



Solution Properties of Polymer by Ultrasound at 1 MHz

H. Ikeda

*Department of Engineering, Tokyo University of Science, Kagurazak, Shinjyuku-ku, 162-8601 Tokyo, Japan,
ike@ci.tus.ac.jp*

ABSTRACT: Partial specific compressibilities ($\bar{\kappa}_2^0$) were obtained by measurements of ultrasonic velocities in polymer solutions. It was found that $\bar{\kappa}_2^0$ depends on the excluded-volume of segment in various polymer solutions. This experimental fact could be explained by presenting the new parameter “the acoustic coefficient (q)”. This new parameter were applied to conformation transition of polymer and phase transition from the theta to the good regimes in polymer solution

1. Introduction

The hitherto-known studies¹⁾ on ultrasonic relaxation for polymer solutions have pointed out that a non relaxation range existed at one or 3 MHz which is intermediate between normal mode motion (Rouse relaxation)²⁾ and local mode motion (Ultrasonic relaxation). This means that the propagation of ultrasonic waves in the megahertz range reflects intermolecular interactions of segment in solution. This is represented as an adiabatic compressibility of solute. On the other hand, overall properties of a polymer such as dimensions of a chain have been investigated statistically on the basis of properties of segment, but such static measurements such as intrinsic viscosity can not give information on segment properties directly.

The present investigation is undertaken to see if the compressibility of solute obtained by ultrasonic method is related to the excluded-volume of segment obtained statistically from values of intrinsic viscosities.

2. Theory

Adiabatic compressibility (κ) of liquid is obtained from measurements of ultrasonic velocity (c) and density (ρ); $\kappa = 1/(\rho c^2)$. The partial specific compressibility of solute ($\bar{\kappa}_2^0$) are used as a compressibility of solute. The partial specific compressibility³⁾ ($\bar{\kappa}_2^0$) of solute is defined as follows

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

where \bar{v}_2 is the partial specific volume of solute and P is pressure, and subscripts 2 and superscript 0 denote solute and infinite dilution, respectively. $\bar{\kappa}_2^0$ corresponds to compressibility of solute in the presence of solvent and so reflects intermolecular forces



between solute and solvent in non-ideal solution.

Adiabatic compressibility of the binary solution (κ) is given as follows

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

where V and P are the volume of solution and pressure. V is expressed in the relation;

$V = n_1 \bar{V}_1 + n_2 \bar{V}_2$, where n and \bar{V} are the mole number and the partial molar volume, and the subscript 1 denotes solvent, respectively. Differentiating the both sides of eq. 2 with respect to mole number of solute gives eq. 3 at infinite dilution.

$$\left(\frac{\partial \kappa}{\partial n_2} \right)_0 = -\frac{\bar{V}_2^0}{V} \left[\kappa_0 + \frac{1}{\bar{V}_2^0} \left(\frac{\partial \bar{V}_2}{\partial P} \right)_0 \right] = \frac{\bar{V}_2^0}{V} [\bar{\kappa}_2^0 - \kappa_1] \quad (3)$$

where \bar{V}_2^0 is the partial molar volume of solute at infinite dilution.

$$\bar{\kappa}_2^0 = \frac{1}{(\bar{V}_2^0/M_2)} \left(\frac{\partial \kappa}{\partial x} \right)_0 + \kappa_1 = \frac{1}{\bar{v}_2^0} \left(\frac{d\kappa}{dx} \right)_0 + \kappa_1 \quad (4)$$

where x is the concentration of solute (g/cm^3).

Thus, $\bar{\kappa}_2^0$ can be obtained experimentally by measurements of the slope of compressibility against concentration and compressibility of solvent. It is known that $\bar{\kappa}_2^0$ coincides with the compressibility of the pure solute in the mixture of organic solvents.

In the dilute solution of polymer, κ is known to decrease linearly with concentration. Thus, the following relation is proposed, in order to examine properties of segment (solute) in the presence of solvent,

$$\kappa = \kappa_1(1 - q\phi_2) \quad (5)$$

where the coefficient (q) represents the properties concerning intermolecular interactions involving intermolecular potential and geometric characteristics (volume and shape) of segment.

At infinite dilution, the acoustic coefficient (q) can be related to $\bar{\kappa}_2^0$, as follows.

$$q = 1 - (\bar{\kappa}_2^0/\kappa_1) \quad (6)$$

The present work is carried out to determine whether q can be related to the excluded volume of segment (β) evaluated from intrinsic viscosity.

The excluded-volume of segment (β) is obtained using the two-parameter theory⁴, $[\eta]/M^{0.5} = K + 0.346\Phi_0 m^2 \beta M^{0.5}$, where m and M are molecular weight of monomer and polymer, respectively. The excluded-volume of segment (β) is represented as follow,



$$\beta = 2 \left(\frac{\phi_1}{N_A} \right) v_1 \left(1 - \frac{\theta}{T} \right) \quad (7)$$

where $v_1(1-\theta/T)$ is a function of temperature, and θ and ϕ_1 are the theta temperature and the entropy coefficient, respectively..

3. Experiments

3.1 Measurements

The adiabatic compressibility of solution were obtained by measurements of ultrasonic velocity and density. The ultrasonic (longitudinal) velocity (c) were measured, within an accuracy of ± 0.1 m/s, by using ultrasonic interferometer at 1 MHz, and density measurements were carried out using Anton Parr digital densimeter, within an error of $\pm 10^{-4}$ b/cm³. The samples were thermostated to better than ± 0.01 °C.

3.2. Materials

Polyvinyl acetate (PVAc, $M=5 \times 10^4$), polymethyl acrylate (PMA, $M=9 \times 10^5$), Polymethyl methacrylate (PMMA $M=18 \times 10^5$) and polystyrene (PST , $M=5 \times 10^4$) were used as polymer samples. Organic solvents purified by distillation after dehydration used as solvents. Concentration of polymer solution was below 5g/dl.

4.Results

Ultrasonic velocity and adiabatic compressibility varied linearly with concentration within experimental error. Thus, $\bar{\kappa}_2^0$ could be obtained using eq.4 for solutions of PVAc, PMMA, PST and PMA, and further the acoustic coefficient (q) were also calculated by using eq.5. These values are given in **Table 1**. The values of $\bar{\kappa}_2^0$ are not inherent in polymer species but depend on solvent power, namely β .

Table 1 Compressibilities of Polystyrene and Polyvinyl acetate in various solvents at 30°C.

PVAc ($M=5 \times 10^4$)	c_1	ρ_1	\bar{v}_{20}	κ_1	$\bar{\kappa}_{20}$	q	$\beta \times 10^{24}$
Solvent	(m/s)	(g/cm ³)	(cm ³ /g)	10^{12} (cm ² /dyne)	(-)	(-)	(cm ³)
Ethylbenzene ($\theta=34^\circ\text{C}$)	1302.0	0.8587	0.844	68.7	36	0.476	-1
3-Heptanone($\theta=29^\circ\text{C}$)	1241.3	0.8095	0.838	80.2	36	0.548	0.7
Acetone	1143.5	0.7793	0.812	98.1	24	0.758	4.4
Butanone	1174.5	0.7949	0.825	91.2	26	0.716	5.4
Ethyl acetate	1120.7	0.8884	0.840	89.6	29	0.674	6.5
Toluene	1287.6	0.8575	0.843	70.4	40	0.433	10.2
Benzene	1278.2	0.8682	0.830	70.5	43	0.390	12.5
1.2-Dichloroethane	1178.0	1.2383	0.845	58.4	48	0.171	16.1

In order to examine if values of q reflect the excluded-volume of segment (β), values of q were plotted against β for solutions of PVAc in **Fig. 1**. It is considered that the value of q is related to the excluded-volume of segment, since the values of q is proportional to the values of β as shown in Fig.1.

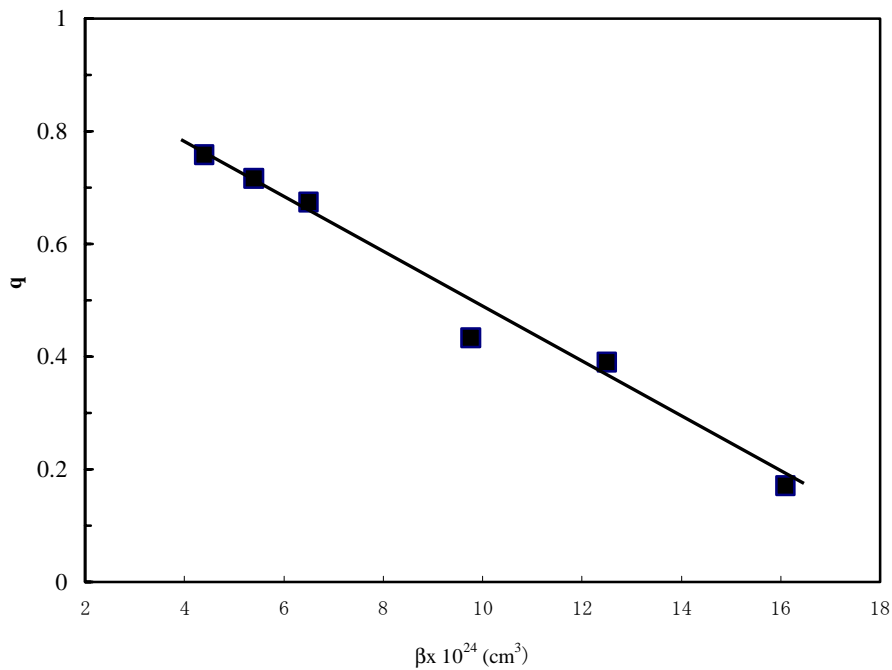


Fig. 1 Plots of q vs the excluded-volume of segment (β) in PVAc solutions at 30°C.

Further, in order to confirm that values of q are a function of the excluded-volume of segment (q), one examine if the relation of q to β is also established for conformation transition of polymer. Temperature dependence of $\bar{\kappa}_2^0$ and q values measured for PMA in toluene at 1 MHz, since thermal transition due to a conformation change has been detected at 55°C for PMA by intrinsic viscosity measurements of n.m.r. and intrinsic viscosity⁵⁾.

Temperature dependence of the excluded-volume of segment (β) obtained by intrinsic viscosity and the acoustic coefficient (q) is shown in Figs.2 and 3, respectively. As shown in Figs. 2 and 3, it is found that $\bar{\kappa}_2^0$ as well as the acoustic coefficient (q) reflect the excluded-volume of segment in polymer solutions. It is interesting that the quantities concerning the excluded-volume of segment obtained at MHz are able to be related to those obtained by viscosity at 0Hz.

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Then, temperature dependence of slope of ultrasonic velocity against concentration is shown as the fundamental data in Fig. 4. This result was given by measurements of slopes of ultrasonic velocity against concentration at each temperature.

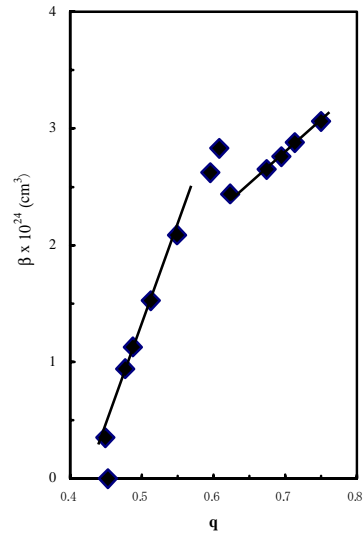
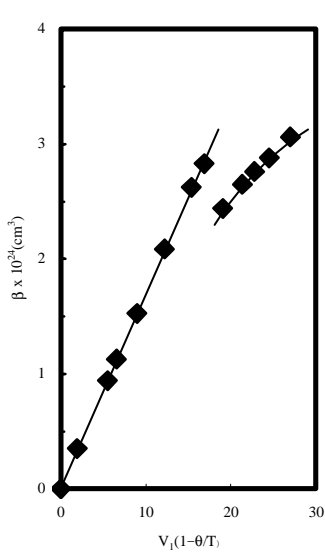


Fig.2 Plots of β vs $V_1(1-\theta/T)$ for PMA in toluene

Fig.3 Plots of B vs q for PMA in toluene

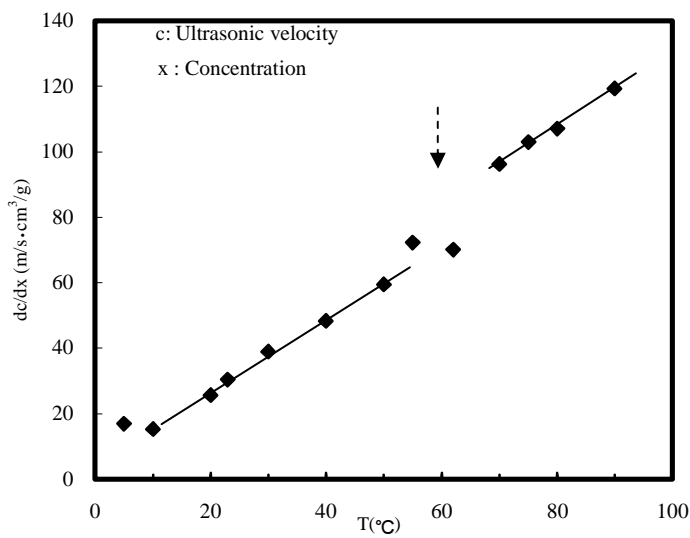
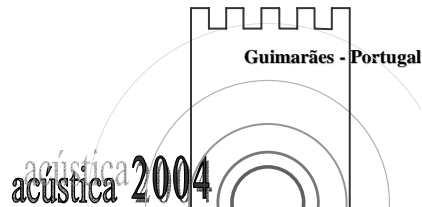


Fig.4 Temperature dependence of ultrasonic velocity for PMA in toluene



5. Conclusion

The partial specific compressibility ($\bar{\kappa}_2^0$) obtained by ultrasonic method at 1 MHz is considered to reflect the excluded-volume of segment (β) obtained at 0Hz, since the acoustic factor (q) is found to be proportional to β in polymer solutions.

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