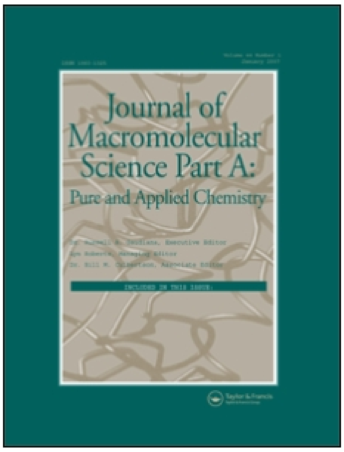

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Effect of S_π on the Polymerization of Liquid Sulfur and the Nature of S_π

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Summary

The Tobolsky-Eisenberg theory serves to explain the equilibrium polymerization of sulfur in terms of the dependence of S_8 (ring) concentration on temperature and the dependence of number-average degree of polymerization on temperature. The predictions of the theory are completely in accord with experiment. In this paper it is shown that it is possible to take the presence of another component in the melt, S_π, into account, using a slightly modified version of the Tobolsky-Eisenberg theory. When this is done it is found that the earlier conclusions remain valid. The molecular complexity and structure of S_π is also discussed.

INTRODUCTION

Sulfur exhibits the curious behavior of changing its melting point during the melting process (*1*,*2*). It first melts at 119.3°C (the "ideal" melting point) and there is then a melting-point depression to 114.5°C (the "natural" melting point). It has been recognized for many years that this phenomenon is due to the formation of a new allotropic form of sulfur in the melt. This form is usually designated S_π (*3*). Thus the melting-point phenomenon is explained as follows: 119.3°C represents the melting point of S_8 (ring) sulfur. Upon melting there is first formed a liquid consisting entirely of S_8 rings.

However, a reaction occurs and there is established an equilibrium between S_8 (rings) and S_π, the S_π serving to depress the melting point. The molecular complexity of S_π has only recently been established by Schenk and Thümmler (*4*). They found it to contain eight sulfur atoms per molecule and thus concluded that S_π must be an eight-membered sulfur chain. These workers also measured the concentration of S_π in the melt as a function of temperature and from these measurements obtained the equilibrium constant for the reaction

$$S_8\text{ (ring)} \xrightarrow{K_8} S_8\text{ (open chain)} \qquad (1)$$

From a van't Hoff plot, $\Delta H°$ for (1) was found to be 7 kcal/mole. It should be noted that S_π cannot be a radical species, since it is present to the extent of 5.5% at the melting point and no electron spin resonance signal is observed in sulfur until temperatures in excess of 200°C are attained (*5,6*).

As liquid sulfur is heated above its melting point it behaves as a normal low-viscosity liquid until a temperature of 159°C is reached, at which point there is an abrupt increase in the viscosity from 10 to 10^3 poises. This viscosity anomaly is interpreted as being due to the polymerization of eight-membered sulfur rings to form long chains which are diradical in nature (*7*). The polymerization of sulfur is very well explained by the equilibrium polymerization theory of Tobolsky and Eisenberg (*8*). This theory predicts two experimental quantities: the equilibrium concentration of S_8 (rings) as a function of temperature, and the number-average degree of polymerization of the sulfur chains as a function of temperature. The equilibrium concentration of S_8 (rings) can, in principle, be obtained by quick quenching liquid sulfur from various temperatures, extracting with CS_2, and weighing the insoluble polymeric sulfur residue. This procedure is only satisfactory over a limited temperature range, owing to the mobility of the equilibrium and the poor heat conduction of sulfur. The average chain length can be obtained from ESR measurements assuming that the polymer is a biradical chain. Measurements of this sort, as well as magnetic susceptibility measurements, confirm the predictions of the equilibrium polymerization theory (*6–8*).

RESULTS AND DISCUSSION

The Tobolsky-Eisenberg theory in its original form ignores the presence of chains containing other than multiples of eight sulfur atoms and the possible presence of n-membered rings, where $n \neq 8$. These assumptions have been removed in a slightly modified treatment (9). Using the extended theory it is possible to consider the effect of the presence of any species of any molecular complexity in the melt. However, as far as we are aware, the only quantitative experimental data available for liquid sulfur concerns S_8 (rings), S_π, and polymeric sulfur, S_μ. At first sight it is difficult to reconcile the presence of S_π with the conclusions of the theory reached earlier. (It must be remembered that the expression for the average chain length is in accord with experiment.) The pertinent expressions, assuming only S_8 rings and chains of all sizes, are (9)

1. In the low-temperature region, below 159°C no polymer is present and

$$\begin{aligned} [S_8] &= [S_8]_0 \\ P &= 8(1 - [S_8]_0^{1/8}\bar{K}_3^{1/8})^{-1} \end{aligned} \tag{2}$$

That is, the liquid is assumed to consist entirely of S_8 (rings).

2. In the high-temperature region

$$\begin{aligned} [S_8] &= \bar{K}_3^{-1} \\ P &= ((\bar{K}_3[S_8]_0^{-1})/8\bar{K}_1)^{1/2} \end{aligned} \tag{3}$$

where $[S_8]$ is the equilibrium concentration of S_8 (rings), $\bar{K}_3$ is the equilibrium constant for the addition of S_8 (rings) to growing polymer chains, $\bar{K}_1$ is the equilibrium constant for the opening of S_8 rings to form S_8 diradical chains, and P is the number average degree of polymerization.

It remains, then, to derive expressions for these quantities using Schenk and Thümmler's experimental results for S_π. The species to be considered are S_8 (rings), S_μ (polymer chains), and S_π. The pertinent expressions from the equilibrium polymerization theory are (9)

$$W = \frac{\bar{K}_1}{8\bar{K}_3} \frac{(\bar{K}_3[S_8])^{1/8}}{\{1 - \bar{K}_3[S_8]^{1/8}\}^2} \tag{4}$$

where W is the total concentration of S_8 units incorporated in the polymer and $\bar{K}_1$ and $\bar{K}_3$ have already been defined:

$$[S_8]_0 = [S_8] + W + [S_\pi] \tag{5}$$

In Eq. (5), $[S_8]_0$ is the total concentration of S_8 units in the melt at all temperatures, $[S_8]$ is the concentration of S_8 rings, and $[S_\pi]$ is the concentration of the "π sulfur" allotrope. Finally, at all temperatures, the number-average degree of polymerization, P, is

$$P = 8(1 - \bar{K}_3[S_8])^{-1/8} \tag{6}$$

Utilizing Eqs. (4), (5), and (6), it is possible to derive expressions for P and $[S_8]$ in both the low- and high-temperature regions taking the presence of S_π into account. To obtain $[S_\pi]$ we proceed as follows:

$$S_8 \text{ (ring)} \xrightleftharpoons{\bar{K}_1} S_8 \text{ (diradical chain)} \tag{7}$$

$$S_\pi \xrightleftharpoons{\bar{K}_8} S_8 \text{ (diradical chain)} \tag{8}$$

Subtracting (8) from (7) there results

$$S_8 \text{ (rings)} \xrightleftharpoons{\bar{K}_1/\bar{K}_8} S_\pi \tag{9}$$

Therefore the experimental equilibrium constant of Schenk, K_s, can be equated to $\bar{K}_1/\bar{K}_8$:

$$[S_\pi] = K_s[S_8] \tag{10}$$

Substituting (10) in (5),

$$[S_8]_0 = [S_8] + W + K_s[S_8] \tag{11}$$

or

$$[S_8]_0 = K_t[S_8] + W \tag{12}$$

where $K_t = 1 + K_s$. Introducing the expressions for W and P [Eqs. (4) and (6)] in (12),

$$[S_8]_0 = \frac{K_t}{\bar{K}_3}\left(\frac{8P-1}{8P}\right)^8 + \frac{\bar{K}_1}{8\bar{K}_3}\, 8P(8P-1) \tag{13}$$

Equations (12) and (13) make it possible to calculate the equilibrium concentration of S_8 rings and the number-average degree of polymerization throughout the entire liquid range. No new parameters have been introduced with the exception of K_t, an experimental quantity.

Two cases are now distinguished:

1. Below the transition temperature of 159°C, $W \approx 0$. From (12),

$$[S_8] = [S_8]_0/K_t \tag{14}$$

Also from (13), with $W=0$,

$$P = 8[1 - (\bar{K}_3/K_t[S_8]_0)^{1/8}]^{-1} \tag{15}$$

2. Above the transition temperature, polymer is formed and W can no longer be neglected. In this region $P \gg 1$, and introducing this approximation in Eq. (13) there results

$$P = [(\bar{K}_3[S_8]_0 - K_t)/8\bar{K}_1]^{1/2} \tag{16}$$

Since $1 - \bar{K}_3[S_8]^{1/8} \ll 1$, it can be expanded and only first-order terms considered. Following this procedure, the expression for $[S_8]$ is

$$\bar{K}_3[S_8] = 1 - (1/P) \tag{17}$$

or, since $1/P \ll 1$,

$$[S_8] = 1/\bar{K}_3 \tag{18}$$

Thus the results obtained taking the presence of S_π into account are essentially equivalent to the earlier results of the equilibrium polymerization theory, as a comparison of Eqs. (2) and (3) with Eqs. (14) to (18) shows.

It remains to consider the nature of the allotrope known as "π sulfur." As mentioned above, Schenk obtained a value of 7 kcal/mole for $\Delta H°$ for the transformation

$$S_8 \text{ (ring)} \rightleftharpoons S_\pi$$

His molecular-weight determinations show that S_π contains eight sulfur atoms and he concludes that the species must therefore be an S_8 chain. However, there is good evidence that the dissociation energy of a sulfur-sulfur bond in the S_8 ring is about 35 kcal/mole. One possible interpretation, suggested by Paddock (*10*), is that S_π may consist of S_8 rings in a conformation other than the normal crown, or puckered ring, conformation. If this were so, it would imply that the "S_π conformation" is strained relative to the normal S_8 conformation to the extent of 7 kcal/mole. In the structural determination of the S_6 ring of Donohue et al. (*11*), it was argued on the basis of bond angles and torsional angles that S_6 was strained relative to S_8 to the extent of approximately 1 kcal/mole per sulfur-sulfur bond. The figure of 7 kcal/mole is therefore not unreasonable for the enthalpy difference between the normal S_8 conformation and the "S_π conformation." In addition, it is known that S_π polymerizes in the solid state (*4*) but no polymerization takes place in the liquid. This would be understandable, provided it were possible for $S\pi$ to change to normal S_8 without breaking any sulfur-

sulfur bonds in the liquid and that this were impossible in the solid. The phenomenon of the polymerization of S_π in the solid state would then be explained on the basis of a kinetic mechanism which requires the formation of polymeric sulfur as an intermediate for the transition from the S_π conformation to the normal conformation. In other words, this process would be analogous to the well-known polymerization of S_6 rings in the solid state (*12*).

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Zusammenfassung

Durch die Tobolsky-Eisenberg Theorie wird das Polymerisationsgleichgewicht des Schwefels erklärt, wobei die S_8-Ring Konzentration und das Zahlenmittel des Polymerisationsgrades von der Temperatur abhängen. Die Voraussagen der Theorie stehen in vollem Einklang mit den experimentellen Befunden. In dieser Arbeit wird gezeigt, dass man die Gegenwart einer weiteren Komponente der Schmelze berücksichtigen kann, nämlich S_π, indem man eine etwas modifizierte Fassung der Tobolsky-Eisenberg Theorie anwendet. Wenn dies getan wird ergibt sich, dass die früher ermittelten Folgerungen gültig bleiben. Die molekularen Verhältnisse und die Struktur des S_π werden ebenfalls diskutiert.

Résumé

La théorie de Tobolsky-Eisenberg sert à expliquer la polymérisation equilibré du soufre sous forme d'une rélation entre la concentration du S_8 (noyau) et la température et entre le degré moyen de polymérisation et la température. Les prévisions de la théorie son en parfait accord avec l'expérience. Dans la présente note on montre qu'il est possible, utilisant une version légerement modifiée de la théorie de Tobolsky-Eisenberg, de prendre à considération un autre composant, S_π, dans la fusion. Dans ce cas on a trouvé que les conclusions précédentes restent valables. On discute aussi le complèx moléculaire et la structure de S_π.