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The liquid-liquid phase diagram of sulfur + biphenyl

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We have studied the liquid-liquid phase diagram of sulfur + biphenyl. Larkin, Katz, and Scott [J. Phys. Chem. **71**, 352 (1967)] reported a liquid-liquid phase separation with an upper critical solution point (UCSP) at 381 K, complete miscibility between 381 K and a lower critical solution point (LCSP) at 494 K, and a polymerization line between the polymerization point of pure sulfur at 432 K and a point on the high temperature coexistence curve near the LCSP. We found that the phase transition temperatures for the higher temperature miscibility gap increased with time. We attribute this shift to chemical reaction between the sulfur and the biphenyl. Therefore, the transition temperatures which we obtain are necessarily upper limits to the true transition temperatures, but are in agreement with the results of Larkin *et al.* We find that the polymerization line meets the coexistence curve at 0.730 ± 0.005 mole fraction sulfur and 498 ± 2 K, whereas the LCSP, as indicated by the ratio of volumes of coexisting phases, is at 0.750 ± 0.005 mole fraction sulfur and 496 ± 3 K. Such a shift of the LCSP away from the end of the polymerization line is consistent with proximity to a nonsymmetrical tricritical point [Wheeler, J. Chem. Phys. **81**, 3635 (1984), and references therein]. If we describe the shape of a branch of the high temperature coexistence curve by $|x - x_c|/x_c = Bt^\beta$, where x is the mole fraction of sulfur, x_c is the mole fraction at the critical point, and t is the reduced temperature $|T - T_c|/T_c$ (with T the temperature and T_c the critical temperature), then the polymer-rich branch for sulfur + biphenyl is described well with $\beta = 0.25$, the value appropriate for a nonsymmetrical tricritical point. The polymer-poor branch could not be described by any of the values of β thought to be possible (i.e., 0.25, 0.325, 0.50, 0.67, or 1.00). We searched carefully for a three-phase region near the LCSP and found none.

I. INTRODUCTION

Sulfur melts at one atmosphere at 393 K and, on further heating to 432 K, exhibits a dramatic transition from a yellow liquid of low viscosity to a red liquid of high viscosity.¹ The transition reverses on cooling. This change in the properties of liquid sulfur is associated with its polymerization: a conversion from rings of eight sulfur atoms to diradical chains of a million or more atoms. In 1959, Tobolsky and Eisenberg² constructed a theory for the polymerization of sulfur by assuming one temperature-dependent equilibrium constant for the opening of the sulfur ring and another for the concatenation of the open rings into long chains. In 1980, Wheeler, Kennedy, and Pfeuty^{3,4} pointed out that the polymerization of sulfur can be viewed as a second-order phase transition (a critical point) with an order parameter n of dimension zero, and that the statistical mechanical models developed for analogous transitions in magnets can be applied to this transition. The theory of Tobolsky and Eisenberg corresponds to the mean field limit of the magnetic model. Calculations of such observables as the heat capacity³ and the density⁵ near the polymerization point using the model of Wheeler *et al.* are in better agreement with experimental results than are calculations from the mean field model.

The consideration of the behavior of pure liquid sulfur led to the consideration of the behavior of sulfur solutions. In 1965, Scott⁶ used the Tobolsky-Eisenberg model for the polymerization of sulfur, together with the Flory-Huggins

model^{7,8} for polymer solutions, to predict the liquid-liquid phase diagrams of sulfur solutions. He predicted that "ordinary" immiscibility between the solvent and unpolymerized sulfur will occur at temperatures low relative to the polymerization temperature of pure sulfur, that the polymerization temperature will increase as the concentration of solvent increases, and that a second region of immiscibility, between the solvent and the (partially) polymerized sulfur, will occur at high temperatures. The low temperature miscibility gap will have at its maximum an upper critical solution point (UCSP), and the high temperature miscibility gap will have at its minimum a lower critical solution point (LCSP). For some solvents, the regions of immiscibility will overlap. In 1967, Larkin, Katz, and Scott⁹ reviewed the experimental literature on sulfur solutions and presented new phase separation data for ten solutions; their data for the mixture sulfur + biphenyl are shown in Fig. 1. The experimental results agree qualitatively with Scott's theory. For example, in the sulfur + biphenyl system, the polymerization line ends near the LCSP.

When, at some point on the phase diagram, three phases become simultaneously indistinguishable from one another, that point is known as a "tricritical point".^{10,11} In 1981, Wheeler and Pfeuty¹² recognized that if a polymerization line is a line of critical points, then its intersection with a critical point for phase separation is a symmetrical tricritical point. The analogous model from the theory of magnets is that of a dilute magnet with $n = 0$. Scott's theory for sulfur solutions is, then, the mean field limit of that model.

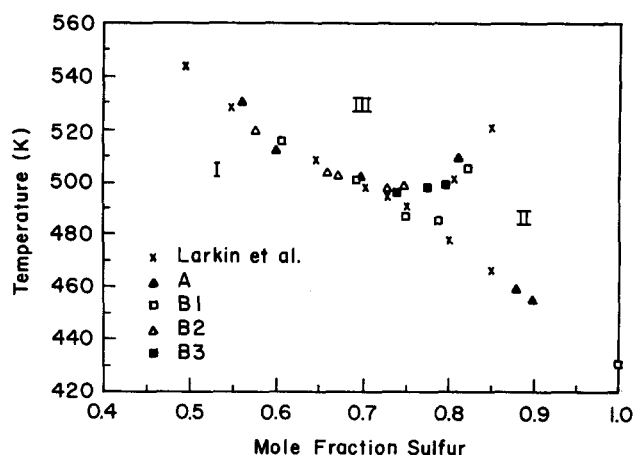


FIG. 1. The high temperature liquid-liquid phase diagram for sulfur + biphenyl. Region I is a region of monomeric sulfur in biphenyl. Region II is a region of partially polymerized sulfur in biphenyl. Regions I and II are separated by the polymerization line. Region III is a region of coexistence of the phases of regions I and II and is defined by the coexistence curve. The key indicates which data points are from Larkin *et al.* (Ref. 9) and which are from the present study, for which there was one set of samples from sulfur of type A (see the text) and three sets of samples using sulfur of type B.

Both Scott's theory and the dilute $n = 0$ magnet theory predict that the coexistence curve should have a leading critical exponent β of unity. That is, if ϕ is the volume fraction of sulfur, ϕ_c its value at the (tri)critical point, T_c the (tri)critical temperature, and t the reduced temperature $|T - T_c|/T_c$, then the sulfur-rich branch of the coexistence curve should have the form

$$(\phi - \phi_c) = Bt^\beta + \dots = Bt + \dots, \quad (1)$$

where the ellipsis represents higher order terms, and the sulfur-poor branch should have the same form:

$$(\phi_c - \phi) = B't + \dots. \quad (2)$$

Thus the coexistence curve is predicted to come to a point at the critical solution point. In addition, the sulfur-poor branch (see Fig. 1) is predicted to be a continuation of the polymerization line. Figure 1 shows that the data of Larkin *et al.*⁹ for sulfur + biphenyl form a rounded, rather than a pointed, coexistence curve, while the sulfur-poor branch is nearly a continuation of the polymerization line. The same rounding was reported by Larkin *et al.* for five other sulfur + solvent systems. The data of Larkin *et al.* for sulfur + biphenyl are closer to the predicted shape for the coexistence curve and the polymerization line than are the data for the other systems. Larkin *et al.* reported that, after the mixtures had been heated above the LCSP, the phase transition temperatures decreased with time. The systems sulfur + biphenyl and sulfur + triphenylmethane showed the least such irreversibility.

The question is: Why is the coexistence curve rounded at the tricritical point in a sulfur + solvent mixture? The following are possible explanations:

(1) Higher order terms ("corrections to scaling") in Eqs. (1) and (2) are important. In the case of critical points in pure fluids, agreement between theory and experiment was not realized until the higher order terms were includ-

ed.¹³ The magnitude of such terms depends on the choice of the variable for the left-hand side of Eqs. (1) and (2).¹⁴ For example, the experiments on sulfur + solvent systems have measured the concentration in terms of mole fraction rather than volume fraction.

(2) The LCSP is not exactly at a tricritical point because of the finite equilibrium constant K_1 for ring-opening below the polymerization line.¹² The finite K_1 corresponds to a nonzero magnetic field in the magnetic model. Wheeler and Pfeuty estimate this effect to be negligible.¹²

(3) The experimental data are distorted by a chemical reaction between the highly reactive sulfur diradicals and the solvent molecules. In the theory, this effect may be viewed¹⁵ as the presence of a magnetic field which produces a new, nonsymmetrical tricritical point which is near the LCSP on the phase diagram. If the LCSP happens to coincide exactly with the nonsymmetrical tricritical point, then the critical exponent β in Eqs. (1) and (2) becomes $1/4$, rather than 1 .

(4) The logarithmic correction factors predicted for tricritical points^{11,16} are important. These corrections lead¹² to a sulfur-rich branch of the form

$$(\phi - \phi_c) = Bt |\ln t|^{7/11} + \dots, \quad (3)$$

and a sulfur-poor branch:

$$(\phi_c - \phi) = B't |\ln t|^{3/22} + \dots. \quad (4)$$

These logarithmic corrections have never been experimentally observed for any tricritical point.

(5) The presence of the UCSP "flattens" the coexistence curve around the LCSP.¹²

(6) Polymeric sulfur can form rings as well as chains, complicating the phase diagram. The theories of Scott⁶ and of Wheeler *et al.*^{3-5,12,15} assume that the only species of importance in liquid sulfur are rings of eight atoms and long diradical chains of thousands of atoms. However, experiments indicate that molecules with a variety of molecular weights exist,¹⁷ and molecular dynamics simulations¹⁸ show the possibility of species which have both ring and chain components in the same molecule ("tadpoles"). It would be particularly interesting if polymeric rings were to form in a significant concentration, for the polymerization to rings is a critical point for which $n = 1$.^{19,20} The two lines ($n = 1$ and $n = 0$) of critical points on the phase diagram for pure sulfur, drawn in field space, will meet at a bicritical point.²¹ This will make possible a tetracritical point in the sulfur + solvent phase diagram.²² The effect of such a tetracritical point on the measured solvent + sulfur phase diagrams has not yet been calculated in detail.

Our aim in this work was to measure a phase diagram with sufficient precision to test the theoretical predictions that have been [Eqs. (1)–(4)], and will be, made for equilibrium polymerization in a two-component system. We have not achieved that aim, but we have learned more about the sulfur + biphenyl system. We believe that there is significant chemical reaction between the sulfur and the biphenyl. This reaction limits the accuracy with which the phase diagram can be measured. We have added to the data available for the coexistence curve near the LCSP and for the poly-

merization line. Our measurements are consistent with those of Larkin *et al.*⁹ We find the polymerization line does not meet the LCSP. The experimental data are not described by Eqs. (1) and (2), nor by Eqs. (3) and (4). We find that the polymer-rich branch can be described by Eq. (1) with $\beta = 0.25$, the value appropriate for a nonsymmetrical tricritical point.¹⁵ We were unable to describe the polymer-poor branch with any value of β thought to be possible: 0.25 (nonsymmetrical tricritical point), 0.325 (nonclassical critical point), 0.50 (classical critical point), 0.67 (tetracritical point²²), 1.00 (symmetrical tricritical point).

II. EXPERIMENTAL METHODS

A. General

Following the approach of Larkin *et al.*,⁹ we determined the temperature–composition phase diagram at 1 atm by making samples of various compositions, then heating those samples and noting the temperatures at which phase transitions occurred. Phase separations were detected visually. Polymerization transitions were detected by measuring the change in viscosity, which was measured as the fall time of a glass ball in the sample.

Larkin *et al.*⁹ had reported that biphenyl and triphenylmethane mixtures with sulfur showed the least irreversibility on heating and cooling of the ten systems they studied. Unpublished work in Scott's laboratory²³ and tests of our own showed that triphenylmethane + sulfur does not show reproducible phase separation temperatures on temperature cycling. We therefore believed the sulfur + biphenyl mixture to be the most promising choice for study.

B. Sample preparation

Sulfur from two different sources was used: (A) “99.999% pure” sulfur powder from Aldrich Chemical Co. (Milwaukee, WI); (B) “99.9999% pure” sulfur powder from Spex Industries, Inc. (Metucken, NJ). We will refer to these as sulfur A and sulfur B, respectively. We believe that sulfur A contained impurities, for two reasons: (1) Melted sulfur A had in it small black specks, which were probably due to organic impurities²⁴; (2) our measurements of the shear viscosity of pure sulfur near the polymerization temperature^{25,26} gave lower viscosity values for sulfur A than for sulfur B, which is the effect most impurities have on the viscosity of sulfur.^{27,28} The biphenyl was “99.99% pure”, from J. T. Baker Chemical Co. (Philipsburg, NJ). All materials and implements were dried for 24 h in a vacuum desiccator. All sample preparation was done in a dry nitrogen atmosphere.

The sample cells were simple Pyrex glass cylinders of 6 mm inside diameter. For samples requiring the monitoring of the viscosity, the cells were 18 cm long, contained a solid glass ball 3 mm in diameter, had a pocket at the top in which to store the ball, and had two fiducial marks for timing the fall of the ball.²⁵ For samples requiring only the visual observation of the phase separation, the cells were 11 cm long and contained no ball. The filled cells were sealed under 1 atm of dry nitrogen by sealing the glass at the tops of the tubes. The volume of the sulfur mixture was 11 cm³ for a viscosity cell

and 5 cm³ for a phase separation cell. The cell under study was held in the temperature-controlled bath in a support which allowed it to be readily rotated and viewed.²⁵

C. Temperature measurement and control

The cells were studied in a well-stirred oil bath, the temperature of which was controlled with an analog controller.²⁵ Dow Corning 710 silicone oil was chosen for the bath oil, since it has an operating temperature range of 273 to 533 K. The temperature fluctuations with time were about 30 mK, peak-to-peak, and temperature gradients in the bath were at most 30 mK.

The temperature was measured with a platinum resistance thermometer, using the circuit described previously.²⁹ It was necessary to reverse the current in the thermometer to account for thermal voltages in the circuit.²⁵ The precision and accuracy of the temperature measurement were limited by the bath control to 30 mK. However, the determinations of the phase transition temperatures were limited by the behavior of the samples, as discussed below.

D. Viscosity measurement

The viscosity was measured by timing the fall of the glass ball between the fiducial marks with a stopwatch. The resolution of the time of fall is limited by the observer response time of 0.1 s. The fall time in the sulfur + biphenyl mixtures ranged from 1 to 5 s. For each datum, the fall time was taken as the average of ten measurements. The *precision* of the viscosity measurement is about 1%. The fall time was converted to units of Pa s by comparing our time of fall data for pure liquid sulfur with the data of Bacon and Fanelli;²⁷ the same calibration constant was used for the (different) balls in the sulfur + biphenyl samples. Thus the *accuracy* of the viscosity measurements for the mixtures was limited by the variation in ball size to about 7%.

E. Procedures

1. Polymerization line

As we will discuss in detail in a later publication,²⁶ the viscosity of pure sulfur, while showing very long relaxation times, was reproducible after cycling through the polymerization transition. For the mixtures of biphenyl + sulfur, however, once polymerization had begun, the viscosity decreased steadily with time and showed no sign of reaching a stable value other than that of unpolymerized sulfur. For this reason, we studied the polymerization line as quickly as possible. We brought each cell to the temperature of interest, stirred the sample thoroughly by rotating it, and allowed only 1 h for equilibration.

2. Phase separation temperatures

Phase separation temperatures were determined by the visual observation of the number of phases present in the sample. The determination of the low temperature coexistence curve, with its “ordinary” critical point, was not a focus of our effort, and only a few observations (see below) were made in that region.

The appearance of a new phase at high temperatures was distinctive and took only about 15 min after a temperature in the two-phase region was reached. However, once such a phase separation had occurred, the transition temperature for that sample became irreproducible, drifting upward with time. Larkin *et al.*⁹ also observed such drifting transition temperatures; they reported that the UCSP increased and the LCSP decreased in most cases; they did not discuss the effect for sulfur + biphenyl in particular. The inability to refine the determination of a transition temperature by repeated cooling and heating of the sample limited the precision of our determination of the coexistence curve. Indeed, this problem limited the accuracy as well, since the observed transition temperatures must be regarded as upper limits on the true transition temperatures. We report as the transition temperature for a given sample that temperature which was midway between the highest temperature at which only one liquid phase was present and the temperature at which the second phase appeared; the uncertainty is taken as half the difference between those two temperatures. For samples near the LCSP in composition, we also noted the volume (i.e., the height in the cell) of each phase at the phase separation temperature as a way of ascertaining the critical composition, at which the volumes of coexisting phases should be equal.

III. RESULTS

A. Phase separation at low temperatures

A sample with a mole fraction of sulfur of 0.5606 separated into two liquid phases at 373.58 K, consistent with the report of Larkin *et al.*⁹ However, after this sample was left overnight at 373.58 K, only one liquid phase was present, and pale yellow crystals had formed. This result suggests that the low temperature liquid-liquid equilibrium reported by Larkin *et al.* is metastable, and that the stable state is solid-liquid equilibrium. We did not make further studies of this region.

B. Polymerization line

The viscosity as a function of temperature was studied for five sulfur + biphenyl mixtures. These data are plotted in Fig. 2 and tabulated in Ref. 25.

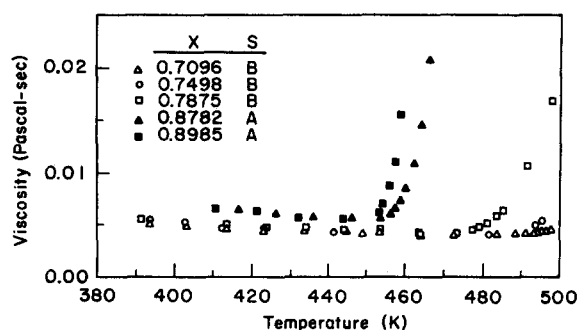


FIG. 2. The viscosities of five sulfur mixtures as functions of temperature. The key indicates the sample compositions (where X is the mole fraction of sulfur) and the source (A or B, see the text) of the sulfur. The viscosity increases upon polymerization of the sulfur. These data were used to obtain the data points for the polymerization line which are listed in Table I.

TABLE I. Features of the liquid-liquid phase diagram of sulfur + biphenyl. The mole fraction of sulfur is denoted by x and its estimated standard deviation is σ_x ; T is the transition temperature in Kelvin and σ_T is the estimate of its standard deviation. The code indicates that the data are from Larkin *et al.* (Ref. 9, as read from their graph) (code L), or, for the new data, that sulfur of type A or B was used. A phase separation point given by Larkin *et al.* at $T = 498$, $x = 0.75$ is plotted in Fig. 1, but was not included in the fits.

No.	x	σ_x	T	σ_T	Code
Upper miscibility gap: Sulfur-poor branch					
1	0.50	0.01	543	2	L
2	0.55	0.01	529	2	L
3	0.5605	0.0005	530	2	A
4	0.5757	0.0005	519.47	0.08	B
5	0.5991	0.0005	512	2	A
6	0.6060	0.0005	515.6	0.2	B
7	0.65	0.01	509	2	L
8	0.6596	0.0005	504.05	0.05	B
9	0.6720	0.0005	502.5	0.1	B
10	0.6944	0.0005	500.9	0.3	B
11	0.6990	0.0005	501.80	0.01	A
12	0.71	0.01	497	2	L
13	0.7290	0.0005	498.3	0.1	B
14	0.73	0.01	495	2	L
15	0.7408	0.0005	496.48	0.06	B
16	0.7492	0.0005	498.4	0.3	B
Upper miscibility gap: Sulfur-rich branch					
17	0.7750	0.0005	498.3	0.1	B
18	0.7971	0.0005	499.4	0.1	B
19	0.81	0.01	501	2	L
20	0.8120	0.0005	509.4	0.3	A
21	0.8217	0.0005	505	1	B
22	0.85	0.01	521	2	L
Polymerization line					
23	0.7498	0.0005	487	2	B
24	0.75	0.01	491	2	L
25	0.7875	0.0005	485	2	B
26	0.80	0.01	478	2	L
27	0.85	0.01	466	2	L
28	0.8782	0.0005	459	1	A
29	0.8985	0.0005	455	1	A
30	1.0000	—	432	2	B

The determination of the polymerization temperatures from the plots of viscosity vs temperature is not without ambiguity. Is the polymerization temperature the point at which the viscosity begins to increase, the point at which the derivative of the viscosity with respect to temperature is a maximum, or the intersection of the straight lines formed by the data well above and well below the transition? Following Larkin *et al.*,⁹ we have taken the polymerization temperature for a given composition to be the intersection of the lines formed by the data far from the transition. The polymerization temperatures are plotted in Fig. 1 and listed in Table I. Our data are in agreement with those of Larkin *et al.*⁹

C. Phase separation at high temperatures

Phase separation temperatures observed at 15 compositions are plotted in Fig. 1 and tabulated in Table I. The uncertainties in the transition temperatures are about 0.2 K. We estimate the LCSP to be at 496 ± 3 K. From the observed volumes of the coexisting phases, we estimate the critical composition to be 0.750 ± 0.005 mole fraction of sul-

fur. By comparison, Larkin *et al.*⁹ report a LCSP at 494 K; they obtained a critical mole fraction of sulfur of 0.76 from a rectilinear diameter and 0.73 from the intersection of the phase boundary and the polymerization line. We find that the polymerization line (as determined from the intersections of lines drawn through the viscosity data away from the polymerization temperature—see above) intersects the phase boundary at 0.730 ± 0.005 mole fraction sulfur and 498 ± 2 K. We note that the two samples at critical mole fraction of 0.75 were clearly below the phase separation when they polymerized. In addition, a polymerization line determined from the viscosity data by the other conceivable methods (see above) would intersect the coexistence curve at a mole fraction even lower than 0.730. Thus we believe that the polymerization line does not meet the LCSP. This conclusion is consistent with the results of Larkin *et al.*

The presence of a three-phase region is predicted by Scott⁶ to occur when the lower temperature miscibility gap intersects the higher temperature miscibility gap, and by Wheeler²² to occur when the polymeric sulfur in solution forms rings as well as chains. We searched carefully in the region of the LCSP for a third phase, allowing overnight equilibration. We never saw a third phase.

We attempted to fit Eqs. (1)–(4) to the data for the upper coexistence curve. We used a standard nonlinear least-squares fitting routine and standard methods of error propagation.³⁰ We used the mole fraction x , rather than the volume fraction ϕ :

$$|x - x_c|/x_c = Bt^\beta. \quad (5)$$

Since the number of data points is small, we fixed x_c , T_c , and β at values known to be reasonable and left the coefficient B as a free parameter. We then varied x_c and T_c in steps for a given choice of β . We attempted to describe the data with β equal to 0.25 (for a nonsymmetrical tricritical point¹⁵), 0.325 (for a nonclassical critical point³¹), 0.50 (for a classical critical point³²), and 1.00 (for a symmetrical tricritical point¹²). We also considered the exponents for a tetracritical point: 0.67 for the unpolymerized branch and 0.33 for the polymerized branch.²²

For the sulfur-poor branch of the coexistence curve, we were unable to find a function which described the entire data set, even leaving β as a free parameter. If we omitted point 6 and the points near the LCSP (points 11–16), then Eq. (5) with $\beta = 0.50$ (and $x_c = 0.73$ or 0.75 , $T_c = 499$ K) described the remaining nine data points, those farthest from the LCSP, within their error. No such fitting function was found for the data very near the LCSP on the sulfur-poor branch. The inclusion of logarithmic correction terms [Eqs. (3) and (4)] did not improve the fits, nor did the addition of corrections to scaling in the form¹³

$$|x - x_c|/x_c = Bt^\beta + B_1 t^{\beta+\Delta} + B_2 t^{\beta+2\Delta} + \dots, \quad (6)$$

with $\Delta = 0.5$.³¹ We also considered the addition of just a term linear to t in Eq. (5), to no avail. Thus we have no satisfactory description from theory for the sulfur-poor branch of the coexistence curve.

For the sulfur-rich branch of the coexistence curve, all six data points were described by Eq. (5) with $\beta = 0.25$, x_c

$= 0.75$, and $T_c = 498$ K. The reduced chi-squared³⁰ was 3.7 rather than unity, but the residuals were randomly distributed, indicating that the actual random errors are about twice those given in Table I. The fit with $\beta = 0.325$ was not bad (with a reduced chi-squared of 8.1 and fairly random residuals), but was not as good as the fit with $\beta = 0.25$. Values of β of 0.50 or 1.00 were definitely excluded. Thus the sulfur-rich branch of the coexistence curve is described by the critical exponent for a nonsymmetrical tricritical point.

IV. CONCLUSIONS

The best explanation at this time for the features of the sulfur + biphenyl phase diagram is that the miscibility gap at high temperatures is near to a nonsymmetrical tricritical point. The irreversible disappearance with time of the viscosity anomaly near the polymerization line is evidence that the components of the mixture react chemically. Such a reaction is equivalent in the magnetic model¹⁵ to the presence of a nonzero magnetic field; in such a field, a nonsymmetric tricritical point is possible, in addition to the symmetric tricritical point present in zero field. Features consistent with the nonsymmetric tricritical point are: (1) The sulfur-rich branch can be described by a critical exponent $\beta = 0.25$; (2) the polymerization line does not meet the lower critical solution point; (3) no three-phase equilibrium is observed. The main problem with this explanation is that $\beta = 0.25$ does not describe the sulfur-poor branch of the coexistence curve.

We have not excluded the possibility that the presence of ring polymers could cause these features. Such considerations will require further theoretical calculations. We also note that in our study of pure liquid sulfur,^{25,26} we observed relaxation times near the polymerization line of days to weeks. It is conceivable that these as yet unexplained long relaxation times are also relevant for sulfur mixtures; on the other hand, the drifts in the transition temperatures showed no signs of abating with time.

It is likely that diradical liquid sulfur will react with any conceivable solvent, so there is little hope of studying a liquid–liquid phase separation in a nonreacting sulfur + solvent system. Organic polymers showing equilibrium polymerization offer better hope for understanding these higher order phase transitions.³³

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