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ADI EISENBERG

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Equilibrium Polymerization under Pressure: The Case of Sulfur

Adi Eisenberg
*Department of Chemistry, University of California, Los Angeles 24, California**

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A previously derived theory of equilibrium polymerization is generalized to take into account the effect of superposed hydrostatic pressure, and the results are applied to the equilibrium polymerization of sulfur. It is shown that the transition which at atmospheric pressure occurs at about 160°C is shifted with pressure toward lower temperatures; at ~850 atm it intersects the melting line, so that above that pressure sulfur melts to a liquid of high viscosity consisting of S_8 rings and diradical terminated chains. The effect of pressure on the equilibrium degree of polymerization and the equilibrium S_8 concentration is also discussed.

I. INTRODUCTION

WHILE it was known for a long time that pressure enhanced the formation of polymer from monomer, it is only recently that pressure effects on addition polymerization have received extensive attention.[1] Some study has also been devoted to the effect of pressure on relatively simple equilibria,[2] and since a theory of equilibrium polymerization has recently been developed[3] and applied to a number of systems at atmospheric pressure,[4] this theory is now extended to account for effects of elevated pressure on equilibrium polymerization; the results of the modified theory are applied to the system of elemental sulfur, for which extensive data are available.

The theory mentioned above differentiates three types of equilibrium polymerization. Case I represents an externally initiated polymerization in which the initiation step is

$$X+M\overset{K}{\rightleftharpoons}XM,$$

where X is the initiator, M the monomer, XM the initiated monomer, and K the equilibrium constant. The propagation equilibria may be represented as

$$XM_n+M\overset{K_3}{\rightleftharpoons}XM_{n+1},$$

where n represents the number of monomer units in the chain and K_3 the equilibrium constant for the propagation reaction, which is independent of the chain length. Case II differs from the above only in the

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* Contribution No. 1537.

[1] K. E. Weale, Quart. Rev. **16,** 267 (1962).

[2] S. D. Hamann, *Physico-Chemical Effects of Pressure* (Butterworths Scientific Publications, Ltd., London, 1957).

[3] A. V. Tobolsky and A. Eisenberg, J. Am. Chem. Soc. **82,** 289 (1960).

[4] (a) A. V. Tobolsky and A. Eisenberg, J. Am. Chem. Soc. **81,** 780 (1959); (b) A. V. Tobolsky and A. Eisenberg, *ibid.*, p. 2302; (c) A. V. Tobolsky and A. Eisenberg, J. Polymer Sci. **45,** 347 (1960); (d) A. V. Tobolsky and A. Eisenberg, *ibid.* **46,** 19 (1960).

absence of the external initiator, the autoinitiating step being

$$M \overset{K}{\rightleftharpoons} M^*,$$

where M* is the initiated monomer. The propagation step may be represented as

$$M_n^* + M \overset{K_3}{\rightleftharpoons} M_{n+1}^*,$$

there being no termination reaction. Finally, Case III represents a reversibly terminated system, for which the initiation and propagation steps may be written as

$$M + M \overset{K}{\rightleftharpoons} M_2,$$

$$M_n + M \overset{K_3}{\rightleftharpoons} M_{n+1}.$$

Case III is algebraically very similar to Case II and is not discussed further; it should be added that both Cases I and III may be divided further into two subcases in which $K = K_3$ or $K \neq K_3$.

The equations correlating the initial experimental values, i.e., M_0 (the original monomer concentration), X_0 (the original initiator concentration, applicable only to Case I), and the equilibrium constants K and K_3 with the degree of polymerization D (formerly written as P but changed here to avoid confusion with pressure, P) for Cases I and II are, respectively,

$$D^2X_0 + D(1/K_3 - M_0) = (K_3M_0 - 1)/K, \qquad (1)$$

$$M_0 = (D-1)/DK_3 + KD(D-1)/K_3. \qquad (2)$$

In the formula for Case I the assumption had to be made that $D \gg 1$ to make the final expression manageable; no such assumption had to be made for Case II. It should be pointed out that in both cases

$$M = (1 - 1/D)/K_3, \qquad (3)$$

or, for $D \gg 1$,

$$M \approx 1/K_3. \qquad (3a)$$

II. ADAPTATION OF THE EQUATIONS TO POLYMERIZATION UNDER PRESSURE

Since no assumptions were made in the derivation which would tend to restrict the applicability of these equations to any particular region of variables, they can be used at elevated pressures if M_0, K, and K_3 are expressed in their pressure-dependent forms. Thus, they become

$$M_0(P) = M_0(0) + \int_0^P (\partial M_0/\partial P)_T dP, \qquad (4)$$

$$\ln K_3(P) = \ln K_3(0) + \int_0^P (\partial \ln K_3/\partial P)_T dP, \qquad (5)$$

$$\ln K(P) = \ln K(0) + \int_0^P (\partial \ln K/\partial P)_T dP, \qquad (6)$$

where (P) indicates the value of the parameter at an elevated gauge pressure P and (0) the value at atmospheric pressure. If we confine ourselves to regions of pressure in which $(\partial M_0/\partial P)_T$, $(\partial \ln K_3/\partial P)_T$, and $(\partial \ln K/\partial P)_T$ are independent of pressure, or in which no significant errors are introduced by making this assumption, the integrals can be solved easily. It is recalled that, in general,[2]

$$d \ln K/dP = \Delta V/RT, \qquad (7)$$

where $\Delta V = V_{\text{reactants}} - V_{\text{products}}$ we obtain, after setting $(\partial M_0/\partial P)_T = \beta_M M_0$, where β_M is the compressibility of the monomer, which is assumed to be constant,

$$M_0(P) = M_0(0) + M_0(0)\beta_M P = M_0(0)[1 + \beta_M P], \qquad (4a)$$

$$\ln K_3(P) = \ln K_3(0) + P\Delta V_P/RT, \qquad (5a)$$

$$\ln K(P) = \ln K(0) + P\Delta V_I/RT, \qquad (6a)$$

where ΔV_I is the difference in molar volume between monomer (plus initiator, where applicable) and initiated monomer and ΔV_P is the difference in molar volume between monomer and polymer. The equation for X_0 is, of course, analogous to that for M_0, except that β_X is needed. For most systems of interest, $M_0 \gg X_0$.

These equations, therefore, allow the prediction of the equilibrium properties of a polymerizing system if the initial conditions, the ΔV values, the compressibilities, and the equilibrium constants at atmospheric pressure are known, and if the assumptions made in their derivations are applicable.

III. APPLICATION TO SULFUR

Very few monomer–polymer equilibria have been investigated extensively, even at atmospheric pressure.[4,5] Of those that have been, the polymerization of sulfur above 160°C, which has been handled as Case II,[4a] is perhaps most amendable to the treatment of its equilibrium polymerization under pressure as outlined in Eqs. (4a) through (6a); sulfur being an element, extensive study has been devoted to many of its physical properties; it is therefore possible to obtain the necessary values from the literature or to estimate them by comparison to other materials.

It has been shown[4a] that sulfur, which undergoes an autoinitiated polymerization, is subject to the following equilibria:

$$M \overset{K}{\rightleftharpoons} M^*,$$

where M represents the S_8 ring and M* the S_8 diradical, and

$$M_n^* + M \overset{K_3}{\rightleftharpoons} M_{n+1}^*.$$

At 160°C, the free energy of the polymerization reaction crosses the zero line, so that, since ΔH_3^0 is positive [4a] polymer (diradical terminated sulfur chains)

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[5] F. S. Dainton and K. J. Ivin, Quart. Rev. 12, 61 (1958).

is stable only above that temperature. Thus, sulfur exhibits the curious phenomenon of a "floor temperature" in contrast to organic polymerizations which exhibit "ceiling temperatures," i.e., temperatures above which high polymer is unstable. In the case of sulfur, as the temperature increases above 160°C, the number average degree of polymerization D, rises, reaches a maximum at $\sim 170°$, and falls slowly as the temperature is raised. The equilibrium monomer concentration $[M]$ below 160°C remains constant and essentially equal to that of the original monomer concentration $[M_0]$ and begins to fall slowly above 160°, more and more monomer being converted to polymer as the temperature rises.

$K(0)$, $K_3(0)$, and $M_0(0)$ are known from the previous work.[4a] To proceed, the following quantities are needed: β_M, ΔV_P, and ΔV_1.

A search through Gmelin's book and *Chemical Abstracts* revealed only two determinations of the compressibility of liquid sulfur, both below 160°. Kleppa,[6] by ultrasonic means, determined the isothermal compressibility of liquid sulfur at 115°C as 34.6×10^{-6} bar^{-1} and the adiabatic compressibility as 30.4×10^{-6} bar^{-1}. Later, Baccareda and Butta[7] determined the adiabatic compressibility of liquid sulfur in the range 120°–143°C, also by ultrasonic means, and found it to be 29.98×10^{-12} cm^2/dyn. Due to the excellent agreement in the two values for the adiabatic compressibility at different temperatures, the isothermal compressibility is taken as 35×10^{-6} atm^{-1} and is assumed not to vary appreciably over the temperature range of interest (120°–160°C).

ΔV_P is calculated from the experimental values of the density of sulfur[8] and the calculated values of the concentration of S_8 (monomer) in the melt.[4a,9] The density of the monomer is known directly at temperatures below 160°; since the density–temperature relationship is linear from the melting point to 160°, the density above the temperature can be estimated by extrapolation. The difference between the experimentally determined density and the value thus obtained must be due to the presence of polymer, the density of which is different from that of the monomer; it can be calculated by use of the relation

$$\rho_{\text{polymer}} = (100-\text{wt.\% monomer}) \bigg/ \left(\frac{100}{\rho_{\text{total}}} - \frac{\text{wt.\% monomer}}{\rho_{\text{monomer}}}\right).$$

The ΔV value for the polymerization reaction is obtained simply from

$$\Delta V_P = 256[1/\rho_{\text{monomer}} - 1/\rho_{\text{polymer}}],$$

the best value being 5.5 ± 0.5 cm^3/mole of S_8.

The value of ΔV_I, the volume change upon ring opening, is, of course, experimentally inaccessible; one must, therefore, resort to a comparison of this system with similar materials which are available both as rings and linear chains. The best example of such systems are the unstrained cycloparaffins ($5\leq n\leq 8$) and the corresponding linear alkenes, with the unsaturation located in any of the permissible positions, data of the physical properties of which are available in the standard reference works.[10,11] The results show a surprising uniformity, i.e., the molar volume of the linear 1-alkene is in all the cases greater than that of the cycloalkane by $16.0\pm0.3\%$. A change in the location of the double bond (or a change from *cis* to *trans* in cases other than the 1-alkenes) does not change that value greatly (2% in the worst case, that of *cis* pentane-2). Since the change in volume upon opening the S_8 ring is experimentally indeterminable, and since no other systems are known to the author which approximate more closely the values to be expected in that reaction, 16% is taken as the approximate increase in molar volume upon opening of the S_8 ring. Since the molar volume of S_8 in the temperature range 120° to 160° is 144 cm^3, ΔV_I is taken as 23 cm^3 per mole.

Calculations of the effect of pressure on the equilibrium polymerization of sulfur can now be carried out; the following being most illuminating:

(a) the change in the transition temperature with pressure;

(b) the change of the degree of polymerization with pressure at constant temperatures, preferably in the transition region;

(c) the change in equilibrium monomer concentration with pressure, also in the transition region;

(d) the initial effect of pressure on the degree of polymerization as a function of temperature.

These are now discussed in the above order.

(a) The transition temperature (floor temperature), i.e., the temperature below which polymer is unstable, occurs when the ΔF of the polymerization reaction changes sign.[5,12] This is equivalent to saying that it occurs at the point at which $K_3M_0=1$, or $\ln K_3 = -\ln M_0$. By use of Eqs. (4a) and (5a), it follows (after setting $\ln[1+\beta_M P]=\beta_M P$) that at that point

$$\ln K_3(0)M_0(0) = -P[(\Delta V_P/RT)+\beta_M],$$

i.e., that

$$P_{\text{tr}} = -[\ln K_3(0)M_0(0)]/[(\Delta V_P/RT)+\beta_M].$$

$K_3(0)$ and $M_0(0)$ can, of course, be written in their temperature-dependent forms. An evaluation of the

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[6] O. J. Kleppa, J. Chem. Phys. **18,** 1303 (1950).

[7] M. Baccareda and E. Butta, Ann. Chim. (Rome) **45,** 50 (1955).

[8] A. M. Kellas, J. Chem. Soc. **113,** 909 (1918).

[9] G. Gee, Trans. Faraday Soc. **48,** 515 (1952); F. Fairbrother, G. Gee, and G. T. Merrall, J. Polymer Sci. **16,** 459 (1955).

[10] "Selected Values of Properties of Hydrocarbons," Natl. Bur. Std. (U. S.), Circ. C461 (1947).

[11] *Faraday's Encyclopedia of Hydrocarbon Compounds* (Chemindex Ltd., Manchester, England, 1946).

[12] A. V. Tobolsky and A. Eisenberg, J. Colloid Sci. **17,** 49 (1962).

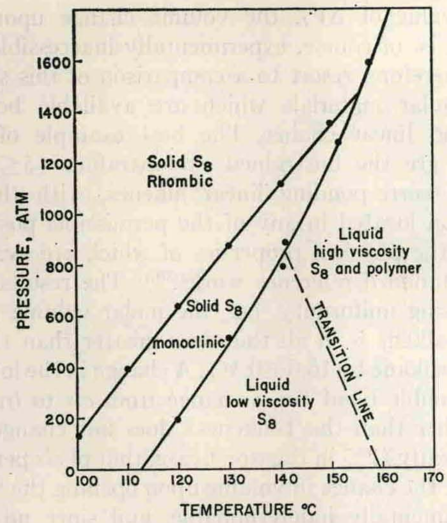

FIG. 1. Modified phase diagram for sulfur. ● Experimental points (Tamann, Ref. 13); - - - this work, calculated.

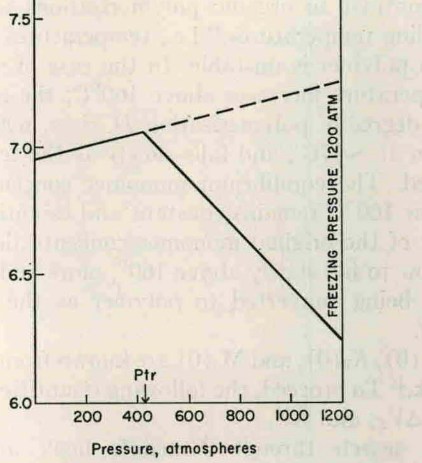

FIG. 3. [M] (in moles/liter) vs P for sulfur at 150°C.

transition temperature as a function of pressure shows that with increasing pressure the transition shifts to lower temperatures (Fig. 1). This is in direct contrast to the behavior expected for organic polymerizations, for which it has been shown[1] (α-methylstyrene, for example) that the transition temperature (ceiling temperature) rises with pressure. The cause of this discrepancy can be seen if it is recalled that for sulfur the $\Delta H(=H_{\text{products}}-H_{\text{reactants}})$ in the equation[1,2]

$$dT_{\text{trans}}/dP=-T(\Delta V/\Delta H)$$

is positive, while in organic polymerizations it is negative; the sign of ΔV $(V_{\text{reactants}}-V_{\text{products}})$ is positive in both instances. Since the melting point of sulfur rises by about 30° per 1000 atm,[13] this means that at approximately 850 atm the melting line intersects the transition line and above that pressure sulfur melts to a liquid of high viscosity, just as selenium does at atmospheric pressure. The low-viscosity form of liquid sulfur is therefore merely a low-temperature and low-pressure phenomenon, the area of stability of which is shown in

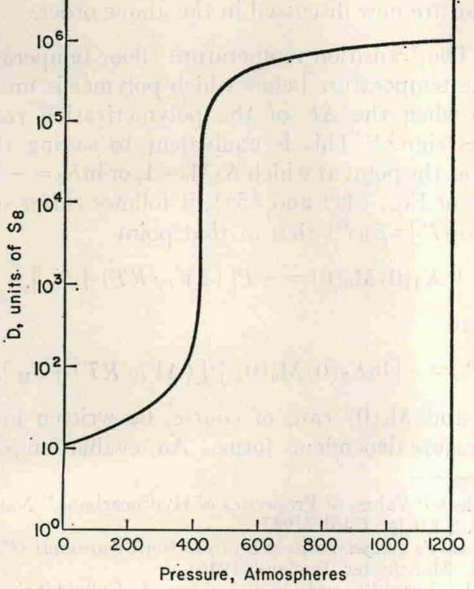

FIG. 2. D vs P for sulfur at 150°C.

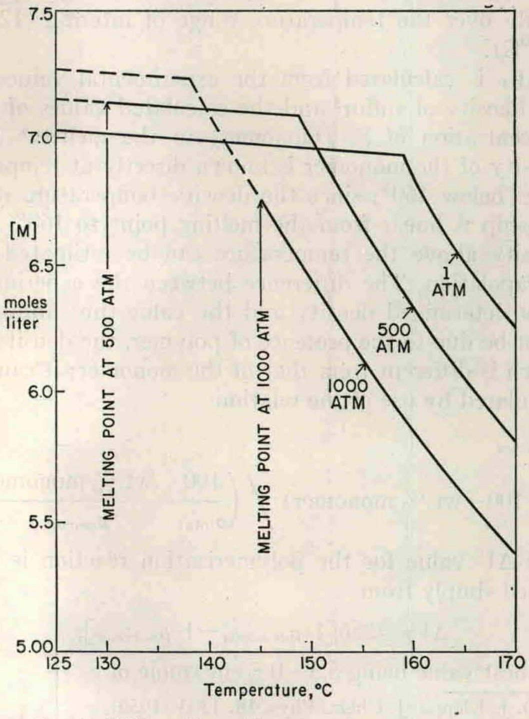

FIG. 4. [M] vs t for sulfur at various pressures.

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[13] Gmelin, *Handbuch der Anorganischen Chemie* (Verlag Chemie, Weinheim, 1953), Vol. 9, p. 529.

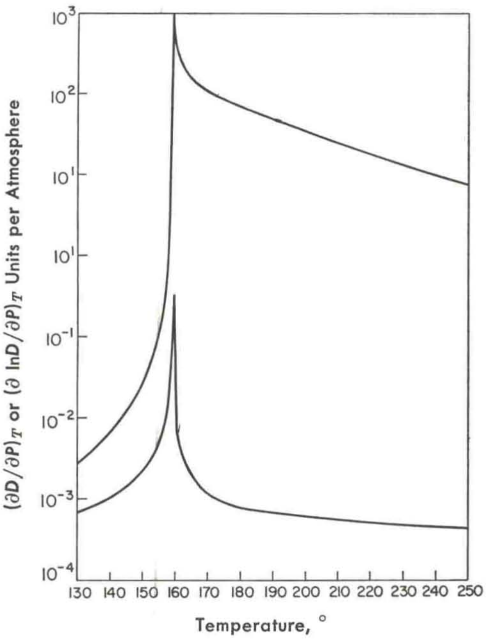

FIG. 5. $\partial D/\partial P$ and $\partial \ln D/\partial P$ vs t. Upper line is $(\partial D/\partial P)_T$; lower line is $(\partial \ln D/\partial P)_T$.

Fig. 1. The melting-point data are those of Tamman,[13] while the dashed line represents the calculated change in transition temperature with pressure.

(b) The calculation of D vs P is most illustrative if performed for a temperature at which a transition occurs between atmospheric pressure and the freezing pressure. A calculation for 150°C (freezing pressure = 1200 atm) is shown in Fig. 2, with the transition occurring at 430 atm. It should be pointed out that in contrast to plots of the degree of polymerization vs temperature which show maxima in D, in this case D rises continuously with P. This becomes quite clear upon inspection of the equation for D vs P. For $D\gg 1$, Eq. (2) becomes

$$D=\{[K_3(P)\mathrm{M}_0(P)-1]/K(P)\}^{\frac{1}{2}}.$$

Since both K_3 and M_0 increase with P while K decreases with P (due to the signs of ΔV_P and ΔV_I), D cannot but rise over the whole range.

(c) A plot of $M(P)$ vs P is shown in Fig. 3 for the entire liquid range at 150°C. It should be pointed out that at the freezing pressure only $\sim 14\%$ by weight of the sulfur is present in the polymeric form. The variation of $[\mathrm{M}]$ with temperature for various pressures is shown in Fig. 4; it should be noted that while the 1-atmosphere line is completely regular down to the lowest temperature shown, the 500-atm plot shows a discontinuity at 130°C (the melting point at that pressure) and the 1000-atm plot at 145°; at the last pressure the material already melts to a mixture of rings and chains.

(d) Finally, Fig. 5 shows the initial effect of pressure on the degree of polymerization, presented both as $d \ln D/dP$ and dD/dP. This is calculated from the temperature derivative of Eq. (2), which is

$$\left(\frac{\partial \ln D}{\partial P}\right)_T$$

$$=\frac{K_3\left(\dfrac{\partial \mathrm{M}_0}{\partial P}\right)_T+K_3\mathrm{M}_0\left(\dfrac{\partial \ln K_3}{\partial P}\right)_T-\left(\dfrac{\partial \ln K}{\partial P}\right)_T(D^2K-DK)}{1/D+2KD^2-KD}.$$

Above the transition temperature $D^2\approx(K_3\mathrm{M}_0-1)/K$ and $D\gg 1$.[4a] Therefore, we can neglect KD and $1/D$ with respect to $2KD^2$, and obtain, upon rearrangement,

$$\left(\frac{\partial \ln D}{\partial P}\right)_T=\frac{1}{2(K_3\mathrm{M}_0-1)}\left[K_3\left(\frac{\partial \mathrm{M}_0}{\partial P}\right)_T\right.$$
$$\left.+K_3\mathrm{M}_0\left(\frac{\partial \ln K_3}{\partial P}\right)_T\right]-\frac{1}{2}\left(\frac{\partial \ln K}{\partial P}\right)_T.$$

Below the transition temperature we cannot make this approximation and,[2a] $1/D\gg 2KD^2$. Incidentally, the last term in the numerator also is negligible[4a] and we are left with

$$\left(\frac{\partial \ln D}{\partial P}\right)_T=\frac{1}{1-K_3\mathrm{M}_0}\left[K_3\left(\frac{d\mathrm{M}_0}{dP}\right)_T+K_3\mathrm{M}_0\left(\frac{d \ln K_3}{dP}\right)_T\right].$$

At the transition temperature, $1/D\approx 2KD^2$, and both terms have to be taken into account. At this point the curve reaches a maximum. The plot of $\partial \ln D/\partial P$ resembles a delta function, just as the heat capacity of sulfur does,[14] but in both cases the curve is at all points continuous and finite.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the benefit of stimulating discussions with A. Darnell of this department in connection with the effect of pressure on the transition temperature.

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[14] E. D. West, J. Am. Chem. Soc. **81**, 29 (1959).