

Power law in properties of sulfur near the polymerization transition

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Sound velocity and attenuation in liquid sulfur have been measured at temperatures from 80 °C in the supercooled state through the melting temperature (about 120 °C) to 200 °C under saturated pressure. The measurements were performed with a pulsed phase sensitive technique at frequencies from 5 to 22 MHz. Accuracy of the sound velocity measurements was 0.1%. A distinct feature in sound velocity was found near 159 °C where sulfur experiences an equilibrium polymerization. However, neither dispersion in the sound velocity nor any appreciable change in sound attenuation was observed. Excess sound velocity (with respect to the monomeric liquid) was extracted from the data and used to estimate the extent of polymerization as a function of the temperature. Both quantities exhibit a similar power law behavior with the exponent close to 0.77.

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INTRODUCTION

Equilibrium polymerization is one of the basic chemical processes that exists in some organic and inorganic systems. Systems polymerizing under equilibrium conditions between polymeric molecules and their respective monomers include certain proteins forming supermolecular structures and variety of organic compounds.^{1,2} Polymerization in liquid sulfur has attracted significant attention over the last century^{3,4} because, in particular, it is the simplest example of such a phenomenon and therefore the most suitable for modeling. In the last few decades both experimental and theoretical progress has occurred with respect to equilibrium polymerization,⁵ but this process still is not well understood even for sulfur. This paper presents an experimental study of the polymerization transition in fluid sulfur through the use of a pulsed phase-sensitive acoustic technique.⁶

Sulfur melts at about 120 °C forming a light yellow liquid, consisting primarily of eight-membered-ring molecules (monomers).³ Near 159 °C sulfur undergoes a polymerization transition at which many of its properties change significantly. All the changes are completely reversible. The most striking effect occurs in the shear viscosity, which increases approximately 10 000 times over a temperature range of about 25 °C.⁷ According to recent data by Ruiz-Garcia *et al.*,⁸ the rise of viscosity can be significantly steeper. Other properties, such as heat capacity,^{9,10} density,^{11–13} optical properties,^{14,15} and the structure factor^{16–19} also exhibit specific changes. In this region the liquid is a solution of linear chain polymeric molecules in a monomeric solvent. According to estimates of Gee,²⁰ the degree of polymerization, P , in sulfur (average number of monomeric units in a chain) reaches its maximum value on the order of 10^5 at the transition temperature, T_p . Further increase of the temperature leads to an increase in the extent of polymerization, Φ_p , (mass fraction of polymers) and a simultaneous decrease in the degree of polymerization. The extent of polymerization saturates at a level of about 50% near 300 °C.^{4,21} This description of the structural changes in the sulfur molecules represents the generally accepted model. Although other scenarios are possible,¹⁷ all the theories of polymerization in sulfur are based on this “standard” model. For this reason

we will also use this model in our discussion of the experimental results.

Wheeler *et al.*²² and Anisimov *et al.*²³ treat the equilibrium polymerization as a second order phase transition similar to magnetization in a weak external field. The order parameters in these theories are proportional, albeit in different ways, to the amount of polymeric component, which is assumed to be zero at $T \leq T_p$, and greater than zero at $T > T_p$. Such an interpretation appears to be consistent with the observed temperature dependence of the heat capacity, which abruptly rises near T_p , and then decreases less rapidly at $T > T_p$. This so-called λ -like feature is typical for second order phase transitions. An earlier model of Tobolsky and Eisenberg,²⁴ that successfully describes a sharp increase in the degree of polymerization at the polymerization temperature, is similar to the mean-field theory of magnetization.²² However, discrepancies between experimental data and these two models do not allow one to make a firm conclusion regarding their adequacy.^{5,17}

A recent model by Dudowicz, Freed, and Douglas (DFD)^{2,25,26} treats the polymerization using a mean-field Flory–Huggins-type incompressible lattice model, in which each monomer and initiator (if applicable) molecules occupy single lattice sites. (An initiator is a substance, which when added to the monomeric system, initiates the polymerization process.) In this model the polymerization is not a second order phase transition, but resembles a glass transition.²⁷ However, in the limit of small values for the initiator constant (in sulfur this constant is on the order of 10^{-12} at the polymerization temperature²²) or small concentrations of the initiator, the polymerization may mimic a second order phase transition. This model defines the temperature of the polymerization transition as the temperature of the maximum in the heat capacity, which coincides with the inflection point in the temperature dependence of the extent of polymerization. However, in view of the incompressibility of the model, it does not apply to such properties as density and compressibility. Therefore, it does not apply to acoustic properties either.

One of the most informative approaches to investigate the nature of phase transitions is to probe them with sound.^{28,29} Information on the acoustical properties of sulfur is mostly

restricted to limited data on sound velocity in samples of different purity at frequencies from 1 to 15 MHz.^{30–34} Typical uncertainties in these data are about 1% while discrepancies between the different results are 2% to 3%. The discrepancies in the sound velocity data near the polymerization temperature are even more significant (see Ref. 34 for a more detailed comparison). There is only one report (Pryor and Richardson³¹) on the measurement of sound absorption. These authors noted the difficulties caused by fluctuating echoes, which were attributed to the formation and collapse of gas bubbles in the liquid. This cavitation makes the reliability of the data questionable.

In the most recent sound velocity measurements, Timrot *et al.*³⁴ used a pulsed multi-echo technique at 2 MHz. The sulfur sample was enclosed in a hermetically sealed quartz cell. The sample length was 30 mm,³⁵ and the accuracy was estimated to be 0.11%. In this work a plateau, whose width is about 2 °C, was found near the polymerization temperature. The authors corrected their results with respect to diffraction effects with the use of an approximate theoretical formula that is partially justified for isotropic solid samples. The magnitude of the corrections made was up to 0.7%. The diffraction effects in this work can be more significant because of the multilayered design of the cell and the small duration of the sound pulses (0.1 μ s).

Anisimov *et al.*²³ discussed the behavior of sound velocity in sulfur near the polymerization temperature within the framework of scaling theory for second order phase transitions. This work predicts a sharp minimum (a dip of approximately 10%) in the thermodynamic sound velocity, which is calculated in the limit of zero frequency. Dynamic scaling theory requires an increase in sound absorption over a broad frequency range around a “characteristic” relaxation frequency, which is determined by the proximity to the phase transition point.³⁶ Scaling theory also predicts dispersion in both the sound velocity and attenuation near the phase transition over the same frequency range. On the other hand, classical hydrodynamic theory suggests a direct proportionality between sound absorption, α , and shear viscosity when $\alpha\lambda \ll 1$, where λ is the wavelength, and stronger dispersion at large sound absorption ($\alpha\lambda \gg 1$).³⁷

Therefore near the polymerization transition in sulfur one expects (a) a minimum in the sound velocity, (b) significant enhancement of sound attenuation, and (c) dispersion in the acoustical properties. The main goal of this study is to check these expectations using a precise acoustic technique.

EXPERIMENT

The principal advantage of the pulsed phase-sensitive technique is that it allows one to perform precise measurements of the variation of the sound propagation time (with an uncertainty of $\pi/1000$, where τ is the period of the sound oscillation) with respect to a reference point. Accurate absolute measurements are also possible but require calibration. Therefore, precise data on sound velocity can be obtained even if the sample length is ≤ 1 mm. This circumstance is especially important for studies of samples with strong attenuation, in particular near phase transitions, where other

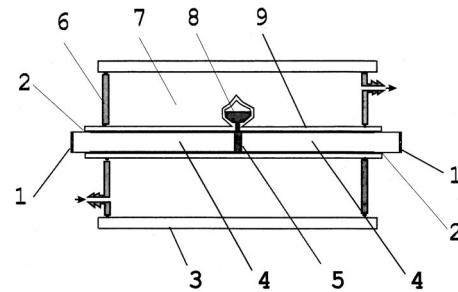


FIG. 1. Schematic of the quartz cell and the oil bath. 1, piezoelectric transducer; 2, glaze seal; 3, glass tube; 4, quartz buffer rod (diameter 12×110 mm); 5, liquid sulfur; 6, flange; 7, silicone oil; 8, reservoir; 9, quartz cell body.

techniques, such as the multi-echo technique, may not be applicable. This technique also allows simultaneous measurements of variations in sound absorption. The technique is described in detail in Ref. 6.

The cell used in this work is shown schematically in Fig. 1. The cell consists of two buffer rods (fused quartz, 12 mm in diameter and 110 mm in length) inserted in a cylindrical cell body (quartz tube, outer diameter 14 mm, 1 mm wall thickness, and 200 mm length). The sample space is a 3-mm slot between the rods. The slot width was measured using a dial Mitutoyo indicator as the difference in the total length of the cell with and without the slot between the rods. The uncertainty of the measurement of the slot width is ± 1 μ m. The rods are hermetically sealed in the tube by a glaze (Vitta PK-1015). Single crystal lithium niobate piezoelectric transducers are attached to the metallized ends of the rods using unpolymerized epoxy resin. The measurements were made with longitudinal sound waves.

Sulfur of purity 0.999 999 (Comico Ltd., Canada) was sublimated into the cell through a reservoir connected to a quartz degassing chamber similar to that used by Zheng and Greer.¹³ After filling, the cell was disconnected from the chamber and sealed by a torch. According to the literature (see, for example, Refs. 3,13,34), sulfur hermetically sealed in an evacuated quartz cell is well preserved against contamination both from reaction with the atmosphere and with the cell walls. Results of our measurements support this statement since there are no changes that can be attributed to contamination of the sample.

The cell was held in an oil bath as shown in Fig. 1. A thermostat (Techne Tempunit TU-16A) controlled the temperature of the oil. The sample temperature was measured by a standard Omega copper-constantan thermocouple attached to the cell body near the sample space. The cold ends of the thermocouple were kept at 0 °C. Uncertainty of the temperature measurements was 0.2 °C.

Experiments were performed at 5, 7, and 22 MHz. The value of the sound velocity at 121 °C from Ref. 33 was used as the reference point. Results of the measurements of sound velocity and the data on variation of sound attenuation are shown in Figs. 2 and 3, respectively. Numerical data on sound velocity are given in the Appendix. The percentage uncertainty of the sound velocity data, as estimated from Eq. (6) of Ref. 6, was 0.1%. The main contribution is determined by

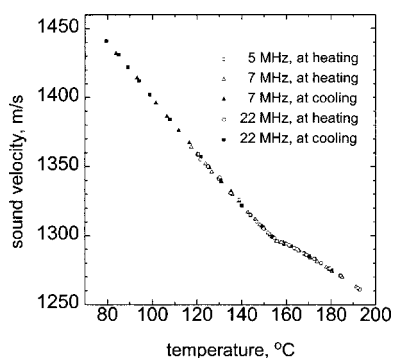


FIG. 2. Sound velocity in liquid sulfur.

the uncertainty of the reference data. The other contributions, which depend on the errors in measurements of the time and the sample length, are smaller by two orders of magnitude. Precision of the data obtained was primarily determined by the temperature instabilities and was close to 0.05% (at the 68% confidence limit). Error bars in Fig. 3 show uncertainties in the data for sound attenuation.³⁸

All the measurements were made under steady state conditions. No appreciable differences were observed in the sound velocity on either heating or cooling the sample. No frequency dependence was observed either.

At temperatures up to 150 °C, the data on sound velocity agree well with those of Timrot *et al.*³⁴ Starting at about 170 °C our data lie systematically higher by about 2 m/s (0.15%). The major discrepancy is near the polymerization temperature where our data exhibit a gradual decrease in slope but do not show a plateau. These discrepancies are probably due to the aforementioned corrections for the diffraction effects in Ref. 34.

DISCUSSION

Sound velocity

The sound velocity in melted, monomeric sulfur (at temperatures up to about 150 °C) depends linearly on the temperature. Such behavior is typical for simple liquids at tem-

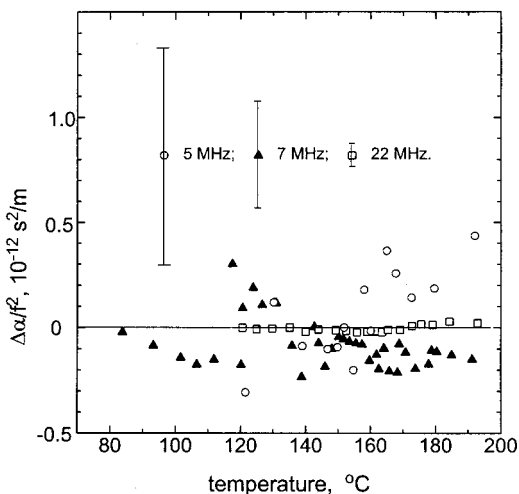


FIG. 3. Variation of sound absorption in liquid sulfur.

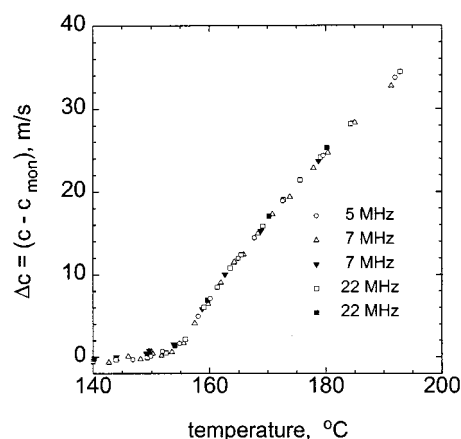


FIG. 4. Excess sound velocity in liquid sulfur with respect to the monomeric liquid.

peratures far from the liquid–gas critical point. Therefore the observed departure from linearity can be associated with the appearance of a polymeric component. If so, the data can be used to extract information about this component. The “excess” sound velocity shown in Fig. 4 is the difference $\Delta c = c - c_m$, where c is the experimental sound velocity, and c_m is the sound velocity in monomeric sulfur. The sound velocity c_m was calculated by linear extrapolation of the temperature dependence obtained between 120 and 150 °C. The standard deviation of the fit is 0.7 m/s; the standard deviation in the slope is $0.01 \text{ m} \cdot (\text{s} \cdot \text{K})^{-1}$. The maximum temperature of the extrapolation is 200 °C, which is still far below the critical temperature of 1040 °C.³⁹ The points obtained in the supercooled (and supposedly monomeric) sulfur were not included in the linear fit because these data exhibit a small, but distinct, change in the slope as seen in Fig. 2. This feature will be explored in future experiments; here we merely note that a change in slope is a common feature of many properties near the glass transition (see Ref. 40, for example).

Because there is no dispersion in the sound velocity over the frequency range studied, one may tentatively assume that the data obtained represent the equilibrium values. Such an assumption is valid for simple liquids but might be questionable for partially polymerized sulfur and must be tested in further experiments at lower frequencies. Although one cannot exclude the possibility that the low-frequency sound velocity exhibits a minimum as predicted in Ref. 23, for now this assumption allows us to extract data on the extent of polymerization.

In Fig. 5 the data on the excess sound velocity Δc are plotted versus $\Delta T = T - T^*$ on a double logarithmic scale. The parameter T^* is chosen to achieve maximum linearity. The value of T^* is 155 ± 0.3 °C. The power law exponent $\kappa \equiv \log(c - c_m) / \log(T - T^*) = 0.77 \pm 0.03$.

To estimate the composition we assume that the two-component solution is homogeneous over the wavelength λ (which is about 50 μm at 22 MHz). That is, λ is significantly greater than a typical cluster size, R . Such an assumption is plausible because the polymers in solution roll up in loose coils with $R \sim N^r$, where N is the number of monomers in the polymer chain, and $r \leq 0.6$.⁴¹ Therefore, the maximum size

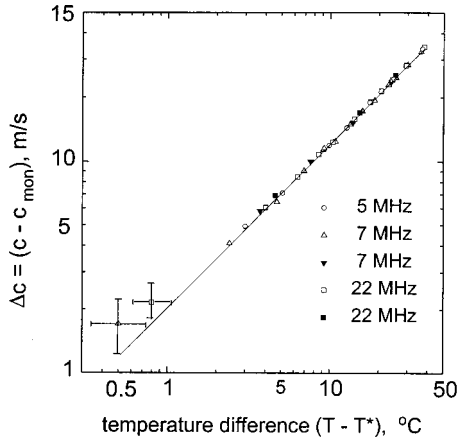


FIG. 5. Log-log plot of excess sound velocity. $T^* = 155^\circ\text{C}$. See text for details.

of the sulfur polymer coils is on the order of 10^2 nm. We also assume that the difference in sound velocities in the monomeric and polymeric components is not large. Under these assumptions one may treat the partially polymerized sulfur as a homogeneous medium, in which the elastic properties are averaged over the volume. Thus for the adiabatic bulk modulus, B , we obtain

$$B = (1/V) \int B_{\text{loc}} dV = \varphi_p B_p + \varphi_m B_m, \quad (1)$$

where V is the volume of the system, B_{loc} is a local value of the bulk modulus, and B_p , B_m , φ_p , and φ_m are the bulk moduli and the volume fractions of polymers and monomers, respectively.

Since $c^2 = vB$, where $v = V/M$ is the specific volume, the sound velocity can be expressed as

$$c^2 = \Phi_m c_m^2 + \Phi_p c_p^2, \quad (2)$$

where c_p and c_m are sound velocities in the pure polymer and pure monomer melts, respectively, $\Phi_p = M_p/M$ is the extent of the polymerization, M is the total mass of the sulfur, M_p is the mass of its polymeric component, and $\Phi_m = 1 - \Phi_p$ is the mass fraction of the remaining monomers.

With these definitions, the polymer fraction can be written as

$$\Phi_p = [(\Delta c/c_m + 1)^2 - 1] / [(c_p/c_m)^2 - 1]. \quad (3)$$

The only unknown quantity in Eq. (3) for Φ_p is the ratio c_p/c_m . With the assumption that the sound velocities in the monomeric and the polymeric melts do not strongly differ at a given temperature, we take this ratio as a constant and treat it as an adjustable parameter. This ratio, calculated from the theoretical results of Tobolsky and Eisenberg at 177°C ,²⁴ equals 1.12. The same ratio calculated from the experimental data of Koh and Klement²¹ is 1.08. Results for Φ_p and their comparison with data from the literature are shown in Fig. 6. The agreement between our data and those from the literature as seen in Fig. 6 leads support to the validity of Eq. (3) and to the assumptions made in its derivation.

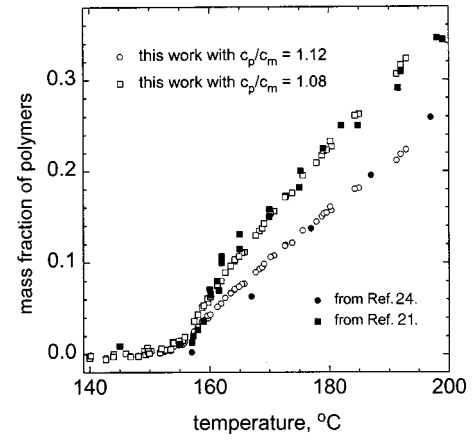


FIG. 6. Mass fraction of polymers in sulfur. See text for details.

A curve for Φ_p obtained in the theory of Wheeler *et al.*²² falls between the two data sets shown in Fig. 6. These theoretical data can also be fitted with results following from Eq. (3) if $c_p/c_m = 1.10$, but only at temperatures greater than 170°C . In the theory of second order phase transitions²² the temperature dependence of Φ_p goes to zero with infinite slope at T_p (159°C). The dependence of Φ_p on T obtained from our data shows an inflection at this temperature. On the other hand, the existence of an inflection point in the extent of polymerization at T_p is consistent with the DFD model.²

For now the data on sound velocity obtained for the polymer-monomer mixture are not sufficient to extract the absolute composition of the mixture.⁴² On the other hand, the existence of a fitting constant in Eq. (3) does not make any difference in behavior $\log \Phi_p$, which should mirror the behavior of $\log \Delta c$ provided that $\Delta c/c_m \ll 1$.

In Fig. 7 the data for the mass fraction of polymers are shown as a function of $(T - T^*)$ on a double logarithmic scale, where $T^* = 155^\circ\text{C}$. As expected, the exponent for the mass fraction of polymers is the same as for the excess sound velocity, namely 0.77 ± 0.03 .

The power law behavior in the extent of polymerization and excess sound velocity differs from the behavior of properties near second order phase transitions.⁴³ In particular, the

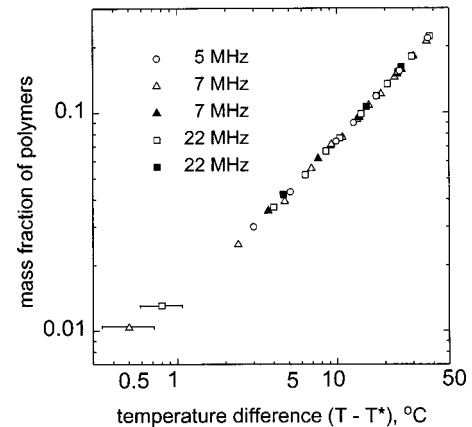


FIG. 7. Mass fraction of polymers on a log-log scale. $T^* = 155^\circ\text{C}$. See text for details.

reduced temperature parameter T^* (see Figs. 5 and 7) is appreciably less than the transition temperature T_p . A similar situation occurs near the glass transition,⁴⁴ where the viscosity and the relaxation time are functions of the reduced temperature $(T - T_0)$, where T_0 is a positive parameter which value is less than the glass transition temperature, T_g .⁴⁵

Sound absorption

Classic hydrodynamics provides the following expression for the sound absorption coefficient, α , in a viscous compressible and thermoconducting liquid when $\alpha\lambda \ll 1$:³⁷

$$\alpha = [(4\eta/3 + \zeta) + \kappa(C_v^{-1} - C_p^{-1})]\omega^2/2\rho c^3, \quad (4)$$

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, $\omega = 2\pi f$ is the angular frequency, and ρ is the mass density. If ω is far from the relaxation frequency, ω_r , the viscosity coefficients do not depend on frequency. Close to ω_r , the bulk viscosity ζ becomes frequency dependent and experiences an enhancement. For simple liquids ω_r ordinarily lies in the GHz range. Near a second order phase transition or a critical point the single relaxation frequency degenerates into a broadband centered around the aforementioned characteristic frequency, which decreases approximately proportionally to the square of the reduced temperature, $t = (T - T_c)/T_c$, where T_c is the transition temperature. Thermal conductivity also increases near T_c . Near the liquid–gas critical point the absorption reaches values close to $0.4/\lambda$; near the critical point of liquid mixtures the absorption is smaller by an order of magnitude.³⁶

In liquid sulfur at temperatures below the polymerization transition the condition $\alpha\lambda \ll 1$ is well fulfilled, and therefore both sound absorption and dispersion should behave similarly to their behavior in simple liquids. In the highly viscous state, viscous forces become comparable with forces contributed by the pressure in the sound wave. Under these conditions coefficients of shear and bulk viscosity become frequency dependent, which should lead to a significant increase in the dispersion of the acoustical properties.³⁶ Therefore, the transition from low to high viscosities (independent of whether there is a thermodynamic phase transition or not) should be accompanied by a proportional increase in sound absorption, which should strongly depend on frequency in the viscous region (viscoelastic effect^{41,46}). Dispersion in the sound velocity should also increase in this region.

However, these expectations are not realized over the frequency range studied. From the data on sound absorption (Fig. 3) we estimate an upper bound for any possible changes in α of at most an order of magnitude at 5 MHz, and significantly less at 22 MHz. From Eq. (4) we estimate that the value of α/f^2 in liquid sulfur at 120 °C is on the order of 10^{-14} s²/m. Similar results, namely a weak variation of sound absorption in sulfur, are reported in Ref. 31.

This behavior for the sound absorption might be a manifestation of the viscoelasticity of the polymeric solution. Viscoelastic systems behave like viscous liquids or like elastic solids depending on the time scale of the process compared

to the relaxation time of the system. Polymer solutions have a complicated relaxation spectrum, depending on the structure of the polymeric molecules and the extent of polymerization.⁴⁶ Ultimately, it will be interesting to investigate this spectrum using methods of physical acoustics, but for now we just mention that the shear viscosity of polymerized sulfur should be dependent on the time scale of the measurements. If so, the difference in data on viscosity obtained by different groups (see Ref. 8) may be attributed not only to differences in purity, but also to differences in the timescales of the methods employed. Therefore, apart from acoustic measurements at lower frequencies, it is interesting to measure viscosity on different timescales, as for example, with a viscometer similar to a Greenspan viscometer for gases.⁴⁷

CONCLUSIONS

We have presented results on the polymerization transition in liquid sulfur. With the use of a pulsed phase-sensitive technique, sound velocity and absorption have been measured at frequencies from 5 to 22 MHz.

The excess sound velocity, Δc , compared to that in pure monomeric sulfur was calculated, and a power law exponent for this quantity was determined. The excess sound velocity mirrors the mass fraction of the polymeric component, Φ_p . The exponents for both Δc and Φ_p are 0.77 ± 0.03 . In contrast to second order phase transitions, but similar to the glass transition, the reduced temperature T^* in the power law expression differs from the transition temperature. Also in contrast to the expectations based on the theory of second order phase transitions, the extent of polymerization does not vanish at the transition temperature, $T_p = 159$ °C, but exhibits an inflection point, as predicted by the DFD model. No minimum in sound velocity is observed, as would be expected from the second order phase transition theory. Thus the current results do not support the interpretation of the polymerization transition as a second order phase transition, but they do support, at least partially, the DFD model.^{2,24,25} The slope of the temperature dependence of the sound velocity in monomeric liquid sulfur changes at the transition to the super cooled state (near 120 °C). In contrast to the sound velocity, no appreciable features are found in the variation of sound absorption as a function of temperature. This behavior of the sound absorption may be due to the viscoelasticity of the polymeric solution. For more firm conclusions it is desirable to perform acoustic measurements at lower frequencies with both longitudinal and transverse sound waves and with better temperature control.

The basic assumption made in this paper is the validity of the standard model for the molecular changes in liquid sulfur. Although we can not exclude the possibility that further experiments will invalidate this model,⁵ the present results appear to be consistent.

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APPENDIX: SOUND VELOCITY IN SULFUR. EXPERIMENTAL POINTS (T , °C; c , m/s).

5 MHz, heating		7 MHz (cont.)		7 MHz, cooling		22 MHz, heating		22 MHz, cooling	
121.5	1355.0	138.8	1325.0	178.8	1276.0	120.6	1359.0	180.2	1275.0
130.2	1342.0	142.7	1317.0	168.8	1286.0	124.9	1350.0	170.2	1285.0
139.0	1326.0	144.0	1315.0	162.6	1292.0	129.7	1341.0	159.6	1294.0
146.8	1310.0	146.0	1312.0	158.7	1295.0	135.1	1331.0	154.0	1299.0
149.9	1305.0	148.1	1308.0	154.0	1299.0	140.0	1322.0	149.7	1306.0
151.9	1302.0	150.2	1305.0	153.8	1299.0	143.9	1315.0	140.2	1322.0
154.8	1298.0	151.7	1302.0	149.6	1306.0	149.3	1306.0	130.7	1340.0
158.0	1295.0	153.5	1299.0	149.1	1307.0	152.5	1301.0	121.8	1357.0
160.1	1294.0	155.5	1296.0	144.0	1315.0	155.8	1296.0	107.8	1384.0
164.9	1290.0	157.4	1295.0	135.2	1332.0	159.0	1294.0	98.8	1402.0
167.7	1287.0	159.7	1294.0	134.9	1331.0	161.3	1293.0	94.1	1412.0
172.6	1283.0	161.9	1292.0	125.5	1349.0	163.5	1291.0	89.1	1422.0
179.6	1276.0	164.1	1290.0	125.3	1350.0	165.4	1289.0	84.9	1431.0
192.0	1262.0	165.8	1289.0	120.1	1359.0	169.1	1286.0	79.4	1441.0
		168.3	1287.0	116.5	1367.0	172.7	1283.0		
		170.8	1284.0	111.8	1376.0	175.6	1280.0		
7 MHz, heating									
120.6	1358.0	173.8	1281.0	106.5	1386.0	179.1	1276.0		
123.8	1352.0	177.9	1277.0	101.6	1396.0	184.3	1271.0		
126.6	1346.0	180.4	1274.0	93.2	1414.0	192.9	1261.0		
130.9	1339.0	185.0	1270.0	83.8	1432.0				
135.8	1330.0	191.3	1263.0						

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