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Acoustical Impedance of Sulfur Near the Polymerization Transition[1]

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The acoustical impedance of liquid sulfur has been measured for the first time for both longitudinal and shear sound waves over the frequency range from 5 to 25 MHz from the melting temperature to 180 °C. The experiment shows that sulfur is not a viscoelastic liquid either below or above the polymerization transition temperature.

KEY WORDS: acoustics; polymerization; sulfur.

1. INTRODUCTION

Liquid sulfur has attracted significant attention for many years [1–3] because of the peculiar appearance of equilibrium polymerization as the temperature exceeds 159°C. Although this phenomenon has been known for many years, there is still no comprehensive understanding. The polymerization transition in sulfur represents one of the most studied liquid–liquid phase transitions, which have been widely discussed over the last few years [4]. Sulfur is the only elementary substance to exhibit the phenomenon of equilibrium polymerization, a phenomenon that is more common for organic and biological systems. The understanding of equilibrium polymerization is also important for practical applications in the polymer industry where the process of polymer fabrication consists of three

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major steps, initiation, propagation, and termination. Equilibrium or "living" polymerization can be viewed as a process in which the third step (termination) is avoided [3].

Sulfur melts at about 120°C, forming a light-yellow liquid of low viscosity. At this temperature, sulfur consists primarily of eight-membered, ring-like molecules. On heating above 120°C, sulfur behaves as an ordinary monomeric liquid, but at 159°C its properties change dramatically. At this temperature the monomeric rings open up and convert to long polymeric chains. This abrupt change is the so-called polymerization transition. Above this transition the viscosity increases by a factor of 10^4 [5], and other properties, such as the density [6], the heat capacity [7], and the sound speed [8], also exhibit interesting features.

The most convincing evidence for the presence of a large fraction of long-chain polymers above the transition temperature comes from electron spin resonance (ESR) measurements [9,10; Kozhevnikov et al., *J. Chem. Phys.* accepted]. At low temperatures, sulfur is a weak diamagnetic liquid [11], but above about 160°C liquid sulfur exhibits a paramagnetic response due to unpaired electrons near the chain ends. As estimated from ESR measurements, the mass fraction of polymers (extent of polymerization) is about 30% and the average number of monomers (eight-atom chain segments) in the chains is on the order of 10^6 near the transition temperature.

Polymerization in sulfur is reversible. No hysteresis has been found in any of the properties. Wheeler et al. [12] and Anisimov et al. [13] have treated polymerization in sulfur as a second-order phase transition in a weak external field. Cordery [14] has applied the Ising model to describe this phenomenon. Wheeler et al. [12] have also shown that an earlier theory of polymerization by Tobolski and Eisenberg [15] can be viewed as a mean-field approximation for a second-order phase transition. However, none of these theories comprehensively describes the experimental data [3]. According to a theory by Dudowicz et al. [16], the polymerization transition is not a true phase transition, but in the presence of an infinitesimally small concentration of initiator, some properties, such as the heat capacity, may behave similar to that at the continuous phase transition.

2. MEASUREMENTS

Acoustical probing provides a sensitive tool for studies of phase transitions [17]. For this reason we recently performed measurements of sound speed and sound absorption in liquid sulfur [8] using a precision pulsed phase sensitive technique [18]. The measurements were done over a frequency range from 5 to 22 MHz. No dispersion in the acoustical properties was observed. We also found that the temperature dependence of the sound speed exhibits a specific feature in the region of the polymerization transition. This feature is consistent with data on the extent of polymerization measured under static conditions [19].

According to classical hydrodynamics [20], sound absorption α in uniform liquids should follow the formula,

$$\alpha = [(4\eta/3 + \zeta) + \kappa(C_V^{-1} - C_P^{-1})]\omega^2/2\rho v^3, \tag{1}$$

where η and ζ are coefficients for the shear and bulk viscosities, respectively, κ is the coefficient of thermal conductivity, C_V and C_P are heat capacities, $\omega = 2\pi\nu$ is the angular frequency, and ρ is the mass density. Therefore, one should expect a strong anomaly (10,000-fold or greater enhancement) for sound absorption at the polymerization transition in sulfur. Surprisingly, we observed no feature in the temperature dependence of the sound absorption near the polymerization transition. We tentatively proposed [8] that the "flat" behavior of sound absorption could be associated with viscoelasticity, a property that is typical for many polymeric solutions [21,22].

Viscoelasticity means that the time dependence of the compliance (strain-to-stress ratio) of a system has a plateau at a time $t < \tau^*$, where τ^* is called the terminal or longest relaxation time. Therefore, for processes occurring on time scales less than τ^*, the system possesses an effective Young's modulus and behaves like an elastic solid. If the time scale is greater than τ^*, the stress is no longer proportional to the strain and the system responds to shear stress like a liquid. The absence of dispersion in the sound speed and the consistency of the sound speed measurements with static data on polymer fraction [8] can be interpreted as though the frequencies of sound in these measurements were *lower* that the relaxation frequency $\nu* = 1/\tau^*$. On the other hand, the viscoelastic interpretation of the data on sound absorption implies that the experimental frequencies are *greater* than ν^*. Clarification of this paradox is the main goal of this paper. An answer to the question of whether the measurements in Ref. 8 were performed above or below the relaxation frequency ν^* is also important for verification of the theoretical predictions made within the framework of second-order phase transition theory [13]. If the frequencies used are greater than ν^*, then the theoretically predicted minimum in sound speed could exist at lower frequencies, and therefore this theory could be valid.

The most convincing test for viscoelasticity is to probe the liquid with transverse sound waves. At $\nu > \nu^*$ viscoelastic liquids support these waves, whereas ordinary liquids (for which ν^* lies in the GHz range) do not.

3. RESULTS

First, we attempted to perform direct measurements of the speed and absorption of transverse sound waves with a sample of about 0.8 mm length. We used a hermetically sealed quartz cell of the same design as that described in Ref. 8. Quartz shear mode transducers with a principal frequency of 5 MHz were employed. The transducers were attached to the buffer rods via hardened epoxy resin. The experiments were performed at sound frequencies of 5, 15, and 25 MHz at temperatures up to 180°C. The transmitted signal disappeared on melting and was reappeared on solidification. No transmitted signal was observed in liquid sulfur either below or above the polymerization transition temperature.

Although suggestive, this negative result cannot be considered as conclusive because the absence of the transmitted signal could result from a large sound absorption for shear waves.

In the second experiment the sound impedance of sulfur was measured. The essence of this approach is as follows. A burst of radio-frequency sound is excited in a quartz rod, and the signal reflected from the end of the rod is measured at two times—first when the rod is in the liquid sulfur and second when the rod is out of the liquid sulfur. A comparison of the amplitudes and phases of the reflected pulses as shown in Fig. 1 yields information on both the real (Z') and imaginary (Z'') components of the acoustical impedance (Z) of the liquid. The sound speed and absorption can then be calculated as follows [23]:

$$Z' = Z_q \frac{1-r}{1+r} = \rho v \tag{2}$$

$$Z'' = Z_q \frac{2r\sin(\theta)}{(1+r)^2} \cong \frac{\alpha \rho v \lambda}{2\pi}, \tag{3}$$

where Z_q is the impedance of the quartz rod, r is the ratio of the amplitude A_f (rod in the liquid) to the amplitude A_0 (rod out of the liquid), ρ is the density of the liquid, v is the sound speed, θ is the phase shift, α is the absorption coefficient of the sound in nepers per centimeter, and λ is the wavelength of the sound (in cm). The impedance of the quartz Z_q is considered real and the absorption is assumed to be small ($\alpha\lambda < 1$).

The measurement procedure is illustrated in Fig. 1. First, the probe and reflected signal are adjusted in magnitude and phase using the pulsed phase-sensitive apparatus described in Ref.19, and the amplitude A_0 is measured. Then the rod is embedded into liquid sulfur, and the amplitude A_f and the phase shift θ are measured.

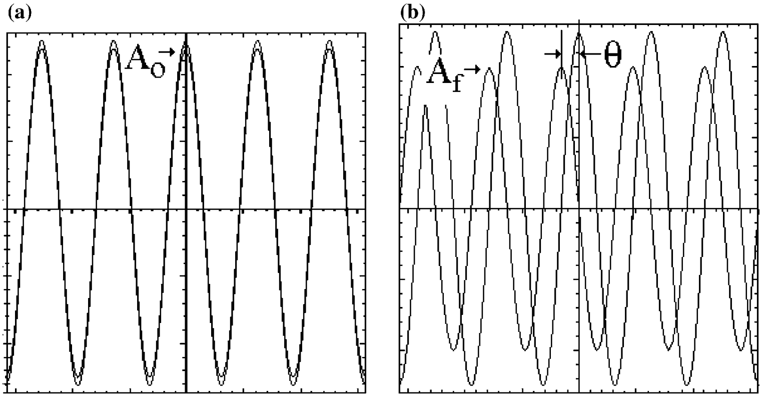

Fig. 1. Probe and reflected radio-pulses as seen at the oscilloscope screen. (a) Rod is out of the sample, probe and reflected signals are overlapped; (b) rod end is in the sample.

The cell is schematically shown in Fig. 2. Sulfur of five nines purity (Alfa Aesar Co.) was loaded into a quartz test tube. The tube was inserted into a copper block with three copper/constantan thermocouples in it. The block was surrounded by a heater. The temperature of the sample was controlled by a temperature controller (Smart-3, Temp, Inc.) and a phase-angle power controller (PC 120/240-PA, Temp, Inc.).

The position of the quartz rod was measured using a micrometer indicator (not shown). In contrast to the first experiment, sulfur was exposed to air in order to remove a drop of liquid sulfur from the end of the rod.

Results of the measurements of r and θ for longitudinal waves are shown in Fig. 3 by solid triangles and squares, respectively. The data obtained agree well with the values calculated from high accuracy data on density [6] and sound speed [8], as shown by the solid curve. Figure 3 also shows that the phase shift for longitudinal waves is essentially zero over the entire temperature range. (It should be noted that the major contribution to the uncertainty in the phase shift θ comes from a slight change in temperature of the rod when it enters the sample.) An estimate for θ obtained from data in the literature yields 10^{-4} radians for low temperatures and close to $\pi/2$ above the transition temperature. Sound absorption was calculated from Eq. (1) using only the shear viscosity term (Stokes' formula [24]). The data on viscosity were taken from Ref. 5. As one can see, the experimental values for θ do not agree with these estimates for polymerized sulfur. On the other hand, the phase shift data are consistent with results obtained in Ref. 8. In particular, *there is no* visible change in the sound absorption in sulfur

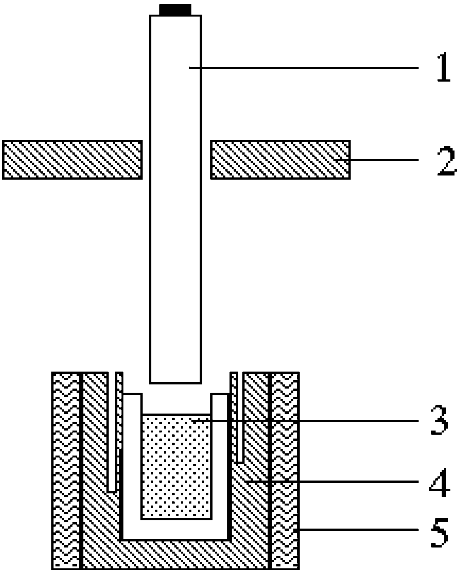

Fig. 2. Schematic of the cell for measurements of ultrasonic impedance. 1, quartz rod with piezoelectric transducer; 2, platform; 3, sulfur in the quartz ampoule; 4, copper block with channels for thermocouples; 5, heater.

near the polymerization transition. As mentioned above, this anomaly can be interpreted as a possible consequence of viscoelasticity.

We next performed the measurements with transverse sound waves at frequencies of 5, 15, and 25 MHz and temperatures up to 180°C. The data obtained for a frequency of 5 MHz are shown in Fig. 3 with open triangles for the amplitude ratio and open squares for the phase shift. No changes either in the amplitude ($r = 1$) or in the phase ($\theta = 0$) of the reflected signal were observed when the rod end was immersed in the liquid sulfur.

Most of the data were obtained with the reflected signal amplitude A_0 close to 3.5 V. To check the shear thinning effect [25], some points at temperature above 160°C were taken with A_0 varied from 0.5 to 5 V. No dependence on the signal amplitude in both r and θ was revealed. No frequency dependence was revealed either. Therefore it is unlikely that the negative result of the transverse sound impedance measurements is due to the shear thinning effect at the quartz–sulfur interface.

It is worth noting that the same result ($r \neq 1$ for longitudinal waves, and $r \equiv 1$ for transverse waves) occurs when sulfur is replaced by water, which is definitely *not a viscoelastic* liquid at ultrasonic frequencies.

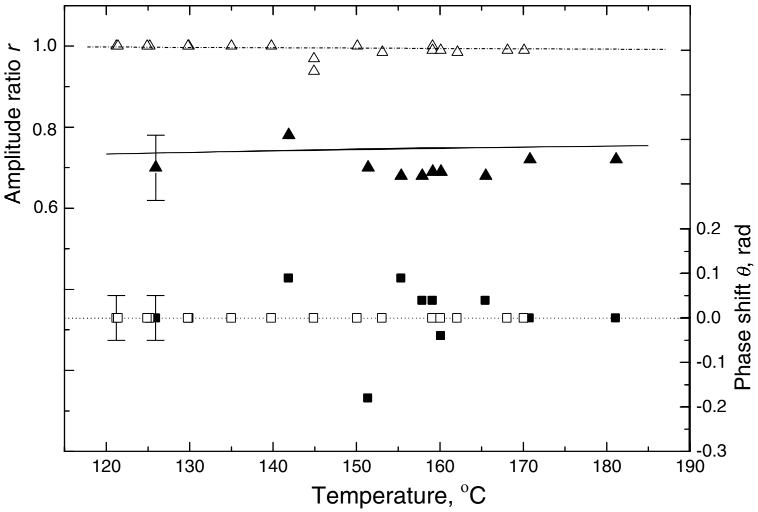

Fig. 3. Experimental data for the amplitude ratio measured with longitudinal (solid triangles) and transverse waves (open triangles); phase shift for longitudinal (solid squares) and shear (open squares) sound. Frequency is 7 MHz. Solid line represents r calculated from data in the literature.

4. CONCLUSIONS

The absence of any change in the reflectivity of transverse sound waves demonstrates that transverse sound does not exit the rod, which means that the transverse acoustical impedance for liquid sulfur in both the low- and high-viscosity regimes is zero. This result is in agreement with that obtained in Ref. 26, where only a longitudinal mode peak was observed in the Brillouin scattering spectrum of liquid sulfur.

In summary, the relaxation frequency ν^* for polymeric sulfur lies well above 25 MHz, and therefore the results obtained for longitudinal waves [8] describe the thermodynamic (zero frequency) sound speed. The minimum in the sound speed near the polymerization transition, which is predicted within the framework of second-order phase transition theory, does not exist, and therefore this theory is not valid for equilibrium polymerization in liquid sulfur. Finally, we were unable to confirm the classical formula for sound absorption in viscous liquids with this study of polymeric sulfur.

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