

## Equilibrium Polymerization under Pressure: The Case of Sulfur

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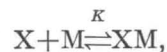
A previously derived theory of equilibrium polymerization is generalized to take into account the effect of superposed hydrostatic pressure, and the results are applied to the equilibrium polymerization of sulfur. It is shown that the transition which at atmospheric pressure occurs at about 160°C is 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<sub>8</sub> rings and diradical terminated chains. The effect of pressure on the equilibrium degree of polymerization and the equilibrium S<sub>8</sub> 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.<sup>1</sup> Some study has also been devoted to the effect of pressure on relatively simple equilibria,<sup>2</sup> and since a theory of equilibrium polymerization has recently been developed<sup>3</sup> and applied to a number of systems at atmospheric pressure,<sup>4</sup> this theory is now extended to account for effects of elevated pressure on equilibrium polymeriza-

tion; 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



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



where *n* represents the number of monomer units in the chain and *K*<sub>3</sub> 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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<sup>1</sup> K. E. Weale, *Quart. Rev.* **16**, 267 (1962).

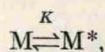
<sup>2</sup> S. D. Hamann, *Physico-Chemical Effects of Pressure* (Butterworths Scientific Publications, Ltd., London, 1957).

<sup>3</sup> A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.* **82**, 289 (1960).

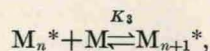
<sup>4</sup> (a) A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.* **81**, 780 (1959); (b) A. V. Tobolsky and A. Eisenberg, *ibid.*, p. 2302; (c) A. V. Tobolsky and A. Eisenberg, *J. Polymer Sci.* **45**, 347 (1960); (d) A. V. Tobolsky and A. Eisenberg, *ibid.* **46**, 19 (1960).



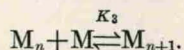
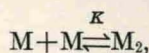
absence of the external initiator, the autoinitiating step being



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



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



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 sub-cases 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,

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

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

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

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

or, for  $D \gg 1$ ,

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

## 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

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

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

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

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,<sup>2</sup>

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

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

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

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

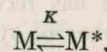
$$\ln K(P) = \ln K(0) + P \Delta V_I / RT, \quad (6a)$$

where  $\Delta V_I$  is the difference in molar volume between monomer (plus initiator, where applicable) and initiated monomer and  $\Delta V_P$  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  $\beta_X$  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  $\Delta V$  values, the compressibilities, and the equilibrium constants at atmospheric pressure are known, and if the assumptions made in their derivations are applicable.

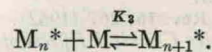
## III. APPLICATION TO SULFUR

Very few monomer-polymer equilibria have been investigated extensively, even at atmospheric pressure.<sup>4,5</sup> Of those that have been, the polymerization of sulfur above 160°C, which has been handled as Case II,<sup>4a</sup> is perhaps most amenable 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<sup>4a</sup> that sulfur, which undergoes an autoinitiated polymerization, is subject to the following equilibria:



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



At 160°C, the free energy of the polymerization reaction crosses the zero line, so that, since  $\Delta H_3^0$  is positive<sup>4a</sup> polymer (diradical terminated sulfur chains)

<sup>5</sup> F. S. Dainton and K. J. Ivin, *Quart. Rev.* **12**, 61 (1958).