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Statistical Mechanics of Dilute Polymer Solutions. IV. Variation of the Osmotic Second Coefficient with Molecular Weight^{1a,b}

BY W. R. KRIGBAUM² AND P. J. FLORY

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Accurate osmotic pressure measurements are reported for seven carefully-fractionated samples of polyisobutylene covering the molecular weight range 38,000–710,000 in cyclohexane, for two of these fractions in benzene, and for six well-fractionated samples of polystyrene varying in molecular weight from 30,800 to 610,000 in toluene. Further measurements are reported five mixtures of two of the polystyrene fractions in toluene, and for two mixtures of two polyisobutylene fractions in cyclohexane. The concentration range covered by these measurements permits reliable evaluation of the second coefficient in the osmotic pressure expansion. π/c plotted against c shows unmistakable upward curvature, the magnitude of which, relative to the slope (second coefficient), stands in close agreement with the calculations on the third coefficient carried out recently by Stockmayer and Casassa. The absolute values of the second coefficient calculated according to recent dilute solution theory agree approximately with those observed; however, the predicted molecular weight dependence of the second coefficient is somewhat smaller than that observed. The increase in the second coefficient with molecular weight heterogeneity predicted by theory has been verified.

The osmotic pressure, π , of a dilute polymer solution may be expressed either in the form³

$$(\pi/c) = RT(A_1 + A_2c + A_3c^2 + \dots) \quad (1a)$$

or, alternately

$$(\pi/c) = (\pi/c)_0[1 + \Gamma_2c + \Gamma_3c^2 + \dots] \quad (1b)$$

The light scattering parameter, Hc/τ , may be similarly expressed in a series form corresponding to equation (1a); *i.e.*

$$Hc/\tau = [A_1' + A_2'c + A_3'c^2 + \dots] \quad (2)$$

According to the early theories of polymer solutions,^{4,5} the second coefficients, A_2 and A_2' , should be constant for a given polymer-solvent pair, *i.e.*, independent of molecular weight and unaffected by molecular heterogeneity. The light scattering second coefficient A_2' as calculated according to these early theories was at one time thought to be sensitive to molecular heterogeneity; however, it

has since been demonstrated that this is not the case.^{6–8} Values of A_2 and A_2' predicted by these theories are in general considerably larger than those observed for dilute polymer solutions. As pointed out several years ago by one of the authors,⁹ the failure of these early theories when applied to the region of low polymer concentration is a consequence of the implicit assumption that when considering the interactions between a particular polymer molecule and all other polymer molecules, segments of the latter molecules may be considered to be randomly distributed throughout the solution. This assumption is permissible for solutions which are sufficiently concentrated to ensure considerable overlapping of the polymer domains; however, it is invalid for dilute solutions, except at the unique temperature Θ (temperature of critical miscibility for a polymer of infinite molecular weight). These theories therefore represent a uniform distribution approximation, and will be so referred to herein.

In a recent statistical treatment of dilute solutions,¹⁰ the excluded volume for a pair of polymer molecules was obtained from consideration of the

(1) (a) This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Synthetic Rubber Division, Reconstruction Finance Corporation. (b) Presented before the Division of Polymer Chemistry at the 121st meeting of the American Chemical Society, Buffalo, N. Y., March 25, 1952.

(2) Duke University, Durham, N. C.

(3) This is the form used by W. G. McMillan and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945); and by B. H. Zimm, *ibid.*, **14**, 164 (1946).

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

(5) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **12**, 425 (1944).

(6) H. C. Brinkmann and J. J. Hermans, *ibid.*, **17**, 574 (1949).

(7) J. G. Kirkwood and R. J. Goldberg, *ibid.*, **18**, 54 (1950).

(8) W. H. Stockmayer, *ibid.*, **18**, 56 (1950).

(9) P. J. Flory, *ibid.*, **13**, 453 (1943).

(10) (a) P. J. Flory, *ibid.*, **17**, 1347 (1949); (b) P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950); (c) W. R. Krigbaum and P. J. Flory, *ibid.*, **20**, 873 (1952).

detailed interactions when two molecules overlap. The values of the osmotic second coefficient A_2 (or of the second coefficient A_2' in the reciprocal turbidity expression) predicted by this dilute solution treatment are generally smaller than those calculated on the basis of the uniform distribution approximation and, furthermore, they decrease with increasing molecular weight and increase with molecular heterogeneity at a fixed average molecular weight. The available dilute solution data obtained by measurement of osmotic pressure¹¹ and turbidity^{12,13} appear to verify these predictions qualitatively.¹³ Osmotic pressure measurements reported in this paper for seven well-fractionated polyisobutylene samples varying in molecular weight from 4×10^4 to 7×10^5 (in cyclohexane), and for six sharp fractions of polystyrene varying in molecular weight from 3×10^4 to 6×10^5 (in toluene), allow a quantitative test of the predicted variation of the second coefficient, A_2 , with molecular weight. Data obtained for five mixtures of two of these polystyrene fractions having molecular weights 6×10^4 and 6×10^5 (in toluene), and for two mixtures of polyisobutylene fractions of molecular weight 8×10^4 and 7×10^5 , respectively (in cyclohexane), permit a test of the predicted variation of the second osmotic coefficient, A_2 , with molecular weight heterogeneity.

Experimental

Fractionation.—Two hundred grams of commercial polyisobutylene¹⁴ designated "Vistanex" LMH and 300 g. of polymer B-100 were fractionated from benzene, using acetone as a precipitant. Duplicate or triplicate batches of 100 g. each were first fractionated, fractions of corresponding molecular weights were then combined for a second fractionation, and this process was continued until sharp fractions were obtained. The initial fractionations were carried out from a 1–2% solution; the concentrations for the final fractionations varied from 0.1–0.5%, depending on the molecular weight. The polymers investigated resulted from the third or fourth successive fractionation.¹⁵

Styrene was freed of inhibitor and polymerized in bulk at 60° to 40% conversion, using benzoyl peroxide as an initiator. Two 300-g. batches having viscosity-average molecular weights of 3×10^4 and 3×10^5 were prepared in this manner, and each was subdivided for subsequent fractionation. Each 150-g. portion was fractionated from a 2% solution in benzene, using methanol as a precipitant. Fractions of corresponding molecular weights were recombined and refractionated, and this process was repeated until sharp fractions were obtained. The final fractionation (the second or third) was effected by the addition of methanol to a 1% solution in butanone. The estimated $\overline{M}_w/\overline{M}_n$

ratios for these fractions were also within the limits given in footnote 12.

Intrinsic Viscosities.—Viscosities of the polyisobutylene fractions investigated osmotically were measured using Ubbelohde viscometers calibrated for kinetic energy corrections. The solvents were freshly distilled before use. In each case measurements were carried out at five concentrations chosen to give relative viscosities in the range 1.2–1.4, and the values of (η_{sp}/c) and $\ln(\eta_{rel})/c$ extrapolated to infinite dilution to obtain the intrinsic viscosity.

Osmotic Pressures.—The osmometers used are a modification of the block type described by Fuoss and Mead,¹⁶ and by Flory.^{11a} Details of their construction are shown in Fig. 1. The brass blocks, measuring $5'' \times 5'' \times 1''$, may be bolted together firmly by eight symmetrically-placed $3/16''$ threaded cap screws. The two blocks are similar in every respect, each bearing a precision-bore 1-mm. capillary (a) and a metal standpipe (b), thereby minimizing the effect of temperature fluctuations. Cells were cut into the blocks by machining, within a 2.25'' circular area, diagonal $1/8''$ channels (c) $1/16''$ deep, spaced $3/16''$ apart center to center. The channels had a semi-circular profile at their base. The two sets of parallel channels, each perpendicular to the other, left $1/16''$ square island points (d) which support the membrane. A "foot" was blown at the base of each capillary, the bottom of which was ground flat. The capillary was sealed into the block against a lead washer (e), pressure being applied to the capillary foot by means of a packing nut and a Teflon gasket (f). Following the design of Sirianni, Wise and McIntosh,¹⁷ a circular groove (g) was cut in the sealing ring on one face, and the ring on the other face bore a matching ridge (h). A lead gasket (i) fitting the sealing ring completely sealed the cells, and also prevented water in the constant temperature bath from coming in contact with the membrane (j).

Sylvania No. 300 regenerated cellophane membranes were used for molecular weights above 50,000. These were found to have a more uniform permeability than the deaerated collodion membranes prepared according to the procedure of Montonna and Jilk.¹⁸ Dried No. 600 untreated cellophane¹⁹ was used for molecular weights below 50,000. The procedure for conditioning the membranes to solvent and for filling the osmometers was essentially that described previously by one of the authors.^{11a} When both cells were filled with solvent, the time required for the difference in the heights of the liquid levels to fall to one-half of its initial value was one hour and ten hours, respectively, for the two types of membranes.

Solutions of the fractionated materials were individually prepared; those for the polymer mixtures were prepared by diluting aliquot portions from a stock solution. Reagent grade toluene ($\rho_{20} = 0.857$), which had been freshly distilled, was used as the solvent for polystyrene, and freshly distilled cyclohexane ($\rho_{20} = 0.769$) or benzene ($\rho_{20} = 0.868$) for polyisobutylene. For the purpose of converting the equilibrium differences in capillary height to osmotic pressures, the densities of the solutions may be taken equal to that of the solvent without introducing appreciable errors within the concentration range of interest.

The osmometers were immersed, except for the tips of the capillaries, in a large thermostated bath at 30°. Temperature fluctuations were held within $\pm 0.001^\circ$ by means of a thyatron relay and mercury contact switch. The osmotic pressures recorded are static values. The time necessary for attainment of equilibrium could be shortened considerably by successively adjusting the liquid levels by means of a threaded rod in each standpipe. A cathetometer reading directly to 0.001 cm. was used to read the heights of the liquid levels in the capillaries. The sum of the heights of the liquid columns decreased approximately 0.003 cm./hr., probably due to evaporation from the capillaries. This decrease did not appear to affect the observed difference in height, however. A comparison with values of π calculated as described below indicates an average error of ± 0.007 g./cm.² for all measurements. This value reflects

(11) (a) P. J. Flory, *THIS JOURNAL*, **65**, 372 (1943); (b) C. R. Masson and H. W. Melville, *J. Polymer Sci.*, **4**, 337 (1949); (c) M. J. Schick, P. Doty and B. H. Zimm, *THIS JOURNAL*, **72**, 530 (1950); (d) C. Bawn, R. Freeman and A. Kamaliddin, *Trans. Faraday Soc.*, **46**, 862 (1950); (e) H. P. Frank and H. Mark, *J. Polymer Sci.*, **6**, 243 (1951); (f) L. A. McLeod and R. McIntosh, *Can. J. Chem.*, **29**, 1104 (1951).

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

(13) T. G. Fox, Jr., P. J. Flory and A. M. Bueche, *THIS JOURNAL*, **73**, 285 (1951).

(14) The two samples of polyisobutylene were supplied by the Standard Oil Company of New Jersey.

(15) The ratio $(\overline{M}_w/\overline{M}_n)$ for each fraction was estimated by assuming that succeeding fractions obtained therefrom were molecularly homogeneous. The ratio $(\overline{M}_w/\overline{M}_n)$ so calculated varied from 1.03 to 1.08 for the polymers entering the final fractionation. The actual heterogeneities of the next to the last fractions are, of course, greater than these ratios indicate, owing to the residual heterogeneity of the final fractions.

(16) R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943).

(17) A. F. Sirianni, L. M. Wise and R. L. McIntosh, *Can. J. Research*, **25B**, 301 (1947).

(18) R. E. Montonna and L. T. Jilk, *J. Phys. Chem.*, **45**, 1374 (1941).

(19) Supplied through the courtesy of E. I. du Pont de Nemours and Company.

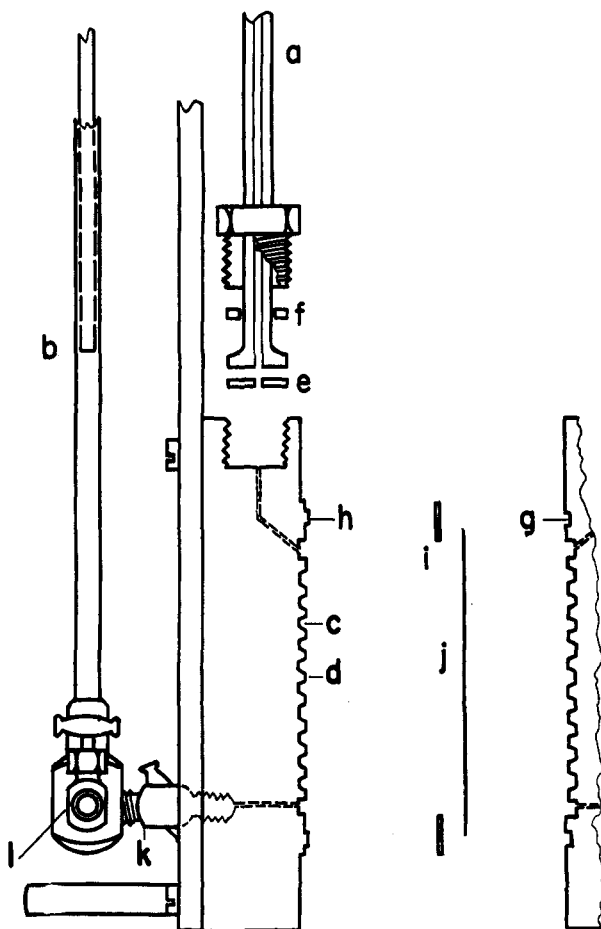


Fig. 1.—Detail of block type osmometers (see text).

errors in concentration and curve fitting, and is therefore considerably larger than the reproducibility of the osmotic results.

Results

Osmotic Pressure-Concentration Relationship.—

The molecular weight may be calculated from the intercept, $(\pi/c)_0$, in the plot of π/c against c according to the van't Hoff relation, which at 30° is

$$\bar{M}_n = 2.57 \times 10^5 / (\pi/c)_0 \quad (3)$$

where π is the osmotic pressure in g./cm.² and c is the solute concentration in g./100 cc. In Fig. 2 values of π/c appear plotted against concentration for two fractions of polyisobutylene in cyclohexane (filled circles), and for a polystyrene fraction in toluene (*cf.* Table I). These data clearly demonstrate curvature in the relation of π/c to c . Curvature concave upward has also been reported heretofore by several authors for $(\pi/c)^{11,17,20}$ and Hc/τ .^{12,13,21}

(20) (a) G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942); (b) G. A. Gilbert and C. Graff-Baker, *J. Polymer Sci.*, **6**, 585 (1951); (c) G. V. Browning and J. D. Ferry, *J. Chem. Phys.*, **17**, 1107 (1949). ADDED IN PROOF.—H. T. Hookway and R. Townsend (*J. Chem. Soc.*, 3190, 4390 (1952)), have recently concluded from osmotic measurements performed on unfractionated polymers that π/c is best represented as a linear function of concentration. However, the concentration ranges covered in their measurements are much too limited to allow a fair test of the third coefficient (in only one case does the ratio $(\pi/c)/(\pi/c)_0$ reach 2).

(21) (a) B. H. Zimm, *ibid.*, **16**, 1099 (1948); (b) P. M. Doty and R. F. Steiner, *J. Polymer Sci.*, **5**, 383 (1950).

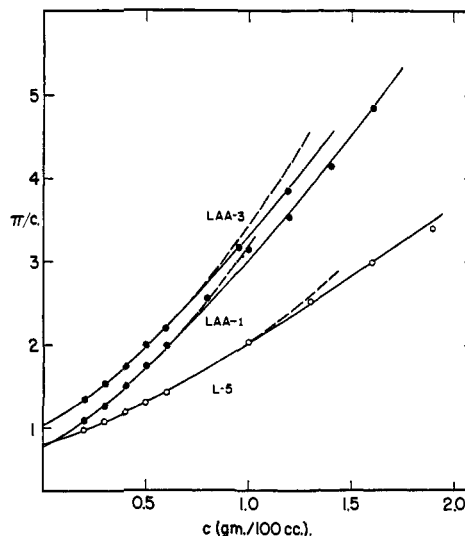


Fig. 2.— π/c ratios plotted against concentration for two polyisobutylene fractions in cyclohexane (filled circles) and for a polystyrene fraction in toluene (open circles). Calculated π/c ratios using $g = 1/4$ are represented by full curves; those using $g = 5/8$, by broken curves.

Restricting ourselves to dilute solutions, the dependence of the osmotic pressure on concentration is expressed adequately by retaining only the first three terms of the virial expansion. Writing the third coefficient $\Gamma_3 = g\Gamma_2^2$, equation (1b) then becomes

$$\pi/c = (\pi/c)_0 [1 + \Gamma_2 c + g(\Gamma_2 c)^2] \quad (4)$$

If the factor g relating the third and second coefficients can be evaluated, the resulting two parameter expression allows the concentration dependence to be fitted conveniently by the procedure described in detail by Fox, Flory and Bueche¹³ and re-examined elsewhere by the present authors.^{22,23} Although the second coefficient may be calculated using a realistic model for the polymer molecule, some approximation is necessary in order to carry through the calculation of the third coefficient. If we assume that the third coefficient is related to the second in the same manner as would apply for hard spheres of a size selected to give the correct second coefficient, then $g = 5/8$.^{10a} Although it was felt that this approximation for the ratio g yields a value for the third coefficient which is too large, its use was tentatively recommended. As shown by the dashed curves in Fig. 2, the π/c ratios calculated using $g = 5/8$ deviate from the experimental points at higher concentrations, indicating that the above mentioned approximation for the third coefficient is too large. On fitting the data appearing in Fig. 2 over the concentration range shown, the empirical factor $g = 1/4$ (yielding the full curves) was found to afford the optimum agreement with the experimental

(22) W. R. Krigbaum and P. J. Flory, *J. Polymer Sci.*, **9**, 503 (1952).

(23) Recently a procedure for the treatment of osmotic data has been proposed by Guggenheim and McGlashan [*Trans. Faraday Soc.*, **48**, 206 (1952)] which involves the assumption that the second and higher coefficients are invariant with molecular weight. Since, as is clearly shown in this paper, the higher coefficients are in fact molecular weight-dependent, the procedure described by them is invalid and must lead to erroneous molecular weight values.

TABLE I
OSMOTIC PARAMETERS FOR POLYISOBUTYLENE IN CYCLOHEXANE AND BENZENE (*) AND FOR POLYSTYRENE IN TOLUENE

Fraction	$g = 1/4$				$g = 5/8$			
	$(\pi/c)_0^a$	M_w	Γ_2^b	RTA_2^b	$(\pi/c)_0^a$	M_w	Γ_2^b	RTA_2^b
A. Polyisobutylene in Cyclohexane or Benzene at 30°								
LD3	6.77	37,900	0.31	2.10	6.84	37,600	0.27	1.85
LC3	3.16	81,400	.59	1.86	3.22	79,800	.50	1.61
LA2	1.52	169,000	1.12	1.70	1.57	164,000	.89	1.40
LAA-3	1.01	254,000	1.60	1.62	1.038	248,000	1.28	1.33
LAA-1	0.76	339,000	2.02	1.53 ⁵	0.785	327,000	1.61 ⁶	1.27
F3B	.463	555,000	3.30	1.53	.492	522,000	2.51	1.23 ⁵
F4	.357	720,000	3.87	1.37	.373	689,000	3.02	1.13
F3B*	.462	556,000	0.45	0.21	.484	530,000	0.35	0.17
F4*	.356	722,000	.52	.18	.37	694,000	.41	.15
B. Polystyrene in Toluene at 30°								
L10-2	8.33	30,900	0.195	1.62	8.41	30,600	0.17	1.43
L-4	6.17	41,700	.251	1.55	6.19	41,500	.23	1.42
O-4	4.18	61,500	.309	1.29	4.22	60,800	.27	1.14
P-5	2.15	120,000	.576	1.24	2.21	116,000	.46	1.02
L-5	0.783	328,000	1.21	0.95	0.815	316,000	.95	0.77
O-5	.42	612,000	2.02	.85	.427	602,000	1.63	.696

^a π in g./cm.² and c in g./100 cc. ^b Γ_2 and RTA_2 expressed in units corresponding to those used for π and c .

results. Recently Stockmayer and Casassa²⁴ have calculated the third coefficient using approximate expressions for the intermolecular free energy. They find g to depend on the factor α by which the linear dimensions of the dissolved polymer molecule are expanded over those of its random-flight counterpart due to intramolecular interactions.²⁵ For the systems appearing in Fig. 2 their calculation predicts $g = 0.25 - 0.28$, in excellent agreement with our empirical value, $1/4$.

In order to test the sensitivity of the values obtained for the first and second coefficients to variations in the ratio g , the data have been fitted by assigning g the values $5/8$, $1/4$ and the values calculated according to the relation of Stockmayer and Casassa. The latter varied for the polyisobutylene fractions from 0.19 for the lowest molecular weight to 0.31 for the highest, and from 0.15 to 0.27 for the corresponding polystyrene fractions. Values of $\log(\pi/c)$ were plotted against $\log c$, as shown in Figs. 3 and 4 for the polyisobutylene and polystyrene data, respectively. Osmotic pressure measurements were carried out for the two highest molecular weight polyisobutylene fractions in a poor solvent (benzene) in order to determine the intercepts more precisely. These data are represented by the open circles in Fig. 3. In Fig. 4 the filled circles represent the observed (π/c) ratios for polystyrene fractions in toluene; the open circles represent (π/c) ratios for mixtures of polystyrene fractions O-4 and O-5. The parameters $(\pi/c)_0$ and Γ_2 were evaluated by fitting the experimental points shown in Figs. 3 and 4 which fall within the range $(\pi/c)/(\pi/c)_0 < 3$ (or 4 for the more accurate g values)²² to the appropriate curve as described elsewhere.¹³ Parameters so obtained for the polyisobutylene fractions in cyclohexane and in benzene and for the polystyrene fractions in toluene, appear in Table I.

(24) W. H. Stockmayer and E. F. Casassa, *J. Chem. Phys.*, **20**, 1560 (1952).

(25) P. J. Flory, *ibid.*, **17**, 303 (1949).

Comparison of the two sets of data shown in the second and sixth column of Table I demonstrates that the choice of g has little effect on the values obtained for the intercept, $(\pi/c)_0$. For the highest molecular weight fractions appearing in Table I, $(\pi/c)_0$ is increased only 6% on decreasing g from $5/8$ to $1/4$. The second coefficient A_2 is somewhat more sensitive to the choice of g , increasing by 15 to 20% as g is decreased from $5/8$ to $1/4$. However, the parameters obtained using the g values calculated according to the relation of Stockmayer and Casassa were, within experimental error, identical with those obtained on setting $g = 1/4$. These have not been included in the Table I, therefore. The π/c ratios calculated according to equation (4), taking $g = 1/4$ and the corresponding values for $(\pi/c)_0$ and Γ_2 , are compared in Figs. 5 and 6 with the experimental values for polyisobutylene and polystyrene, respectively.

The above experimental results, as well as those of McLeod and McIntosh,^{11f} show²² that the earlier value of $5/8$ for g is definitely too large. Although the indicated revision of g by a factor of about $2/5$ of its previously recommended value ($5/8$) scarcely alters the results obtained for the first coefficient, $(\pi/c)_0$, it must not be inferred that further reduction of g to zero would likewise be inconsequential in this respect. The assumption that π/c is linear with concentration, *i.e.*, that $g = 0$, results in molecular weights which are too high (except near the condition for which π/c is independent of c , *i.e.*, near the Θ temperature). The magnitude of the error committed by extrapolating linearly varies from a few per cent. for a molecular weight of 50,000 to 30-40% at 500,000 according to the data reported in this paper.²⁶ The comparative insensitivity of $(\pi/c)_0$ to the value of g over the range $g = 1/4$ to $5/8$ is a consequence of the implicit dependence of the third coefficient on the square second. Exaggeration of the third coefficient

(26) See also H. L. Wagner and P. J. Flory, *THE JOURNAL*, **74**, 195 (1952).

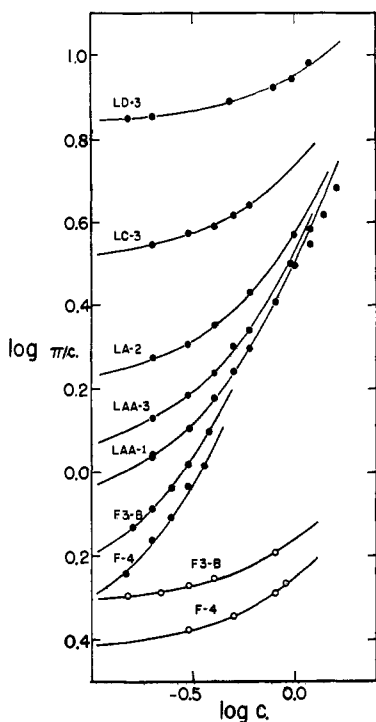


Fig. 3.—Log (π/c) vs. $\log c$ for polyisobutylene fractions in cyclohexane at 30° (filled circles) and in benzene at 30° (open circles). The curves shown were fitted to the data taking $g = 5/8$.

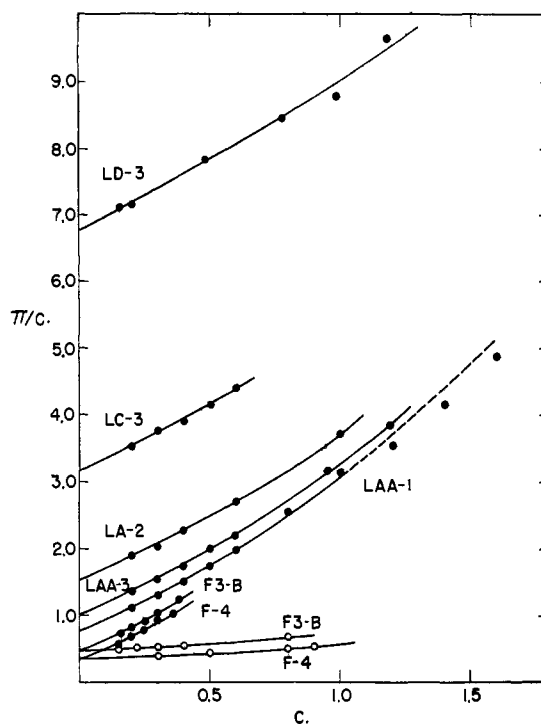


Fig. 5.— π/c vs. c for polyisobutylene in cyclohexane (filled circles) and in benzene (open circles). The curves represent π/c ratios calculated according to equation (4) taking $g = 1/4$.

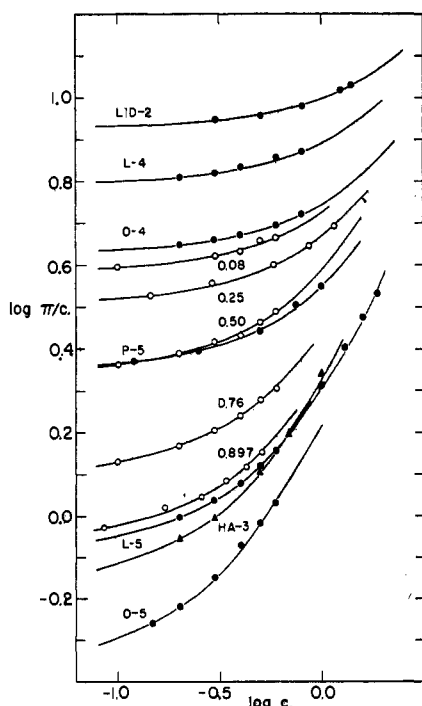


Fig. 4.—Log-log plot of π/c vs. c for polystyrene fractions (filled circles) in toluene at 30° and for mixtures of fractions 0.4 and 0.5 (open circles). The weight fraction of polymer 0.5 is given with the curve for each mixture. The curves shown were fitted using $g = 1/4$.

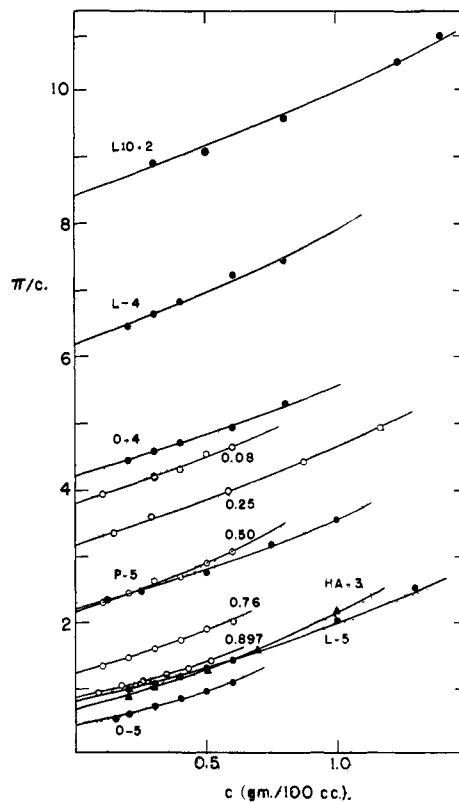


Fig. 6.— π/c vs. c for polystyrene in toluene (see caption of Fig. 4), the curves were calculated according to equation (4), taking $g = 1/4$.

through use of a g which is too great is largely compensated in fitting experimental data by choice of a second coefficient which is somewhat too small.

Intrinsic Viscosity-Molecular Weight Relationship for Polyisobutylene.—Intrinsic viscosities for

the seven polyisobutylene fractions measured in diisobutylene at 20° and in cyclohexane at 30° appear together with the number-average molecular weights in Table II. These intrinsic viscosities

TABLE II

INTRINSIC VISCOSITIES OF POLYISOBUTYLENE FRACTIONS

Fraction	\bar{M}_n	DIB, 20°	C ₆ H ₁₂ , 30°
LD3	37,800	0.308	0.388
LC3	80,600	.487	0.638
LA2	167,000	.823	1.12
LAA-3	251,000	1.04	1.50
LAA-1	333,000	1.27	1.81
F3B	540,000	1.68	2.48
F4	710,000	1.96	2.87

are shown in Fig. 7 as a log-log plot against molecular weight (filled circles). Values previously ob-

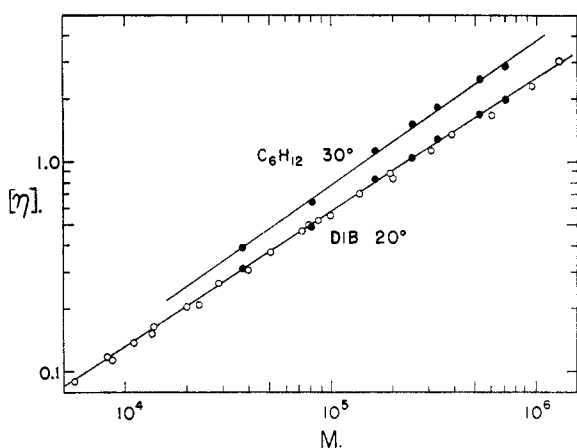


Fig. 7.—Log-log plot of intrinsic viscosity against molecular weight for polyisobutylene in diisobutylene at 20° and in cyclohexane at 30°.

tained by one of the authors^{11a} for polyisobutylene in diisobutylene at 20° appear in Fig. 7 as open circles. The best straight line through the filled circles representing polyisobutylene in diisobutylene at 20° is

$$\log M = 5.376 + 1.56 \log [\eta] \quad (5a)$$

and in cyclohexane at 30°

$$\log M = 5.159 + 1.45 \log [\eta] \quad (5b)$$

Equation (5a) is in excellent agreement with that previously reported for diisobutylene at 20°^{11a}

$$\log M = 5.378 + 1.56 \log [\eta] \quad (6a)$$

and equation (5b) is in good agreement with the relation obtained by Fox and Flory²⁷ for cyclohexane at 30° by comparing intrinsic viscosities in these two solvents

$$\log M = 5.184 + 1.45 \log [\eta] \quad (6b)$$

Variation of the Second Osmotic Coefficient with Molecular Weight.—According to the theory of dilute solutions when applied to homogeneous polymers, the parameter Γ_2 occurring in equation (1b) is given by^{10a,10b}

$$\Gamma_2 = M(\bar{v}^2/v_1)(\psi_1 - \kappa_1)F(X) \quad (7)$$

where v is the partial specific volume of polymer

²⁷ T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949).

and v_1 the molar volume of solvent. ψ_1 and κ_1 are entropy and heat parameters, the standard state free energy²⁸ of formation of a polymer-solvent contact pair being expressed as $kT(1/2 - \psi_1 + \kappa_1)$.²⁹ The parameter A_2 of equation (1a) is given by Γ_2/M , or

$$A_2 = (\bar{v}^2/v_1)(\psi_1 - \kappa_1)F(X) \quad (8)$$

The theories based on the random distribution approximation, when modified through introduction of the arbitrary entropy parameter ψ_1 in place of $1/2$ as obtained from lattice theory, yield relations differing from equations (7) and (8) through omission of the molecular weight dependent factor $F(X)$, given by

$$F(X) = 1 - X/2!2^{3/2} + X^2/3!3^{3/2} - \dots \quad (9)$$

Literal application of the theory of intramolecular interactions²⁵ leads to the relationship^{10b}

$$X = 2(\alpha^2 - 1) \quad (10)$$

the factor, α , by which the linear dimensions of the molecule are expanded over those of its random-flight counterpart being given by

$$\alpha^5 - \alpha^3 = 2C_M(\psi_1 - \kappa_1)M^{1/2} \quad (11)$$

where C_M is a constant for a particular polymer-solvent system at a specified temperature. C_M may vary slightly with temperature, depending on the polymer³⁰; it may be deduced from knowledge of the ratio r_0^2/M of the unperturbed mean-square end-to-end length of the molecule to its molecular weight, as obtained from viscosity measurements in an "ideal" solvent. It is evident from eq. (11) that α is molecular-weight dependent; hence, X , $F(X)$, and the second coefficients Γ_2 and A_2 must likewise be molecular weight-dependent according to the dilute solution treatment. Since the expansion factor α and the thermodynamic parameters ψ_1 and κ_1 may be evaluated from viscosity measurements,³⁰ values of the osmotic second coefficient can be calculated if the appropriate viscosity data are available and the molecular weight is known.

The experimental second coefficients for polyisobutylene in cyclohexane are shown in Figs. 8 and 9, where $\log \Gamma_2$ and $\log RTA_2$, respectively, are plotted against $\log M$. In these figures the lines marked "a" represent experimental values for the second coefficient obtained using $g = 1/4$; those designated "b" represent experimental values (not shown) fitted using $g = 5/8$. Coefficients deduced from the present measurements appear in these figures as filled circles; those obtained by fitting the earlier polyisobutylene data^{11a} appear as open circles. The equations of the lines marked "a" ($g = 1/4$) are

$$\log \Gamma_2 = -4.446 + 0.85 \log M \quad (12a)$$

$$\log RTA_2 = 0.964 - 0.14 \log M \quad (12b)$$

and of the lines designated "b" ($g = 5/8$)

$$\log \Gamma_2 = -4.364 + 0.83 \log M \quad (13a)$$

$$\log RTA_2 = 1.046 - 0.17 \log M \quad (13b)$$

Theoretical second coefficients, Γ_2 and RTA_2 , as

(28) E. A. Guggenheim, *Trans. Faraday Soc.*, **44**, 1007 (1948).

(29) For previous discussion of these parameters see ref. (7b); also, "Thermodynamics of High Polymer Solutions," by P. J. Flory and W. R. Krigbaum, a chapter in the "Annual Review of Physical Chemistry," Vol. 2, Annual Reviews, Inc., Stanford, California, 1951.

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

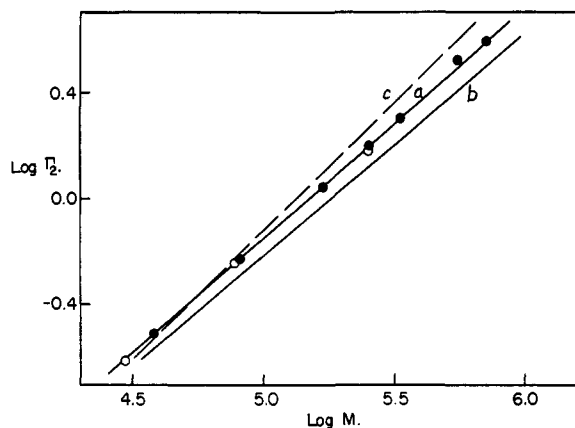


Fig. 8.— $\log \Gamma_2$ vs. logarithm of the molecular weight for polyisobutylene in cyclohexane. Line "a" and the experimental points shown were obtained on setting $g = 1/4$. Line "b" represents the observed second coefficients taking $g = 5/8$, experimental points being omitted for purposes of clarity. Predicted values are represented by the dashed line "c."

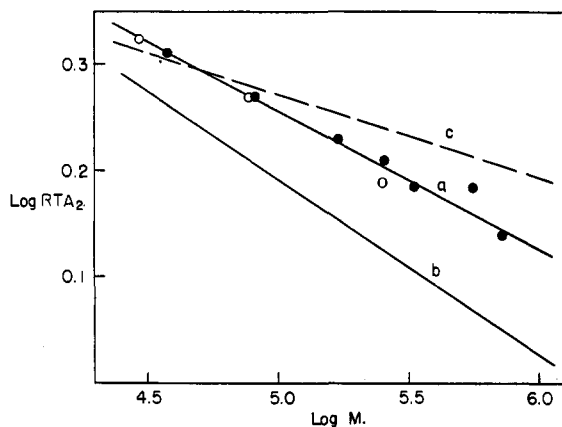


Fig. 9.— $\log RTA_2$ vs. logarithm of the molecular weight for polyisobutylene in cyclohexane. Letters "a," "b" and "c" have the same significance as in Fig. 8.

calculated from equations (7) and (8) taking $v_1 = 109$ cc., $\bar{v}_{30} = 1.097$ cc./g. (obtained by extrapolating the volume-temperature relation for polyisobutylene³¹ above the second order transition to 30°) and $(\psi_1 - \kappa_1) = 0.081$ as deduced by Fox and Flory³² from intrinsic viscosity measurements, are given by $\Gamma_2 = 8.91 \times 10^{-6} MF(X)$ and, converting to units consistent with those used for c and π , $RTA_2 = 2.30 F(X)$. X was calculated from equation (10) using values of α given by the relationship $\alpha^5 - \alpha^3 = 5.02 \times 10^{-3} M^{1/2}$, likewise based on viscosity measurements.³² The value of $F(X)$ corresponding to each calculated X was taken from a graph of this function plotted against X which appeared in a previous paper of this series.^{10b} Both $\log \Gamma_2$ and $\log RTA_2$ so calculated were very nearly linear with $\log M$. The equations of the dashed lines "c" in Figs. 8 and 9, representing the theoretical relationships for Γ_2 and RTA_2 , respectively, for polyisobu-

(31) T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **55**, 221 (1951).

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

tylene in cyclohexane at 30° , are

$$\log \Gamma_2 = -4.737 + 0.92 \log M \quad (14a)$$

$$\log RTA_2 = 0.673 - 0.08 \log M \quad (14b)$$

It is evident from Figs. 8 and 9 that the second coefficients obtained for polyisobutylene are molecular weight dependent. Furthermore, the calculated values of Γ_2 and RTA_2 are the right order of magnitude and the molecular weight dependence as predicted by theory is also qualitatively correct; however, the observed molecular weight dependence is not accurately represented by equations (7) and (8) using values of the parameters deduced from viscosity measurements. Inasmuch as fitting the data using two widely different values of g , $5/8$ and $1/4$, yields substantially the same molecular weight dependence, we conclude that this discrepancy is not a result of the procedure used to deduce the second coefficients from the experimental data.

Turning now to the polystyrene-toluene systems, the experimental values obtained for Γ_2 and RTA_2 taking $g = 1/4$ (Table I) are represented by the filled circles in Figs. 10 and 11, where their

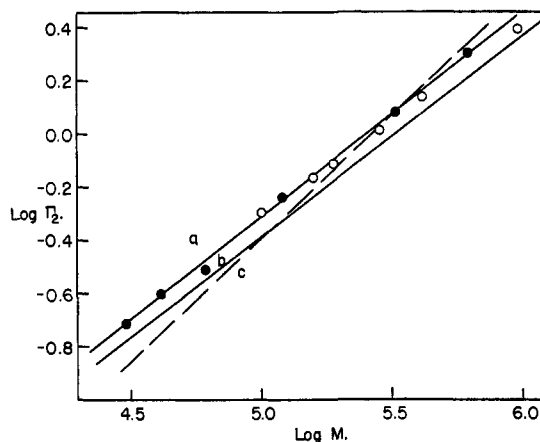


Fig. 10.— \log - \log plot of Γ_2 against molecular weight for polystyrene in toluene at 30° (filled circles). Values obtained by fitting the data of Bawn, *et al.*,^{11d} and Frank and Mark^{11e} appear as open circles. Line "a" and the points shown represent experimental values using $g = 1/4$. Line "b" represents experimental values (not shown for purposes of clarity) obtained using $g = 5/8$. Γ_2 's calculated as described in the text are represented by dashed line "c."

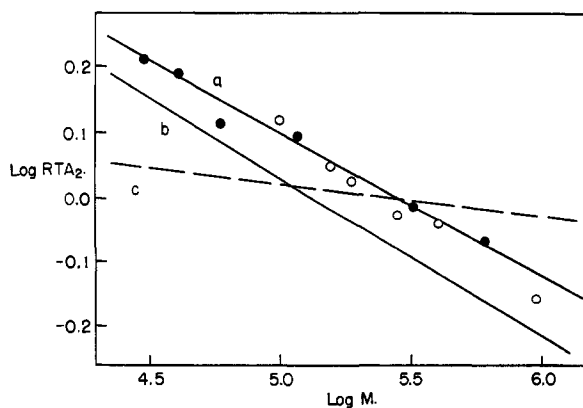


Fig. 11.— \log - \log plot of RTA_2 against molecular weight. (All symbols have the same significance as in Fig. 10.)

logarithms are plotted against $\log M$. The open circles represent values obtained by applying the same procedure to the data of Bawn, *et al.*,^{11d} and of Frank and Mark^{11e} for polystyrene in toluene at $\sim 25^\circ$. Bawn, *et al.*, found that their values of the second coefficient for polystyrene in toluene could be represented empirically as a linear function of $1/M$; however, the present data for polystyrene which extend to lower molecular weights (and the polyisobutylene data as well) do not conform to such a relation. The solid lines marked "a" in Figs. 10 and 11 represent the best straight lines passing through the experimental points obtained using $g = 1/4$. The equations of these lines are

$$\log \Gamma_2 = -4.210 + 0.78 \log M \quad (15a)$$

$$\log RTA_2 = 1.200 - 0.22 \log M \quad (15b)$$

Lines marked "b" represent the best straight lines drawn through the points (not shown) obtained taking $g = 5/8$. The equations of these lines are

$$\log \Gamma_2 = -4.130 + 0.75 \log M \quad (16a)$$

$$\log RTA_2 = 1.280 - 0.25 \log M \quad (16b)$$

Theoretical values for the second coefficients, Γ_2 and RTA_2 , calculated as before from equations (7) and (8) taking $v_1 = 106$ cc., $\bar{v}_{30} = 0.93$ cc./g. (obtained by extrapolating the volume-temperature relation of Fox and Flory³³ for polystyrene above the second order transition temperature to 30°), and $(\psi_1 - \kappa_1) = 0.058$ as deduced from viscosity measurements,³⁴ are given by $\Gamma_2 = 4.82 \times 10^{-6} MF(X)$ and, converting to units consistent with those used for c and π , $RTA_2 = 1.24 F(X)$. X was again calculated from equation (10) using values of α given by the relationship $\alpha^2 - \alpha^3 = 3.18 \times 10^{-3} M^{1/2}$, likewise based on viscosity measurements.³⁴ Both $\log \Gamma_2$ and $\log RTA_2$ so calculated were very nearly linear with $\log M$. The equations of the dashed lines "c" in Figs. 10 and 11, representing the calculated values of Γ_2 and RTA_2 , respectively, for polystyrene in toluene at 30° , are

$$\log \Gamma_2 = -5.121 + 0.947 \log M \quad (17a)$$

$$\log RTA_2 = 0.289 - 0.053 \log M \quad (17b)$$

The second coefficients shown in Figs. 10 and 11 for the polystyrene-toluene systems are clearly molecular-weight dependent. As was the case for polyisobutylene in cyclohexane, the values of the second coefficient for the polystyrene-toluene systems calculated according to theory are the correct order of magnitude, and vary with molecular weight in the observed direction. However, the molecular weight dependences calculated according to equations (7) and (8), using values for α and the thermodynamic parameters deduced from intrinsic viscosity, differ appreciably from those observed. In particular, the calculated $\log RTA_2$ decreases much less rapidly with increasing molecular weight than is observed. This discrepancy for the polystyrene-toluene system is even more marked than that for polyisobutylene-cyclohexane. Comparison of equations (15) and (16) again reveals that fitting the data with the use of two widely different values of g (*i.e.*, $5/8$ and $1/4$) does not alter the observed molecular weight dependence very much; hence, the

procedure used to deduce the second coefficient from the experimental data does not appear to be responsible for the discrepancy.

An attempt was made, therefore, to achieve agreement between theory and experiment by choosing arbitrary values for the parameters occurring in the equations without altering their form. The relation $X = 2(\alpha^2 - 1)$ was derived from the treatment²⁵ of an isolated polymer molecule in solution using approximations the effect of which is difficult to assess. We have attempted to fit the observed molecular weight dependence by replacing the factor "2" by an arbitrary number, n , letting $(\psi_1 - \kappa_1)$ assume values as required but retaining the values for α deduced from intrinsic viscosity. Although the $F(X)$ vs. X curve may be fitted by this device to the RTA_2 values for polyisobutylene, the slope of the steepest region of this curve is somewhat too shallow to fit the observed molecular weight dependence of the second coefficient for polystyrene in toluene. Thus, although the observed molecular weight dependence could be more closely approximated by substituting other values for the thermodynamic parameters entering into equations (7) and (8), and by replacing the factor "2" in equation (10) by an arbitrary number, no choice of values will allow an accurate description of the molecular weight dependence using the function $F(X)$ as given by equation (9). We conclude, therefore, that the observed discrepancy arises from a defect in the function $F(X)$.

The function $F(X)$ occurs in the expression for the volume excluded to a pair of polymer molecules, *i.e.*

$$u = (\bar{v}^2/N_{01})(\psi_1 - \kappa_1)M^2F(X) \quad (18)$$

where N is the Avogadro number. Equation (9) was derived with the assumption that the distribution of segments representing each polymer molecule remains undistorted when two molecules overlap. We have investigated the possibility that when two molecules overlap each may be "flattened" along the axis passing through the centers of the two molecules and expanded perpendicular to this axis. On taking this type of distortion into account, the function $F(X)$ is reduced by approximately 10% over the range of X values of interest, hence all RTA_2 and Γ_2 values would be diminished by this constant factor. It does not appear, therefore, that molecular distortion can account for the observed discrepancy in the function $F(X)$.

Variation of the Osmotic Second Coefficient with Heterogeneity.—According to the dilute solution treatment, A_2 for a molecularly heterogeneous polymer is given by^{10b}

$$A_2 = (\bar{v}^2/v_1)(\psi_1 - \kappa_1)\Upsilon \quad (19)$$

which differs from equation (8) for a homogeneous polymer through replacement of $F(X)$ by Υ , where

$$\Upsilon = \sum_i \sum_j w_i w_j F(X_{ij}) \quad (20)$$

In equation (20) w_i and w_j represent the weight fractions of polymer species i and j , respectively, and each summation extends over all polymer species. For a mixture of two polymer species, i and j , X_{ij} may be calculated according to the relation^{10b}

$$(X_{ij}/M_i M_j) = \left[\frac{2(X_{ii}/M_i^2)^{2/3} (X_{jj}/M_j^2)^{2/3}}{(X_{ii}/M_i^2)^{2/3} + (X_{jj}/M_j^2)^{2/3}} \right]^{3/2} \quad (21)$$

(33) T. G. Fox, Jr., and P. J. Flory, *J. App. Phys.*, **21**, 581 (1950).

(34) W. R. Krigbaum and P. J. Flory, unpublished results.

TABLE III
OSMOTIC PARAMETERS FOR MIXTURES OF POLYSTYRENE FRACTIONS IN TOLUENE

Polymer	w_{05}	$(\pi/c)_{0^a}$	$\bar{M}_n^{g=1/4}$	Γ_2	RTA_2	$(\pi/c)_{0^a}$	$\bar{M}_n^{g=5/8}$	Γ_2	RTA_2
O-4	0.000	4.18	61,500	0.309	1.29	4.22	60,800	0.27	1.14
Mixture O-4 and O-5	.080	3.80	67,700	.349	1.33	3.82	67,300	.32	1.22
	.250	3.16	81,300	.427	1.35	3.17	81,000	.38	1.21
	.500	2.16	119,000	.646	1.40	2.17	118,000	.57	1.24
	.760	1.23	209,000	.933	1.14	1.25	206,000	.82	1.03
	.897	0.86	299,000	1.106	0.95	0.86	299,000	.98	0.84
O-5	1.000	.427	612,000	2.02	0.85	.43	602,000	1.63	.696
HA-3652	394,000	1.62	1.06	.69	373,000	1.23	.85
					(0.89) ^b				(.72) ^b

^a π in g./cm.² and c in g./100 cc. Γ_2 and RTA_2 in units corresponding to those used for π and c . ^b RTA_2 interpolated for a homogeneous polymer whose molecular weight equals the weight-average of the mixture.

TABLE IV
OSMOTIC PARAMETERS FOR POLYISOBUTYLENE FRACTIONS IN CYCLOHEXANE

Polymer	w_{F4}	$(\pi/c)_{0^a}$	$\bar{M}_n^{g=1/4}$	Γ_2	RTA_2	$(\pi/c)_{0^a}$	$\bar{M}_n^{g=5/8}$	Γ_2	RTA_2
LC3	0.000	3.16	81,400	0.590	1.86	3.22	79,800	0.502	1.61
Mixture LC3 and F4	.111	2.89	89,000	.663	1.92	2.92	88,000	.563	1.64
	.250	2.50	103,000	.774	1.94	2.50	103,000	.651	1.62
F4	1.000	0.357	720,000	3.87	1.38	0.373	689,000	3.02	1.13

^a π in g./cm.² and c in g./100 cc. Γ_2 and RTA_2 in units corresponding to those used for π and c .

Equations (19)–(21) predict an increase in the second coefficient, A_2 , with heterogeneity. For a mixture of two polymer species differing only in molecular weight, A_2 should exhibit a maximum at some intermediate weight fraction according to these relations.

In order to test these predictions, osmotic pressure measurements were carried out on five mixtures of polystyrene fractions 0-4 and 0-5 (cf. Table I), and on a polystyrene sample designated HA-3 which had been obtained by a single-step fractionation, and therefore had a rather broad molecular weight distribution. Observed π/c ratios for the ternary systems are indicated in Figs. 4 and 6 by open circles (the weight fraction of polymer species 0-5 is given for each curve), and for polymer HA-3 by triangles. π/c ratios were also measured for two mixtures of polyisobutylene fractions LC3 and F4; these appear in Fig. 12, where $\log(\pi/c)$ is plotted against $\log c$. The weight fraction of species F4 is indicated in the figure for each mixture. Experimental values for the osmotic parameters, fitted with $g = 1/4$ and $5/8$ are given in Table III for the polystyrene-toluene systems, and those for the polyisobutylene-cyclohexane systems in Table IV.

It is evident from the sixth and tenth columns of Tables III and IV that heterogeneity increases the second coefficient, A_2 , as expected according to theory. This may also be seen by comparing the π/c curves shown in Fig. 6 for polystyrene fraction P-5 with that for the 50-50 mixture of fractions 0-4 and 0-5. Although these two polymers have about the same number-average molecular weight, it is evident that the π/c curve for the mixture has a steeper initial slope. Values of RTA_2 expected for a sharp fraction having the same weight-average molecular weight as polymer HA-3 (broad molecular weight distribution³⁵), as calculated according to equations

(35) The ratio (\bar{M}_w/\bar{M}_n) for polymer HA-3 estimated as described in footnote (15), but taking into account the residual heterogeneity of succeeding fractions, was 1.25.

(15b) and (16b), are shown in parentheses at the foot of Table III. Comparison with the experimental values reveals that RTA_2 for this polymer obtained by a single-step fractionation is 18% larger than the interpolated value for a homogeneous polymer having the same weight-average molecu-

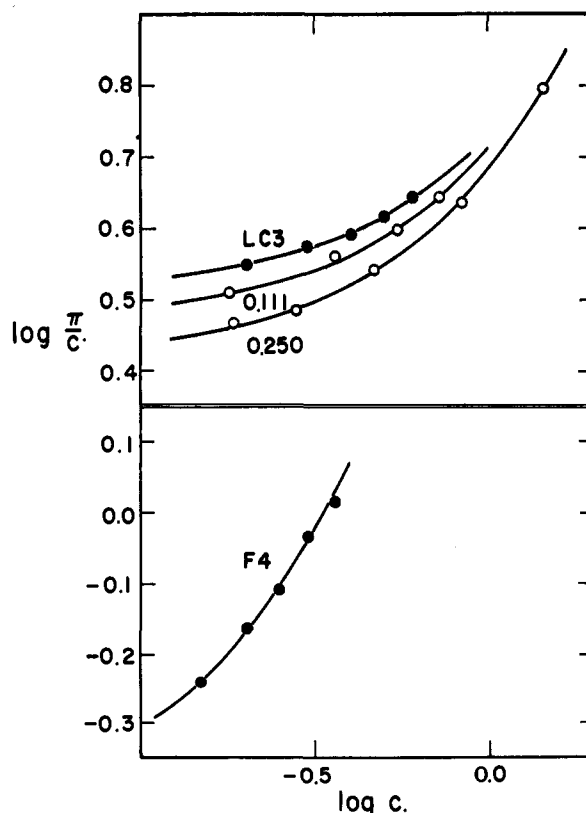


Fig. 12.—Log-log plot of π/c vs. c for two polyisobutylene fractions (filled circles) in cyclohexane at 30° and for two mixtures of these fractions (open circles). The weight fraction of polymer F4 is indicated for each mixture.

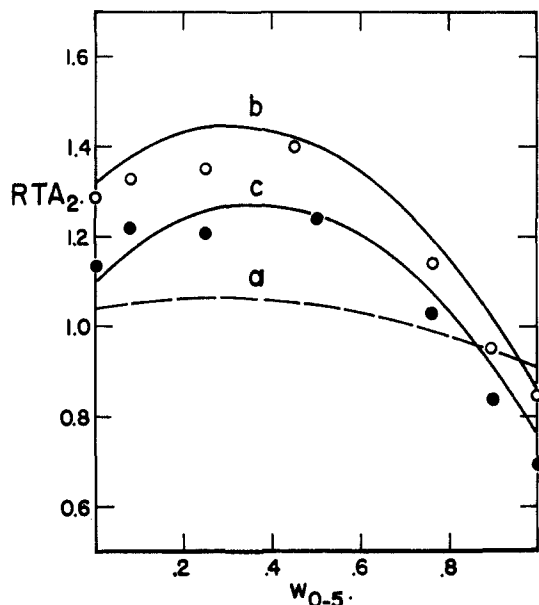


Fig. 13.— RTA_2 for polystyrene fractions 0-4 and 0-5 and for five mixtures of these two fractions, plotted against weight fraction 0-5. Open circles designate experimental values obtained using $g = 1/4$; filled circles, using $g = 5/8$. Curves "a," "b" and "c" were calculated as described in the text.

lar weight. Comparison at constant number-average molecular weight reduces this difference somewhat; on this basis RTA_2 for polymer HA-3 is 10% larger than the interpolated value for the homogeneous species.

Experimental RTA_2 values for polystyrene fractions 0-4 and 0-5, and for five mixtures of these two fractions, appear in Fig. 13 plotted against the weight fraction of high molecular weight species 0-5. Open circles represent values obtained using $g = 1/4$; filled circles, taking $g = 5/8$. The maximum predicted by theory is clearly exhibited. Experimental values of RTA_2 obtained using $g = 1/4$ for polyisobutylene fractions LC3 and F4, and for two mixtures of these fractions, appear in Fig. 14 plotted against the weight fraction of high molecular weight species F4. In Figs. 13 and 14 the dashed lines marked "a" were calculated according to equations (19)–(21), using values of α and the thermodynamic parameters deduced from intrinsic viscosity measurements. Since the variation of RTA_2 with molecular weight for homogeneous polymers calculated in this manner is too small, it is not surprising that the predicted variation of RTA_2 with heterogeneity is likewise much smaller than that observed. As described above, the molecular weight dependence for the homogeneous polymers may be fitted ap-

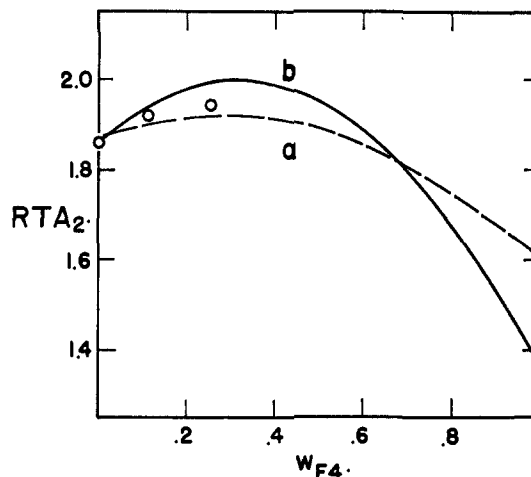


Fig. 14.—Experimental RTA_2 values (fitted with $g = 1/4$) for polyisobutylene fractions LC3 and F4, and for two mixtures, plotted against weight fraction F4. Curves "a" and "b" were calculated as described in text.

proximately by adjusting the arbitrary parameter n in the relation $X = n(\alpha^2 - 1)$, allowing $(\psi_1 - \kappa_1)$ to assume values as required. Using values of n and $(\psi_1 - \kappa_1)$ so obtained, equations (19)–(21) yield theoretical RTA_2 values for the mixtures lying on curves "b" (for RTA_2 fitted with $g = 1/4$) and "c" (with $g = 5/8$). The curves so calculated match the observed values within the error of these measurements.

Conclusions.—On the basis of the results presented in this paper we conclude that the dilute solution theory represents a considerable improvement over the earlier theories making the uniform distribution approximation. The theory correctly predicts a variation of the osmotic second coefficient with molecular weight and with heterogeneity, and allows a prediction of the magnitude of the second coefficient. The theoretical values for the second coefficient vary less rapidly with molecular weight than those observed, this discrepancy probably being due primarily to a defect in the function $F(X)$. On the other hand, the predicted heterogeneity dependence for mixtures of two polymer homologs appears to be substantially correct.

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