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Partial Specific Compressibility of Polystyrene

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Synopsis

The partial specific compressibilities of polystyrene at infinite dilution in such solvents as methyl ethyl ketone, toluene, dioxane, and a mixture of methanol and toluene were determined by ultrasonic velocity measurements and were compared with the intrinsic viscosities. The limiting partial specific compressibility decreased with decreasing solvent power. The variation of this quantity was ascribed to the increase in the segment-segment contacts on the basis of a macroscopic model. The limiting partial specific compressibility is a measure of the compactness of the polymer molecule.

INTRODUCTION

The acoustical properties of dilute polymer solutions have attracted the attention of several workers.[1,2] A previous series of our papers[3-6] dealt with the partial specific compressibility of poly(vinyl acetate) at infinite dilution determined by the ultrasonic velocity measurement in the dilute solution. This quantity varied linearly with the intrinsic viscosity among various solvents.[4] It is a problem to find the physical meaning of this quantity in connection with solution properties of polymer.

In the present paper, the limiting partial specific compressibility of polystyrene is compared with the intrinsic viscosity for such solvents as methyl ethyl ketone, toluene, dioxane, and a mixture of methanol and toluene, and the results are discussed on the basis of a macroscopic model.

NOTATIONS AND MODEL

Limiting Partial Specific Compressibility

The limiting partial specific compressibility (LC) is defined as

$$\bar{\kappa}_{20} = -(1/\bar{v}_{20})\,(\partial\bar{v}_2/\partial P)_0 \qquad (1)$$

where ν_2 is the partial specific volume of a solute, P the pressure, and the subscript zero refers to the infinite dilution. LC is given from the data of compressibility and density of the dilute solution by extrapolation to infinite dilution as follows:

$$\bar{\kappa}_{20} = -\,(\kappa_1/\bar{v}_{20})\lim_{x\to 0} K_x$$

$$K_x = \left(\frac{d-x}{d_1} - \frac{\kappa}{\kappa_1}\right)\frac{1}{x} \qquad (2)$$

where d and κ are, respectively, the density and compressibility of the solution, x is the concentration of the solute in grams per cubic centimeter of the solution, and the subscript 1 refers to the solvent. For nonelectrolytic solutions, the plot of $(d-x)/d_1 - \kappa/\kappa_1$ against x varies almost linearly in the concentration range $x = 0$–0.1. The limiting value of K_x can be estimated from the slope of the plot at $x = 0$.

Mechanical Model of Polymer Molecule

To give a physical meaning to LC, a mechanical model of polymer molecule in the dilute solution under static compression is assumed. The schematic diagram is shown in Figure 1, where a region A is the volume of occluded, immobilized, and/or solvated solvent (hereafter refers to solvation region). The region B is the volume of polymer molecule, which is composed of segment–segment and segment–solvent interspaces. After simple calculations (see Appendix), we have

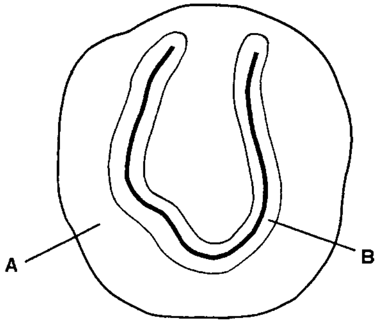

Fig. 1. Mechanical model of polymer molecule in solution: (A) solvation region; (B) molecular volume.

$$\bar{\kappa}_{20} = \kappa_2 + \frac{n_s v_1}{v_2}(\kappa_s - \kappa_1) \tag{3}$$

where κ_2 is the compressibility of the region B, κ_s that of the solvation region, v_1 and v_2 are, respectively, the specific volume of solvent and solute, and n_s is the gram number of solvent in the solvation regions per gram of the solute. In the derivation, the volume contraction of the solvent due to the solvation was neglected. A similar model has been used to estimate the hydration number of sugars[7] and the compressibility of protein molecule.[8]

EXPERIMENTAL

The ultrasonic velocity was measured with an ultrasonic interferometer, details of which were reported in the previous paper.[3] The frequency of ultrasonics was 1.0001 Mcycle/sec. The density and viscosity were measured, respectively, with an Ostwald picnometer and a Wada's tilting vis-

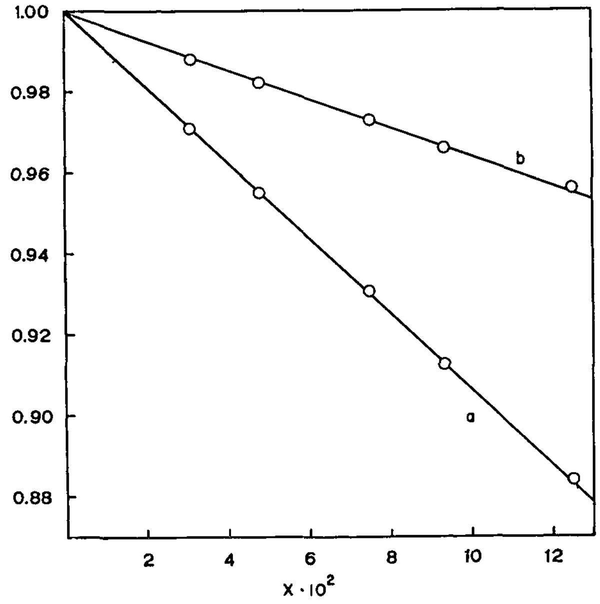

Fig. 2. Plots of (*a*) $(d - x)/d_1$; (*b*) κ/κ_1.

cometer.[9] The intrinsic viscosity at zero shear rate was determined according to the method described in the previous paper.[4]

The polystyrene sample was Asahi-Dow Styron 683–7. The weight-average molecular weight determined by light scattering was 27–30 × 10^4 and the number-average molecular weight obtained with a Spinco E ultracentrifuge was 24 × 10^4 as calculated by the equation[10] $S_0 = 0.01835 \times M^{0.47}$ in toluene. Pure grade solvents, dried and freshly distilled, were used.

RESULTS AND DISCUSSION

To illustrate the accuracy of extrapolation, $(d-x)/d_1$ and κ/κ_1 are plotted against x for dioxane at 35°C. in Figure 2. The limiting value of K_x was estimated from the slopes of these two lines. The experimental values of LC, intrinsic viscosity, and partial specific volume of polystyrene in methyl ethyl ketone, toluene, dioxane, and a mixture of methanol and toluene (23.1:76.9 by volume)* at 30, 34, and 40°C. are collected in Table I.

As is seen in the table, the values of LC in poor solvents such as methyl ethyl ketone and the methanol–toluene mixture are lower than those in the good solvents such as dioxane and toluene. A similar relationship between LC and intrinsic viscosity has also been found for poly(vinyl acetate),[4] as is shown in Table II.

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* Theta solvent at 25°C. The measurement of ultrasonic velocity at 25°C. in the present concentration range was impossible owing to the low solubility.

TABLE I
Limiting Partial Specific Compressibility, Intrinsic Viscosity, and Partial Specific Volume of Polystyrene

Temp., °C.	Solvent	$\bar{\kappa}_{20} \times 10^{12}$, cm.^{2}/dyne	[η], cc./g.	$\bar{v}_{20}$, cc./g.
30	Dioxane	36.8	76	0.927
	Toluene	31.9	79	0.920
	MEK	15.3	50	0.920
34	Dioxane	34.9	75	0.920
	Toluene	32.2	80	0.920
	MEK	20.7	49	0.920
	Mixture[a]	15.7	44	0.915
40	Dioxane	36.5	76	0.922
	Toluene	33.0	78	0.920
	MEK	18.0	48	0.920
	Mixture[a]	20.0		0.925

[a] Methanol:toluene = 23.1:76.9 by volume.

TABLE II
Limiting Partial Specific Compressibility and Intrinsic Viscosity of Poly(vinyl Acetate) at 30°C.

Solvent	$\bar{\kappa}_{20} \times 10^{12}$, cm.^{2}/dyne	[η], cc./g.
Ethylene chloride	49	95
Cyclohexanone	43	84
Benzene	42	83
Toluene	39	72
MEK	25	56
Acetone	24	52
Methanol	1	39

TABLE III
Limiting Partial Specific Compressibility of Vinyl Acetate Monomer ($\kappa = 90 \times 10^{-12}$ cm.^{2}/dyne) at 30°C.

Solvent	$\bar{\kappa}_2 \times 10^{12}$, cm.^{2}/dyne
Ethylene chloride	91
Cyclohexanone	78
Benzene	90
Toluene	90
MEK	92
Acetone	89
Methanol	92

In an ideal liquid mixture, LC is equal to the compressibility of the solute liquid as is seen from its definition, and in the oridinary liquid mixture LC is not so much different from that of the solute. As an example, the values of LC for vinyl acetate monomer in various solvents are listed in Table III.[11] On the other hand, the compressibility of solid polymer is about 20×10^{12} cm. ^{2}/dyne.[12] In our results, LC of the polymer ranges from the compressibility of liquid to that of solid in magnitude.

If it is assumed that the compressibility of the solvation region is identical with that of bulk solvent, the LC becomes the compressibility of the polymer molecule, which is determined by the segment–solvent and segment–segment interactions. In a sufficiently good solvent, each segment in the random coil behaves like a solute molecule, forming a liquid mixture with neighboring solvent molecules. The compressibility of the molecule in such solvent would be, therefore, as high as that of liquid. When the solvent power of the medium is lowered, the coil shrinks, and the hydrodynamic volume of molecule is reduced, as is shown by the decrease in the intrinsic viscosity.[13,14] The reduction of solvent power increases the segment–segment contacts, resulting in the lowering of the compressibility of molecule. Thus in a poor solvent, either the intrinsic viscosity or the LC is lowered, as is shown in the present results.

The LC is decreased also by the increase in amount and intensity of solvation (increase of n_s and decrease in κ_s) as is shown by eq. (3). Actually, the decrease in the compressibility of the solvation region should be taken into account to some extent.

The limiting partial specific compressibility is a measure of solution properties of polymer and is related to the compactness of the molecule.

APPENDIX

The pressure derivative of the partial specific volume at infinite dilution is given by

$$\left(\frac{\partial \bar{v}_2}{\partial P}\right)_{n_2\to 0} = \left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial n_2}\right)_{n_1}\right]_{n_2\to 0} = \left\{\left[\frac{\partial}{\partial n_2}\left(\frac{\partial V}{\partial P}\right)\right]_{n_1}\right\}_{n_2\to 0}$$

$$= \lim_{x_2\to 0}\frac{\left(\frac{\partial V}{\partial P}\right)_{n_1 n_2} - \left(\frac{\partial V}{\partial P}\right)_{n_1,0}}{n_2} = \lim_{x\to 0}\frac{\kappa_1}{x}\left(\frac{d-x}{d_1}-\frac{\kappa}{\kappa_1}\right) \qquad (1)$$

where V is the volume of solution, and n_1 and n_2 are, respectively, gram number of the solvent and solute. Putting

$$K_x = \left(\frac{d-x}{d_1}-\frac{\kappa}{\kappa_1}\right)\frac{1}{x} \qquad \text{(A2)}$$

we have

$$\tilde{\kappa}_{20} = -(\kappa_1/\bar{v}_{20})\lim_{x\to 0} K_x \qquad \text{(A3)}$$

K_x is related to the molal compressibility ΦK_2 by the equation

$$K_x = -\frac{\Phi K_2}{\kappa_1 M_2}$$

where M_2 is the molecular weight of solute. The molal compressibility is defined as[15]

$$\Phi K_2 = (1000/c)\kappa - [(1000\, d/c) - M_2](\kappa_1/d)_1$$

where c is the molarity.

If the solute molecule is represented by the model shown in Figure 1, the volume of solution is given by

$$V = (n_1 - n_s n_2)v_1 + n_2\,(v_2 + n_s v_s) \tag{A4}$$

where v_1, v_2, and v_s are, respectively, the specific volume of solvent, solute, and the solvent in the solvation region, and n_s is the gram number of solvent in the solvation regions per one gram of solute. The partial specific volume of the solute is given by

$$\bar{v}_2 = \partial \bar{V}/\partial n_2 = v_2 + n_s\,(v_2 - v_1) \tag{A5}$$

Differentiating with respect to the pressure, we have

$$(\partial \bar{v}_2/\partial p)_0 = -\,v_2\kappa_2 - n_s(v_s\kappa_s - v_1\kappa_1)$$

where κ_1, κ_2, and κ_s are, respectively, the compressibility of the solvent, solute, and solvent in the solvation region. If the volume contraction due to the solvation is negligible in order of magnitude, we have

$$\begin{aligned} v_s &= v_1 \\ \bar{v}_{20} &= v_2 \end{aligned} \tag{A6}$$

and

$$\bar{\kappa}_{20} = \kappa_2 + (n_s v_1/v_2)\,(\kappa_s - \kappa_1) \tag{A7}$$

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Résumé

On a déterminé les compressibilités spécifiques partielles, à dilution infinie du polystyrène dans des solvants tels que la méthyléthylcétone, le toluène, le dioxanne et dans un mélange d'alcool méthylique et de toluène par des mesures de la vitesse des ultrasons et on a comparé ces résultats aux viscosités intrinsèques. La compressibilité spécifique partielle limite diminue avec l'abaissement du pouvoir solvatant. On a attribué la variation de cette propriété à l'augmentation du contact segment-segment que l'on peut déduire d'un modèle macroscopique. La compressibilité spécifique partielle limite est une mesure du taux de compacité de la molécule polymérique.

Zusammenfassung

Die partielle spezifische Kompressibilität von Polystyrol bei unendlicher Verdünnung in Lösungsmitteln wie Methyläthylketon, Toluol, Dioxan sowie einer Mischung von Methanol und Toluol wurde durch Ultraschallgeschwindigkeitsmessungen bestimmt und mit der Viskositätszahl verglichen. Der Grenzwert der partiellen spezifischen Kompressibilität nimmt mit abnehmender Güte des Lösungsmittels ab. Die Änderung dieser Grösse wird auf der Grundlage eines makroskopischen Modells der Zunahme der Segment-Segment-Kontakte zugeschrieben. Der Grenzwert der partiellen spezifischen Kompressibilität ist ein Mass für die Kompaktheit des Polymermoleküls.

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