[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Intrinsic Viscosity–Temperature Relationships for Polyisobutylene in Various Solvents[1]

BY T. G FOX, JR.,[2] AND P. J. FLORY

Intrinsic viscosities of polyisobutylene fractions ($M = 1.8 \times 10^5$ to 1.88×10^6) have been determined in various pure solvents, and in several solvent mixtures also, over wide temperature ranges. The measurements have been corrected to zero rate of shear in addition to the usual extrapolation to infinite dilution. The results provide a rigorous test of the recent theory relating the intrinsic viscosity to polymer chain structure and to thermodynamic parameters governing the interaction between polymer and solvent. Theory applies quantitatively within the limit of the experimental error in the results. The parameter K in the equation $[\eta] = KM^{1/2}\alpha^3$ is the same in different solvents, but decreases somewhat with temperature (1.08×10^{-3} at 24° to 0.91×10^{-3} at 105°). For poor solvents the value of Θ in the equation $\alpha^5 - \alpha^3 = 2\psi_1 C_M \cdot (1 - \Theta/T)M^{1/2}$ agrees with the independently determined critical miscibility temperature for $M = \infty$. The entropy of dilution parameter ψ_1 varies over a fourfold range for different solvents, contrary to current theories of non-polar mixtures.

The constant Φ in the relationship $K = \Phi(\overline{r_0^2}/M)^{3/2}$ has the approximate value 2.1×10^{21}, which should be the same for all polymers. The root-mean-square end-to-end distance $\sqrt{\overline{r_0^2}}$ unperturbed by intramolecular interactions (other than hindrance to free rotation) for a polyisobutylene molecule with $M = 10^6$ is computed to be 795 Å. at 25°. This is appreciably greater than the length, 412 Å., calculated for free rotation. In cyclohexane, a good solvent, $\alpha = 1.54$ and $\sqrt{\overline{r_0^2}} = 1225$ Å.

Introduction

The dependence of the intrinsic viscosity of a polymer solution on polymer–solvent interaction and on inherent structural features affecting the chain configuration has been discussed in preceding papers.[3,4,5] In particular, it has been shown from theoretical considerations that the intrinsic viscosity should depend on the molecular weight M, temperature T and solvent type in accordance with the relationships

$$[\eta] = KM^{1/2}\alpha^3 \tag{1}$$

and

$$\alpha^5 - \alpha^3 = 2\psi_1 C_M(1 - \Theta/T)M^{1/2} \tag{2}$$

The quantities occurring in these equations are defined in a preceding paper.[5] A preliminary investigation[4] of intrinsic viscosities of polyisobutylene fractions in several solvents confirmed the adequacy of these relationships over wide ranges in molecular weight and temperature.

In the work reported in this paper, equations (1) and (2) have been subjected to more rigorous experimental test with the aid of more accurate measurements of intrinsic viscosities in a greater variety of solvents over wide ranges of temperature. The relationships established in the preceding paper[6] have been employed in order to extrapolate the viscosity measurements to zero shear rate. This is important when measurements made in the same viscometer at different temperatures are to be compared, owing to the increase in rate of shear as the absolute viscosity of the solution is decreased with rise in temperature. Critical miscibility measurements leading to the independent determination of Θ also have been carried out. The parameters occurring in equations (1) and (2) have been evaluated for various solvents according to the methods discussed previously.[5]

Experimental

Materials.—Three polyisobutylenes were fractionated by the addition of acetone to their benzene solutions at 30°,[4] and five of the fractions so prepared were selected for the work reported here (Table I). Viscosity average molecular weights $\bar{M}_v$ were calculated from the intrinsic viscosities in the solvents listed in Table I by the equation

$$[\eta] = K'\bar{M}_v^a \tag{3}$$

where the respective values of K' and a have been reported elsewhere.[4] Viscosity–temperature relationships were obtained for three of these fractions; for these the tabulated values of $\bar{M}_v^{1/2}$ are precise to ±2%.

TABLE I

POLYISOBUTYLENE FRACTIONS

Designation	% of whole polymer	$\bar{M}_v$	$\bar{M}_v^{1/2}$	Solvents employed in mol. wt. detn.
250-2	..	(15,000,000)	..	C_6H_{12}(40°)
PB5F1	23	1,880,000	1371	C_6H_{12}(30°); DIB(20°); C_6H_6(25°)
PB5F2	12	1,460,000	1210	C_6H_{12}(30°); DIB(20°); C_6H_6(25°)
PB3F2	18	180,000	424	C_6H_6(25°)
PB3F4	2	54,000	..	CCl_4(30°)

The solvents employed were of high purity. They were distilled and dried over anhydrous magnesium sulfate before use.

Viscosity Determinations.—Two Ubbelohde viscometers having efflux times for water at 20° of 100 and 250 sec., respectively, were calibrated for the kinetic energy correction term.[7] Solutions were prepared by weighing the polymer in a 50- or 100-ml. flask and diluting at a known temperature, the concentration c, in grams/100 ml., being calculated at other temperatures from the expansion coefficient of the solvent. The solutions were filtered into the viscometer through a medium sintered glass filter. Efflux times, which were measured with an accurate electric timer reading to 0.0001 minute, were generally reproducible to ±0.001 minute. Viscosities of a given solution were measured at several temperatures with the aid of a series of constant temperature water-baths each controlled to ± 0.01° at the desired temperature. Duplicate measurements on a given solution at the lowest temperature made before and after the observations at higher temperatures were in good agreement. In those poor solvents wherein the polymer was kept at high temperatures for as much as several days, it was necessary to add a small amount (0.05 g./100 ml.) of phenyl-

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[1] This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

[2] Rohm and Haas Company, Inc., Philadelphia, Pa.

[3] P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

[4] T. G Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949).

[5] P. J. Flory and T. G Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

[6] T. G Fox, Jr., J. C. Fox and P. J. Flory, *ibid.*, **73**, 1901 (1951).

[7] A. S. T. M. Designation D445-39T.

β-naphthylamine in order to prevent degradation of the polymer. Extrapolation of the specific viscosity η_{sp} to zero rate of shear was accomplished in each case from the actual rate of shear, calculated from the dimensions of the viscometer and the viscosity of the solution, and the relationships of the previous paper.[6] The magnitude of this correction at infinite dilution is indicated in each case in Table II.

Determination of Precipitation Temperatures.—The critical temperature T_c for complete miscibility in a given solvent should depend on the molecular weight of the polymer as

$$\Theta/T_c = (1 + \sqrt{x})^2/x \qquad (4)$$

where x represents the ratio of the molar volumes of polymer and solvent according to the theory of polymer solutions published some years ago.[8] Expanding in series and replacing x with $M\bar{v}/\mathrm{v}_1$ where $\bar{v}$ is the specific volume of the polymer and v_1 is the molar volume of the solvent

$$T_c \cong \Theta(1 - b/M^{1/2}) \qquad (4')$$

where $b = 2(\mathrm{v}_1/\bar{v})^{1/2}$ according to equation (4). Introduction of the arbitrary entropy parameter ψ_1 should not affect the form of (4′), although it will alter the value of b. However, it is sufficient here to treat b merely as an empirical parameter. The desired quantity, Θ, is obtained as the intercept in the plot of T_c *vs.* $M^{-1/2}$.

The critical precipitation temperature for a polyisobutylene fraction in a chosen solvent, or solvent mixture, was determined by preparing several solutions at concentrations in the vicinity of the theoretical critical volume fraction of polymer: v_2 (crit.) $= 1/x^{1/2}$.[8] The temperature at which the stirred solution became turbid on slow cooling was recorded for each concentration. Since the precipitation temperature is relatively insensitive to concentration in this range, the maximum temperature T_c for the co-existence of two phases was obtained with adequate precision ($\pm 0.3°$) from measurements at several concentrations. Results for a solvent mixture consisting of three parts by volume of ethylbenzene and one of diphenyl ether are shown in Fig. 1. The predicted linear relationship between T_c and $M^{-1/2}$ is confirmed. From the intercept and slope of the line, Θ = 300.0 °K., or 26.8°C., and b = 13. Other values for Θ given in Table III and in the second column of Table IV were obtained for the fraction

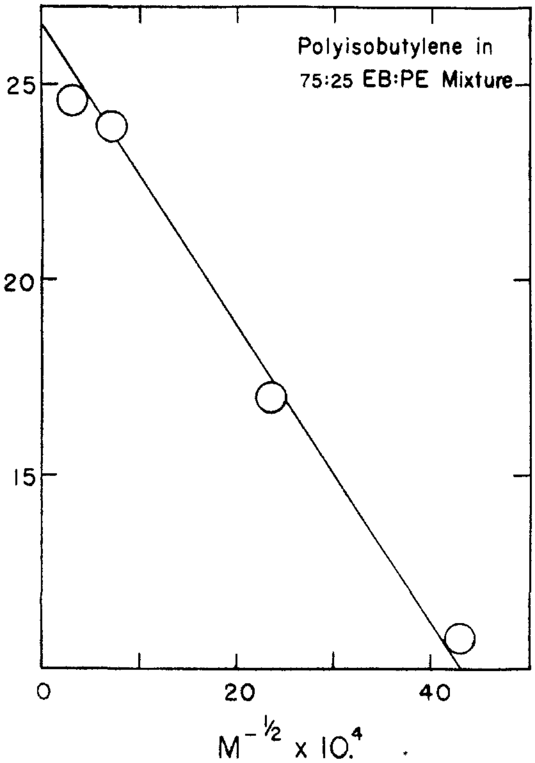

Fig. 1.—A plot illustrating the observed dependence on molecular weight of the critical temperature for miscibility of polyisobutylene fractions in a 3-1 mixture of ethylbenzene and diphenyl ether.

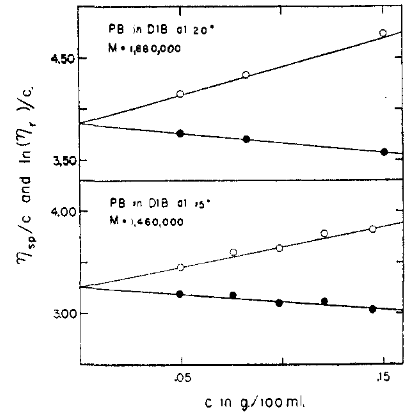

Fig. 2.—Solution viscosity-concentration relationships for polyisobutylene fractions in diisobutylene: the open circles and the closed circles represent η_{sp}/c and $(\ln \eta_r)/c$, respectively.

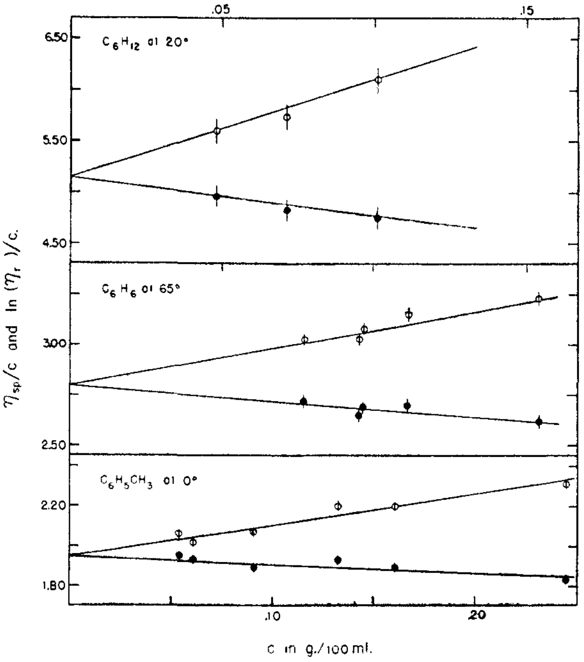

Fig. 3.—The dependence of η_{sp}/c (open circles) and $(\ln \eta_r)/c$ (closed circles) on concentration for a polyisobutylene fraction of M = 1,460,000 in various solvents.

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[8] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942). Equation (4) corresponds to (24) of this reference with K (critical) replaced by $2B\mathrm{v}_1/RT_c = 2\Theta/T_c$.

TABLE II

INTRINSIC VISCOSITY-TEMPERATURE RELATIONSHIPS

Solvent	T, °C.	Corrn. in $[\eta]$ on extrapn. to zero rate of shear, %	k	$[\eta]$, Obsd.	$[\eta]$ Calcd.
	PB5F1, M = 1,880,000				
Benzene	25	0.32	0.47	1.58	1.55
	35	0.69	.375	2.26	2.25
	50	1.41	.35	2.93	2.89
	65	2.20	.35	3.39	3.34
Ethylbenzene	0	0.58	0.375	2.63	2.66
	30	1.32	.375	3.35	3.40
	50	1.99	.375	3.68	3.67
	75	2.85	.375	3.97	3.95
Diisobutylene	20	1.67	0.37	3.86	3.91
	45	2.16	.37	3.85	3.81
	60	2.47	.37	3.83	3.83
	85	3.01	.37	3.70	3.73
75:25[a]	25	0.19	Curved	1.32	1.37
EB:PE	26	.19	Curved	(1.43)	1.45
	45	.73	0.40	2.34	2.40
	65	1.40	0.40	2.89	2.96
50:50[a]	71.5	0.20	Curved	1.36	1.38
EB:PE	74	.20	Curved	(1.55)	1.55
	85	.52	0.40	2.06	2.11
Phenetole	86	.24	Curved	1.25	
Anisole	105.5	.30	Curved	1.25	
	PB5F2, M = 1,460,000				
Benzene	25	0.40	0.47	1.37	1.37
	35	0.79	.375	1.90	1.92
	50	1.60	.35	2.51	2.44
	65	2.28	.35	2.80	2.82
Cyclohexane	20	3.13	.36	5.15	5.13
	30	3.67	.36	5.15	5.13
	45	4.55	.36	5.15	5.11
	60	5.50	.36	5.15	5.14
Toluene	0	0.66	0.375	1.97	1.98
	20	1.44	.34	2.56	2.59
	40	2.39	.34	3.00	2.96
	60	3.35	.34	3.25	3.24
	85	4.51	.34	3.45	3.48
Diisobutylene	15	1.88	0.37	3.26	3.27
	30	2.22	.37	3.25	3.25
	45	2.57	.37	3.24	3.21
	60	2.92	.37	3.05	3.11
n-Heptane	0	2.00	0.34	3.22	3.18
	25	2.59	.34	3.18	3.12
	50	3.20	.34	2.97	3.01
	80	3.97	.34	2.88	2.93
Triptane	0	1.56	0.34	3.60	3.56
	25	2.23	.34	3.53	3.48
	50	2.50	.34	3.28	3.38
	65	3.08	.34	3.31	3.32
n-Hexadecane	25	0.24	0.34	2.52	2.53
	50	.40	.34	2.54	2.53
	75	.58	.34	2.53	2.54
	100	.78	.34	2.50	2.55
	PB3F2, M = 180,000				
Benzene	18	0.20	Curved	0.39	0.38
	20	.21	Curved	$.40_5$	$.40_5$
	22	.24	Curved	.42	.43
	24	.27	0.50	.45	.45
	45	.62	.35	.59	.60
	65	.95	.35	.68	.68

[a] Parts by volume of ethylbenzene (EB) and phenyl ether (PE), respectively.

of highest molecular weight (1,880,000) assuming values of b corresponding to that given above.[9]

Results

Dependence of the Specific Viscosity on Concentration.—For each combination of polymer fraction, solvent and temperature, viscosities were measured at several concentrations so chosen as to yield relative viscosities η_r in the range from 1.1 to 1.6. After correction to zero rate of shear,[6] both η_{sp}/c and $(\ln \eta_r)/c$ were plotted against concentration as illustrated by the examples shown in Figs. 2 and 3. The intrinsic viscosity was taken as the common ordinate intercept for the straight lines drawn through the two sets of points; their slopes are related to one another in accordance with the mutually related equations[10]

$$\eta_{sp}/c = [\eta] + k[\eta]^2c \qquad (5)$$

$$(\ln \eta_r)/c = [\eta] - (0.50 - k)[\eta]^2c \qquad (5')$$

where k is a constant characteristic of the given solvent–polymer pair and independent of the molecular weight of the latter. Values found for k are included in Table II. In good solvents these plots are linear, k is about 0.34 to 0.40, and the uncertainty in the intrinsic viscosity introduced by extrapolation does not exceed ± 1%. In poor solvents at temperatures near Θ the value of k increases, and in many cases the plots become curved as illustrated in Fig. 4; the uncertainty in the extrapolation arising from curvature may introduce an error as great as ± 4% in the intrinsic viscosity. Instances in which curvature was observed are indicated in Table II.

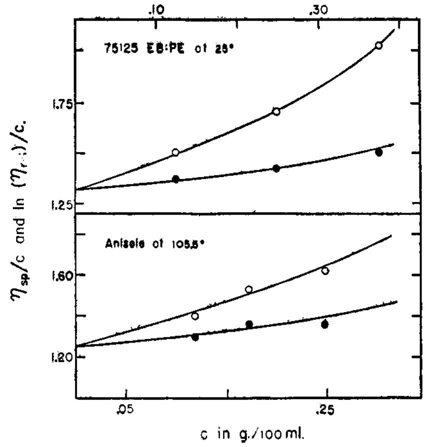

Fig. 4.—The dependence of η_{sp}/c (open circles) and $(\ln \eta_r)/c$ (closed circles) on concentration for solution of a polyisobutylene fraction of M = 1,880,000 at T = Θ in two solvents. (Although the data for anisole could be represented by two straight lines, the sum of their slopes would not equal the required value of 0.5.)

The intrinsic viscosities are presented in Table II and representative plots of $[\eta]$ *vs.* T are shown in Figs. 5 and 6.

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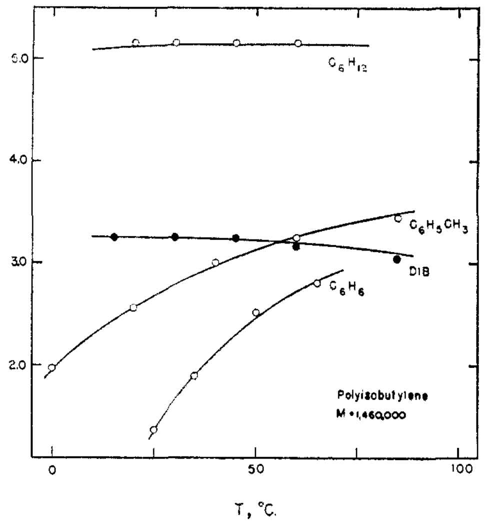
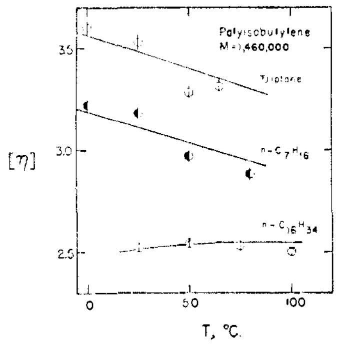
[9] Further work, as yet unpublished, shows that values of b are roughly the same for different solvents which do not differ too greatly in molar volume. Hence, the above procedure, involving extrapolations of only about 2°, is adequate for ascertaining values of Θ which are correct within ±1°.

[10] M. L. Huggins, THIS JOURNAL, 64, 2716 (1942).





Figs. 5, 6.—[η]–T relationships for a polyisobutylene fraction of M = 1,460,000 in several solvents. The experimental data are given by the circles; the curves represent the theoretical relationships expressed in equations (1) and (2).

Determination of Primary Parameters.—Intrinsic viscosities in various solvents interpolated to $T = \Theta$ in each case are given in Table III. Values of K calculated as the ratio of these intrinsic viscosities to the square root of the molecular weight[5] are given in the last column. Confirming theoretical predictions, K appears to be independent of M and of the solvent at a given temperature. Aside from the unexplained anomalous result for the 50:50 ethylbenzene–diphenyl ether mixture, a decrease in K with increase in temperature is indicated.

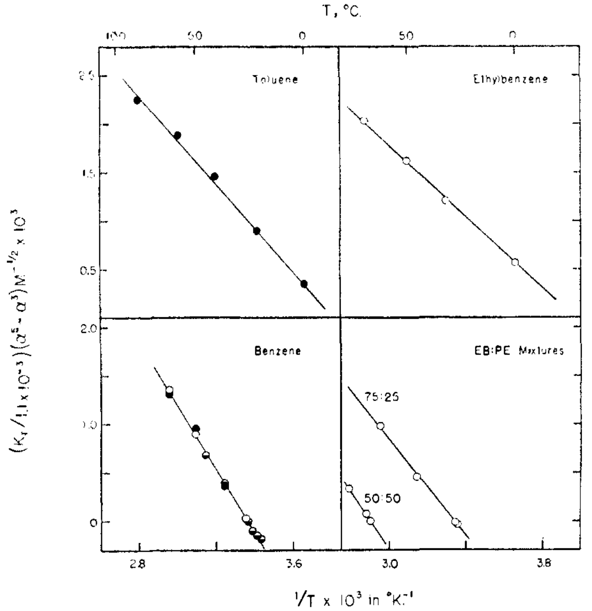
Table III

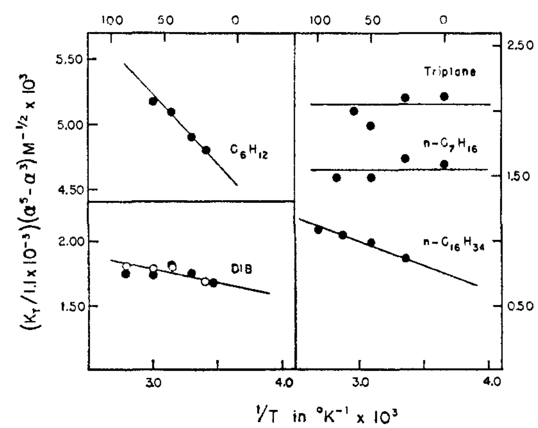
Values of K Determined in Various Solvents

Solvent	Θ, °C.	Polymer	[η] at $T = \Theta$	$K \times 10^3$
Benzene	24	PB5F1	1.48[a]	1.08 ± 0.02
		PB5F2	1.28[a]	1.06 ± 0.03
		PB3F2	0.45	1.06 ± 0.04
75:25 EB:PE	26.8	PB5F1	1.49[a]	1.08 ± 0.04
50:50 EB:PE	76	PB5F1	1.61[a]	1.17
Phenetole	86	PB5F1	1.25	0.91 ± 0.05
Anisole	105.5	PB5F1	1.25	0.91 ± 0.05

[a] Interpolated or extrapolated from the data of Table II.

For the purpose of calculating values of α, the small decrease in K with temperature was assumed to be linear; values of 1.10×10^{-3} and 0.93×10^{-3} were assigned for 0 and 100°, respectively. The α for each polymer–solvent–temperature combination was calculated from the intrinsic viscosity using equation (1) and the linearly interpolated value of K at the temperature T, which we will designate as K_T. The parameters Θ and $\psi_1 C_M$ (for C_M at 0°) were then evaluated according to the procedure previously outlined[5] by plotting $(K_T/1.10 \times 10^{-3})\ (\alpha^5 - \alpha^3)/M^{1/2}$ against $1/T$. In Figs. 7 and 8 these plots are observed to be accurately linear, and data for fractions of different molecular weight in the same solvent fall on the same straight line in conformity with theory. The values of Θ and $\psi_1 C_M$ (at 0°) deduced from the intercepts and slopes of these lines are given in Table IV. The intrinsic viscosities included in the last column of Table II have been calculated, using equations (1) and (2), from these parameters and K as specified above





Figs. 7, 8.—Plots of $(K_T/1.1 \times 10^{-3})(\alpha^5 - \alpha^3)M^{-1/2}$ vs. $1/T$ for polyisobutylene fractions in various solvents. The data for fractions with molecular weight of 1,880,000, 1,460,000 and 180,000 are represented by the open, closed and half-closed circles, respectively.

(assuming that C_M changes inversely as K with temperature[5]). The agreement with the observed values is excellent.

TABLE IV

VALUES OF INTERACTION PARAMETERS

Solvent	Θ °K. From pptn. measurement	Θ °K. From $[\eta] - T$ data	100 $\psi_1 C_M$ at 0°C.	$\psi_1 C_M v_1$ at 25°C.
Benzene	297	297	0.55	0.51
Cyclohexane	...	126	.42	.47
Toluene	260	261	.43	.48
Ethylbenzene	249	251	.37	.47
75:25 EB:PE	300	299	.42	.58
50:50 EB:PE	349	344	.48	.70
Diisobutylene	...	84	.12	.19
n-Heptane	...	0	.08	.12
Triptane	...	0	.10	.16
n-Hexadecane	...	175	.11	.32
Anisole	377	...	..	..
Phenetole	357	...	..	..
Phenyl ether	421	...	..	..
Ethyl heptylate[a]	306	...	..	(0.1–0.15)
Ethyl caproate[a]	330	...	..	(0.1–0.15)

[a] The parameters for these solvents are only approximate.

Discussion

The results presented above demonstrate that the theory embodied in equations (1) and (2) is adequate for the representation of the temperature dependence of the intrinsic viscosity of polyisobutylene in a wide variety of solvents. In fact, there is no indication of any systematic deviation exceeding the experimental error. The ability of these relationships to account for the dependence of the intrinsic viscosity on molecular weight over a wide range was established in a previous investigation.[4] This is implicit also in the plots of Figs. 7 and 8, where data for polymers of different molecular weight are superimposed. In particular, these results again emphasize that K is independent of M and the solvent (at a given temperature) within experimental error. It follows that Φ (see ref. (5)) is essentially constant at a value inappreciably below its asymptotic upper limit throughout the range investigated. Further confirmation of the theory is provided by the excellent agreement between the values of Θ obtained from precipitation studies in the poorer solvents and those deduced from the viscosity–temperature measurements (Table IV). In the better solvents, Θ is too low to be determined from precipitation measurements, and the long extrapolation required for its determination from intrinsic viscosity–temperature data increases the uncertainty to perhaps ± 20°.

Evaluation of Φ.—Values of $\bar{r}^2$ obtained by Kunst[11] from the angular dissymmetry of scattered light for polyisobutylene solutions permit estimation of the value of Φ according to the relationship $\Phi = [\eta]M(\bar{r}^2)^{-3/2}$ (see ref. (5), equation (17)). His results for a polyisobutylene fraction in *n*-heptane and various *n*-heptane–*n*-propanol mixtures are given in Table V. The molecular weight, 1.9×10^6, reported by Kunst is lower than the value, 2.5×10^6, computed from the intrinsic viscosity in *n*-heptane using equations (1) and (2) and the parameters given above.[12] Φ's calculated using each of these molecular weights are given in the last two columns of Table V. Variations within each column probably are not greater than the experimental error in $(\bar{r}^2)^{3/2}$. Similar calculations[13] from corresponding data for dilute solutions of polystyrene[14] give $\Phi = 2.1 \times 10^{21}$, in agreement with the mean values based on Kunst's data for polyisobutylene in conjunction with our estimate of the molecular weight. This is somewhat smaller than the theoretical value,[5] 3.6×10^{21}, based on the Kirkwood–Riseman theory.[15] Considering approximations in the theory, the agreement probably is satisfactory. The value 2.1×10^{21} will be assumed in subsequent calculations.

TABLE V

ESTIMATION OF Φ FROM THE RESULTS OF KUNST

Solvent	T, °C.	$(\bar{r}^2)^{1/2}$, Å.	$[\eta]$	$\Phi \times 10^{-21}$ calcd. using: $M = 1.9 \times 10^6$	$\Phi \times 10^{-21}$ calcd. using: $M = 2.5 \times 10^6$
n-Heptane	25	1860	4.50	1.33	1.75
	60	1750	4.00	1.41	1.86
n-Heptane + 10% propanol	25	1710	4.00	1.52	2.00
n-Heptane + 20% propanol	25	1320	2.30	1.90	2.50
	60	1640	3.50	1.51	1.98
n-Heptane + 27% propanol	60	1330	2.40	1.94	2.56
			Average	1.6 ± 0.2	2.1 ± 0.3

Dimensions of the Randomly Coiled Polymer Chain.—The normal mean-square end-to-end distance $\bar{r}_0^2$, *i. e.*, the mean-square r in the absence of effects due to interactions between the segments and their environment, for a molecule of molecular weight M may be calculated from K, using the above value of Φ.[5] Thus, values of the ratio $\bar{r}_0^2/M$ at 0, 25 and 100° as given in Table VI were computed from K using equation (16) of reference (5). Similarly, $\overline{\cos \phi}$ was computed from equation (20) of that paper; corresponding values of arc cosine $(\overline{\cos \phi})$ also are included in Table VI. For purposes of illustration, root-mean-square end-to-end distances $\sqrt{\bar{r}_0^2}$ for $M = 10^6$, calculated from the results given in the third column of Table VI, are given in the fifth column. The corresponding values calculated from equation (19) of reference (5) assuming free rotation, *i. e.*, assuming that $\overline{\cos \phi} = 0$, and taking $\theta = 109.5°$ and $l_0 = 1.54$ Å., are given in the sixth column. Finally, comparisons are shown between the actual chain and the equivalent freely jointed chain[3] comprised of Z segments of length l, each segment being free to orient at random with respect to its neighbors.

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[11] E. D. Kunst, *Rec. trav. chim.*, **69**, 125 (1950).

[12] The molecular weights used in the present paper are based primarily on the relationship between molecular weight and intrinsic viscosity in diisobutylene published by one of us several years ago. See, THIS JOURNAL, **65**, 372 (1943).

[13] T. G Fox, Jr., and P. J. Flory, THIS JOURNAL, **73**, 1915 (1951).

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

[15] J. G. Kirkwood and J. Riseman, *ibid.*, **16**, 565 (1948).

Taking $\overline{r_0^2} = Zl^2$ and $nl_0 = Zl$, it follows from equation (19) of reference (5) that

$$n/Z = l/l_0 = [(1 - \cos\theta)/(1 + \cos\theta)]\,[(1 + \overline{\cos\phi})/(1 - \overline{\cos\phi})] \quad (6)$$

Table VI

Normal Dimensions of the Randomly Coiled Polyisobutylene Chain Unperturbed by Thermodynamic Interactions

				$(\overline{r_0^2})^{1/2}$ in Å. for $M = 10^6$			
T, °C.	$K \times 10^3$	$(\overline{r_0^2}/M) \times 10^{17}$	Arc cosine $(\overline{\cos\phi})$	Calcd. from col. 3	Calcd. for free rot.	Ratio	n/Z number of chain atom per equivalent segment
0	1.10	6.49	54.3°	806	412	1.95	7.6
25	1.06	6.32	54.8°	795	412	1.93	7.4
100	0.93	5.80	56.9°	762	412	1.85	6.8

The size of the statistical segment at different temperatures as given in the last column of Table VI was computed from this equation. The absolute magnitudes of the dimensional parameters given in Table VI are, of course, subject to the uncertainty in the numerical value of Φ. Comparisons of the relative values of the calculated dimensions for different temperatures, however, are significant.

Inspection of Table VI demonstrates that hindrance to rotation increases the average linear dimensions of the polyisobutylene chain by a factor of approximately two. Increasing the temperature apparently has the effect of preferentially overcoming the barrier to rotation in the direction of increasing ϕ, inasmuch as $\overline{r_0^2}$ decreases slightly with elevation of the temperature.

The dimensions of the coiled polymer chain in a given solvent depend on the thermodynamic interaction with that solvent. For a polyisobutylene molecule of $M = 10^6$ at 25° in cyclohexane, $\alpha = 1.54$ and $(\overline{r^2})^{1/2} = 795 \times 1.54$ or 1220 Å.; in benzene at 24°, $\alpha = 1$ and $(\overline{r^2})^{1/2} = 795$ Å. Thus, for a high molecular weight polyisobutylene in a *good solvent* the two factors responsible for the increase in size of the molecule over that for the random flight configuration with free rotation appear to be comparable in magnitude.

Estimation of Thermodynamic Parameters.—Employing $\overline{r_0^2}/M$ from Table VI and taking 1.10 for the specific volume of polyisobutylene, the value of $C_M v_1$ at 25° as computed by equation (12) of reference (5) is approximately equal to 3.4. ψ_1 and κ_1 (Table VII) were obtained according to the methods previously discussed[5] from this value of $C_M v_1$ and the figures listed in Table IV for $\psi_1 \times C_M v_1$ and Θ. ψ_1 appears in all cases to be much less than one-half, the approximate value given by the lattice theory of polymer solutions.[8,16] Since the numerical coefficient in equation (12) of ref. (5) may be somewhat in error owing to inaccuracies in the theory,[5] the above value of C_M and the absolute magnitudes of ψ_1 (and of κ_1 as well) are correspondingly uncertain. The relative values of ψ_1 (and of κ_1) in the various solvents, however, are significant. The unexpectedly large variations (fourfold) in the entropy coefficient ψ_1 shown in Table VII appear to be related to the spatial character of the solvent molecules. For those solvents having cyclic structures, which are relatively compact and symmetrical (*e. g.*, benzene, toluene and cyclohexane), $\psi_1 = 0.15$, but it is consistently lower for the less symmetrical acyclic solvents capable of assuming a number of different configurations. There appears to be no correlation between ψ_1 and the heat of mixing. This is demonstrated by the presence of "good" and "poor" solvents in each of the above groups; *e. g.*, both benzene and cyclohexane have similar values for ψ_1, and for both *n*-heptane and ethyl heptylate ψ_1 is lower by a factor of three or four. The conclusion drawn from these results that ψ_1 varies so greatly with the geometrical character of the solvent is supported by the work of Schick, Doty and Zimm[17] on osmotic pressure–concentration–temperature relationships for polystyrene in various solvents. Current theories[8,16] of polymer solutions fail to take into account the specific geometrical character of the solvent in relation to the polymer segment. It is obvious from the above results that this is a serious deficiency which must be borne in mind in applications of these theories.

Table VII

The Thermodynamic Interaction Parameters at 25°

Solvent	ψ_1	κ_1
Benzene	0.15	0.15
Cyclohexane	.14	.059
Toluene	.14	.12
Ethylbenzene	.14	.117
75:25 EB:PE	.17	.17
50:50 EB:PE	.21	.24
Diisobutylene	.056	.016
n-Hexadecane	.094	.055
n-Heptane	.035	0
Triptane	.047	0

Values of κ_1 given in Table VII indicate that heats of mixing of polyisobutylene are very low for aliphatic solvents but are much higher in aromatic solvents and in ethers, as would be expected.

Solvents for a non-polar polymer such as polyisobutylene may be classified according to the values found for the intrinsic viscosity and for its temperature coefficient. Thus in a "geometrically good" solvent, where the entropy of mixing (as measured by ψ_1) is high the observed intrinsic viscosity will be relatively high, or will approach a high value at high temperatures. In a "geometrically poor" solvent (where ψ_1 is small) the viscosity will be relatively low. In either case, in a "thermally good" solvent wherein the heat of mixing (as measured by κ_1) is low, the viscosity–temperature coefficient will be low; while in a "thermally poor" solvent (wherein κ_1 is large), this coefficient will be relatively high. A possible complication could arise from the variation of $[\eta]$ with T due to a decrease in K with T. This variation is small in the present case, but in some instances might be large.

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(16) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(17) M. J. Schick, P. Doty and B. H. Zimm, This Journal, **72**, 530 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Intrinsic Viscosity Relationships for Polystyrene[1]

BY T. G FOX, JR.,[2] AND P. J. FLORY

Intrinsic viscosities of polystyrene fractions ($M = 7.0 \times 10^4$ to 1.27×10^6) have been determined in various solvents at several temperatures. Critical miscibility temperatures Θ in the limit of infinite molecular weight were found to be 307 and 343°K. for polystyrene in cyclohexane and in ethylcyclohexane, respectively. From intrinsic viscosities measured in these solvents at temperatures equal to their respective Θ's, K in the equation $[\eta] = KM^{1/2}\alpha^3$ was found to be about 8.0×10^{-4} at 34° and about 7.3×10^{-4} at 70°. Present data, as well as other data from the literature, are well represented by the above equation in conjunction with the relationship $\alpha^5 - \alpha^3 = 2\psi_1 C_M(1 - \Theta/T)M^{1/2}$ where α is the factor representing the linear expansion of the polymer coil due to interactions. The entropy of dilution parameter ψ_1 has been found to be about 0.1 for the solvents with cyclic structures; ψ_1 for methyl ethyl ketone is about 0.01. The universal viscosity constant Φ in the relationship $K = \Phi(\overline{r_0^2}/M)^{3/2}$ has been calculated to be 2.1×10^{21} on the basis of data of Outer, Carr and Zimm on molecular dimensions of polystyrene in solution as deduced from the dissymmetry of scattered light. The root-mean-square distance $\sqrt{\overline{r_0^2}}$ separating the ends of a polystyrene chain in the absence of interactions of the polymer segments with their environment, apart from hindrances to free rotation, is calculated to be 730 Å. at 25° for a polystyrene of $M = 10^6$; the calculated distance for free rotation is 302 Å. In benzene, a good solvent, at 25°, $\alpha \cong 1.5$ and the root-mean-square distance between the ends of the chain is *ca.* 1100 Å. The polystyrene molecule appears to be more extended than is one of polyisobutylene having the same number of chain atoms.

Introduction

The results of the application of the theory of intramolecular interactions in dissolved polymer molecules to the interpretation of their intrinsic viscosities are summerized in the equations[3,4]

$$[\eta] = KM^{1/2}\alpha^3 \tag{1}$$

$$\alpha^5 - \alpha^3 = 2\,\psi_1 C_M(1 - \Theta/T)M^{1/2} \tag{2}$$

$$K = \Phi(\overline{r_0^2}/M)^{3/2} \tag{3}$$

$$\begin{aligned} C_M &= 27(2^{5/2}/\pi^{3/2}N)(\bar{v}^2/V_1)(M/\overline{r_0^2})^{3/2} \\ &= 1.4 \times 10^{-24}\,(\bar{v}^2/V_1)(\Phi/K) \end{aligned} \tag{4}$$

The various quantities appearing in these equations are defined in preceding papers.[4,5]

Equations (1) and (2) have been subjected to rigorous test in their application to precisely measured intrinsic viscosities of polyisobutylenes[6,7] over wide ranges in molecular weight and temperature and in a number of different solvents. The adequacy of these relationships has been confirmed and the various parameters have been evaluated. The present paper is concerned with the similar treatment of intrinsic viscosities of polystyrene, and with the deduction from such data of the ratio $\overline{r_0^2}/M$ characterizing the configuration of the chain, and the determination of the thermodynamic parameters Θ and ψ_1 for polystyrene in several solvents. Experimental data on the dependence of intrinsic viscosities of polystyrenes on molecular weight[8] and on solvent and temperature[9,10] have been reported by several investigators, and more recently the mean-square extension $\overline{r^2}$ of polystyrene chains has been obtained in various solvents through measurements on the angular dissymmetry of light scattered by dilute solutions.[10,11] For the successful application of equations (1) and (2), however, intrinsic viscosities at the temperature $T = \Theta$ are virtually required for reliable evaluation of K; this constitutes the first step in the determination of all other quantities appearing in the above equations. Such measurements have been carried out in the present investigation. With their aid, previously reported intrinsic viscosity data (and some additional results reported here) and results of chain dimension measurements are interpreted in the light of the relationships presented above.

Experimental

Materials.—Four polystyrenes were prepared by bulk polymerizations of styrene at 60° in the presence of benzoyl peroxide according to the method described elsewhere.[12] Details of the polymerizations are summarized in Table I. The polymers were fractionated by the addition of methanol to their dilute (1 to 2 g./100 cc.) solutions in methyl ethyl ketone at 30°.[12] Seven of the fractions were selected for the work reported here. The percentage of the corresponding whole polymer represented by each of these fractions, together with their viscosity-average molecular weights $\bar{M}$ are listed in Table I. The latter were calculated from the intrinsic viscosities in benzene using the relationship[8]

$$\log \bar{M}_v = (\log [\eta] + 4.013)/0.74 \tag{5}$$

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[1] This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

[2] Rohm and Haas Company, Inc., Philadelphia, Penna.

[3] P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

[4] P. J. Flory and T. G Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

[5] See also in this connection, P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

[6] T. G Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949).

[7] T. G Fox, Jr., and P. J. Flory, THIS JOURNAL, **73**, 1909 (1951).

[8] R. H. Ewart and H. C. Tingey, Abstracts of papers presented at the 111th Meeting of the American Chemical Society, Atlantic City, N. J., April 14-18 (1947).

[9] L. H. Cragg and J. E. Simkins, *Can. J. Research*, **B27**, 961 (1949).

[10] F. D. Kunst, *Rec. trav. chim.*, **69**, 125 (1950).

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

[12] T. G Fox, Jr., and P. J. Flory, THIS JOURNAL, **70**, 2384 (1948).