Excluded-Volume Effects in Dilute Polymer Solutions. 7. Very High Molecular Weight Polystyrene in Benzene and Cyclohexane

Y. Miyaki, Y. Einaga,* and H. Fujita

Department of Polymer Science, Osaka University, Toyonaka, Osaka, 560 Japan.

Received July 5, 1978

ABSTRACT: Light-scattering measurements were made on six polystyrene fractions of very high molecular weight in benzene at 25 °C and in cyclohexane at 34.5 °C by use of a Fica 50 photometer and a homemade laser scattering photometer designed to permit accurate measurements down to a scattering angle of 5°. The weight-average molecular weights $\overline{M}_w$ and the square roots of mean-square radius of gyration $\langle S^2\rangle_z^{1/2}$ in benzene ranged from $8.7_6 \times 10^6$ to $56._8 \times 10^6$ and from 16_4 to 50_6 nm, respectively. The molecular size 506 nm of the highest molecular weight sample is the largest one determined so far by light scattering. Except for the highest molecular weight fraction, the asymptotic behavior of light scattering at large angles in the theta state gave about 1.15 for $\overline{M}_w/\overline{M}_n$ and values smaller than 1.10 for $\overline{M}_z/\overline{M}_w$. The expansion factor α_s^2 increased in proportion to $\overline{M}_w^{1/5}$, for α_s^2 larger than 2–3 in good agreement with the numerical studies on lattice chains.

Light-scattering measurements of molecular weight M, mean-square radius of gyration $\langle S^2\rangle$, and second virial coefficient A_2 on very high molecular weight polymers in good solvent are essential for elucidation of the problem that has attracted polymer physical chemists since Flory in the 1940's,[1] i.e., excluded-volume effects on polymer behavior in dilute solution at very large values of the excluded volume parameter z. Slagowski et al.[2,3] were probably the first to attempt this kind of measurement. They examined benzene and cyclohexane solutions of polystyrene samples, the highest molecular weight of which approached approximately 50×10^6. However, their data somewhat badly scatter, and they have not yet published other than a short communication.[3] Fukuda et al.[4] reported light-scattering studies on high molecular weight polystyrenes in benzene and *trans*-decalin, but they did not go beyond a molecular weight of about 13×10^6.

The present paper describes our light-scattering experiment done on the same systems as treated by Slagowski et al.[2,3] Our polystyrene fractions ranged in weight-average molecular weight from 8×10^6 to 60×10^6. As far as we know, this last molecular weight is the largest so far determined for synthetic polymers by any absolute method including the light-scattering technique. We owe the samples of this study to the Japan Synthetic Rubber Co. (JSR), which has recently succeeded in synthesizing ultra-high molecular weight linear polystyrene by a special emulsion polymerization technique.

Soon after we started this work it was recognized that our Fica 50 photogoniometer would not be available for accurate evaluation of the molecular quantities of polystyrene fractions of M higher than 30×10^6 in benzene and that for this purpose we would have to get a new instrument which hopefully permits an accurate intensity measurement down to a scattering angle lower than 10°. Thus, with the cooperation of Union Giken Co., Osaka, Japan, we designed and constructed a computer-operated photogoniometer with the He–Ne laser as the light source. Although this instrument was a vital part of the present work, we shall report on its details, calibration, and illustrative data in a separate paper.[5]

Experimental Section

Polymer Samples. Two unfractionated samples of JSR polystyrene designated IK1500 and BK2500 by the company were made available by Dr. T. Inoue. Before fractionation, they were thoroughly purified by extraction with methanol. First, each of them was separated into several parts by fractional precipitation, in which the polymer was dissolved in a benzene–methanol mixture (76:24 by volume) and the solution was cooled in stepwise fashion from 30 to 23 °C. Each of the fractions obtained was then subjected to a similar process of fractional precipitation, with the mixed-solvent composition properly adjusted. This operation was iterated at least three more times. No combination of fractions of similar intrinsic viscosities was made. No mechanical stirring was applied to the solution at any stage during these fractionation processes. To obtain fractions as homogeneous as possible in molecular weight the initial concentrations of polymer in the final fractionations were lowered to about 10^{-4} g cm^{-3}. Six fractions were selected for the present physical measurements from a number of final fractions and were designated IK1500-1, IK1500-2, BK2500-1, BK2500-2, BK2500-3, and BK2500-4.

Solvents and Preparation of Solutions. Benzene and cyclohexane as the solvents for the present light-scattering measurements were extensively purified by the standard procedures immediately before use.[6]

Solutions were gravimetrically prepared. Great care was taken to prevent the polymer solute from shear degradation in dissolving it in a given solvent. The flasks containing polymer and solvent were stood still in a dark room, at room temperature for benzene solutions and at 40–45 °C for cyclohexane solutions. No mechanical stirring was applied to the solutions. After the solution had appeared to be homogenized, the flask was gently shaken for 1 or 2 days to promote complete dissolution. The solutions shaken for 1 day and those shaken for 2 more days did not show any difference in relative viscosity. The entire process took about 2 weeks. The cyclohexane solutions were kept warm to prevent precipitation of the polymer solute.

Light-Scattering Photometry. All six fractions were examined in benzene at 25 °C and in cyclohexane at 34.5 °C (chosen as the Θ temperature for polystyrene) by use of a Fica 50 photogoniometer. We followed the procedures established at our laboratory on the basis of experiences over the past decade. The test solutions were first made optically clean by centrifugation at about 25 000 g for benzene solutions and 13 000 g for cyclohexane solutions for about 2 h in a Sorvall RC2-B centrifuge, and then directly pipetted into light-scattering cells. No change in relative viscosity was detected before and after centrifugation. The measuring cells and pipets used were cleaned by rinsing with acetone vapor in distillation columns. To prevent shear degradation of polymer chains the tip of each pipet was not made sharp pointed and the rate of flow out of it was suppressed below 15 cm^3 min^{-1}. Intensities of scattered light were measured at angles from 13 to 150° with vertically polarized light of 436 and 546 nm in wavelength as the incident beam. Measurement on pure benzene showed that readings can be made within errors of ±1% in this range of scattering angles. At each scattering angle the measurement was repeated several times and the average of the data was taken to be the desired one; each measurement did not scatter more than ±1% of the average at any angle.

0024-9297/78/2211-1180$01.00/0

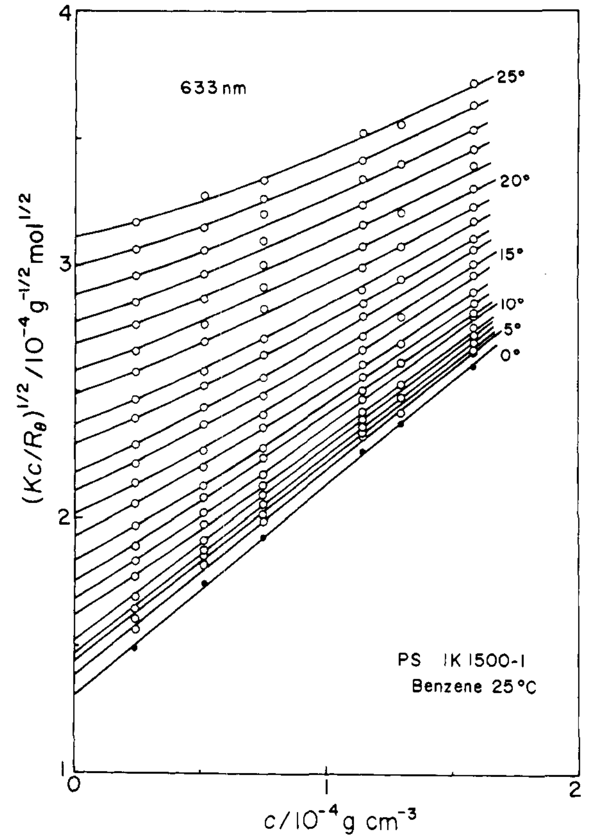

Figure 1. Reciprocal square root of reduced scattering intensity at indicated angles as a function of polymer concentration for sample IK1500-1 in benzene at 25 °C. Closed circles represent the values extrapolated to zero scattering angle.

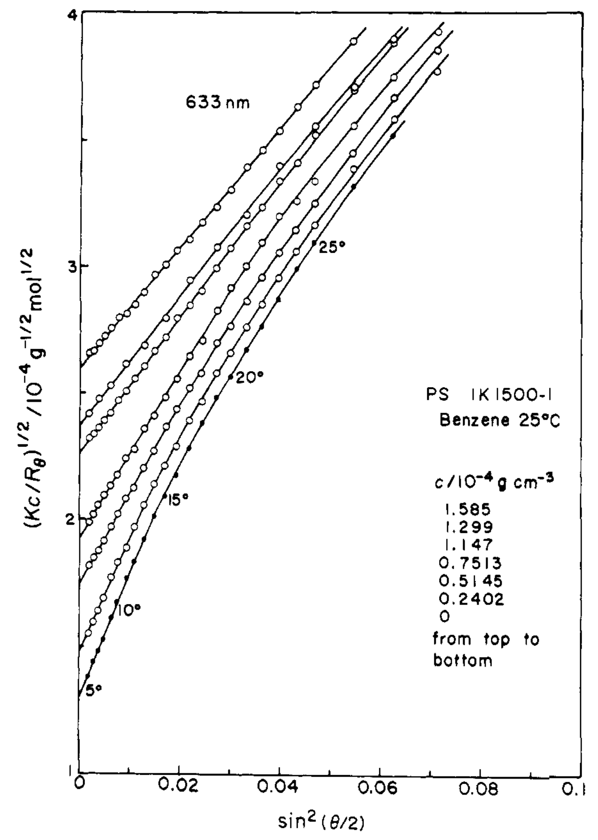

Figure 2. Angular dependence of reciprocal square root of reduced scattering intensity at indicated concentrations for sample IK1500-1 in benzene at 25 °C. Closed circles represent the values obtained by extrapolation to zero concentration.

For the three highest molecular weight fractions, i.e., IK1500-1, IK1500-2, and BK2500-1, in benzene at 25 °C the data were also taken by use of the laser-scattering photogoniometer mentioned in the introduction. The measurement was made at angles from 5 to 150° with vertically polarized light of 633 nm as the incident beam. The value of 11.84×10^{-6} cm^{-1} reported by Pike et al.[7] was assumed for the absolute Rayleigh ratio of benzene at 633 nm to compute Rayleigh ratios of benzene solutions of polystyrene at this wavelength.

For the specific refractive index increments $\partial n/\partial c$ of polystyrene in benzene at 25 °C for light of 436 and 546 nm we chose the values reported by Bodmann:[8] 0.1094 cm^3 g^{-1} at 436 nm and 0.1062 cm^3 g^{-1} at 546 nm. The $\partial n/\partial c$ value of this system for light of 633 nm was estimated from these data by use of the equation for simple Cauchy dispersion,[8] because no literature value was available and also because our differential refractometer was not yet ready for the measurement with light of 633 nm wavelength. The computed $\partial n/\partial c$ was 0.104_7 cm^3 g^{-1}. The values of $\partial n/\partial c$ for polystyrene in cyclohexane at 34.5 °C for light of 436 and 546 nm were directly determined by use of a differential refractometer of the modified Schulz–Cantow type. The results were 0.180_7 cm^3 g^{-1} at 436 nm and 0.170_9 cm^3 g^{-1} at 546 nm.

Results

Light-Scattering Envelopes. In Figures 1 and 2 are presented the data on benzene solutions of the sample IK1500-1, the highest molecular weight polystyrene examined in this study. The data are plotted according to Berry's method,[9] in which the reciprocal square root of reduced intensity of scattered light, i.e., $(Kc/R_\theta)^{1/2}$, is taken as the ordinate. Figure 1 shows the concentration dependence of reduced intensity of scattered light at fixed scattering angles between 5 and 25°. The data points for scattering angles smaller than 8° follow a straight line, thus enabling us to extrapolate them to zero concentration with precision. However, those for the larger scattering angles show an upward curvature as the concentration is lowered, and the curvature becomes more pronounced as the scattering angle gets larger. Thus we find it necessary to measure scattering intensities down to a progressively lower concentration, in order to extrapolate the data at higher scattering angles to infinite dilution. The lowest polymer concentration studied on the sample IK1500-1 in benzene at 25 °C was 2.402×10^{-5} g cm^{-3}. At this concentration, the scattering intensity of the solution was only about twice that of pure benzene when compared at 30°. For this reason, the data obtained at angles larger than 25° have been discarded.

The closed circles in Figure 1 show values of $(Kc/R_0)^{1/2}$ extrapolated to zero scattering angle. The extrapolations were made on the graph shown in Figure 2. The straight line fitting these extrapolated points gives $\bar{M}_w = (56.8 \pm 1.0) \times 10^6$ and $A_2 = (1.09 \pm 0.05) \times 10^{-4}$ cm^3 mol g^{-2} for the sample IK1500-1 in benzene at 25 °C, where $\bar{M}_w$ is the weight-average molecular weight of the polymer solute and A_2 is the second virial coefficient of the solution.

Figure 2 illustrates the angular dependence of reduced intensity of scattered light at different polymer concentrations. At concentrations higher than about 10^{-4} g cm^{-3} the plotted points follow a straight line at scattering angles lower than 25°. But as the concentration is lowered, the range of scattering angles in which $(Kc/R_\theta)^{1/2}$ varies linearly with $\sin^2(\theta/2)$ becomes narrower and the slope of the linear portion of the plot becomes steeper. Thus if measurements had not been extended down to scattering angles below 15°, the intercepts of the plots for such low concentrations would have been seriously overestimated. In our experiment, this uncertainty was largely suppressed by the advantage of a laser scattering photogoniometer, which made it possible to obtain data down to a scattering angle as low as 5°.

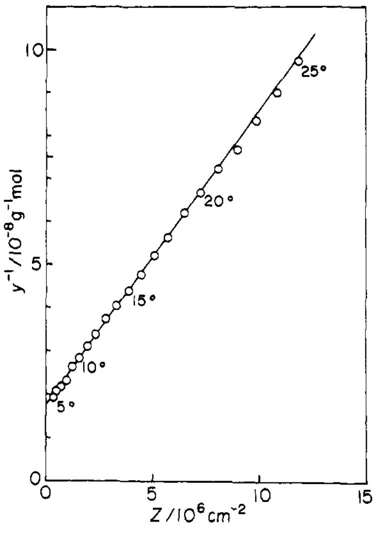

Figure 3. Fujita's plot for sample IK1500-1 in benzene at 25 °C: $y = (R_\theta/Kc)_{c=0}$, $Z = (yu^2)^{-1} \int_0^u yu'^2\, du'$, and $u = (4\pi/\lambda)^2 \sin^2(\theta/2)$.

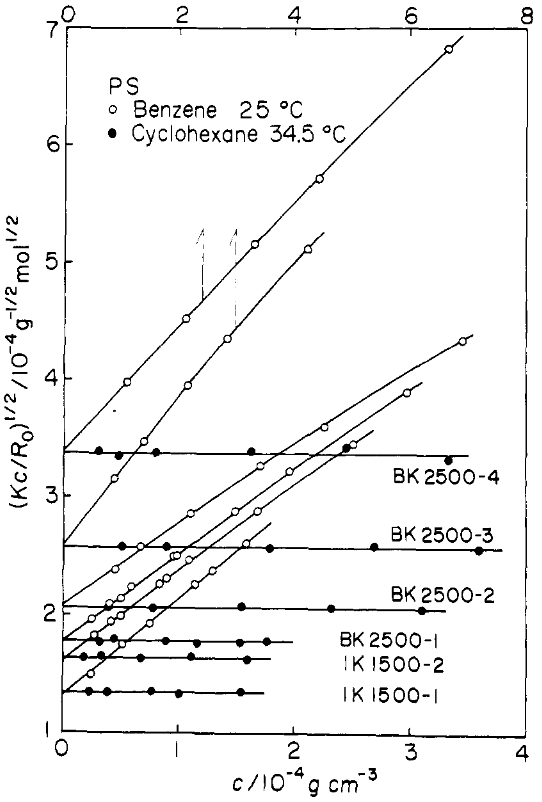

Figure 4. Reciprocal square root of reduced scattering intensity at zero scattering angle as a function of concentration for six polystyrene samples in benzene at 25 °C and in cyclohexane at 34.5 °C.

The closed circles in Figure 2 represent the infinite-dilution values of $(Kc/R_\theta)^{1/2}$ obtained by extrapolating the solid curves in Figure 1. The smooth curve fitting them gives $\overline{M}_w = (56.8 \pm 1.0) \times 10^6$ from its intercept at zero scattering angle. This is in agreement with the value derived above from Figure 1. However, the initial slope of this curve cannot be determined unequivocally. In such circumstances, it would be worthwhile to try the method proposed a few years ago by one of the authors.[10] Figure 3 shows that the data points on the Fujita plot follow very closely a straight line over the range of the variable Z. The slope of the line gives $\langle S^2\rangle_z^{1/2} = 506 \pm 10$ nm for the sample IK1500-1 in benzene at 25 °C.

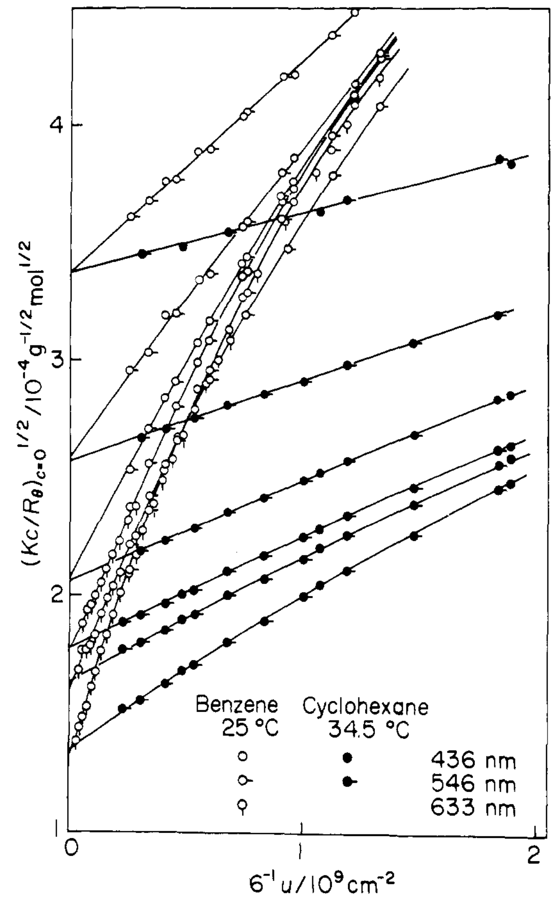

Figure 5. Reciprocal square root of reduced scattering intensity at zero concentration and at indicated incident wavelengths as a function of u for six polystyrene samples in benzene at 25 °C and in cyclohexane at 34.5 °C. Here $u = (4\pi/\lambda)^2 \sin^2(\theta/2)$. Polystyrene samples are BK2500-4, BK2500-3, BK2500-2, BK2500-1, IK1500-2, and IK1500-1 from top to bottom.

The presentation of the original light-scattering data for other samples in benzene at 25 °C and for all the samples in cyclohexane at 34.5 °C is omitted here in order to save space. Only the extrapolated data at zero scattering angle and at zero polymer concentration for these systems are illustrated in Figures 4 and 5. In these figures, the open and closed circles refer to benzene solutions and cyclohexane solutions, respectively. Also, in Figure 5, the data for different wavelengths are distinguished by pips. A few points may be made.

(1) For each of the six samples studied, essentially identical weight-average molecular weights were obtained from both benzene and cyclohexane solutions.

(2) In either of these solutions the data for a given polymer sample at different wavelengths fell on a single line.

(3) The cyclohexane data in Figure 4 gave $A_2 = 0$ for all the polystyrene samples studied. The benzene plots in the same figure were linear below $c = 2 \times 10^{-4}$ g cm^{-3}, and presented no difficulty in determining A_2 from their initial slopes. The points (1) and (2) support the accuracy and reliability of the present measurements, because they are the basic requirements from the theory of light scattering.

The values of $\overline{M}_w$, A_2, and $\langle S^2\rangle_z^{1/2}$ determined from the smooth curves in Figures 4 and 5 are summarized in Table I. It is instructive to note that the molecular diameter of the highest molecular weight sample in benzene amounts to over 1 μm. This size and the molecular weight as well are probably the largest values determined so far for synthetic polymers by light scattering.

Table I
Results of Light-Scattering Measurements on Polystyrene in Benzene at 25 °C and Cyclohexane at 34.5 °C

	in benzene at 25 °C		(A_2, cm³ mol g⁻²) × 10⁴	in cyclohexane at 34.5 °C	
samples	$\bar{M}_w \times 10^{-6}$	$\langle S^2\rangle_z^{1/2}$, nm		$\bar{M}_w \times 10^{-6}$	$\langle S^2\rangle_{0z}^{1/2}$, nm
IK1500-1	$56._8 \pm 1.0$	$50_6 \pm 10$	$1.0_9 \pm 0.05$	$55._7 \pm 1.2$	$22_8 \pm 5$
IK1500-2	$39._0 \pm 1.0$	$39_2 \pm 8$	$1.2_2 \pm 0.03$	$38._0 \pm 0.7$	$18_3 \pm 4$
BK2500-1	$31._9 \pm 0.6$	$35_3 \pm 7$	$1.2_8 \pm 0.04$	$32._0 \pm 0.6$	$16_7 \pm 4$
BK2500-2	$23._2 \pm 1.0$	$29_7 \pm 9$	$1.4_4 \pm 0.05$	$23._5 \pm 0.5$	$14_5 \pm 3$
BK2500-3	$15._0 \pm 0.6$	$22_7 \pm 7$	$1.6_6 \pm 0.05$	$15._2 \pm 0.3$	$11_6 \pm 2$
BK2500-4	$8.7_6 \pm 0.3$	$16_4 \pm 4$	$1.8_2 \pm 0.05$	$8.7_9 \pm 0.2$	$87._9 \pm 2$

Determination of Number-Average and *z*-Average Molecular Weight. It follows from the Debye theory[11] that the particle scattering function $P(\Theta)$ of a molecular-weight polydisperse sample of linear flexible polymer in the unperturbed state is represented by

$$yu^2 = \frac{2}{A'^2}\int_0^\infty \frac{f(M)}{M} e^{-A'uM}\,\mathrm{d}M - \frac{2}{A'^2}\int_0^\infty \frac{f(M)}{M}\,\mathrm{d}M + \frac{2}{A'}u \quad (1)$$

where

$$y = \bar{M}_w P(\Theta) = (R_\Theta/Kc)_{c=0} \quad (2)$$

$$u = (4\pi/\lambda)^2 \sin^2(\theta/2) \quad (3)$$

$$A' = \langle S^2\rangle_0/M \quad (4)$$

and $f(M)$ is the weight distribution of molecular weights in the sample. In these expressions, Θ is the scattering angle, λ is the wavelength of incident light in the solution, and $\langle S^2\rangle_0$ is the unperturbed mean-square radius of gyration of a monodisperse sample with molecular weight M, so that A' is a constant for the polymer under consideration. If the polydisperse sample has high-average molecular weights and, in addition, its molecular weight distribution is narrow (more correctly, it has a negligible trail in the low molecular weight region), the first term on the right-hand side of eq 1 may be dropped in comparison with the remaining two terms when values of u are sufficiently large. Then we have

$$yu^2 = -\frac{2}{A'^2\bar{M}_n} + \left(\frac{2}{A'}\right)u \quad (5)$$

where $\bar{M}_n$ is the number-average molecular weight of the sample. Thus it can be expected that, under the conditions mentioned above, plots of yu^2 against u should approach a straight line as u increases and that the intercept and slope of the straight line allow A' and $\bar{M}_n$ to be evaluated. It is a simple matter to show that the z-average molecular weight $\bar{M}_z$ of a polydisperse sample of a polymer is related to A' and the z-average unperturbed mean-square radius of gyration $\langle S^2\rangle_{0z}$ by

$$\bar{M}_z = (1/A')\langle S^2\rangle_{0z} \quad (6)$$

Since $\langle S^2\rangle_{0z}$ can be measured by conventional light scattering, the evaluation of A' allows $\bar{M}_z$ to be determined. These theoretical predictions are not new,[11] but, as far as we know, none of the previous investigators have presented experimental data which made them applicable for molecular characterization of polymer samples. Now, as is illustrated below, such data have become available from our measurements on very high molecular weight polystyrene samples in cyclohexane.

Figure 6 shows the yu^2 vs. u plots for six samples in cyclohexane at 34.5 °C. The data points for each sample follow a straight line at u values above a certain limit. The straight lines for different samples are almost parallel, in good agreement with the prediction from eq 5 (note that A' is a constant for a given polymer–solvent pair). Table II gives the values of A', $\bar{M}_w/\bar{M}_n$, and $\bar{M}_z/\bar{M}_w$ determined from the slopes and intercepts of these lines together with the values of $\bar{M}_w$ and $\langle S^2\rangle_{0z}$ for cyclohexane solutions listed in Table I. It is seen that all the samples examined have $\bar{M}_z/\bar{M}_w$ ratios smaller than the corresponding $\bar{M}_w/\bar{M}_n$ ratios and unexpectedly close to unity. This suggests that their molecular weight distributions are quite narrow. It

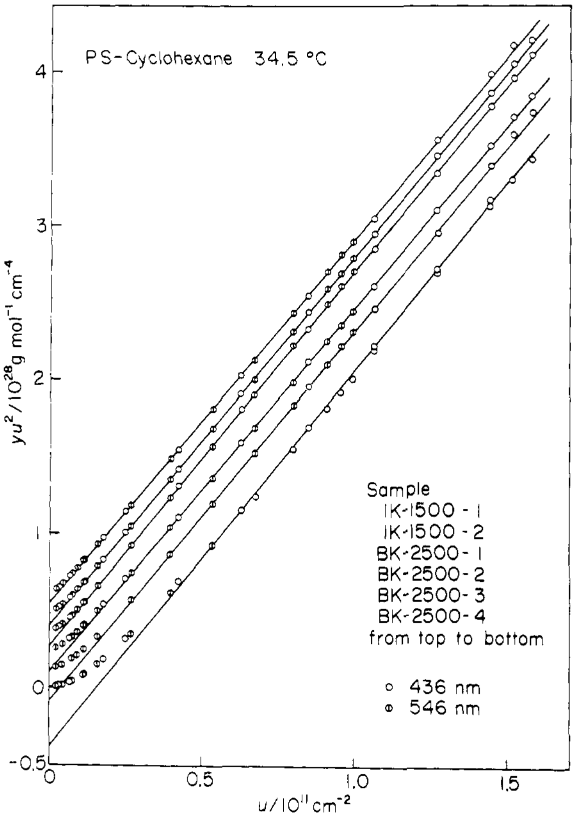

Figure 6. Plots of yu^2 vs. u for polystyrene samples in cyclohexane at 34.5 °C: $y = (R_\Theta/Kc)_{c=0}$ and $u = (4\pi/\lambda)^2 \sin^2(\Theta/2)$. Except for sample BK2500-4, the data points for different samples are shifted upward by different amounts. It is to be understood that they tend to zero intercepts.

Table II
Values of $\bar{M}_w/\bar{M}_n$, $\bar{M}_z/\bar{M}_w$, and A' Estimated from Light-Scattering Asymptotes in Cyclohexane at 34.5 °C

samples	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$	(A', cm²) × 10¹⁸ [a]
IK1500-1	$1.4_4 \pm 0.15$	$1.1_0 \pm 0.04$	$8.4_6 \pm 0.2$
IK1500-2	$1.1_4 \pm 0.1$	$1.0_5 \pm 0.03$	$8.4_0 \pm 0.2$
BK2500-1	$1.1_3 \pm 0.1$	$1.0_6 \pm 0.03$	$8.2_1 \pm 0.2$
BK2500-2	$1.1_7 \pm 0.1$	$1.0_5 \pm 0.03$	$8.5_1 \pm 0.2$
BK2500-3	$1.1_5 \pm 0.06$	$1.0_6 \pm 0.03$	$8.3_2 \pm 0.2$
BK2500-4	$1.1_4 \pm 0.05$	$1.0_7 \pm 0.03$	$8.2_2 \pm 0.2$

[a] The average value of A' is $(8.3_5 \pm 0.2) \times 10^{-18}$ cm².

Table III
Typical Reported Values of $\langle S^2\rangle_{0z}/\overline{M}_w$ for Polystyrene in Cyclohexane at the Θ Temperature

($\langle S^2\rangle_{0z}/\overline{M}_w$, cm^2) × 10^{18}	ref	($\langle S^2\rangle_{0z}/\overline{M}_w$, cm^2) × 10^{18}	ref
8.8	present data	9.00	Krigbaum and Carpenter[14]
9.36	Outer et al.[12]		
7.95	Notley and Debye[13]	7.6	Berry[9]
		8.4	Yamamoto et al.[15]

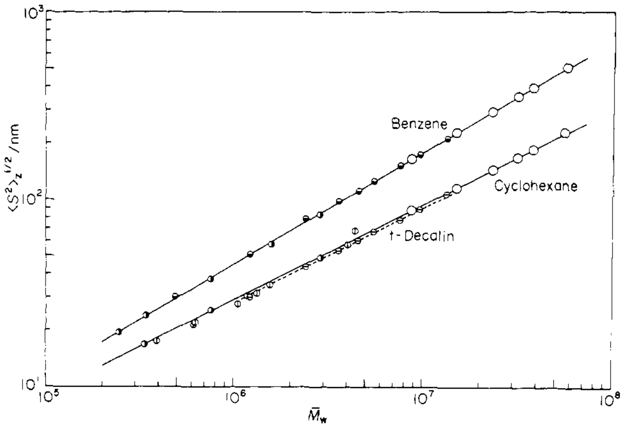

Figure 7. Molecular weight dependence of root-mean-square radius of gyration for polystyrene in benzene, in cyclohexane, and in *trans*-decalin. ○, in benzene at 25 °C and in cyclohexane at 34.5 °C (present data); ◑, in benzene at 30 °C and in cyclohexane at 34.5 °C (Yamamoto et al.[15]); ◒, in benzene at 30 °C (Fukuda et al.[4]); ⊖, in *trans*-decalin at 20.4 °C (Fukuda et al.[4]); ⦶, in cyclohexane at 34.8 °C (Berry[9]).

must be noted, however, that no great accuracy can be claimed for the $\overline{M}_w/\overline{M}_n$ ratios, because, as can be seen from Figure 6, the intercepts of the asymptotic lines are quite small. On the other hand, the factor A' (and hence $\overline{M}_z/\overline{M}_w$ as well) can be determined with high accuracy.

The $\overline{M}_w/\overline{M}_n$ ratio for the sample IK1500-1 is much larger than those of the other samples examined, suggesting that this highest molecular weight fraction contained a considerable amount of relatively low molecular weight fractions which had not been removed by precipitation fractionation. In this connection it is interesting to see in Figure 5 that the light-scattering envelope for the sample IK1500-1 at infinite dilution intersects that for IK1500-2, the next highest molecular weight sample.

Discussion

Factor A'. The values of A' shown in Table II range from $8.2_1 \times 10^{-18}$ to $8.5_1 \times 10^{-18}$ cm^2 and give $8.3_5 \times 10^{-18}$ cm^2 as an average. As far as we know, this is the first time that the value of A' for a monodisperse polymer was experimentally estimated. The average of $\langle S^2\rangle_{0z}/\overline{M}_w$ calculated from the cyclohexane data shown in Table I is (8.8 ± 0.2) × 10^{-18} cm^2. Its difference from A' is an index of the average polydispersity of the fractions studied. In Table III, we list some literature values (averages) of $\langle S^2\rangle_{0z}/\overline{M}_w$ for polystyrene in cyclohexane at the Θ temperature. The scatter of these values is undoubtedly ascribed to both experimental errors and polydispersities of the samples used.

Radius of Gyration. The values of $\langle S^2\rangle_z^{1/2}$ in benzene at 25 or 30 °C and of $\langle S^2\rangle_{0z}^{1/2}$ in cyclohexane at 34.5 °C are double-logarithmically plotted against $\overline{M}_w$ in Figure 7. The graph includes not only our data but also some reported values by previous authors.[4,9,15] The present data for both benzene and cyclohexane solutions fall on a smooth extension of these previous data. No anomaly appears in molecular weight dependence of $\langle S^2\rangle$ even at very high molecular weights available in this study. For benzene solutions the plotted points are all fitted closely by an empirical equation

$$\langle S^2\rangle_z = (1.47 \pm 0.05) \times 10^{-18}\overline{M}_w^{\,1.19\pm0.01} \text{ (in cm}^2\text{)} \quad (7)$$

and the corresponding empirical equation for cyclohexane solutions is

$$\langle S^2\rangle_{0z} = (8.8 \pm 0.2) \times 10^{-18}\overline{M}_w \text{ (in cm}^2\text{)} \quad (8)$$

if Berry's data are ignored. The solid lines in Figure 7 have been drawn according to these equations. It is interesting to see that the data points by Fukuda et al.[4] for polystyrene in *trans*-decalin at the Θ temperature appear slightly below the cyclohexane line. We do not know whether this difference is due to the solvent effect or not.

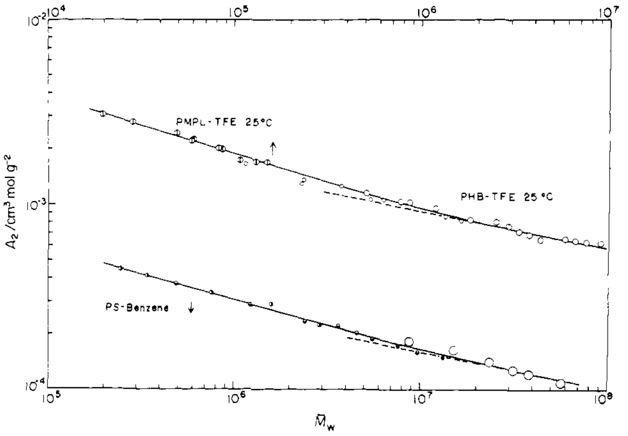

Figure 8. Molecular weight dependence of second virial coefficient A_2 for polystyrene in benzene and for poly(D-β-hydroxybutyrate) (◯, ○) and poly(β-methyl-β-propiolactone) (⦶) in trifluoroethanol at 25 °C.[16] The other marks have the same meaning as in Figure 7. The broken lines have slope −0.20.

Second Virial Coefficient. Double logarithmic plots of A_2 vs. $\overline{M}_w$ for benzene solutions of polystyrene are shown in Figure 8. The data points again include the reported values by Yamamoto et al.,[15] and by Fukuda et al.[4] All the plotted points are fitted approximately by a single curve which slightly bends upward. This behavior is quite similar to that we have observed recently for fractions of poly(D-β-hydroxybutyrate) in trifluoroethanol.[16] For the convenience of comparison, the data on this bacterium-produced polyester are also plotted in Figure 8. The dashed lines in the figure have been drawn with slope −0.20. This slope value is expected as the limiting one for very large molecular weights from the current theories of flexible linear polymers in dilute solution.

Expansion Factor $\alpha_s(z)$. The two-parameter theory[17] of flexible polymers in dilute solution indicates that the expansion factor α_s of such a polymer, which is defined by

$$\alpha_s^2 = \langle S^2\rangle/\langle S^2\rangle_0 \quad (9)$$

is a universal function of a single variable z called the excluded-volume parameter. The definition of z is

$$z = (1/4\pi)^{3/2}(B/A'^{3/2})M^{1/2} \quad (10)$$

where

$$B = \beta/M_0^2 \quad (11)$$

Here M_0 is the molar weight of a repeat unit of the polymer, β is the binary cluster integral for interaction

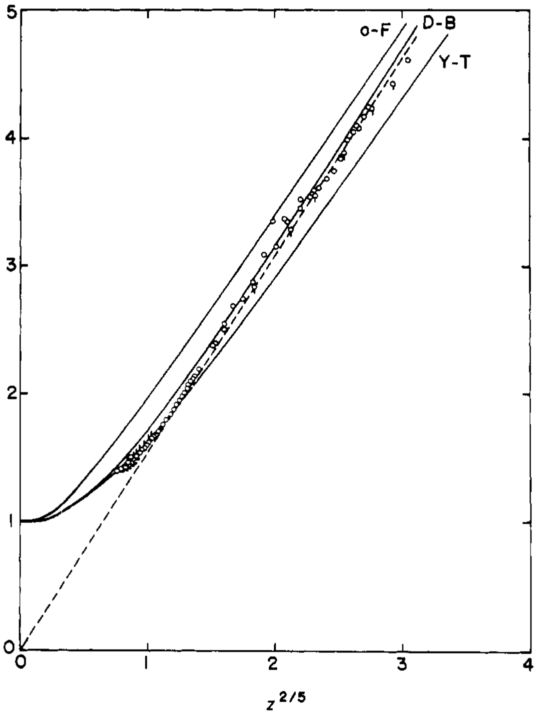

Figure 9. Plots of α_s^2 vs. $z^{2/5}$ for various lattice chains. O, diamond lattice (Wall and Erpenbeck,[18] Suzuki,[20] Wall and Hioe,[26] and Jurs and Reissner[24]); ⚲, simple cubic lattice (Kron and Ptitsyn[19] and Domb and Hioe[27]); ȯ, face-centered cubic lattice (Domb and Hioe[27]); o-, body-centered cubic lattice (Domb and Hioe[27]). The solid lines O-F, D-B, and Y-T are the theoretical values by the original Flory equation,[29] the Domb-Barrett equation,[33] and the Yamakawa-Tanaka equation,[37] respectively. The broken line represents eq 15.

between repeat units, and A' has the same meaning as defined above. Despite the great many efforts of theoreticians, no exact form of $\alpha_s(z)$ has yet been established. This is expected because we must solve a complicated many-body problem to approach it.

In the past two decades, many attempts have been made, with the aid of computers, to calculate average dimensions of lattice chains and/or off-lattice chains (real chain models) with volume exclusion by the Monte-Carlo method[18-25] or by direct enumeration.[26-28] From these studies it has become clear that for very many walks, N, on the lattice and for large values of β

$$\langle S^2\rangle \propto \langle R^2\rangle \propto N^{1.2} \tag{12}$$

and

$$\langle S^2\rangle/\langle R^2\rangle = 0.156 \pm 0.001 \tag{13}$$

regardless of the type of lattice in space. Here $\langle R^2\rangle$ denotes the mean-square end-to-end distance of the chain. It should be remarked that the proportionality between $\langle R^2\rangle$ and $N^{1.2}$ conforms not only to the simple theory of Flory[1,29] based on the mean-field approximation but also to the recent theoretical conclusion derived by much more sophisticated approaches.[30,31] The point is that these recent approaches have not as yet predicted a numerical value of the factor for this proportionality relation.

Recently, Domb et al.[32-35] have suggested an empirical relation

$$\alpha_R^2 = 1.64z^{2/5} \tag{14}$$

"as providing the best fit to the data of lattice chains currently available" in the range of z from 6 to 40. Here α_R is the expansion factor defined in terms of $\langle R^2\rangle$. These authors[33] also have proposed a semiempirical equation of closed form for $\alpha_R(z)$. However, its asymptotic form for large z gives 1.66 for the coefficient in eq 14.

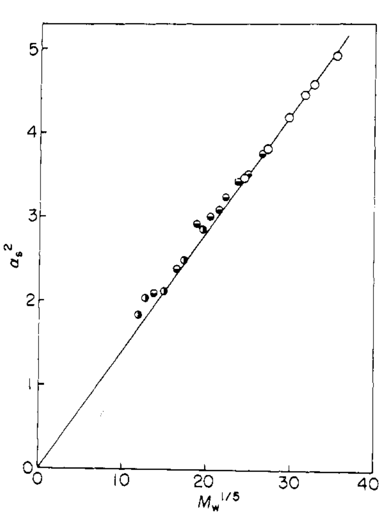

Figure 10. Plot of α_s^2 vs. $\bar{M}_w^{1/5}$ for polystyrene in benzene. Various marks have the same meaning as in Figure 7.

Now, combining eq 13 with 14 and using the well-known relation $\langle S^2\rangle_0/\langle R^2\rangle_0 = {}^1/_6$, we obtain the asymptotic relation between α_s and z:

$$\alpha_s^2 = (1.53 \pm 0.01)z^{2/5} \tag{15}$$

In Figure 9 we have collected some typical lattice chain data in the form of α_s^2 plotted against $z^{2/5}$. Here $\langle S^2\rangle_0$ necessary for the computation of α_s^2 were calculated for random-flight chains with no restriction of fixed bond angle, and β needed for the computation of z were obtained according to the method of Stockmayer.[36] It is seen that values of α_s^2 for different types of lattice fall approximately on a single curve, which is fitted closely by eq 15 for α_s^2 larger than about 2.

In order to see whether this result from lattice chain computations is obeyed by real polymer solutions, we have plotted three sets of observed data for polystyrene in benzene in Figure 10 in the form of α_s^2 versus $\bar{M}_w^{1/5}$ (note that z is proportional to $M^{1/2}$ for a given polymer-solvent pair). The data points associated with the work of Fukuda et al.[4] were obtained by using eq 8 to estimate $\langle S^2\rangle_0$, instead of using their measured $\langle S^2\rangle_{0z}$ in *trans*-decalin at the Θ temperature. It is observed that the plotted points not only fall approximately on a single curve, but also fit a straight line passing through the origin (0,0) at α_s^2 larger than about 2.5. This behavior of the experimental results is quite similar to that of the calculated points in Figure 9.

Figure 11 shows similar plots made on the basis of our previous data on poly(D-β-hydroxybutyrate) and its stereoisomer poly(β-methyl-β-propiolactone) in trifluoroethanol[16] and on polyisobutylene in cyclohexane[38] as well as the data of Kato et al.[39] on poly(α-methylstyrene) in toluene. The values of α_s^2 for the first two polymers were calculated by use of an $\langle S^2\rangle_{0z}/\bar{M}_w$ which had been redetermined from intrinsic viscosity data for poly(β-methyl-β-propiolactone) in a Θ solvent *n*-butyl chloride at 13 °C. This point will be expounded in detail in a forthcoming paper.[40] For polyisobutylene and poly(α-methylstyrene) the directly measured values of $\langle S^2\rangle_{0z}$ were taken from the respective papers. The behavior of the experimental points in Figure 11 is also consistent with the one shown in Figure 9. It appears that the asymptotic proportionality between α_s^2 and $\bar{M}_w^{1/5}$ (and hence $z^{2/5}$) is reached when α_s^2 exceeds a value between 2 and 3. At

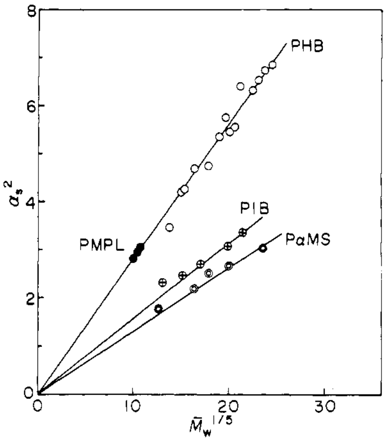

Figure 11. Plots of α_s^2 vs. $\bar{M}_w^{1/5}$ for various polymer–solvent systems at 25 °C. ○, poly(D-β-hydroxybutyrate) in trifluoroethanol (Miyaki et al.[16] and Hirosye et al.[40]); ●, poly(β-methyl-β-propiolactone) in trifluoroethanol (Miyaki et al.[16] and Hirosye et al.[40]); ⊕, polyisobutylene in cyclohexane (Matsumoto et al.[38]); ◎, poly(α-methylstyrene) in toluene (Kato et al.[39]).

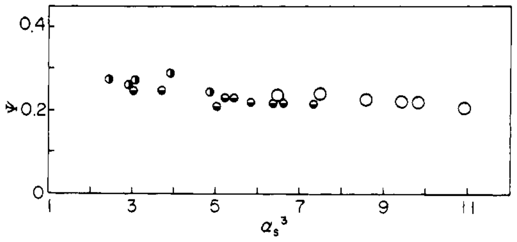

Figure 12. Plot of interpenetration function Ψ vs. α_s^3 for polystyrene in benzene. Various marks have the same meaning as in Figure 7.

Table IV
Values of β Estimated from the Straight Lines in Figures 10 and 11

polymers	solvents	temp, °C	(β, cm^3) × 10^{24}
polystyrene	benzene	25, 30	34
poly(D-β-hydroxybutyrate)	trifluoroethanol	25	160
poly(β-methyl-β-propiolactone			
polyisobutylene	cyclohexane	25	14
poly(α-methylstyrene)	toluene	25	32

present, we have available only a few light-scattering data which may be used to check the lattice chain behavior of $\alpha_s^2(z)$ over a wide range of α_s. Thus although we must avoid saying this conclusively, it seems that the expansion factors of real polymer–solvent systems behave approximately as predicted by artificial self-avoiding lattice chains.

The values of the binary cluster integral β computed from the slopes of the lines in Figures 10 and 11 by using eq 14 are given in Table IV. Note that the β value for poly(D-β-hydroxybutyrate) in trifluoroethanol differs from the one reported in our previous paper.[16]

Interpenetration Function Ψ(*z*). According to the two-parameter theory, the interpenetration function Ψ(*z*) defined by

$$\Psi(z) = A_2M^2/(4\pi^{3/2}N_A\langle S^2\rangle^{3/2})$$

is a universal function of *z*. It also may be considered a universal function of α_s, because α_s is such a function. Figure 12 shows plots of Ψ vs. α_s^3 for polystyrene in benzene. It is seen that Ψ gradually decreases in the range of α_s^3 from 2 to 10 and appears to approach the asymptotic value 0.22 which was estimated from the data on poly(D-β-hydroxybutyrate) in trifluoroethanol.[16] This behavior of Ψ may be ascribed to the molecular weight dependence of A_2 shown in Figure 8, which follows a curve convex downward and approaches the asymptotic slope −0.2 only at very high molecular weights, while the exponent in eq 7 remains close to the limiting value 1.20 over the entire range of $\bar{M}_w$ studied.

Acknowledgment. The authors thank the Japan Synthetic Rubber Co. for having made the polystyrene samples used available to us. Thanks are due to Union Giken Co., which helped us in constructing the laser scattering photogoniometer. Partial support from the Ministry of Education is gratefully acknowledged.

References and Notes

(1) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, Chapter XII.
(2) E. L. Slagowski, Ph.D. Thesis, University of Akron, 1972.
(3) D. McIntyre, L. J. Fetters, and E. Slagowski, *Science*, **17**, 1041 (1972).
(4) M. Fukuda, M. Fukutomi, Y. Kato, and T. Hashimoto, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 871 (1974).
(5) T. Mitani, Y. Einaga, and H. Fujita, to be published.
(6) J. A. Riddick and E. E. Toops, Eds., "Organic Solvents", Interscience, New York, 1955.
(7) E. R. Pike, W. R. M. Pomeroy, and J. M. Vaughan, *J. Chem. Phys.*, **62**, 3188 (1975).
(8) M. B. Huglin, "Light Scattering from Polymer Solutions", M. B. Huglin, Ed., Academic Press, London and New York, 1972, Chapter 6.
(9) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).
(10) H. Fujita, *Polym. J.*, **1**, 537 (1970).
(11) See, for example, P. Kratochvil, ref 8, Chapter 7.
(12) P. Outer, C. I. Carr, and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).
(13) N. T. Notley and P. J. W. Debye, *J. Polym. Sci.*, **17**, 99 (1955).
(14) W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, **59**, 1166 (1955).
(15) A. Yamamoto, M. Fujii, G. Tanaka, and H. Yamakawa, *Polym. J.*, **2**, 799 (1971).
(16) Y. Miyaki, Y. Einaga, T. Hirosye, and H. Fujita, *Macromolecules*, **10**, 1356 (1977).
(17) H. Yamakawa, "Modern Theories of Polymer Solutions", Harper and Row, New York, N.Y., 1971.
(18) F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.*, **30**, 634 (1959).
(19) A. K. Kron and O. B. Ptitsyn, *Vysokomol. Soedin., Ser. A*, **9**, 759 (1967).
(20) K. Suzuki, *Bull. Chem. Soc. Jpn.*, **41**, 538 (1968).
(21) Z. Alexandrowicz and Y. Accad, *Macromolecules*, **6**, 251 (1973).
(22) C. Domb, *Adv. Chem. Phys.*, **15**, 229 (1969).
(23) F. L. McCrackin, J. Mazur, and C. M. Guttman, *Macromolecules*, **6**, 859 (1973).
(24) P. C. Jurs and J. E. Reissner, *J. Chem. Phys.*, **55**, 4948 (1971).
(25) N. C. Smith and R. J. Fleming, *J. Phys. A: Math., Nucl. Gen.*, **8**, 929, 938 (1975).
(26) F. T. Wall and F. T. Hioe, *J. Phys. Chem.*, **74**, 4416 (1970).
(27) C. Domb and F. T. Hioe, *J. Chem. Phys.*, **51**, 1915 (1969).
(28) A. Bellemans, *Physica*, **68**, 209 (1973).
(29) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).
(30) S. F. Edwards, *Proc. Phys. Soc., London*, **85**, 613 (1965).
(31) P. G. de Gennes, *Phys. Lett. A*, **38**, 339 (1972).
(32) C. Domb, A. J. Barrett, and M. Lax, *J. Phys. A: Math., Nucl. Gen.*, **6**, L82 (1973).
(33) C. Domb and A. J. Barrett, *Polymer*, **17**, 179 (1976).
(34) A. J. Barrett, *J. Phys. A: Math., Nucl. Gen.*, **9**, L33 (1976).
(35) M. Lax, A. J. Barrett, and C. Domb, *J. Phys. A: Math. Nucl. Gen.*, **11**, 361 (1978).
(36) W. H. Stockmayer, *Makromol. Chem.*, **35**, 54 (1960).
(37) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **47**, 3991 (1967).
(38) T. Matsumoto, N. Nishioka, and H. Fujita, *J. Polym. Sci., Part A-2*, **10**, 23 (1972).
(39) T. Kato, K. Miyaso, I. Noda, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 777 (1970).
(40) T. Hirosye, Y. Einaga, and H. Fujita, to be published.