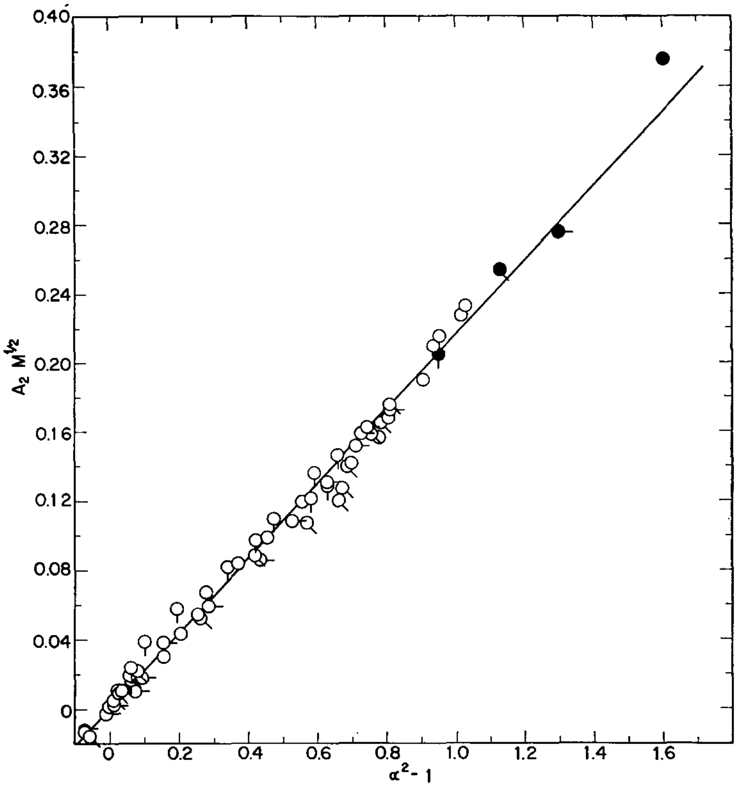

FIG. 16. $A_2M^{1/2}$ as a function of α^2-1 for data on decalin, ○, and toluene, ●. The polymers are identified in Fig. 5.

The value of $10^{18}(\langle s^2\rangle/M)_0$ calculated from the slope is 7.5 compared to the directly observed value of 7.6, and the plot is seen to be linear over a wide span in thermodynamic conditions. Rearrangement of Eq. (23) yields the result

$$\frac{A_2M^{1/2}}{4N_a\pi^{3/2}/a_1} = -\left(\frac{\langle s^2\rangle}{M}\right)_0^{3/2} + \left(\frac{\langle s^2\rangle}{M}\right)_0^{1/2}\frac{\langle s^2\rangle}{M} \tag{24}$$

which should prove useful in determining $(\langle s^2\rangle/M)_0$ from plots of A_2M versus $(\langle s^2\rangle/M)$ for data confined to good solvent conditions.

V. CONCLUSION

The first objective of this work has been to determine by experiment, as accurately as possible, the dependence of the mean-square molecular radius and the second virial coefficient on temperature and molecular weight for a single polymer, polystyrene, in decalin. All data are found to be consistent with the assumption that the expansion of the radius above the Flory temperature Θ and the virial coefficient are both functions of the single statistical variable z, defined above, in which the temperature dependence of the segment pair excluded volume β is given by

$$\beta=\beta_0[1-(\Theta/T)].$$

Consequently the adequacy of the fundamental assumptions of the various "two-parameter" statistical-mechanical treatments—that intersegmental interactions are short range and pairwise additive—is supported. Our results provide evidence in support of the following statements:

(1) The prediction of statistical mechanical calculations that both $A_2M^{1/2}(s^2/M)_0^{-3/2}$ and α^2 are functions only of the interaction parameter z is verified.

(2) The temperature dependence of the thermodynamic parameter B may be taken as $B=B_0[1-(\Theta/T)]$ over a 100 C° temperature interval for polystyrene–decalin solutions.

(3) The dependence of α^2 on z is given adequately by Eqs. (7) and (13) for the range in z covered here.

(4) The dependence of $A_2M^{1/2}(s^2/M)^{-3/2}$ on z/α^3 is given by Eq. (15) combined with either Eq. (19), with $K_1=3.10$, or with Eq. (20), with $K_2=2.37$.

(5) The empirical plot of $A_2M^{1/2}(\langle s^2\rangle/M)_0^{-3/2}$ versus z given in Fig. 10 should be useful in analysis of data confined to good solvents to obtain $(\langle s^2\rangle/M)_0$ and B.

(6) $A_2M^{1/2}$ is linear in α^2-1 with a slope that yields directly $(\langle s^2\rangle/M)_0$ for data covering a large span in α^2.

The establishment of these relations over a certain range of temperature and molecular weight obviously does not guarantee that the same functions must apply outside this range; *however, these relations will presumably hold over the same range of z for any flexible polymer in dilute solution,* at least for nonpolar nonionic systems in which only short-range forces are operative.

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APPENDIX

Substitution of Eqs. (11) and (12) in Eq. (10) gives

$$\alpha^2=\int_0^\infty x^2\phi d\ \ln x \Big/ \int_0^\infty \phi d\ \ln x, \tag{A1}$$

where $x^2=s^2/\langle s^2\rangle_0$ and

$$\ln\phi=-(1+\nu)x^2-Kz/x^3+2(1+\nu)\ \ln x. \tag{A2}$$

Grimley[37] approximated Eq. (A1) by substituting a delta function peaked at the most probable value of $s^2/\langle s^2\rangle_0=\alpha_0^2$ for the function ϕ, to obtain the result $\alpha^5-\alpha^3=3Kz/2(1+\nu)$. Inspection reveals marked similarity between ϕ and the log-normal distribution function ϕ^* given by

$$\phi^*=\phi_0\ \exp[-(1+\nu)(5\alpha_0^2-3)(\ln\alpha/\alpha_0)^2], \tag{A3}$$

with ϕ_0 the value of ϕ for $x=\alpha_0$. This suggests that ϕ^* might represent a better approximation to ϕ than a delta function. Expansion of ϕ/ϕ^* in terms of $\ln\alpha/\alpha_0$ shows that the approximation $\phi=\phi^*$ is valid to order $(\ln\alpha/\alpha_0)^3$. Thus, the approximation is better the larger is Kz (or α_0). Equation (A1) is easily integrated after replacing ϕ by ϕ^* to obtain the result

$$\alpha^2=\alpha_0^2\ \exp[1/(1+\nu)(5\alpha_0^2-3)], \tag{A4}$$

where $\alpha_0^0-\alpha_0^3=3Kz/2(1+\nu)$.

Equation (A4) agrees very well with the numerical integration of Eq. (10) with $F(s^2)$ given by Eq. (11).[35] The approximation could be carried to still smaller Kz by including correction terms of order $(\ln\alpha/\alpha_0)^3$ and higher, if desired.

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Hauffe–Ilschner Transition during Thermal Oxidation

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Numerical computations together with physical considerations are used to argue that a transition proposed by Hauffe and Ilschner from electron tunneling to nonlinear ionic diffusion as rate-limiting mechanisms during thermal oxidation is not to be expected. The results indicate instead that the reverse transition is likely to occur. This in turn has serious implications regarding the oxidation kinetics and limiting thicknesses as a function of temperature deduced from the Mott–Cabrera theory.

I. INTRODUCTION

A TRANSITION from an electron-tunneling rate-limiting stage to an ionic diffusion rate-limiting stage with increasing oxide film thickness during the thermal oxidation of metals at temperatures below 300°K has been postulated by Hauffe and Ilschner.[1] The purpose of this work is to illustrate that this postulated transition is not physically realistic, but that the opposite transition (i.e., from ionic diffusion rate-limiting to electron-tunneling rate-limiting stages) is actually to be expected. In order to prove this, it is first necessary to review briefly the second theory of Mott[2] and the deduction of a transition by Hauffe and Ilschner.

II. CONCEPT OF THE TRANSITION

The following equation for the ionic current is basic to the second Mott theory[2] for thermal oxidation of metals:

$$J_i=2N\nu\{\exp(-U/kT)\}\ \sinh(-Z_i\,|\,e\,|\,aV/kTL), \tag{1}$$

where V is the electrical potential across the oxide of thickness L due to transfer of electrons from metal to the O^- state of adsorbed oxygen. The several parameters are defined as follows: N is the surface density of ions at the rate-limiting activation barrier, U is the height of this activation barrier, ν is the characteristic ionic jump frequency, $2a$ is the distance between interstitial positions, $Z_i\,|\,e\,|$ is the charge per ion, $|\,e\,|$ is the magnitude of the electronic charge, and kT is the product of Boltzmann's constant and temperature.

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