

Absorption of 10-MHz to 110-MHz Ultrasonic Waves by Solutions of Polystyrene

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ABSTRACT: The absorption of ultrasonic waves over the frequency range of 10 kHz to 110 MHz was measured for solutions of polystyrene in xylene. The samples were anion-polymerized, atactic polystyrenes with three different molecular weights. Both the strength and frequency of the low-frequency relaxation occurring between 10 and 100 kHz were found to depend on the molecular weight and were ascribed to heat-transfer between the polymer sphere (a polymer chain with included solvent) and the surrounding solvent. Spectra of the high-frequency relaxations observed at frequencies from 1 to 100 MHz were found to be independent of molecular weight and decomposed into two single relaxations. The high-frequency relaxation is concluded to arise from the volume change accompanying an internal rotation of a backbone segment consisting of a few monomeric units. The splitting into two mechanisms is interpreted on the basis of the tacticity of atactic polystyrene. The ultrahigh-frequency relaxation around 500 MHz which is discerned by replotting the data by Mikhailov and Safina is attributed to the relaxation of vibrational specific heat of the phenyl groups.

KEY WORDS Ultrasonic Wave / Absorption / Relaxation / Polystyrene / Tacticity / Solution / Crank-Shaft Motion / Micro-brownian Motion / Phenyl Vibration /

Many authors have reported ultrasonic studies of synthetic polymers in organic solvents and among the polymers polystyrene has received the most attention. The absorption of ultrasonic waves in polystyrene solutions has been studied in various solvents at frequencies from 1 to 70 MHz by Bauer, Hässler, and Immendörfer,^{1,2} and by Nomura, Kato, and Miyahara.³⁻⁷ A prominent relaxation was located around several megahertz, with the relaxation frequency somewhat depending on the solvent species. The dispersion of sound velocity associated with the relaxation was observed for solutions of polystyrene in benzene and carbon tetrachloride by Bader and Cerf.⁸ The data by Bauer, *et al.*, and Nomura, *et al.*, show a high-frequency limit of absorption coefficient somewhat higher than that of the solvent, indicating the possibility of another relaxation at a higher frequency.

More recently, Ludlow, Wyn-Jones, and Rassing⁹ observed the absorption of *N,N*-dimethylformamide (DMF) solutions of polystyrene

at frequencies up to 100 MHz and concluded the relaxation consists of two single relaxations, one having a relaxational frequency at 6 MHz and the other at 75 MHz. Lemaréchal¹⁰ extended the frequency range up to 145 MHz and, by revising the high-frequency limit of absorption in Ludlow's paper, concluded the relaxation frequencies are located at 5.8 MHz and 35 MHz. Mikhailov and Safina¹¹ measured the ultrasonic absorption up to 900 MHz in toluene and methyl-ethylketone (MEK) solutions of polystyrene. Their results were originally presented as the excess absorption coefficient divided by the square of the frequency, $\Delta\alpha/f^2$. As will be described in later sections, the data clearly indicate, when converted into the excess absorption per wavelength plotted against frequency, two relaxations below 100 MHz and furthermore a new relaxation around 500 MHz.

Ohsawa and one of the present authors (Wada)¹² extended the frequency down to 10 kHz with the resonant reverberation technique

developed by them¹³ and found that solutions of radically polymerized polystyrene exhibit a relaxation at frequencies of 10 to 100 kHz. Both the relaxation strength and relaxation frequency of this low-frequency relaxation largely depend on the molecular weight of the polymer.

The molecular mechanism of the two high-frequency relaxations, which will be called the HF-I and HF-II relaxations in order of increasing frequency, is still obscure at present. Hässler and Bauer¹ claim that the relaxation results from kink formation in the polymer chain. Nomura and his coworkers attributed the relaxation to internal rotation of a segment whose end bonds are collinear. For interpreting the splitting into two relaxations, Ludlow, Wyn-Jones, and Rassing⁹ assumed a three-state model for the internal rotation, while Fünfschilling, Lemaréchal, and Cerf¹⁴ who observed two relaxations in a solution of poly(2-vinyl pyridine) suggested two kinds of segments with different lengths. In any case, the high frequency acoustic relaxation of polymer solutions may be a key to revealing the dynamic character of the elementary process for the microbrownian motion of a polymer chain in solution.

The mechanism of the low-frequency relaxation (LF relaxation) observed by Ohsawa and Wada and that of the ultrahigh-frequency relaxation (UHF relaxation) discerned in the data by Mikhailov and Safina are entirely open to question at present.

In the present study, the absorption of ultrasonic waves from 10 kHz to 110 MHz was measured for solutions of atactic polystyrenes in xylene. The samples were polymerized by anionic polymerization and consequently their molecular-weight distribution was expected to be narrow. Three experimental methods were combined to cover this wide frequency range: the resonance reverberation method, the pulse technique, and the Bragg reflection method. The results provided the molecular-weight dependence of characteristic parameters of the LF relaxation.

The origin of the LF relaxation is discussed on the basis of the molecular-weight dependence of the relaxation strength and relaxation frequency. The parameters of the HF relaxation,

which were found to be independent of molecular weight, are compared with those obtained by various authors for polystyrene solutions in different solvents. The molecular mechanism of the HF relaxations is discussed on the basis of these data, taking into account the tacticity of atactic polystyrene. In the last section, an interpretation of the UHF relaxation is suggested.

SAMPLES

Three kinds of atactic polystyrene with different molecular weights were prepared by anionic polymerization following the procedures described by Wyman, Elyash, and Frazer.¹⁵ After elimination of the inhibitor, styrene monomer was purified by fractional distillation *in vacuo* with nitrogen being used as the carrier gas to control the pressure at *ca.* 50 mmHg. The monomer thus purified was dried for several days over calcium hydride. The monomer was repeatedly degassed by freezing and melting and distilled in vacuum.

Polymerization was carried out in a mixed solvent of benzene and tetrahydrofuran (THF) in weight ratio of 100:1. Benzene was treated by ordinary purification techniques for elimination of thiophene and water. After that, for the purpose of removing impurities which may react with anion, small amounts of styrene monomer and *n*-BuLi were added until the solution was colored by the formation of polystyryllithium. Finally, the colored solution thus obtained was distilled. THF was first treated by ordinary purification techniques for elimination of water, and for the same purpose as in benzene, the solvent was refluxed with sodium and anthracene until a permanent dark color was observed, and then distilled in vacuum. The initial monomer concentration was 10% and *n*-BuLi was used as an initiator. The temperature was kept below 50°C during the polymerization.

After 1 to 2 hr, termination of the polystyryllithium was accomplished by the introduction of methanol. The polymer thus obtained was precipitated by adding a large amount of methyl alcohol, and then vacuum-dried at 100°C. The average molecular weights of three polystyrenes, A, B, and C as denoted in order of increasing

molecular weight, were obtained from the intrinsic viscosity in benzene as 2.1×10^5 , 3.7×10^5 , and 1.0×10^6 , respectively. Commercial oligostyrene with molecular weight of 2100 was also used.

Solutions of polystyrene in xylene were used in concentrations of 1 to 2 g/100 ml for the reverberation method below 200 kHz and 7 g/100 ml for the reverberation method around 500 kHz, the pulse technique and the Bragg reflection method. Xylene used in this experiment was a mixture of *p*-, *m*-, and *o*-xylenes and ethyl benzene.

EXPERIMENTAL METHODS

In the present study, the absorption of ultrasonic waves in xylene solutions of polystyrene is measured in a wide frequency range from 10 kHz to 110 MHz by combining three different techniques, the resonant reverberation method, the pulse method, and the Bragg reflection method.

The absorption of ultrasonic waves at 3 and 10 MHz was measured by the pulse technique with the substitution method,¹⁶ which has advantages in eliminating the effect of sound diffraction and obtaining in a direct manner the excess absorption coefficient of solution over solvent. A polyethylene film 70 microns thick was used as a membrane between the solution and solvent. The separation between the transmitting quartz transducer in the solvent and the receiving one in the solution was kept constant at 11 cm and the transducer assembly was moved in the direction of sound propagation. The change in the received pulse height with this motion is directly proportional to the excess absorption of the solution. The cell was immersed in a water bath of a constant temperature.

The absorption of ultrasonic waves above 50 MHz was obtained from diffraction of a laser beam by a sound field at the Bragg angle.¹⁷ A block diagram of the apparatus is drawn in Figure 1.

The light beam from a He—Ne laser was diffracted by progressive, continuous ultrasonic waves and was detected by a photodiode. The sample cell was mounted onto a rotatable plate which was further set on a plate moving in the

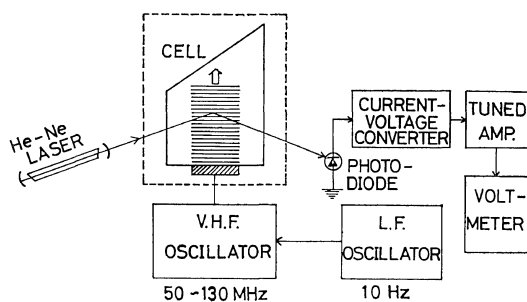


Figure 1. Block diagram of the Bragg reflection method for measuring wavelength and absorption coefficient of ultrasonic waves in a liquid.

direction of sound propagation. The ultrasonic waves were amplitude-modulated at 10 Hz. The signal from the photodiode was amplified with a tuned amplifier working at the modulation frequency. The Bragg angle was determined by obtaining the maximum intensity of diffracted light. The wavelength of sound could be calculated from the Bragg angle θ_B and the wavelength of light. Since the intensity of diffracted light is proportional to that of sound, the signal level in db plotted against the displacement of the ultrasonic cell in the direction of sound propagation, keeping the incident angle at θ_B , gives twice the absorption coefficient. The ultrasonic waves were sufficiently weak to avoid heating of the sample liquid. Water at a constant temperature was circulated around the sample cell. An absolute accuracy of 3% was estimated for the measurement of the absorption in water.

The resonance reverberation method was employed in the lowest frequency range, 10 kHz to 700 kHz. The method was essentially similar to that described by Ohsawa and Wada¹³ and consisted of measuring the free decay-rate D of acoustic energy in the liquid contained in a spherical glass vessel. For the purpose of eliminating effects from the vessel, D in neper/sec in the solution and D_0 in the solvent were compared at the same resonance mode. Since the effects from the vessel are the same in both cases,

$$d\left(\frac{D}{u}\right) = \frac{D}{u} - \frac{D_0}{u_0} = \alpha - \alpha_0 \quad (1)$$

where α and α_0 are absorption coefficients in neper/cm of solution and solvent, respectively, and u and u_0 are sound velocities in cm/sec.

In the case of a polymer solution which has a much higher viscosity than the solvent, however, the loss in the boundary layer on the surface of vessel might be different between solution and solvent, if the liquid moves tangentially to the wall. In the present case, however, this effect was proved to be negligible from both experiment and theory as described below.

Resonance modes of a spherical resonator are identified by two integers, n and σ ¹⁸: n is the number of nodal plane passing through the center and σ is the number of nodal plane in a radial direction. For modes of $n=0$, motion of the liquid is completely radial and no tangential motion takes place. On the other hand, tangential motion takes place in modes of $n \geq 1$. In the present experiment no difference was discerned in the frequency dependence of $\Delta(D/u)$ between two series of modes, $n=0$ and $n=1$. Furthermore, changing the vessel from 6 l to 10 l, which would change the relative contribution of shear viscosity, did not result in a change in the observed curve of $\Delta(D/u)$ vs. frequency even for modes of $n=1$.

These experimental observations are theoretically supported by the following reasons: Boundary layer effects, if any, should be the highest when the vessel wall is rigid. The boundary layer loss for a viscous liquid in a rigid spherical vessel was theoretically treated by Lamb.¹⁹ For modes of $n=1$, the decay-rate D_s due to the boundary layer loss is given by the equation,

$$D_s = \sqrt{\frac{2\omega\eta}{\rho a^2}} \frac{1}{(ka)^2 - 2}, \quad k = 2\pi/\lambda \quad (2)$$

where ω is the angular frequency, a is the radius of the vessel, ρ and η are the density and the shear viscosity of liquid, respectively, and λ is the wavelength. In the present case, D_s was calculated from eq 2 by using the dynamic shear viscosity of the polystyrene solution and, above 30 kHz, D_s was found to be negligible compared with the observed decay-rate. Below 30 kHz, however, D_s in eq 2 could not be neglected for a solution of sample A, which has the highest dynamic shear viscosity but the

lowest absorption. Actually, however, the vessel wall is not rigid but highly elastic because the vessel wall is thin, and yields a much lower value of D_s than expected from eq 2.

The acoustic system of the resonance reverberation method employed in the present study was just the same as has been described in a previous paper.¹³ A 6-l pyrex glass flask was used for frequencies below 200 kHz and one of 120 ml for frequencies around 500 kHz. The electronic system was, however, greatly improved in the present study by use of integrated circuits for obtaining a high S/N ratio and a small distortion in the signal. A detailed description of the circuit will be given in a future paper.

RESULTS

Figure 2 illustrates the absorption coefficient in excess of solvent at 20°C divided by squared frequency, $\Delta(\alpha/f^2) = (\alpha - \alpha_0)/f^2$ (α_0 = solvent absorption) obtained by three methods. The value is reduced to unit concentration by dividing the observed value by the concentration c because a dilute solution was used in low frequencies and, at high frequencies, the absorption has been proved to be proportional to c up to a rather high concentration.³⁻⁷ Figure 3 shows the data at 30°C, where low-frequency values were observed only for sample A.

In Figures 2 and 3, a remarkable relaxation

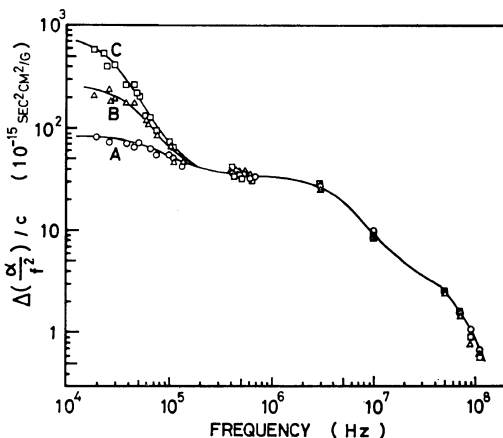
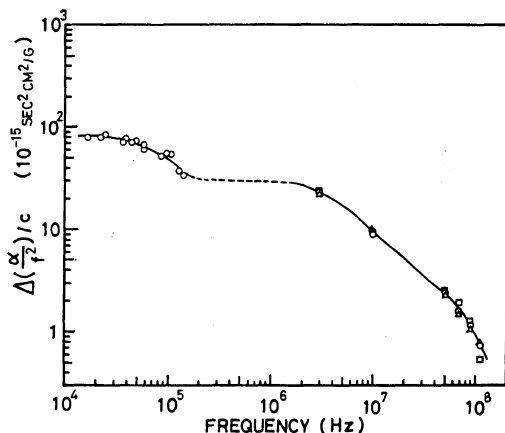
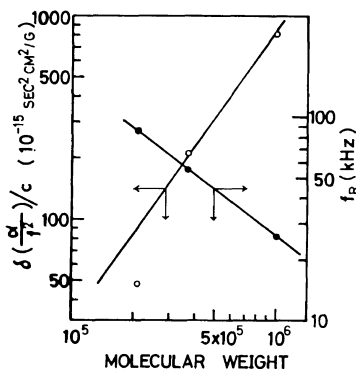


Figure 2. Absorption in excess of solvent at 20°C in xylene solutions of three polystyrenes: A (circle), $MW=2.1 \times 10^5$; B (triangle), $MW=3.7 \times 10^5$; C (square), $MW=10.0 \times 10^5$.

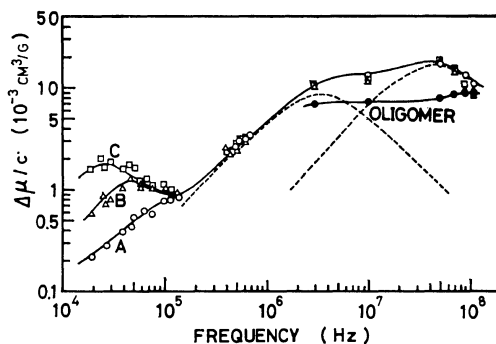
Table I. Characteristic values for low-frequency relaxation of polystyrene solutions in xylene at 20°C

Molecular weight, 10^5	$[\eta]$ in xylene, $10^2 \text{ cm}^3/\text{g}$	$\delta(\alpha/f^2)/c$, $10^{-15} \text{ sec}^2 \text{ cm}^2/\text{g}$	f_R , kHz	$\frac{\delta(\alpha/f^2)f_R}{c[\eta]}$, $10^{-12} \text{ sec}/\text{cm}$
2.1	0.81	48	85	50.4
3.7	1.14	211	55	102
10.0	2.06	816	26	103

**Figure 3.** Absorption in excess of solvent at 30°C in xylene solutions of polystyrene. Symbols are identified as in Figure 2.**Figure 4.** Molecular weight dependence of drop in α/f^2 and relaxation frequency for low-frequency relaxation in xylene solutions of polystyrene at 20°C.

is found around 50 kHz for each sample. The relaxation strength of this LF relaxation increases and the relaxation frequency decreases with increasing molecular weight.

In Figure 4, the excess absorption at a suffi-

**Figure 5.** Absorption in excess of solvent per wavelength at 20°C in xylene solutions of polystyrene with best fit single relaxation curves (dashed lines). Symbols are identified as in Figure 2 and dots represent oligostyrene ($MW=2100$).

ciently low frequency and the relaxation frequency of the LF relaxation are plotted against molecular weight. The former, $\delta(\alpha/f^2)$, is obtained as the difference in $\Delta(\alpha/f^2)$ between 10 kHz and 500 kHz, and the latter is defined as the frequency where $\Delta(\alpha/f^2)$ falls by a half of $\delta(\alpha/f^2)$. The values for sample A seem to be somewhat erroneous because of small excess absorption. A summary of these characteristic parameters associated with the LF relaxation is in Table I.

In contrast to the LF relaxation, the absorption above 1 MHz is quite independent of molecular weight as clearly indicated in Figure 5 where the excess absorption per wavelength $\Delta\mu$ is plotted against frequency. This agrees with the conclusion by Ludlow, *et al.*⁹ In Figure 5 the HF relaxation is decomposed into two single relaxations as drawn by the broken lines. The data for oligostyrene are also represented in Figure 5 for comparison.

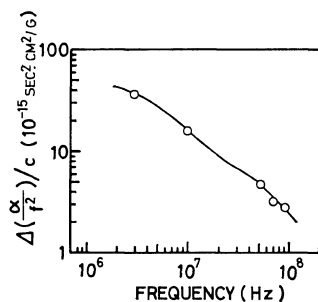


Figure 6. Absorption in excess of solvent at 20°C in a decalin solution of polystyrene ($MW=2.1 \times 10^5$).

Nomura, *et al.*,⁶ reported a high absorption in a polystyrene solution in decalin. Figure 6 gives out result for sample A in decalin, which provides somewhat smaller values than reported by Nomura, *et al.*,⁶ but still considerably larger than those in a xylene solution.

COMPARISON WITH SHEAR VISCOELASTICITY

The absorption of acoustic (longitudinal) waves in a liquid is generally expressed in terms of the dynamic volume viscosity κ' and the dynamic shear viscosity η' as

$$\frac{\alpha}{f^2} = \frac{2\pi^2}{\rho u^3} \left(\kappa' + \frac{4}{3} \eta' \right) \quad (3)$$

The dynamic shear viscosity of a solution of polystyrene was measured by Rouse and Sittel²⁰ at frequencies from 100 Hz to 100 kHz and by Moore and McSkimin^{21,22} at frequencies from 23 MHz to 300 MHz. These data are approximately fitted by the Rouse theory²³ based on the bead-spring model of a polymer chain:

$$\eta' = \eta_0 + \frac{cRT}{M} \sum_p \frac{\tau_p}{1 + (2\pi f \tau_p)^2} \quad (4)$$

where η_0 is the shear viscosity of the solvent, c is the weight concentration of the polymer, R is the gas constant, T is the absolute temperature, and M is the molecular weight of the polymer. The relaxation times of shear viscosity, τ_p , are given by

$$\tau_p = \frac{6(\eta - \eta_0)M}{\pi^2 p^2 cRT} \quad (p=1, 2, \dots) \quad (5)$$

where η is the steady-flow viscosity of the solution.

The values of $(\kappa' + 4\eta'/3)$ calculated by eq 3 from the observed absorption in Figure 2 are found much larger than η' calculated by eq 4 through the entire frequency range in this study.

According to the theory on volume viscosity of a polymer solution by Okano,²⁴ who employed the bead-spring model of a dilute polymer solution, κ' is equal to $2\eta'/3$ if the energy loss is assumed only due to friction of beads against solvent in a way analogous to the shear viscosity.

The above facts indicate that the observed absorption is for the most part ascribed to the volume viscosity which is essentially different in its origin from the shear viscosity. The observed relaxation frequencies for the LF relaxations are 55 kHz and 26 kHz for samples B and C, respectively, which are located in the vicinity of the lowest relaxation frequencies of shear viscosity, $f_{\text{shear}} = 1/2\pi\tau_1$, which are respectively 140 kHz and 4.6 kHz at 20°C as calculated by eq 5. However, this may be rather accidental. In fact, the Rouse theory predicts f_{shear} is proportional to the inverse square of molecular weight but the LF relaxation frequency does not have such a strong dependence on molecular weight as is illustrated in Figure 4.

In the sound field, where pressure is adiabatically changed, both pressure and temperature are varied sinusoidally with time. In the following sections, mechanisms for the LF relaxation, the HF relaxation and the UHF relaxation of polystyrene solutions will be discussed on the basis of temperature and/or pressure changes in the system.

DISCUSSION ON LOW-FREQUENCY RELAXATION

The essential features of the LF relaxation are that, as has been described in the preceding section, both the relaxation strength and the relaxation frequency depend on the molecular weight. This would mean that the relaxation may be related to a global motion of a polymer chain.

A polymer chain in a dilute solution takes a randomly coiled conformation. Furthermore, a chain with included solvent may be assumed to be a sphere of radius d which will be called a polymer sphere in the following discussion.

When a homogeneous system is compressed adiabatically, the temperature rise due to pressure change is given by thermodynamics as

$$a = \left(\frac{\partial T}{\partial p} \right)_S = \frac{T\beta}{c_p} \quad (6)$$

where p is the pressure, S is the entropy, β is the thermal expansion coefficient, and c_p is the specific heat per unit volume at constant pressure. In the case of a dispersed system, the value of a for the dispersed particle is in general different from that of the medium, resulting in a temperature difference and irreversible heat flow between them. The absorption of ultrasonic waves caused by this mechanism was theoretically treated by Isakovitch²⁵ and Ratinskaya.²⁶ According to them,

$$\delta \left(\frac{\alpha}{f^2} \right) = \frac{2\pi^2}{3} \phi T \rho u c_{p2}^2 d^2 \left(\frac{1}{5\kappa_2} + \frac{1}{\kappa_1} \right) \left(\frac{\beta_1}{c_{p1}} - \frac{\beta_2}{c_{p2}} \right)^2 \quad (7)$$

if the frequency is sufficiently lower than a critical frequency f_c ,

$$f_c = \frac{\kappa_2}{\pi d^2 c_{p2}} \quad (8)$$

In eq 7 and 8, ϕ is the volume fraction of dispersed spheres of radius d , and κ is the thermal conductivity. Quantities without subscript denote those of the whole system and subscripts 1 and 2 identify quantities belonging to the medium and the sphere, respectively. In the following paragraphs the LF relaxation is discussed along with this theory regarding the polymer sphere as the dispersed particle.

In comparing the theory with the experiment, the thermal conductivity of the polymer sphere κ_2 is most difficult to estimate. The thermal conductivity of bulk polystyrene in the molten state²⁷ is comparable with that of xylene. Since the polymer sphere is a mixture of polymer and solvent, its thermal conductivity may be lower than those of solvent and bulk polymer. It may be possible, therefore, to employ an approximation in eq 7,

$$\frac{1}{5\kappa_2} + \frac{1}{\kappa_1} \simeq \frac{1}{5\kappa_2} \quad (9)$$

The volume fraction of polymer sphere ϕ is related to polymer concentration c as

$$\phi = \frac{N_A c}{M} v, \quad v = \frac{4\pi}{3} d^3 \quad (10)$$

where N_A is Avogadro's number and v is the volume of polymer sphere. The volume v is related to the intrinsic viscosity $[\eta]$ by

$$[\eta] = \Phi \frac{v}{M} \quad (11)$$

where Φ is a constant nearly independent of molecular weight.²⁸

The difference $(\beta_1/c_{p1} - \beta_2/c_{p2})$ on the right-hand side of eq 7 is a small quantity as compared with β_1/c_{p1} because the volume fraction of polymer chain is fairly low in the polymer sphere. We therefore put

$$\frac{\beta_1}{c_{p1}} - \frac{\beta_2}{c_{p2}} = \frac{\beta_1}{c_{p1}} \delta \quad (12)$$

where $|\delta| \ll 1$.

Assuming f_c is equal to the relaxation frequency f_R , by combining eq 7 to 12, we obtain the approximate equation,

$$\frac{\delta(\alpha/f^2)f_R}{c[\eta]} \simeq \frac{2\pi N_A T \rho u c_{p2}}{15\Phi} \left(\frac{\beta_1}{c_{p1}} \right)^2 \delta^2 \quad (13)$$

In Table I, it is found that the values of $\delta(\alpha/f^2)f_R/c[\eta]$ for samples B and C are nearly equal, being independent of molecular weight. The value for sample A is smaller than the others, but, as is seen in Figure 4, the characteristic values for sample A seem somewhat erroneous because of the small excess absorption. In the right-hand side of eq 13, the quantities which might depend on molecular weight are c_{p2} and δ , but the above result suggests that these quantities do not strongly depend on molecular weight. On this basis, we may approximate c_{p2} by c_{p1} and, using experimental values of ρ and u and literature values of $\beta_1 = 0.99 \times 10^{-3} \text{ K}^{-1}$ and $c_{p1} = 1.49 \text{ J/K, cm}^3$, eq 13 is written as

$$\frac{\delta(\alpha/f^2)f_R}{c[\eta]} \simeq 2.80 \times 10^{-6} \delta^2 \quad (\text{sec/cm}) \quad (14)$$

In this calculation, we employed $\Phi = 9.40 \times 10^{23} \text{ mole}^{-1}$ according to Pyun and Fixman,²⁸ assuming the radius of a polymer sphere is equal to the radius of gyration of the polymer chain. By using experimental values of the left-hand

side of eq 14, we get $|\delta|=6 \times 10^{-3}$ for sample B, being much smaller than unity as expected.

A crude estimate of δ is made as follows. If we assume additivity for the thermal expansion coefficient and specific heat per unit volume, then,

$$\left. \begin{aligned} \beta_2 &= \beta_1(1-x) + \bar{\beta}x \\ c_{p2} &= c_{p1}(1-x) + \bar{c}_p x \end{aligned} \right\} \quad (15)$$

where x is the volume fraction of polymer chain in the polymer sphere and $\bar{\beta}$ and \bar{c}_p are quantities of polymer chain itself. The value of x is estimated by the relationship

$$x = \frac{Mv_0}{M_0v} = \frac{v_0}{M_0} \frac{\Phi}{[\eta]} \quad (16)$$

where M_0 and v_0 are the molecular weight and volume of a monomeric unit of the polymer. For sample B the value of x is 0.017.

If we take the thermal expansion coefficient and specific heat of bulk polystyrene in the molten state (at 120°C) in place of $\bar{\beta}$ and \bar{c}_p ($\bar{\beta}=0.74 \times 10^{-3} \text{ K}^{-1}$ ²⁵ and $\bar{c}_p=1.86 \text{ J/K cm}^3$ ²⁹), we obtain from eq 12 and 15 $\delta=8 \times 10^{-3}$ for sample B. This is in a satisfactory agreement with that from eq 14.

In eq 8 d increases with increasing molecular weight, resulting in a decrease of f_c in accordance with the experimental result in Figure 4. Estimation of f_c from eq 8 is difficult because we cannot expect an additivity law for a transport coefficient such as thermal conductivity. On the contrary we can estimate (κ_2/c_{p2}) from eq 8 by use of the observed value of $f_R(=f_c)$ and d calculated by eq 11. The result indicates $(\kappa_2/c_{p2})=0.8 \times 10^{-6} \text{ cm}^2/\text{sec}$ for sample B, which is less than $\bar{\kappa}/\bar{c}_p=0.8 \times 10^{-3} \text{ cm}^2/\text{sec}$ for bulk polystyrene at 120°C as well as $\kappa_1/c_{p1}=0.96 \times 10^{-3} \text{ cm}^2/\text{sec}$ for xylene at 20°C.

The present theory assumes that the polymer chain is confined in a sphere with the radius equal to the radius of gyration. This assumption seems plausible in discussing the relaxation strength but not plausible in describing the relaxation time. In the latter case, we must take into account the dimension of a polymer chain in the solution in more detail.

DISCUSSION ON HIGH-FREQUENCY RELAXATION

As has been described in the first section, ultrasonic absorption measurements in polystyrene solutions have been made in the megahertz range on a series of solvents.^{1-7,9-11} In Figures 7 and 8, the existing data are reproduced in the form of excess absorption per wavelength plotted against frequency. The curves from 1 to 100 MHz seem to be resolved into two single relaxations, HF-I and HF-II. The parameters of two relaxations are listed in Table II. Since the data by Nomura, *et al.*,³⁻⁶ and Bauer, *et al.*,¹² are limited to below 70 MHz, parameters for the HF-II relaxation were not obtained. As Lemaréchal has pointed out, the parameters for the HF-II relaxation depend on the estimation of the limiting absorption at frequencies higher

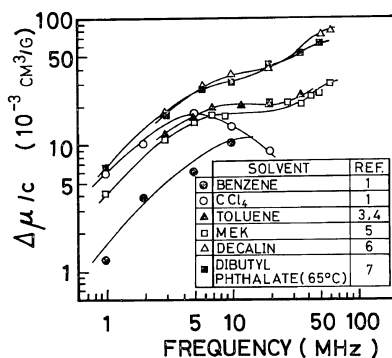


Figure 7. Excess absorption per wavelength for polystyrene in various solvents at 20°C (65°C for dibutyl phthalate).

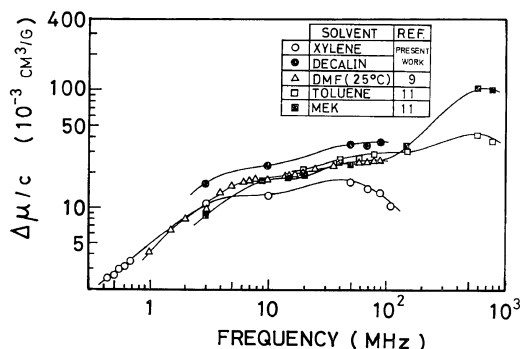


Figure 8. Excess absorption per wavelength for polystyrene in various solvents at 20°C (25°C for *N,N*-dimethyl formamide).

Table II. Characteristic values for high-frequency relaxations of polystyrene solutions

Solvent	Temp, °C	Solvent viscosity, cP	Molar volume of solvent, cm ³ /mol	$(\Delta\mu/c)_{\max}$, 10 ⁻³ cm ³ /g		f_R , MHz		Ref
				HF-I	HF-II	HF-I	HF-II	
Benzene	20	0.65	88.8	11.2	—	13	—	1
Toluene	20	0.59	106	15.5	—	6.4	—	3,4
Toluene	20	0.59	106	9.2	24	7	55	11
Xylene	20	0.67	123	8.5	16.6	3.4	46	* ^a
CCl ₄	20	0.97	96.6	17.5	—	5.8	—	1
MEK	20	0.44	89.6	15.2	—	7.6	—	5
Decalin	20	2.40	159	21.4	—	6.3	—	6
Decalin	20	2.40	159	20.5	34.6	7.5	98	* ^a
DMF	25	0.9	77.4	12	23	6	75	9
DMF	25	0.9	77.4	10.7	13.3	5.8	35	10
DBP	65	4.5	275	21.2	—	5	—	7

^a Present work.

than the HF-II relaxation. This limiting value includes absorptions due to vibrational modes in polymers as well as other absorptions, and should not be assumed to be zero.

As is readily seen in Table II, no correlation is found between solvent viscosity and relaxation frequency. Benzene and xylene exhibit a nearly equal viscosity but the relaxation frequency is higher in benzene. Dibutyl phthalate (DBP) has the largest viscosity in Table II, but the relaxation frequency is not the lowest. This would mean that the HF relaxations are not concerned with translational motion of polymer chains. The kink model proposed by Bauer, *et al.*,^{1,2} therefore, should be rejected because the model assumes the translation of the chain portion between kink and chain end.

Anyway, the HF relaxations in polystyrene solutions, as have been already pointed out by various authors,^{4-7,9} are to be ascribed to local internal rotation of a small segment. For the local rotation to occur without being accompanied by translation, the segment must have collinear end bonds and rotates around this axis. If a chain of C—C bonds is assumed to lie on the diamond lattice, the shortest segment with collinear end bonds is the crank-shaft conformation^{30,31} as illustrated in Figure 9.

As shown in Figure 5, the absorption of the oligostyrene solution (degree of polymerization=21) is about a half of the polystyrene solution. This would mean that a half of the chain (*ca.* 10 monomeric units) is effective in the HF re-

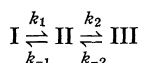
laxations; in other words, five monomeric units at each chain end are more mobile and contribute to another relaxation at a much higher frequency. This is reasonable with reference to our assumption that a few monomeric units form the segment.

In the case of polystyrene, the potential for this rotation is determined by the diad configuration at the two ends of the rotatable segment because the relative position of a pair of phenyl groups at the end of the segments is changed with the rotation. The diad sequence of polystyrene was investigated with NMR by Matsuzaki, Uriu, Osada, and Kawamura.³² They concluded that atactic polystyrene prepared by either radical polymerization or ionic polymerization is rich in syndiotactic diad, and syndiotactic and isotactic diads are distributed randomly in the chain. The fraction of syndiotactic diad is *ca.* 70% almost irrespective of polymerization condition.

Therefore, the probability of segments with two syndiotactic ends is $0.7 \times 0.7 = 0.49$, that with one end syndiotactic and the other isotactic is $2 \times 0.7 \times 0.3 = 0.42$, and that with two isotactic ends is $0.3 \times 0.3 = 0.09$. It may be concluded that the HF-I and HF-II relaxations correspond to the first two and the last case with the small probability does not appear as an observable relaxation. We have no evidence at present which of the first two might correspond to either the HF-I or HF-II relaxation.

Fünfschilling, Lemaréchal, and Cerf¹⁴ assumed

two kinds of segments of different lengths for the two relaxations but it must be mentioned that the potential for the internal rotation is mostly determined by the configuration near the rotating bonds and not by the length of the segment. Ludlow, Wyn-Jones, and Rassing⁹ proposed a three-state model for the rotation. It is in general very unusual, however, that two relaxations arising from the three-state rotation have almost the same relaxation strength as is the present case. They assumed a three state mechanism such as



and concluded from their results that $k_1 = 3.8 \times 10^7 \text{ sec}^{-1}$, $k_2 = 4.7 \times 10^8 \text{ sec}^{-1}$, and $K_1 > 10$ and $K_2 < 0.1$ where K_1 and K_2 are respective equilibrium constants for the steps $I \rightleftharpoons II$ and $II \rightleftharpoons III$. This would mean the state II has a higher energy but a considerably lower free energy than the state I. This may not be impossible but is not easy to imagine.

Previous authors^{1-7,9} assumed thermal relaxation for the HF relaxation of the polymer solution. According to this assumption, it follows that³³

$$\left(\frac{\Delta\mu}{c}\right)_{\text{max}} = \frac{\pi(\gamma-1)}{2c_p M_s} g R f(x) \quad (17)$$

$$f(x) = \frac{2x^2 \exp(-x)}{[1 + 2 \exp(-x)]^2}, \quad x = \Delta H/RT \quad (18)$$

where γ is the ratio of specific heat of the solvent at constant pressure to that at constant volume and c_p is the specific heat (at constant pressure) per unit volume of the solvent, M_s is the molecular weight of the rotating segment, g is the fraction of rotatable segments in the polymer chain, and ΔH is the enthalpy difference between the two states, the upper state of which is assumed to have a two-fold degeneracy because the rotation of C—C bond exhibits three energy minima.

The temperature dependence of $\Delta\mu_{\text{max}}$ is determined by the function $f(x)$, which first increases with increasing temperature, reaches a maximum of 0.761 at $x=2.7$ and then decreases. The temperature dependence of $\Delta\mu_{\text{max}}$ was observed by Bauer, *et al.*,¹ and Nomura, *et al.*³⁻⁷

for the HF-I relaxation. The temperature coefficient of $\Delta\mu_{\text{max}}$ is positive for polystyrene solutions in CCl_4 ,¹ but negative in toluene³ and decalin,⁶ and slightly negative in MEK.⁵ In the case of dibutyl phthalate as a solvent,⁷ $\Delta\mu_{\text{max}}$ first increases with increasing temperature and reaches a maximum at 45°C. Nomura, *et al.*,⁴⁻⁷ fitted the variation of $\Delta\mu_{\text{max}}$ with temperature to the function $f(x)$ and estimated the values of ΔH for the HF-I relaxation as 1.66 (dibutyl phthalate⁷), 1.02 (decalin⁶), 0.41 (toluene⁴), and 1.7 kcal/mol (MEK⁵).

In this paper, the absolute value of $\Delta\mu_{\text{max}}$ will be discussed in what follows. Since $f(x)$ in eq 17 has a maximum at $x=2.7$ which corresponds to $\Delta H=1.54 \text{ kcal/mol}$ at 20°C, the inequality should hold for xylene solutions,

$$\left(\frac{\Delta\mu}{c}\right)_{\text{max}} < 0.65 \times 10^{-2} g \quad (\text{cm}^3/\text{g}) \quad (19)$$

where the literature values for c_p and γ are used, and M_s is assumed to be 300 (three monomeric units; see Figure 9). Using the sum of $(\Delta\mu/c)_{\text{max}}$ for the HF-I and HF-II relaxations in the present work, we obtain $g > 3.8$. The increase in M_s would result in the increase in g . This is quite unreasonable because g should be smaller than unity. The above considerations eliminate the possibility of a purely thermal relaxation for the HF relaxation.

Therefore we discard the assumption of thermal relaxation and turn to the assumption of volume relaxation. The volume change due to the internal rotation arises from the change of packing near the rotating bonds, especially the packing of adjacent phenyl groups. Solvent molecules can enter between phenyl groups if there is sufficient free space, but cannot if the

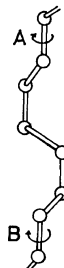


Figure 9. Crank-shaft conformation. A and B represent collinear end bonds.

space is narrowed by internal rotation. Therefore the volume change, ΔV , on the rotation of one mole segments may be a fraction of the molar volume of the solvent.

From this assumption, it follows³³ that for the two-state model, with a degenerated upper state,

$$\left(\frac{\Delta\mu}{c}\right)_{\max} = \frac{\pi\rho u^2}{2M_s\Delta H}(\Delta V)^2 gh(x) \quad (20)$$

$$h(x) = \frac{2x \exp(-x)}{[1 + 2 \exp(-x)]^2}, \quad x = \frac{\Delta H}{RT} \quad (21)$$

where ΔV is the volume change with the rotation of one mole segments. Since the function $h(x)$ in eq 20 has a maximum of 0.337 at $x=1.9$ (this implies $\Delta H=1.09$ kcal/mol at 20°C), we obtain, assuming $M_s=300$,

$$\left(\frac{\Delta\mu}{c}\right)_{\max} < 6.54 \times 10^{-4} \frac{(\Delta V)^2}{\Delta H} g \quad (\Delta V \text{ in cm}^3/\text{mol}, \Delta H \text{ in kcal/mol}) \quad (22)$$

Using values of $\Delta H=1.09$ kcal/mol and $\Delta V=20$ cm³/mol (one-fifth of the molar volume of a phenyl group), eq 21 is rewritten as

$$\left(\frac{\Delta\mu}{c}\right)_{\max} < 0.24g \text{ (cm}^3/\text{g)} \quad (23)$$

Substituting the sum of $(\Delta\mu/c)_{\max}$ for the HF-I and HF-II relaxations in the present work, $g >$

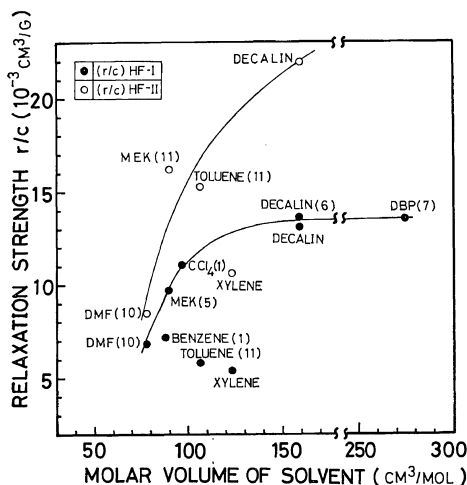


Figure 10. Relaxation strengths for the HF-I (dot) and the HF-II (circle) relaxations of polystyrene in various solvents plotted against the molar volume of the solvents.

0.106 which may be a plausible value.

From the above considerations we conclude the HF relaxations of polystyrene are predominantly volume relaxations. In fact, as is seen in Table II, the relaxation is strongest in DBP which has the largest molar volume among the solvents in Table II. Figure 10 indicates the correlation between the relaxation strength and the molar volume of the solvent. A positive correlation is found for a series of solvents, DMF, MEK, CCl₄, decalin, and DBP. The series of benzene, toluene, and xylene seems to be somewhat different. These three solvents whose molecular form is similar to that of the phenyl group may be more closely packed in between the phenyl groups, providing smaller values of ΔV .

DISCUSSION ON ULTRAHIGH-FREQUENCY RELAXATION

As is illustrated in Figure 7, the data by Mikhailov and Safina¹¹ for polystyrene solutions in MEK and toluene indicate another acoustic relaxation around 500 MHz.

Since polystyrene possesses no long side chain, the relaxation may be attributed to vibration of phenyl groups in a way similar to the γ relaxation in bulk polystyrene which appears at -70°C when measured at 34 kHz.³⁴ The extrapolation of the activation plot of the γ relaxation to room temperature indicates the frequency for maximum loss should be located around 500 MHz.

The general expression of relaxation strength for vibrational relaxation is³³

$$\left(\frac{\Delta\mu}{c}\right)_{\max} = (\gamma - 1) \frac{n C_{\text{vib}}}{c_p} \quad (24)$$

where c_p is the specific heat of the solvent at constant pressure per unit volume, C_{vib} is the specific heat of the vibrator in question, and n is the number of vibrators per unit volume of solution of unit polymer concentration. The specific heat of the vibrator is given by the Einstein equation,

$$C_{\text{vib}} = k \left(\frac{h\nu}{kT}\right)^2 \frac{\exp(-h\nu/kT)}{[1 - \exp(-h\nu/kT)]^2} \quad (25)$$

where ν is the characteristic frequency of the

vibrator, k is the Boltzmann constant, and h is the Planck constant.

The vibrational frequency of the phenyl group around the C— ϕ bond in polystyrene is calculated from the van der Waals potential between the phenyl group and neighbor atoms in the main chain as $\nu=1.54 \times 10^{12}$ Hz.³⁵ By use of this value, the calculated value of $(\Delta\mu/c)_{\max}$ is $0.015 \text{ cm}^3/\text{g}$ for MEK and $0.021 \text{ cm}^3/\text{g}$ for toluene. On the other hand, the observed values are $(\Delta\mu/c)_{\max}=0.03$ for MEK and 0.06 for toluene. The observed and calculated values agree within an order of magnitude.

The experimental values in Figure 7 seem somewhat erroneous because the values were derived from the small difference in (α/f^2) between solution and solvent. The theoretical value may also be in error because the vibrational frequency was calculated by only taking into account the interaction between the phenyl group and neighboring hydrogen atoms. Considering these facts, the agreement between experiment and theory may be rather satisfactory.

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