Thermal Analysis of Polymers. VIII. Dilatometric and Thermal Optical Behavior of Sulfur

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Synopsis

The use of combined modes of thermal analysis by differential thermal analysis (DTA), thermomechanical analysis, and thermal depolarization analysis (TDA) presents a more illustrative picture of the phase transitions and behavior of the allotropes of sulfur. Volumetric changes suggest the T_g of polymeric sulfur to occur at 35°C. Changes in depolarized light level and an abrupt change in volume at 77°C identify this change as a first-order fusion. The depolarized light behavior of sulfur, which has been quenched from 200°C to − 190°C, illustrates the probable existence of a mesomorphic state of sulfur between 100° and 122°C. Polymeric sulfur is thermally bleached near −150°C.

INTRODUCTION

The allotropic forms of sulfur have been studied by a number of authors, and the results and conclusions of these studies up until 1965 are contained in two major texts.[1,2] Of the many reported allotropes, most are not easily prepared. The thermodynamically stable form is orthorhombic sulfur, usually designated as S_α, which is reported to melt at 119.3°C.[2] This form of sulfur is believed to exist as octahedral rings of sulfur atoms. A second allotropic form, called S_ω, can be obtained commercially under the tradename Crystex (Stauffer Chemical Company). This allotrope is obtained by rapid quenching to room temperature of sulfur which has been heated above 160°C, and it is often purified of residual octahedral sulfur by extraction with carbon disulfide. Crystex differs from rhombic sulfur in its specific volume change at 75°C, and apparently the conversion of this form to the orthorhombic sulfur becomes rather rapid above 90°C.[3] A third type of sulfur results from the rapid quenching from 200°C to about −70°C, and this form is known as elastic or polymeric sulfur. It is a mixture of polymeric sulfur and S_8 rings and exhibits a second-order change in specific volume at −30°C. Tobolsky has attributed the depression of the second-order change in Crystex from 75°C to −30°C as being due to the plasticizing affect of the monomeric sulfur.[2] The glass transition by dilatometry has been reported to occur at −29°C for elastic sulfur.[4] Das and Ghosh[5] have reported that elastic sulfur contains both S_α and S_ω.

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This work was undertaken to demonstrate a total characterization of sulfur by thermal analysis, studying the material by the techniques of differential thermal analysis (DTA), dilatometry, depolarized light intensity, and white light transmission as a function of temperature and to show that the analogies and behavior between sulfur and other polymeric systems are more easily interpreted when characterized by a total thermal analysis system.

EXPERIMENTAL

Commercially available sulfur, which had been sublimed, was used in this work. Differential thermal measurements were carried out on the du Pont 900 standard DTA cell at a heating rate of 10°C/min in air. Sample size was 10 mg.

The dilatometric results were obtained using the dilatometric attachment for the du Pont 941 TMA at a heating rate of 3°C/min for a 20-mg sample. The derivative signal was recorded by a developmental operational amplifier circuit whose gain is greater than that of a conventional RC circuit. The description and procedure of this measurement has been reported elsewhere.[6]

The thermal depolarization results were measured on an apparatus which piped a light beam through a furnace to a phototube. A polarizer and analyzer were positioned before and after the furnace, respectively. The output from the phototube was fed to an electrometer which was connected to the du Pont 900 thermal analyzer. A quartz-iodine lamp with a Wanless transformer, rated at 5 volts, furnished the illumination to the sample. For white light measurements, the analyzer was removed from the light beam and a neutral density filter was inserted to cut down the intensity of the light beam. An interference filter with a peak maximum of 530 nm was inserted between the light and the polarizer to approach monochromatic irradiation. The phototube was a Tung Sol DT 933A. Thermal optical measurements were made at a heating rate of 5°C/min, and, except where noted, programmed cooling at 5°C/min was standard. The silver block furnace was surrounded by a cooling jacket through which nitrogen vapor was passed for controlled cooling.

RESULTS AND DISCUSSION

Differential Thermal Analyses

Figure 1 shows the DTA response for both flowers of sulfur and sulfur which had been quenched from 200°C to liquid nitrogen temperatures. The two endothermal peaks at 111° and 122°C are always observed via DTA for what is initially rhombohedral sulfur. Small peaks occur at 116° and 184°C. The endotherms at 111° and 122°C represent the so-called melting point depression of monoclinic sulfur and melting of the rhombic form, S_α respectively. The 116°C transition could be another form of
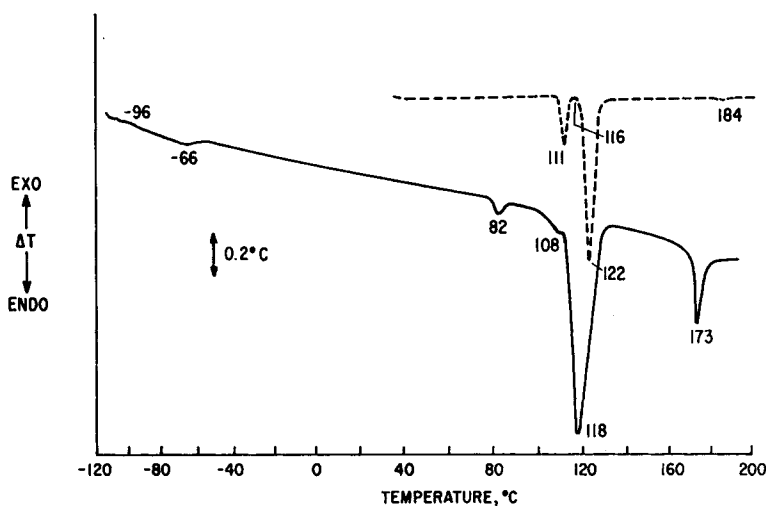
Fig. 1. DTA response of sublimed (---) and polymeric (——) sulfur.

melting point depression of S_α. The small change at 184°C may be due to the so-called lambda transition ($S_\lambda \rightarrow S_\pi, S_\mu$).[2]

Now when sulfur is quenched rapidly from 200°C to liquid nitrogen temperatures, a mixture of polymorphic forms of sulfur is obtained, consisting of six-membered and eight-membered sulfur rings and long-chain polymer (S_ω). Hence, in going from liquid nitrogen temperatures and traversing the whole melting range of sulfur, most or all of these species should be detected, and indeed changes are observed at −96°, −66°, 82°, 108°, 118°, and 173°C. These latter three temperature changes agree well with the visual DTA observations of Chiu.[7] The endotherm occurring at 173°C is caused by the fusion of the lambda form of sulfur. The endotherm at 118°C is the normal melting point of S_α, and the 108°C peak represents the depressed melting point or monoclinic form. The small endotherm occurring at 82°C is puzzling in the absence of other data, and its sharpness is affected by its cooling history, i.e., if the polymeric material is cooled slowly, the 82°C transition does not occur or at least is not easily detectable. This small endotherm, however, could be due to a small amount of Crystex-type sulfur, which has been reported to exhibit a transition near 75°C, and it is probable that by rapid quenching, this elastic form of sulfur could be observed by DTA as a component in the mixture of sulfur states that occur during the quenching process.

Whereas a change is observed at −29°C in the specific volume–temperature plot of quickly quenched sulfur,[3] a very small change in specific heat at −96° and a broad endotherm at −66°C are seen by DTA. The −66°C peak could be due to long-range rotational or torsional motions within the backbone of the linear polymeric sulfur chain, and the −96°C transition could be the initiation of very short-range rotational motions, occurring as

the initiation of molecular motion for the Crystex or elastic sulfur whose fusion occurs near 82°C. The lower temperature of $-66°C$ rather than the second-order change at $-29°C$ occurs as a result of more complete quenching from the melt with liquid nitrogen than with CO_2–solvent mixtures.

Dilatometry

The dilatometric results in Figure 2 support the observations in Figure 1. The volumetric response of the rhombohedral sulfur showed distinct changes at 110° and 113°C, with a volume decrease at 122°C. On quickly quenching the sulfur from 200°C to liquid nitrogen temperatures, volume changes were observed at 35°, 77°, 100°, and 119°C. No volumetric changes were observed between $-100°$ and 20°C. The change at 119°C is that of the melting of the prismatic form of the monoclinic modification of sulfur, formed during quenching, whereas the volume change at 100°C lies between the temperature of fusion of the rhombic form at 113°C and its normal range of existence reported as below 95.5°C.[8] Crystals of the rhombic form have been reported to be transformed to monoclinic crystals at 100°C within several hours,[8] and consequently the existence of the two forms of monoclinic crystals, prismatic which melts at 119°C and nacreous which melts at 107°C, can be present to some degree in the polymeric form of sulfur. The change at 77° in Figure 2 is that due to the elastic sulfur, which appears to be typically first order. The change at 35°C, appearing as a second-order transition via the derivative of the volume, will be discussed later. Hence, the three other transition changes are all first order.

The volume decrease at 119°C, while representing a first-order change, is inverted, and this is due to the conversion of S_α to liquid sulfur S_λ whose viscosity is less than that of water. Because of the voids between particles
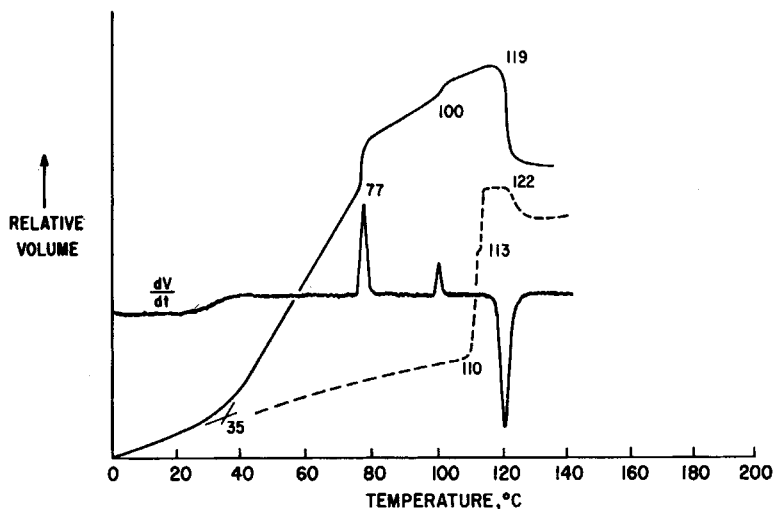

Fig. 2. Dilatometric behavior of sublimed (---) and polymeric (———) sulfur.

making up the filling medium for the dilatometer, the liquid sulfur penetrates these voids and, rather than expanding further, causes the appearance of a volume contraction. This points out the limitation of a broad-range dilatometric filling medium, but this filling medium is adequate to describe volume changes for materials whose viscosities are in the range of 5000 poises or larger.

Depolarized Light Behavior

In Figure 3 we see that large effect of the light scattering and lack of forward transmission of the flowers of sulfur on the fusion point at 122°C, at which point there is a sharp spike in the TDA curve and lack of depolarization thereafter. The lack of transmission prior to the fusion point is due to a large amount of light scattering, whereas that after the fusion point is due to the isotropic character of the liquid sulfur. When the liquid sulfur is quenched from 200° to −100°C, the elastic form of sulfur predominates. The heating curve for the elastic form (Fig. 3) shows a slight increase in depolarization at −36°, a slight decrease in polarization peaking at +20°C, and an increase in depolarization between 20° and 24°C. Apparently complete fusion occurs at 75°C, as noted by a very sharp drop in the intensity of the depolarized light.

However, after reaching zero light level, the sulfur appeared as if it formed a new crystalline substance at 100°C, indicated by an increase in the depolarization of light with a peak and final fusion occurring at 119°C, again to the isotropic liquid indicated by zero light level. On cooling from the melt at a controlled rate of 5°C/min, the molten sulfur recrystallized at 63°C to a high level of depolarization, dropping off in intensity as the tem-
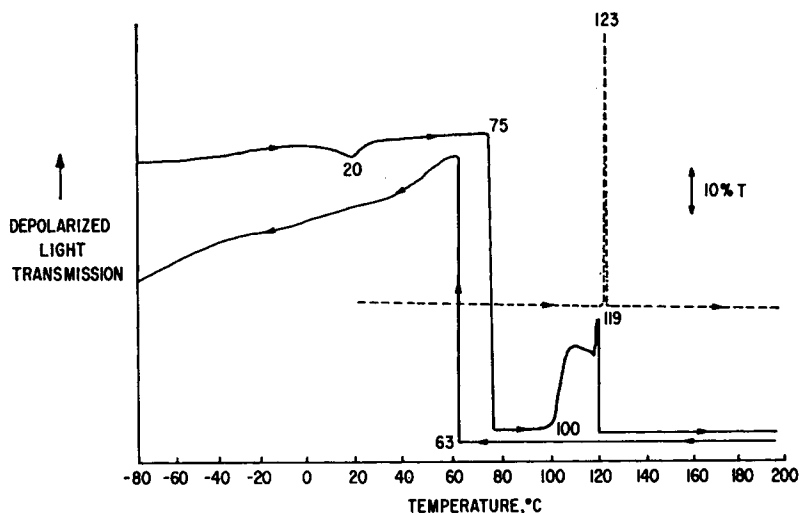

Fig. 3. TDA response of sublimed (---) and polymeric (——) sulfur.

p- AZOXYPHENETOLE

Cooling Rate: 5°/min.
Heating Rate: 5°/min.
1.0% T/in.

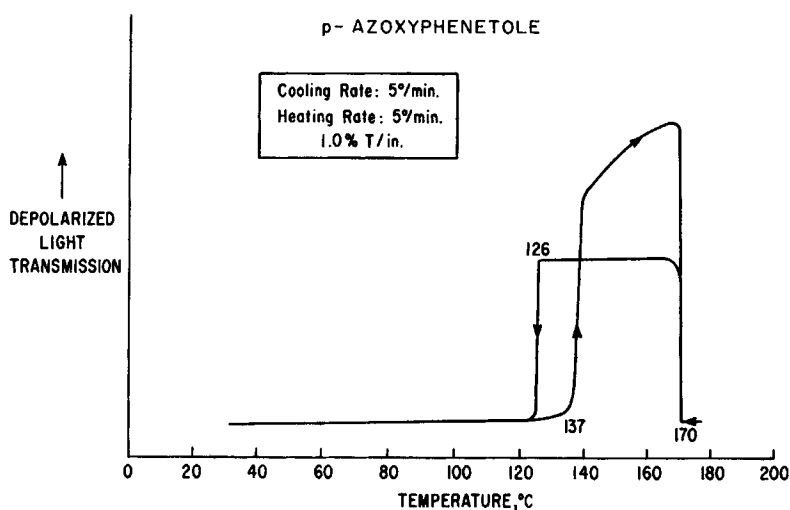DEPOLARIZED
LIGHT
TRANSMISSION

126

137

170

TEMPERATURE,°C

Fig. 4. TDA response of p-azoxyphenetole.

perature was lowered.   This high level of depolarization is a consequence of the crystalline character of the elastic form of sulfur.

The initiation of an increase in depolarized light intensity at 20°C corresponds with the onset of volume change for the glassy form of sulfur shown in Figure 2.   Even though the extrapolated value is 35°, a careful examination of the volume–temperature plot shows that the volume change begins at 20°C.   The first-order volume change at 77°C in the dilatometric scan is confirmed in the 75°C occurrence of fusion via TDA measurements.

The 100° and 119°C changes appear from the TDA data to be conversions to possibly a crystalline mesomorph, as evidenced by the shape of the TDA curve.   This mesomorphic behavior might be brought about by the plasticizing effect of the long, molten sulfur chains on the lattice array normally taken by monoclinic sulfur, and this interference with three-dimensional molecular ordering or the spacing of the linear sulfur chains by S_8 octahedra may leave the nematic state as the preferred orientation.   Reference to Figure 4 shows the same type of curve for the mesomorphic behavior of p-azoxyphenetole (PAP).   These mesomorphic transitions are usually typified by an increase in depolarized light transmission on changing from the crystalline to the mesomorphic state (nematic), with a possible increase, decrease, or leveling of the transmitted light during the temperature span in which the mesomorphic state exists.   When final fusion occurs, the depolarized light transmission decreases to zero level, noted as 170°C for PAP and 119°C for sulfur.   Contrary to the cooling curve in Figure 4, the mixture of sulfur states supercools to a greater extent than the crystalline PAP monomer, since the mesomorphic state of sulfur may result from a mixture of monoclinic and elastic sulfur, the latter of which has been shown to be fibrous in nature.

White Light Characteristics

Since the purely rhombic form of sulfur, such as that present in flowers of sulfur, scatters a great deal of light and is highly crystalline, no transmission of white light is expected prior to fusion. This is confirmed in Figure 5, wherein a sharp increase in white light intensity occurs at 120°C, exhibiting two peaks at 122° and 124°C, and slowly decreasing in value from 125° to 165°. At this latter temperature, there is a reasonably abrupt change in slope extending beyond 180°C. Curve (a) represents the change in white light intensity as the liquid sulfur is cooled at 5°C/min, as shown before with depolarized light (Fig. 3). Contrary to depolarized light, the white light shows a change in the intensity at 167°C and an abrupt decrease in light level at 53°C.

On reheating this sample at 5°C/min, curve (b) results, which shows a gradual increase in light intensity beginning near 35° and finally bottoming out at 90°C, at which temperature an increase in light intensity occurs, with changes in the curve at 90°C, 120°C, and 122°C, all of which increase the light level. A slight decrease in the light level occurs at 166°C. When the molten sulfur is rapidly quenched from 190°C, the white light intensity shows a very abrupt drop beginning near 35°C and decreasing rapidly until the temperature is near 60°C, at which point it begins to level off. The white light level begins to increase rapidly at 100°C, with a very sharp change occurring at 119°C. Again, the transmission level decreases for the lambda transition ($S_\lambda \rightarrow S_\pi, S_\mu$) at 164°C.

This white light behavior correlates well with the behavior observed by TDA, DTA, and volume measurements. While the volume change at 35°C
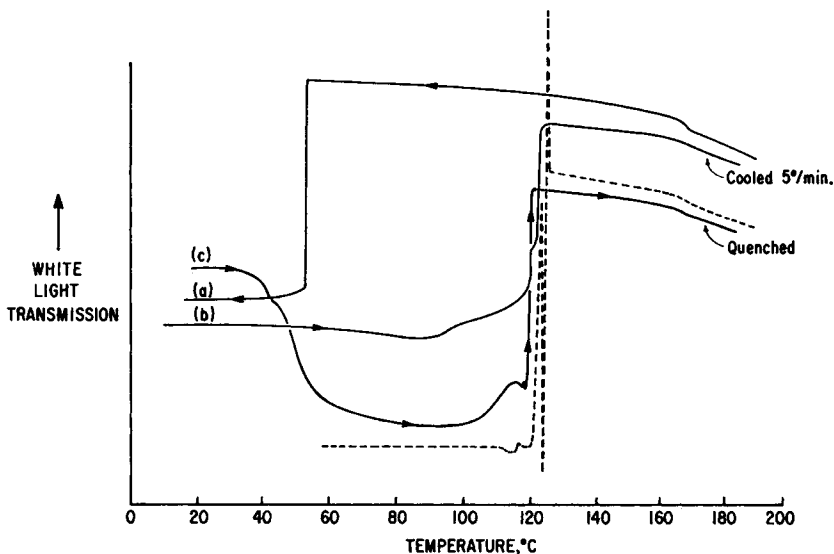

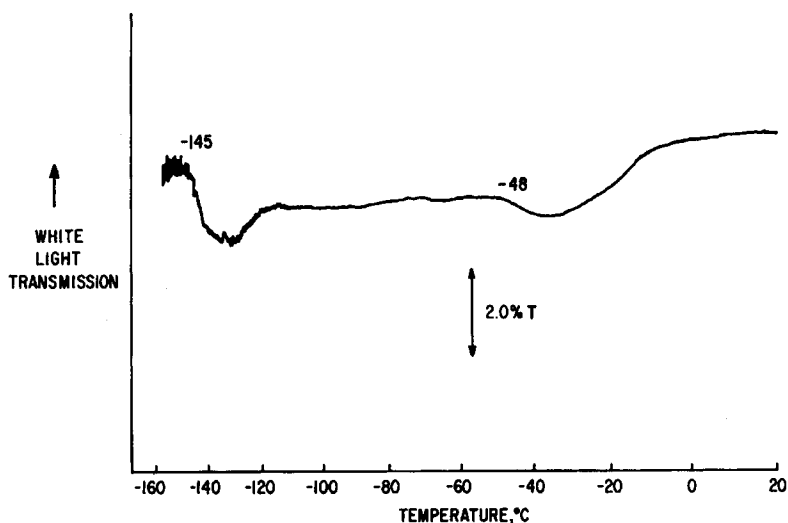Fig. 5. White light characteristics of sublimed (---) and polymer (——) sulfur.

Fig. 6. Low temperature profile of white light transmission for polymeric sulfur.

was not picked up by depolarization or differential thermal analysis, the change in white light intensity that occurs in that region is significant. This indication of decrease in light level without significant change in the depolarization at that temperature could be due to the transition from glassy to monoclinic sulfur, whereas the increase in white light level near 106°C correlates well with the endothermic transition by DTA and is probably due to the fusion of the nacreous form of monoclinic sulfur. The abrupt change in white light level is coincident with the melting of S_α at 119°C. The lambda form of sulfur, which apparently melts near 173°C by DTA, shows a change in white light at 167°, but no change is observable at this temperature with depolarized light transmission.

During the light transmission studies, the quenching of the molten sulfur was accomplished by removing the sulfur from the optical analyzer and quenching it immediately in liquid nitrogen. During this maneuver, it was observed that as the molten sulfur was quenched and approached the temperature of liquid nitrogen, the yellow color that was typically sulfur was bleached so that the sulfur sample appeared to be colorless and optically transparent. As the sulfur sample was warmed, the yellow color abruptly reappeared within the sample, and increased in intensity as the sample was warmed to room temperature. This behavior was viewed with white light, and the white light characteristics are shown in Figure 6. The decrease in light level at −145°C is that accompanying a change from the colorless, transparent form of sulfur to the yellow form of sulfur, and this change amounts to a 2% decrease in transmission. The initial yellow color is a very faint canary-like color. On increasing the temperature, the transition temperature changes in Figure 5, curve (c), are observed as well as a change at −48°C which could be synonymous with the specific volume

change for elastic sulfur when the sulfur is quenched to a much lower temperature than perhaps that which was achieved by cooling a mixture of solid CO_2 and acetone.[3]

CONCLUSIONS

The thermal characterization of sulfur shows it, like any other polymer, to be strongly dependent on the thermal history of the sample.   Apparently reasonable cooling rates, that is, those of 5°C or greater, induce a mixture of allotropic forms in a given sulfur sample.   The existence of the monoclinic, rhombic, and elastic forms of sulfur as well as other allotropic forms may be readily recognized with thermal analysis.

Tables I and II summarize the fusion temperatures for various allotropes of sublimed and polymeric sulfur.

TABLE I
Allotropic Forms Present in Sublimed Sulfur

Allotropic forms	Fusion temperature, °C			
	DTA	Volume	TDA	White light
Nacreous monoclinic, S_γ	111	110	—	—
Prismatic monoclinic, S_β	116	113	—	—
Rhombic, S_α	122	122	122	122,124
Amorphous, S_λ	184	—	—	165

TABLE II
Allotropic Forms of Sulfur Observed on Quenching from the Molten State

Allotropic forms	Fusion temperature, °C			
	DTA	Volume	TDA	White light
Elastic, S_ω	82	77	77	90
Nacreous monoclinic, S_γ	108	100	100	99
Prismatic monoclinic, S_β	118	119	119	120,122
Amorphous, S_λ	173	—	—	166

The volumetric changes raise the question that the T_g of polymeric sulfur, identifiable in its volumetric behavior with glycerine,[9] may occur at 35°C. Changes in the depolarized light behavior of only quenched sulfur occur in the range 20°–40°C, and no change is observed in C_p in this temperature interval.   While it has been observed that no change in depolarization occurs at the T_g for glycerin, glassy glucose, and sucrose solutions,[9] the occurrence of a small change in depolarized light could accompany the T_g transition. More information will be published to satisfy this relationship.   The lack of observation of a change in C_p near 35°C may be due to the small amount of heat necessary for the occurrence of T_g.   Volumetric determinations often exhibit more resolution and sensitivity than corresponding heat capac-

ity measurements as the latter are a derivative thermodynamic property. All the changes above this temperature are apparently first order.

Changes in the depolarized light transmission, which are a consequence of molecular ordering or disordering, confirm the volumetric response at 77°C as being a first-order transition by showing a decrease in the depolarized light to *zero light level*, which is normally identifiable by depolarization as a crystalline fusion phenomenon.[10]   The great similarities in the depolarized light behavior between the glassy form of sulfur formed by quick quenching to −190°C and the TDA response of *p*-azoxyphenetole could well illustrate the mesomorphic character of elastic sulfur in the temperature range of 100° to 122°C.   The thermal bleaching of glassy sulfur near liquid nitrogen temperatures is intriguing and warrants further research.

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