



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,<sup>13</sup> 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

$$D = \{[K_3(P)M_0(P) - 1]/K(P)\}^{\frac{1}{2}}$$

Since both  $K_3$  and  $M_0$  increase with  $P$  while  $K$  decreases with  $P$  (due to the signs of  $\Delta V_P$  and  $\Delta V_T$ ),  $D$  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 ~14% by weight of the sulfur is present in the polymeric form. The variation of  $[M]$  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

$$\left(\frac{\partial \ln D}{\partial P}\right)_T = \frac{K_3 \left(\frac{\partial M_0}{\partial P}\right)_T + K_3 M_0 \left(\frac{\partial \ln K_3}{\partial P}\right)_T - \left(\frac{\partial \ln K}{\partial P}\right)_T (D^2 K - DK)}{1/D + 2KD^2 - KD}$$

Above the transition temperature  $D^2 \approx (K_3 M_0 - 1)/K$  and  $D \gg 1$ .<sup>4a</sup> Therefore, we can neglect  $KD$  and  $1/D$  with respect to  $2KD^2$ , and obtain, upon rearrangement,

$$\left(\frac{\partial \ln D}{\partial P}\right)_T = \frac{1}{2(K_3 M_0 - 1)} \left[ K_3 \left(\frac{\partial M_0}{\partial P}\right)_T + K_3 M_0 \left(\frac{\partial \ln K_3}{\partial P}\right)_T \right] - \frac{1}{2} \left(\frac{\partial \ln K}{\partial P}\right)_T$$

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

$$\left(\frac{\partial \ln D}{\partial P}\right)_T = \frac{1}{1 - K_3 M_0} \left[ K_3 \left(\frac{\partial M_0}{\partial P}\right)_T + K_3 M_0 \left(\frac{\partial \ln K_3}{\partial P}\right)_T \right]$$

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,<sup>14</sup> 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.

<sup>14</sup> E. D. West, J. Am. Chem. Soc. **81**, 29 (1959).