References and Notes

(1) This work is part 42 of the series; for part 41 see M. Palumbo, G. M. Bonora, C. Toniolo, E. Peggion, and E. S. Pysh, "Proceedings Vth American Peptide Symposium", M. Goodman, Ed., San Diego, Calif., in press.
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Solution Properties of Poly(D-β-hydroxybutyrate). 2. Light Scattering and Viscosity in Trifluoroethanol and Behavior of Highly Expanded Polymer Coils

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ABSTRACT: This paper aims to investigate solution properties of flexible linear polymers with very large values of the excluded volume parameter z by utilizing a previous finding that trifluoroethanol (TFE) is an unusually good solvent for bacterium-synthesized poly(D-β-hydroxybutyrate) (PHB). A series of PHB fractions with $\overline{M}_w$ up to 10 million are prepared and their TFE solutions at 25 °C are subject to accurate light-scattering and viscosity measurements. After the characteristic parameters for unperturbed chains and the binary cluster integral for segment–segment interactions are estimated by use of Yamakawa's modified Stockmayer–Fixman equation, α_s (linear expansion factor), Ψ (interpenetration function), and α_η (viscosity expansion factor) are calculated as functions of z from observed results. Three findings of principal interest are as follows. (1) As predicted by many theories, $\alpha_s{}^5$ becomes asymptotically proportional to z, and the Domb–Barrett semiempirical equation closely describes the observed relation between these two quantities. (2) Ψ is essentially constant (0.22 ± 0.01) for $\alpha_s{}^3 > 7$. Before approaching this asymptotic behavior, the curve of Ψ vs. $\alpha_s{}^3$ shows a slight decline, in contrast to the prediction from the current two-parameter theories. (3) Plots of $\alpha_\eta{}^3$ vs. $\alpha_s{}^3$ on a log–log graph are asymptotically represented by a straight line with a slope of 0.90 ± 0.02. This behavior indicates that the Flory viscosity factor Φ decreases steadily as the polymer coils undergo increasing expansion by volume exclusion.

In Part 1[1] of this series we concluded from a variety of experimental observations that the molecular chain of a bacterium-produced poly(D-β-hydroxybutyrate) (PHB) in such solvents as trifluoroethanol (TFE), ethylene dichloride (EDC), and chloroform assumes randomly coiled conformation and undergoes unusually large excluded volume effects. In fact, the observed molecular weight dependence of $\langle S^2 \rangle$ (mean-square radius of gyration), A_2 (second virial coefficient), and $[\eta]$ (intrinsic viscosity) for the polymer in TFE approached one which may be expected from the current theories of dilute polymer solutions for very large values of β, the binary cluster integral for segment–segment interaction. It occurred to us that such features of the system PHB–TFE could be utilized for exploring one of the yet unsettled problems in polymer physical chemistry. It is the asymptotic behavior of linear polymers in dilute solution in the limit of large values of the familiar excluded volume parameter z. The study reported in the present paper is an outcome from such anticipation.

In order to access sufficiently large z the experimentalist must find a polymer–solvent pair which satisfies at least the following two conditions. (a) The solvent must be markedly nonideal for the polymer, which means a sufficiently large value of β. (b) The polymer must be such that sharp fractions can be prepared over a very wide range of molecular weights. From our previous study it was quite certain that condition (a) is almost ideally fulfilled by the system PHB–TFE. The highest molecular weight (in terms of weight-average molecular weight $\overline{M}_w$) treated in part 1 was about 3 million, and one might consider that this would be high enough to meet condition (b). However, it was found from a preliminary analysis that a much higher molecular weight sample would have to be prepared to approach the asymptotic behavior in question. We also recognized that for an accurate determination of $\overline{M}_w$, $\langle S^2 \rangle$, and A_2 of very high molecular weight polymers in extremely good solvent, the case considered here, light-scattering measurements must be extended down to much lower scattering angles and polymer concentrations than examined in our previous work.

For these reasons we considered it worthwhile to repeat a similar study to that reported in part 1, this time by paying much more attention to the technical aspects of the light-scattering experiment and also trying to biosynthesize much higher molecular weight PHB. The present paper describes the experimental results from such efforts, together with a discussion in terms of the two-parameter theory for flexible linear polymers in solution.

To evaluate excluded volume effects we must separate the contributions of short-range effects on observed data for $\langle S^2 \rangle$ and $[\eta]$. This can be done by knowing the values of these quantities for unperturbed chains. Such values are directly measurable by light scattering and viscometry if an appropriate theta solvent for the given polymer is available. After considerable effort, however, we were unable to find any theta solvent for PHB. Therefore we were obliged to have recourse to an indirect method for the estimation of these quantities, and the conventional Stockmayer–Fixman method[2] seemed relevant as such. Unfortunately, it was found that the molecular weights of the PHB samples available to us were too high to extrapolate Stockmayer–Fixman plots to zero molecular weight with reasonable accuracy. In order to obviate this difficulty we resolved to take a bold step and assume that the isotacticity of the PHB chain has little effect on its overall conformations and average size in solution. This seemed reasonable because neighboring asymmetric carbon atoms on the PHB chain are separated by three skeletal bonds. So we prepared relatively low molecular weight samples of equimolar copoly(D-L-β-methyl β-propiolactone) (PMPL), a stereoisomer of PHB, and studied their behavior in TFE at 25 °C by light scattering and viscometry. As anticipated, the copolymer data supplemented the homopolymer data in the region of low molecular weights and enabled accurate extrapolation of the Stockmayer–Fixman plot for PHB to zero molecular weight.

Despite their fundamental importance for a deeper understanding of polymer solution, experimental explorations of the behavior of polymer coils undergoing very large excluded volume effects are still meager in the literature. We may cite as such only the recent investigations by Slagowski,[3] Burmeister and Meyerhoff,[4] and Fukuda et al.,[5] all concerned with very high molecular weight samples of polystyrene in benzene or toluene. It is hoped that the work reported below will stimulate further research in this little explored field of polymer physical chemistry.

Experimental Section

Samples of PHB. With an incubator of 1000-L capacity and following a similar method to that described in part 1,[1] we attempted a large-scale biosynthesis of PHB and obtained 54 g of polymer from the bacterial cells, 790 g in dry weight. The intrinsic viscosity of the sample in chloroform at 30 °C was 11.1 dL/g.

The entire sample was separated into a number of fractions by preliminary fractional precipitation with chloroform as the solvent and a mixture of chloroform and propylene glycol (1:2 by volume) as the precipitant. Pure propylene glycol was not useful as a precipitant because its addition caused partial gelatinization before the solution reached the turbidity point and the gel formed was hard to redissolve by agitation. The crude fractions obtained were properly combined according to their intrinsic viscosities, and each of the combined samples was chosen as a starting material for a series of extensive refractionations. In each of these refractionations, a given sample was dissolved in a chloroform–propylene glycol mixture of fixed composition (about 0.35 in the volume fraction of the latter component) and fractions of decreasing molecular weight were successively extracted by stepwise cooling of the solution from 31 to 23 °C. To obtain fractions as homogenous as possible the initial concentrations in this series of refractionations were successively lowered, finally reaching the range 0.04–0.07 g/dL. Twelve fractions were chosen out of the final 23 for the present study. It is shown below that these ranged from about 5×10^5 to 100×10^5 in $\overline{M}_w$. Strangely, no fraction with a molecular weight less than this lower bound was extractable from our original PHB sample. This was the reason we were forced to evaluate the behavior of low molecular weight PHB using its stereoisomer PMPL.

Samples of PMPL. Though the details are described elsewhere,[6] the necessary samples of PMPL were obtained by polymerizing an equimolar mixture of D- and L-β-methyl β-propiolactone with the system diethylzinc-water as a catalyst.[7] Each sample was fractionated by using the system chloroform–propylene glycol, and ten of the resulting fractions were chosen for the present study. Their gel permeation chromatograms suggested that they were quite homogeneous in molecular weight, almost comparable to Toyo Soda's standard samples of living polystyrene. Differing from PHB, PMPL dissolved in a great many organic liquids.[6]

Light-Scattering Measurement. The light-scattering behavior of PHB and PMPL in TFE at 25 °C was investigated with a Fica 50 photogoniometer, according to the procedures described in part 1.[1] However, the present measurements on PHB were extended down to a scattering angle of 18° and to much lower polymer concentrations than in the previous measurements. Thus for the highest molecular weight fraction Y-11 the lowest concentration was 0.0011 g/dL and even for the lowest molecular weight fraction Y-62 it was 0.04 g/dL. Since TFE is extremely nonideal for PHB it was crucial for an accurate determination of $\overline{M}_w$, $\langle S^2 \rangle$, and A_2 of high molecular weight fractions to go down to as low scattering angles and concentrations as possible.

The corresponding measurements on PMPL were terminated at an angle of 30° and at relatively high concentrations because of the comparatively low molecular weights of the samples treated. Reliable values of $\langle S^2 \rangle$ were determined only for three PMPL fractions.

The observed data for PHB and PMPL with $\overline{M}_w$ less than 5×10^6 were analyzed by Berry's square-root plot[8] and those for the higher molecular weight PHB by Fujita's plot.[9]

The previously determined specific refractive index increments (dn/dc)[1] were used for the analysis of data on PHB. The values of dn/dc for PMPL in TFE at 25 °C for the wavelengths 436 and 546 nm were found to be 0.153_2 and 0.150_8 mL/g, respectively. These agree with the values for the system PHB–TFE within experimental errors.

Viscosity Measurement. Intrinsic viscosities $[\eta]$ of PHB and PMPL in TFE at 25 °C were determined with conventional capillary viscometers of the Ubbelohde type for fractions with $[\eta]$ smaller than 7 dL/g and with a variable-torque rotational viscometer of the Zimm–Crothers type[10,11] for all other fractions. The results obtained with the capillary viscometers were not corrected for shear-rate effect, while those with the rotational viscometer were extrapolated to zero rate of shear according to the theory described below.

The steady-state motion of the rotor in a Zimm–Crothers rotational viscometer obeys the equation[11]

$$c(\omega_m - \omega_r) + d = 8\pi^2 L R_o^2 R_i^2 \omega_r \eta / (R_o^2 - R_i^2) \qquad (1)$$

where ω_m and ω_r are the angular speeds of the magnet and the rotor, R_o and R_i are the radii of the outer stator and the inner rotor, L is the effective length of the rotor, η is the viscosity coefficient of the fluid,

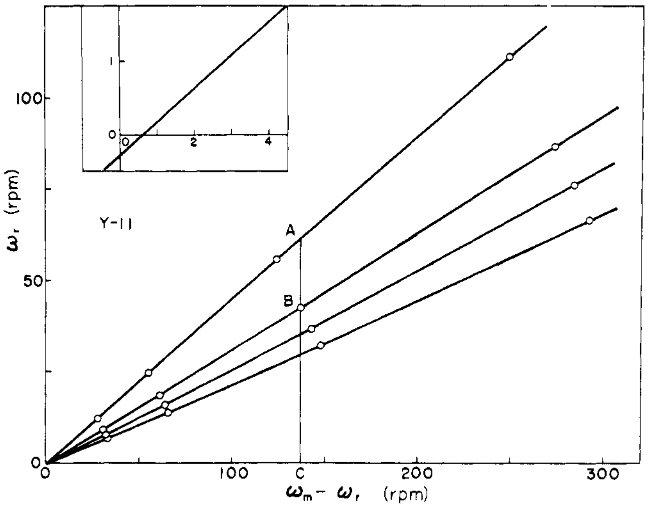

Figure 1. Relationships between rotor speed ω_r and relative speed of magnet $\omega_m - \omega_r$ for TFE solutions of sample Y-11 and pure TFE at 25 °C. The lines correspond to polymer concentrations 0 (pure TFE), 0.01123, 0.01659, and 0.02258 in g/dL, from top to bottom. The straight line fitting data for pure TFE at very small $\omega_m - \omega_r$ is enlarged in the insert.

and c and d are constants for the instrument. In this equation, the first term on the left-hand side represents the torque produced by eddy current interaction between the magnet and the metal ring fixed inside the rotor tube, while the second term represents a constant hysteresis torque associated with ferromagnetic materials contained in the ring. In the viscometer we used, the drive ring was made of aluminum or copper, and hence the second term was considered negligible in comparison with the first term. Thus, according to eq 1, ω_r and hence the driving torque on the rotor could be varied by changing the angular speed of the magnet.

The apparent rate of shear, G, produced in the fluid is given by

$$G = 8\pi\omega_r R_o^2 R_i^2 (R_o^2 - R_i^2)^{-2} \ln (R_o/R_i) \quad (2)$$

Hence the value of G corresponding to a rotor speed ω_r can be calculated if R_o and R_i are separately determined.

To compute η from measured values of ω_m and ω_r by use of eq 1 we must determine the constants c and d in advance. This requires calibration of the instrument with a liquid of known viscosity coefficient. However, what we need is the relative viscosity η_{rel}, i.e., the ratio of the viscosity coefficients of a solution and its solvent, rather than the absolute viscosity coefficient. With this point in mind, we devised a method which can be conveniently escaped from the calibration and used it throughout the present study.

Writing eq 1 for both solvent and solution it follows that η_{rel} is given by

$$\eta_{rel} = \omega_r^0/\omega_r \quad (3)$$

if $\omega_m - \omega_r$ and $\omega_m^0 - \omega_r^0$ are chosen equal. Here the superscript 0 refers to the solvent. To put eq 3 in actual use we may measure ω_r as a function of ω_m for both solvent and solution, plot ω_r against the corresponding $\omega_m - \omega_r$, and then find a pair of ω_r and ω_r^0 for a given abscissa value from the resulting plots for the solution and the solvent. When substituted into eq 3 these paired rotor speeds allow η_{rel} to be computed. The corresponding rate of shear G is obtained by inserting that ω_r into eq 2. Repetition of similar operations at different values of $\omega_m - \omega_r$ yields G dependence of η_{rel} for a given solution, and the result may be used to estimate η_{rel} at zero rate of shear by suitable extrapolation. For an illustration of this method the plots of ω_r vs. $\omega_m - \omega_r$, three TFE solutions of the sample Y-11, and the solvent are shown in Figure 1. The ratio of the ordinates for points A and B gives η_{rel} for the solution with c = 0.01123 g/dL at a shear rate corresponding to the ω_r for point B.

Experimental Results

Molecular Weight and Second Virial Coefficient. Figure 2 displays, on Berry's square-root plot, the reduced intensities of scattered light at zero angle, Kc/R_o, for PHB fractions in TFE at 25 °C as a function of the polymer mass concentration c. The graph includes the remeasured data for the samples A-12 and AB-22 which had been prepared in part 1.[1] It is seen that the present measurements were performed down to so low a polymer concentration that virtually no difficulty is encountered in extrapolating the data to infinite

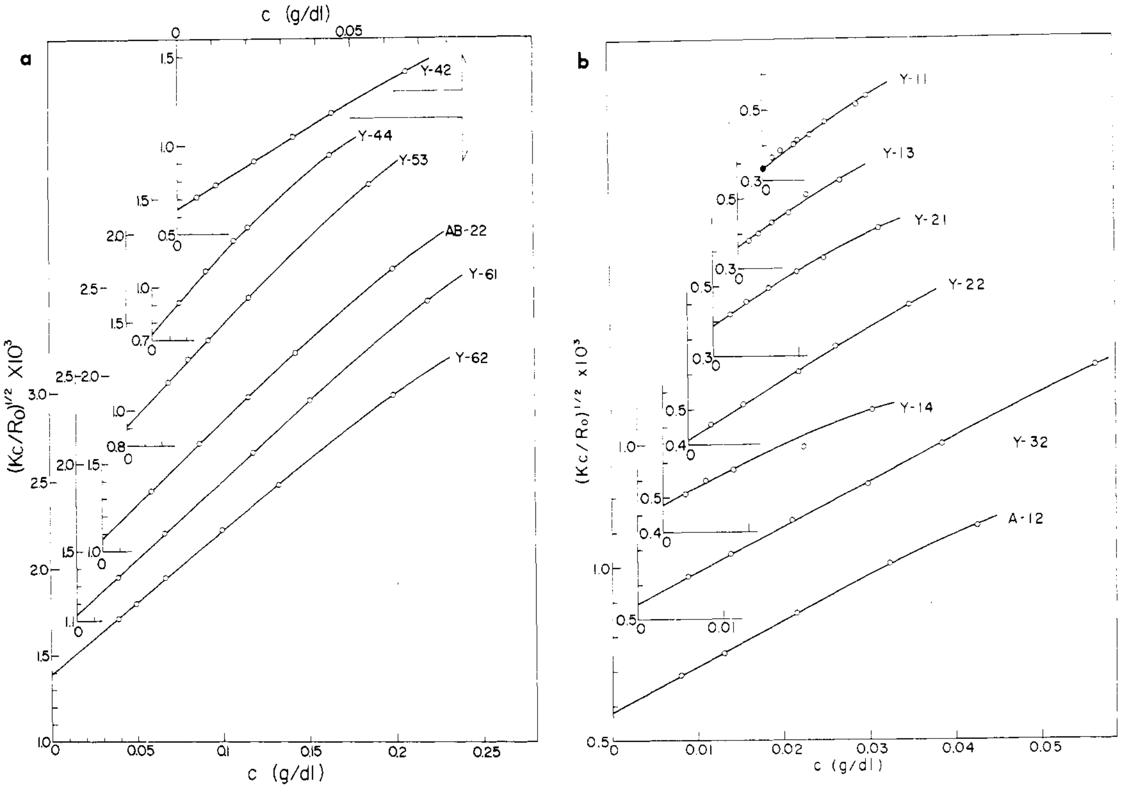

Figure 2. Square root of reduced scattering intensity at zero angle $(Kc/R_o)^{1/2}$ as a function of polymer concentration c for PHB in TFE at 25 °C: (a) for samples with $\overline{M}_w < 252 \times 10^4$; (b) for samples with $\overline{M}_w > 295 \times 10^4$. The points for the four highest molecular weight samples and the intercept for sample Y-11 were obtained by treating the original data in terms of Fujita's plot.

Table I
Results from Light-Scattering Measurements on PHB and PMPL in TFE (Trifluoroethanol) at 25 °C

Sample code	$\overline{M}_w \times 10^{-4}$, g mol^{-1}	$A_2 \times 10^4$, cm^3 mol g^{-2}	$\langle S^2 \rangle^{1/2}$, Å
PHB (Poly(D-β-hydroxybutyrate))			
Y-11	910 ± 20	6.20 ± 0.2	2560 ± 50
Y-13	761 ± 30	6.28 ± 0.2	2320 ± 50
Y-14	434 ± 20	6.46 ± 0.4	1710 ± 50
Y-21	667 ± 20	6.38 ± 0.2	2140 ± 50
Y-22	590 ± 10	6.52 ± 0.2	1980 ± 20
Y-31	380 ± 10	6.88 ± 0.2	1490 ± 20
Y-32	335 ± 5	7.12 ± 0.2	1387 ± 20
Y-42	252 ± 5	8.06 ± 0.2	1191 ± 20
Y-44	183 ± 2	8.24 ± 0.2	952 ± 15
Y-53	120 ± 1	9.56 ± 0.1	769 ± 5
Y-61	77.9 ± 1	10.2 ± 0.1	586 ± 10
Y-62	51.0 ± 0.5	11.4 ± 0.1	431 ± 5
A-12[a]	295 ± 4	7.64 ± 0.1	1339 ± 20
AB-22[a]	86.9 ± 1	10.2 ± 0.1	623 ± 10
PMPL (Copoly(D–L-β-methyl β-propiolactone))			
L-1	15.0 ± 0.5	16.9 ± 0.3	225 ± 10
L-2	13.0 ± 0.5	17.0 ± 0.3	201 ± 10
L-3	10.7 ± 0.5	17.2 ± 0.3	178 ± 10
L-4	8.65 ± 0.2	19.7 ± 0.2	(151)
L-5	8.28 ± 0.2	20.1 ± 0.2	
L-6	5.89 ± 0.2	22.0 ± 0.5	
L-7	6.01 ± 0.2	22.5 ± 0.5	
L-8	4.91 ± 0.1	24.1 ± 0.5	
L-9	2.85 ± 0.1	27.9 ± 1	
L-10	1.96 ± 0.05	30.3 ± 1	

[a] Two of the fractions prepared in part 1.[1]

dilution. The values of $\overline{M}_w$ and A_2 determined from the curves in Figure 2 are collected in Table I. This table also gives the values of these quantities for PMPL in TFE at 25 °C.

The values of A_2 given in Table I and those obtained for the same system in part 1 are plotted double logarithmically against $\overline{M}_w$ in Figure 3. Note that for the fractions A-12 and AB-22 the remeasured values are shown. It is seen that all the plotted points are fitted closely by a smooth curve having a slight upward curvature. One of the implications of this result is that, at high dilutions, TFE solutions of PHB and PMPL are thermodynamically indistinguishable, despite a definite difference in tacticity between the molecular chains of these two polymers. The solid curve in Figure 3 approaches a limiting slope of −0.20 at molecular weights higher than 10^6. This slope agrees with the value expected from current theories of flexible polymers for very large values of the excluded volume parameter z.[12]

Radius of Gyration. Figure 4 depicts, on Berry's square-root plot, the particle scattering functions $P(\theta)$ for all the PHB fractions studied in TFE at 25 °C. Here the ordinate $(\overline{M}_w Kc/R_\theta)_{c=0}{}^{1/2}$ is actually the square root of $P(\theta)$. Note that the graph includes the redetermined data for our previously prepared fractions A-12 and AB-22. It is seen that, with increasing molecular weight (i.e., going from the bottom to the top in the graph), the curves fitting the data points become progressibly more convex upward and the correct determination of the initial slope becomes more difficult. Such strongly curved $P(\theta)$ is a manifestation of the great expansion of the polymer coil in the solvent studied, and thus it is consistent with the conclusion, derivable from the comparatively large values of A_2 found in Table I, that TFE ought to be a very good solvent for PHB.

Except for the four highest molecular weight fractions Y-11, Y-13, Y-21, and Y-22, the initial tangents shown in Figure 4 were used to evaluate $\langle S^2 \rangle$ of the respective fractions. For these four fractions all the data were retreated in terms of the Fujita plot to estimate $\langle S^2 \rangle$. Figure 5 illustrates the application of the Fujita plot to the fraction Y-11. Although Fujita's original formulation was developed for the state of infinite dilution, its formal application to data at finite concentration finds no reason to be declined and is worth attempting. In fact, as seen from Figure 5, the data points on Fujita's plot exhibit much less curvature regardless of the concentration of the solution and allow the behavior at finite dilution to be extrapolated with a high degree of certainty.

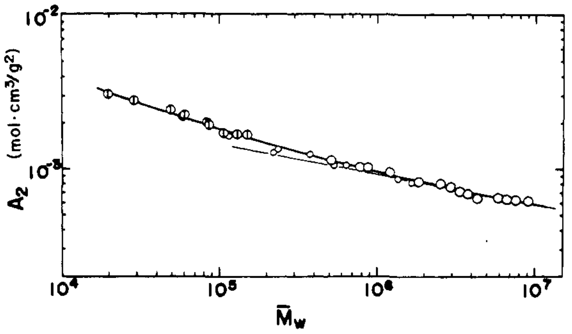

Figure 3. Molecular-weight dependence of the second virial coefficient A_2 for PHB and PMPL in TFE at 25 °C. Large circles, present work (○, PHB; ⦶, PMPL). Small circles, previous work of Akita et al.[1] The thin line represents slope −0.20.

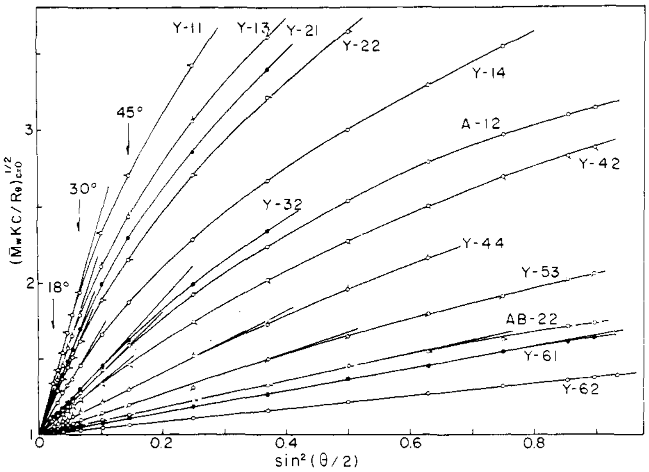

Figure 4. Angular dependence of particle scattering function $P(\theta)$ represented as $(\overline{M}_w Kc/R_\theta)_{c=0}{}^{1/2}$ vs. $\sin^2(\theta/2)$ for PHB in TFE at 25 °C. Values of $\sin^2(\theta/2)$ for scattering angles 18, 30, and 45° are shown by vertical arrows.

The values of $\langle S^2 \rangle^{1/2}$ for PHB and PMPL fractions in TFE at 25 °C are given in Table I. They are plotted against $\overline{M}_w$ on a log–log graph in Figure 6, where the corresponding data obtained in part 1 are also indicated for comparison. All the plotted points may be fitted by a straight line as indicated. Thus we get for PHB or PMPL in TFE at 25 °C

$$\langle S^2 \rangle^{1/2} = 1.69 \times 10^{-9} \overline{M}_w{}^{0.60 \pm 0.005} \tag{4}$$

where $\langle S^2 \rangle^{1/2}$ is expressed in centimeters. Three points are worth mentioning. First, the data points for PMPL fall on a smooth extension of those for PHB. This result is in accord with the suggestion in the introductory section that the isotacticity of the PHB chain has negligible effect on its overall conformation and dimensions in dilute solution. Second, the exponent 0.60 in eq 4 is the asymptotic limit that the fifth-power theories for the expansion factor predict in the limit of large values of the excluded volume parameter z.[12] Third, when scrutinizing Figure 6, we find that the radii of gyration estimated in part 1 were a little too small. This may be primarily attributed to the fact that our previous light-scattering

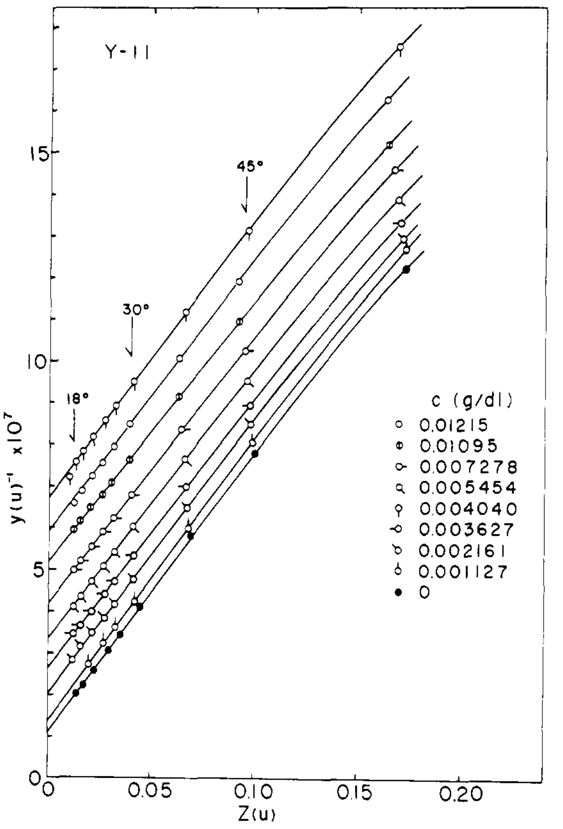

Figure 5. Fujita's plots for sample Y-11 in TFE at 25 °C at different polymer concentrations. Here $y(u)^{-1} = Kc/R_\theta$, $u = \sin^3(\theta/2)$, and $Z(u) = [y(u)u^{4/3}]^{-1} \int_o^u y(u)u\,du$. The data points are shifted upward by: (○) 5×10^{-7}; (○) 3×10^{-7}; (⊕) 2.5×10^{-7}; (○) 2×10^{-7}; (○) 1.5×10^{-7}; (○) 1×10^{-7}; (○) 5×10^{-8}.

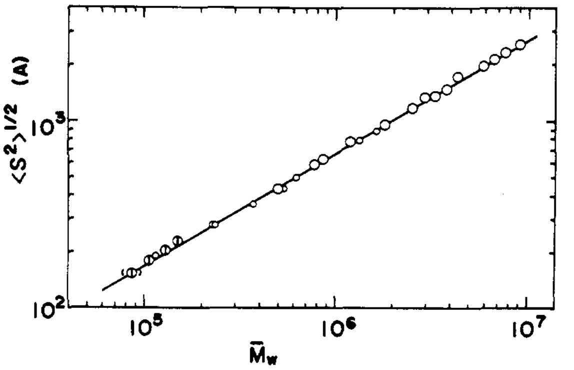

Figure 6. Molecular-weight dependence of root-mean-square radius of gyration $\langle S^2\rangle^{1/2}$ for PHB and PMPL in TFE at 25 °C. The symbols are the same as in Figure 3.

measurements were terminated at a scattering angle of 30° and also at relatively high polymer concentrations. In fact, when remeasured at much lower angles and concentrations, we found about 10% corrections for the $\bar{M}_w$ of the sample A-12 and for the $\langle S^2\rangle^{1/2}$ of the sample AB-22.

Intrinsic Viscosity. Figure 7 illustrates shear-rate dependence of η_{sp}/c and $(\ln \eta_{rel})/c$ for the sample Y-11 in TFE at 25 °C. The solid lines have been drawn to extrapolate the data to zero rate of shear. Marked non-Newtonian behavior is worth noting.

Table II summarizes the values of $[\eta]$ obtained for PHB and PMPL in TFE at 25 °C. All values larger than 7 dL/g refer to zero rate of shear. Figure 8 shows a log–log plot of $[\eta]$ vs. $\bar{M}_w$ prepared from the data in Table II. The graph also includes our previous data for the system PHB–TFE. As was the case

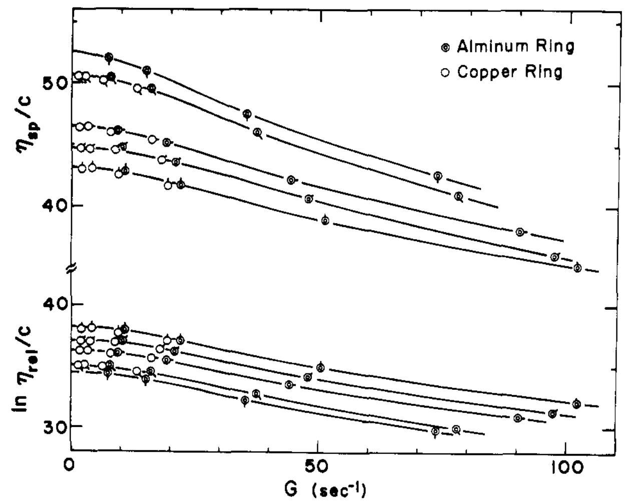

Figure 7. Dependence of η_{sp}/c and $\ln \eta_{rel}/c$ on apparent shear rate G for sample Y-11 in TFE at 25 °C. Polymer concentrations are: pip up, 0.00790 g/dL (the data points for $\ln \eta_{rel}/c$ are shifted upward by 1); successive clockwise 45° rotations of pip corresponding to 0.00987, 0.01316, 0.01974, and 0.02258 g/dL, respectively.

Table II
Intrinsic Viscosities of PHB and PMPL in TFE at 25 °C

PHB		PMPL	
Sample code	$[\eta]$, dL/g	Sample code	$[\eta]$, dL/g
Y-11	40.6	L-1	1.93
Y-13	34.0	L-2	1.67
Y-21	33.3	L-3	1.48
Y-22	28.4	L-4	1.26
Y-31	21.4	L-7	0.924
Y-42	15.1	L-8	0.800
Y-53	8.88	L-9	0.514
Y-61	6.23	L-10	0.388
Y-62	4.61		

with $\langle S^2\rangle$, the data points for both PHB and PMPL are fitted by a single straight line, which gives

$$[\eta] = 2.22 \times 10^{-4}\bar{M}_w^{0.76\pm0.01} \quad \text{(in TFE at 25 °C)} \qquad (5)$$

where $[\eta]$ is expressed in dL/g.

The exponent in this equation is smaller by 0.04 than that derived from our previous measurements.[1] The alteration reflects the expanded range of molecular weights of the present measurements. The point to note is that the exponent 0.76 is significantly lower than the value 0.8 which is usually anticipated as the asymptotic limit for very nonideal polymer solutions. In contrast to this result, we have seen that both molecular dimensions and second virial coefficients of PHB in TFE exhibit the theoretically predicted asymptotic behavior in the range of molecular weights treated in the present study.

Discussion

Excluded volume effects on dilute polymer solutions are usually discussed in terms of three dimensionless quantities defined by[12]

$$\alpha_s^2 = \langle S^2\rangle/\langle S^2\rangle_0 \qquad (6)$$

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \qquad (7)$$

$$\Psi = A_2M^2/(4\pi^{3/2}N_A\langle S^2\rangle^{3/2}) \qquad (8)$$

where $\langle S^2\rangle_0$ and $[\eta]_\theta$ are the mean-square radius of gyration and the intrinsic viscosity for a polymer molecule not perturbed by excluded volume effect, M is the molecular weight, and N_A is Avogadro's number. The quantities α_s, α_η, and Ψ

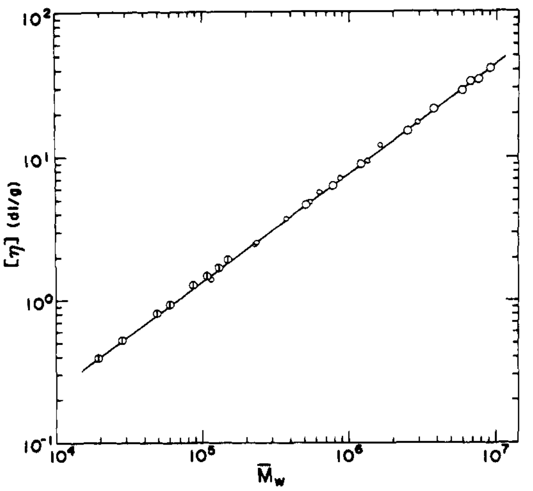

Figure 8. Molecular weight dependence of intrinsic viscosity $[\eta]$ for PHB and PMPL in TFE at 25 °C. The symbols are the same as in Figure 3.

are called the linear expansion factor, the viscosity expansion factor, and the interpenetration function, respectively. According to the two-parameter theory of polymer solutions,[12] both α_s and Ψ are expected to depend only on the excluded volume parameter z, which is defined by[12]

$$z = (3/2\pi)^{3/2}(B/A^3)M^{1/2} \tag{9}$$

where

$$A^2 = 6\langle S^2\rangle_0/M \tag{10}$$

$$B = \beta/M_0^2 \tag{11}$$

with M_0 being the molar weight of a repeat unit of the polymer and β the binary cluster integral for segment–segment interaction. Note that both A and B are independent of M. Thus z is proportional to $M^{1/2}$ for a homogeneous series of polymers in a given solvent. Despite the great many efforts in the past three decades no exact forms of $\alpha_s(z)$ and $\Psi(z)$ have as yet been established. One of the primary aims of the present study was to explore their asymptotic behavior for very large values of z.

Ample experimental evidence is now available showing that α_η also depends only on z, but no success has yet been achieved in deriving the exact form of $\alpha_\eta(z)$. Its asymptotic behavior for large z was another point of interest which motivated us to the present work.

According to Flory and Fox, [13] we may write $[\eta]$ in the form

$$[\eta] = 6^{3/2}\Phi(\langle S^2\rangle/M)^{3/2}M^{1/2} \tag{12}$$

where Φ is called the Flory viscosity factor. This expression gives for the unperturbed state of polymer

$$[\eta]_\theta = 6^{3/2}\Phi_0\,(\langle S^2\rangle_0/M)^{3/2}M^{1/2} \tag{13}$$

where the subscript 0 refers to unperturbed chain. Division of eq 12 by eq 13 yields

$$\alpha_\eta^3 = (\Phi/\Phi_0)\alpha_s^3 \tag{14}$$

Thus if α_η is a function of z only, Φ/Φ_0 also should depend only on z, and, as sometimes done, we may use this ratio to discuss the excluded volume effect on intrinsic viscosity.

Evaluation Parameters A, β, and Φ_0. Once the parameter A is known we can compute $\langle S^2\rangle_0$ as a function of M from eq 10. Since it follows from eq 13 that

$$[\eta]_\theta = KM^{1/2} \tag{15}$$

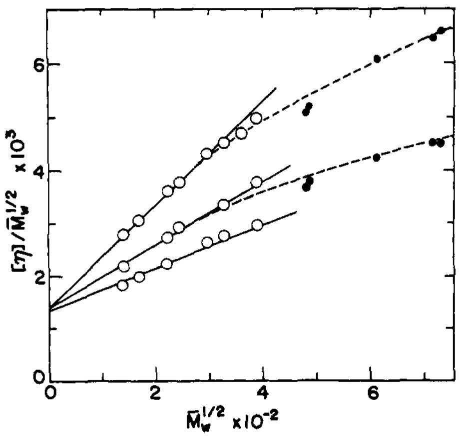

Figure 9. Stockmayer–Fixman plots for PMPL (open circles) and PHB (closed circles). The lines correspond to TFE at 25 °C, chloroform at 30 °C, and EDC at 30 °C from top to bottom.

with

$$K = \Phi_0 A^3 \tag{16}$$

We can calculate $[\eta]_\theta$ as a function of M if A and Φ_0 are known. Thus what we need for evaluating α_s and α_η as functions of z are the values of three parameters A, β, and Φ_0.

If an appropriate θ solvent is available for PHB or PMPL, A and Φ_0 for these polymers can be evaluated by measuring $\langle S^2\rangle_0$ and $[\eta]_\theta$ as functions of M and analyzing the data in terms of eq 10, 15, and 16. Since, however, this was not the case we were compelled to adopt an indirect method. Thus we attempted to estimate K in eq 15 by applying the conventional Stockmayer–Fixman method[2] to the data for PMPL (as mentioned in the introductory section, the molecular weights of our PHB fractions were too high to use this method effectively) and Φ_0 by extrapolating the Φ values computed from actual data on PHB and PMPL in TFE at 25 °C to $M = 0$.

Figure 9 illustrates the Stockmayer–Fixman plots for PMPL in three solvents. The data in EDC and chloroform were added to ensure the extrapolation of the plot for TFE solutions. The intercept of the lines for TFE and chloroform solutions was set equal to $1.05K$ according to eq 17 below, while that for EDC solutions was equated to K according to eq 18 also given below. Thus we found $K = 1.33 \times 10^{-3}$ from either of the two intercepts.

There was a considerable uncertainty in estimating Φ_0 by the method mentioned above (see Figure 13). However, the values in the range 1.8×10^{23}–2.2×10^{23} seemed reasonable, and we performed all the subsequent computations with $\Phi_0 = 2.0 \times 10^{23}$. This extrapolated value is more than 30% lower than 2.86×10^{23} that is expected theoretically for Gaussian chains at the nondraining limit.[12] The difference may primarily be attributed to the molecular weight heterogeneity of our polymer fractions, but there may also be other reasons for the discrepancy.

No general method for the evaluation of β is as yet established. However, Yamakawa has shown in his recently published book[12] that a reasonable value of B may be obtained by fitting empirically derived equations (modified Stockmayer–Fixman equations)

$$[\eta]/M^{1/2} = 1.05K + 0.287\Phi_0 BM^{1/2} \qquad (0 < \alpha_\eta^3 < 2.5) \tag{17}$$

$$[\eta]/M^{1/2} = K + 0.346\Phi_0 BM^{1/2} \qquad (0 < \alpha_\eta^3 < 1.6) \tag{18}$$

to the initial linear portion of a Stockmayer–Fixman plot. We applied this method to the three lines shown in Figure 9 and computed the corresponding β with K and Φ_0 derived above.

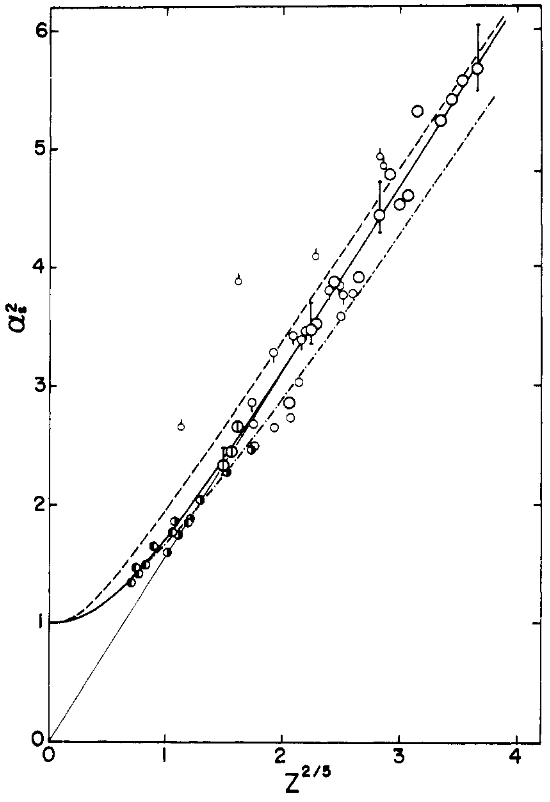

Figure 10. Plots of α_s^2 vs. $z^{2/5}$: (○) PHB in TFE at 25 °C (present data); (⦶) PMPL in TFE at 25 °C (present data); (o) PHB in TFE at 25 °C (Akita et al.[1]); (⫰) polysytrene in benzene at 40 °C (Slagowski[3]); (⫯) polystyrene in benzene at 30 °C (Fukuda et al.[5]); (◐) polychloroprene in n-butyl acetate at 25 °C, and (◑) polyshloroprene in carbon tetrachloride at 25 °C (Norisuye et al.[14]); (- - -) original Flory equation;[17] (—) Domb–Barrett equation;[19] (-·-) Yamakawa–Tanaka equation.[18]

The results are as follows.

Solvent	$\beta \times 10^{24}$, cm^3
TFE (25 °C)	126
Chloroform (30 °C)	$77._7$
EDC (30 °C)	$43._6$

Expansion Factor $\alpha_s(z)$. In Figure 10, the values of α_s^2 for PHB and PMPL in TFE at 25 °C are plotted against $z^{2/5}$, with all these values calculated by using A, β, and Φ_0 estimated above. This type of graph is useful because many typical theories of flexible linear polymers predict that α_s^5 should become asymptotically proportional to z.[12] The figure includes for comparison the data points derived from previous work on other polymer–solvent systems: polystyrene (narrow distribution) in benzene (Slagowski[3] and Fukuda et al.[5]) and polychloroprene (sharp fractions) in carbon tetrachloride and in n-butyl acetate (Norisuye et al.[14]). The values of A and Φ_0 for these systems were computed from the actual data obtained in an appropriate theta solvent, while their β values were taken from recent articles by Yamakawa,[15,16] who estimated them by analyzing reported intrinsic viscosity data in terms of eq 17 or 18.

Except for some points most of which include our previous data on PHB and those on Slagowski's polystyrene, the plotted points are approximately fitted by a single curve which is closely linear in the region where a majority of data points appear. This behavior lends support to the theoretical predictions that α_s is a universal function of z and that α_s^5 becomes proportional to z as z increases. Presumably this is the first experimental demonstration of the asymptotic proportionality between α_s^5 and z.

A great number of approximate closed expressions for $\alpha_s(z)$ have been proposed[12,15] since the pioneering work by Flory[17] in 1949, but none of them appear to have been compared with experimental data covering a sufficiently broad range of z. Now that such data have been in hand it is of interest to compare them with some typical theories.

In this place we choose three of them. They are the original Flory equation[17]

$$\alpha_s^5 - \alpha_s^3 = 2.60z \tag{19}$$

the Yamakawa–Tanaka equation[18]

$$\alpha_s^2 = 0.541 + 0.459(1 + 6.40z)^{0.46} \tag{20}$$

and the Domb–Barrett equation[19]

$$\alpha_r^2 = [1 + 10z + (70\pi/9 + 10/3)z^2 + 8\pi^{3/2}z^3]^{2/15} \tag{21}$$

with

$$\alpha_s^2/\alpha_r^2 = 0.933 + 0.067 \exp[-(0.85z + 1.39z^2)] \tag{22}$$

The last one is a kind of semiempirical equation that has been deduced from computer enumeration of self-avoiding walks on various types of lattice. It is designed so as to agree with eq 20 for very small values of z, while it becomes almost indistinguishable from eq 19 for very large z. The dashed, solid, and dot–dash lines in Figure 10 are graphical representations of eq 19, 20, and 21, respectively. It is interesting to see that the Domb-Barrett equation closely fits a majority of plotted points. Apparently, either eq 19 or 20 is less satisfactory.

It follows from this finding that consistent values of β may be obtained from an analysis of intrinsic viscosity data by the Yamakawa eq 17 or 18 and that of expansion factor data by the Domb-Barrett eq 21.[23] Since these equations are still semiempirical, it would be hazardous to claim on the basis of such internal consistency alone that the β values obtained by them must be close to the correct one of a given polymer–solvent system. Nonetheless the result found here seems to be a significant step toward the resolution of an as yet unsettled problem in polymer solution theory, i.e., establishing an acceptable means for the estimation of β.

The value of β chosen to compute z for the polystyrene–benzene system in Figure 10 is 34.2×10^{-24} cm^3. The β value for our system PHB–TFE is about four times as large as this, implying that PHB undergoes far more expansion by volume exclusion in TFE than does polystyrene in a typical good solvent benzene. At present, we are unable to explain why TFE acts as so good a solvent for PHB. The maximum z in Figure 10 corresponds to a PHB fraction of about 10 million molecular weight. It exceeds the z value for the 50 million molecular weight sample of polystyrene treated by Slagowski.[3] This difference is another manifestation of an unusually large β of PHB in TFE.

The data points for PHB and PMPL in Figure 10 have been derived by assuming 2.0×10^{23} for Φ_0. Since, as mentioned above, there is some freedom in the choice of Φ_0 it would be fair to examine how much the data points depart from the Domb-Barrett line when Φ_0 is varied within an appropriate range. The vertical segments in Figure 10 indicate the ranges in which the respective points shift as Φ_0 is allowed to change from 2.2×10^{23} to 1.9×10^{23}. They are comparable to experimental errors for mean-square radii of gyration and give rise to no substantial alteration of the conclusion.

Interpenetration Function $\Psi(z)$. Figure 11 shows values of the function Ψ for PHB and PMPL in TFE and that for polystyrene in benzene. Here, as is often done, we have chosen not z itself but its function α_s^3 as the abscissa. The solid line is an approximate fit to the plotted points. For α_s^3 above about 7 it is horizontal, giving 0.22 ± 0.01 as an asymptotic value of Ψ. This value, however, should not be taken too literally, be-

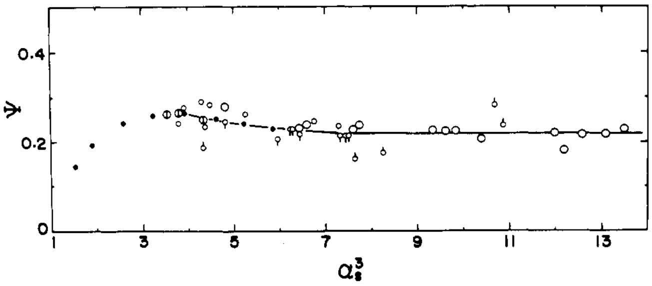

Figure 11. Plots of interpenetration function Ψ vs. α_s^3. Closed circles are values calculated by Gobush et al.[20] The other symbols are the same as in Figure 10.

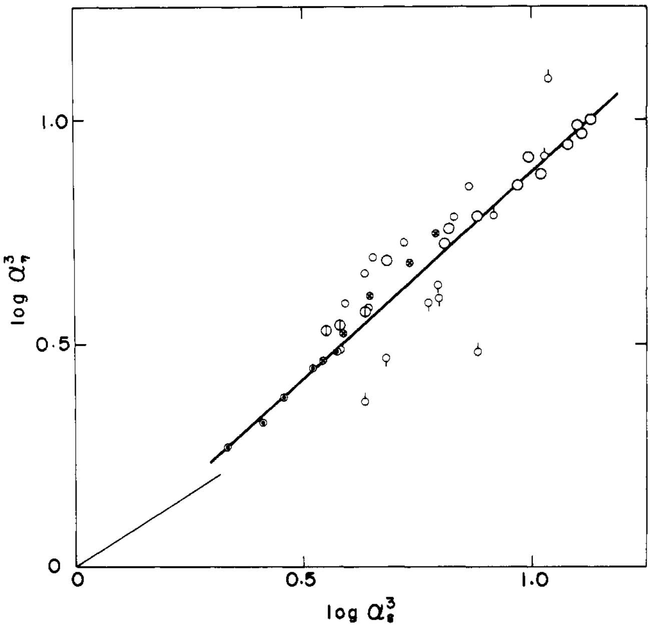

Figure 12. Relationship between log α_η^3 and log α_s^3. Data for polyisobutylene in n-heptane and in cyclohexane at 25 °C (Matsumoto et al.[21]) are indicated by marks ⊙ and ⊗, respectively. The other symbols are the same as in Figure 10. The thin straight line represents the initial tangent calculated by Fujita et al.[22]

cause the determination of Ψ is sensitive not only to errors in the measurements of its constituent quantities but also to polydispersity of the sample used. The point to note is a slight upswing of the line for α_s^3 below 7, which none of the existing approximate theories for Ψ predict.[12] The closed circles, which represent the results of a recent computer calculation by Gobush et al.,[20] exhibit a similar trend. However, this agreement is a mere artifact, arising from the fact that the computation became less accurate with increasing chain length because of a concomitant attrition of chain samples. One might suspect that the upswing would be no more than the error in experimental determination of Ψ, but we believe it to be a real effect. In fact, if the molecular weight dependence of A_2 becomes stronger as the molecular weight is decreased, with the molecular weight dependence of $\langle S^2 \rangle$ essentially unchanged, it is possible that Ψ in a *fixed* solvent goes up monotonically with decreasing molecular weight or α_s. The present data for A_2 and $\langle S^2 \rangle$ in Figures 3 and 6 display just such a molecular weight dependence.

In this connection it can be shown mathematically that all the currently available expressions of A_2 for flexible linear polymers predict a curve convex upward for the relation between ln A_2 and ln M of a given polymer–solvent pair. However, we have not seen any actual system which obeyed this prediction. Our A_2 data for PHB and PMPL in TFE exhibit a small but opposite curvature, and it is our usual experience to observe an essentially linear relation between ln A_2 and ln M over a broad range of molecular weights. These facts suggest that the current theories of A_2 for solutions of flexible linear polymers still require improvement.

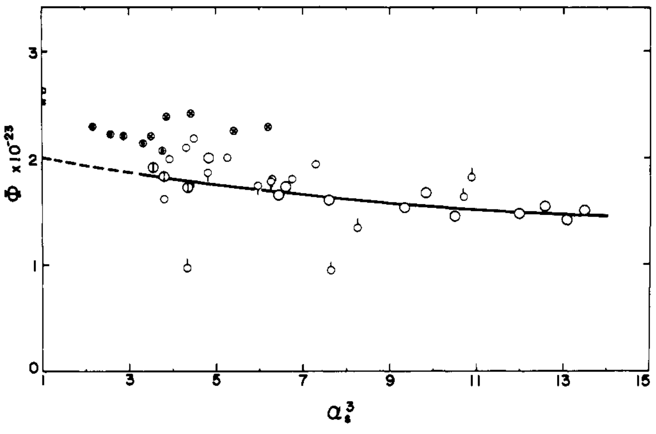

Figure 13. Plots of Flory viscosity factor Φ vs. α_s^3. The open and closed squares on the ordinate axis represent Φ_0 values determined by Matsumoto et al.[21] (for polyisobutylene) and by Fukuda et al.[5] (for polystyrene), respectively. The other symbols are the same as in Figure 12.

Viscosity Expansion Factor α_η. Figure 12 presents, on a log–log graph, α_η^3 vs. α_s^3 relations for PHB and PMPL in TFE, together with those for polystyrene in benzene and polyisobutylene in cyclohexane and n-heptane.[21] Although the plotted points scatter considerably, mainly owing to the difficulty in experimental determination of $\langle S^2 \rangle$, we may conclude that α_η is, to a good approximation, a universal function of α_s and hence z. The solid line indicated is a tentative fit to the plotted points and has a slope of 0.90 ± 0.02, in contrast to the early theory of Flory and Fox[13] who predicted unity for the slope. The line is drawn not to pass through the origin by considering a recent theoretical conclusion by Fujita et al.,[22] who showed that the initial tangent of ln α_η^3 vs. ln α_s^3 ought to have a slope of about $\frac{2}{3}$, as indicated by a thin solid line in Figure 12.

It is seen that the small open circles in Figure 12, which represent our previous data on PHB, scatter considerably above the straight line fitting most of our present data. This is another manifestation of the fact that our previous light-scattering experiment by and large underestimated mean-square radii of gyration. We are hesitant to comment on the large deviations in data of other authors.

Finally, in Figure 13, the values of Flory's viscosity factor Φ for the same polymer–solvent system as in Figure 12 are plotted against α_s^3. We see even more appreciable scatter of the plotted points and acknowledge great difficulty in the experimental determination of this factor. The solid curve has been drawn to fit our present data on PHB and PMPL. The value of 2.0 × 10^{23} assumed for Φ_0 to compute A and β for these polymers was determined by extrapolation to $\alpha_s = 1$ as indicated. The point to observe is a slow but steady decline of the solid curve with increasing expansion of polymer coil by volume exclusion. This behavior explains why the slope of the line in Figure 12 is smaller than unity or, more concretely, why the Mark–Howink–Sakurada index for the system PHB–TFE (0.76) does not approach 0.8 despite the condition that TFE is an unusually good solvent for PHB.

Conclusions and Remarks. The principal conclusions from the present study on PHB may be summarized as follows.

(1) α_s^5 becomes asymptotically proportional to z as has been predicted by many theoreticians since Flory in 1949, and the

actually observed relation between these two quantities is described closely by Domb–Barrett's semiempirical equation proposed very recently. This fact affords a method for evaluating the binary cluster integral β for a given polymer–solvent system from measurement of α_s.

(2) As the polymer coil undergoes increased expansion by volume exclusion, Ψ becomes constant (0.22 ± 0.01) for $\alpha_s^3 > 7$. Before reaching this asymptotic limit Ψ decreases slightly with increasing α_s, in disagreement with the predictions of any two-parameter theories available at present for A_2.

(3) Log–log plots of α_η^3 vs. α_s^3 are approximately fitted by a straight line with a slope of 0.90 ± 0.02, except in the region of α_s near unity. This result indicates that the Flory viscosity factor Φ decreases steadily as the polymer coil is expanded more by volume exclusion.

The maximum value of α_s (about 2.4) attained in the present work is the largest of those reported so far, as far as we know. Our experimental results indicate that the behavior of a polymer coil in dilute solution already enters into the asymptotic region when it is expanded by excluded volume effect above α_s as large as 2. It is hoped that further studies are attempted to check this conclusion with data on other polymer–solvent systems.

Finally, we must refer to an important point which has not been given a serious consideration in the above presentation. It is the polydispersity of the polymer fractions used in this work. Actually, we had no adequate means to estimate it. For example, conventional osmometry did not seem adaptable to our polymer fractions, because their number-average molecular weights were supposed to be quite high. No conventional solvent was applicable for their examination by gel-permeation chromatography. For these and other reasons we had to be content with leaving all the measured values uncorrected for polydispersity. Apparently, this fact makes the above-stated conclusions less definitive.

As a tentative attempt and as sometimes done we assume that correction of $\langle S^2 \rangle$ for polydispersity is the most crucial among others and design a 10% reduction to convert the observed z average $\langle S^2 \rangle^{1/2}$ to weight average values. Then our observed values of Ψ, Φ, and Φ_0 are raised approximately by 30%, but those of α_s, α_η, and z remain unchanged. Thus if the major polydispersity correction is restricted to $\langle S^2 \rangle$, conclusions (1) and (3) stated above hold as they stand.

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(23) Figure 10 suggests that, for $\alpha_s^2 > 3$, plots of α_s^2 vs. $M^{1/5}$ are fitted by a straight line through the origin and that the slope of the line may be equated to $1.55(3/2\pi)^{3/5}(B/A3)^{2/5}$. This fact may be conveniently used to estimate B and β.

Chain Transfer in Radical Polymerizations and End Group Content of Resultant Polymers

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ABSTRACT: The radical polymerization of vinyl monomers was carried out in the presence of reactive chain transfer agents possessing functional groups and the weight fractions of the resultant polymers bearing functional groups from the transfer agents were determined with a thin-layer chromatographic method. The monomer–chain-transfer agent combination chosen in the present work is styrene–trichloroacetyl chloride and methyl methacrylate–2-aminoethanethiol hydrochloride. The chain-transfer polymerizations were expected to produce polystyrene with an acyl chloride end group and poly(methyl methacrylate) with an amino end group in a high yield. The end group content of resultant polymers determined by the thin-layer chromatography was in both cases in good agreement with that predicted from the polymerization kinetics, suggesting that the thin-layer chromatography can be effectively applied to the end group determination.

When transfer reaction takes place to an added chain-transfer agent, each transfer causes one molecule of the transfer agent to become incorporated in polymer.[1] Although factors influencing the chain transfer and effects of the chain-transfer agent on reduction in polymer chain length have been extensively investigated, there have been published