

NOTES

A Simple Mathematical Model of Frontal Polymerization

In this paper we present the simplest mathematical description of frontal polymerization. Earlier¹ we pointed out that the existence of a saturated gel layer of poly(methyl methacrylate) (PMMA) in methyl methacrylate (MMA) at the interface between solid polymer and monomer (where the polymerization is autoaccelerated) is the source of frontal polymerization. It has also been shown² that an early convection process completed in a few minutes after contact of the solid PMMA and the liquid monomer produced a uniform "initial" initiator concentration C_I^0 in the MMA solution. Since the overall polymerization takes several days, we take the start of the polymerization process after this convective uniformization of the initiator is completed. The basic simplification of the kinetics comes about by the replacement of the gel layer whose thickness is several millimeters by an infinitely thin gel layer at the solid PMMA interface, taken at $X = X(t)$. This permits us to neglect diffusion in the gel layer and describe the process by means of ordinary differential and algebraic equations. The concentration of monomer in the gel layer C_M^g is directly proportional to the monomer concentration in the liquid $C_M = C_M(t)$, $X(t) < x < l$, where l is the height of the liquid and

$$C_M^g = \kappa C_M \quad (\kappa < 1) \quad (1)$$

where κ is an effective partition coefficient (probably close to the equilibrium value at the given temperature). The rate of polymerization at the gel layer, at $x = X(t)$, is autoaccelerated (due to the Trommsdorff effect) and very much larger than in the bulk of the liquid.

We represent the autoaccelerated rate of polymerization in the gel, by assuming that the termination rate coefficient K_t is significantly smaller than K_t^0 , the termination rate constant in the bulk at small conversion. We approximate K_t , which is a decreasing function of the conversion by the exponential relation:

$$K_t = K_t^0 e^{-\omega(1-\kappa C_M/C_M^0)} \cdot e^{\omega(1-\kappa)} = K_t^0 e^{-\omega\kappa(1-C_M/C_M^0)} \quad (2)$$

where the coefficient ω is a function of the temperature, which effectively vanishes above T_c and C_M^0 is the initial

concentration of monomer. As the solid PMMA advances, the remaining concentration of initiator, C_I , increases at a rate proportional to the decrease of the volume of the liquid, which in turn is proportional to dX/dt in the reaction vessel of fixed cross section. At the same time C_I decreases by the thermal first order decomposition. Thus the overall change in C_I is given by

$$\frac{dC_I}{dt} = -K_i C_I + \gamma \frac{d(X/X_0)}{dt} C_I \quad (3)$$

where X_0 is the initial location of the solid interface and γ is proportionality constant, which is in turn directly proportional to the fixed cross-sectional area of the reaction vessel. The corresponding contribution to dC_M/dt arising from dX/dt is negligible for the monomer solution since it is close to being pure monomer. Under the "steady state" assumption, the rate of polymerization in the liquid is

$$\frac{dC_M}{dt} = -K_p \left(\frac{2fK_i}{K_t^0} \right)^{1/2} \cdot C_M C_I^{1/2} \quad (4)$$

where K_p is the polymerization rate constant, K_i is the rate constant for the first-order thermal decomposition, and f is the initiation efficiency. The increase of the volume of the solid PMMA is proportional to the rate of polymerization in the gel times the specific volume of the polymer, V_p :

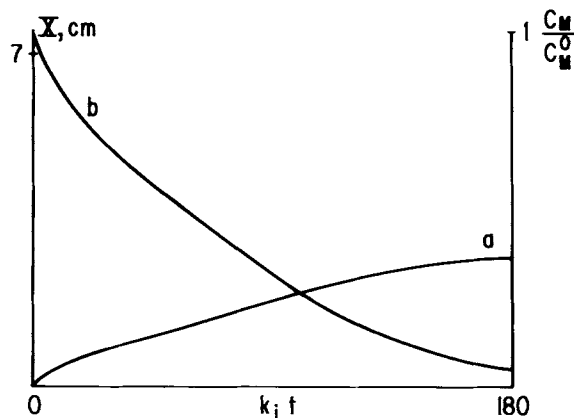


Figure 1 The graph of X and C_M/C_M^0 versus $k_i t$ for $\omega = 2$ ($T < T_c$): (a) $X(t)$; (b) C_M/C_M^0 .

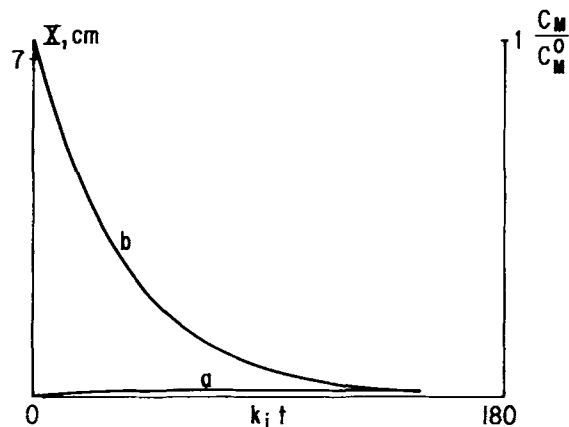


Figure 2 The graph of X and C_M/C_M^0 versus $k_i t$ for $\omega = 0.1$ ($T \approx T_c$): (a) $X(t)$; (b) C_M/C_M^0 .

$$\frac{d(X/X_0)}{dt} = V_p \cdot K e^{(\omega\kappa/2)(1-C_M/C_M^0)} \cdot \kappa C_M \cdot Z^{1/2} C_I^{1/2} \quad (5)$$

where the concentration of the initiator in the gel C_I^g is related to that in the bulk by the effective initiator partition coefficient Z , viz.,

$$C_I^g = Z C_I \quad (6)$$

and

$$K = K_p \left(\frac{2f K_i}{K_t} \right)^{1/2} \quad (7)$$

One finds by elementary means the implicit solution for C_M :

$$t = \int_{C_M^0}^{C_M} \frac{d\eta}{F(\eta)} \quad (8)$$

where

$$F(\eta) = \eta \left[\exp \left(\beta \int_{C_M^0}^{C_M} e^{(\omega\kappa/2)(1-\eta/C_M^0)} d\eta \right) \times \left[(K_i/2) \int_{C_M^0}^{C_M} (1/\eta) \right] \times \exp \left(-\beta \int_{C_M^0}^{C_M} e^{(\omega\kappa/2)(1-\eta/C_M^0)} d\eta \right) - K C_I^{1/2} \right] \quad (9)$$

with

$$\beta = V_p \cdot Z^{1/2} \cdot \kappa \cdot \gamma / 2. \quad (10)$$

Noting that $-1/K(d \ln C_M/dt) = C_I^{1/2}$, we obtain the explicit solution of (5)

$$X/X_0 = V_p \kappa \times Z^{1/2} (2C_M^0/\omega\kappa) (e^{(\omega\kappa/2)(1-C_M/C_M^0)} - 1) \quad (11)$$

which shows that $X(t)$ is an exponential function of conversion in the liquid $(1 - C_M/C_M^0)$, determined by the parameter ω . Clearly for $T > T_c$ for which ω vanishes X remains essentially at zero. For $T < T_c$, ω is finite and X increases significantly with time. This is shown below in Figures 1 and 2 obtained by carrying out the numerical quadrature for C_M , which was then substituted in eq. (11), for the parameter values $C_I^0 = 0.00001$, $C_M^0 = 9.4$, $Z = 0.1$, $\kappa = 0.7$, $\gamma = 2.0$, and $\omega = 2.0$ and 0.1 . These curves are in semiquantitative agreement with experiment.

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