New Techniques for Measuring Complex Shear Viscosity of Dilute Polymer Solutions at Frequencies from 2 to 300 kHz

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ABSTRACT: Two new techniques for measuring complex shear viscosity ($\eta' - i\eta''$) of a liquid, especially of a dilute solution of polymer including polyelectrolyte, have been developed. The first of them, "the travelling torsional wave method", consists essentially of measuring incremental attenuation and phase retardation of torsional waves travelling along a long circular rod when a liquid is applied around the rod. The waves are generated and received by a quartz torsional resonator soldered on the top of the rod. Electronic circuits are designed so as to observed frequency ranges from 20 to 300 kHz and the error is within 1% for the sample with the viscosity of 10^{-2} poise. A sample of 10 cc is required for the measurement.

The second method, "the torsional reverberation method", employs the same vibration system as the above but the system is excited into a resonant oscillation. The method consists of measuring decrease in resonant frequency and increase in decay-rate when a liquid is applied around the rod. The method can be used at a fundamental resonance and overtones, 2 to 10 kHz in the present case. The accuracy is of the order of 1% for the sample with viscosity of 10^{-2} poise.

KEY WORDS Complex Viscosity / Technique / Polymer Solution /
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A technique for measuring complex shear viscosity of a liquid was first proposed by Mason¹ who measured variation in resonant frequency and equivalent resistance of a torsional quartz resonator when the liquid was applied. The method covered the frequency range from 20 to 200 kHz by use of resonators of different length. Torikai and Negishi² employed a phase-sensitive detector for measuring the equivalent resistance of the resonator. Application of this technique to dilute polymer solutions was made by Tanaka, Sakanishi, and Furuichi.³ One of the present authors (Wada) and his coworkers⁴ employed a modification of this method, which is applicable to an electrically conductive liquid. In this case, the lower one-fourth of the resonator was dipped into the liquid.

The viscosity of a liquid at higher frequencies is obtained from the complex reflectivity of shear waves at the solid-liquid interface.⁵

This method has been extended by McSkimin and his coworkers^{6,7} up to 300 MHz. The low-frequency complex shear viscosity of dilute polymer solutions has been studied by several investigators using the apparatus by Birnboim and Ferry,⁸ which is useful in the frequency range from 10^{-2} to 400 Hz.

In the present paper, two new techniques will be presented for measuring complex shear viscosity of liquids. The first, the travelling torsional wave method, is an improvement on McSkimin's one,⁹ in which attenuation and phase-shift of torsional waves are measured which travel along a circular rod with an applied liquid. The waves are excited by a quartz torsional resonator soldered on the top of the rod. The improvement is made to attain high accuracy so that the method can be applied to measurement of a dilute polymer solution. The method covers the frequency range from 20 to 300 kHz.

The second method reported in this paper consists essentially of measurement of decay-rate and resonant frequency of torsional oscillation of the circular rod around which a liquid is applied. The same vibration system as the first method is used and the oscillation is excited and detected by means of the quartz torsional resonator.

The two methods can be applied to electrically conductive liquids as well as nonconductive ones, and require about 10 cc of specimen solutions. The error is less than 1 % for a liquid of viscosity of 10^{-2} poise in the first method, and in the order of 1 % in the second one.

TRAVELLING TORSIONAL WAVE METHOD

Principle of the Method

The travelling torsional wave method which had been first developed by McSkimin⁹ was improved in several aspects for the purpose of attaining a sufficient accuracy to measure dilute polymer solutions. This method has advantages over the torsional resonator technique¹ when applied to an electrically conductive solution with continuously varied frequencies.

Figure 1. View of the mechanical system of travelling torsional wave method and torsional reverberation method: 1, silica gel; 2, metal shield; 3, torsional quartz resonator; 4, rubber O-ring; 5, circular rod of fused quartz; 6, test liquid; 7, coaxial glass cylinder; 8, needle support; 9, water-jacket; 10, air-jacket; 11, U-tube of polyethylene; 12, liquid reservoir; 13, piston; 14, thermometer.

Figure 1 represents the vibration system, where the torsional pulsed waves are generated by a torsional quartz resonator at the top of the rod and run along a circular rod of fused quartz. The pulse is reflected from the bottom of the rod, then again reflected from the top and so on, and multiple echoes are received by the resonator.

A liquid is applied around a given length h of the rod. The increase in attenuation ΔA in nepers and the phase retardation ΔB in radians of the n -th echo are then measured. Unless the loading is very high, the equivalent plane-wave shear impedance $Z = R + iX$ of the liquid is given⁹ by

$$R = \frac{\rho_0 V_0 a}{4nh} \Delta A, \quad X = \frac{\rho_0 V_0 a}{4nh} \Delta B \quad (1)$$

where ρ_0 is the density of the rod, a the radius of the rod, and V_0 the velocity of propagation of torsional waves in the rod without the liquid.

Complex shear viscosity $\eta^* = \eta' - i\eta''$ of the liquid is calculated from the well-known equations;¹

$$\eta' = \frac{2RX}{\omega\rho}, \quad \eta'' = \frac{R^2 - X^2}{\omega\rho} \quad (2)$$

where ρ is the density of liquid and ω the angular frequency.

Electronic Circuit

Figure 2 illustrates the block diagram of the entire electronic system. Some improvements have been made upon the circuit by McSkimin⁹

Figure 2. Block diagram of electronic system of travelling torsional wave method.

with the purpose of observing the n -th echo in a high S/N value. The value of n is to be taken as large as possible to attain high accuracy and in the present study, n was taken as 10 to 100, depending on the loss of liquid.

The frequency of the hf continuous waves from the variable frequency oscillator (1) (20—500 kHz) is reduced by a factor of *ca.* 10^{-4} with the frequency divider (5), which consists of a three-stage fantastron circuit and a six-stage flip-flop circuit. The low-frequency output from (5) is formed into a pulsed wave by the pulse forming circuit (4). The purpose of frequency division is to synchronize the carrier of waves with the pulse envelope and hence the reduction ratio of frequency is not significant.

The duration of the pulse is variable in the range of 10 to 100 msec. A pulse from an appropriate stage of the frequency divider (5) is used to trigger the horizontal sweep of the oscilloscope (11). The order n of the echo pulse which is displayed on the oscilloscope is determined by the stage of frequency divider from which the trigger pulse is taken out.

The hf waves from (1) are gated by the gate-1 (2) and then by the gate-2 (3) into pulsed hf waves. Since the gate signal from (4) has been synchronized with the original hf waves, the hf signal displayed on the oscilloscope is perfectly clear when the oscilloscope is triggered by

the signal from (5). Two gates are used in order to keep the leak level out of the gate time as low as possible. The output from the power amplifier in the driving circuit (7) has a level ratio in and out of the gate time of 120 db.

Figure 3 illustrates the detailed circuit diagram of the main part of Figure 2, gate-2 (3), and the driving and receiving circuits (7). The bridge circuit is used following McSkimin⁹ so as to balance out the current through the clamped admittance of the quartz resonator. Values of C and R are adjusted to be equal to the clamped capacitance (capacitance of the resonator and the cable) and the clamped resistance (leak resistance of the resonator), respectively. The inductance L is varied so as to make resonance with C to the hf signal. The applied voltage to the quartz resonator is as high as 10^3 V p-p, but the signal level at point A in Figure 3 against ground corresponds to the excess of motional admittance over clamped admittance of the resonator.

This signal with received multiple-echo signals goes into the preamplifier and then to the mixer (9) in Figure 2, in which they are mixed with original hf waves attenuated by the attenuator (8). The signal from (9) is amplified by the untuned amplifier (10) and displayed on the oscilloscope (11) in which the horizontal sweep is triggered by the pulse from (5).

Acoustic Circuit

Two torsional quartz resonators with resonant frequencies of 40 kHz and 100 kHz are used and the frequency range from 20 kHz to 300 kHz is covered. Rods of fused quartz of the same size are used for two resonators, respectively. The length of the rods is 79 cm and the radius is the same as the resonator, 0.25 cm. As is illustrated in Figure 1, the rod (5) is supported by a rubber O-ring (4) at an upper part and by a needle support (8) at the center of the bottom end surface.

The rod is placed in a coaxial glass cylinder (7). The gap between the rod and the cylinder wall is 0.5 mm, and the specimen of about 10 cc is necessary to fill the gap to $h = 70$ cm. The specimen liquid is easily taken out of the cylinder by use of a U-tube (11) into a reservoir

Figure 3. Circuit diagram of gate-2 and driving and receiving circuits in Figure 2.

(12) in which pH or concentration of the specimen solution is varied. The solution stirred by a magnetic stirrer in the reservoir.

The temperature of the specimen is controlled by an inner water-jacket (9) which is further surrounded by an outer air-jacket (10). Water of a constant temperature is circulated through the inner jacket. The temperature is measured by a thermometer (14) in the inner jacket.

The torsional resonator is attached to the top end of the rod by use of indium solder after the surfaces have been plated with silver. An adhesive such as epoxy resin was proved unsuitable to measurements with varied temperature because of high-temperature coefficient of loss. The resonator is surrounded by a metal shield (2) including silica gel (1) as a desiccant. The shield serves also as the electrostatic shield and is useful at the same time to keep the temperature of resonator constant.

Performance

By varying the delay time of the triggering signal, an echo of an appropriate order can be displayed on the oscilloscope. The order n of echo is determined by counting the number of echoes with slow sweep on the oscilloscope. The value of n is not necessary in usual measurements because the measurement is made by use of calibration curves which have been obtained by use of standard solutions of known viscosity at the same value of n .

Principles for measuring ΔA and ΔB are essentially similar to those of McSkimin.⁹ The n -th echo is mixed with the continuous carrier signal and eliminated by adjusting the attenuator and frequency. Then increase in the attenuator reading, ΔN in db, with an applied liquid gives ΔA as

$$\Delta A = \frac{\Delta N}{8.686}. \quad (4)$$

The value of ΔB is obtained from the equation,⁷

$$\Delta B = 2\pi \frac{f_r - f}{f_r - f_r'} \quad (5)$$

where f_r and f_r' are two adjacent frequencies for balancing without the liquid and f the frequency for balancing with the liquid. The phase shifter employed by McSkimin is therefore unnecessary. The accuracy of the attenua-

tor is 0.1 db and that of the frequency counter is 0.1 Hz.

Some Experimental Results

Figure 4 illustrates an example of the data. The specimens are dilute aqueous solutions of glycerine at 30°C. Experimental conditions are $n = 16$, $h = 70.5$ cm, and $f = 32.03$ kHz. Since

Figure 4. Attenuation ΔA (filled circle) and phase retardation ΔB (open circle) of torsional waves propagating along a rod plotted against $\sqrt{\omega\rho\eta/2}$ in water-glycerine mixtures at 30°C; $n = 16$, $h = 70.5$ cm, and $f = 32.03$ kHz.

glycerine-water mixtures exhibit no relaxation at this frequency, $\eta'' = 0$ and hence both R and X are equal to $(\omega\rho\eta/2)^{1/2}$ where η is the steady-flow shear viscosity. The steady-flow viscosity was measured by means of an Ostwald viscometer. In Figure 4, observed values of ΔA and ΔB are plotted against $(\omega\rho\eta/2)^{1/2}$. The straight lines in Figure 4 represent the theoretical slope predicted from eq 1, which agrees well with the observed ones. Values of ΔB extrapolated to $(\omega\rho\eta/2)^{1/2} = 0$ do not vanish probably because of the effect of the liquid surface. This surface acts as an excess mechanical impedance to waves propagating along the rod and the result in Figure 4 indicates that the surface impedance is rather reactive than resistive.

For the measurement of a specimen with unknown η' and η'' , calibration curves as illustrated in Figure 5 are used which are obtained for aqueous solutions of glycerine or sucrose and over the required range of R and X for the same conditions (frequency, temperature,

Figure 5. An example of calibration curves obtained for water-glycerine mixtures at 30°C; $n = 16$ and $h = 70.5$ cm.

Figure 6. Frequency f (open circle) and attenuation N (filled circle) of torsional waves travelling along a rod plotted against the depth of water around the rod; $n = 12$. Zero level of N is taken arbitrarily.

h and n) as those for a specimen. The accuracy of the present technique is better than 10^{-4} poise as will be expected from linearity and scatter in the calibration curves.

Figure 6 illustrates the effect of the liquid depth h on the attenuation and phase shifts. The measurement was made for water at 20°C, at 128 kHz and $n = 12$. The result reveals that both the attenuation and the phase shifts are linear against h as predicted from eq 1.

Figure 7 shows the behavior at small values of h for water at 25°C. Points A correspond to the state without liquid and points B to the liquid just on the bottom surface of the rod. The difference between A and B gives, therefore, the effect of liquid on the bottom surface. Points C extrapolated to $h = 0$ from finite values of h do not coincide with points B because of

Figure 7. Frequency f (open circle) and attenuation N (filled circle) of torsional waves travelling along a rod plotted against the depth of water around the rod; $n = 26$. Zero level of N is taken arbitrarily. A, B and C are identified in the text.

the effect of liquid level rise due to surface tension.

Data in Figures 6 and 7 have been obtained in the preliminary stage of this study and the rod used was different from other experiments. Rods in those cases were made of pyrex glass and the diameters were 0.5 and 1.2 cm in Figures 6 and 7, respectively.

One of the results for a viscoelastic solution is drawn in Figure 8, in which $\eta' - \eta_s$ (η_s = solvent viscosity) and η'' of a poly(glutamic acid) solution at 113 kHz are plotted against pH. The solvent is a mixture of dioxane and water including 0.2 N NaCl. Polymer concentra-

Figure 8. Complex shear viscosity $\eta' - i\eta''$ of a poly(glutamic acid) solution plotted against pH. Open and filled circles represent $\eta' - \eta_s$ and η'' , respectively. Concentration, 0.7 g/100 cc; solvent, a mixture of water (0.2 N NaCl) and dioxane (2.1 in volume); temperature, 30°C; frequency, 113 kHz.

tion is 0.7 g/100 cc. Sharp maxima in both η' and η'' at the region of helix-coil transition of this polymer reflect the maximum in relaxation time.^{4,10} Details will be discussed in a future paper.

TORSIONAL REVERBERATION METHOD

Principle of the Method

With the purpose of extending the frequency range to lower than the travelling torsional method, a new technique called "torsional reverberation method" has been developed. The mechanical system is quite the same as the previous method in Figure 1 but, in the present method, the rod with the quartz resonator is excited into a torsional resonant vibration. In this case, the fundamental mode has a frequency of about 2.2 kHz, and this mode with several overtones up to 10 kHz can be used.

The principle of the method is essentially to measure the resonant frequency and the decay-rate of free oscillation after the excitation has been stopped with and without an applied liquid. In the case of a nonconducting liquid, the whole vibrating system can be dipped into the liquid. Then the lowering of resonant frequency Δf is proportional to X , the imaginary part of shear impedance of the liquid, and the increase of decay-rate ΔD (neper/sec) is proportional to R , the real part of the impedance. The complex viscosity $\eta' - i\eta''$ can be calculated from X and R by eq 2. The proportional constant is obtained theoretically or by calibrating the system with a nonrelaxing reference liquid in which $\eta'' = 0$ and $\eta' = \text{steady-flow viscosity}$.

In case of a conducting liquid, however, the vibrating rod is partly dipped into the liquid. In this case, in contrast to the travelling wave method, Δf and ΔD are not proportional to the liquid-level height h because the amplitude is not uniform along the rod. The reference liquid and the test liquid should be compared, therefore, at exactly the same value of h .

Under assumptions that (1) the vibrating rod is a series connection of two parts, one with the length $l - h$ being not loaded and the other with the length h loaded by a liquid of shear wave impedance $R + iX$, (2) both ends of the

rod are free, and (3) the effect of liquid surface is negligible, the resonant frequency f_n and the decay-rate D_n of the n -th overtone can be obtained from the transmission-line analysis as

$$f_n = f_n^0 - \frac{2Xf_n^0}{n\pi\rho_0V_0a} \left(h + \frac{l}{2n\pi} \sin \frac{2n\pi h}{l} \right) \quad (6)$$

$$D_n = D_n^0 + \frac{4Rf_n^0}{n\rho_0V_0a} \left(h + \frac{l}{2n\pi} \sin \frac{2n\pi h}{l} \right) \quad (7)$$

where ρ_0 , V_0 and a have the same significance as in eq 1, and f_n^0 and D_n^0 are values without liquid.

In the case of such a low-frequency measurement, a bending mode of the rod may be coupled with the torsional mode. In the present case, the fundamental frequency of bending of the rod is as low as 20 Hz but some overtones of bending might be close to the torsional frequency. The occurrence of bending oscillation was proved by detecting pressure changes in the water-jacket by means of a hydrophone. The frequency of pressure changes was equal to that of an hf signal applied to the quartz resonator. Since the frequency of bending oscillation depends greatly on the liquid height h , the excitation of bending at a resonant frequency for torsional oscillation, in other words, the coupling between bending and torsional vibration, occurs at discrete values of h . The choice of h for the torsional-reverberation method, therefore, is of great importance in avoiding this coupling.

For the purpose of completely eliminating the effect of bending, a thick rod in which a fundamental resonant frequency of bending is higher than resonant frequencies of torsion can be employed but this may require a larger amount of test liquid.

Electronic Circuit and Performance

Figure 9 illustrates the block diagram of the entire system. The frequency of hf waves from the variable oscillator (2) are divided by a four-stage flip-flop circuit (3) into 2 to 10 kHz. This is necessary for high accuracy of frequency measurement and making the oscillator (1) in Figure 2 appropriate for this purpose.

The carrier waves are gated by the gate-1 (5) and successively by the gate-2 (6). The gating signal is a square wave which is fed from the

Figure 9. Block diagram of electronic system of torsional reverberation method.

9-stage flip-flop circuit (4) and has a frequency of $f/2^9$ (f = carrier frequency) and a duration time of a half period. The ratio of carrier-wave levels in and out of the gate time is as high as 140 db, which is necessary to detect small free-decay signals free from the leakage of carrier waves.

The detailed circuit diagram of gate-2 (6) and

Figure 10. Circuit diagram of gate-2 and driving and receiving circuit (T, torsional quartz resonator).

driving and receiving circuits (7) is illustrated in Figure 10. The SCR element is used to provide a high-voltage square wave with a low output impedance. The variable inductance L in Figure 10 is tuned to make a series resonance with the capacitance of transducer and hence the driving voltage to the transducer is as high as 2×10^3 volts. The resonance is also effective to depress higher harmonics, if any. The resonant circuit is coupled with the buffer amplifier tube 6DJ8 through a small capacitance (50 pF) because, if not, the circuit might be short-circuited by the grid current of the tube.

The output signal from (7) is mixed in the mixer (10) with a reference wave which has quite the same frequency and the opposite phase

(a)

(b)

(c)

Figure 11. Example of oscilloscope pattern of torsional reverberation method at 2.2 kHz: (a) exponential decay of free oscillation (output from (7) in Figure 9), (b) mixed signal (output from (10)), and (c) enlarged pattern of zero-level point of (b).

as the output signal but the level of which is a constant independent of the output signal. The reference wave is formed by a Schmitt trigger and monostable multivibrators (8) and attenuated by a definite amount by the attenuator (9).

The mixed signal from (10) is fed to the twin-T tuned amplifier (11) and then to the oscilloscope (12), in which the horizontal sweep is triggered by the delayed signal from (4).

The pattern on the oscilloscope screen is illustrated in Figure 11, in which the point of zero level indicates the time at which the exponentially decaying signal reaches a definite level N determined by the attenuator. The resonance is detected by adjusting the carrier-wave frequency so that the decay-rate is the lowest. Then the reading of the electronic counter (1) divided by 16 ($= 2^4$; four-stage flip-flop circuit (3) in Figure 9) gives the resonant frequency.

The attenuator is then varied to a lower value N_0 so as to shift back the zero-level time by a definite time interval t . The readings N and N_0 of the attenuator are related to the decay-rate D as

$$D = \frac{N - N_0}{8.868 t} \quad (8)$$

It is of course possible to measure the decay-rate directly by use of a logarithmic amplifier

Figure 12. Decrease in resonant frequency of torsional oscillator plotted against level height of an aqueous solution of sucrose; ($n=1$ and $f^0 = 2.154$ kHz). Solid line represents theoretical curve from eq 6.

Figure 13. Increase in decay-rate of torsional oscillation plotted against level height of an aqueous solution of sucrose; $n=1$ and $f^0 = 2.154$ kHz. Solid line represents theoretical curve from eq 7.

Figure 14. Example of calibration curves obtained for aqueous solutions of sucrose at 30°C. Resonant frequency multiplied by 16 and signal level N at 57 msec after the excitation has been stopped are plotted against $\sqrt{\rho\eta}$; $n=1$ and $h=28$ cm.

and level comparators as has been done by Ohsawa and one of the present authors (Wada).¹¹

Some Experimental Results

Figures 12 and 13 illustrate an example of observed values of decrease in resonant frequency Δf and increase in decay-rate ΔD plotted against the liquid-level height h . Solid lines represent calculated values from eq 6 and

Figure 15. Real and imaginary parts (open and filled circles, respectively) of complex shear viscosity of a poly(glutamic acid) solution at 2.15 kHz plotted against pH. Polymer concentration, solvent, and temperature are the same as in Figure 8. Dashed line represents the steady-flow viscosity of solution and the solvent viscosity is 13.08×10^{-3} cgs.

7. The value of t was 43.15 msec in this case.

Discrepancies of observed values from theoretical ones occur around $h = 40$ cm indicating the coupling of a bending mode. Two minor discrepancies of experimental points from theory are found around $h = 19$ cm and $h = 61$ cm. The output of the hydrophone in the water-jacket exhibits maxima at these points. These data indicate that h should be taken as *ca.* 25 cm to avoid the bending effect.

For the purpose of measurement of the viscoelastic behavior of a polymer solution, calibration curves covering the required range of R and X are necessary. Figure 14 shows an example of calibration curves obtained for

aqueous solutions of sucrose of different concentrations. The ordinate represents the resonant frequency multiplied by 16 and, in place of decay-rate D , the signal level N in db at 57 msec after the excitation has been stopped. As far as the exciting voltage of torsional resonator and the time t are kept constant for reference and test liquids, N is a function of R alone.

Figure 15 indicates results for the same poly-(glutamic acid) solution as in Figure 8. Detailed discussion of this result will be given in a future paper.

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