Transport Properties of Polyisobutylene in Dilute Solution

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ABSTRACT: The dilute-solution transport properties of polyisobutylene (PIB) fractions have been measured under Θ conditions and in good solvents of varying thermodynamic quality. The translational diffusion coefficients were evaluated via photon correlation spectroscopy and coupled with the results from intrinsic viscosity and low-angle laser light scattering experiments to yield the appropriate size parameters. The results allow a comparison of the properties of PIB with those of other flexible chains and with various theoretical predictions.

Introduction

During the last half century a number of studies on the dilute-solution properties of polyisobutylene (PIB) have appeared. Notable among these reports are the pioneering works of Flory, Fox, and Krigbaum[2-8] and those of Fujita and co-workers.[9,10] Recently the configuration of the PIB chain, in bulk and in dilute solution, has been probed by neutron and X-ray scattering.[11,12] Identical chain dimensions in the bulk and in the Θ solvent benzene-d_6 were observed.

Theoretical studies of the conformational characteristics of PIB have also been reported.[13-21] A rotational isomeric state (RIS) model for PIB has been developed,[22] which predicts values of the characteristic ratio, C_∞,[23] and the variation of this parameter with temperature, in accord with experiment.[5,8,9,11,12,24-26]

Despite the extensive studies on PIB in dilute solution, measurements of D_T, the translational diffusion coefficient, have not heretofore been reported. In this paper the results from photon correlation spectroscopy (PCS) and intrinsic viscosity experiments on some fractionated PIB chains are presented. Data are reported for PIB in solvents of varying thermodynamic quality, thereby permitting the comparison of the hydrodynamic or transport properties of PIB with those of other flexible chains and with various theoretical predictions.

Experimental Section

Materials and Static Methods. The PIB chains examined in this work were obtained from three sources: Exxon Commercial material (sample designation C), Exxon Chemicals laboratory samples (L; supplied by Dr. H. C. Wang), and Polysciences, Inc. (PS). Solvent–nonsolvent fractionations (toluene–methanol) were performed to generate samples of reduced dispersity and symmetrical distributions. Two of the three Polysciences samples exhibited narrow and symmetrical distributions as ascertained by size-exclusion chromatography (SEC) and were therefore used as received. The third sample was used both in the unfractionated and fractionated states.

Static properties of the chains were determined by SEC and low-angle laser light scattering (LALLS). Two different chromatography units were employed. One system (Exxon) consisted of a Waters 150C equipped with a seven-column "ultra-Styragel" set having one linear column and six columns with a continuous porosity range of 10^2–10^6 Å. The second instrument (UAB) incorporated a Waters Model 510 pump, a Waters Model 410 differential refractometer, and two "linear ultra-Styragel" columns with the same porosity range as the seven-column set. For all separations on either system, tetrahydrofuran (30 °C) was used as the mobile phase at a flow rate of 1 mL min^{-1}. A minimum of two runs per sample were done with the Exxon instrument.

Weight-average molecular weights and second virial coefficients, M_w and A_2, respectively, were determined in *n*-heptane and/or cyclohexane at 23 °C using a Chromatix KMX-6 photometer ($\lambda_0 = 632.8$ nm). Specific refractive index increments, $\partial n/\partial c$ values, were measured at the same incident wavelength as for the LALLS experiments with the Chromatix KMX-16 differential refractometer. Values of 0.143 and 0.0947 mL g^{-1} were obtained for solutions of PIB in *n*-heptane and cyclohexane, respectively.

The solvents used for the LALLS and refractometry experiments were distilled-in-glass grade from Burdick & Jackson Labs, Inc., and were further purified by refluxing over CaH_2 followed by distillation. The middle fractions were used in scattering experiments by filtration through Teflon membrane filters (Millipore) with 0.2-μm nominal pore size.

M_w and A_2 values were obtained by linear regression analysis of plots of $Kc\bar{R}_\theta^{-1}$ against c where K is the optical constant, c the solute concentration, and $\bar{R}_\theta$ the excess Rayleigh ratio. Analysis of the same data by square-root plots[27] yielded M_w and A_2 values within 3% of those values calculated from the standard plots. M_w values determined from the same samples in *n*-heptane and cyclohexane agreed to within 4%.

Transport Property Determinations. Intrinsic viscosities were measured in cyclohexane, *n*-heptane, and benzene by using Cannon-Ubbelohde dilution viscometers or a Schott Gërate automatic viscometric system. Temperature control of the viscometry bath was maintained to within 0.02 °C of the measurement temperature through the use of a water bath equipped with a heater/circulator. The limiting viscosity number, $[\eta]$, and the Huggins coefficient, k_H, were obtained from the equation

$$\eta_{sp}/c = [\eta](1 + k_H[\eta]c + ...) \quad (1)$$

where η_{sp} is the specific viscosity. Measurement conditions were such so as to eliminate the need to apply kinetic energy corrections.

Cyclohexane (Aldrich, HPLC grade >99.9%) and *n*-heptane (Fisher, spectrograde) were used as received. Benzene (Fisher reagent grade) was further purified by treatment with concentrated sulfuric acid followed by distillation over sodium. All solvents were filtered through Acrodisc CR Teflon membrane filters of 1.0-μm nominal pore diameter directly into the viscometers.

PCS measurements were performed as described previously.[28] Electric field correlation functions, $g'(\tau)$, obtained from the corresponding intensity functions using the expression derived by Siegert[29] were analyzed by the method of cumulants[30]

$$b^{1/2} \ln g'(\tau)/B = \ln b^{1/2} - \Gamma(\tau) + \mu_2(\tau)/2 \quad (2)$$

Here b is an optical (system response) constant, B the base line,

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Table I
Molecular Characteristics of Polyisobutylene

	cyclohexane		*n*-heptane		SEC results: Exxon		SEC results: UAB	
sample[a]	$M_w \times 10^{-5}$, g mol^{-1}	$A_2 \times 10^4$, mL mol g^{-2}	$M_w \times 10^{-5}$, g mol^{-1}	$A_2 \times 10^4$, mL mol g^{-2}	M_z/M_w	M_w/M_n	M_z/M_w	M_w/M_n
1PS	0.135				1.07	1.06		
2PS	0.270	9.7_6			1.09	1.10	1.11	1.09
3C	0.640[b]				1.12	1.14		
4C	0.840[b]				1.10	1.10	1.09	1.14
5PS	1.08	6.7_7			1.16	1.21		
6C	1.26	5.4_6	1.27	3.3_5	1.14	1.15		
7C	1.29	5.5_0			1.16	1.13		
8PS[c]	1.33	6.4_7			1.05	1.14	1.05	1.08
9C	1.67	5.5_1	1.66	3.1_1	1.13	1.18	1.18	1.23
10L[d]	2.21	5.6_3			1.84	1.93		
11L	3.25	5.3_0			1.38	1.37		
12C	3.30	5.2_2			1.24	1.29	1.25	1.33
13L[d]	3.40	5.5_6	3.19	2.8_3	1.92	1.96		
14L	4.36	5.4_2			1.40	1.44		
15C	4.49	5.7_9	4.46	2.8_8	1.54	1.47	1.47	1.44
16L[d]	6.32	4.8_5			1.91	1.98		
17C	7.46	4.5_1	7.43	2.3_3	1.27	1.31	1.26	1.29
18C[d]	10.1	4.2_6			2.04	2.28		
19C	15.4	3.7_3	14.2	2.2_2	1.24	1.25	1.23	1.23
20C	16.1	3.8_0	16.1	1.9_9	1.52	1.53		

[a] C = commercial sample; L = lab sample; PS = Polysciences. [b] Via SEC. [c] Obtained from 5PS via removal of low molecular weight material: Sample 5PS was found to have a bimodal molecular weight distribution. The lower molecular weight component had a peak molecular weight (SEC) virtually half that of the majority (~85% by weight) component.

τ the time delay, Γ the effective decay constant, and μ_2 the second moment. Values of B were determined from averaging either the contents of the eight correlator channels delayed 1024 in τ (calculated) or from those channels delayed sufficiently in τ so as to attaion a constant value (measured). In all cases the base lines agreed to within 0.02%.

The effective decay constant, Γ, is related to the apparent z-average translational diffusion coefficient by

$$\Gamma = D_{app,z} q^2 \tag{3}$$

with the wave vector q defined as

$$q = (4\pi n_0/\lambda_0) \sin(\theta/2) \tag{4}$$

with $\lambda_0 = 632.8$ nm. In most cases correlograms were measured at a scattering angle, θ, of 25°. Values of $D_{app,z}$ at $\theta = 25°$ agreed with those at 20°, indicating proper optical alignment of the spectrometer and contributions from stray light were negligible. This latter result was consistent with the flat correlation functions determined at the start of each experiment from the solvent.

Solvents and solutions were clarified by closed-loop filtration. Cyclohexane and *n*-heptane were the same as for the viscometry experiments. Isoamyl isovalerate (IAIV) was obtained from Pfaltz and Bauer and was determined to be greater than 99.5% pure by GC/MS. IAIV was observed to attack the solvent-resistant tubing normally used with the peristaltic pump/closed-loop filtration apparatus. Consequently, an apparatus consisting of Teflon tubing, stainless steel and Teflon connections, an appropriate filter, and an HPLC pump was assembled. Filters of either 0.2-μm (Anotec) or 0.45-μm (Gelman Acrodisc CR) mean pore diameters were employed. A flow rate of 1 mL min^{-1} was not exceeded during any of the filtration cycles. Filtration for a period of approximately 15 min was normally sufficient in order to attain a constant (less than 2% fluctuations) reading on the pulse counter.

Limiting diffusion coefficients, D_z, were determined from measured values of $D_{app,z}$ according to[31,32]

$$D_{app,z} = D_z(1 + k_d c + ...) \tag{5a}$$

where the diffusion virial coefficient, k_d, is given by

$$k_d = 2A_2M - k_f - v_2 \tag{5b}$$

with k_f the frictional virial coefficient and v_2 the partial specific volume of the solute. In all cases $D_{app,z}$ was linearly proportional to c.

The z-average frictional coefficient, f_z, was calculated by using the Stokes–Einstein relation

$$D_z = kT/f_z \tag{6a}$$

where k is Boltzmann's constant and T is the absolute temperature. Equivalent spherical hydrodynamic radii were calculated from

$$f_z = 6\pi\eta_0 R_{H_z} \tag{6b}$$

At 25 °C *n*-heptane and cyclohexane are reported[33] to have viscosities of 0.3967 and 0.8980 cP, respectively. The solvent viscosity of isoamyl isovalerate at 22.1 °C was 1.3656 cP as measured by calibrated viscometers.

Results

Values of M_w and A_2 from the static scattering experiments along with the sample dispersity ratios M_z/M_w and M_w/M_n from SEC are collected in Table I. The good agreement of the weight-average molecular weights determined from the solutions of PIB in cyclohexane and in *n*-heptane and the consistent polydispersities obtained from the chromatographic systems seemingly confirm the accurate determination of the primary chain properties. The following analysis employs the fractionated samples and the molecular weights calculated from the LALLS experiments in cyclohexane and *n*-heptane. Average molecular weight values are used when appropriate.

The second virial coefficients of the fractionated PIB's in cyclohexane (T = 23 °C) depend on M_w according to

$$A_2 = 6.88 \times 10^{-3} M_w^{-0.203} \text{ (mL mol g}^{-2}\text{)} \tag{7}$$

$$0.27 \times 10^5 \le M_w \le 16.1 \times 10^5 \text{ g mol}^{-1}$$

The correlation coefficient of the linear regression fit, r, was calculated as 0.9452. Statistical analysis of the thermodynamic terms for PIB in *n*-heptane yielded

$$A_2 = 3.08 \times 10^{-3} M_w^{-0.188} \text{ (mL mol g}^{-2}\text{)} \tag{8}$$

$$1.67 \times 10^5 \le M_w \le 16.1 \times 10^5 \text{ g mol}^{-1}$$

with r equal to 0.9718.

Table II
Intrinsic Viscosities and Huggins Coefficients for Polyisobutylene

sample	$M_w \times 10^{-5}$, g mol^{-1}	$[\eta]^{25°C}_{CYC}$, dL g^{-1}	k_H	$[\eta]^{25°C}_{HEP}$, dL g^{-1}	k_H	$[\eta]^{25°C}_{BEN}$, dL g^{-1}	k_H
1PS	0.135	0.175	0.45	0.150	0.36	0.123	0.59
2PS	0.270	0.276	0.48	0.213	0.42	0.171	0.61
3C	0.640	0.480	0.49				
4C	0.840	0.584	0.42	0.419	0.41	0.283	0.71
5PS	1.08	0.722	0.40				
6C	1.27	0.778	0.44				
7C	1.29	0.811	0.45				
8PS	1.33	0.847	0.40	0.600	0.40	0.395	0.68
9C	1.67	1.02	0.40	0.713	0.40	0.441	0.72
10L	2.21	1.16	0.38				
11L	3.25	1.63	0.40				
12C	3.30	1.68	0.39	1.07	0.34	0.590	0.77
13L	3.30	1.68	0.36				
14L	4.36	1.98	0.36				
15C	4.48	2.07	0.32	1.37	0.34	0.706	0.79
16L	6.32	2.54	0.36				
17C	7.45	2.97	0.34	2.06	0.25	0.930	0.81
18C	10.1	3.75	0.34				
19C	14.8	4.82	0.31	3.10	0.33	1.28	0.96
20C	16.1	5.33	0.34				

Table II contains the intrinsic viscosities and Huggins coefficients measured at 25 °C in cyclohexane, *n*-heptane, and benzene. The associated Mark–Houwink–Sakurada plots are presented in Figure 1. The data are described by the following power laws, strictly valid for the molecular weight ranges indicated

$$[\eta]^{25°C}_{CYC} = 1.35 \times 10^{-4} M_w^{0.740} \text{ (dL g}^{-1}\text{)} \quad (9)$$

$$0.64 \times 10^5 \le M_w \le 16.1 \times 10^5 \text{ g mol}^{-1}$$

$$[\eta]^{25°C}_{HEP} = 1.58 \times 10^{-4} M_w^{0.697} \text{ (dL g}^{-1}\text{)} \quad (10)$$

$$0.84 \times 10^5 \le M_w \le 14.8 \times 10^5 \text{ g mol}^{-1}$$

$$[\eta]^{25°C}_{BEN} = 1.00 \times 10^{-3} M_w^{0.504} \text{ (dL g}^{-1}\text{)} \quad (11)$$

$$0.135 \times 10^5 \le M_w \le 14.8 \times 10^5 \text{ g mol}^{-1}$$

where CYC = cyclohexane, HEP = *n*-heptane, and BEN = benzene. The coefficient r was ≥0.9990 for all three expressions. The lowest M_w samples were not used in calculating the power laws for PIB in cyclohexane and *n*-heptane, owing to the decrease of excluded volume[8,28,34-36] in the low-M_w regime.

Limiting values of the *z*-average translational diffusion coefficients, hydrodynamic radii, and diffusion virial coefficients are collected in Table III. Figure 2 shows D_z against M_w for PIB in the three solvents. The following expressions have been calculated:

$$D^{25°C}_{z,CYC} = 1.78 \times 10^{-4} M_w^{-0.572} \text{ (cm}^2 \text{ s}^{-1}\text{)} \quad (12)$$

$$1.33 \times 10^5 \le M_w \le 14.8 \times 10^5 \text{ g mol}^{-1}$$

$$D^{25°C}_{z,HEP} = 4.10 \times 10^{-4} M_w^{-0.560} \text{ (cm}^2 \text{ s}^{-1}\text{)} \quad (13)$$

$$0.64 \times 10^5 \le M_w \le 14.8 \times 10^5 \text{ g mol}^{-1}$$

$$D^{22.1°C}_{z,IAIV} = 5.94 \times 10^{-5} M_w^{-0.493} \text{ (cm}^2 \text{ s}^{-1}\text{)} \quad (14)$$

$$0.64 \times 10^5 \le M_w \le 14.8 \times 10^5 \text{ g mol}^{-1}$$

The term r was ≥0.9992 for all the power laws. Corresponding plots of R_H against M_w are given in Figure 3.

Discussion

Comparison of Previous Work. The second virial coefficients in cyclohexane (Table I) and those reported by Matsumoto et al.[9] for somewhat narrower distribution PIB fractions are plotted as a function of M_w in Figure 4. It was originally anticipated that the thermodynamic terms determined in this work, because of slightly greater polydispersity, would tend to larger values than those previously reported; however, the values in Table I are consistently smaller. The coefficients obtained for our unfractionated samples are generally observed to fall between the power laws of the two data sets (Figure 4). While we do not offer an explanation for this disagreement with the previous work, we do note that the trend in A_2 values for the fractionated and unfractionated chains (Table I) is consistent based on the sample polydispersities.

The second virial coefficients measured in *n*-heptane are plotted against M_w in Figure 5where the results from ref 9 are also shown. Contrary to the coefficients in cyclohexane, good agreement is noted in *n*-heptane.

The MHS expressions obtained in this work can be compared to the studies of Matsumoto et al.,[9] Krigbaum and Flory,[8] and Gundert and Wolf.[37,38] The power law for PIB in *n*-heptane (eq 10) is in good agreement with that reported in ref 9 ($[\eta] = 1.63 \times 10^{-4} M_w^{0.70}$). However, for PIB in cyclohexane and in benzene (Figure 6), the $[\eta]$ values of Table II are in accord with those measured by Gundert and Wolf[37,38] and Krigbaum and Flory[8] while somewhat smaller than those presented in ref 9. This disagreement may be directly related to the similar problem of the second virial coefficients in cyclohexane.

Polydispersity effects were not detected in correlating the cyclohexane-based limiting viscosity numbers (Table II) measured in the two laboratories (Exxon and UAB). Analysis of the data, including the unfractionated samples, in cyclohexane leads to

$$[\eta] = 1.35 \times 10^{-4} M_w^{0.739} \quad (15)$$

Comparison with eq 9 reveals only a slight decrease in the exponent. The term r was found to go from 0.9996 (eq 9) to 0.9995 (eq 15).

In passing, it is noted that correction of the MHS power law for PIB in benzene (near-Θ condition) with the Burchard–Stockmayer–Fixman[39,40] (BSF) extrapolation yields a K_Θ value in good agreement with that of Krigbaum and Flory[8] and Gundert and Wolf[38] (Table IV). Taking ϕ as

Table III
Translational Diffusion Coefficients, Hydrodynamic Radii, and Diffusion Virial Coefficients for Polyisobutylene

		cyclohexane, 25 °C			n-heptane, 25 °C			IAIV, 22.1 °C		
sample	$M_w \times 10^{-5}$, g mol^{-1}	$D_z \times 10^8$, cm^2 s^{-1}	R_H, nm	k_d, mL g^{-1}	$D_z \times 10^8$, cm^2 s^{-1}	R_H, nm	k_d, mL g^{-1}	$D_z \times 10^8$, cm^2 s^{-1}	R_H, nm	k_d, mL g^{-1}
3C	0.64				83.5	6.59	−3.7	24.8	6.45	−5.2
8PS	1.33	20.8	11.7	14				18.4	8.69	−19
9C	1.67	18.1	13.4	22						
12C	3.30	12.4	19.6	95	33.4	16.5	44	11.2	14.3	−36
15C	4.48	10.2	23.6	112				9.69	16.5	−53
17C	7.44	7.79	31.2	186	21.1	26.1	54	7.72	20.6	−77
19C	14.8	5.21	46.7	446	14.4	38.2	222	5.34	29.9	−237

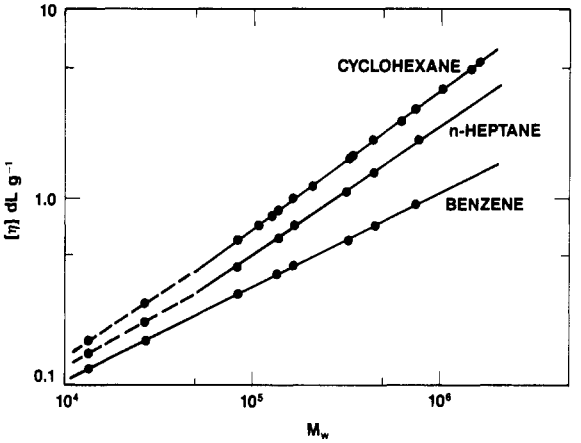

Figure 1. Intrinsic viscosity–molecular weight plots for PIB.

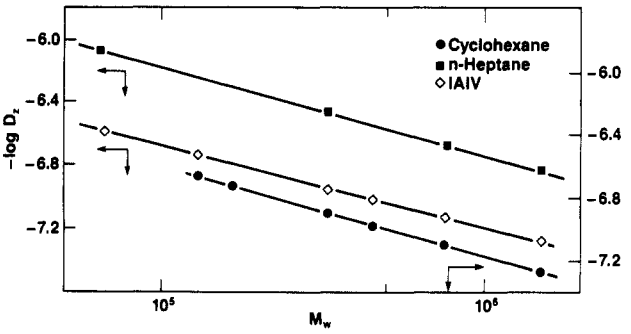

Figure 2. Diffusion coefficient–molecular weight plots for PIB.

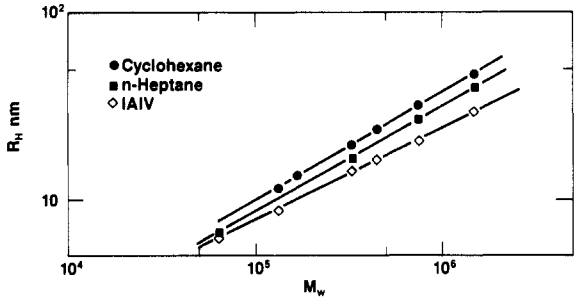

Figure 3. Hydrodynamic radii–molecular weight plots for PIB.

2.5×10^{21} [41,42] allows a determination of Flory's characteristic ratio, C_∞, by

$$C_\infty = \lim_{n\to\infty} \frac{\langle R^2\rangle_0}{nl^2} \tag{16}$$

Here $\langle R^2\rangle_0$ is the mean-square end-to-end distance of the Θ chain, n is the number of main-chain bonds, and l is the effective bond length (0.153 nm). The values of C_∞ (excluding the intrinsic viscosity based values on Fujita et al.[9,10]) range from 6.6 to 6.8. These are in excellent agreement with those calculated from the corrected four-state RIS model of Suter, Saiz, and Flory.[22] Concurrent with this agreement is the average experimental value[10,24-26]

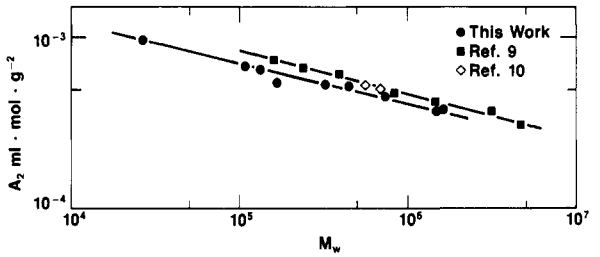

Figure 4. Virial coefficient–molecular weight plots for PIB in cyclohexane.

of ca. -0.2×10^3 deg^{-1} for d ln $\langle R^2\rangle_0/dT$, which agrees well with those calculated within the framework of the four-state RIS model.[22]

Transport Virial Coefficients. The Huggins coefficients (Table II) are slightly larger in cyclohexane than in n-heptane, although the differences are probably within experimental error (for the PIB–cyclohexane system, Gundert and Wolf[37] have reported values virtually identical with ours for k_H). This is somewhat surprising based on the larger second virial coefficients observed in cyclohexane. The k_H values in both solvents are, however, typical of those found for other chains in thermodynamically good solvents. As expected the k_H terms in benzene are larger than those determined in cyclohexane and in n-heptane. The Θ solvent values scale with M_w according to

$$k_{H,\Theta} = 0.233 M_w^{-0.095} \tag{17}$$

with $r = 0.967$. The molecular weight dependence of k_H, observed here as well as in previous studies,[43-45] makes comparison to existing theories, none of which predict a power law behavior, difficult. Forced averaging of the data yielded $k_{H,\Theta} = 0.738 \pm 0.11$. This quantity is, therefore, considered to be in good semiqualitative agreement with the theoretical efforts of Freed and Edwards[46] (0.757) and of Brinkman[47] (0.76). The experimental average is somewhat less than that calculated by Peterson and Fixman[48] (~0.9) but considerably larger than the value of $^1/_3$ recently reported by Perico, La Ferla, and Freed,[49] the latter quantity being typical of a polymer in a good solvent.

The diffusion virial coefficients of Table III are positive in the good solvents and negative in IAIV.[50] In all cases, the absolute value of k_d is an increasing function of $\bar{M}_w$. Taking v_2 as 1.09 mL g^{-1},[51] the frictional virial coefficient k_f can be calculated with eq 5b. In turn the reduced quantity k_f^* can be obtained[52] from

$$k_f^* = k_f(M/N_A V_H) \tag{18}$$

where N_A is Avogadro's number and V_H is the effective spherical hydrodynamic volume ($V_H = (4/3)\pi R_H^3$). The corresponding k_f^* values for the measurements in the three solvents are collected in Table V. The general trends in k_f^* are similar to those observed for the Huggins coeffi-

Table IV
Unperturbed Parameters for Polyisobutylene

method	solvent	$K_\Theta \times 10^3$,[a] g dL^{-1}	$\langle R^2\rangle_0/M$, $\times 10^3$ nm^2	C_∞	temp, °C	ref
intrinsic viscosity	IAIV[b]	1.14	5.92	7.1	22.1	9
	IANB[b]	1.16	5.99	7.2	28.0	10
	IABE[b]	1.13	5.89	7.0	23.7	10
	EH[b]	1.04[c]	5.57	6.7	38[c]	38
	benzene	1.23	6.23	7.5	22.8[d]	10
		1.12	5.87	7.0	25.0	9
		1.07	5.68	6.8	25.0	5, 8
		1.05	5.61	6.7	25.0	this work
light scattering	IAIV/IANB[b]		5.69	6.8	22.1/28.0	9, 10
neutron scattering	PIB-d_8		5.70	6.8[e]	RT	11, 12
	benzene-d_6		5.49	6.6	26.4	11, 12

[a] Via BSF extrapolation procedure. [b] IAIV = isoamyl isovalerate; IANB = isoamyl *n*-butyrate; IABE = isoamyl benzyl ether; EH = ethyl heptanoate. [c] Interpolated value (see the Appendix). [d] The PIB used in the work of ref 10 contained 1.6 mol % of isoprene. [e] The statistical segment length, a, for PIB is 0.56_3 nm; where $a^2 = 6R_G^2/N_2$ and N_w denotes the weight-average degree of polymerization.

Table V
Reduced Frictional Virial Coefficients of Polyisobutylene in Various Solvents

		k_f*		
sample	$M_w \times 10^{-5}$, g mol^{-1}	cyclohexane	*n*-heptane	IAIV
3C	0.64			0.4
8PS	1.33	5.16		1.5
9C	1.67	4.95		
12C	3.30	4.15	4.1	1.6
15C	4.48	4.59		2.1
17C	7.44	4.85	4.8	2.6
19C	14.8	3.50	4.6	5.3

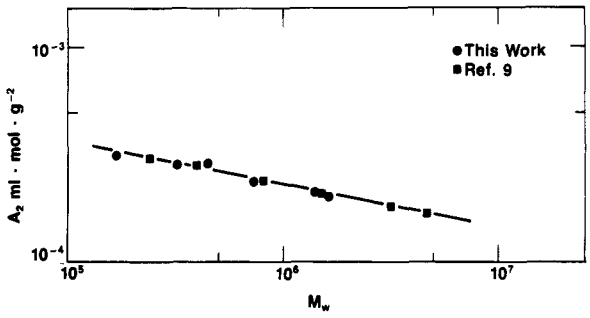

Figure 5. Virial coefficient–molecular weight plots for PIB in *n*-heptane.

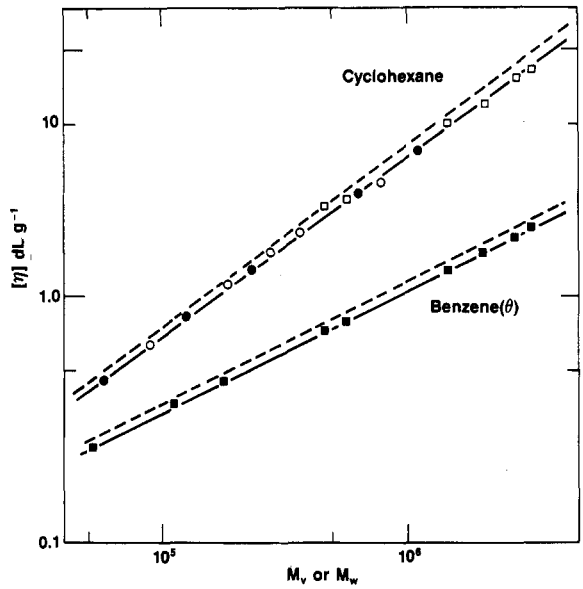

Figure 6. Intrinsic viscosity–molecular weight plots for PIB. Solid lines are based on eqs 9–11 while the dashed lines represent the data of Fujita et al.[9] The M_n data of refs 7 and 8 have been converted to M_w via the use of an M_w/M_n ratio of 1.1.

cients (Table II). The values of k_f*, like those of k_H, are essentially the same for PIB in cyclohexane and in *n*-heptane. Neglecting the highest molecular weight sample (19C) in the Θ solvent IAIV, the term k_f* is observed to increase with an increase in molecular weight. A similar trend is observed for k_H in benzene where the thermodynamic contribution to η_{sp}/c and therefore $[\eta]$ and k_H is negligible.

The k_f* terms in cyclohexane and *n*-heptane are in good agreement with those reported (4.8–5.2) for polyisoprene[53,54] and polybutadiene[55] in good solvents. These values are, however, less than the theoretical estimates of 7.16[56] and 6.36[57] and also less than the experimental results for polystyrene[52] (6.3) and poly(α-methylstyrene)[28] (7.0) in toluene.

Although not formally correct, an average of 2.25 (1.64 neglecting sample 2C) is obtained for k_f* in IAIV. This quantity is in reasonable agreement with that calculated by Yamakawa (2.34).[58] An increase of k_f* with increasing molecular weight has been reported for polybutadiene at high M_w under Θ conditions.[55]

Dilute-Solution Behavior of PIB. The strength of the excluded-volume interaction and the relative extent of solvent permeation on the behavior of PIB can be determined through the analysis of standard quantities and subsequent comparisons. From the data of Tables I–III the Mandelkern–Flory–Scheraga parameter β and the ratio π can be calculated via

$$\beta = (M[\eta]/100)^{1/3}/[\mathrm{f}]\ \mathrm{mol}^{-1/3} \tag{19}$$

and

$$\pi = A_2M/[\eta] \tag{20}$$

where the intrinsic frictional coefficient $[\mathrm{f}] = 6\pi R_H$ and $[\eta]$ is expressed in cubic centimeters per gram. The radius of gyration (R_G)–molecular weight power laws for PIB have been reported,[9,10] and are given by

$$R_G(\text{cyclohexane}) = 1.66 \times 10^{-2} M_w^{0.580}\ \mathrm{nm} \tag{21}$$

$$R_G(n\text{-heptane}) = 1.34 \times 10^{-2} M_w^{0.584}\ \mathrm{nm} \tag{22}$$

and

$$R_G(\text{IAIV}) = 3.08 \times 10^{-2} M_w^{0.500}\ \mathrm{nm} \tag{23}$$

where the expression for IAIV has been corrected to the Θ condition.[59] Further combination of the data reported in this work with that for R_G allows determination of the parameter ρ, the Flory–Fox viscosity term, ϕ, and the

Table VI
Solution Parameters for Polyisobutylene in Cyclohexane

sample	$M_w \times 10^{-5}$, g mol^{-1}	$\beta \times 10^{-6}$, mol$^{-1/3}$	ρ	$\phi \times 10^{23}$	ψ	π
8PS	1.33	2.19	1.33			1.02
9C	1.67	2.19	1.32			0.90
12C	3.30	2.21	1.35			1.03
14L	4.36			1.95	0.26	1.19
15C	4.48	2.16	1.32	2.00	0.25	1.12
16L	6.32			1.90	0.25	1.21
17C	7.45	2.23	1.37	1.96	0.24	1.13
18C	10.1			1.97	0.25	1.15
19C	14.8	2.16	1.34	1.89	0.24	1.15
20C	16.1			1.97	0.25	1.15
		2.19 ● 0.03	1.34 ± 0.02	1.95 ± 0.04	0.25 ± 0.01	NA

interpenetration function, ψ, by

$$\rho = R_G/R_H \tag{24}$$

$$\phi = [\eta]M/(6^{3/2}R_G{}^3) \tag{25}$$

and

$$\psi = A_2M^2/(4\pi^{3/2}N_AR_G{}^3) \tag{26}$$

All of the parameters are comprised of a static and a dynamic contribution except ψ, which is a purely static property. In this regard, it should be noted that the limiting viscosity number has been expressed as[60,61]

$$[\eta] \sim R_G{}^2R_H/M \tag{27}$$

and therefore reflects both contributions.

In a recent paper Freed et al.[62] analyzed the PIB data of Matsumoto et al.[9] and concluded, without diffusion results, that PIB in cyclohexane conforms to the least draining limit. (Here the term least draining limit is adopted to reflect the finite solvent permeation calculated for a chain at Θ.[63]) The consideration of the frictional properties of the macromolecule is, however, crucial for the analysis of draining since $[\eta]$ reflects mainly the static contribution (see eq 27) whereas [f] corresponds to the hydrodynamics only. The data reported in this work therefore allow a more stringent test of the renormalization group (RG) theory.

Calculated results for the parameters are collected in Table VI for PIB in cyclohexane and in Table VII for PIB in *n*-heptane and at the Θ condition. The quantities in Table VI are nearly constant with the exception of π, which initially increases at low molecular weights and levels off above $M_w = 4.36 \times 10^5$ g mol^{-1}. The lack of any discernible trend, albeit over a narrow range of molecular weight and for a limited number of samples, is believed to correspond to the self-avoiding (SA) limit.

This behavior is depicted graphically in Figures 7–9 where π, ψ, and ϕ/ϕ_0 are plotted against different representations of the radius of gyration expansion factor, $\alpha_G = R_G/R_{G_o}$ (subscript o denotes the Θ condition). The results for PIB in *n*-heptane are also shown. (The solid lines in all three figures denote the experimental averages.) Enhanced permeation of cyclohexane through the PIB coil is, based on Table VI and Figures 7–9, a minor effect.

A number of theoretical calculations have been reported for chains in the SA least draining limit. These include Douglas and Freed's[64] extension of the two-parameter theory using RG concepts, the numerical quadrature analysis of Barrett,[65] and the $1^1/_2$ order in excluded-volume dynamic RG theory developed by Oono.[66]

The average for π, 1.16, is similar to the theoretical values of Douglas and Freed, 1.10, Barrett, 1.167, and Oono, 1.196. Comparison of the mean for β, 2.19×10^6 mol$^{-1/3}$, reveals agreement with the work of Douglas and Freed, 2.16×10^6 mol$^{-1/3}$, but not with those values reported by Barrett or Oono (2.4×10^6 mol$^{-1/3}$ and 2.36×10^6 mol$^{-1/3}$, respectively). Some of the theoretical values for ψ are in good agreement with the experimental result of 0.25. In particular, the second-order RG theory of des Cloizeaux[67] predicts 0.269 while that of Douglas and Freed yields 0.268. Barrett's calculated value of 0.24 is also in accord with the experimental result. The only value that, within experimental error, does not agree with that reported here is the RG result of Oono (0.219).

Table VII
Solution Parameters for Polyisobutylene in *n*-Heptane and under Θ Conditions

sample	$M_w \times 10^{-5}$, g mol^{-1}	$\beta \times 10^{-6}$, mol$^{-1/3}$	ρ	$\phi \times 10^{23}$	ψ	π
		n-Heptane				
3C	0.64		1.31			
12C	3.30		1.36			0.87
15C	4.48			2.15	0.22	0.94
17C	7.45	2.35	1.39	2.20	0.20	0.84
19C	14.8	2.31	1.41	1.97	0.23	1.01
		Θ Conditions[a]				
3C	0.64		1.19			
8PS	1.33		1.28			
9C	1.67	2.19				
12C	3.30	2.15	1.22			
15C	4.48	2.16	1.22	2.51		
17C	7.45	2.18	1.22	2.61		
19C	14.8	2.17	1.22	2.54		

[a] IAIV, 22.1 °C. Benzene, 25 °C.

The ρ values in Table VI are smaller than those determined either from the literature or through experiment for polystyrene in benzene, toluene, and ethylbenzene or for poly(α-methylstyrene) in toluene.[68] The experimental result of 1.35 is similar to that, 1.39, reported for polyisoprene[50,51] and polybutadiene,[55] therefore implying that ρ depends on the intrinsic stiffness or flexibility of the chain along with the extent of draining.

The theoretical values of ρ 1.50,[64] 1.64,[65] and 1.56[66] are considerably larger than the result obtained here and reflect, in part, the preaveraging approximation involved in the calculation of D_T (Kirkwood–Riseman theory). Zimm[41] and Garcia de la Torre et al.[69] have, for chains at Θ, calculated errors of 13 and 14%, respectively. Wang et al.[70] estimate a necessary correction of 26% for a Gaussian chain and 16% for a chain in the SA limit in qualitative agreement with the simulations cited above. Other possible factors that may be responsible for the disagreement between theory and experiment are the rigid-body assumption in the K–R theory[71] and internal friction.[72] Fixman has noted that an increase in ρ over that obtained at $T = \Theta$ cannot be predicted unless the internal friction contribution is incorporated. By this interpretation, therefore, the PIB chains exhibit some draining.

An average for ϕ/ϕ_0 of 0.77 is calculated here from the experimental results. The ϕ_0 value of 2.55×10^{23} (Table VII) is in accord with the Monte Carlo simulation of Zimm[41]

Table VIII
Size Parameters for Polyisobutylene[a]

		cyclohexane, 25 °C			*n*-heptane, 25 °C				Θ conditions			
sample	$M_w \times 10^{-5}$, g mol^{-1}	R_G[b]	R_H	R_V	R_T	R_G[c]	R_H	R_V	R_T	R_G[d]	R_H	R_V
3C	0.64	10.2		7.86		8.59	6.59			7.79	6.45	
8PS	1.33	15.6	11.7	12.1	10.4					11.2	8.69	9.40
9C	1.67	17.8	13.4	13.9	11.5							10.5
12C	3.30	26.4	19.6	20.6	17.8	22.4	16.5	17.7		17.7	14.3	14.6
15C	4.48	31.5	23.6	24.5	21.8					20.6	16.5	17.7
17C	7.45	42.2	31.2	32.7	29.2	36.0	26.1	29.0	23.4	26.6	20.6	22.2
19C	14.8	62.9	46.7	48.4	43.3	53.8	38.2	41.7	36.4	37.5	29.9	31.1

[a] Size parameter units in nanometers. [b] Via eq 20. [c] Via eq 21. [d] Via eq 22.

Table IX
Power Law Relationships for Polyisobutylene Size Parameters

size	cyclohexane		*n*-heptane		Θ condition[a]	
param, nm	$K \times 10^{-2}$	α	$K \times 10^{-2}$	α	$K \times 10^{-2}$	α
R_G[b]	1.66	0.580	1.34	0.584	3.08	0.500
R_H	1.38	0.572	1.38	0.560	2.49	0.500
R_V[c]	1.29	0.580	1.35	0.566	2.54	0.500
R_T[c]	0.850	0.601	0.672	0.604		

[a] Θ condition expressions were derived by using the Burchard–Stockmayer–Fixman and Baumann extrapolation procedures. [b] Reference 9. [c] Based on $[\eta]$ and A_2 values for fractionated samples (Table I).

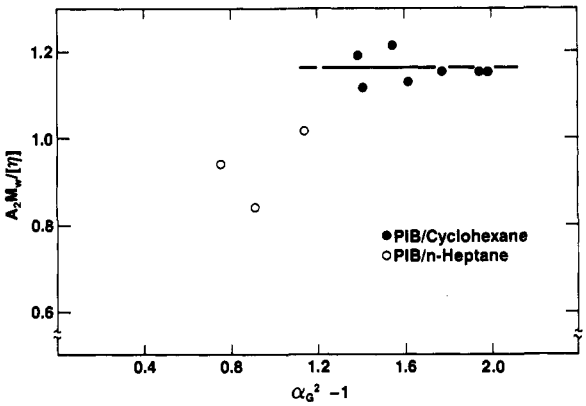

Figure 7. Plot of $A_2M_w/[\eta]$ against $\alpha_G^2 - 1$ where α_G^2 is the expansion factor for the root-mean-square radius of gyration.

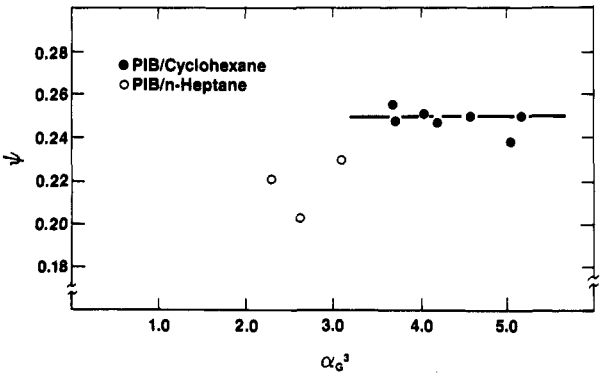

Figure 8. Plot of ψ against α_G^3.

and the experimental results for a number of flexible chains at Θ.[42,66] The mean for ϕ/ϕ_0 lies between the calculations of Rey et al.[73] (0.87) and Freed and Douglas[64] (0.87) and that reported by Oono[66] (0.707). Barrett's calculations[65] yield $\phi/\phi_0 = 0.66$, which is considerably lower than the experimental result.

Further evidence supporting the premise that PIB in cyclohexane conforms to the SA least draining limit is contained in the power law exponents. Representation of the Einstein expression followed by linear regression of the equivalent radius, R_V, as a function of M_w yielded an

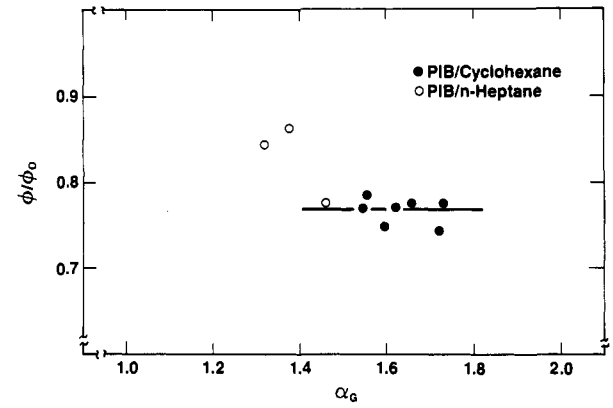

Figure 9. Plot of the universal ratio ϕ/ϕ_0 against the expansion factor for the radius of gyration.

exponent of 0.58. A slightly larger exponent of 0.601 was calculated from the thermodynamic radii, R_T, data, obtained from the reported second virial coefficients of Table I. The exponents are similar to that obtained by Matsumoto et al.[9] (eq 20). A theoretical value of 0.588 has been reported for the SA least draining limit.[74]

As noted previously the existence of the diffusion data allows a direct comparison to the RG theory of Wang et al.[61] One of the theoretical predictions is that the ratio $\alpha_\eta^3/\alpha_G^2\alpha_H$ where α_η and α_H are the expansion factors for the intrinsic viscosity, $[\eta]/[\eta]_0$, and hydrodynamic radius, R_H/R_{H_0}, respectively, is a universal (non-system-specific) constant, independent of the extent of draining, and equal to 0.888. The average experimental value observed here is 0.845, which is in good agreement. A second prediction of the theory is that the strength of the excluded volume and that of draining can be qualified through analysis of the power law exponents. The MHS exponent a is represented by

$$a = 2\nu_G\lambda_2 - 1 + \nu_H \tag{28}$$

where ν_G and ν_H are the radius of gyration–M_w and hydrodynamic radius–M_w powers and λ_2 is a phenomenological excluded-volume parameter representable in terms of Z. The power ν_H is given by

$$\nu_H = 1/2 + [(2\nu_G - 1)/2]\lambda_2\lambda_{\xi D} \tag{29}$$

here $\lambda_{\xi D}$ is an associated parameter that describes the extent of draining. The term λ_2 varies between 0 at the Θ state and 1 at the SA limit while $\lambda_{\xi D}$ equals 1 in the SA least draining limit and decreases with increasing draining. By use of eqs 9, 12, and 21, λ_2 was found to equal 1.0 and λ_D was determined as 0.85. The latter quantity seems to indicate weak draining. It should be noted that if the extent of permeation is large those ratios from eqs 19, 20, 24, and 25 would vary with molecular weight. Further comparison of the two phenomenological parameters for PIB with several other flexible linear chains will be reported elsewhere.[68]

Taken together, the results for PIB in cyclohexane indicate that the chains behave as self-avoiding least

Table X
Size Ratios for Polyisobutylene[a]

model/polymer–solvent syst	R_T/R_G	R_T/R_H	R_H/R_G	R_V/R_G	R_V/R_H	ref
hard sphere	1.29	1.00	1.29	1.29	1.00	72
unperturbed Gaussian coil			0.81	0.82	1.02	62
PIB/Θ			0.81	0.82	1.02	this work
self-avoiding random walk	0.66	1.04	0.64	0.73	1.14	62
PIB/cyclohexane	0.67–0.72	0.88–0.95	0.76–0.72	0.78–0.76	1.02–1.05	this work
PIB/*n*-heptane	0.63–0.67	0.80–0.95	0.78–0.71	0.82–0.76	1.05–1.08	this work

[a] Over the M_w range of 10^5–5×10^6.

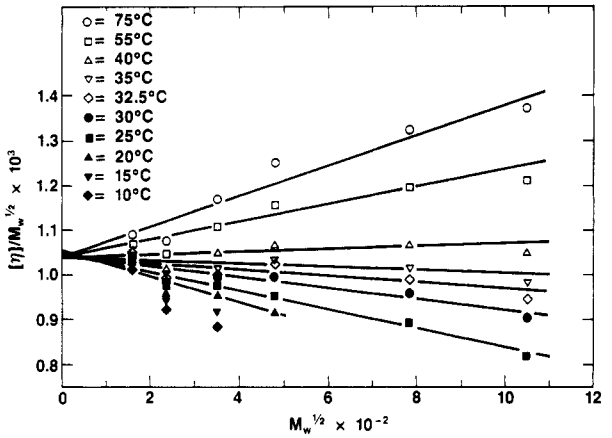

Figure 10. Burchard–Stockmayer–Fixman plot for PIB in ethyl heptanoate. Data used are from ref 38.

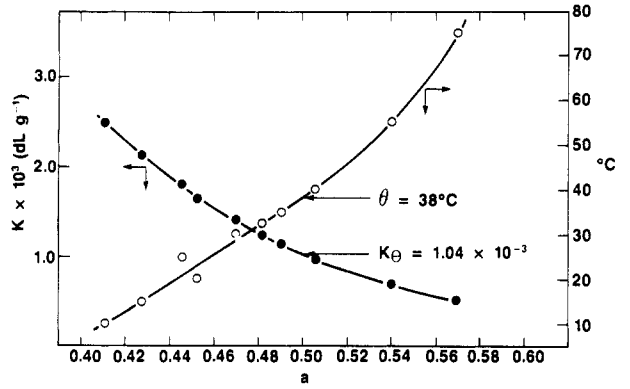

Figure 11. Mark–Houwink–Sakurada exponent plotted as a function of K_Θ and temperature for PIB in ethyl heptanoate. Data are from ref 38.

draining coils. Although the values of ρ and $\lambda_{\xi D}$ imply some draining, the constant nature of all of the other parameters implies the absence of a significant draining effect. This assignment is independent of the comparison to theory; however, fair agreement with the theory of Douglas and Freed[64] is observed.

Close examination of Tables VI and VII reveals some unusual factors in comparing the results for PIB in cyclohexane and in *n*-heptane. The parameters π, ϕ, and ψ take on smaller values in *n*-heptane typical of a chain in an intermediate solvent. The factors β and ρ are, however, larger in *n*-heptane than in cyclohexane. This is a curious result, and recent studies on solutions of polystyrene and poly(α-methylstyrene) in *n*-butyl chloride exhibit similar increases in ρ and β when compared to polystyrene in benzene.[75] One explanation for this behavior is that the frictional and static properties of the coil scale with solvent power differently.[59] Without additional data it seems premature to fully consider the behavior of both ρ and β in *n*-heptane.

In closing this discussion, we note that the average value of ρ in IAIV, once eq 14 is corrected to true Θ conditions, is equal to 1.22. This quantity is somewhat less than the ρ ratio calculated from examination of the literature data for polystyrene in cyclohexane 1.28[76] and may reflect differences in the ternary interaction[77] of the two systems at Θ. Alternatively, the recent theory of Yamakawa[78] predicts a decrease in ρ with an increase in chain flexibility. On the basis of the characteristic ratios for polystyrene, 10.7 (at 34.5 °C) and that for PIB, 6.7, the smaller ρ for PIB is understandable. Further comparison of the ρ values for a variety of linear chains with the theory will be reported in due course.[68]

Acknowledgment. We thank Dr. H. C. Wang, Exxon Chemicals, for providing PIB samples 10L, 13L, and 16L. We also thank Dr. J. Douglas of NIST for comments on any early draft of this work.

Appendix

PIB Chain Dimensions. The size radii R_V and R_T can be calculated from the experimental values of $[\eta]$ and A_2, respectively. The essential ansatz upon which these calculations are based is that flexible polymer chains in dilute solution can be approximately modeled as hard spheres of volume V. Thus

$$[\eta] = (5/2)N_A V/M \tag{A1}$$

$$A_2 = 4N_A V/M^2 \tag{A2}$$

These expressions lead directly to

$$R_V = 5.41 \times 10^{-9}(M[\eta])^{1/3} \tag{A3}$$

$$R_T = 4.63 \times 10^{-9}(M^2 A_2)^{1/3} \tag{A4}$$

These calculated radii along with those of R_G and R_H are given in Table VIII for samples for which R_H is available in one or more solvents. Via the use of all of the available data, the various power law relationships emerge (Table IX). From the use of these power law relationships the size ratios such as R_T/R_H, R_V/R_H, etc., can be calculated. The results of this exercise are given in Table X. The Θ condition results for PIB show good agreement with the predictions of Oono,[66] although, with the exception of the R_T/R_G ratio, less satisfactory agreement is found for the good-solvent case.

Gundert and Wolf[38] have presented a considerable amount of intrinsic viscosity data in ethyl heptanoate over the temperature range of 10–75 °C (Figure 10). Their data, Figure 11, yield a K_Θ of 1.05×10^{-3}, a value in agreement with that of Fox and Flory[5,8] and our work. These findings yield a C_∞ of 6.8, which agrees with that deduced from the Θ-temperature light scattering results of Fujita et al.[9,10] and the neutron scattering findings[11,12] (Table IV). Conversely, the intrinsic Θ-condition viscosity data of Fujita et al.[9,10] yield values of C_∞ that range from 7.0 to 7.5. We have no explanation for this discrepancy.

The intrinsic viscosity PIB results of Gundert and Wolf[38] yield a Θ temperature of 38 °C (Figure 11) for the PIB–

ethyl heptanoate system. This value is in accord with the estimate available from their reported[38] temperature dependence of A_2.

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