BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 997—1000 (1971)

Osmotic Pressures of Polystyrene, Poly-*p*-chlorostyrene and Poly-*o*-chlorostyrene Solutions

Kenji Kubo and Kazuyoshi Ogino
Department of Pure and Applied Sciences, College of General Education, The University of Tokyo, Tokyo

(Received November 30, 1970)

Second virial coefficients for polystyrene (PS), poly-*p*-chlorostyrene (PPCS), and poly-*o*-chlorostyrene (POCS) were determined in various solvents by osmotic-pressure measurements. Free-energy parameters, χ, were estimated from the values of the second virial coefficients. It was shown that the values of χ in each solvent at 30°C became larger in the following order: PS, POCS, PPCS in toluene; PS, PPCS, POCS in chlorobenzene; PPCS, PS, POCS in *n*-butyl acetate. It was indicated that, in addition to the effect of intermolecular forces, another parameter related to the stiffness of the polymer chains should be considered in order to discuss the thermodynamic properties of polymer solutions. It was shown that the values of χ for two polychlorostyrenes in *n*-butyl acetate increased with an increase in the temperatures, unlike the behavior of PS in the same solvent.

In a preceding paper,[1] it was shown that the thermodynamic properties of solutions of poly-*p*-chlorostyrene (PPCS) were markedly different from those of polystyrene (PS) because of the effect of the polar substituent at the para position.

In this paper, the variation in the thermodynamic properties due to the various positions of substituent was examined by osmotic-pressure measurements for PS, PPCS, and poly-*o*-chlorostyrene (POCS) in different solvents.

Experimental

Materials. *o*-Chlorostyrene, a monomer, was prepared from commercial *o*-chlorobenzaldehyde by the following process: *o*-chlorophenylmethylcarbinol was synthesized by a Grignard reaction and was then dehydrated by potassium bisulfate.[2] The monomer was polymerized in bulk at 60°C, in the presence of azo-bis-isobutyronitrile as an

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[1] K. Kubo, K. Ogino, and T. Nakagawa, *Nippon Kagaku Zasshi*, **88**, 1254 (1967).

[2] L. A. Brooks, *J. Amer. Chem. Soc.*, **66**, 1295 (1944).

initiator, under nitrogen gas. The polymer was fractionated from a dilute benzene solution by a successive precipitation procedure using methanol. One separate from nine fractions was used for the osmotic-pressure measurements.

Each fraction of PPCS was the same as has been described in the previous paper.[1] The monodispersed polystyrene used in this experiment was from the Pressure Chemical Company; we assumed that this will not be of the isotactic type, for it was soluble in 2-butanone.

The solvents were dried, toluene and chlorobenzene with calcium chloride, and *n*-butyl acetate with magnesium sulfate, and were freshly distilled before each measurement.

Measurements. The osmotic pressures were determined using a Hewlett-Packard High Speed Membrane Osmometer (Model 503) and Schleicher & Schuell membranes (Type 08) at various temperatures; in toluene and chlorobenzene at 30°C and in *n*-butyl acetate at 5, 30, and 55°C. Pycnometer was used in determining the partial specific volumes in benzene at 30°C; these volumes were found to be 0.797 for PPCS and 0.792 (cc/g) for POCS.

Results

The second virial coefficient, A_2, was obtained from the osmotic pressure by the use of the following equation;

$$\pi/c = \boldsymbol{R}T(1/M_n + A_2c) \tag{1}$$

or;

$$(\pi/c)^{1/2} = (\boldsymbol{R}T/M_n)^{1/2}(1 + M_nA_2c/2) \tag{2}$$

where π is the osmotic pressure; c, the concentration; M_n, the number-average molecular weight; $\boldsymbol{R}$, the gas constant, and T, the absolute temperature. The data observed in toluene and chlorobenzene fit Eq. (2), and those in *n*-butyl acetate fit Eq. (1); several examples are shown in Figs. 1 and 2. The results for M_n and A_2 are summarized in Table 1.

According to the lattice theory of polymer solutions by Flory and Huggins, the free-energy parameter, χ, is related to A_2 by the following relation;

$$A_2 = (1/2 - \chi)\bar{v}_2^2/V_1 \tag{3}$$

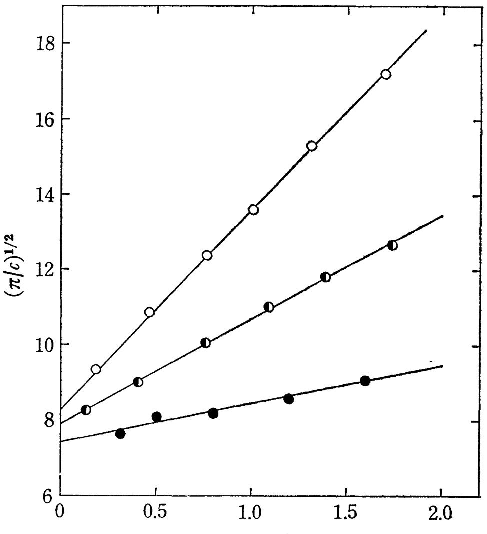

Fig. 1. Plots of $(\pi/c)^{1/2}$ against c in toluene at 30°C. ○ for PS, ◐ for POCS, and ● for PPCS-f6

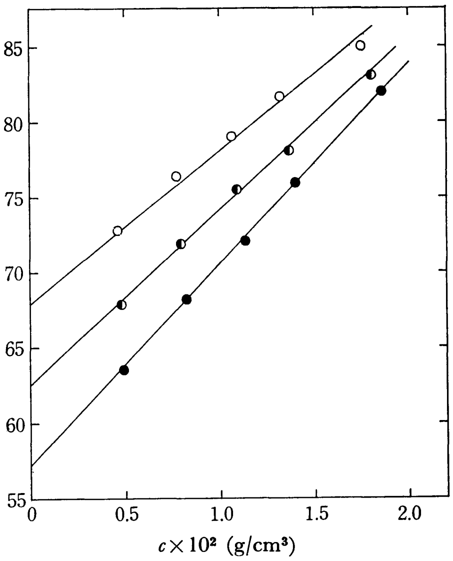

Fig. 2. Plots of π/c against c for POCS in *n*-butyl acetate. ● at 5°C, ◐ at 30°C, and ○ at 55°C

where $\bar{v}_2$ is the partial specific volume of the polymer and where V_1 is the molar volume of the solvent. Since a strong molecular-weight dependence of A_2 in dilute solutions has been observed, especially in good solvents, it is not reasonable, in a strict sense, to discuss the thermodynamic properties of polymer solutions in terms of χ values estimated from Eq. (3). In dilute polymer solutions, A_2 is generally given by the relation using Flory's notation:

$$A_2 = (1/2 - \chi)(\bar{v}_2^2/V_1)h(z/\alpha_s^3) \tag{4}$$

with:

$$z = 2(3/2\pi)^{3/2}(\bar{v}_2^2/N_AV_1)(\overline{r^2}_0/M)^{-3/2}M^{1/2}(1/2 - \chi). \tag{5}$$

Here, N_A is Avogadro's number, $\overline{r^2}_0$ is the unperturbed mean-square end-to-end distance of the polymer, and the latter is proportional to the molecular weight, M. The α_s quantity is the expansion factor related to the statistical radius. Several forms of $\alpha_s(z)$ consistent with $h(z/\alpha_s^3)$ have been reported. Recently, it has been shown by Fujita *et al.* that their experimental results can be explained well[3] by a combination of $\alpha_s(z)$ and $h(z/\alpha_s^3)$, which Yamakawa and his coworkers presented.[4,5] Therefore, employing their results we estimated χ as:

$$\alpha_s^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \tag{6}$$

and:

$$h(z/\alpha_s^3) = \{1 - (1 + 4.454z/\alpha_s^3)^{-0.2867}\}/1.277(z/\alpha_s^3). \tag{7}$$

The value of χ is obtained as follows: by combining Eqs. (4)—(7), $A_2M^{1/2}(\overline{r^2}_0/M)^{-3/2}$ can be represented, and plotted, as a function of z only. The value of z, which corresponds to the A_2 and M_n values obtained from the osmotic-pressure measurements, can be found on the graph when we know the value of $(r_0^2/M)^{1/2}$.

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3) T. Norisuye, K. Kawahara, A. Teramoto, and H. Fujita, *ibid.*, **49**, 4330 (1968).

4) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **47**, 3991 (1967).

5) H. Yamakawa, *ibid.*, **48**, 2103 (1968).

TABLE 1. EXPERIMENTAL RESULTS OF OSMOTIC PRESSURE MEASUREMENTS AND VALUES OF FREE ENERGY PARAMETERS FOR POLYSTYRENE, POLY-*p*-CHLOROSTYRENE AND POLY-*o*-CHLOROSTYRENE IN VARIOUS SOLVENTS

Polymer -Fract.	Solvent	Temp. °C	$M_n \times 10^{-4}$	$A_2\times 10^4$ $\left(\frac{\text{cm}^3\cdot\text{mol}}{g^2}\right)$	χ[a)]	χ[b)]
PS	Toluene	30	37.3	3.45	0.456	0.383
	Chlorobenzene	30	38.8	3.77	0.454	0.370
	n-Butyl acetate	5	41.1	1.88		
		30	40.4	2.08	0.466	0.423
		55	40.2	2.00		
PPCS-f6	Toluene	30	46.3	0.625	0.489	0.483
-f7	Chlorobenzene	30	31.6	2.17	0.465	0.411
-f8	*n*-Butyl acetate	5	18.0	2.96		
-f8		30	17.6	2.39	0.448	0.380
-f8		55	16.5	1.90		
POCS	Toluene	30	40.7	1.73	0.470	0.435
	Chlorobenzene	30	40.6	1.72	0.472	0.439
	n-Butyl acetate	5	41.5	0.570		
		30	40.3	0.449	0.490	0.488
		55	40.1	0.337		

a) Estimated from Eq. (3).
b) Estimated from Eqs. (4)—(7).

Then, the value of χ corresponding to the z can be readily obtained from Eq. (5). The values of χ, summarized in Table 1, are estimated, using the values of $\bar{v}_2$ in cc/g and $(\overline{r^2_0}/M)^{1/2}$ in cm·mol$^{1/2}$/g$^{1/2}$, to be as follows:

	$\bar{v}_2$	$(\overline{r^2_0}/M)^{1/2}\times 10^{11}$
PS	0.920[6)]	670[7)]
PPCS	0.797	584[1)]
POCS	0.792	633[8)]

The values of χ obtained from Eq. (3) are also summarized in Table 1.

Discussion

A free-energy parameter, χ, is resolved into an enthalpy term, χ_h, and an entropy term, χ_s. The enthalpy term is represented by Hildebrand's expression:[9)]

$$\chi = V_1(\delta_s - \delta_p)^2/RT. \qquad (8)$$

Here, the solubility parameter, δ, is given by $(\Delta E/V)^{1/2}$, where ΔE is the molar energy of vaporization, and the suffix s or p represents the solvent or the polymer respectively. It was shown by Huggins that χ_s is expressed as $1/z$ (z: coordination number); thus, χ should increase in accordance with $|\delta_s - \delta_p|$. From the results in toluene, taking account of δ_s (toluene) = 8.9 and δ_p (PS) = 9.3,[10)] it seems to be reasonable to assume that δ_p increases in the order of PS, POCS, and PPCS. The assumption that the δ_p of POCS is smaller than that of PPCS suggests that the effect of the *o*-chlorine atom on an intermolecular force is not so large as that of the *p*-chlorine atom because of the screening effect by a main chain for the *o*-chlorine atom.

If the order of δ_p shown above can be used, and in view of δ_s (chlorobenzene) = 9.50, the increase in χ does not correspond to the order of $|\delta_s - \delta_p|$ in chlorobenzene. Therefore, in addition to the effect of intermolecular forces, another parameter may be introduced so as to represent the difference in the thermodynamic properties of polymer solutions. Thus, it is reasonable to take into account a theory of the average-potential method proposed by Prigogine and his co-workers.[11)] In this theory, external degrees of freedom of r-mer are defined as the remainder left by internal degrees associated with intramolecular valence forces from a total of $3r$ degrees of freedom; they are taken to be $3c$ in number. With a sufficiently large r, c/r tends to 0 for a "perfect rigid r-mer" and to 2/3 for a "perfect flexible r-mer." The parameter c has a value which decreases with an increase in the "stiffness' of the polymer chain. The intermolecular potential energy between elements of i and j is taken to be a Lennard-Jones 6-12 potential-energy type with characteristic parameters for the pair, ε^*_{ij} and r^*_{ij}, where r^*_{ij} is the distance between the centers of the elements, at a minimum potential energy of ε^*_{ij}. The element of the monomer is the monomer itself, and the submolecule of the polymer is treated as an element. If the "sizes" of the elements of A (monomer) and B

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6) M. Griffel, R. S. Jessup, J. A. Cogliano, and R. P. Park, *J. Research NBS*, **52**, 217 (1954).

7) M. Kurata and W. H. Stockmayer, *Fortscr. Hochpolym.-Forsch.*, **3**, 196 (1963).

8) K. Matsumura, *Makromol. Chem.*, **124**, 204 (1969).

9) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Dover Publications Inc., New York, N.Y. (1964), p. 131.

10) T. G. Fox, *Polymer*, **3**, 111 (1962).

11) I. Prigogine (with the collaboration of A. Bellemans and V. Mathot), "The Molecular Theory of Solutions," North-Holland Publishing Co., Amsterdam (1957), Chapters 16 and 17.

(r-mer) are equal,

$$r^*_{\mathrm{AA}} = r^*_{\mathrm{BB}} = r^*_{\mathrm{AB}}. \tag{9}$$

If the minima of potential energies are also equal,

$$\varepsilon^*_{\mathrm{AA}} = \varepsilon^*_{\mathrm{BB}} = \varepsilon^*_{\mathrm{AB}}. \tag{10}$$

The free-energy parameter in the (r-mer)-monomer system can, then, be approximately represented by this theory by the relation:

$$\chi = 1/z + (C_{\mathrm{P,A}}/2R)(1 - c_{\mathrm{B}}/q_{\mathrm{B}})^2 \tag{11}$$

where $C_{\mathrm{P,A}}$ is the molar configurational heat capacity of the monomer and where q_{B} is given by $(rz-2r+2)/z$. Using the parameters assumed by Eqs. (9) and (10) along with Eq. (11), it can readily be understood that χ is larger in positive value the stiffer the polymer. The systems of polychlorostyrenes-chlorobenzene are treated as such cases in a crude sense. On the basis of this crude assumption, the χ values for these systems are not worth discussing quantitatively, but the finding that the value of χ for POCS in chlorobenzene is larger than the corresponding value for PPCS may be qualitatively attributed to the enlarged chain stiffness of POCS, which in turn may be due to the steric hindrance of the rotation of the main chain by the chlorine atom at the ortho position.

The second virial coefficients for PPCS and POCS in *n*-butyl acetate decrease with an increase in the temperature. This behavior is different from that of PS in the same solvent, and it is equivalent to a decrease in the intrinsic viscosity with an increase in the temperature, as has been reported previously for PPCS in *n*-butyl acetate.[1] In view of an inappreciable temperature coefficient of $\bar{r}_0^2$ for PPCS in the same solvent,[12] it seems reasonable to conclude that the values of χ for PPCS, and perhaps for POCS in *n*-butyl acetate, increase with an increase in the temperatures. This fact may suggest the existence of a strong interaction between the chlorine atom in the polymer and the solvent molecule. The solubility of POCS in *n*-butyl acetate in poorer than that of PPCS. This fact may be attributed to the difference in stiffness between the two polychlorostyrenes.

From the relations for A_2 and M_n reported in the literature, the values of A_2 can be estimated for polymers with the same molecular weights as those of the polymer fractions employed in this work. The values of A_2 thus obtained are 3.67[13] and 3.54×10^{-4}[14] for atactic PS in toluene; a value of 3.45×10^{-4} (cm^3·mol/g^2) is obtained by us, which is slightly smaller than the former and is nearly equal to the latter. The values of A_2 for PPCS in toluene, 0.80[15] and 1.00×10^{-4},[16] are slightly larger than our corresponding value, 0.625×10^{-4} (cm^3·mol/g^2). These discrepancies may be partly attributed to the difference in the molecular-weight distributions of the polymers; the deduced conclusion seems not to be affected by these discrepancies. The results for A_2 obtained from light scattering for poly-*m*-chlorostyrene in toluene[17] were not taken into account of our present discussion, because a value of A_2 obtained from such a measurement is not essentially equivalent to that obtained from osmotic pressure for a polymer fraction with a molecular-weight distribution.

The difference in solubility between PS and various polychlorostyrenes in toluene has been represented by Matsumura[8] on the basis of the data of the polymer-coil dimensions as measured by light scattering. The order of the solubilities of PS and PPCS among these polymers is the reverse of that estimated from our osmotic-pressure measurements. From the fact that our results on osmotic pressure for PS and PPCS in toluene are essentially identical with the corresponding data in the literature cited here, we have some question about the results of light scattering which have been referred to by Matsumura.[18,19]

We intend to proceed with our studies in concentrated polymer solutions by means of vapor-pressure measurements, by which a free-energy parameter is directly estimated; it seems that it will be interesting to discuss quantitatively the effect of the stiffness of a polymer chain on the thermodynamic properties, basing our discussion on the average-potential method or on Flory's method, presented lately.[20]

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12) K. Kubo and K. Ogino, *Rep. Prog. Poly. Phys. Japan*, **10**, 111 (1967).

13) W. R. Krigbaum and P. J. Flory, *J. Amer. Chem. Soc.*, **75**, 1775 (1953).

14) F. Danusso and G. Moragrio, *J. Polymer. Sci.*, **24**, 161 (1957).

15) N. Kuwahara, K. Ogino, A. Kasai, S. Ueno, and M. Kaneko, *ibid.*, **A3**, 985 (1965).

16) K. Takamizawa, This Bulletin, **39**, 1186 (1965).

17) K. Matsumura, *ibid.*, **42**, 1874 (1969).

18) T. Oyama and K. Kawahara, *Nippon Kagaku Zasshi*, **78**, 484 (1957).

19) T. Saito, This Bulletin, **35**, 1580 (1962).

20) P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965).