[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCMASTER UNIVERSITY]

Intrinsic Viscosities of Polystyrene Fractions in a Variety of Solvents. A Test of the Flory–Fox Treatment[1]

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Intrinsic viscosities of a fraction of polystyrene ($M = 9.8 \times 10^5$), measured in 12 solvents at several temperatures in the range 15 to 65°, have been used to calculate the thermodynamic interaction parameters, θ, $\psi_1 C_M$, ψ_1 and κ_1, of the Flory–Fox treatment of intrinsic viscosities of high polymers. Values of intrinsic viscosity were then calculated from the Flory–Fox equation for other fractions in the molecular-weight range 9.5×10^4 to 1.11×10^6 in the same solvents at 25 and 65°, and these were found to be in good agreement with measured values. The values obtained for the entropy of dilution parameter ψ_1 support the conclusion that the entropy of dilution is related to the shape of the solvent molecules, being significantly greater for solvents whose molecules have a cyclic, and therefore compact, structure.

Introduction

In a series of recent papers[2-4] Flory and Fox have extended the theoretical treatment of the intrinsic viscosity of linear high polymers in solution to take account of the configuration of the polymer molecules and the effect on it of the length of the polymer chain, the nature of the solvent, and the temperature. Their treatment leads to the equations

$$[\eta] = KM^{1/2}\alpha^3 \qquad (1)$$

and

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

where K is a factor independent of the solvent and (except for short chain molecules) of the molecular weight, and $\psi_1 C_M$ and θ have constant values for a given polymer–solvent system. Hence α, the "extensibility coefficient" for the polymer, is dependent on the solvent, the temperature and the molecular weight.

Fox and Flory[5] have subjected these relationships to a thorough experimental testing using solutions of polyisobutylene in several different solvents over a range of temperatures and have obtained excellent agreement between theory and experiment. In a recent paper[6] they reported that preliminary measurements of their own and data from the literature indicate that the theory applies also to polystyrene. Nevertheless, Flory has suggested that a more rigorous test of the relationships with polystyrene would be desirable. The necessary experiments, involving a wider range of temperatures and higher molecular weights, are well under way in this Laboratory. In the meantime, however, we can report evidence that the relationships satisfactorily predict the behavior of polystyrene in a wide variety of solvents.

In their paper, Fox and Flory used data from this Laboratory[7] obtained with toluene solutions of three polystyrene fractions (F 3, F 21, F 35) provided by Dr. E. H. Merz.[8] In an experimental comparison of various criteria of solvent power we have measured the intrinsic viscosity of F 3 at 25, 35, 45, 55 and 65°, in 13 solvents: benzene, bromobenzene, *o*-dichlorobenzene, cyclohexanone, 2,5-dimethylfuran, dioxane, ethyl acetate, ethylbenzene, ethyl chloroacetate, methyl *n*-amyl ketone, 1-nitropropane, pyridine and toluene. With these values, and the values of K already obtained by Fox and Flory, it was possible to evaluate θ and $\psi_1 C_M$ for each of the 13 polymer–solvent systems and hence to calculate $[\eta]$ for other values of M at any accessible temperature T. Other fractions, F 1, F 6, F 21, F 22, F 35 and F 36, of the same series as F 3 were available. Accordingly, their molecular weights were determined viscometrically, and values of $[\eta]$ were calculated at 25° and 65° for F 21 and F 35 (and in a few instances for one or more of F 1, F 6, F 22 and F 36) in the 13 solvents. These were then compared with values of $[\eta]$ experimentally determined.

Experimental

A. Materials 1. Polymers.—The seven polystyrene fractions used were all products of a single fractionation described by Merz and Raetz,[8] and were generously supplied to us by Dr. Merz. (One fraction of the series, F 5, was distributed to laboratories coöperating in a comparative study by the Commission on Macromolecules of the International Union of Chemistry.) Molecular weights of the seven fractions were calculated from our viscosity data, using the relationship of Ewart and Tingey[9] as modified by Fox and Flory,[6] and are given in Table I.

TABLE I

Fraction	F 1	F 3	F 6	F 21	F 22	F 35	F 36
Mol. wt. $\times 10^{-4}$	111	97.5	84.6	44.5	42.1	14.5	9.45

2. **Solvents.**—All the solvents used were of C.p. grade except 1-nitropropane, which was practical grade. Each was carefully distilled immediately before use, a middle fraction of constant refractive index being collected.

B. Procedure 1. Viscosity Determinations.—Measurements on F 3 were made according to the procedure described by Cragg and Simkins,[7] using two Ostwald–Cannon–Fenske viscometers (ASTM-50). These had been carefully calibrated, and kinetic energy corrections were applied to all the data. All other viscosity measurements were made in two Ubbelohde viscometers, modified to allow dilution in the viscometer, and designed so that the kinetic energy effect would be negligible.[10] With these viscometers no correction was necessary, and t_s/t_0 could be taken as equal to ν_s/ν_0.

In these latter measurements the procedure was as follows. Approximately 0.2 g. of polymer was placed in a weighed 50-ml. flask and accurately weighed, after which 30 ml. of solvent was added, and the flask shaken to hasten solution. After thermal equilibration in a bath at 25.0°, the solution was diluted with solvent, also at 25.0°, to

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[1] This work was supported by a grant from the National Research Council of Canada through its Associate Committee on Synthetic Rubber Research. It was reported to the Royal Society of Canada, Section III, meeting in Montreal, June, 1951.

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

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

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

[5] T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1909 (1951).

[6] T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1915 (1951).

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

[8] See E. H. Merz and R. W. Raetz, *J. Polymer Sci.*, **5**, 587 (1950).

[9] For reference see Fox and Flory.[6]

[10] D. A. Henderson and N. R. Legge (Polymer Corporation, Sarnia), private communication.

50.0 ml. The concentration at other temperatures was obtained by correcting for the change in density (d_t/d_{25} is with sufficient precision the same for solution as for pure solvent). The solution was filtered through a medium sintered-glass filter. After 10 min. equilibration at 25.0°, solution (10.00 ml.) was added to the viscometer by pipet and the flow-time determined to ±0.1 sec. Solvent (5.00 ml.) was then added from the same pipet and the flow-time of the diluted solution determined after thorough shaking. Two further dilutions were made with 10.00-ml. portions of solvent, giving four concentrations per run.

When viscosity determinations were made at temperatures other than 25.0°, a separate portion of the master solution was used and diluted as required. Measurements of volume, both of master solution and of diluent, were made after equilibration at 25.0°, but before measurement of flow-times the viscometer and liquid were allowed to stand in the bath at the other temperature for 15 minutes.

Intrinsic viscosities were determined by graphical extrapolation to $c = 0$ of $(\ln \eta_s/\eta_0)/c$ vs. c curves (η_s/η_0 being taken as equal to ν_s/ν_0, since with sufficient precision $d_s/d_0 = 1$ for the solutions investigated). They are expressed in the units dl./g.

Results

Intrinsic viscosities of fraction F 3, determined in twelve different solvents at various temperatures in the range 15 to 65°, are recorded in Table II. The solvents are listed in order of decreasing solvent power as measured by the intrinsic viscosity at 25°. (Bromobenzene is included in the table for completeness, although the intrinsic viscosity values listed are for F 21—the supply of F 3 having been exhausted.)

TABLE II

INTRINSIC VISCOSITIES OF F 3

Solvent	[η]					
	15°	25°	35°	45	55°	65°
Benzene		2.54	2.54	2.55	2.56	2.57
Bromobenzene[a]		1.35				1.32
Toluene		2.32	2.32	2.29	2.29	2.30
o-Dichlorobenzene	2.22	2.27	2.32			
Pyridine	2.17	2.18	2.18	2.18		
Ethylbenzene		2.17	2.16	2.16	2.15	2.14
1,4-Dioxane		2.11	2.07	2.13	2.14	2.14
2,5-Dimethylfuran		2.04	2.00	2.03	2.00	1.99
Cyclohexanone		1.97	1.97	1.97	1.98	1.98
Methyl *n*-amyl ketone	1.25	1.27	1.27	1.28		
Ethyl chloroacetate		1.26	1.30	1.34	1.37	1.39
Ethyl acetate		1.06	1.06	1.06	1.06	1.06
1-Nitropropane		1.00	1.04	1.08	1.10	1.10

[a] Intrinsic viscosities for F 21.

From the data of Table II values of intrinsic viscosity for other fractions in the 13 solvents, at 25 and 65°, were calculated using the Flory–Fox equations (the method of calculation is described elsewhere[4,5]); and, corresponding to each of these predicted values, an intrinsic viscosity was obtained experimentally. These calculated and observed values are recorded in Tables III and IV, side by side for convenience of comparison.

TABLE III

COMPARISON OF CALCULATED AND OBSERVED INTRINSIC VISCOSITIES

Temperature →	25°				65°			
Fraction →	F 21		F 35		F 21		F 35	
Solvent [η] →	Obsd	Calcd.	Obsd.	Obsd.	Obsd.	Calcd.	Obsd.	Calcd.
Bromobenzene			0.64	0.61			0.58	0.58
o-Dichlorobenzene	1.26	1.29	.56	.59	1.23	1.33	.55	.60
Pyridine	1.21	1.26	.53	.57	1.20	1.22	.53	.55
Ethylbenzene	1.24	1.26	.54	.57	1.20	1.21	.52	.55
1,4-Dioxane	1.24	1.23	.54	.56	1.18	1.22	.52	.55
2,5-Dimethylfuran			.48	.46				
Cyclohexanone	1.21	1.16	.54	.53	1.20	1.12	.55	.54
Methyl *n*-amyl ketone	0.75	0.78	.37	.40	0.77	0.77	.38	.38
Ethyl chloroacetate	.77	.77	.38	.39	.79	.82	.37	.39
Ethyl acetate	.72	.73	.36	.37	.73	.73	.37	.36
1-Nitropropane	.65	.64	.34	.34	.70	.68	.34	.34

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED INTRINSIC VISCOSITIES

Solvent	Fraction no.	25°		65°	
		$[\eta]_{obsd.}$	$[\eta]_{calcd.}$	$[\eta]_{obsd.}$	$[\eta]_{calcd.}$
Toluene	F 1	2.56	2.51	2.46	2.43
	F 6	1.99	2.00	1.94	1.99
	F 21	1.30	1.30		
	F 22	1.25	1.23		
	F 35	0.57	0.59		
	F 36	0.42	0.44		
Benzene	F 1	2.80	2.80		
	F 21	1.42	1.48		

Discussion

It is evident from Tables III and IV that with the Flory–Fox equations prediction may be made with remarkable precision. The agreement between the calculated and observed results is often within the precision of measurement of intrinsic viscosities. In Fig. 1, $[\eta]_{obsd.}$ is plotted against $[\eta]_{calcd.}$; the radius of each circle indicates a precision of ±4%, and the line representing the equation $[\eta]_{obsd.} = [\eta]_{calcd.}$ passes through most of the circles. The agreement becomes even more gratifying when all the circumstances are considered. The measurements with F 3, from which the calculated values of $[\eta]$ are derived, were quite independent of the measurements which gave the observed values of Tables III and IV: the viscometers were different (and of a different type), the solvents used were from different batches (and sometimes from entirely different sources),[11] and the measurements were made independently by two different experimenters, the interval between the two series of measurements being two years.

Moreover, the predicted values were for two temperatures 40° apart, for molecular weights from 0.9 × 10^5 to 11 × 10^5, and for solvents varying considerably in molecular structure and in solvent power. Their close agreement with observed values therefore constitutes, we believe, persuasive testimony to the usefulness of the Flory–Fox equations.

The data may also be used to calculate the thermodynamic parameters ψ_1 and κ_1 related, respectively, to the entropy of mixing and the heat of mixing of polymer and solvent.[4] The values of $\psi_1 C_M$ and θ (of equation 2), obtained graphically[4] from the data of Table II and used in calculating the values of $[\eta]_{calcd.}$ in Tables III and IV, are listed in col-

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[11] The relatively poor agreement obtained with *o*-dichlorobenzene as solvent may be due in part to differences in the relative proportion of the other isomers present as impurities.

TABLE V

PROVISIONAL VALUES OF THERMODYNAMIC INTERACTION PARAMETERS AT 25°. POLYSTYRENE IN VARIOUS SOLVENTS

Solvent	θ, °K.	$10^2 \times \psi_1 C_M$ at 25°C.	$\psi_1 C_M V_1$ at 25°C.	ψ_1	κ_1
Benzene	100	0.29	0.26	0.09	0.03
Bromobenzene	115	.25	.27	.09	.03
Toluene	160	.32	.35	.12	.06
o-Dichlorobenzene	220	.52	.54	.18	.13
Pyridine	161	.28	.23	.08	.04
Ethylbenzene	156	.27	.33	.11	.06
1,4-Dioxane	198	.36	.31	.10	.07
2,5-Dimethylfuran	145	.24	.26	.09	.04
Cyclohexanone	170	.23	.24	.08	.05
Methyl *n*-amyl ketone	210	.10	.14	.05	.04
Ethyl chloroacetate	255	.19	.23	.08	.07
Ethyl acetate	222	.09	.10	.03	.02
1-Nitropropane	272	.12	.11	.04	.04

umns 1 and 2 of Table V. The former multiplied by V_1, the molar volume of the solvent concerned, yielded values of $\psi_1 C_M V_1$ (column 3), whence values of ψ_1 (column 4) were obtained by dividing by the value of $C_M V_1$ (3.0) calculated for polystyrene at 25° by Fox and Flory.[6] Finally, the values of κ_1 (column 5) were calculated using the relationship $\kappa_1 = \psi_1 \theta / T$.[6]

Table V, then, constitutes an extension of Table V of the paper by Fox and Flory,[6] providing values for an additional 11 solvents. Our values of ψ_1 and κ_1 are subject to almost all the uncertainties mentioned by Fox and Flory. In other words, these values too are only approximate.

Nevertheless they are good enough to reinforce the conclusions that Fox and Flory drew from their more limited data, namely, that solvents of cyclic molecular structure have higher values of ψ_1 than those whose molecules are acyclic. If we include their data, the values of ψ_1 for the 10 cyclic solvents all lie above 0.08, whereas the values of ψ_1 for the 6 acyclic solvents are all below 0.09 (and all but one below 0.06).

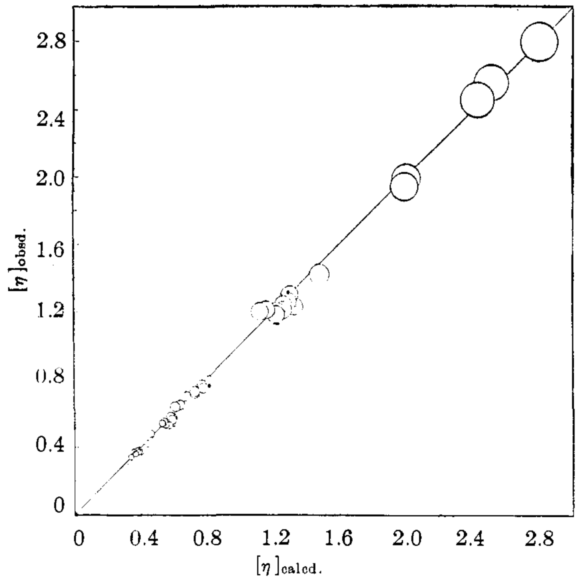

Fig. 1.—System polystyrene-solvent at 25° and 65°: 6 polystyrene fractions, mol. wt. 0.9 × 10^5 to 1.1 × 10^6; 13 solvents (ranging from good to poor).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Flow Birefringence in Arrested Clotting Systems[1]

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Flow birefringence measurements have been made on fibrinogen–thrombin mixtures to which hexamethylene glycol had been added at various stages of the clotting reaction. The extinction angle and birefringence data indicate that the early stages of the clotting process involve end-to-end aggregation, which is reversible upon dilution with solvent containing hexamethylene glycol.

In recent physical chemical studies of the fibrinogen–fibrin reaction attention has been directed toward the early stages of the thrombin-induced polymerization of fibrinogen. It is important to have information about the nature of the polymers produced in the initial part of the reaction, before gelation, where the degree of polymerization is very low. From sedimentation and viscosity studies of inhibited fibrinogen–thrombin systems Shulman and Ferry[2] suggested that an elongated polymer is produced in the clotting reaction in the presence of hexamethylene glycol. The flow birefringence technique is especially suitable for the study of the structure of asymmetrical molecules such as fibrinogen.[3] It is applied here in an investigation of the nature of the polymerized products formed in the early stages of the reaction when bovine thrombin is added to bovine fibrinogen solutions and the clotting process arrested, after a time, by the addition of hexamethylene glycol. It has been shown[2] that this inhibitor does not destroy fibrinogen or thrombin.

Experimental

Materials.—Armour bovine fraction I was refractionated according to Laki's procedure[4] yielding solutions containing 10–15 mg./ml. of fibrinogen as determined by Morrison's method.[5] The protein, analyzed by Laki's method,[4] was

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(1) This work was carried out in connection with project N6-onr 26414 supported by the Office of Naval Research.

(2) S. Shulman and J. D. Ferry, *J. Phys. Colloid Chem.*, **55**, 135 (1951).

(3) C. S. Hocking, M. Laskowski, Jr., and H. A. Scheraga, THIS JOURNAL, **74**, 775 (1952).

(4) K. Laki, *Arch. Biochem. Biophys.*, **32**, 317 (1951).

(5) P. R. Morrison, THIS JOURNAL, **69**, 2723 (1947).