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Osmotic Pressure Measurements for Poly-*p*-Chlorostyrene Solutions

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Osmotic pressure measurements were made on poly-*p*-chlorostyrene fractions in toluene. Their intrinsic viscosities were measured in toluene, butanone, and chlorobenzene at 30°C. The intrinsic viscosity - molecular weight relationships of these systems were then evaluated for the monodisperse homologue by applying the proper correction for the heterogeneity in the sample. The unperturbed dimension of the polymer was estimated by the Kurata-Stockmayer method. A comparison of this estimate with that for polystyrene indicated that the chlorine atom at the para-position had no appreciable effect on the hindrance to the internal rotation of chain. The heat of the dilution of the polymer in toluene and chlorobenzene was also determined from measurements of the temperature coefficient of the osmotic pressure. It was endothermic in toluene and approximately zero in chlorobenzene. These results were then discussed in relation to the cohesive energy densities of the polymer and the solvents.

In the study of high polymers, the osmotic pressure is a primary source of information on the number average molecular weights of polymers and on the thermodynamic properties of polymer-solvent systems. In the measurement, however, we often encounter many technical difficulties which have not yet been completely solved. The main difficulty arises from solute permeation through semi-permeable membranes.[1,2] In practice, however, we may avoid this difficulty in the measurement of fractionated samples with molecular weights higher than 2×10^4 by making a suitable choice of the semi-permeable membrane.

A large number of experimental and theoretical work has been carried out in an effort to elucidate the solution properties of high polymers. It is interesting to examine how these properties are influenced by the structural units of the polymer molecule. In this connection, light-scattering measurements carried out in our laboratory have shown that, in comparison with a polystyrene chain, the chain extension of poly-*p*-chlorostyrene is modified in solution, possibly because of the polar character of its structural unit.[3]

The present investigation was undertaken in order to make a further study of the solution behavior of poly-*p*-chlorostyrene. As is well known, this behavior, for example, the relation between the intrinsic viscosity and the molecular weight, is affected by the heterogeneity in molecular weight. This difficulty can apparently be overcome by estimating the relation corresponding to a homogeneous homologue, using an appropriate molecular weight distribution function and the data for weight- and number-average molecular weights for each fraction of the fractionated sample. Furthermore, the temperature dependence of the osmotic pressure of the system was also measured in order to examine the way in which a polar group substituted in the polymer molecule affects the polymer-solvent interaction.

Experimental

Materials.—The poly-*p*-chlorostyrene fractions used were those described in a previous report.[3] The sample had been thermally polymerized at 100°C for 48 hr. and then fractionated by a successive precipitation procedure employing butanone as a solvent and methanol as a precipitant. The steps followed were to dissolve the fraction in butanone (about 2 per cent concentration) and then to pour the solution into excess methanol, which had previously been cooled by a dry ice - methanol mixture, before filtering and drying the sample in a vacuum (below 10^{-4} mmHg) for 10 hr. at 60°C.

Each solvent was purified in the usual manner.

Osmometry.—The osmotic pressure measurements were carried out with modified Zimm-Myerson osmometers. This type of osmometer was preferred because of its simple construction and operation.[4] Further, some investigators have developed refinements in the use of this instrument.[5-10] Our modification of the

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[1] A. V. Staverman, *Rec. trav. chim.*, **70**, 344 (1951); **71**, 623 (1952).

[2] F. Alvang and O. Samuelson, *J. Polymer Sci.*, **24**, 353 (1957).

[3] T. Saito, This Bulletin, **35**, 1580 (1962).

[4] B. H. Zimm and I. Myerson, *J. Am. Chem. Soc.*, **68**, 911 (1946).

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[7] S. H. Pinner and J. V. Stabin, *J. Polymer Sci.*, **9**, 575 (1952).

[8] E. H. Immergut and J. V. Stabin, ibid., **14**, 209 (1954).

[9] H. Takenaka and T. Ikeda, The 5th Annual Meeting of the Society of Polymer Science, Japan, May, 1956.

[10] T. Matsuo, *Chem. High Polymers Japan* (*Kobunshi Kagaku*), **15**, 640 (1958).

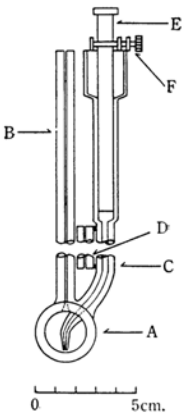

Fig. 1. Modified cell of Zimm-Myerson osmometer.
A, cell; B, measuring capillary; C, filling tube; D, reference capillary; E, positioning rod; F, screw cock

cell is presented in Fig. 1. The glass cell is 1.2 cm. deep and 2 cm. in inner diameter. The filling tube (in. diam. 2 mm.) extends from the side of the cell to within a few millimeters of the bottom, and the measuring capillary (int. diam. 0.8 mm.) extends to the top of the cell so that air bubbles in the cell may be easily eliminated. The filling tube is closed by a glass rod with a mercury seal, similar to that devised by Takenaka and Ikeda,[9] the rod being used to adjust the meniscus level of the solution. Membranes are clamped on by means of 18—8 stainless-steel plates with Teflon packings. The cell is filled and emptied with a hypodermic syringe fitted with a long needle. The osmometer cell is held in a large glass cylinder containing the solvent.

Gel-cellophane ♯300* was used as the semi-permeable membrane. After the membranes had been allowed to swell in water, they were clamped on the cell and then conditioned to a measuring solvent by a procedure similar to that proposed by Carter and Record.[11] Namely, they were transferred to toluene through 50/50 water-ethanol, absolute ethanol and 50/50 ethanol-toluene, being allowed to remain in each solvent for two days. Before measurements the membranes on the cell were immersed in toluene for at least two weeks.

The osmotic pressure measurements for the poly-p-chlorostyrene fractions were performed at 30.0 and 60.0°C by employing toluene and chlorobenzene as solvents. Though the osmometer was cotrolled in an thermostat within ± 0.001°C at 30°C and ± 0.005°C at 60°C, the results did not stabilize because of fluctrations of the room temperature; therefore, the thermostat was then placed in an air-bath, one controlled to within ± 0.1°C of the measuring temperature.

In order to eliminate effects due to the absorption of the solute on the membranes,[2] new membranes were further conditioned with a solution at a higher concentration before use, and then the cell was rinsed three times with the solution to be measured. In the third rinsing it was immersed for a period of 0.5 to 1 hr. The osmotic pressure data were obtained by reading the height differences over 24 to 48 hr., since at least 5 hr. were required to attain equilibrium. No lowering of the height of the solution meniscus, which is possibly due to the permeation of the solute through the membranes, was observed during the measurement except in the case of the most concentrated solution (about 2.5 g./100 cc.). The dynamic osmotic procedure failed to give any reliable results because the relation between the rate of solvent permeation and the pressure difference was not linear. Membrane symmetries were assured within a range of ± 0.01 cm. during each measurement.

Viscometry.—Viscosity was measured at 30 ± 0.01°C with an Ubbelohde viscometer which had been modified to facilitate successive dilutions. Its flowing volume was about 2 cc., and the length of the capillary was 10 cm. The flow time of butanone was about 200 sec., permitting us to ignore the kinetic energy correction. The solvents used were toluene, butanone and chlorobenzene. The data obtained were treated according to Huggins' equation.

Results and Discussion

Extrapolation to Infinite Dilution.—Most of the fractions were osmotically measured in toluene at 30.0°C in a concentration range of 0.2 to 1×10^{-2} g./cm³. The values of the reduced osmotic pressure, π/c, are plotted against the concentration, c, in Fig. 2 (π in g./cm² and c in g./cm³). They are apparently represented by this equation:

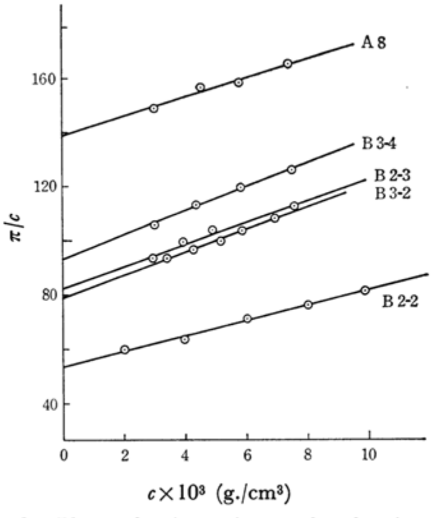

Fig. 2. Plots of π/c against c for fractions of poly-p-chlorostyrene in toluene at 30°C.

$$\pi/c = \boldsymbol{RT}[(1/M_n) + A_2c] \tag{1}$$

where $\boldsymbol{R}$ is the gas constant in g.cm./deg.mol.; M_n, the number-average molecular weight, and A_2, the second virial coefficient in cm³mol./g². The constants, M_n and A_2, were evaluated by the method of least squares, where Eq. 1 was rewritten

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[11] S. R. Carter and B. R. Record, *J. Chem. Soc.*, **1939**, 664.

* This was kindly supplied by the Tokyo Cellophane Co., Ltd.

in the form expressed as a c series, as recommended by Ducker et al.[12] Figure 2 apparently shows a good agreement between the experimental points and the rectilinear relation.

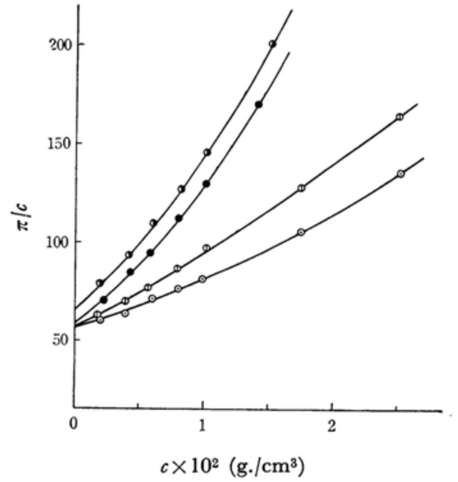

Fig. 3. Plots of π/c against c for fraction of B 2-2 in toluene (⊙ at 30°C, ⦶ at 60°C) and in chlorobenzene (● at 30°C, ◑ at 60°C).

TABLE I. OSMOTIC PRESSURE DATA FOR THE FRACTION B 2-2

Temp. °C	$c\times10^2$ g./cm³	π g./cm²	π/c
Toluene solution			
30	0.200	0.120	60
	0.398	0.253	64
	0.601	0.428	71
	0.801	0.610	76
	0.989	0.804	81
	1.751	1.855	106
	2.513	3.418	136
60	0.178	0.112	63
	0.392	0.274	70
	0.570	0.436	77
	0.792	0.686	87
	1.016	0.988	97
	1.751	2.250	129
	2.504	4.129	165
Chlorobenzene solution			
30	0.224	0.157	70
	0.426	0.360	85
	0.579	0.549	95
	0.799	0.900	113
	1.013	1.320	130
	1.408	2.402	171
60	0.196	0.154	79
	0.421	0.394	94
	0.605	0.666	110
	0.820	1.044	127
	1.010	1.474	146
	1.511	3.036	201

On the other hand, the osmotic pressures of toluene solutions of the fraction B 2-2 were measured over a larger concentration range, up to 2.5×10^{-2} g./cm³, at two different temperatures, 30.0 and 60.0°C. Furthermore, the osmotic pressure of the fraction in chlorobenzene was measured at the same temperatures. A plot (Fig. 3) of the observed data, listed in Table I, shows that the values for both solvents fit curves with an upward curvature. Therefore, the relationship between π/c and c should be represented by an equation with larger virial coefficients:

$$\pi/c = \boldsymbol{R}T[(1/M_n) + A_2c + A_3c^2] \tag{2}$$

where A_3 is the third virial coefficient in cm⁶mol./g³. In this case, there are two methods of analyzing the observed data; one is to determine the most possible curve for the experimental points by the least squares technique, as has been previously described, while the other is to fit the curve according to the equation derived from Flory's theory of dilute polymer solutions, i. e.,

$$\pi/c = (\boldsymbol{R}T/M_n)(1 + \Gamma_2c + g\Gamma_2{}^2c^2) \tag{3}$$

where g is a factor whose value depends on the intermolecular potential energy.[13] As the theoretical work of Stockmayer and Casassa gave $g=1/4$, Eq. 3 may be written as:

$$(\pi/c)^{1/2} = (\boldsymbol{R}T/M_n)^{1/2}[1 + (\Gamma_2/2)c] \tag{4}$$

This equation gives a linear relation between $(\pi/c)^{1/2}$ and c.[14]

The data observed for the fraction B 2-2 were treated by both methods; the results, i. e., M_n, A_2, and A_3, are summarized in Table II. The plots of $(\pi/c)^{1/2}$ against c, also shown in Fig. 4, indicate that they apparently obey a linear relationship. From Table II, however, it appears that the values of M_n and A_2 are nearly the same for both treatments, while the agreement between those of A_3 is far from satisfactory. The standard deviations of the observed values of π from those calculated by Eq. 3 with $g=1/4$ are larger than those obtained from Eq. 2. However, because the osmotic pressures of the fractions in toluene, except that of B 2-2, were measured for only a few concentrations and over a smaller concentration range, it may be better if the data for the fractions are treated by Flory's equation with $g=1/4$. The results are summarized in Table III, which contains the weight average molecular weight, M_w, as determined by Saito from light-scattering measurements.[3]

The Dependence of Solution Properties on the Molecular Weight.—The plot of the

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[12] E. Ducker, E. C. Fieller, H. T. Hookway and R. Townsend, *J. Chem. Soc.*, **1952**, 4390.

[13] P. J. Flory, *J. Chem. Phys.*, **17**, 1347 (1949); P. J. Flory and W. R. Krigbaum, ibid., **18**, 1086 (1950).

[14] W. H. Stockmayer and E. F. Casassa, ibid., **20** 1560 (1952).

TABLE II. COMPARISON OF THE VALUES, FOR M_n, A_2, AND A_3, FOR THE FRACTION B 2-2, CALCULATED FROM THE METHOD OF LEAST SQUARES (Eq. 2) AND FROM THE FLORY EQUATION USING $g=1/4$ (Eq. 3)

Solvent	Temp. °C	Eq.	$M_n\times10^{-4}$	$A_2\times10^4$ cm^{3}mol./g^2.	$A_3\times10^3$ cm^{6}mol./g^3.
Toluene	30	2	45.4	0.80	1.7
		3	48.3	0.98	1.2
Toluene	60	2	51.0	1.33	0.9
		3	47.3	1.12	1.2
Chlorobenzene	30	2	42.9	1.86	8.5
		3	50.3	2.16	5.9
Chlorobenzene	60	2	42.5	2.04	7.3
		3	45.5	2.32	6.2

TABLE III. EXPERIMENTAL RESULTS FOR THE POLY-p-CHLOROSTYRENE FRACTIONS

Fraction	$M_n\times10^{-4}$	$A_2\times10^4$ cm^{3}mol./g.^{2}	$M_w\times10^{-4}$	[η] Toluene	Butanone	Chlorobenzene
A 2	50.7	—	115	—	1.11_4	1.39_6
B 2-2	47.2	0.96	99	0.85_0	0.91_5	1.24_7
B 2-3	30.9	1.47	75	0.65_8	0.73_5	0.92_2
B 3-2	31.9	1.42	66	0.65_2	0.71_2	0.91_8
B 3-4	27.2	1.54	47	0.55_6	0.59_4	0.75_3
A 8	19.2	1.69	31	0.39_5	0.43_5	0.53_7

Intrinsic viscosity is expressed in 100 ml./g.

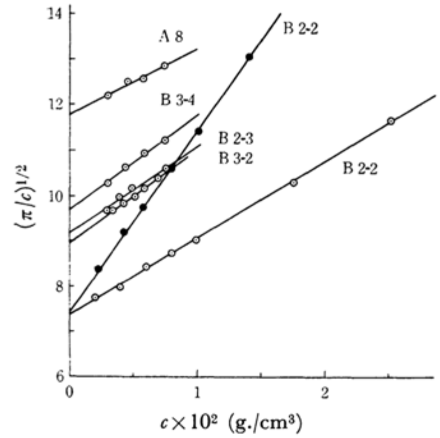

Fig. 4. Plots of $(\pi/c)^{1/2}$ against c according to Eq. 4 for fractions in toluene (open circles) and in chlorobenzene (filled circles) at 30°C.

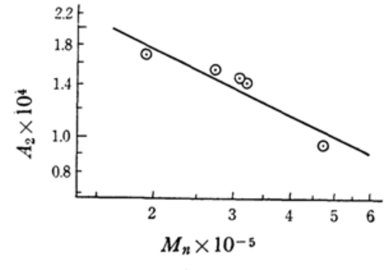

Fig. 5. Dependence of second virial coefficient on molecular weight for poly-p-chlorostyrene fractions in toluene at 30°C.

second virial coefficient against the molecular weight is shown in Fig. 5. It appears that A_2 decreases as M_n increases, as is generally recognized, and has a linear logarithmic relationship to M_n, corresponding to $A_2 \propto M_n^{-0.6}$. The osmotic second virial coefficients have slightly higher values and a more marked dependence on the molecular weight than that determined by light-scattering measurements. This may be partly attributed to the molecular weight distribution of the fractions.

As a result of light-scattering measurements, it has been shown that the presence of a polar group in the molecule of poly-p-chlorostyrene has a marked influence on its solution behavior and increases its solubility in polar solvents. This tendency may be deduced from the fact that A_2 in a chlorobenzene solution is remarkably higher than that in toluene, as is shown in Table II, and also from the fact that the magnitude of the intrinsic viscosity of the fractions in toluene, butanone, and chlorobenzene increases as the polarity of the solvent is increased. The data for the intrinsic viscosity, [η], are also summarized in Table III. The plot of [η] against M_n for each solvent (Fig. 6) shows that the relation for each solution is apparently linear on a log-log scale. However, it is known that the degree of homogeneity with respect to the molecular weight has a much greater effect on the relation between [η] and M_n than on that between [η] and M_w. For comparison, the plot of [η] against M_w is also shown in Fig. 6. These plots represents the effect of the heterogeneity on the Mark-Houwink equation:

$$[\eta]=KM^{\alpha} \qquad (5)$$

It is desirable that the equation be established for a homogeneous homologue of the polymer

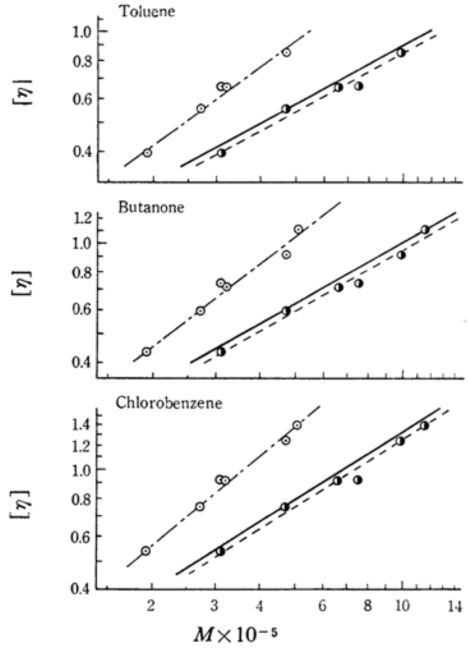

Fig. 6. Relation between intrinsic viscosity and molecular weights. Open circles, $[\eta]$-M_n; half-filled circles, $[\eta]$-M_w; full line, relation corresponding to homogeneous homologue.

before entering into a precise discussion. The K-value corresponding to homogeneous samples may be estimated from the experimental values, i. e., K_w in the $[\eta]$-M_w or K_n in the $[\eta]$-M_n relation, by assuming that the molecular weight distribution for each of the fractions is represented by the familiar Schulz-Zimm function:

$$w(M) = [y^{h+1}/\Gamma(h+1)]M^h \exp(-yM)$$

where

$$y = h/M_n = (h+1)/M_w$$

where Γ represents the gamma function, and where the value of the exponent, α, is approximately the same for the $[\eta]$-M_w relationship. The parameter, h, characterizing the heterogeneity of each fraction was experimentally determined. Therefore, the K value may be calculated by the equation:

$$K = K_w\Gamma(h+1)(h+1)^\alpha/\Gamma(\alpha+h+1)$$

or $$K = K_n\Gamma(h+1)h^\alpha/\Gamma(\alpha+h+1)$$

A detailed discussion will be given elsewhere. Thus, the relations were evaluated for the homogeneous homologue:

$$[\eta] = 1.29 \times 10^{-4} M^{0.64} \text{ (in toluene)}$$

$$[\eta] = 0.96 \times 10^{-4} M^{0.67} \text{ (in butanone)}$$

$$[\eta] = 0.48 \times 10^{-4} M^{0.74} \text{ (in chlorobenzene)}$$

They are shown by the full curves in Fig. 6. They show that the molecule of poly-*p*-chlorostyrene assumes the largest dimension in chlorobenzene and the smallest in toluene, and that the magnitude of the exponent increases with an increase in the polarity of the solvent.

Unperturbed Dimension.—According to the theory of the excluded volume effect, developed by Kurata, Stockmayer and Roig,[15] it may be possible to evaluate an unperturbed dimension of a polymer molecule from its $[\eta]$-M relationships. Recently a detailed review of the procedure has been presented.[16] Their theory results in the following equation:

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + Bg(\alpha_\eta)M^{2/3}/[\eta]^{1/3} \tag{6}$$

where K_θ is K in Eq. 5, corresponding to the theta condition; B, the constant which depends on the structure of the polymer molecule and the polymer-solvent interaction, and α_η, the hydrodynamic linear expansion factor, $([\eta]/[\eta]_\theta)^{1/3}$. The function of α_η, $g(\alpha_\eta)$, is given by the equation:

$$g(\alpha_\eta) = 8\alpha_\eta^3/(3\alpha_\eta^2+1)^{3/2} \tag{7}$$

From the first plot of $[\eta]^{2/3}/M^{1/3}$ against $M^{2/3}/[\eta]^{1/3}$, K_θ was approximately estimated by an extrapolation according to Eq. 6, and the α_η value for each fraction was evaluated. Then, $[\eta]^{2/3}/M^{1/3}$ was plotted against $g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}$, using the estimated α_η value, thus affording an improved value for K_θ.

Our data were repeatedly analyzed with the least-square technique of Deming until K_θ converaged to a constant value. In this case the effect of the molecular weight distributions of each fraction was taken into account. That is, the observed value of $[\eta]$ for each fraction was corrected to that corresponding to a homogeneous sample by assuming the Schulz-Zimm distribution function. From the intercepts of the Kurata-Stockmayer plots for poly-*p*-chlorostyrene, which are shown in Fig. 7, the values of K_θ in toluene, butanone, and chlorobenzene are derived as

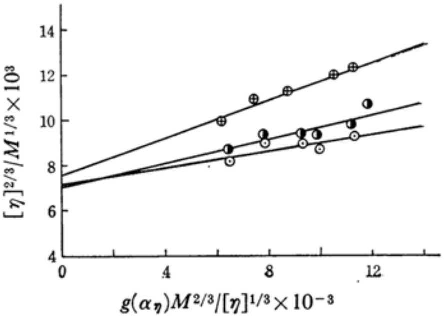

Fig. 7. Kurata-Stockmayer viscosity plots for poly-*p*-chlorostyrene fractions in toluene (open circles), butanone (half-filled circles), and chlorobenzene (crossed circles).

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[15] M. Kurata, W. H. Stockmayer and A. Roig, *J. Chem. Phys.*, **33**, 151 (1960).

[16] M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolymer Forsch.*, **3**, 196 (1963).

6.1, 5.9, and 6.6×10^{-4} respectively. These values are considered to be in excellent agreement and give $K_\theta = (6.1 \pm 0.4) \times 10^{-4}$. The unperturbed end-to-end distance of a polymer chain, $\langle r^2 \rangle_0^{1/2}$, in cm., may be calculated by the equation:

$$\langle r^2 \rangle_0^{1/2} = (K_\theta / \Phi)^{1/3} M^{1/2} \tag{8}$$

where Φ is a universal constant, given as 2.87×10^{21} for monodispersed systems. The σ factor may be generally used as a measure of the hindrance to internal rotations about the single bonds of the chain; it is defined as the ratio of $\langle r^2 \rangle_0^{1/2}$ to the dimension, $\langle r^2 \rangle_{0f}^{1/2}$, which corresponds to the model with fixed valence angles and a completely free internal rotation. In the case of poly-*p*-chlorostyrene, this gives a value for σ of 2.30 ± 0.06, which is slightly higher than that, 2.18 ± 0.07, cited in the literature.[16] On the other hand, the σ value for polystyrene is 2.22 ± 0.05.[16] It appears that the chlorine atom at the para-position has only a small effect on the hindrance to the internal rotations, whereas the presence of this polar group remarkably modifies the solubility of the polymer in comparison with that of polystyrene.

Thermodynamic Properties. — In examining polymer-solvent interactions, the results are usually expressed in terms of a purely empirical parameter, χ_1, which is expressed according to the Flory-Huggins lattice theory of polymer solutions by the equation:

$$A_2 = [(1/2) - \chi_1] / V_1 d_2^2 \tag{9}$$

where V_1 is the molar volume of the solvent and d_2, the density of the polymer. The density of the polymer was calculated from the relation between the solution density and the weight fraction of the polymer, the additivity of the partial volumes being assumed. The χ_1 values for the fraction B 2-2 at 30°C are 0.483 in toluene and 0.462 in chlorobenzene. Ogino reported that the values of the parameter for polystyrene and poly-*p*-chlorostyrene in benzene, as determined by the measurement of initial stress-strain relations for gels in the solvent, were 0.47 for the former system and 0.49_5 for the latter.[17] From the osmotic pressure measurements, Bawn et al. obtained χ_1 values of 0.443 to 0.447 for polystyrene solutions in toluene and of 0.484 to 0.487 for butanone solutions.[18] These figures show that toluene, as well as benzene, is a poor solvent for poly-*p*-chlorostyrene, and that the better solvent has a structure similar to that of the monomer unit of the polymer, i. e., chlorobenzene for poly-*p*-chlorostyrene and toluene for polystyrene.

Further information can also be obtained from the measurement of the temperature dependence of the osmotic pressure. According to thermodynamic relationships, the excess molar heat of dilution, Δh_1^{E}, and the excess entropy of dilution, Δs_1^{E}, are given by the temperature coefficients of the second and third virial coefficients, i. e.,

$$\begin{aligned} \Delta\mu_1^{\mathrm{E}}/c^2 V_1 &= -\boldsymbol{R}T(A_2 + A_3 c) \\ \Delta h_1^{\mathrm{E}}/c^2 V_1 &= \boldsymbol{R}T^2\{(\partial A_2/\partial T) + (\partial A_3/\partial T)c\} \\ T\Delta s_1^{\mathrm{E}}/c^2 V_1 &= \boldsymbol{R}T\{A_2 + T(\partial A_2/\partial T) + \\ &\qquad A_3 c + T(\partial A_3/\partial T)c \end{aligned}$$

where $\Delta\mu_1^{\mathrm{E}}$ represents the excess free energy of dilution. The results are summarized in Table IV, in which the values of A_2 and A_3, evaluated by means of the method of the least squares, were used. The heat of dilution in chlorobenzene could be taken to be zero within the limits of experimental error over the concentration range from zero to 2×10^{-2} g./cm³. With a toluene solution the values show an endothermic heat of dilution. Bawn and Wajid reported that the heat of dilution in a polystyrene-toluene system was zero at all concentrations.[19] Polystyrene has a cohesive energy density (C. E. D.) of 82 cal./cm³, as elucidated by swelling experiments.[20] On the other hand, the value of the Hildebrand solubility parameter for toluene is reported to be 8.90 (cal./cm³)$^{1/2}$ at 25°C; i. e., the C. E. D. of toluene is 79 cal./cm³. The solubility behavior of the polystyrene-toluene system may be interpreted in terms of their C. E. D.'s and in terms of the resemblance of the solvent molecule to the structural unit of the polymer. If this situation also holds in the case of a poly-*p*-chlorostyrene - chlorobenzene system, the C. E. D. of poly-*p*-chlorostyrene may lie near the value of that of chlorobenzene, i. e., 91 cal./cm³.

TABLE IV. EXCESS THERMODYNAMIC FUNCTIONS OF DILUTION FOR POLY-*p*-CHLOROSTYRENE IN TOLUENE AND CHLOROBENZENE AT 30°C (cal.cm³/g.²)

$c \times 10^2$ g./cm³	$\Delta\mu_1^{\mathrm{E}}/c^2V_1$	$\Delta h_1^{\mathrm{E}}/c^2V_1$	$T\Delta s_1^{\mathrm{E}}/c^2V_1$
	Toluene solution		
0	-0.048 ± 0.002	0.32 ± 0.04	0.37 ± 0.04
1	-0.058 ± 0.003	0.27 ± 0.04	0.33 ± 0.04
2	-0.069 ± 0.003	0.23 ± 0.04	0.30 ± 0.04
	Chlorobenzene solution		
0	-0.112 ± 0.007	0.11 ± 0.09	0.22 ± 0.09
1	-0.163 ± 0.007	0.04 ± 0.10	0.20 ± 0.10
2	-0.215 ± 0.008	-0.04 ± 0.10	0.18 ± 0.10

Summary

The osmotic pressure of poly-*p*-chlorostyrene fractions in toluene and the intrinsic viscosities at 30°C in toluene, in butanone, and in chlorobenzene have been measured. The relation

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[17] K. Ogino, This Bulletin, **32**, 553 (1959).

[18] C. E. H. Bawn, R. J. F. Freeman and A. D. Kamaliddin, *Trans. Faraday Soc.*, **46**, 862 (1950).

[19] C. E. H. Bawn and M. A. Wajid, *J. Polymer Sci.*, **12**, 109 (1954).

[20] R. E. Boyer and R. S. Spencer, ibid., **3**, 97 (1948).

between the intrinsic viscosity and the molecular weight corresponding to a homogeneous homologue has been determined, taking into consideration the effect of the heterogeneity of each fraction on this relationship. The unperturbed dimension of the polymer, as evaluated by Kurata-Stockmayer's plots, showed that the polar group at the position of the benzene ring does not appreciably affect the hindrance to internal rotations about single bonds of its chain in comparison with the polystyrene chain. The heat of the dilution of poly-*p*-chlorostyrene in chlorobenzene and toluene has been determined from measurements of the temperature coefficients of the osmotic pressure. In the concentration range up to 2.5×10^{-2} g./cm^3, the $\Delta h_1^{E}/c^2V_1$ value, where V_1 is the molar volume of the solvent, was approximately zero in chlorobenzene and 0.3 cal. cm^3/g.^{2} in toluene. The results have been discussed in relation to the cohesive energy densities of the polymer and the solvents.

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