TRANSITION PHENOMENA IN EQUILIBRIUM POLYMERIZATION

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ABSTRACT

Rather surprisingly an *exact* treatment of equilibrium polymerization by the law of mass action predicts the existence of unusually sharp transitions under certain circumstances. We here derive the complete mathematical equations for these transition phenomena, and apply them to the ceiling temperature of α-methylstyrene and the floor temperature of sulfur. Our description of the transition phenomena goes beyond the discussion of Dainton and Ivin in yielding exact (*mathematical*) expressions for the degree of polymerization, size distribution, and monomer concentration throughout the entire transition region. For sharp transitions two equilibrium constants are required.

INTRODUCTION

A great variety of chemical compounds can polymerize (or associate) to form linear polymers. In many cases polymerization proceeds under conditions of equilibrium between polymer and monomer. In some cases an initiator enters into the polymerization equilibria.

A general theory for equilibrium polymerization has been developed (1), which is based on two equilibrium constants: an equilibrium constant K for initiation and an equilibrium constant K_3 for propagation. The two experimental observables, namely, the equilibrium monomer concentration and the equilibrium degree of polymerization, can be expressed in terms of the initial (unreacted) monomer concentration M_0, the initial initiator concentration X_0, and the two equilibrium constants K and K_3.

In this paper we shall develop a very surprising aspect of equilibrium polymerization, namely, the existence of unusually sharp "transitions." In certain cases, there exists a sharply defined "ceiling temperature" *above* which high polymer is thermodynamically unstable with respect to monomer; in other cases there exists a sharply defined floor "temperature" *below* which polymer is unstable with respect to monomer. We shall show that both of these results can be explained quantitatively in terms of the general theory of equilibrium polymerization. We shall first specialize our treatment to two cases: the equilibrium polymerization of α-methylstyrene in the presence of an ionic initiator and the equilibrium polymerization of sulfur.

CEILING TEMPERATURE FOR α-METHYLSTYRENE

Consider the equilibrium polymerization of α-methylstyrene in the presence of an anionic initiator. We shall (postulate for reasons of mathematical simplicity) assume that the reaction between the initiator R^-Na^+ and the monomer M goes to completion. This happens only for certain initiators, as has been shown before (2, 3). The species RM^-Na^+ is formed which may be regarded as the effective initiator (this is essentially equivalent to case I-b of the general theory (1)). The reaction sequence is as follows:

$$RM^-Na^+ \;+\; M \;\overset{K_3}{\rightleftharpoons}\; RM_2^-Na^+$$

$$RM_2^-Na^+ \;+\; M \;\overset{K_3}{\rightleftharpoons}\; RM_3^-Na^+$$

$$RM_n^-Na^+ \;+\; M \;\overset{K_3}{\rightleftharpoons}\; RM_{n+1}^-Na^+$$
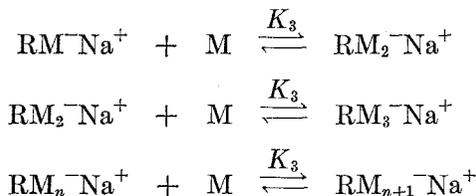
This assumption that all growth steps have the same equilibrium constant may not be exact for low degrees of polymerization (4), but this does not affect our general result or conclusions. Moreover, the assumption has given very satisfactory results for α-methylstyrene (2) and ϵ-caprolactam (5).

Let us take the initial concentration of initiator RM^-Na^+ to be X_0 moles per kilogram (which will be our concentration unit); X_0 is also the original concentration of R^-Na^+. Let the initial concentration of monomer be M_0, the equilibrium concentration of monomer be M, the equilibrium concentration of RM^-Na^+ be X, and the equilibrium degree of polymerization be P. The exact relations between P, M, and X, and M_0, X_0, and K_3 are as follows (1).

$$P = \frac{1}{(1 - K_3 M)} \tag{1}$$

$$M_0 = M(1 + K_3 XP^2); \tag{2}$$

$$X_0 = X(1 + K_3 MP) = XP. \tag{3}$$

The following derived relationships are also useful:

$$P = \frac{(M_0 - M)}{(X_0 - X)}; \tag{4}$$

$$P^2(K_3 X_0) - P(K_3 X_0 - 1) - 1 = 0. \tag{5}$$

A transition temperature occurs as a direct mathematical consequence of these equations at the temperature for which $K_3 M_0 = 1$ (the reason for this will be given subsequently). This will be a ceiling temperature if $\Delta H_3°$ is negative, and a floor temperature if $\Delta H_3°$ is positive. In the case of α-methyl-

styrene $\Delta H_3°$ is negative, and hence we have ceiling temperature phenomena. In this section we shall present only the results of the calculations. The treatment is given in the appendix.

For temperatures above the ceiling temperature, since polymer is thermodynamically unstable with respect to the monomer, the equilibrium monomer concentration equals approximately the original monomer concentration, i.e.,

$$M_0 \approx M; \qquad [2a]$$

and therefore

$$P \approx \frac{1}{(1 - K_3 M_0)}. \qquad [1a]$$

At the ceiling temperature, we obtain the following approximations (see appendix)

$$P_t \approx (K_3 X_0)^{-1/2}; \qquad [6]$$

$$(M_0 - M)_t \approx \left(\frac{X_0}{K_3}\right)^{1/2}; \qquad [7]$$

the subscript t denotes the transition (floor or ceiling) temperature.

The steepness of the transition can be indicated by the value dP/dT at the ceiling temperature

$$\left(\frac{dP}{dT}\right)_t \approx \frac{\Delta H_3°}{RT^2[2K_3 X_0 - (K_3 X_0)^{3/2}]}. \qquad [8]$$

Since the ceiling temperature is defined by the relation $K_3 M_0 = 1$, we also get a transition at a fixed temperature by varying the initial monomer concentration M_0. All the equations given above, except Eq. [8], are valid for this case too. We add another equation which defines the sharpness of the transition as a function of M_0 in the range of the critical M_0 concentration at constant temperature

$$\left(\frac{dP}{dM_0}\right)_t \approx \frac{X_0}{2}. \qquad [9]$$

All these relations, which are direct mathematical consequences of Eqs. [1], [2], and [3], and therefore exact consequences of the law of mass action, are derived in the appendix. We shall now apply these equations numerically to α-methylstyrene and show how sharp the transitions are.

Numerical Results for α-Methylstyrene

Equations [1] to [9] were applied numerically to α-methylstyrene. Using the data of Worsfold and Bywater (6) and also of McCormick (7), we ob-

tain the following result for K_3 (our concentration units are still moles/kg. and the standard state is 1 mole/kg.).

$$K_3 = \exp(\Delta S_3^\circ/R) \exp(-\Delta H_3^\circ/RT);$$

$$\Delta H_3^\circ = -7{,}720 \text{ cal./mole};$$

[10]

$$\Delta S_3^\circ = -27.6 \text{ cal./deg. mole.}$$

For an initiator concentration of 0.001 mole/kg. and for two values of
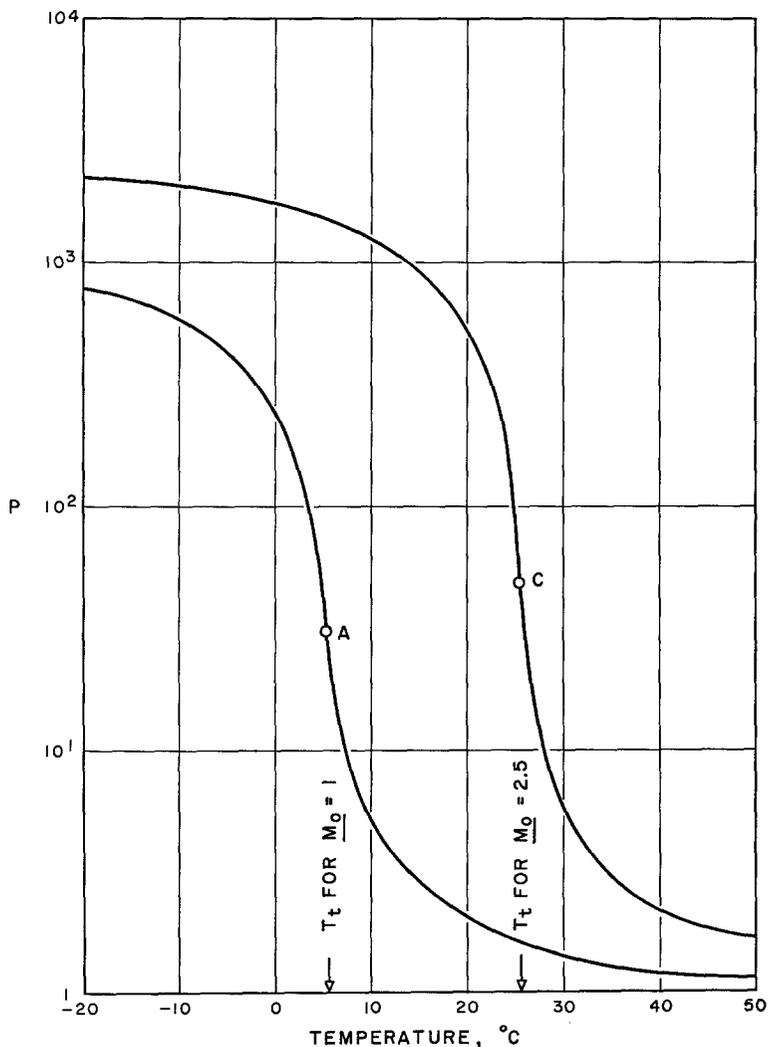
FIG. 1. Degree of polymerization vs. temperature in °C. for α-methylstyrene for $M_0 = 1$ and $M_0 = 2.5$ moles/kg. $X_0 = 0.001$ mole/kg.
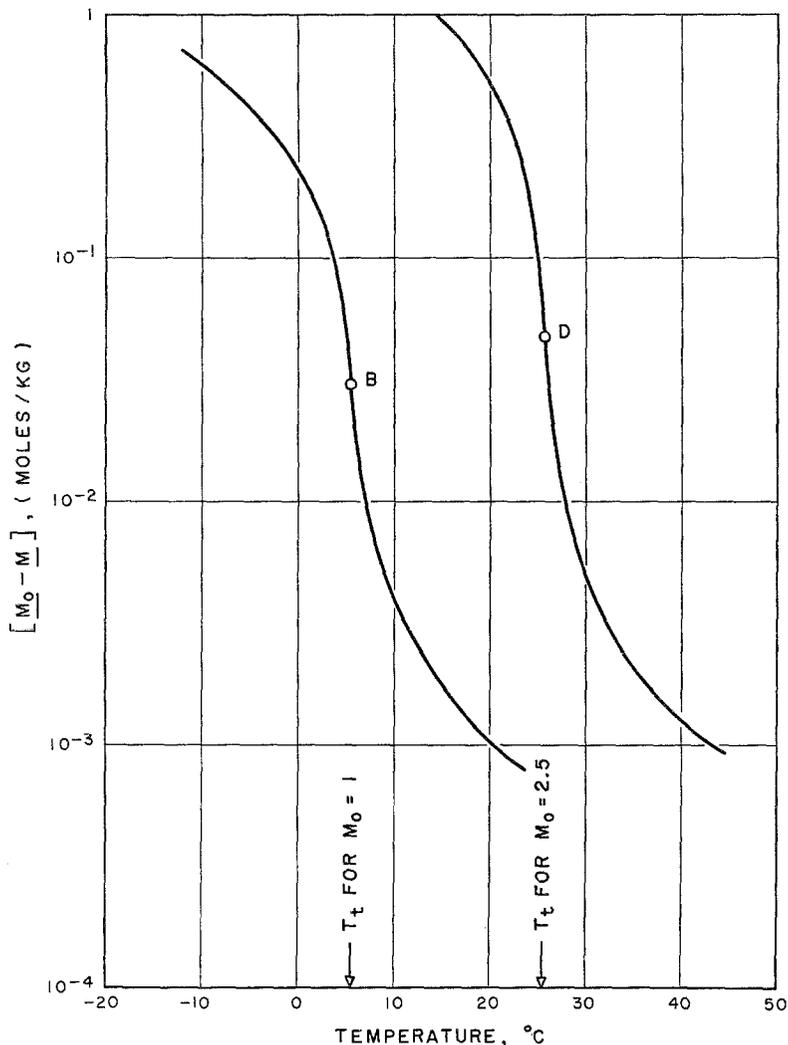
FIG. 2. $(M_0 - M)$ moles/kg. vs. temperature for α-methylstyrene for $M_0 = 1$ and $M_0 = 2.5$ moles/kg. $X_0 = 0.001$ mole/kg.

M_0, namely, 1.0 and 2.5 moles/kg., we have computed P vs. T according to Eqs. [1a], [5], and [6]. This is shown in Fig. 1. From Eqs. [3], [4], and [7] we have obtained $(M_0 - M)$ versus temperature for these same conditions. In Fig. 2 we have plotted $(M_0 - M)$, obviously equal to the total weight concentration (of polymer), as a function of temperature.

We have computed P versus M_0 at two different temperatures, $+5.6°C$. and $-7.6°C$., for the same initiator concentration using Eq. [5]. This is
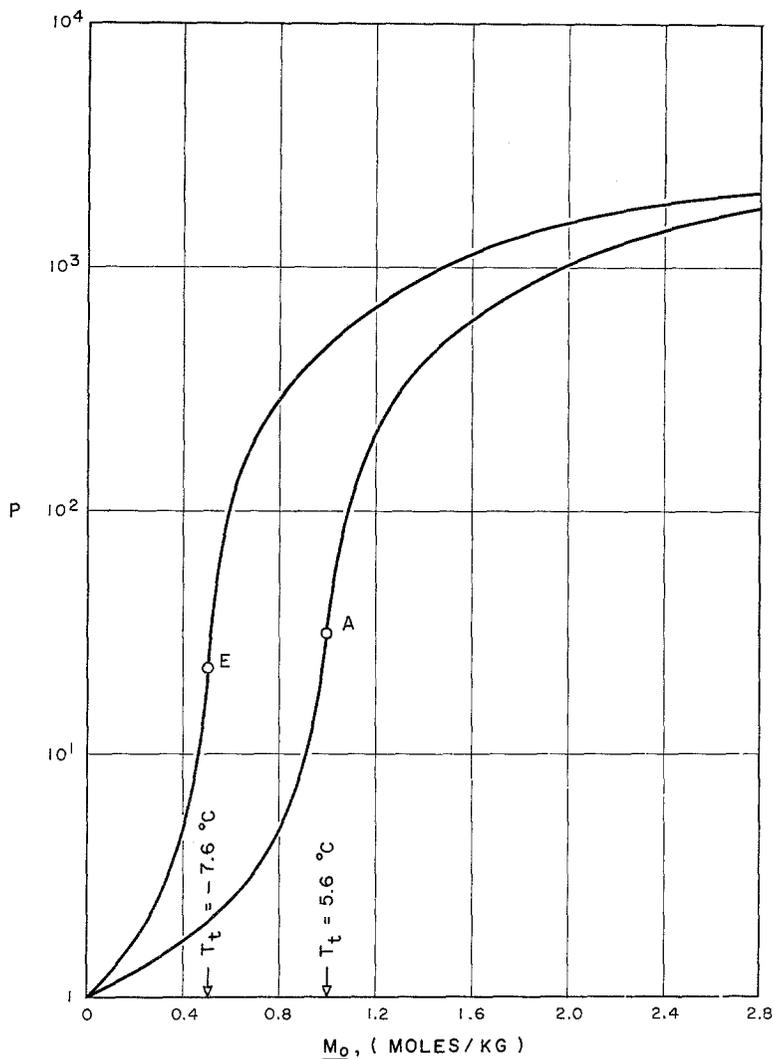
FIG. 3. Degree of polymerization vs. M_0 moles/kg. for α-methylstyrene for $T = +5.6°C$. and $T = -7.6°C$. $X_0 = 0.001$ mole/kg.

shown in Fig. 3. We have also computed $M_0 - M$ for the same conditions using Eqs. [3] and [4]. The results are shown in Fig. 4.

The numerical values for the transition points (indicated on the graphs as $A, B, C \cdots$) are:

For $M_0 = 1$ (Figs. 1 and 2)

$$T_t = 5.6°C.$$

$$P_t = 31.6 \text{ (Point } A\text{)}$$

$$(M_0 - M)_t = 0.0306 \text{ mole/kg. (Point } B)$$

$$(dP/dT)_t = -24.7 \text{ units/degree}$$

$$[d(M_0 - M)/dT]_t = -0.0247 \text{ mole/kg./degree}$$

For $M_0 = 2.5$ (Figs. 1 and 2)

$$T_t = 25.6°C.$$
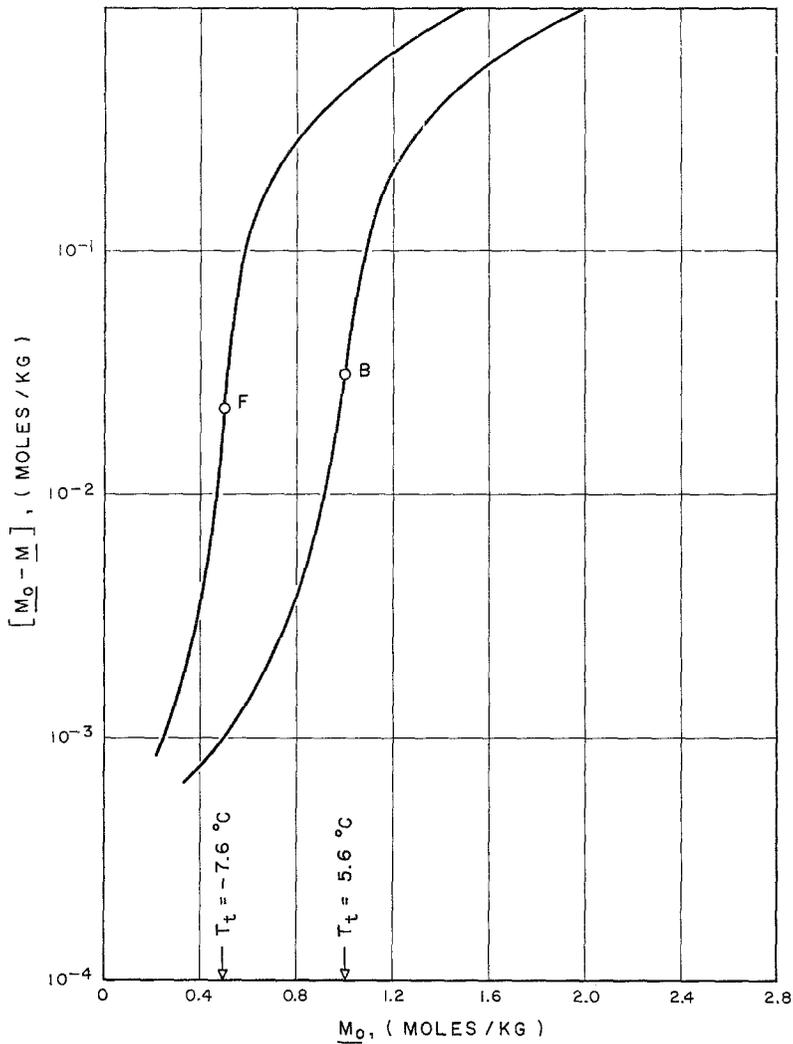
FIG. 4. $(M_0 - M)$ moles/kg. vs. M_0 moles/kg. for α-methylstyrene for $T = 5.6°C$. and $T = -7.6°C$. $X_0 = 0.001$ mole/kg.

$$P_t = 50 \text{ (Point } C)$$

$$(M_0 - M)_t = 0.0490 \text{ mole/kg. (Point } D)$$

$$(dP/dT)_t = -53.1 \text{ units/degree}$$

$$[d(M_0 - M)dT]_t = -0.0531 \text{ mole/kg. /degree}$$

For $K_3 = 1$ ($t = 5.6°C.$, Figs. 3 and 4)

$$P_t = 31.6 \text{ (Point } A)$$

$$(M_0 - M)_t = 0.0306 \text{ mole/kg. (Point } B)$$

$$(dP/dM_0)_t = +500 \text{ units/degree}$$

$$[d(M_0 - M)/dM_0]_t = 0.500$$

For $K_3 = 2$ ($t = -7.6°C.$, Figs. 3 and 4)

$$P_t = 22.4 \text{ (Point } E)$$

$$(M_0 - M)_t = 0.0214 \text{ mole/kg. (Point } F)$$

$$(dP/dM_0)_t = 500 \text{ units/mole/kg.}$$

$$[d(M_0 - M)/dM_0]_t = 0.500$$

The absolute numerical values of $[d(M_0 - M)/dT]_t$ seem small, but in view of the magnitude of $(M_0 - M)_t$, the slopes are quite large. The values for the rates of change of P with M_0 seem to be greater than those of the rate of change with T, whereas the graph seems to indicate approximately equal rates; this is, of course, due only to the units on the abscissa; while on the T axis we plot 70°, we show only 2.8 monomer concentration units on the M_0 axis. It should also be pointed out that in a three-dimensional construction of P vs. M_0 vs. T, points A and B of Figs. 1 and 2 would be identical with points A and B of Figs. 3 and 4. It is also apparent that the two graphs of P vs. T (Fig. 1) are sections of this three-dimensional construction perpendicular to the M_0 axis at points $M_0 = 1$ and $M_0 = 2.5$. The above arguments are equally valid for the graphs of $(M_0 - M)$ vs. T and for Figs. 3 and 4.

FLOOR TEMPERATURE FOR SULFUR

Sulfur polymerizes in the absence of an initiator. We consider the following equilibria:

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

$$M^* + M \overset{K_3}{\rightleftharpoons} M_2^*$$

$$M_n^* + M \overset{K_3}{\rightleftharpoons} M_{n+1}^*$$
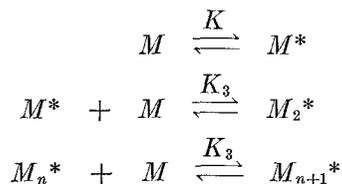
The eight-membered sulfur ring is considered as one monomer unit; the asterisk denotes a diradical. Let the initial concentration of monomer be M_0, the equilibrium monomer concentration, as before, M, and the equilibrium degree of polymerization P. The exact relations between P and M and M_0, K_3, and K are (8):

$$P = \frac{1}{(1 - K_3 M)}. \tag{1}$$

$$M_0 = M(1 + KMP^2). \tag{11}$$

Another derived relationship of great usefulness:

$$K_3 M_0 = \frac{(P - 1)}{P} + KP(P - 1). \tag{12}$$

These relationships are generally valid for case II polymerization (1).

Here also a transition occurs at the temperature for which $K_3 M_0 = 1$. For bulk sulfur $M_0 = 3.90$, and this transition occurs at 159°C., a temperature at which the liquid suddenly seems to acquire a very high viscosity. The $\Delta H_3°$ is positive in this case, so we have a "floor" temperature.

For the temperature region in which high polymer is stable, i.e., above the floor temperature, P is $\gg 1$, and Eq. [12] becomes

$$P \approx \left(\frac{M_0 K_3 - 1}{K}\right)^{1/2}. \tag{12a}$$

In regions below the floor temperature, Eqs. [1a] and [2a] hold.
At the transition point, the following relationships hold:

$$P_t \approx \frac{1}{K^{1/3}}; \tag{13}$$

$$(M_0 - M)_t \approx \frac{K^{1/3}}{K_3}; \tag{14}$$

$$\left(\frac{dP}{dT}\right)_t \approx \frac{(\Delta H_3°/KP - P\Delta H°)}{3RT^2}; \tag{15}$$

$$\left(\frac{dP}{dM_0}\right)_t \approx \frac{K_3}{3KP}. \tag{16}$$

NUMERICAL RESULTS FOR SULFUR[1]

The above equations were applied quantitatively to sulfur. Using the figures of P vs. T and M vs. T obtained by G. Gee (9), we calculated the thermodynamic constants as follows (8):

$$\Delta H° = 32{,}800; \qquad \Delta S° = 23.0$$

$$\Delta H_3° = 3{,}170; \qquad \Delta S_3° = 4.63.$$

We have calculated the P vs. T curves for M_0 values of 3.90 moles/kg. (bulk), 3.50 moles/kg., and 3.00 moles/kg. These are shown in Fig. 5. All the curves exhibit transitions at that temperature at which $K_3 M_0 = 1$, go through a maximum, and drop off as the temperature increases. The criteria for the occurrence of this maximum are obtained easily by differentiating Eq. [12a] (since we are in the high-polymer region) with respect to T and
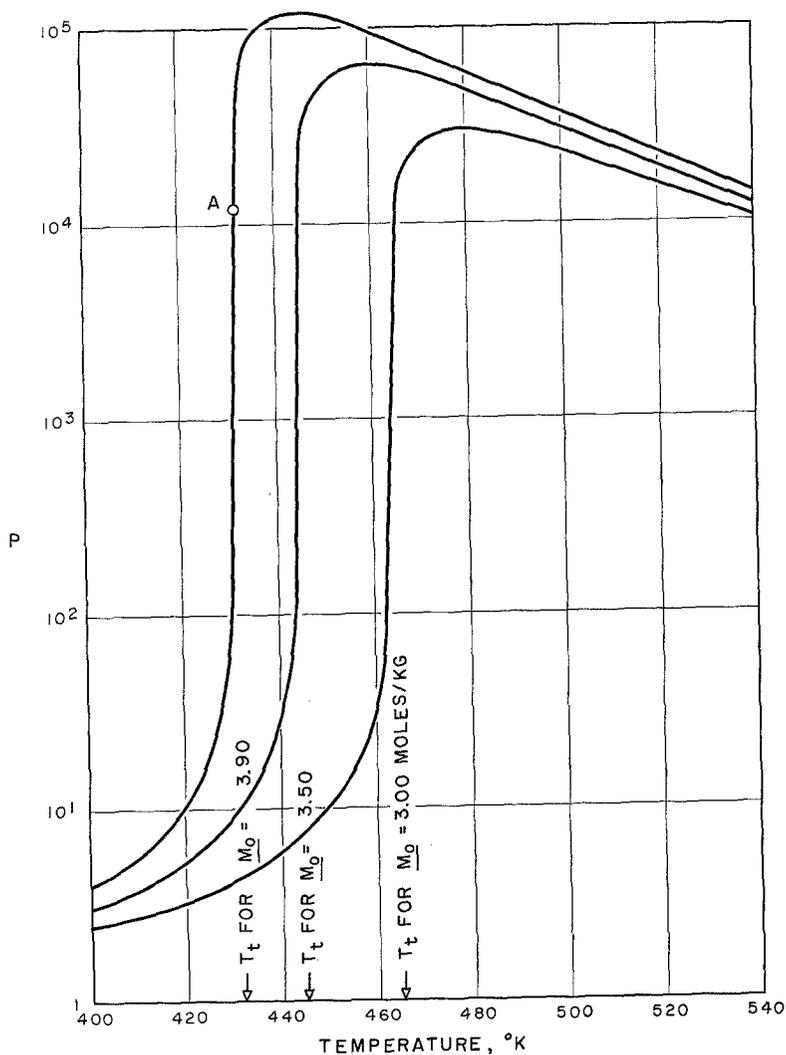

FIG. 5. Degree of polymerization vs. temperature in °C. for sulfur in bulk (3.90 moles/kg.), and two dilutions (3.50 and 3.00 moles/kg.).

setting $dP/dT = 0$. The result is

$$T_{\max} = \frac{\Delta H_3^{\circ}}{S_3^{\circ} + R\ln[M_0(\Delta H^{\circ} - \Delta H_3^{\circ})/\Delta H^{\circ}]}. \qquad [17]$$

We have also computed the curves of P vs. M_0 for two temperatures, 167°C. and 187°C. These are shown in Fig. 6. The corresponding curves for $(M_0 - M)$ vs. M are shown in Fig. 7. The transitions in this case are much more pronounced than in α-methylstyrene. Representative numerical values were calculated in this instance for Point A (Fig. 5), Point B (Fig. 6), and Point C (Fig. 7).

For Point A

$$T_t = 432°K. = 159°C.$$

$$P_t = 1.2 \times 10^4 \text{ units}$$

$$(M_0 - M)_t = 3.24 \times 10^{-4} \text{ mole/kg.}$$

$$(dP/dT)_t = 1.35 \times 10^5 \text{ units/degree}$$

For Points B and C

$$P_t = 3 \times 10^3$$

$$(M_0 - M)_t = 9.4 \times 10^{-4} \text{ mole/kg.}$$

$$(dP/dM_0)_t = 9.54 \times 10^4 \text{ units/mole/kg.}$$

$$[d(M_0 - M)/dM_0]_t = 0.667$$

Case III

As was mentioned before, the equilibrium polymerization of α-methylstyrene is characteristic of Case I-b of the general theory, while sulfur is an example of Case II. Although we have no specific example for Case III-a, we shall present the pertinent formulas for the sake of completeness:[2]

$$P = \frac{1}{(1 - K_3 M)} + 1 = \frac{1}{(1 - K_3 M)} \qquad \text{for } P \gg 1. \quad [18]$$

$$M_0 = KM^2 \left[\frac{(2 - K_3 M)}{(1 - K_3 M)^2}\right] \approx \frac{KM^2}{(1 - K_3 M)^2} \qquad \text{for } P \gg 1. \quad [19]$$

A derived relationship of theoretical interest is:

$$K_3 M_0 \approx 1 + \frac{KP^2}{K_3}. \qquad [20]$$

[2] In the paper describing the general treatment of equilibrium polymerization[1], we presented only the approximate formulas for Case III-a. We are indebted to Dr. B. Nam of I.C.I. for calling to our attention the fact that the formulas originally presented were approximate and for suggesting the corrections.

In the region of high-polymer instability, Eq. [2a] maintains its validity. At the transition temperature, the following equations apply:

$$P_t \approx \left(\frac{K_3}{K}\right)^{1/3}. \tag{21}$$

$$(M_0 - M)_t \approx \frac{KP^2}{K_3{}^2}. \tag{22}$$

$$\left(\frac{dP}{dT}\right)_t \approx \frac{(P^2\Delta H_3{}^\circ - P\Delta H^\circ)}{3RT^2}. \tag{23}$$

$$\left(\frac{dP}{dM_0}\right) \approx \frac{K_3{}^2}{3KP}. \tag{24}$$

If K equals K_3 no sharp transition occurs.

EXPERIMENTAL CONFIRMATION

In general, the results presented for α-methylstyrene have been confirmed experimentally. The work of Worsfold and Bywater and of McCormick has yielded the curve of temperature vs. equilibrium monomer concentration. Unpublished results of Rembaum and Szwarc (10) have shown the existence of small amounts of low molecular weight polymer above the ceiling temperature for α-methylstyrene (using a similar anionic initiator); this supports our calculations qualitatively.

The motion of the floor temperature in liquid sulfur to higher temperatures with increasing dilution has been confirmed qualitatively (11), as has also the variation of equilibrium monomer concentration with temperature for bulk sulfur (9). There are no reliable experimental data for the chain length as a function of temperature, but work of Gardner and Frankel (12) has yielded the degree of polymerization at one temperature, which is in essential agreement (within a factor of 2) with the calculation of Gee (9) and with our work (1).

PREVIOUS CONCEPTION OF CEILING TEMPERATURE PHENOMENA

The occurrence of ceiling temperatures in certain polymerization reactions was noticed over twenty year ago, and discussed by Dainton and Ivin from a kinetic and thermodynamic point of view in a comprehensive review article on the thermodynamics of polymerization. Their kinetic treatment is based on the fact that at the ceiling temperature the rate of propagation equals the rate of depropagation, or, using their symbols

$$T_c = \frac{\Delta H_p}{R \ln\left(\dfrac{A_p M_1}{A_d}\right)}, \tag{25}$$
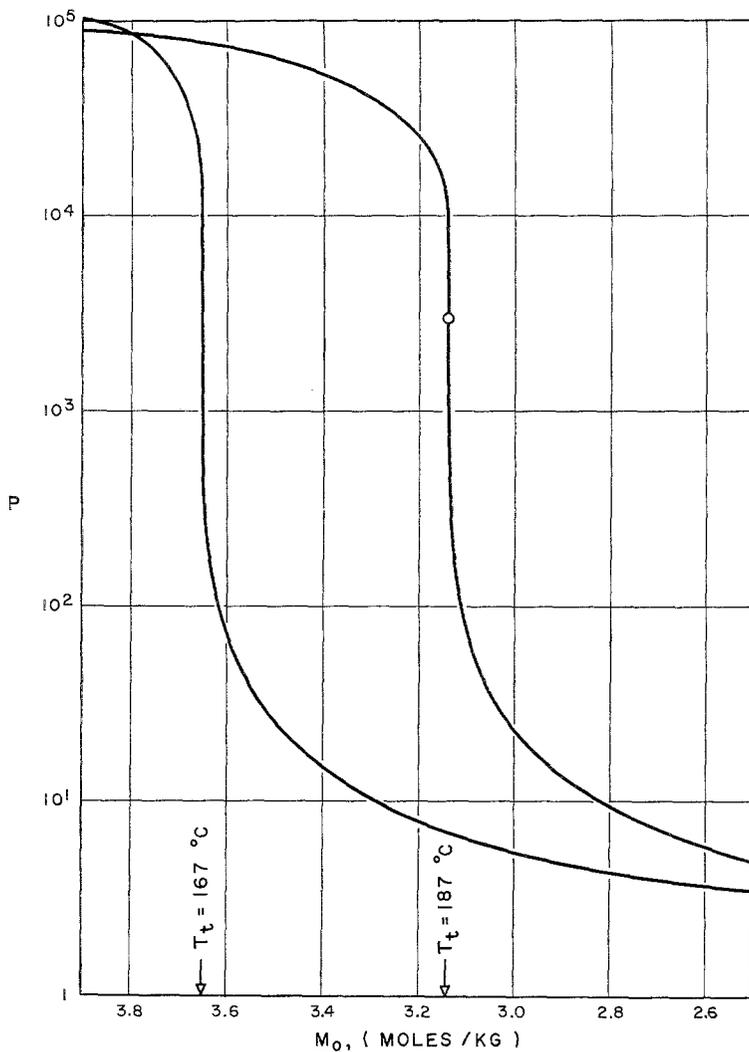
FIG. 6. Degree of polymerization vs. M_0 moles/kg. for sulfur at 167°C. and 187°C.

where ΔH_p is the heat change (of the polymerization reaction) under the prevailing experimental conditions, M_1 is the monomer concentration, and A_p and A_d are the frequency factors in the Arrhenius expression for the rate constants of the propagation and depropagation reactions [$k_d = A_d \exp{(-E_d/RT)}$]. This treatment is satisfactory for polymerization reactions in which the degree of polymerization is determined from kinetic considerations, i.e., the relative magnitudes of the rates of initiation, propagation, termination, etc. However, it seems to us to be inadequate
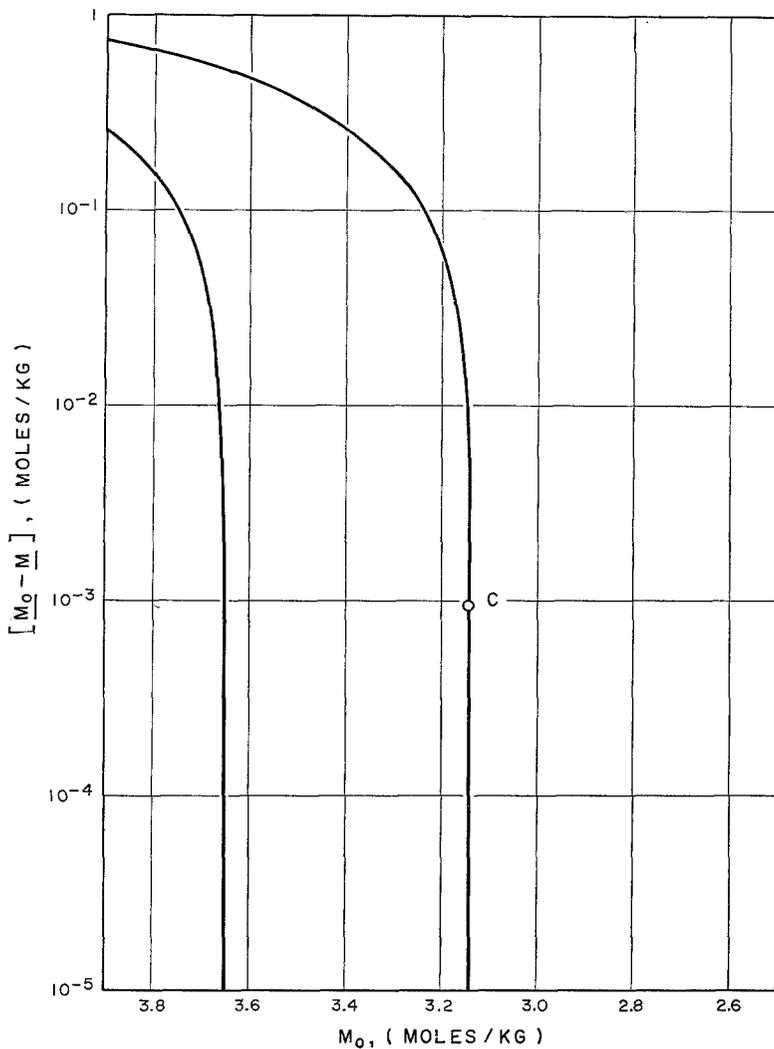
FIG. 7. $(M_0 - M)$ moles/kg. vs. M_0 moles/kg. for sulfur at 167°C. and 187°C.

for systems for which polymer is in equilibrium with its monomer at all temperatures as in α-methylstyrene initiated by organometallics. In such systems the rate of depropagation of the polymer equals the rate of propagation at all temperatures, not only at the ceiling temperature.

Thermodynamically, Dainton and Ivin conceive the ceiling temperature to be that temperature at which the free energy of polymerization (for long-chain polymers) passes from a negative to a positive value as the tempera-

ture is raised, i.e.,

$$T_c = \frac{\Delta H_p}{\Delta S_p},$$

or, defining $\Delta S_p{}^\circ$ as the entropy change for $M_1 = 1$ mole/liter of monomer,

$$T_c = \frac{\Delta H_p}{(\Delta H_p{}^\circ + R \ln M_1)}. \qquad [26]$$

In our treatment, the transition occurs at $K_3 M_0 = 1$. Written in another way, this is

$$M_0 \exp\left(\frac{\Delta S_3{}^\circ}{R}\right) \exp\left(\frac{-\Delta H_3{}^\circ}{RT_t}\right) = 1$$

or

$$\ln M_0 = \frac{-\Delta S_3{}^0}{R} + \frac{\Delta H_3{}^0}{RT_t},$$

which yields

$$T_t = \frac{\Delta H_3{}^\circ}{(\Delta S_3{}^\circ + R \ln M_0)},$$

which is equivalent to equation 26 of Dainton and Ivin. However, the thermodynamic theory of Dainton and Ivin does not yield any indication of the sharpness of the transition or expressions of P versus T and M versus T in the neighborhood of T_t, which our theory has now accomplished.

To obtain sharp transitions it is necessary that K is much smaller than K_3 or that there is a very small amount of initiator in the system.

Molecular Weight Distribution in Equilibrium Polymerization

It can easily be shown that the distribution in equilibrium polymerization, even in the presence of an initiator, is the random distribution. For example, the expression for the mole fraction of x-mers (obtained by dividing the expression for the absolute concentration of x-mers by the total concentration of polymer (1, 8, 13)) is

$$\frac{N_x}{N} = n_x = (K_3 M)^{n-1}(1 - K_3 M).$$

This, by the well-known principles of step reaction polymerization, leads to

$$P_n = 1/(1 - K_3 M);$$

$$P_w = \frac{(1 + K_3 M)}{(1 - K_3 M)};$$

and the heterogeneity index is

$$\text{H.I.} = 1 + K_3 M = 2 - 1/P \approx 2.$$

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APPENDIX

Derivation of formulae, valid exactly at the transition temperature

A. Case I-b

1. Determination of P_t

After setting $K_3 M_0 = 1$ and solving Eq. [5] by the general method for quadratic equations, we obtain

$$P_t = (\tfrac{1}{2}) + [1 + (4/K_3 X_0)]^{1/2}/2.$$

For $P \gg 1$, which is easily obtained with $X_0 \lll 1$, we have

$$P_t \approx (K_3 X_0)^{-1/2}.$$

2. Determination of $(M_0 - M)_t$

Rewriting Eq. [2] as

$$M_0 - M = K_3 X M P^2$$

and substituting

$$M = (1 - 1/P)/K_3$$

and

$$P_t \approx (K_3 X_0)^{-1/2}$$

we obtain

$$(M_0 - M)_t \approx (X_0/K_3)^{1/2}$$

3. Determination of $(dP/dT)_t$.

Since $(dP/dT)_{M_0,X_0} = (dP/dK_3)_{T,M_0,X_0} (dK_3/dT)_{P,M_0,X_0}$, we solve Eq. [5] for $(dP/dK_3)_{T,M_0,X_0}$, Eq. [10] for $(dK_3/dT)_{P,M_0,X_0}$, and eliminate $(X_0/K_3)^{1/2} - 1/K_3$ in the numerator since it is much smaller than $M_0/(K_3X_0)^{1/2}$, we obtain

$$(dP/dT)_t \approx \Delta H_3°/RT_t{}^2[2K_3X_0 - (K_3X_0)^{3/2}]$$

4. Determination of $(dP/dM_0)_t$

We differentiate Eq. [5] with respect to M_0, set $K_3 M_0 = 1$, $(2P - 1) \approx 2P$, and obtain

$$(dP/dM_0)_t \approx \tfrac{1}{2}X_0$$

5. Determination of $[d(M_0 - M)/dT]_t$

Since $M_0 - M \approx PX_0$,

$$d(M_0 - M)/dT \approx X_0(dP/dT).$$

Therefore

$$[d(M_0 - M)/dT]_t \approx X_0\Delta H_3°/RT_t{}^2[2K_3X_0 - (K_3X_0)^{3/2}]$$

6. Determination of $[d(M_0 - M)/dM_0]_t$

Since $M_0 - M \approx PX_0$

$$[d(M_0 - M)/dM_0]_t \approx X_0(dP/dM_0)_t .$$

Therefore

$$[d(M_0 - M)/dM_0]_t \approx \tfrac{1}{2}$$

B. The methods outlined above for obtaining the formulas for Case I-b are very similar to those used in calculating the results for Cases II and III-a. These calculations, therefore, will not be presented here.