Polymer Journal, Vol. 21, No. 11, pp 905—913 (1989)

Ultrasonic Viscoelasticity and Excess Absorption in Polymer Solution

Haruyo YOSHIZAKI

Department of Materials Science and Engineering, Defense Academy,
Hashirimizu 1-10-20, Yokosuka 239, Japan

(Received May 12, 1989)

ABSTRACT: Shear moduli are measured by the reflection method for many polymer-toluene solutions. The results have good agreement with theoretical values by Rouse and Lamb. Longitudinal velocity and absorption are measured for poly(vinylisobuthylether) solution in toluene by the interferometric method. Comparing both moduli, it is found that the ratio of the dynamic volume viscosity to the dynamic shear one is 20—40. The phenomena are discussed on the basis of several theories and found to be well described by the concentration fluctuation theory by V. P. Romanov and V. A. Solove'ev.

KEY WORDS Shear Impedance / Acoustical Excess Absorption / Concentration Fluctuation Theory / Rouse's and Lamb's Theory / Poly(vinylisobuthylether) / Polymer Solution /

Recently, the relaxation properties of longitudinal waves of relatively dilute solutions in the 100 MHz region have been studied by many scientists, because the rate process for an interaction between solution and solvent lie in this frequency range. However, data of transverse wave have not been reported, owing to difficulty of measurement. To avoid difficulty in the transverse wave, the reflecting method is used, counting as many pulsed echoes as possible. The method is able to measure the real part of shear impedance, $\rho v_s'^2$, where ρ is the density of sample and v_s' is the real part of the complex shear velocity. The measured values of $\rho v_s'^2$ are compared with Rouse's theory, to test its validity at very high frequencies. The measurement is conducted on toluene solution of polybutene (HV-1900), poly(vinylisobuthylether) (J-30) and polystyrene (PS). The longitudinal velocity and absorption are also measured for J-30, indicating that the ratio of the observed absorption to the classical Stokes–Kirchhoff loss is 20—40. Since the classical theory considers only the shear viscosity, a total viscous contribution indicating the effects arising from the volume viscosity η_v and shear viscosity η_s to ultrasonic absorption must be taken into account. In the case of structural relaxation, the ratio η_v/η_s is essentially temperature independent and rarely higher than 10 or less than 0.5. The theory has been applied to associated liquids such as water and various alcohols.[1] On the other hand, in the case of nonassociated liquids, the ratio η_v/η_s is often very high (>20). The phenomena have been successfully interpreted in terms of the thermal relaxation mechanism, which is due to the time lag for transition of energy from the transitional freedom of molecules to the internal freedom, vibration and rotation. However, there are some difficulties in application of the theory to the present results; 1) the incremental specific heat δC_p derived from the measurement is larger than the theoretical value estimated from thermal relaxation mechanism; 2) the thermal relaxation theory is only valid for a pure liquid. Bauer[2] linearly extrapolated δC_p in 5—20%

solution into the pure liquid state and compared it with Shottky's function. The consistency has not appeared in the present data obtained by the difference of losses between solution and solvent directly; 3) the spectra of the absorption per wavelength are broad, indicating the presence of the cooperative phenomena.[4] This type of cooperation is in contrast to the thermal relaxation mechanism which should show a single relaxation,[3] because it arises from the internal freedom of rotation independent of the cooperative motion in the relatively dilute state solution.

Here, a new analysis for the excess absorption is proposed, following concentration fluctuation theory predicted by Romanov and Solov'ev.[5] This approach affords a better understanding of the observed phenomena.

A necessary consequence of the random motion of the molecules is that the number of molecules per unit volume, in any volume element, is not at every instance equal to its average value but instead fluctuates about this average. The theory of concentration fluctuation in a gas was first developed by Smoluchowski in 1908 and found to be true by the explanation of blue sky with light scattering. It was found that the fluctuation theory held also for colloidal suspensions, for which Svedberg observed particles directly with a microscope in 1912. Vucks and Lisnyanskii postulated that sound absorption of solutions, like light scattering, is related to concentration fluctuations, in 1962. Remanov and Solov'ev calculated the acoustic absorption due to fluctuations, molar enthalpy H and molar volume V to depend on mean fluctuation. When we apply an ultrasonic sound wave to the specimen, adiabatic compression and expansion arise in it. Variation in the pressure p and temperature T in the sound wave alters the magnitude of fluctuation, and a new distribution is established by diffusion. This phenomena is a relaxation process, where the time lag accompanied by diffusion causes sound absorption of solutions.

EXPERIMENTAL

The reflection method is used to determine the real part of $\rho v_s'^2$. A shear impedance cell is similar to the one constructed by Clark and Litovitz.[6] A 2-cm-diam. 2-cm-long AC-cut crystalline quartz rod was used in frequencies of 8.6, 20, 60, and 100 MHz. This method, in which real and imaginary part of rigidity cannot be obtained directly, has the advantage of easy treatment. Further, it has no loss of contact between the transducer and quartz rod, so that one can measure over fifty or more echos and determine a low value of $\rho v_s'^2$ in solution state. Following the theory by Mason[7] and Piccirelli and Litovitz,[4] the value $\rho v_s'^2$ is expressed by

$$\rho v_s'^2 = (Z_q^2/\rho)\{\tanh[D_w(T)/40 \log e]\}^2 \tag{1}$$

where ρ is the density of sample, v_s' is the real part of the complex shear velocity, Z_q ($=8.78 \times 10^5$ g cm^{-2} s^{-1}) is the shear impedance of AC cut quartz and $D_w(T)$ is the differences between the losses, expressed in decibels per echo, when the quartz is terminated in the liquid and then in air at the same temperature. The amplitude in db *versus* number of echo is shown in Figure 1 as an example. The least square fit, indicated in the solid line, determins $D_w(T)$.

The usual interferometric technique[8] was used to measure the longitudinal wave velocity and absorption at frequencies of 1, 3, 5, 20, 60, 100, 140, and 180 MHz.

Viscosities are measured by a Cannon Fenske viscometer.

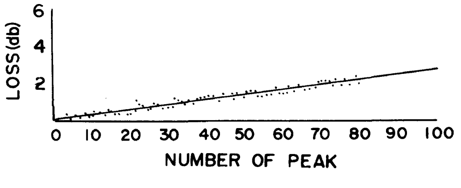


Figure 1. Example of the amplitude in db *versus* the number of echos.

Table I. Molecular weights of samples

Sample	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Z[a]	M_0[b]
Polybutene (HV-1900)	2350	2.1	42	56
Poly(vinylisobutylether) (J-30)	5700	2.2	57	100
Polystyrene (P.S.)	10000	1.06	95	105

[a] Z, degree of polymerization; Nq, $q=5$.
[b] M_0, molecular weight of monomer.

Volume expansion coefficient is measured by a picnometer modified by the author.

The molecular characteristics of the samples are listed in Table I. The distribution curves of molecular weight of HV-1900 and J-30 are obtained by gel permeation chromatograph.

RESULTS AND ANALYSIS

a) *Shear Moduli*

The values of $\rho v_s'^2$ *versus* frequency are shown in Figure 2. For the monodisperse in case of PS, the theoretical curve is derived from Rouse's theory,[9] in which real and imaginary parts of rigidity are, respectively, represented by

$$G_1=\frac{CRT}{M}\sum_{p=1}^{N}\frac{(\omega\tau_p)^2}{1+(\omega\tau_p)^2}, \tag{2}$$

$$G_2=\frac{CRT}{M}\sum_{p=1}^{N}\frac{\omega\tau_p}{1+(\omega\tau_p)^2}+\omega\eta_s, \tag{3}$$

where C is the concentration ($\mathrm{g\,cm^{-3}}$), R is the gas constant, T is the absolute temperature, M is the molecular weight, ω is the angular frequency (radian), χ_p is the relaxation time of the pth mode of motion, and η_s is the viscosity of solvent. The value of τ_p is given by

$$\tau_p=\frac{1}{\sin^2\left[\dfrac{p\pi}{2(N+1)}\right]}\,\frac{M(\eta-\eta_s)}{CRT\displaystyle\sum_{p=1}^{N}\frac{1}{\sin^2[p\pi/2(N+1)]}}, \tag{4}$$

where $p=1, 2, \cdots, N$, N is the number of segment, η is the static viscosity of solution, and $\eta-\eta_s$ is the contribution of polymer to the viscosity of the solution in steady flow. When the Rouse mode number N is large,

$$\tau_p=\frac{6}{\pi^2p^2}\,\frac{M(\eta-\eta_s)}{CRT}, \tag{5}$$

$$\tau_1=\frac{6}{\pi^2}\,\frac{M(\eta-\eta_s)}{CRT}. \tag{6}$$

For HV-1900 and J-30 with a most probable distribution of molecular weights ($\bar{M}_w/\bar{M}_n=2$), the following relations[10] are used.

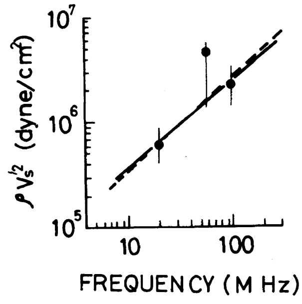
$$G_1=\frac{CRT}{M}\sum_{p=1}^{N}\int_0^\infty\frac{(\omega\tau_1)^2\mu^4/p^4}{1+(\omega\tau_1)^2\mu^4/p^4}\exp(-\mu)\mathrm{d}\mu, \tag{7}$$

$$G_2=\frac{CRT}{M}\sum_{p=1}^{N}\int_0^\infty\frac{\omega\tau_1\mu^2/p^2}{1+(\omega\tau_1)^2\mu^4/p^4}\exp(-\mu)\mathrm{d}\mu+\omega\eta_s, \tag{8}$$

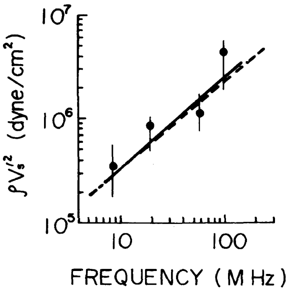
where $\mu=M/\bar{M}_n$ and $\tau_1=3\eta\bar{M}_n/(\pi^2CRT)$. The Rouse mode number N is given by the relation $Nq=Z$, where q is the number of monomer units in a segment and Z $(=M/M_0)$ is the degree of polymerization. The values of G_1 and G_2 are estimated from $N=11$ and $q=5$ in eq 7 and 8. The value of N in the eq 2, 3, 7, and 8 is estimated as 11, with $q=5$ as obtained from the results of oligostyrene and oligobutene in previous papers.[11,12] Knowing G_1 and G_2, $\rho v_s'^2$ is calculated by

$$\rho v_s'^2=\frac{G_1}{2}\left\{1+\left[1+\left(\frac{G_2}{G_1}\right)^2\right]^{1/2}\right\}. \tag{9}$$

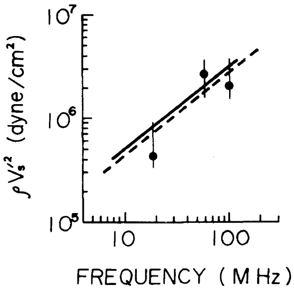
In Figure 2, the solid lines show the composit values of eq 2 and 3; the dotted lines indicate those of eq 7 and 8. The difference between mono and poly disperse systems was found to have little effect on the value of $\rho v_s'^2$ in this high frequency region with respect to a dilute solution. Regardless of differencies in molecular weights (*cf.*, Figure 2a and 2b), concentration (*cf.*, Figure 2b and 2c), temperature (*cf.*, Figures 2b and 2e), and distribution of


HV-1900, toluene 5 g/100 ml 23°C

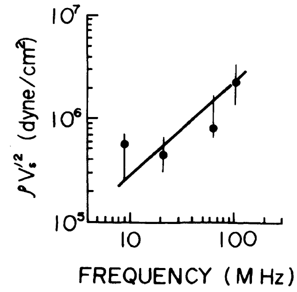
(a)


J-30, toluene 5 g/100 ml 23°C

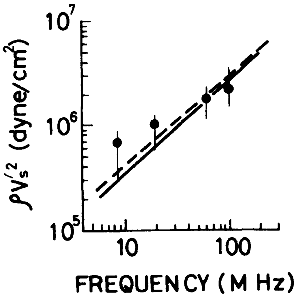
(b)


J-30, toluene 10 g/100 ml 23°C

(c)


P.S. (10,000), toluene 5 g/100 ml 23°C

(d)


J-30, toluene 5 g/100 ml 3°C

(e)

Figure 2. The values of $\rho v_s'^2$ *versus* frequency of (a) HV-1900, toluene (5 g/100 ml) at 23°C, (b) J-30, toluene (5 g/100 ml) at 23°C, (c) J-30, toluene (10 g/100 ml) at 23°C, (d) P.S. (10,000), toluene (5 g/100 ml) at 23°C, (e) J-30, toluene (5 g/100 ml) at 3°C. The top and bottom of error bar show the maximum and minimum of measured values. The dots show mean values.

molecular weight (*cf.*, Figures 2b and 2d), the measured values of $\rho v_s'^2$ match the theoretical values. This consistency enables us to estimate the values of G_1 and G_2 by knowing only temperature, concentration and molecular weights of the samples.

b) *Longitudinal Moduli*

The complex bulk modulus is written as $K = K_1 + iK_2 = K_1 + i\omega\zeta'$ and the complex shear modulus $G^* = G_1 + G_2 = G_1 + i\omega\eta'$, where ζ' is dynamic volume viscosity and η', the dynamic shear viscosity. If the complex longitudinal wave modulus is written as $M^* = M_1 + iM_2$, the relation among the velocity of longitudinal waves v_1, the attenuation of longitudinal waves α_1 in neper cm^{-1} and the modulus can be shown as follows

$$M_1 = \rho v_1{}^2 \frac{1-(\alpha_1 v_1/\omega)^2}{(1+\alpha_1{}^2 v_1{}^2/\omega^2)^2} = K_1 + \frac{4}{3}G_1, \quad (10)$$

$$M_2 = \rho v_1{}^2 \frac{2\alpha_1 v_1/\omega}{(1+\alpha_1{}^2 v_1{}^2/\omega^2)^2} = K_2 + \frac{4}{3}G_2. \quad (11)$$

Using eq 11, the following equation is obtained for $\alpha_1 v_1/\omega \ll 1$,

$$\frac{\alpha_1}{f^2}=\frac{2\pi^2}{\rho v_1{}^3}\left(\zeta'+\frac{4}{3}\eta'\right). \qquad (12)$$

If the differences between solution and solvent in absorption of longitudinal waves, dynamic volume and shear viscosities are written as $\Delta\alpha_1$, $\Delta\zeta'$, and $\Delta\eta'$, respectively, the following equation is obtained;

$$\frac{\Delta\alpha_1}{f^2}=\frac{2\pi^2}{\rho v_1{}^3}\left(\Delta\zeta'+\frac{4}{3}\Delta\eta'\right). \qquad (13)$$

The difference in shear, $\Delta\alpha_s$ is derived from the second term of eq 13 and given by

$$\frac{\Delta\alpha_s}{f^2}=\frac{8\pi^2}{3\rho v_1{}^3}\Delta\eta', \qquad (14)$$

where the value of $\Delta\eta'$ can be determined by estimation of the first term in the right side of eq 8 which should be $\omega\Delta\eta'$. The values of τ_1 are obtained from eq 6 and shown in Table II. The value of $\Delta\alpha_s/f^2$ can be calculated from eq 14 in which $\Delta\eta'$ is replaced by the factor $(G_2-\omega\eta_s)/\omega$ and the results are shown by the solid line in Figure 3 and Table II. Then $\Delta\zeta'$ in Table II is calculated from eq 13 and 14.

DISCUSSION

It is seen in Figure 3 and Table II that the experimental values of longitudinal excess absorption $\Delta\alpha_1$ are much larger than those of shear absorption $\Delta\alpha_s$ with a ratio of $\Delta\zeta'/\Delta\eta>20$. At first sight, the phenomena with high value of $\Delta\zeta'/\Delta\eta$ seem to be due to a thermal relaxation mechanism. However, there are three reasons why this mechanism is not adequate to explain the results; First, thermal relaxation theory[13] proposes that δC_p as referring to one mole can be written as

$$\delta C_p=\frac{2\Delta\mu_{\max}}{\pi}\frac{C_p}{\gamma-1}, \qquad (15)$$

where $\Delta\mu_{\max}$ is the maximum value of absorption per wave length $\Delta\mu$ $(=\Delta\alpha\lambda)$, γ is C_p/C_v and C_p and C_v are specific heats at constant pressure and volume, respectively. Using the values of v_1, C_p, $\mu_{\max}$, and coefficient of expansion θ, δC_p is obtained as shown in Table III, where $\gamma-1$ is calculated from the relation $v_1{}^2=(\gamma^{-1})JC_p/\theta^2 T$,[14] where $J=4.187\,\text{J}\,\text{cal}^{-1}$. On the other hand Shottky introduced the contribution to specific heat due to a doubly excited energy state above a nondegenerated ground state, giving

$$\delta C_p=R\left[\frac{\Delta H^0}{RT}\right]^2\frac{2\exp(-\Delta H^0/RT)}{[1+2\exp(-\Delta H^0/RT)]^2}, \qquad (16)$$

where ΔH^0 is the difference in enthalpy between ground and excited states. The form of eq 16 *versus* $\Delta H^0/RT$ has been given by Litovitz,[6] showing that the maximum value of δC_p occurring at $\Delta H=2.4RT$ is 1.52 cal mol^{-1} °C^{-1}. Comparing the results in Table III, it is clear that the difference between them is far beyond experimental error. Next, the validity of eq 16 is only for the case of unimolecular reaction.[13] Its application to the

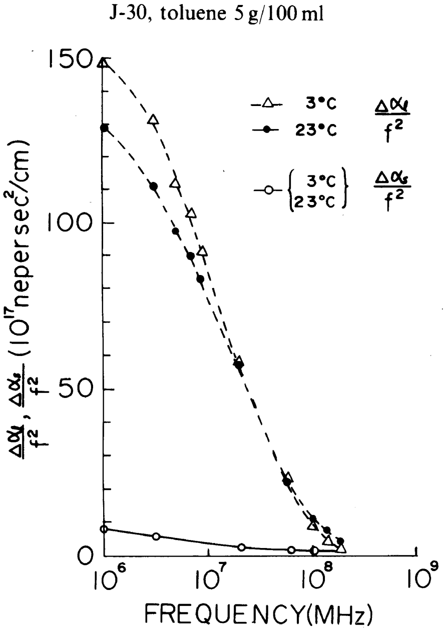


Figure 3. Values of $\Delta\alpha_1/f^2$ and $\Delta\alpha_s/f^2$ *versus* frequency. The dots and triangles are measured values. The solid line and circles are theoretical values by Lamb's theory.

Table II. Acoustical quantities of J-30, toluene mixture

Temp		Frequency	$\Delta\alpha_s/f^2$	$\Delta\alpha_l/f^2$	$\Delta\zeta'$	$\Delta\zeta'/\Delta\eta'$
°C		MHz	$s^2\,cm^{-1} \times 10^{-17}$	$s^2\,cm^{-1} \times 10^{-17}$	$g\,cm^{-1}\,s^{-1} \times 10^{-3}$	
3	$\rho=0.8825$ ($g\,cm^{-3}$)	1	7.6	148	183	24.6
	$v_l=1.402\times10^5$ ($cm\,s^{-1}$)	3	5.3	131	155	31.6
	$\tau_l=1.59\times10^{-8}$ (1/s)	5	3.9	114	136	37.8
	$\eta=1.291\times10^{-2}$ (poise)	7	3.4	105	125	39.8
	$\eta_s=7.77\times10^{-3}$ (poise)	9	2.9	92.0	110	41.0
	$G/CRT=2.01\times10^5$	20	1.5	57.6	68.4	34.4
	$N=11$	60	0.99	16.7	19.8	21.2
		100	0.67	7.62	8.56	13.8
		140	0.50	4.11	4.45	9.63
		180	0.41	2.82	2.97	7.84
23	$\rho=0.8630$ ($g\,cm^{-3}$)	1	7.5	128	120	21.4
	$v_l=1.313\times10^5$ ($cm\,s^{-1}$)	3	5.4	111	105	26.1
	$\tau_l=1.06\times10^{-8}$ (1/s)	5	4.3	97.1	91.8	28.7
	$\eta=9.73\times10^{-3}$ (poise)	7	3.8	89.4	84.7	30.0
	$\eta_s=6.02\times10^{-3}$ (poise)	9	3.5	83.8	79.5	30.7
	$G/CRT=2.16\times10^5$	20	2.3	59.5	56.7	33.3
	$N=11$	60	1.2	21.8	20.5	23.8
		100	0.80	10.8	9.90	16.7
		140	0.61	6.52	5.85	12.9
		180	0.50	4.27	3.73	10.0

Table III. Estimation of δC_p derived from experimental values

Temp	C_p	$\gamma-1$[a]	$\Delta\mu_{max}$	δC_p
°C	$erg\,g^{-1}$			$cal\,mol^{-1}$
3	1.63×10^7	0.374	1.7×10^{-3}	2.13
23	1.68×10^7	0.341	1.9×10^{-3}	2.34

[a] $\gamma-1$ was calculated from the relation $v_l{}^2=(\gamma-1)JC_p/\theta^2T^{14}$, where $\theta=1.06\times10^{-3}$.

solution is doubtful. The third weak point is the fact that the thermal relaxation has difficulty in explaining the broadness of the spectrum of $\Delta\mu$. Figure 4 shows the curve of $\Delta\mu$ *versus* frequency where the dots and triangles are experimental values and the solid line is a single relaxation curve characteristic of the thermal relaxation and clearly deviates from the experimentals. Thus neither structural relaxation nor thermalrelaxation can account for the excess absorption data.

The most probable interpretation should be a concentration fluctuation mechanism predicted by Romanov and Solov'ev,[5] because the present system is a mixture. They attribute the excess absorption to fluctuation which is treated as regions of variable concentration in the volume devided into elements dV, and assume that the resorption of the fluctuation proceeds according to the diffusion equation $\partial x/\partial t = D\nabla^2 x$, where x is the concentration in the volume dV and D is diffusion constant. The amplitudes involved in expansion into the Fourier spectrum of concentration fluctuation B_f vary according to the equation,

$$\frac{\partial B_f}{\partial t} = -\frac{1}{\tau_f}(\bar{B}_f - B_f)\,, \qquad (17)$$

where $\bar{B}_f$ is the average value of B_f for given p and T, f is the wave number of the Fourier

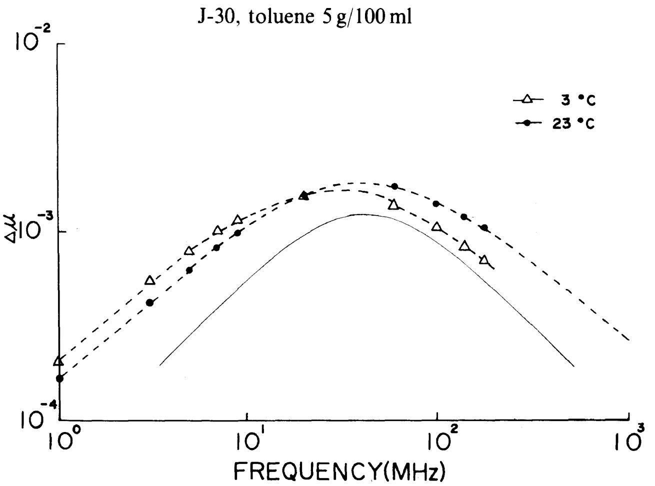


Figure 4. Curve of $\Delta\mu(=\Delta\alpha\lambda)$ *versus* frequency. The dots and triangles are measured values. The solid line is the theoretical value of a single relaxation and its maximum frequency is plotted in the same manner as that of the measured curve on 23°C.

spectral expansion, and τ_f is relaxation time and defined as

$$\tau_f = 1/Df^2 \,. \tag{18}$$

The excess volume viscosity coefficient $\Delta\zeta'$ should be presented by the following equations,

$$\Delta\zeta' = AK_\infty{}^2 T\frac{f_m}{D}L\left(\frac{\omega}{Df_m{}^2}\right), \tag{19}$$

$$L\left(\frac{\omega}{Df_m{}^2}\right) = \frac{1}{f_m\sqrt{D/\omega}}\int_0^{f_m\sqrt{D/\omega}}\frac{x^4}{1+x^4}\mathrm{d}x\,, \tag{20}$$

$$A = \frac{V^2k}{4\pi^2\psi^2}\left(\frac{v}{V}-\frac{a_\infty}{C_{p\infty}}h\right)^2, \tag{21}$$

where K_∞ is the instantaneous adiabatic modulus, V is molar volume, k is Boltzman constant, $\psi=\partial^2\Phi_0/\partial c^2$ where Φ_0 is the molar thermodynamic potential in the absence of fluctuation, $v=\partial^2 V_0/\partial c^2$ where V_0 is the molar volume in the absence of fluctuation, a_∞ is instantaneous molar heat capacity, $C_{p\infty}$ is instantaneous molar heat capacity, $h=\partial^2 H_0/\partial c^2$ where H_0 is molar enthalpy in the absence of fluctuation, and f_m is the maximum wave number of Fourier spectral expansion of fluctuation. The value of A involves a large amount of uncertainty,[15] so an explicit calculation was not given. This term can be considered a constant with temperature.[5] Taking into account the smallness of G_1 and the difference between K_∞ and K_0 which is the equilibrium modulus, the temperature dependence of K_∞ should be indentified with M_1.

In dilute solutions of linear polymer, the molecular motions are non-cooperative and hence segments can freely rotate. An individual molecule forms a random coil, the most probable shape on the basis of statistical theory. The mean square end-to-end distance of molecule L^2 is represented by

$$L^2 = Na^2\,, \tag{22}$$

where N is the total number of segments, and a is the length of a segment. When isolated polymer molecules move through the surrounding fluid unperturbed by the movement of other polymer molecules, D is represented by the Einstein relation,[16]

$$D = kT/Nf'\,, \tag{23}$$

where f' is a submolecule friction constant and Nf', a molar friction constant.

One may deduce a relation between D and $\eta-\eta_s$. According to Debye,[17] the value of

$\eta - \eta_s$ is given by

$$\eta - \eta_s = \frac{nL^2 Nf'}{36}, \qquad (24)$$

where n is the number of molecules per unit volume of solution. Eliminating Nf' from eq 23 and 24, one obtains

$$D(\eta - \eta_s) = \frac{kTnL^2}{36} \qquad (25)$$

Putting $n = 0.05\,(\mathrm{g\,cm^{-3}})\,6.03 \times 10^{23}/5700\,(\mathrm{g}) = 5.29 \times 10^{18} \times 1\,\mathrm{cm^{-3}}$, $a = 4 \times 1.5 \times 10^{-8} \times 5\,\mathrm{cm}$ and the values of η, η_s, and N given in Table II into eq 22 and 25, one obtains the value of D given in Table IV.

First, the volume viscosities $\Delta\zeta'$ are plotted *versus* frequency. Comparing the plots with the theoretical value of $L(\omega/Df_m^2)$ *versus* frequency, f_m can be determined from $\omega/Df_m^2 = 1$ on the horizontal axis. The results are shown in Table IV which indicates that f_m is constant with temperature. Secondly, the values of $\Delta\zeta'/(K_\infty^2 Tf_m/D)$ *versus* ω/Df_m^2 are plotted as shown in Figure 5, where the values of $L(\omega/Df_m^2)$ are also plotted against ω/Df_m^2. The value of A is determined as the value of the vertical axis of $\Delta\zeta'/(K_\infty^2 Tf_m/D)$ which corresponds to the unit value of $L(\omega/Df_m^2)$. The values of $\Delta\zeta'$ reduced by $K_\infty^2 Tf_m/D$ fit very well with the values of $L(\omega/Df_m^2)$ at both 3°C and 23°C.

The value of f_m defines the limit of applicability of the model proposed by Romanov and Solov'ev and the validity of $f_m \sim 10^7\,\mathrm{cm^{-1}}$ is supported by them. If a molecule in a solvent is like a rod, it should be assumed that $f_m \sim 1/L$. Putting the value of $N = 11$ and $a = 4 \times 1.5 \times 10^{-8} \times 5\,\mathrm{cm}$ into eq 22, $1/L$ is estimated as $1.01 \times 10^6\,\mathrm{cm^{-1}}$. The mean length between molecules r is related to $1/r \sim (N_A/V)^{1/3}$, where N_A is Avogadro's number. Since $N_A = 6.02 \times 10^{23}$, $V = 100\,(\mathrm{cm^3}) \times 5700/5$, $1/r$ is nearly equal to $1.74 \times 10^6\,\mathrm{cm^{-1}}$. These values give the relation $f_m > 1/r > 1/L$, which suggests the shape of molecule in a solvent to be more like a sphere than a rod.

Table IV. Values of D and f_m

Temp °C	D $\mathrm{cm^2\,s^{-1}}$	f_m $\mathrm{cm^{-1}}$	τ_{fm} s	τ_1/τ_{fm}
3	8.09×10^{-7}	1.91×10^7	3.38×10^{-9}	4.70
23	1.20×10^{-6}	1.90×10^7	2.31×10^{-9}	4.59

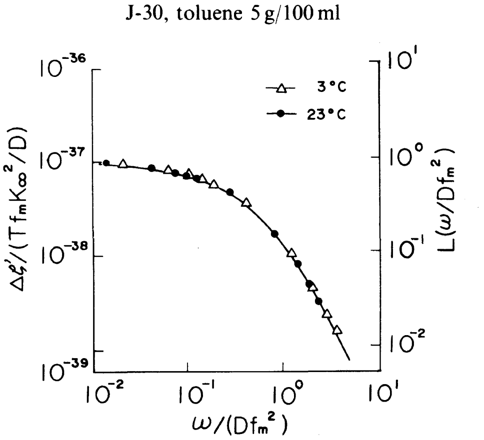


Figure 5. Plots of $\Delta\zeta'/(K_\infty^2 Tf_m/D)$ and $L(\omega/Df_m^2)$ *versus* ω/Df_m^2. The dots and triangles are measured values. The solid line is the theoretical value of $L(\omega/Df_m^2)$.

The relaxation time of concentration fluctuation, τ_f can be estimated by eq 18 and the value of f_m, as shown in Table IV. Comparing τ_f with the relaxation time of Rouse mode motion τ_1, the ratios of τ_1/τ_f are 4.70 and 4.59 for 3°C and 23°C, respectively. On the basis of eq 5 and 6, this means that the minimum relaxation time of fluctuation corresponds to the second mode motion of the Rouse mode. Considering τ_1 has the order of time necessary for movement of whole one molecule in shear deformation, about half the length of one molecule is the minimum size of fluctuation, where there is one or no molecule. This is very reasonable for all points of the fluctuation theory.

CONCLUSIONS

Shear moduli were measured for some polymer toluene solutions, and the results had good agreements with those expected from Rouse's and Lamb's theory. It was found that the concentration fluctuation theory by Romanov–Solovev explains the acoustic excess absorption of poly(vinylisobutylether) solution in toluene very well.

Acknowledgment. The author wishes to thank Mr. Yoshida of Shimadzu Co., Ltd. for the measurements of molecular weight distribution of HV-1900 and J-30 using GPC.

REFERENCES

1. N. Hirai and H. Eyring, *J. Appl. Phys.*, **29**, 810 (1958).
2. H. J. Bauer and H. Hässler, *The 6th International Congress on Acoustics*, J-69.
3. H. Nomura, S. Kato, and Y. Miyahara, *Nihon Kagaku Zasshi*, **90**, 40 (1969); *ibid.*, **91**, 837 (1970).
4. R. Piccirerei and T. A. Litovitz, *J. Acoust. Soc. Am.*, **29**, 1009 (1957).
5. V. P. Romanov and V. A. Solov'ev, *Soviet Physics-Acoustics*, **11**, 68 (1965).
6. A. E. Clark and T. A. Litovitz, *J. Acoust. Soc. Am.*, **32**, 1221 (1960).
7. W. P. Mason, *Phys. Rev.*, **73**, 1074 (1948).
8. for instance, Heuter and Bolt, "Sonics," John Wiley & Sons, New York, N. Y., 1965, p 338.
9. P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).
10. A. J. Barlow, G. Harrison, and J. Lamb, *Proc. R. Soc. A*, **282**, 228 (1964).
11. R. Kono and H. Yoshizaki, *J. Appl. Phys.*, **47**, 5319 (1976).
12. H. Yoshizaki and R. Kono, *Acoustica*, **37**, 326 (1977).
13. J. Lamb, in "Physical Acoustics," Vol. II, W. P. Mason, Ed., Academic Press, New York, N. Y., 1965, Part A, p 222.
14. J. Lamb, in "Physical Acoustics," Vol. II, W. P. Mason, Ed., Academic Press, New York, N. Y., 1965, Part A, p 224.
15. V. A. Solovyev, C. J. Montrose, M. H. Watkins, and T. A. Litovitz, *J. Chem. Phys.*, **48**, 2155 (1968).
16. F. Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).
17. P. Debye, *J. Chem. Phys.*, **14**, 636 (1946).