SHORT COMMUNICATIONS

Compressibility of Rodlike and Coiled Polymers in Solution

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Solution properties of polymer solution should be investigated from the viewpoint of intermolecular potentials of segment and geometric properties such as volume or shape of a segment in the presence of solvent molecules. A measurement method at high frequencies appropriate to detect molecular interactions of segment is required, since measurement in low frequency range reflects the overall properties of a polymer chain such as dimensions obtained by intrinsic viscosity and those at too high frequencies give information on the local properties such as microstructures or internal motions of substituents smaller than a segment. In the megahertz range, propagation of ultrasonic longitudinal wave and/or the adiabatic compressibility in organic liquids has been explained by intermolecular potentials of liquid molecules.¹

For polymer solutions, the ultrasonic method in the megahertz range was used to observe molecular interactions of a segment. The reason is as follows: the propagation of ultrasonic longitudinal waves in the megahertz range reflects intermolecular interactions of segments and solvent molecules in polymer solutions, in that the non-relaxation range exists in the megahertz range intermediate between Rouse relaxation (normal mode motion)² and ultrasonic relaxation (local mode motion).³ In this case, even if local and/or normal-mode motion remains in the megahertz range, the dispersion of ultrasonic velocity is negligible small. In this study, two compressibilities of solute were obtained for the first time by measurement of ultrasonic velocity and density in solutions of poly- γ -benzyl-L-glutamate (PBLG). Compressibilities of the rodlike polymer were compared with those of coiled polymers such as polystyrene.

THEORY

Adiabatic compressibility (κ) of liquid is obtained from measurement of ultrasonic velocity (c) and den-

sity (ρ); $\kappa = 1/(\rho c^2)$. Two compressibilities of solute are presented as compressibility of solute: partial specific compressibility of solute ($\bar{\kappa}_2^0$) and compressibility of mixing unit (κ_2 and/or κ'_2). The partial specific compressibility ($\bar{\kappa}_2^0$) of solute is defined as,⁴

$$\bar{\kappa}_2^0 \equiv -\frac{1}{\bar{v}_2^0} \left(\frac{\partial \bar{v}_2}{\partial P} \right)^0 \quad (1)$$

where $\bar{v}_2$ is the partial specific volume of solute and P is pressure, and subscripts 2 and 0 denote solute and infinite dilution, respectively.

Adiabatic compressibility of solution (κ) is given as,

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right) \quad (2)$$

where V and P are the volume of solution and pressure. V is expressed as,

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad (3)$$

where n and $\bar{V}$ are mole number and the partial molar volume, and the subscripts 1 and 2 denote solvent and solute, respectively. Substituting eq 3 into eq 2 gives,

$$\begin{aligned} \kappa &= \frac{1}{V} \left(\frac{\partial(n_1 \bar{V}_1 + n_2 \bar{V}_2)}{\partial P} \right) \\ &= \frac{1}{V} \left[\frac{n_1 \bar{V}_1}{\bar{V}_1} \left(\frac{\partial \bar{V}_1}{\partial P} \right) + \frac{n_2 \bar{V}_2}{\bar{V}_2} \left(\frac{\partial \bar{V}_2}{\partial P} \right) \right] \\ &= \phi_1 \bar{\kappa}_1 + \phi_2 \bar{\kappa}_2 \end{aligned} \quad (4)$$

where ϕ is the volume fraction and $\bar{\kappa}$ is the partial molar (specific) compressibility. By substituting $\phi_2 = x \bar{v}_2$ given by x (g/cm³) as the solute concentration and partial specific volume of solute $\bar{v}_2$ (cm³/g) in eq 4, eq 5 is obtained,

$$\bar{\kappa}_2 = \frac{\kappa - \bar{\kappa}_1}{x \bar{v}_2} + \bar{\kappa}_1 = \frac{1}{\bar{v}_2} \left(\frac{\kappa - \bar{\kappa}_1}{x} \right) + \bar{\kappa}_1 \quad (5)$$

$\bar{\kappa}_2$ at infinite dilution is given as,

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$$\bar{\kappa}_2^0 = \frac{1}{\bar{v}_2^0} \left(\frac{\kappa - \kappa_1}{x} \right)^0 + \kappa_1 = \frac{1}{\bar{v}_2^0} \left(\frac{d\kappa}{dx} \right)^0 + \kappa_1 \quad (6)$$

$\bar{\kappa}_2^0$ may thus be obtained experimentally from the plots of compressibility vs. concentration and compressibility of solvent.

$\bar{\kappa}_2^0$ coincides with the compressibility of pure solute liquid in ideal solution but becomes often negative in aqueous solution.

Molecular compressibility⁵ ($W = (M/\rho)\kappa^{-1/7}$) and molecular sound velocity⁶ ($R = (M/\rho)\rho(\kappa')^{-1/6}$) are presented as the molecular constant, parachor, by Wada and Rao, respectively. These molecular constants (W and R) have been explained on the basis of the Lennard-Jones potential by Kishimoto–Nomoto¹ and Swamy.⁷

Nomoto presented two additivities⁸ of these molecular constants for binary solution on the basis of the principle of additives of intermolecular forces, as follows.

$$\kappa^{-1/7} = \phi_1 \kappa_1^{-1/7} + \phi_2 \kappa_2^{-1/7} \quad (7)$$

$$(\rho\kappa)^{-1/6} = \phi_1 (\rho_1 \kappa_1)^{-1/6} + \phi_2 (\rho_2 \kappa_2')^{-1/6} \quad (8)$$

where ρ_1 is the density of solvent and ρ_2 is equal to $1/\bar{v}_2^0$.

κ_2 and κ_2' obtained as compressibilities of solute according to eqs 7 and 8, respectively, are compressibilities of mixing units due to molecular compressibility (W) and molecular sound velocity (R), respectively. κ_2 and κ_2' are designated as Wada's and Rao's compressibilities of mixing units, respectively. The difference in physical meaning between κ_2 and κ_2' does not exist essentially.

Differentiation of eqs 7 and 8 with respect to mole number of solute give relations of $\bar{\kappa}_2^0$ to κ_2 and κ_2' , respectively.

$$\bar{\kappa}_2^0 = 7\kappa_1 \left[\frac{8}{7} - \left(\frac{\kappa_1}{\kappa_2} \right)^{-1/7} \right] \quad (9)$$

$$\bar{\kappa}_2^0 = 6\kappa_1 \left[\frac{8}{6} - \frac{\rho_2}{6\rho_1} - \left(\frac{\rho_2 \kappa_2'}{\rho_1 \kappa_1} \right)^{-1/6} \right] \quad (10)$$

κ_2 and κ_2' may be calculated from $\bar{\kappa}_2^0$ according to eqs 9 and 10, respectively.

EXPERIMENTAL

Rodlike and coiled polymers were used as solutes in this study.

Polystyrene (PST) and polyvinyl acetate (PVAc) and polymethyl acrylate (PMA) were used as representative samples of the coiled polymer. Commercial PST (AMCO Inc.) was purified by benzene as solvent and

methanol as precipitant, and PVAc (Aldrich Chemical Co., Inc.) was subjected to successive fractionating dissolution using acetone and water as solvent and precipitant, respectively. Molecular weights of PST and PVAc were $\bar{M}_w = 5.1 \times 10^4$ by light scattering and $\bar{M}_v = 5.2 \times 10^4$ by intrinsic viscosity,⁹ respectively. $\bar{M}_w/\bar{M}_n$ for PST and PVAc were determined to be below 1.10 and 1.45 by the GPC method, respectively.

Polymethyl acrylate ($\bar{M}_v = 90 \times 10^4$) was also used as a coiled polymer.¹⁰ All solvents used were good or marginal solvents.

Poly- γ -benzyl-L-glutamate (PBLG) was used as a rodlike polymer. A helical structure is formed for PBLG in organic solvents such as 1,4-dioxane (Dioxane) and *N,N'*-dimethylformamide (DMF). The molecular weight of PBLG used was $\bar{M}_v = 10.3 \times 10^4$, according to H–M–S relation.¹¹

All solvents were purified by distillation after dehydration.

Propagation velocity of ultrasonic waves was measured by a variable-path interferometer at 1 MHz, within an accuracy of 0.15 m/s. This interferometer gives the absolute value of ultrasonic velocity. The constancy of oscillator frequency, checked using a digital frequency counter, was 0.5 in 10^6 . The density measurements were carried out using a precision digital densimeter (Anton Paar K.G. Model DMA 50), within an error of 0.5×10^{-4} g/cm³. The sample was thermostated within ± 0.01 °C. Adiabatic compressibility (κ) was obtained with an experimental error of less than $\pm 0.04\%$.

The propagation velocity of ultrasonic longitudinal wave (c) at 1 MHz and density (ρ) were measured for solutions of the coiled polymers at six concentrations (0, 1, 2, 3, 4, 5 g/dL) at 30 °C and for solutions of rodlike polymers at three or five concentrations (0, 0.5, 1, 1.5, 2) at 20 °C. Ultrasonic velocity, density and compressibility varied linearly with concentration within experimental error. $\bar{\kappa}_2^0$ was obtained using eq 6.

Measurement of intrinsic viscosity reflecting dimensions of a chain was carried out using an Ubbelohde-type viscometer at 30 °C.

To compare compressibilities of the coiled polymers with those of rodlike ones, compressibilities of PMA ($\bar{M}_v = 55 \times 10^4$) in toluene, PST ($\bar{M}_v = 18 \times 10^4$) in *p*-xylene and PBLG in two solvents were measured, as a function of temperature ranging from 25 to 50 °C. The viscosity-average molecular weight, $\bar{M}_v$, of PST was determined by intrinsic viscosity in benzene.¹³

RESULTS

Ultrasonic velocity and density increased linearly with concentration in all polymer solutions studied

in this study. Compressibility (κ) decreased linearly with concentration, so the partial specific compressibility ($\bar{\kappa}_2^0$) of solute was obtained according to eq 6. κ_2 and κ'_2 were calculated using eqs 9 and 10, respectively. Compressibility of a solute is considered to be independent of molecular weight of polymer, since measurement was carried out at high frequency. This is supported by the result of Table I. Solvent dependence of the two compressibilities of the coiled polymers such as polystyrene were measured as a function of intrinsic viscosity, as given in Table II. Density (ρ_1), ultrasonic velocity (c_1) and adiabatic compressibility (κ_1) of solvent and partial specific volume ($\bar{v}_2^0$) of solute are also given in Tables I and II.

$\bar{\kappa}_2^0$ did not depend on molecular weight but increased with dimensions of a chain at least for coiled polymers in good solvents. Therefore, $\bar{\kappa}_2^0$ would not de-

pend on polymer dimensions but on solvent power or intermolecular interactions of segment or local chain.

Two compressibilities of mixing unit (κ_2 and κ'_2) are independent of molecular weight and solvent, as given in Tables I and II. Therefore, κ_2 and κ'_2 give values intrinsic to polymers, irrespective of solvent and molecular weight.

A comparison of compressibilities of the coiled polymer with those of the rodlike polymer is attempted by employing was made using PBLG as a rodlike polymer.

Compressibility of PBLG was measured as a function of temperature from 25 to 50 °C, in Dioxane and DMF. For comparison with the coiled polymers, compressibility of PMA in toluene and PS in *p*-xylene was also measured at 30 to 40 °C. The results for PBLG and the coiled polymers are given in Table III-1 and III-2, respectively.

$\bar{\kappa}_2^0$, κ_2 and κ'_2 for PBLG, PMA and PST were almost constant with temperature. The results for PST agreed with those for PST in some solvents.¹²

To compare the amplitude in compressibility of solute for coiled and rodlike polymers, compressibility of mixing unit (κ_2) was used as representative compressibility of solute. As shown in Figure 1, κ_2 for PBLG was smaller than for the coiled polymers such as PMA and PST: $\kappa_2 = 30$ to 31×10^{-12} cm²/dyn for PBLG and $\kappa_2 = 40$ to 50×10^{-12} cm²/dyn for coiled polymers. This is because that the helix structure of PBLG

Table I. $\bar{\kappa}_2^0$, κ_2 and κ'_2 at each fraction for PVAc in benzene at 30 °C

$\bar{M}_v \times 10^{-4}$ (g/mol)	$\bar{v}_2^0$ (cm ³ /g)	$\bar{\kappa}_2^0$ 10 ¹² (cm ² /dyn)	κ_2 10 ¹² (cm ² /dyn)	κ'_2 10 ¹² (cm ² /dyn)	$[\eta]$ (cm ³ /g)
41	0.83	43	48	49	127
36	0.83	43	48	49	110
27	0.83	43	48	49	91
24	0.83	43	48	49	87
16	0.83	43	48	49	64
9	0.83	43	48	49	42
5	0.83	43	48	49	32

Table II. Compressibilities of polystyrene, polyvinyl acetate and polymethyl acrylate in various solvents at 30 °C

PST ($M = 5 \times 10^4$)		ρ_1	$\bar{v}_2^0$	c_1	κ_1	$\bar{\kappa}_2^0$	κ_2	κ'_2	$[\eta]$
Solvent		(g/cm ³)	(cm ³ /g)	(m/s)	10 ¹² (cm ² /dyn)				(cm ³ /g)
Ethyl acetate		0.8885	0.91	1120.5	90	20	45	45	21
<i>sec</i> -BB		0.8544	0.94	1297.0	70	33	44	44	24
DCE		1.2385	0.94	1179.2	58	41	43	44	26
Benzene		0.8684	0.92	1279.2	70	35	44	45	28
Average values			0.92				44	45	
PVAc ($M = 5 \times 10^4$)		ρ_1	$\bar{v}_2^0$	c_1	κ_1	$\bar{\kappa}_2^0$	κ_2	κ'_2	$[\eta]$
Solvent		(g/cm ³)	(cm ³ /g)	(m/s)	10 ¹² (cm ² /dyn)				(cm ³ /g)
Acetone		0.7793	0.82	1143.5	98	24	48	52	26
EA		0.8884	0.84	1120.5	90	29	47	48	29
TOL		0.8576	0.84	1279.3	70	40	46	48	34
Benzene		0.8682	0.83	1182.3	71	43	48	49	36
DCE		1.2383	0.84	1178.2	58	48	49	49	40
Average values			0.84				48	49	
PMA ($M = 9 \times 10^5$)		ρ_1	$\bar{v}_2^0$	c_1	κ_1	$\bar{\kappa}_2^0$	κ_2	κ'_2	$[\eta]$
Solvent		(g/cm ³)	(cm ³ /g)	(m/s)	10 ¹² (cm ² /dyn)				(cm ³ /g)
Toluene		0.8575	0.82	1285.3	71	33	42	45	105
Ethyl acetate		0.8885	0.81	1120.7	90	14	42	44	175
Benzene		0.9375	0.82	1282.2	70	34	43	45	215
MCB		1.0963	0.82	1254.2	58	42	43	45	240
Average values			0.81				42	44	

Table III.

1 Compressibilities of PBLG in 1,4-dioxane and DMF at each temperature

T (°C)	ρ_1 (g/cm ³)	$\bar{v}_2^0$ (cm ³ /g)	c_1 (m/s)	κ_1	$\bar{\kappa}_2^0$	κ_2	κ'_2
				10 ¹² (cm ² /dyn)			
in 1,4-dioxane							
25	1.0277	0.77	1346.2	53.7	19	30	30
28	1.0243	0.77	1334.1	54.9	20	30	30
30	1.0222	0.77	1324.9	55.7	20	30	30
32	1.0199	0.78	1316.0	56.6	19	30	31
36	1.0153	0.78	1298.8	58.4	20	31	31
40	1.0107	0.80	1283.1	60.1	19	31	31
45	1.0051	0.78	1261.0	62.6	19	32	33
50	0.9983	0.77	1240.1	65.1	19	33	33
Average values		0.78			19	30	31
in <i>N,N'</i> -dimethyl formamide							
28	0.9410	0.78	1449.3	50.6	21	29	30
30	0.9391	0.78	1440.1	51.3	20	28	29
35	0.9343	0.78	1424.2	52.8	21	30	31
38	0.9311	0.78	1410.8	54.0	21	31	32
40	0.9296	0.78	1401.1	54.8	21	30	31
44	0.9258	0.79	1385.2	56.3	21	31	32
50	0.9201	0.80	1362.0	58.6	19	31	32
Average values		0.78			21	30	31

2 Compressibilities of the coiled polymers in solvents at each temperature

T (°C)	ρ_1 (g/cm ³)	$\bar{v}_2^0$ (cm ³ /g)	c_1 (m/s)	κ_1	$\bar{\kappa}_2^0$ 10^{12} (cm ² /dyn)	κ_2	κ_2'
Polymethyl acrylate ($M = 55 \times 10^4$) in toluene							
30	0.8575	0.81	1282.8	71	34	43	46
35	0.8528	0.81	1261.2	74	34	44	47
40	0.8481	0.81	1239.4	77	34	45	48
Polystyrene ($M = 18 \times 10^4$) in <i>p</i> -xylene							
30	0.8522	0.92	1287.8	71	32	42	43
35	0.8478	0.92	1267.7	73	31	42	43
40	0.8435	0.92	1246.6	76	31	43	44

Figure 1. Temperature dependence of κ_2 for coiled and rod-like polymers in solvent.

formed by strong intermolecular forces such as hydrogen bonding.

$\bar{\kappa}_2^0$ obtained for PBLG was also independent of sol-

vent, since dimensions are affected little by an organic solvent.

CONCLUSIONS

In the megahertz range, two compressibilities of the coiled polymers were measured in good solvents: partial specific compressibility of solute ($\bar{\kappa}_2^0$) and compressibilities of mixing unit (κ_2 and κ'_2). $\bar{\kappa}_2^0$ depended on solvent power in solutions of coiled polymer.

Compressibilities of mixing unit (κ_2 and κ'_2) were intrinsic to polymer species irrespective of solvent and molecular weight. Differences in amplitude for κ_2 and κ'_2 were only slight, since both depend on the basis of intermolecular force.^{1,7}

Compressibility of solute was measured for PBLG in two organic solvents. $\bar{\kappa}_2^0$ and the compressibilities of mixing unit (κ_2 and κ'_2) were independent of solvent and temperature, because PBLG behaved as a rod in the solvents.

Comparison of compressibilities of solute between PBLG and coiled polymers is shown in Figure 1. Compressibilities of mixing unit (κ_2 and κ'_2) of PBLG were smaller than for coiled polymers, since the helix structure of PBLG is formed by hydrogen bonding.

Therefore, rodlike and coiled polymers thus behave as rods and segments (or local chain), respectively.

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