to the retention of the long chains.

The diffusion kinetics of both species has been examined. In a dilute regime, it stays unchanged for both types of chain by the presence of another solute. Increasing the short chain concentration at fixed long chain concentration, we have observed an enhanced diffusion of the long chains. We interpret this effect as due to an increase of the long chain partition coefficient from the pores when short chains are added to the solution. A simple virial expansion model is in good quantitative agreement with our results, when the same parameters are used as in the analysis of single-chain diffusion kinetics presented in the accompanying paper.[1] The acceleration of the long chain diffusion is, however, less important by addition of short chains than by increase of long chain concentration. We show that this is due to the low exclusion of the short chains from the pores. The deswelling of the long chains by the short chains does not seem to play an important role in the explored concentration range. We have also observed in one experiment performed in an initial concentration regime of dilute short chains and overlapping long chains an acceleration of the short chain diffusion. We qualitatively attribute this effect to the fact that two driving forces should be effective in the presence of two solutes.

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Registry No. Polystyrene, 9003-53-6; bisphenol A polycarbonate (copolymer), 25037-45-0; bisphenol A polycarbonate (SRU), 24936-68-3.

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Measurement of Chain Dimensions in Dilute Polymer Solutions: A Light Scattering and Viscometric Study of Linear Polyisoprene in Cyclohexane

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ABSTRACT: Several methods for obtaining the size of macromolecules in dilute solution were applied to a series of linear polyisoprenes in the thermodynamically good solvent cyclohexane. The polymers, prepared by anionic polymerization, cover a wide range in molecular weight ($1.5 \times 10^4 < M < 3.4 \times 10^6$) and have narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.1$). The viscometric radius R_V, the radius of gyration R_G, the hydrodynamic radius R_H, and the thermodynamic radius R_T were determined by viscometry and by static and dynamic light scattering. The molecular weight dependences of all four size measures are well-described by power laws ($R \propto M^a$). The exponents obtained for R_H, R_V, and R_T agree fairly well with the predicted value of 0.588 for good solvents. The exponent obtained for R_G is smaller, although R_G/R_H in fact changes rather little over the range of available data. The values of R_G/R_H, R_V/R_H, and R_T/R_H are in reasonable accord with the theory for self-avoiding coils and with results for polystyrene and poly(α-methylstyrene) in good solvents.

Introduction

Several methods are available for determining the size of polymer molecules in dilute solution. Some provide the radius of gyration R_G (angular dependence of light or neutron scattering intensity[1,2]), others the hydrodynamic radius R_H (diffusion[3,4] and sedimentation coefficients[5]) or some combination of R_G and R_H (intrinsic viscosity[6]), and still others a thermodynamic or excluded volume radius R_T (second virial coefficient in good solvents[6,7]). Such data are used extensively to test dilute solution theories predicting the influence of chain length, chain architecture,

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and polymer–solvent thermodynamic interactions.

Many previous comparisons among these methods have employed polystyrene,[5-14] available in nearly monodisperse form for a very wide range of molecular weights and architectures through anionic polymerization. Here we examine another flexible chain species, polyisoprene, to compare several types of size measurements for linear chains and to furnish tests of dilute solution theory for an additional system. Samples with constant microstructure and narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n < 1.1$) were prepared by anionic polymerization. The diffusion coefficient D, the intrinsic viscosity $[\eta]$, the second virial coefficient A_2, and the radius of gyration were determined for a wide range of molecular weight M in dilute solutions of cyclohexane, a thermodynamically good solvent for polyisoprene. The data were obtained by quasi-elastic light scattering (QELS), by viscometry, and by low-angle laser light scattering (LALLS) and wide-angle light scattering (WALS) intensity measurements.

Background

The polymers used in the study have very narrow molecular weight distribution. Errors arising from neglecting the finite distribution breadth will be very small, so we summarize here only the equations for monodisperse systems.

The light scattering intensity due to optically isotropic polymer coils in dilute solution is governed by[1]

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{MP(q)} + 2A_2c + ... \qquad (1)$$

where ΔR_θ is the excess Rayleigh ratio at polymer concentration c (wt/vol) and scattering angle θ, K is an optical constant which is obtainable separately, $P(q)$ is the single particle scattering factor for the coils, and q is the magnitude of the scattering vector:

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \qquad (2)$$

When the coil dimensions are much smaller than the wavelength λ

$$P(q) = 1 - R_G{}^2q^2/3 + ... \qquad (3)$$

The intrinsic viscosity is obtained from the viscosities of dilute solutions

$$\frac{\eta - \eta_s}{\eta_s c} = [\eta][1 + k_H[\eta]c + ...] \qquad (4)$$

where η and η_s are the solution and solvent viscosities and k_H is the Huggins coefficient.

Quasi-elastic light scattering in dilute solutions provides the translational diffusion coefficient D. When the chains are small ($qR_G \ll 1$) and move independently[4]

$$\frac{\langle I(t)I(0)\rangle}{\langle I\rangle^2} = 1 + B \exp[-2Dq^2t] \qquad (5)$$

where $\langle I\rangle$ is the average scattering intensity at q, $\langle I(t)I(0)\rangle$ is the intensity correlation function at q for time separation t, and B is an instrumental constant of order unity. The diffusion coefficient in dilute solutions depends on concentration according to

$$D = D_0(1 + k_Dc + ...) \qquad (6)$$

where[6]

$$k_D = 2A_2M - k_\zeta - \bar{v} \qquad (7)$$

in which $\bar{v}$ is the partial specific volume of the polymer and k_ζ governs the concentration dependence of the molecular friction coefficient

$$\zeta = \zeta_0(1 + k_\zeta c + ...) \qquad (8)$$

The values of ζ_0 and D_0 are connected by the Einstein equation

$$D_0 = kT/\zeta_0 \qquad (9)$$

where k is the Boltzmann constant and T is the temperature. The hydrodynamic radius of the coils is related to ζ_0 by the Stokes equation

$$\zeta_0 = 6\pi\eta_sR_H \qquad (10)$$

To a first approximation, polymer chains in good solvents behave both hydrodynamically and thermodynamically like impenetrable spheres in such experiments. For spheres of volume V[6]

$$[\eta] = {}^5\!/\!_2N_a\frac{V}{M} \qquad (11)$$

$$A_2 = 4N_A\frac{V}{M^2} \qquad (12)$$

where N_a is the Avogadro number. Thus, with $V = {}^4\!/\!_3\pi R^3$, one can define viscometric and thermodynamic radii for the chains

$$R_V = 5.41 \times 10^{-9}([\eta]M)^{1/3} \qquad (13)$$

$$R_T = 4.63 \times 10^{-9}(A_2M^2)^{1/3} \qquad (14)$$

From eq 9 and 10, the hydrodynamic radius is given by

$$R_H = 0.0531\frac{kT}{\eta_sD_0} \qquad (15)$$

For monodisperse spheres, these three radii are of course identical and larger than the radius of gyration R_G by a factor of $({}^5\!/\!_3)^{1/2}$. For sufficiently long flexible chains in good solvents these radii are expected to differ from one another but to vary with molecular weight in the same way. According to recent theory[15]

$$R_G \propto M^{0.588} \qquad (16)$$

in the asymptotic range of strong excluded volume effects, a prediction which describes the neutron and light scattering data on polystyrene rather well. On the other hand, experimental results for R_H and R_V indicate a weaker dependence over the same range of M. It has been argued that R_H is significantly more sensitive to short-range correlations than R_G so that the conditions for observing the asymptotic behavior of R_H are less easily satisfied.[16]

Experimental Methods

1. Materials and Characterization. Linear polyisoprenes with constant microstructure (~70% cis, 23% trans, and 7% 3,4 units) and narrow molecular weight distribution were synthesized by organolithium-initiated anionic polymerization at room temperature in benzene or benzene/cyclohexane mixtures.[17] Samples PLS-95, -135, and -305 were purchased from Polymer Laboratories, Ltd.; all other samples were prepared under vacuum line conditions in this laboratory or at the University of Akron. Molecular weight characterization was carried out by a combination of light scattering measurements and size exclusion chromatography. The latter measurements were made with a Waters 150C SEC instrument using μ-Styragel columns and tetrahydrofuran as the elution solvent. The instrument was calibrated with well-characterized standards run under the same operating conditions. The results were used primarily to assess polydispersity in samples with $M < 10^6$. The ratios $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$ were well below 1.1 for samples used in the subsequent measurements.

Cyclohexane (distilled in glass, Burdick and Jackson) was the solvent used in all experiments. For viscometry the solvent was used without further purification. For the light scattering

Table I
Results on Small-Angle Light Scattering and Viscometry Measurements on Polyisoprene Solutions in Cyclohexane

sample	$10^{-4}M^a$	10^4A_2, mL g^{-1}	$[\eta]$, dL g^{-1}	k_H
PI-V	1.5_2	$14._5$		
PI-III	2.3_4	$12._8$		
DSP-4	(4.7_0)		0.54_4	0.35
DSP-1	(5.2_5)		0.59_0	0.37
PI-II	6.2_0	$10._2$	0.63_7	0.34
PLS-95	$10._1$	9.1		
PLS-135	$(12._9)$		1.11	0.34
DSP/GVS-1	$15._6$	8.0	1.29	0.32
PLS-305	$30._2$	6.6	2.01	0.38
DSP-5	$(36._6)$		2.3_5	0.33
PI-12	$58._1$	6.2	3.3_5	0.34
PI-LF1	$92._0$	5.4	4.6_6	0.31
PI-L17	167	4.8	7.0_2	0.33
DSP/GVS-3	342	4.1	11.2^b	0.37^b

[a] Weight-average molecular weight. Values in parentheses were assigned by SEC, the calibration having been constructed with M and SEC measurements on the other samples in the table. Molecular weights calculated from $[\eta]$ by using eq 22 are in excellent agreement in all cases. [b] Values may be slightly affected by shear rate (see text).

Table II
Results of Wide-Angle Light Scattering Measurements on Polyisoprene Solutions in Cyclohexane

sample	$10^{-4}M^a$	10^4A_2, mL g^{-1}	R_G,^{b} nm
A	$11._2$	7.8	$17._7$
B	$16._4$	7.9	$19._4$
C	$23._1$	7.0	$24._3$
D	$29._7$	6.8	$26._2$
E	$31._6$	6.5	$28._0$
F	$35._0$	5.9	$31._2$
G	$50._0$	5.5	$37._0$
H^c	$58._1$	5.5	41
I	$94._2$	4.7	48
J	139	4.6	65
K	160	3.7	68

[a] Weight-average molecular weight. [b] z-average radius of gyration. [c] Sample H is sample PI-12 (see other tables).

Table III
Results of Quasi-Elastic Light Scattering Measurements on Polyisoprene Solutions in Cyclohexane

sample	$10^{-4}M$	10^7D_0, cm^2 s^{-1}	k_D, mL g^{-1}	k_0
PI-V	1.5_2	6.9_9	$10._9$	4.6
PI-III	2.3_4	5.5_2	$14._6$	4.8
PI-II	6.2_0	3.1_6	$37._8$	4.7
DSP-GVS-1	$15._6$	1.8_4	$78._6$	4.6
PLS-305	$30._2$	1.2_6	125	4.5
PI-L12	$58._1$	0.85_4	210	5.0
PI-LF1	92	0.67_2	26_9	5.6
PI-L17	167	0.44_7	46_9	4.6
DSP/GVS-3	342	0.29_4	66_6	5.1

measurements, the solvent was refluxed over calcium hydride and distilled prior to use. At 25 °C and $\lambda = 633$ nm the refractive index of cyclohexane is 1.425_4, the Rayleigh ratio R_θ is 5.30×10^{-6} cm^{-1}, and the specific refractive index increment dn/dc for polyisoprene in cyclohexane is 0.106 mL g^{-1}. The viscosity η_s of cyclohexane at 25 °C is 0.897 cP.

2. LALLS Measurements. Molecular weights and second virial coefficients (see eq 1) were obtained with a Chromatix KMX-6 low-angle light scattering photometer operating at $\lambda = 633$ nm (He–Ne laser). Integrated intensity was measured at $\theta \approx 3°$–$6°$ ($P(q) \approx 1$ in this range for all samples) and converted to Rayleigh ratio by application of known attentuation and geometrical factors. Calibration was checked repeatedly by measurements of R_θ for pure cyclohexane. Measurements were made at ambient temperature, $T = 23 \pm 1$ °C, on pure cyclohexane and a series of dilutions of polyisoprene stock solutions, filtered (Gelman Alpha-450, pore diameter 0.3–0.45 μm), and pumped slowly through the sample cell. For each polymer sample, measurements were performed on five or more dilutions in the range $0.1c^*$ to $0.6c^*$, where c^* is the coil overlap concentration, estimated as $[\eta]^{-1}$. The data were analyzed according to the Berry method[18] in which the series expansion of eq 1 is truncated at the c^2 term, the third virial coefficient A_3 is approximated by ${}^1/_3MA_2{}^2$, and $(Kc/\Delta R_\theta)^{1/2}$ is plotted against c. The optical constant K was calculated from λ and the optical properties of polyisoprene-cyclohexane solutions given above.[1] The intercept and slope were obtained by least squares; the resulting values of M and A_2 are recorded in Table I.

3. WALS Measurements. Table II contains the values of second virial coefficient and radius of gyration obtained for a separate series of polyisoprenes. These samples were prepared by anionic polymerization at Akron University; the measurements were made with a Sofica light scattering photometer at ambient temperatures. Solutions in cyclohexane were prepared and filtered as described above. The light source was a mercury vapor lamp in this case, equipped with filters to isolate the mercury blue line ($\lambda = 436$ nm). The photometer was calibrated with polystyrene standards. Incident beam and scattering intensities were measured in the angular range $30° \leqslant \theta \leqslant 150°$, the values of $Kc/\Delta R_\theta$ were calculated from the calibration and optical parameters appropriate for polyisoprene–cyclohexane solutions at $\lambda = 436$ nm. Zimm plots were constructed according to the Berry method,[18] and values of M, A_2, and R_G were determined from the intercept and slopes.[1]

4. QELS Measurements. The scattering intensity correlation function $\langle I(t)I(0)\rangle$ was measured for the polyisoprene–cyclohexane solutions at 25 °C over a range of scattering angles with a Brookhaven Instruments Co. photometer and correlator. Scattered light (He–Ar laser, $\lambda = 633$ nm) was collected through a defining pinhole mounted in front of the photomultiplier, the resulting signal being passed via an amplifier/discriminator to a 72-channel photon correlator. The delay time between channels was selected to achieve a correlation decay of approximately two decades in the first 64 channels. A much longer delay time was used for the last 8 channels to establish the base line, $\langle I\rangle^2$. A function proportional to the field correlation function $g_1(t)$ was then generated from the intensity correlation

$$g_1(t) = \beta\left[\frac{\langle I(0)I(t)\rangle}{\langle I\rangle^2} - 1\right]^{1/2} \tag{17}$$

where $\beta = B^{-1/2}$ (see eq 5) is an instrumental constant.[9,19] This experimental function was fitted by using a weighted least-squares technique to a second-order cumulant expansion[20]

$$\ln g_1(t) = \ln \beta - \mu_1{}^* + \frac{\mu_2}{2!}t^2 \tag{18}$$

where μ_1 is $\bar{\Gamma}$, the mean decay constant (the exponential coefficient Dq^2 if $g_1(t)$ is a single exponential), and $\mu_2/\bar{\Gamma}^2$ is a measure of variance from the single exponential form.

Values of μ_1 and μ_2 were obtained at several scattering angles from 30° to 90° for each of several concentrations ($c < c^*$). The correlation function was adequately described by a single exponential for all samples except the two of highest molecular weight. Thus $\mu_2/\bar{\Gamma}^2$ from the cumulant fit was smaller than 0.1 and highly variable from run to run. Values of $\bar{\Gamma}$ were reproducible and obeyed the anticipated q^2 dependence from 30° to 90°. For those samples $D = \bar{\Gamma}/q^2$ was plotted vs. c and D_0 and k_D were determined from the intercept and slope (eq 6). The values obtained are recorded in Table III.

Departure from single exponential decay was evident for solutions of the two samples with highest molecular weight. Reproducible values of $\mu_2/\bar{\Gamma}^2 \approx 0.25$ were obtained for high scattering angles with progressively smaller and more erratic values as the angle was decreased, and $\bar{\Gamma}$ did not vary as q^2. Such behavior is expected when qR_G is not negligibly small and requires an extrapolation of $\bar{\Gamma}/q^2$ to zero angle to obtain the diffusion coefficient. For scatterers of finite size at finite concentration the first departures from q^2 dependence are described by[4]

$$\bar{\Gamma} = D_0q^2(1 + \alpha R_G{}^2q^2 + k_Dc + ...) \tag{19}$$

where α is a dimensionless coefficient dependent on the geometry and internal dynamics of the scatterers. Figure 1 illustrates the

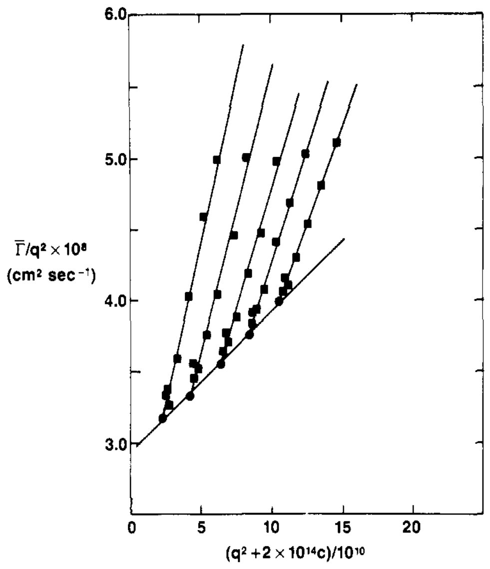

Figure 1. Double extrapolation plot of mean decay constant from QELS to zero scattering angle and zero polymer concentration. The polymer is sample DSP/GVS-3 ($M = 3.42 \times 10^6$); lines of constant concentration extrapolated to zero scattering angle are shown. Extrapolation to zero concentration of the $q = 0$ intercepts gives D_0.

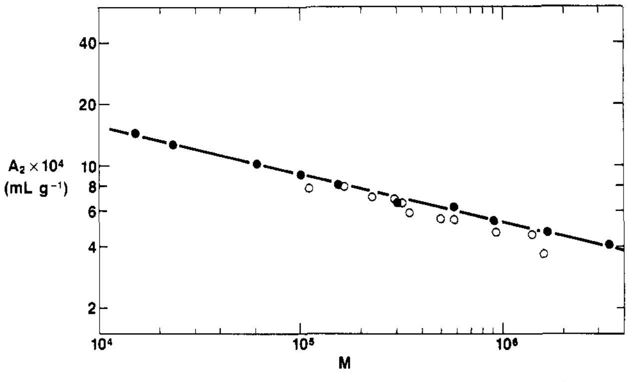

Figure 2. Second virial coefficient as a function of molecular weight for linear polyisoprene in cyclohexane. The filled circles are data obtained by LALLS experiments (Table I); the open circles are data obtained by WALS experiments (Table II).

extrapolation procedure.[19] The resulting D_0 and k_D for these two samples are also recorded in Table III.

5. Intrinsic Viscosity. Flow times for solvent and several concentrations of each polymer were measured in Cannon–Ubhelohde capillary viscometers at 25 ± 0.02 °C. The flow rates were slow enough to make kinetic energy corrections negligible. Values of $[\eta]$ and k_H were obtained from the intercept and slope of a Huggins plot (eq 4) and are recorded in Table I. Shear rate effects should be negligible for all samples except DSP/GVS-3: the value of $[\eta]$ obtained for that sample may be slightly smaller than the zero shear rate limit.[21]

Analysis of Data

Values of A_2 from LALLS (Table I) and WALS (Table II) are plotted as a function of polyisoprene molecular weight in Figure 2. The WALS results, which cover a relatively narrow range of molecular weights, are more scattered and lie slightly below the LALLS results which we believe to be more reliable. The values from LALLS are well-described by a power law over the full range:

$$A_2 = 1.32 \times 10^{-2}\ M^{-0.23}\ \text{mL g}^{-1} \qquad (20)$$

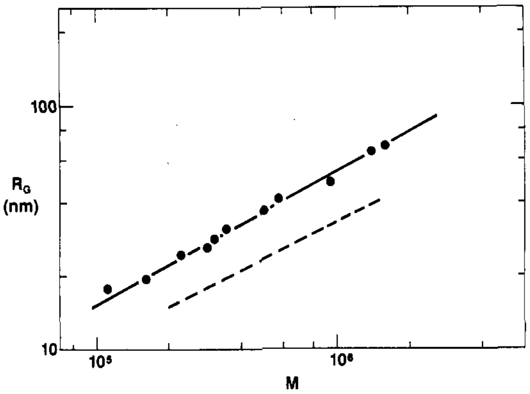

Figure 3. Radius of gyration as a function of molecular weight for linear polyisoprene in cyclohexane. The filled circles are data given in Table II. The dashed line is R_G vs. M for polyisoprene at the θ condition (dioxane at 34 °C[22]).

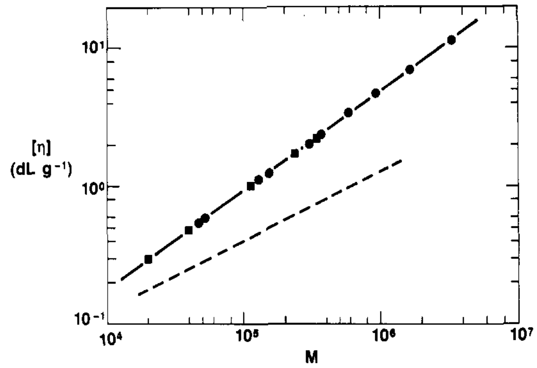

Figure 4. Intrinsic viscosity as a function of molecular weight for linear polyisoprene in cyclohexane. The circles are data given in Table II; the squares are data from ref 23. The dashed line is $[\eta]$ vs. M for polyisoprene at the θ condition.[22]

Values of R_G from WALS (Table II) are plotted as a function of molecular weight in Figure 3. The precision of the measurement decreases with decreasing M, the value from sample A ($M = 11.2 \times 10^4$) being rather less certain than the others. The results from $M = 16.4 \times 10^4$ to $M = 160 \times 10^4$ are described reasonably well by a power law

$$R_G = 2.84 \times 10^{-2}\ M^{0.545}\ \text{nm} \qquad (21)$$

with an uncertainty in the exponent of ±0.02. The relationship between R_G and M for polyisoprene at the Θ condition[22] is shown by a dashed line in Figure 3.

Values of $[\eta]$ (Table I) are plotted as a function of molecular weight in Figure 4. The data are well-described by a power law

$$[\eta] = 2.05 \times 10^{-4}\ M^{0.730}\ \text{dL g}^{-1} \qquad (22)$$

which is based only on results obtained from samples for which absolute molecular weights were available, but with sample DSP/GVS-3 omitted because of suspected shear rate dependence. With DSP/GVS-3 included the exponent decreases to 0.718 and the front factor increases to 2.37×10^{-4}. Data reported elsewhere for polyisoprene in cyclohexane[23] (measurements at 35 °C; $\bar{M}_n$ converted to $\bar{M}_w$ by assuming a constant $\bar{M}_w/\bar{M}_n = 1.05$ for those samples) are shown in Figure 4 for comparison. Agreement with eq 22 is excellent. The relationship between $[\eta]$ and M for polyisoprene at the θ condition[22] is shown by the dashed line in Figure 4.

Values of D_0 and k_D (Table III) are plotted as functions of molecular weight in Figures 5 and 6. The data are well-described by power laws:

$$D_0 = 1.98 \times 10^{-4}\ M^{-0.584}\ \text{cm}^2\ \text{s}^{-1} \qquad (23)$$

$$k_D = 6.70 \times 10^{-3}\ M^{0.775}\ \text{mL g}^{-1} \qquad (24)$$

Values of R_H, R_V, and R_T were calculated from D_0 (eq 15), $[\eta]$ (eq 13), and A_2 (eq 14), respectively, for the samples in this study. The results are shown in Table IV along with

Table IV
Coil Size for Polyisoprene in Cyclohexane Obtained by Several Methods

sample	10^4M	R_H,[a] nm	R_V, nm	R_T, nm	R_G,[b] nm
PI-V	1.5_2	3.4_9		3.2_2	(5.4_2)
PI-III	2.3_4	4.4_2		4.1_1	(6.8_6)
DSP-4	(4.7_0)	(6.5_8)	7.4_0		$(10._0)$
DSP-1	(5.2_5)	(6.9_8)	7.8_9		$(10._6)$
PI-II	6.2_0	7.7_2	8.5_5	7.3_0	$(11._7)$
PLS-95	$10._1$	$(10._3)$		9.7_3	$(15._2)$
PLS-135	$(12._9)$	$(11._9)$	$13._2$		$(17._4)$
DSP/GVS-1	$15._6$	$13._3$	$14._7$	$12._5$	$19._3$
PLS-305	$(30._2$	$19._4$	$21._3$	$18._2$	$27._6$
DSP-5	$(36._6)$	$(21._8)$	$23._9$		$30._6$
PI-12	$58._1$	$28._6$	$31._4$	$27._5$	$39._5$
PI-LF1	92	$36._3$	$40._8$	$35._7$	$50._7$
PI-L17	167	$54._6$	$57._1$	$51._0$	$70._2$
DSP/GVS-3	342	$83._0$	$(84._7)$[c]	$78._1$	(104)

[a] Values in parentheses were obtained with D_0 calculated from eq 23. [b] All values were obtained from eq 21; values in parentheses apply to molecular weights that lie outside the range covered by the WALS measurements. [c] Value may be slightly too small owing to a shear rate effect on $[\eta]$ for this sample.

Table V
Comparison of Coil Size for Polyisoprene in Cyclohexane Obtained by Several Methods

sample	$10^{-4}M$	R_V/R_H	R_T/R_H	R_G/R_H[a]
PI-V	1.5_2		0.92	(1.55)
PI-III	2.3_4		0.93	(1.55)
DSP-4	(4.7_0)	1.13		(1.52)
DSP-1	(5.2_5)	1.13		(1.52)
PI-II	6.2_0	1.11	0.95	(1.52)
PLS-95	$10._1$		0.94	(1.48)
PLS-135	$(12._9)$	1.11		(1.46)
DSP/GVS-1	$15._6$	1.11	0.94	1.45
PLS-305	$30._2$	1.10	0.94	1.42
DSP-5	$(36._6)$	1.10		1.40
PI-12	$58._1$	1.10	0.96	1.38
PI-LF1	92	1.12	0.98	1.40
PI-L17	167	1.05	0.93	1.29
DSP/GVS-3	342	(1.02)[b]	0.94	(1.25)

[a] Ratios in parentheses obtained with R_G values outside the range covered by WALS measurements. (See footnote *b* on Table IV. [b] Value may be influenced by shear rate effects on $[\eta]$.

R_G calculated from eq 21. The values of R_G for molecular weights outside the range of the WALS data ($16.4 < 10^{-4}M < 160$) are enclosed in parentheses. The size ratios R_V/R_H, R_T/R_H, and R_G/R_H are given in Table V.

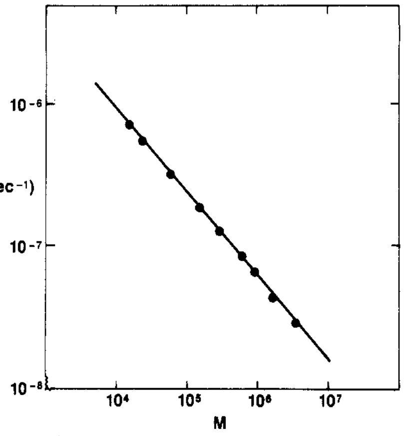

Figure 5. Infinite dilution diffusion coefficient as a function of molecular weight for linear polyisoprene in cyclohexane.

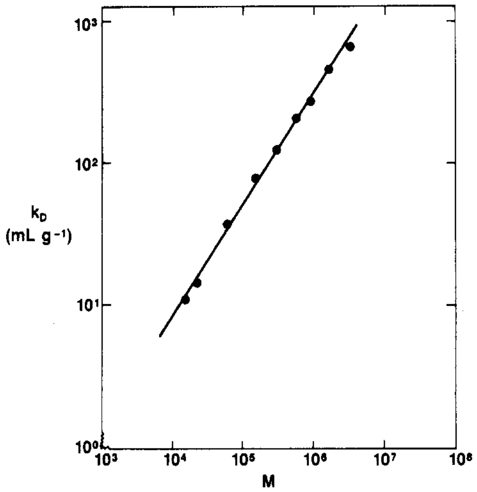

Figure 6. Coefficient of concentration dependent for diffusion as a function of molecular weight for linear polyisoprene in cyclohexane.

Discussion

The following expressions for the hydrodynamic, viscometric, and thermodynamic radii were calculated from the correlations for D_0 (eq 23), $[\eta]$ (eq 22), and A_2 (eq 20)

$$R_H = 1.23 \times 10^{-2}\, M^{0.584} \text{ nm} \tag{25}$$

$$R_V = 1.48 \times 10^{-2}\, M^{0.577} \text{ nm} \tag{26}$$

$$R_T = 1.09 \times 10^{-2}\, M^{0.590} \text{ nm} \tag{27}$$

with uncertainties in the exponents of ±0.004, ±0.002, and ±0.002, respectively. Within these limits the R_H and R_T exponents agree with the theoretical prediction of 0.588,[15] while the exponent for R_V is only marginally different. The exponent obtained for R_G (eq 21) is considerably smaller than theory, however. These results are thus contrary to observations on polystyrene where, in benzene for example, the R_G exponent agrees well with theory,[24] but the R_H exponent is smaller.[9] We are unable to offer an explanation for this reversal. On the other hand, such differences in exponents should perhaps not be strongly emphasized. Thus, recent work on polystyrene suggests that specific solvent effects may be important and may influence some size measurements more than others.[13] Also, our results for R_H, R_V, and R_T were obtained with a common set of polyisoprenes and cover at least two decades of M. Our confidence in those exponents is therefore greater than in the R_G exponent that was obtained with a different series

Table VI
Comparison of Experimental and Theoretical Size Ratios

polystyrene	solvent	R_G/R_H	R_T/R_H	R_V/R_H	k_0	ref
polystyrene	benzene (toluene)	1.51	1.01	1.03	6.3	5, 12, 24
poly(α-methylstyrene)[a]	benzene (toluene)	1.55	1.05	1.11	7.2	25–27
polyisoprene	cyclohexane	1.39	0.95	1.11	4.8	this work
spheres (theory)		0.775	1.0	1.0	7.18	6, 28
unperturbed coils (theory)		1.24	0	1.23	2.23	28–30
self-avoiding coils (theory)		1.56	1.02	1.12		30

[a] Values of R_G/R_H, R_V/R_H, and k_0 given here for poly(α-methylstyrene) are based on revised molecular weights for the results in ref 26.[27] Light scattering molecular weights reported there were obtained with dn/dc = 0.108 mL g⁻¹ at 630 nm, whereas the correct value for high molecular weight poly(α-methylstyrene) in toluene is 0.122 mL g⁻¹.[31]

of samples covering barely one decade of M.

The difference among the several measurements of size as obtained on individual samples are shown in Table V. The ratio R_T/R_H is insensitive to molecular weight over the full range with an average value of 0.95. The ratio R_V/R_H is similarly insensitive to molecular weight except at very high M where shear rate might have affected the value of R_V; the average is 1.11 when the value for the highest molecular weight sample DSP/GVS-3 is omitted. The average value of R_G/R_H is 1.39 over the range of molecular weights where R_G was determined. However, R_G/R_H decreases slowly but perceptibly with M even over this limited range; the hydrodynamic size and physical size of polyisoprene coils seem clearly to vary with molecular weight in slightly different ways even in the high M range.

Values of k_ζ were calculated from experimental values of k_D, A_2, and M using eq 7. According to theory[6]

$$k_\zeta = k_0 N_a (V_H/M) \qquad (28)$$

where V_H is the hydrodynamic volume of the coil $4\pi R_H^3/3$ and k_0 is a dimensionless constant of order unity. Values of k_0 calculated from k_ζ with eq 28 are given in Table III. No trend with molecular weight is apparent; the average value of k_0 is 4.8 ± 0.4. The constancy of k_0 is not a very sensitive test of the particular form of eq 28 however. Thus, for example, $k_\zeta \propto [\eta]$ fits the data nearly as well, although giving a slightly different value of the proportionality constant.

A comparison of results obtained for a few other polymer species in good solvents is shown in Table VI. Theoretical predictions for spheres, random coils (θ condition), and self-avoiding coils (good solvents) are also listed there. The experimental ratios are averages of values calculated or interpolated from data on individual samples in the high molecular weight range. Despite differences in the reported molecular weight exponents, the trend in the ratios is rather weak and nearly within the experimental scatter. The averages of R_G/R_H for polystyrene and poly(α-methylstyrene) in benzene or toluene are in reasonable agreement with each other and with the theory of self-avoiding coils; the average for polyisoprene in cyclohexane is smaller by about 10%. The averages of R_T/R_H are all near unity as predicted for both spheres and self-avoiding coils. The averages of R_V/R_H for all three species are in reasonable agreement with theory. Averages of k_0 lie between the theoretical values for spheres and random coils but vary noticeably from one polymer system to another. This variation of k_0 is in contrast with the constancy of the Huggins coefficient. The average of values obtained here, $k_H = 0.34$ (Table I), is typical of results found for many species of linear polymers in good solvents. Unfortunately the theory for k_0 and k_H for self-avoiding coils is still unsettled.

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Registry No. Polyisoprene, 9003-31-0; cyclohexane, 110-82-7.

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