

A Model of Frontal Polymerization Including the Gel Effect

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Frontal polymerization is a process in which a spatially localized reaction zone propagates into a monomer, converting it into a polymer. This new approach to polymer production requires both theoretical and experimental study. Agreement between the existing theoretical and experimental work done on this subject has generally been fairly good. However, experimental results tend to show a higher degree of conversion than theoretical results. The reason for this discrepancy may be attributed to an autoacceleration of the polymerization rate which occurs when conversion has reached a certain point. This autoacceleration is due to a decrease in the termination rate caused by a phenomenon known as the gel effect. In this paper, we develop a mathematical model of the frontal polymerization process, taking the gel effect into consideration. Specifically, we determine how it will affect the degree of conversion, maximum temperature, and propagation velocity of the system.

Keywords: Frontal polymerization; Mathematical modeling; Gel effect

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1. INTRODUCTION

Frontal polymerization is a process in which a spatially localized reaction zone propagates into a monomer, converting it into a polymer. This new approach to polymer production requires both theoretical and experimental study. Agreement between the existing

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theoretical and experimental [3–6,19–25] work done on this subject has generally been fairly good. However, experimental results tend to show a higher degree of conversion than theoretical results [7]. The reason for this discrepancy may be attributed to an autoacceleration of the polymerization rate which occurs when conversion has reached a certain point (for methyl methacrylate in a benzene solution, for example, this point has been shown to be at approximately 50% conversion [14]). This result may, at first, seem counterintuitive, as many theoretical models have shown that the polymerization rate would decrease over time, due to reductions in the concentration of monomer and initiator. If the amount of initiator and fresh monomer is depleted, it would make sense that conversion would slow down, for the simple reason that there will not be large amounts of monomer present to convert. What actually occurs, though, is the opposite. Up until a certain point, the rate of polymerization *does* decrease steadily. However, after this point (the gel point) it actually begins to *increase*. This autoacceleration is due to a decrease in the termination rate caused by a phenomenon known as the gel effect. This phenomenon was first noted in the 1940s [17,26] in the polymerization of methyl methacrylate with a benzoil peroxide initiator, and has since then been studied extensively in batch reactors (see, for example the references in [9]), and in the frontal regime [7,15].

A simplified description of how the gel effect works is as follows. Once the gel effect has occurred, polymer molecules that reach a certain chain length become entangled with other polymer molecules. At this point, the mobility of these molecules (specifically the mobility of the chain ends where the active sites are located) becomes severely reduced. Because of this decrease in mobility, the probability of two polymer chains reacting with each other (a termination reaction) is much lower, greatly reducing the value of the termination rate constant k_t .

In addition, experiments in the non-frontal regime have shown that the initiation and propagation reactions may be similarly affected, but only for temperatures below a certain point (the glass transition temperature) [2]. For the case of frontal polymerization, however, the temperatures are necessarily above this point, so for the system described in this paper, the initiation and propagation reactions are not appreciably affected by the gel effect [7].

Thus beyond the gel point, the system will consist of a combination of large, relatively immobile polymer molecules with many active sites, and smaller monomer molecules whose mobility is comparatively undeterred by the gel effect. The propensity will be for the monomer molecules to attach themselves to the polymers, providing a noticeable increase in the rate of conversion. Again, this was a simplified description of the gel effect, the purpose of which was to provide the necessary background for this paper.

In this paper, we develop a mathematical model of the frontal polymerization process, taking the gel effect into consideration. Specifically, we determine how it will affect the degree of conversion, maximum temperature, and propagation velocity of the system.

2. MATHEMATICAL MODEL

The propagation of free-radical polymerization fronts involves the usual free-radical mechanism [12] consisting of decomposition, initiation, propagation and termination reactions. For the process studied in this paper, the characteristic scale of the polymerization wave is much smaller than the vessel through which it propagates, so that the test vessel (usually a test tube) can be treated as infinite on the scale of the polymerization wave. To study polymerization waves that propagate at a constant speed and do not change their profile in the course of propagation, we introduce a moving coordinate system attached to the wave, in which the wave is a stationary solution. Thus a traveling wave coordinate (x) may be introduced. At one side of the vessel ($x = -\infty$) there is a fresh mixture of monomer and initiator, and on the other side ($x = \infty$) there is the inactive polymer, or products, that are left behind in the wave's wake. The kinetic equations describing this system are written as

$$uI' + k_d I = 0, \quad (2.1)$$

$$uR' - 2fk_d I + k_p RM + k_t R\dot{P} = 0, \quad (2.2)$$

$$uM' + k_p RM + k_p M\dot{P} = 0, \quad (2.3)$$

$$u\dot{P}' - k_p RM + k_t R\dot{P} + k_t \dot{P}^2 = 0, \quad (2.4)$$

$$uP' - k_t R\dot{P} - k_t \dot{P}^2 = 0, \quad (2.5)$$

where u is the propagation velocity of the wave which must be determined in the course of solution of the problem. Here I , R , M , and P denote the concentrations in mol/L of the initiator, free radicals, monomer, and inactive polymer, \dot{P} is the concentration of the polymer radicals, and prime denotes the derivative with respect to x . The quantities k_d , k_p , and k_t are the rate constants for the decomposition, propagation, and termination reactions, respectively, that are all taken in the form of Arrhenius exponentials

$$k_d = k_d^0 \exp(-E_d/R_g T), \quad k_p = k_p^0 \exp(-E_p/R_g T), \\ k_t = k_t^0 \exp(-E_t/R_g T),$$

where R_g is the gas constant, T is the temperature of the mixture, and k_d^0, k_p^0, k_t^0 , and E_d, E_p, E_t are respectively the frequency factors and activation energies of the three types of reactions.

In order to account for the gel effect, we assume that the frequency factor for the termination reaction, k_t^0 , depends on the degree of conversion of the monomer. Specifically,

$$k_t^0 = \begin{cases} k_{t1}^0, & M > M_g, \\ k_{t2}^0, & M \leq M_g, \end{cases} \quad (2.6)$$

where M_g is the prescribed amount of monomer remaining when the gel point is reached, k_{t1}^0 is the frequency factor for the termination reaction prior to, and k_{t2}^0 the frequency factor after, the gel effect has begun (where $k_{t1}^0 > k_{t2}^0$ because termination will be less likely once the gel effect has begun).

Equation (2.1) describes the consumption of the initiator occurring in the decomposition reaction. Here f is an efficiency factor which is necessary to account for the fact that not all of the radicals produced survive to initiate polymer chains. Equation (2.2) describes both the production (the $2fk_dI$ term) and consumption (the k_pRM and $k_tR\dot{P}$ terms) of the free radicals. These radicals are produced in the initiator decomposition reaction and consumed in the propagation and termination reactions. In a similar way, the remaining Eqs. (2.3)–(2.5) describe the change in the concentration of the monomer, polymer radicals and inactive polymer, respectively. Once the gel effect has occurred, it is clear from Eq. (2.4) why the rate of polymerization would be increased.

These kinetic equations must be supplemented by the energy balance in the system, which accounts for thermal diffusion and heat release in the polymerization process. Since the heat release occurs mainly in the propagation step [16], the energy balance takes the form

$$\kappa T'' - uT' + qk_p(RM + M\dot{P}) = 0, \quad (2.7)$$

where κ is the thermal diffusivity of the mixture (assumed to be constant), and q is the increase in temperature associated with converting 1 mol/L of monomer into polymer.

We will study a simplified kinetic system by using a steady state assumption regarding the total concentration of the radicals [8]. It has been documented, initially by Norrish and Brookman [18], that in the bulk polymerization of methyl methacrylate, the steady state assumption does not hold true with the onset of the gel effect. In a later work by Hayden and Melville [13], however, it was shown that the steady state assumption is indeed valid for high enough temperatures, which are achieved in the frontal regime. Under this assumption, the rate of change of the concentration of the radicals, R and \dot{P} , is much smaller than the rates of their production and consumption, so that there is a simple algebraic balance between the amounts of radical and initiator. Under this assumption, Eqs. (2.2)–(2.4) can be reduced to a single equation:

$$uM' - k_{\text{eff}}\sqrt{IM} = 0, \quad (2.8)$$

where the effective rate constant, k_{eff} , preexponential factor, k_{eff}^0 , and activation energy, E_{eff} , are given by

$$k_{\text{eff}} = k_{\text{eff}}^0 \exp(-E_{\text{eff}}/R_g T), \quad k_{\text{eff}}^0 = k_p^0 (2fk_d^0/k_t^0)^{1/2},$$

$$E_{\text{eff}} = E_p + (E_d - E_t)/2.$$

Thus, our model consists of the mass and energy balances (2.1), (2.7), and (2.8), and the boundary conditions at the left ($x = -\infty$) and right ($x = \infty$) ends of the tube. For calculational simplicity, we make a change of variables for the initiator, $I = J^2$, and for

convenience write the modified equations as

$$uJ' + Jk_1(T) = 0, \quad (2.9)$$

$$uM' + JMk_2(T) = 0, \quad (2.10)$$

$$\kappa T'' - uT' + qJMk_2(T) = 0, \quad (2.11)$$

and the boundary conditions at the cold ($x = -\infty$) and hot ($x = +\infty$) boundaries

$$x = -\infty: \quad M = M_0, \quad T = T_0, \quad J = J_0; \quad x = +\infty: \quad T' = 0. \quad (2.12)$$

Here T_0 is the initial temperature, J_0 and M_0 are the amounts of (modified) initiator and monomer present in the initial mixture, and

$$k_1(T) = k_d(T)/2 = k_{01} \exp(-E_1/R_g T), \quad k_{01} = k_d^0/2, \quad E_1 = E_d, \\ k_2(T) = k_{\text{eff}}(T) = k_{02} \exp(-E_2/R_g T), \quad k_{02} = k_{\text{eff}}^0, \quad E_2 = E_{\text{eff}}.$$

With the reaction rates in the form of Arrhenius exponentials, this problem is quite difficult to study analytically. In previous works [10,11] the authors of this paper have circumvented this complexity by replacing the Arrhenius dependence of the reaction rates on temperature, $k_n(T)$ ($n = 1, 2$), by step functions with heights equal to the maximum of the Arrhenius function, and integral values over the range T_0 to T_b being approximately equal. This approach has proven to provide results that are not only correct qualitatively, but also quantitatively. Applying this approach to the problem at hand requires a slight modification to account for the gel effect:

$$\hat{k}_1(T) = \begin{cases} 0, & T < T_1, \\ A_1(T_b), & T > T_1, \end{cases} \quad (2.13)$$

and

$$\hat{k}_2(T) = \begin{cases} 0, & T < T_2, \\ A_2(T_b), & T_2 < T < T_g, \\ A_{2g}(T_b), & T > T_g, \end{cases} \quad (2.14)$$

with

$$\begin{aligned} T_n &= T_b(1 - \epsilon_n), \quad \epsilon_n = R_g T_b / E_n, \quad A_n(T_b) = k_n(T_b) \quad (n = 1, 2), \\ A_{2g}(T_b) &= k_g A_2(T_b), \end{aligned} \quad (2.15)$$

where $k_g = (k_{11}^0/k_{12}^0)^{1/2}$ is a parameter describing the relative strength of the gel effect. Here, T_n ($n = 1, 2$) are the temperatures at which the reactions begin, T_g is the temperature at which the gel point is reached (i.e. where $M = M_g$), ϵ_n are small dimensionless parameters, A_1, A_2, A_{2g} are the heights of the step functions, and $k_1(T_b)$ and $k_2(T_b)$ are the reaction rates evaluated at the maximum temperature, T_b .

It is important to notice that $\hat{k}_2(T)$ is affected by the gel effect, while $\hat{k}_1(T)$ is not. The reason for this, as was mentioned above, is that the only reaction that is appreciably affected by the gel effect in this system is the termination reaction, of which $\hat{k}_1(T)$ is independent.

Since the typical situation is that the activation energy for the decomposition reaction, E_1 , is greater than that for the polymerization reaction, E_2 , formally it is possible for the polymerization reaction to occur prior to the decomposition reaction, which is not consistent with the nature of this model. In order to make up for this inaccuracy of the steady state approximation, we introduce the Heaviside function, $\chi(J_0 - J)$, in the polymerization reaction, rewriting Eqs. (2.10) and (2.11) as

$$uM' + JM\chi(J_0 - J)k_2(T) = 0, \quad (2.16)$$

$$\kappa T'' - uT' + qJM\chi(J_0 - J)k_2(T) = 0. \quad (2.17)$$

Thus, both reactions will begin simultaneously as a result of the Heaviside function, χ . Since the set of equations is invariant under spatial translation, we let the point in space where both reactions begin be $x = 0$. Because we have replaced the Arrhenius-type reaction rates with step functions, the spatial region from $x = -\infty$ to $x = +\infty$ can be divided into three regions: one where neither reaction has begun ($x < 0$, $k_1(T) = k_2(T) = 0$), one in which both reactions have occurred but the gel point has not yet been reached ($0 < x < x_g$, $k_1(T)k_2(T) \neq 0$), and one after the gel point ($x > x_g$, $k_1(T)k_2(T) \neq 0$). Thus Eqs. (2.9), (2.16), and (2.17) can be stated for each of the three

regions as

$$uJ' = 0, \quad uM' = 0, \quad \kappa T'' - uT' = 0, \quad \text{for } x < 0; \quad (2.18)$$

$$\begin{aligned} uJ' + J(x)A_1 &= 0, & uM' + J(x)M(x)A_2 &= 0, \\ \kappa T'' - uT' + qJ(x)M(x)A_2 &= 0, & \text{for } 0 < x < x_g; \end{aligned} \quad (2.19)$$

$$\begin{aligned} uJ' + J(x)A_1 &= 0, & uM' + J(x)M(x)A_{2g} &= 0, \\ \kappa T'' - uT' + qJ(x)M(x)A_{2g} &= 0, & \text{for } x > x_g. \end{aligned} \quad (2.20)$$

The boundary conditions are given in (2.12). In addition, there are the following matching conditions at $x=0$ and $x=x_g$ that constitute continuity of the mass, temperature and temperature gradient distributions in the polymerization wave:

$$\begin{aligned} J(0^-) &= J(0^+), & M(0^-) &= M(0^+), \\ T(0^-) &= T(0^+) = T_1, & T'(0^-) &= T'(0^+), \end{aligned} \quad (2.21)$$

$$\begin{aligned} J(x_g^-) &= J(x_g^+), & M(x_g^-) &= M(x_g^+) = M_g, \\ T(x_g^-) &= T(x_g^+) = T_g, & T'(x_g^-) &= T'(x_g^+). \end{aligned} \quad (2.22)$$

3. SOLUTION

Solution of the Eqs. (2.18) in the $x < 0$ region, satisfying the boundary conditions (2.12), as well as the third condition in (2.21) can be readily found as

$$J(x) = J_0, \quad (3.1)$$

$$M(x) = M_0, \quad (3.2)$$

$$T(x) = T_0 + (T_1 - T_0)e^{(u/\kappa)x}. \quad (3.3)$$

Solution of the Eqs. (2.19) in the $x_g > x > 0$ region satisfying the matching conditions (2.21) are given by

$$J(x) = J_0 e^{-(A_1/u)x}, \quad (3.4)$$

$$M(x) = M_0 \exp[(A_2/A_1)(J(x) - J_0)], \quad (3.5)$$

$$\begin{aligned} T(x) &= T_0 + (T_1 - T_0)e^{-(u/\kappa)x} + q(M_0 - M(x)) \\ &\quad - (qA_2/u)e^{-(u/\kappa)x} \int_0^x J(\tau)M(\tau)e^{-(u/\kappa)\tau} d\tau. \end{aligned} \quad (3.6)$$

Solution of the Eqs. (2.20) in the $x > x_g$ region satisfying the matching conditions (2.22) are given by

$$J(x) = J_0 e^{-(A_1/u)x}, \quad (3.7)$$

$$M(x) = M_0 \exp[(A_2/A_1)[(J(x_g) - J_0) - k_g(J(x_g) - J(x))]], \quad (3.8)$$

$$T(x) = T_0 + (T_1 - T_0)e^{-(u/\kappa)x} + q(M_0 - M(x)) \\ - (qA_2/u)J_0M_0e^{-(u/\kappa)x-\alpha}(I_1(0) - k_gGI_2(x)), \quad (3.9)$$

where

$$I_1(\zeta) = \int_{\zeta}^{x_g} \exp[\alpha e^{-(A_1/u)\tau} - (A_1/u)\tau - (u/\kappa)\tau] d\tau,$$

$$I_2(\zeta) = \int_{x_g}^{\zeta} \exp[k_g\alpha e^{-(A_1/u)\tau} - (A_1/u)\tau - (u/\kappa)\tau] d\tau,$$

$$\alpha = A_2J_0/A_1 \quad \text{and} \quad G = \exp[\alpha e^{-(A_1/u)x_g(1-k_g)}].$$

These equations involve an unknown propagation velocity u , the gel point x_g , and the maximum temperature T_b . Taking the limit as $x \rightarrow \infty$ in (3.8), (3.9) we find that

$$M_b = M_0 G e^{-\alpha}, \quad (3.10)$$

$$T_b = T_0 + q(M_0 - M_b), \quad (3.11)$$

$$T_b(1 - \epsilon_1) = T_0 + (qA_2/u)J_0M_0e^{-\alpha}(I_1(0) + k_gGI_2(\infty)). \quad (3.12)$$

Equation (3.12) was derived from Eq. (3.9), using the condition that the gradient of the temperature must be zero at $x = \infty$.

Finally, taking Eq. (3.8) at the gel point gives us an equation for x_g :

$$M_g = M_0 \exp[\alpha(e^{-(A_1/u)x_g} - 1)]. \quad (3.13)$$

Thus, we have derived four equations (3.10)–(3.13), for the four unknown quantities u , T_b , M_b , and x_g . To study these equations it is convenient to define the following non-dimensional parameters:

$$\xi = (u/\kappa)x_g, \quad v = \kappa A_2 J_0 / u^2, \quad m = M_b / M_0, \quad \text{and} \quad m_g = M_g / M_0, \quad (3.14)$$

where ξ is a non-dimensional spatial parameter, v is related to the propagation velocity, m is the ratio of remaining monomer to initial monomer, and m_g is the ratio of monomer remaining at the gel point to initial monomer. We can now rewrite Eqs. (3.10)–(3.13) as

$$m = 1 - (T_b - T_0)/qM_0, \quad (3.15)$$

$$m = Ge^{-\alpha}, \quad (3.16)$$

$$T_b(1 - \epsilon_1) = T_0 + qM_0 v e^{-\alpha} (u/\kappa) (I_1(0) + k_g G I_2(0)), \quad (3.17)$$

$$m_g = \exp \left[\alpha \left(e^{-(v/\alpha)\xi} - 1 \right) \right]. \quad (3.18)$$

Eliminating m from (3.15) and (3.16) we derive an equation for T_b

$$Ge^{-\alpha} = 1 - (T_b - T_0)/qM_0. \quad (3.19)$$

In order to derive an expression for u , the propagation velocity, we must examine Eq. (3.17). The expression involving integrals in Eq. (3.17), $(u/\kappa)(I_1(0) + k_g G I_2(\infty))$, can be rewritten as

$$(\alpha/v) \left(\int_{e^{-(v/\alpha)\xi}}^1 e^{\alpha y} y^{\alpha/v} dy + k_g G \int_0^{e^{-(v/\alpha)\xi}} e^{k_g \alpha y} y^{\alpha/v} dy \right). \quad (3.20)$$

These integrals can be further simplified. First, portions of the arguments of the integrals can be approximated by realizing that certain quantities are small relative to others. Similarly to previous work [11], we will assume that

$$v = \kappa A_2 J_0 / u^2 = O(1/\epsilon) \gg 1,$$

which, along with the fact that

$$\alpha = A_2 J_0 / A_1 = O(1),$$

allows us to make the approximation

$$y^{\alpha/v} \sim 1 + (\alpha/v) \ln y.$$

Next, from Eq. (3.18),

$$e^{-(v/\alpha)\xi} = 1 + \ln(m_g)/\alpha.$$

Substituting these results as well as the definitions of v and ϵ_1 given in Eqs. (2.15) and (3.14) into Eq. (3.17) and simplifying gives us an expression for the (dimensional) propagation velocity

$$u = (T_b/\alpha) [(\kappa A_2 R_g J_0)/(E_1 q M_0 \sigma)]^{1/2}, \quad (3.21)$$

where

$$-\sigma = e^{-\alpha} \left(\int_{1+\ln(m_g)/\alpha}^1 e^{\alpha y} \ln y dy + G k_g \int_0^{1+\ln(m_g)/\alpha} e^{k_g \alpha y} \ln y dy \right).$$

4. RESULTS

Examining Eqs. (3.15), (3.19), and (3.21) numerically, we were able to observe how variation of the ratio of the rate constants for the termination reactions before and after the gel effect (k_g) affected the maximum temperature in the front (T_b), the final degree of conversion of the monomer (M_b), and the propagation velocity (u).

The following parameter values were used [1]:

$$\begin{aligned} k_d^0 &= 4 \cdot 10^{12} / \text{s}, & k_p^0 &= 5 \cdot 10^6 \text{ L}/(\text{s mol}), & k_{t1}^0 &= 3 \cdot 10^7 \text{ L}/(\text{s mol}), \\ E_d &= 27 \text{ kcal/mol}, & E_p &= 4.7 \text{ kcal/mol}, & E_t &= 0.7 \text{ kcal/mol}, \\ q &= 33.24 \text{ L} \cdot \text{K/mol}, & \kappa &= 0.0014 \text{ cm}^2/\text{s}. \end{aligned} \quad (4.1)$$

In addition, we fixed the initial temperature (T_0) at 300 K, the initial amount of monomer present (M_0) at 6 mol/L, and the gel point (M_g) at $\frac{1}{2}M_0$.

Increases in k_g (achieved by decreasing k_{t2}) caused marked increases in polymerization (Fig. 1). In fact, when k_g was increased to 10 (i.e., $k_{t2} = \frac{1}{10}k_{t1}$), conversion was nearly complete. This is quite different from previous theoretical results [10] where the maximum conversion achieved was never more than ninety percent. This increase in conversion is, as was mentioned above, due to the lower termination rate coupled with a negligible change in the rates of initiation and propagation. These results can also be predicted by

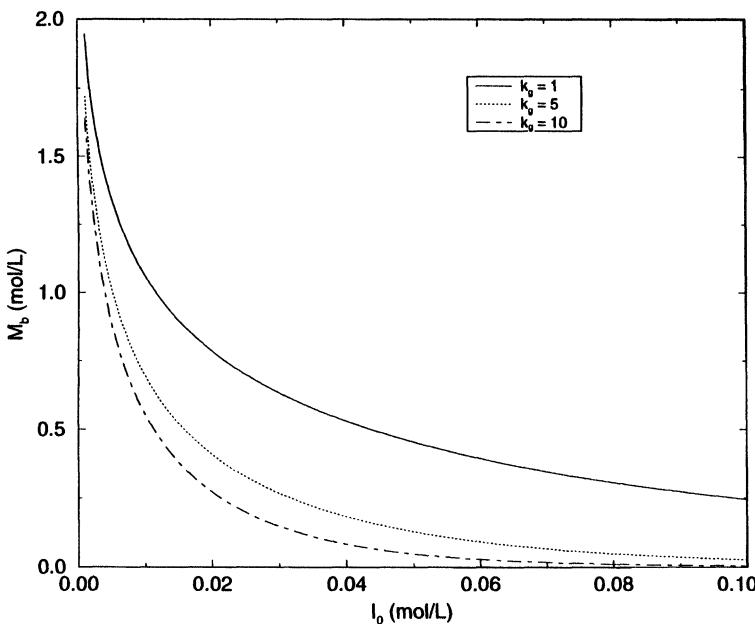


FIGURE 1 Effect of changes in k_g on the degree of conversion.

examining Eq. (3.10)

$$M_b = M_0 G e^{-\alpha}.$$

As k_g increases linearly, G will decrease exponentially, with M_b following suit.

With increases in k_g , the propagation velocity of the system was higher (Fig. 2). This result can be explained by the fact that with termination being less likely, the propensity will be for more propagation reactions to occur. Because the propagation reactions are highly exothermic, the more of them that take place, the greater the amount of heat that will be produced, which will in turn cause increases in the front velocity. Another way to understand this result is by examining the equation for σ . The quantity preceding the second integral, Gk_g , will become very small for large values of k_g . The result of this will be a decrease in the value of σ , and (see Eq. (3.21)) a corresponding increase in the front velocity.

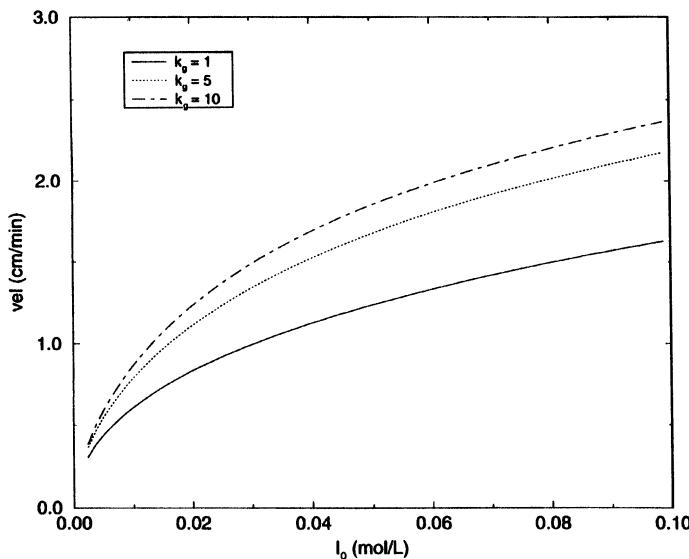


FIGURE 2 Effect of changes in k_g on the propagation velocity.

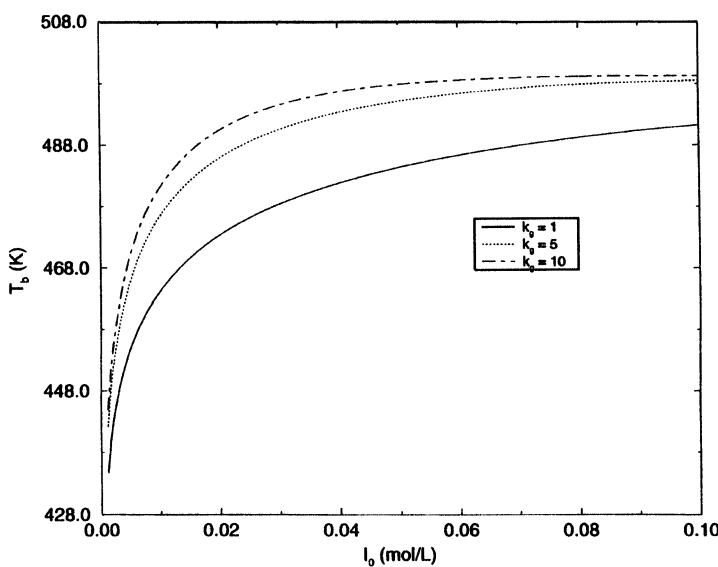


FIGURE 3 Effect of changes in k_g on the maximum temperature of the system.

The maximum temperature of the system tended to increase with increases in k_g (see Fig. 3). The reason for this higher temperature can be seen by examining Eq. (3.11)

$$T_b = T_0 + q(M_0 - M_b).$$

As the gel effect becomes more pronounced, conversion increases, decreasing the value of M_b , thereby increasing the maximum temperature.

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