

# Frontal polymerization with encapsulated monomer

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**Abstract** Thermal frontal polymerization (TFP) is the process that converts monomers into polymers by means of a spatially localized self-propagating thermal reaction wave. Free radical frontal polymerization systems can suffer from a limited pot life, i.e. the systems will spontaneously polymerize while remaining at ambient pressure and temperature before they can be used. One way to avoid this undesirable spontaneous polymerization is by microencapsulating the monomer. The release of monomer from its shell can be modeled as a temperature dependent or temperature independent reaction; we consider both cases. Conditions are established which reduce the current model to the standard FP model and extinction limits are determined by employing an asymptotic analysis of the reaction zone in the limit as the reaction zone shrinks to an interface.

**Keywords** Frontal polymerization · Mathematical modeling · Traveling wave · Encapsulated monomer

## 1 Introduction

Frontal polymerization (FP) is the process in which a spatially localized reaction zone propagates through a mixture of monomer and initiator converting it into polymer. In TFP, the polymerization wave propagates due to diffusion of heat released in exothermic chemical reactions. In the simplest case, a test tube filled with a monomer/initiator mixture is heated at one end causing primary radicals formed by the initiator decomposition to react with monomer molecules thereby beginning the polymer chain.

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The chemical reactions that lengthen the polymer chain are exothermic. The heat released by these reactions diffuse into adjacent layers of the reactant mixture and initiate the reactions there. The process repeats, and in this way, a self-sustained polymerization wave propagates along the tube. Under appropriate conditions, the wave propagates uniformly with constant velocity with unreacted monomer in its path and polymer in its wake.

It is the apparent simplicity of FP which has made it an attractive way of synthesizing polymeric materials. One advantage of FP is the ability to prepare materials quickly and to vary the morphology in a controlled manner. Another advantage of FP is that in energy savings. FP is an approach to polymer synthesis which exploits the heat released by the chemical reactions. Therefore, no further energy input is needed to sustain the wave, just the temporary heat source applied to start the reactions.

Frontal polymerization studies began in the former Soviet Union in 1972 by Chichilo et al. [1] to synthesize polymethyl methacrylate. This process was performed as a polymerization analog to the Self—propagating High—temperature synthesis (SHS) of materials in which combustion waves are used to make a wide range of ceramics and intermetallic compounds. The experiments were carried out in high pressure conditions ( $>3,000$  atm) to suppress instabilities and monomer boiling [2,3]. It was found that the front velocity increased with increasing initiator concentration and pressure. Methyl methacrylate (MMA) as the monomer was used for many years in early studies but extensive boiling at high temperatures made this monomer of limited use. The discovery that methacrylic acid made possible the formation of a traveling front at ambient pressure and temperature gave impetus to FP as a way of synthesizing new materials [4]. Much interest was generated in discovering new chemical systems capable of polymerizing frontally. Subsequent experimental work demonstrated the feasibility of propagating fronts in solutions of thermal free-radical initiators in a variety of high boiling point monomers—both liquid [4–6] and solid [7,8]. The first mathematical model was proposed by Goldfeder et al. which addressed several important characteristics of FP such as the speed of the polymerization wave, the final amount of reacted monomer, and the temperature inside the reaction zone [9]. Subsequent work by Goldfeder et al. used the same model but this time took into account heat losses [10]. A more thorough analysis of nonadiabatic FP was conducted by Spade [11] and several other mathematical studies expanded the scope of polymerization kinetics [12–14]. This gave the mathematical backing to FP experiments where the authors utilized different techniques to affect the morphology and microstructure of the final product as a way to synthesize materials with specific properties [15,16].

FP is often not useful in real world applications because the monomer/initiator systems can suffer from a limited pot life, meaning that over a period of time the systems will polymerize before they can be used. This is called spontaneous polymerization (SP). In experiments, this can compete with and sometimes extinguish FP waves [17]. To be effective, the polymerization system should be almost inert at room temperature and highly reactive when heated. Typically, an additive is used in the mixture to increase pot life [17,18]. Another way to extend pot life is by encapsulating the initiator. This prevents radicals formed by initiator decomposition from coming into contact with the monomer molecules. This was done by Pojman et al. and they observed increases in pot life for different polymerization systems [19].

They observed dramatic increases in pot life from hours to weeks in some systems and from a few days to several weeks in other systems. We deduce that microencapsulating the monomer molecules will also extend pot life. If instead the monomer molecules are protected by a shell, then free-radicals will be prevented from reacting with the monomer molecules, thus preventing SP.

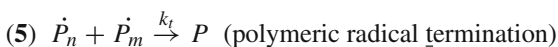
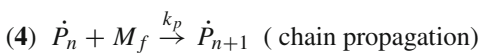
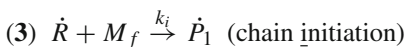
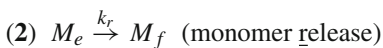
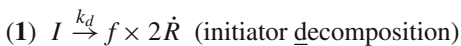
In the present work, we formulate a non-adiabatic free-radical frontal polymerization model with encapsulated monomer. Experimental and numerical results motivate us to seek one-dimensional traveling wave solutions to the problem. We then examine under what conditions the current model simplifies to the standard FP model in the absence of heat losses. Lastly, we take into account heat losses and derive an extinction limit to the traveling wave.

## 2 Mathematical model

The model of thermal free-radical polymerization was first proposed in [9] and studied in more detail in [11]. FP with microencapsulated monomer involves the following steps:

1. upon heating, an unstable initiator molecule decomposes (usually a peroxide or a nitrile) to form “primary” free radicals,
2. the monomer molecules are released from the microcapsule shells when a certain temperature is attained,
3. once released, the monomer molecules react with the free radicals to initiate a polymer chain,
4. the polymer chain is lengthened by successive addition of monomer molecules,
5. two polymer radicals are neutralized by combination

Polymerization stops when the initiator is depleted. Some of the assumptions made in [11] are repeated here for convenience. The phenomenon of free-radical frontal polymerization with microencapsulated monomer involves the following five step chemical process:



where  $I$ ,  $\dot{R}$ ,  $M_e$ ,  $M_f$ ,  $\dot{P}_n$ , and  $P$  represent initiator, free radical, microencapsulated monomer, free monomer, polymer radical with  $n$  monomer units, and a neutralized polymer radical respectively. The assumed mode of termination of two polymer radicals is by combination. This is also true for free radicals formed by the initiator. Due to their proximity when they appear in the reactant mixture, a non-negligible amount

of free radicals are terminated by combination. As a result, only a certain amount of free radicals are available to initiate polymer chains. The fraction of free radicals that are active compared to the total number of radicals formed by the initiator is called the *efficiency* ( $f$ ) [20]. It is an empirical parameter which is determined experimentally.

$$f = \frac{\text{radicals incorporated into polymer}}{\text{radicals formed by initiator}}$$

The inclusion of  $f$  in reaction (1) takes into account  $\dot{R} + \dot{R} \rightarrow R - R$  as a side reaction. The coefficient 2 represents the fact that two radicals are formed by decomposition of one initiator molecule. The reaction rate parameters have the form of Arrhenius exponentials

$$k_j = k_j(T) = k_j^0 \exp(-E_j/(R_g T)), \quad j = r, d, i, p, t$$

where  $R_g$  is the gas constant,  $T$  is the temperature of the mixture and  $k_j^0$  and  $E_j$  are the pre-exponential factor and activation energy respectively of the reaction designated by  $j$ . The subscripts correspond to the five reaction steps – initiator decomposition  $d$ , monomer release  $r$ , chain initiation  $i$ , chain propagation  $p$ , and polymer radical termination  $t$ . The change of the concentrations of the different species with time can be described by the following kinetic equations:

$$\frac{d\tilde{I}}{d\tilde{t}} = -k_d \tilde{I}, \tag{2.1}$$

$$\frac{d\tilde{R}}{d\tilde{t}} = 2fk_d \tilde{I} - k_i \tilde{R} \tilde{M}_f, \tag{2.2}$$

$$\frac{d\tilde{M}_e}{d\tilde{t}} = -k_r \tilde{M}_e, \tag{2.3}$$

$$\frac{d\tilde{M}_f}{d\tilde{t}} = k_r \tilde{M}_e - k_i \tilde{R} \tilde{M}_f - k_p \tilde{P} \tilde{M}_f, \tag{2.4}$$

$$\frac{d\tilde{P}}{d\tilde{t}} = k_i \tilde{R} \tilde{M}_f - k_t \tilde{P}^2, \tag{2.5}$$

$$\frac{d\tilde{P}}{d\tilde{t}} = k_t \tilde{P}^2, \tag{2.6}$$

where  $\tilde{I}$ ,  $\tilde{R}$ ,  $\tilde{M}_e$ ,  $\tilde{M}_f$ ,  $\tilde{P}$ , and  $\tilde{P}$  represent the concentrations in mol/L of the corresponding species. The notation for the polymer radical concentration contains an implied summation (i.e.,  $\tilde{P} = \sum_n \tilde{P}_n$ ). These equations must be supplemented by the energy balance in the system, which accounts for thermal diffusion and heat release in the polymerization process. Reactions (1) and (2) are typically endothermic whereas reactions (3)–(5) are exothermic. Although all the reactions contribute to the enthalpy of the system, the heat release due to the chain initiation and chain propagation reactions is most significant [21]. Considering the heat release due to reactions (3) and (4)

and ignoring all other heats of reaction, the energy balance takes the form of a reaction diffusion equation

$$\frac{\partial T}{\partial \tilde{t}} = \kappa \frac{\partial^2 T}{\partial \tilde{x}^2} + q \tilde{M}_f (k_i \tilde{R} + k_p \tilde{P}) - \tilde{\alpha} (T - T_0), \quad (2.7)$$

where  $\kappa > 0$  is the thermal diffusivity of the mixture,  $q > 0$  is the rise in temperature induced per unit concentration of reacted monomer,  $\tilde{\alpha} \geq 0$  is the heat loss parameter, and  $T_0$  is the ambient temperature. We reduce the number of reaction rate parameters by assuming that  $k_i = k_p$  [11]. Also, by assuming  $\tilde{R} \ll \tilde{P}$  [11] and introducing the combined concentration of radicals  $\tilde{D} \equiv \tilde{R} + \tilde{P}$ , we can reduce the number of equations by summing Eqs. (2.2) and (2.5)

$$\frac{\partial \tilde{I}}{\partial \tilde{t}} = -k_d \tilde{I}, \quad (2.8)$$

$$\frac{\partial \tilde{D}}{\partial \tilde{t}} = 2f k_d \tilde{I} - k_t \tilde{D}^2, \quad (2.9)$$

$$\frac{\partial \tilde{M}_e}{\partial \tilde{t}} = -k_r \tilde{M}_e, \quad (2.10)$$

$$\frac{\partial \tilde{M}_f}{\partial \tilde{t}} = k_r \tilde{M}_e - k_p \tilde{D} \tilde{M}_f, \quad (2.11)$$

$$\frac{\partial \tilde{P}}{\partial \tilde{t}} = k_t \tilde{D}^2, \quad (2.12)$$

$$\frac{\partial T}{\partial \tilde{t}} = \kappa \frac{\partial^2 T}{\partial \tilde{x}^2} + q k_p \tilde{M}_f \tilde{D} - \tilde{\alpha} (T - T_0). \quad (2.13)$$

Now that we have an equation describing the total radical concentration with time, we can use the steady state assumption (SSA) to obtain an approximate solution for the total radical concentration. It means that the rate of appearance of  $\tilde{D}$  is equal to its rate of disappearance which corresponds to steady state conditions. It mathematically means that when the system of equations is appropriately nondimensionalized, the equation for  $\tilde{D}$  has a small parameter in front of its time derivative. Setting this parameter to zero means that we disregard a short transient from the initial state to the steady state and consider only the outer solution. Setting  $\partial \tilde{D} / \partial \tilde{t} = 0$  we have

$$\tilde{D} \approx \sqrt{\frac{2f k_d \tilde{I}}{k_t}}.$$

which upon substitution in Eqs. (2.11) and (2.13), together with Eqs. (2.8) and (2.10) yields

$$\frac{\partial \tilde{I}}{\partial \tilde{t}} = -k_d \tilde{I}, \quad \tilde{I}(0) = I_0 \tag{2.14}$$

$$\frac{\partial \tilde{M}_e}{\partial \tilde{t}} = -k_r \tilde{M}_e, \quad \tilde{M}_e(0) = M_0 \tag{2.15}$$

$$\frac{\partial \tilde{M}_f}{\partial \tilde{t}} = k_r \tilde{M}_e - k_{eff} \tilde{M}_f \sqrt{\tilde{I}}, \quad \tilde{M}_f(0) = 0 \tag{2.16}$$

$$\frac{\partial T}{\partial \tilde{t}} = \kappa \frac{\partial^2 T}{\partial \tilde{x}^2} + q k_{eff} \tilde{M}_f \sqrt{\tilde{I}} - \tilde{\alpha}(T - T_0), \quad T(\tilde{x}, 0) = T_0 \tag{2.17}$$

where  $k_{eff} \equiv k_p \sqrt{2fk_d/k_t}$ . Since  $\tilde{P}$  decouples from Eqns. (2.8)–(2.11) and (2.13), we can disregard it since we are only concerned with the evolution of the monomer, the initiator, and the temperature. The boundary conditions will be prescribed later. We now look to nondimensionalize Eqns. (2.14)–(2.17).

### 2.1 Nondimensionalization

It is convenient to nondimensionalize Eqns. (2.14)–(2.17) with the following variables

$$\theta = \frac{T - T_a}{T_a - T_0}, \quad M_e = \frac{\tilde{M}_e}{M_0}, \quad M_f = \frac{\tilde{M}_f}{M_0},$$

$$I = \frac{\tilde{I}}{I_0}, \quad x = \tilde{x}/x_*, \quad t = \tilde{t}/t_*$$

and the following nondimensional parameters

$$Z_i = \frac{E_i(T_a - T_0)}{RT_a^2}, \quad \delta = \frac{T_a - T_0}{T_a}, \quad A_d = k_d(T_a)t_*$$

$$A_r = k_r(T_a)t_*, \quad \alpha = \tilde{\alpha}t_*$$

using the following time and spatial scales respectively

$$t_* = \left( k_{eff}(T_a)\sqrt{I_0} \right)^{-1}, \quad x_* = \sqrt{\kappa t_*}.$$

Here,  $T_a = T_0 + qM_0$  is the adiabatic reaction temperature. Next,  $Z_i$  is the Zeldovich number which can be thought of as the nondimensional activation energy of the corresponding reaction. The subscript  $i$  is  $r$  for release,  $d$  for decomposition, and  $e = eff$  for polymerization. The resulting nondimensional system of equations is

$$\frac{\partial I}{\partial t} = -A_d e^{\frac{Z_d \theta}{1+\delta \theta}} I, \quad I(0) = 1, \tag{2.18}$$

$$\frac{\partial M_e}{\partial t} = -A_r e^{\frac{Z_r \theta}{1+\delta \theta}} M_e, \quad M_e(0) = 1, \tag{2.19}$$

$$\frac{\partial M_f}{\partial t} = A_r e^{\frac{Z_r \theta}{1+\delta \theta}} M_e - e^{\frac{Z_e \theta}{1+\delta \theta}} M_f \sqrt{I}, \quad M_f(0) = 0, \tag{2.20}$$

**Table 1** Values used in paper

$k_d^0$	[1/s]	$4 \times 10^{12}$	$q$	[L K/mol]	33
$k_p^0$	[L/s mol]	$5 \times 10^6$	$\kappa$	[cm <sup>2</sup> /s]	0.0014
$k_r^0$	[L/s mol]	$3 \times 10^7$	$M_0$	[mol/L]	6
$E_d$	[kJ/mol]	113	$I_0$	[mol/L]	0.01
$E_p$	[kJ/mol]	20	$T_0$	[K]	300
$E_t$	[kJ/mol]	3	$R_g$	[kJ/mol K]	0.008315

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial x^2} + e^{\frac{Z_e \theta}{1 + \delta \theta}} M_f \sqrt{I} - \alpha(\theta + 1), \quad \theta(x, 0) = -1. \quad (2.21)$$

A typical value for  $f$ , and one that is often found in the literature is 0.5 [20]. Since there are no predetermined values for  $k_r^0$ ,  $E_r$ , or  $\tilde{\alpha}$ , the parameters  $A_r$ ,  $Z_r$ , and  $\alpha$  will be adjusted. For the remainder of the paper, we will use the parameter values [9] presented in Table 1 to obtain the numerical results found in the figures. The corresponding nondimensional parameter values are

$$A_d = 2.27, \quad Z_d = 10.85, \quad Z_e = 7.2, \quad \text{and} \quad \delta = 0.4.$$

The numerical results were computed using MATLAB's ode45 differential equation solver.

## 2.2 Traveling wave

We now look for polymerization waves traveling along a tube of length  $\ell$ . We introduce the traveling wave coordinate  $\xi = x + ut$ , where  $u$  is the speed of the polymerization wave that has to be found in the course of the solution of the problem. The region over which the major variations of temperature and species concentrations occur are typically much smaller than the length of the tube, therefore, on the scale of the polymerization wave, the tube can be considered infinite. Ahead of the polymerization wave where reactions have yet to take place, the initial temperature and species concentrations are

$$\xi \rightarrow -\infty : \quad \theta = -1, I = 1, M_e = 1, M_f = 0$$

and the final state behind the wave when all the reactions have come to completion

$$\xi \rightarrow \infty : \quad \frac{d\theta}{d\xi} = 0.$$

The system of equation written in the moving coordinate system is

$$u \frac{dI}{d\xi} = -k_d(\theta)I, \quad I(0) = 1, \quad (2.22)$$

$$u \frac{dM_e}{d\xi} = -k_r(\theta)M_e, \quad M_e(0) = 1, \tag{2.23}$$

$$u \frac{dM_f}{d\xi} = k_r(\theta)M_e - k_e(\theta)M_f\sqrt{I}, \quad M_f(0) = 0, \tag{2.24}$$

$$u \frac{d\theta}{d\xi} = \frac{d^2\theta}{d\xi^2} + k_e(\theta)M_f\sqrt{I} - \alpha(\theta + 1), \quad \theta(0) = \theta_{ig}, \quad \left. \frac{d\theta}{d\xi} \right|_{\xi \rightarrow \infty} = 0 \tag{2.25}$$

where

$$k_i(\theta) = A_i \exp(Z_i\theta/(1 + \delta\theta)) \quad \text{for } i = d, e, r.$$

Here,  $\theta_{ig}$  is the Arrhenius cut-off temperature. We introduce this temperature because we assume that below some temperature, reactions do not take place. Also,  $\theta$  reaches  $\theta_{ig}$  at  $\xi = 0$ . Due to the translational invariance of the problem,  $\theta$  could reach  $\theta_{ig}$  at any point along the  $\xi$ -axis, but zero is a natural starting point.

We first consider the adiabatic problem in which case  $\alpha = 0$ . Adding Eqs. (2.23), (2.24), and (2.25) with  $\alpha = 0$  and applying the boundary condition as  $\xi \rightarrow -\infty$ , we obtain the first integral of the system

$$\frac{d\theta}{d\xi} = u(M_e + M_f + \theta). \tag{2.26}$$

Evaluating (2.26) as  $\xi \rightarrow \infty$  allows us to express  $M_b \equiv M_f|_{\xi \rightarrow \infty}$  in terms of the temperature inside the reaction zone  $\theta_b$  as

$$M_b = -\theta_b.$$

This is true because in the adiabatic case, the temperatures in the reaction zone and at infinity are equal. We have set  $M_e|_{\xi \rightarrow \infty}$  equal to zero because the exact solution of  $M_e$  is

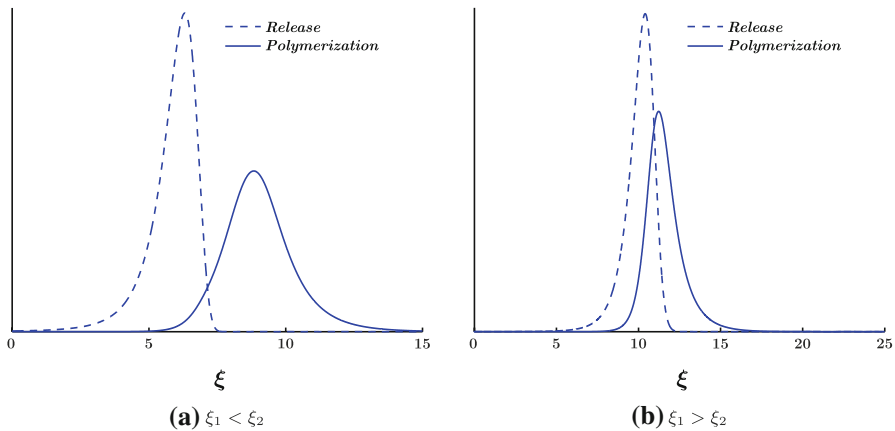
$$M_e(\xi) = \exp\left(-\frac{1}{u} \int_0^\xi k_r[\theta(\tau)] d\tau\right)$$

and  $k_r[\theta(\tau)]$  is positive.

### 3 Separated reactions

One limiting case of thermal FP with microencapsulated monomer is when a sufficient amount of monomer is released ahead of the reaction zone. The wave then travels as if the monomer was never initially encapsulated. This corresponds to a regular FP wave. Therefore, theoretically, the polymerization wave velocity, the final degree of conversion, and the final temperature of the system should in fact agree with the same





**Fig. 1** Release reaction rate ( $r_1$ ) and polymerization reaction rate ( $r_2$ ) profiles that are **a** separated and **b** unseparated in space

quantities as those found from the standard FP model [22]. In this section, we consider under what conditions the FP model with microencapsulated monomer reduces to the standard FP model. To make comparisons with the standard model, we set  $\alpha = 0$ .

If a sufficient amount of monomer is released ahead of the reaction zone, then the release reaction occurs in a different region than the polymerization reaction. For the reactions to be considered separated in space, we require that the second point of inflection  $\xi_1$  of the release reaction rate profile be less than the first point of inflection  $\xi_2$  of the polymerization reaction rate profile. Figure 1 illustrates this idea. The equations for  $\xi_1$  and  $\xi_2$  are found by calculating the second derivative with respect to  $\xi$  of the first and second terms of the right hand side of Eq. (2.24), respectively and setting them to zero.

$$R(\xi) \equiv \frac{d^2}{d\xi^2} (k_r(\theta) M_e) = 0, \quad R(\xi_1) = 0$$

$$S(\xi) \equiv \frac{d^2}{d\xi^2} (k_e(\theta) M_f \sqrt{I}) = 0, \quad S(\xi_2) = 0$$

At the point  $\xi_1$ , we assume that polymerization has not yet begun and therefore, the amount of monomer is conserved, i.e.  $M_e + M_f = 1$ . This allows us to write  $R$  as a function of  $\theta$  rather than a function of  $\xi$ . This motivates us to look not for a point along the  $\xi$ -axis, but rather the temperature at the point on the  $\xi$ -axis. Therefore, instead of requiring that  $\xi_1 < \xi_2$ , we now require that  $\theta_1 < \theta_2$  where  $\theta_{1,2} = \theta(\xi_{1,2})$ . This is true because  $\theta(\xi)$  is non-decreasing. Near  $\theta_1$ ,

$$R(\theta) \sim k_r(\theta) \left( \frac{1}{u^2} k_r(\theta) - 3Z_r \frac{1 + \theta}{(1 + \delta\theta)^2} \right) \quad (3.1)$$

At the point  $\xi_2$ , we assume that  $M_e(\xi)$  has approached its steady state which involves setting  $M_e(\xi) = 0$ . We also assume that polymerization has just only begun, there-

fore, only a small amount of monomer and initiator have been consumed and they are still approximately at their initial concentrations. Moreover, the activation energy of decomposition in free-radical polymerization is typically much larger than the activation energies of the propagation and termination reactions and thus govern the kinetics of the polymerization process. As a result,  $Z_d > Z_e$  which implies that  $k_d(\theta) < k_e(\theta)$  for  $\theta$  not too close to zero. With this information, we are able to write  $S$  as a function of  $\theta$ . Near the point  $\theta_2$ ,

$$S(\theta) \sim Z_e u^2 \frac{1 + \theta}{(1 + \delta\theta)^2} \left( Z_e u^2 \frac{1 + \theta}{(1 + \delta\theta)^2} - k_e(\theta) \left( 3 + \frac{1}{1 + \theta} \right) \right). \tag{3.2}$$

By requiring that  $\theta_1 < \theta_2$  where  $\theta_1$  and  $\theta_2$  are the roots of Eqs. (3.1) and (3.2), respectively, we are able to establish a lower bound on  $A_r$

$$A_r > 3u_0^2 Z_r \exp \left( \frac{\theta_2(1 - 2\delta - Z_r)}{1 + \delta\theta_2} \right) \tag{3.3}$$

where  $\theta_2$  is given approximately by setting  $S(\theta)$  to zero, taking the logarithm, using a two-term Taylor expansion for  $\theta$  small, and solving. If  $A_r$  satisfies (3.3), then the reactions are separate and the model simplifies to the standard FP model. That being the case, we can use the velocity formula [22] which applies to a regular FP wave.

$$\tilde{u}^2 = \frac{\kappa k_d^0 R_g T_b^2}{2q M_0 E_d} \exp \left( j_0 - \frac{E_d}{R_g T_b} \right) \left( \int_0^{j_0} \frac{e^s - 1}{s} ds \right)^{-1}, \quad u_0 = \frac{t_*}{x_*} \tilde{u} \tag{3.4}$$

where

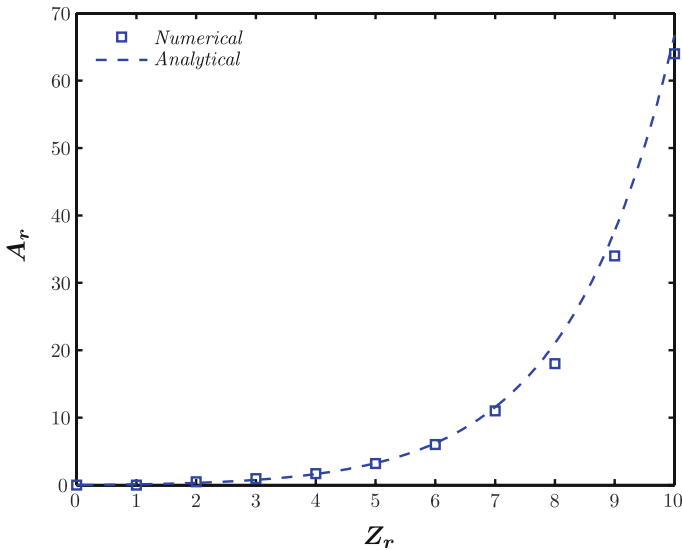
$$j_0(T_b) \equiv \frac{2\sqrt{I_0} k_{eff}^0}{k_d^0} \exp \left( \frac{E_d - E_{eff}}{R_g T_b} \right),$$

and  $T_b$  is determined by the equation

$$T_b = T_0 + q M_0 \left( 1 - e^{-j_0(T_b)} \right). \tag{3.5}$$

This is why we replaced  $u$  in (3.3) with  $u_0$ . To test the accuracy of the restriction imposed on  $A_r$ , we compared numerical results with inequality (3.3) as shown in Fig. 2. There appears to be very good agreement between the results. As  $Z_r$  increases,  $A_r$  must increase exponentially fast. This is not surprising. As  $Z_r$  gets large, the release reaction zone shrinks to an interface. This can be seen by looking at the solution of  $M_e(\theta)$  for  $Z_r$  large,

$$M_e(\theta) = \exp \left( -\frac{k_r(\theta)(1 + \delta\theta)^2}{Z_r u^2(1 + \theta)} \right), \quad Z_r \rightarrow \infty$$



**Fig. 2** Inequality (3.3) gives a region in the  $(Z_r, A_r)$ -plane. For  $A_r$  above the dotted line/boxes, the release reaction occurs ahead of the polymerization reaction

which is found by using Laplace's method for integrals. This has the effect of moving the point of inflection of the reaction rate curve  $r_1$  (see Fig. 1) to the right where  $r_1$  is near zero. This in effect makes it more difficult to separate the two regions.

#### 4 Heat losses

We now study FP with microencapsulated monomer in the presence of heat losses. The existence of the traveling wave will depend on the parameter  $\alpha$ . If the heat loss level is too high for a given amount of available monomer, the wave will be extinguished. We assume that the release reaction rate  $k_r(\theta)$  is temperature independent and attempt to derive an analytical expression for the extinction limit. The extinction limit  $\alpha_{cr}$  is the threshold value in which for  $\alpha > \alpha_{cr}$ , no traveling wave solutions exist.

The monomer is released into the mixture once the temperature reaches  $\theta_{ig}$ . Since the monomer is sequestered from the initiator, if  $\theta_{ig}$  is too high, the microcapsules will not release the monomer upon heating and polymerization will not occur. In order for this type of FP to work, the microcapsules must release the monomer below the temperature in the reaction zone.

The structure of the wave is as follows. There are two regions to be studied.

*Region 1:*  $-\infty < \xi < 0$  The temperature is too low for reactions to begin. At  $\xi = 0$ ,  $\theta_{ig}$  is reached and the monomer is released at a temperature independent rate  $A_r M_e$ .

*Region 2:*  $0 \leq \xi < L$  The monomer is being released. Polymerization and decomposition reactions occur at  $\xi = L$  where the point  $L$  is the location of the reaction zone.

We assume that the reaction zone shrinks to an interface at an unknown point  $L$ . This behavior occurs if  $Z_d$  is sufficiently large. We conclude that ahead of the reaction zone, for  $\xi < L$ , neither decomposition nor polymerization reactions have begun. In region 1, the temperature satisfies the following boundary value problem

$$\frac{d^2\theta}{d\xi^2} - u \frac{d\theta}{d\xi} - \alpha(\theta + 1) = 0, \quad \theta(-\infty) = -1, \quad \theta(0) = \theta_{ig} \tag{4.1}$$

yielding

$$\theta(\xi) = -1 + (1 + \theta_{ig})e^{\mu\xi}, \tag{4.2}$$

where  $\mu = u(1 + \sqrt{1 + 4\beta})/2$  and  $\beta = \alpha/u^2$ . Also in this region,

$$I(\xi) = 1, \quad M_e(\xi) = 1, \quad M_f(\xi) = 0.$$

In region 2, the temperature Eq. (4.2) still holds true since polymerization has not yet begun. Here too  $I(\xi) = 1$ , but  $M_e$  and  $M_f$  are no longer constant. They satisfy the equations

$$\frac{dM_e}{d\xi} = -\frac{A_r}{u}M_e, \quad \frac{dM_f}{d\xi} = \frac{A_r}{u}M_e \tag{4.3}$$

with the boundary conditions  $M_e(0) = 1$  and  $M_f(0) = 0$  so that

$$M_f(\xi) = 1 - e^{-\frac{A_r}{u}\xi}, \quad M_e(\xi) = e^{-\frac{A_r}{u}\xi}$$

At the point  $L$ :

$$\theta(L) \equiv \theta_L = -1 + (1 + \theta_{ig})e^{\mu L}, \tag{4.4}$$

$$M_f(L) \equiv M_L = 1 - e^{-\frac{A_r}{u}L}. \tag{4.5}$$

From Eq. (3.4), we are given the velocity of the wave as a function of the temperature  $T_b$  inside the reaction zone. After nondimensionalizing and using  $\theta_L$  instead of  $\theta_b$  as the reaction zone temperature [23], we get

$$u^2 = \frac{k_d(\theta_L)(1 + \delta\theta_L)^2}{2Z_dM_L} f(j_0), \tag{4.6}$$

where

$$f(j_0) = e^{j_0} \left( \int_0^{j_0} \frac{e^s - 1}{s} ds \right)^{-1}, \quad j_0 \equiv 2 \frac{k_e(\theta_L)}{k_d(\theta_L)}.$$

By analyzing the equations in the reaction zone (for a more complete analysis of these equations see [22]),

$$M_b = M_L e^{-j_0}. \quad (4.7)$$

The jump in the temperature gradient across the reaction zone is [22]

$$\left. \frac{d\theta}{d\xi} \right|_{\xi=L^+} - \left. \frac{d\theta}{d\xi} \right|_{\xi=L^-} = -u(M_L - M_b).$$

Assuming that  $\left. \frac{d\theta}{d\xi} \right|_{\xi=L^+}$  is negligible as is the case with normal FP [22, 23], the above equation together with (4.2) yields

$$\mu(1 + \theta_{ig})e^{\mu L} = u(M_L - M_b). \quad (4.8)$$

From Eq. (4.4)

$$(1 + \theta_{ig})e^{\mu L} = (1 + \theta_L)$$

so that Eq. (4.8) becomes

$$\mu(1 + \theta_L) = u(M_L - M_b). \quad (4.9)$$

Five equations have been derived for the five unknown quantities  $L$ ,  $\theta_L$ ,  $M_b$ ,  $M_L$ , and  $u$ . They are repeated here for convenience.

$$M_b = M_L e^{-j_0} \quad (1)$$

$$M_L = 1 - e^{-\frac{A_r}{u}L} \quad (2)$$

$$\theta_L = -1 + (1 + \theta_{ig})e^{\mu L} \quad (3)$$

$$u^2 = \frac{k_d(\theta_L)(1 + \delta\theta_L)^2}{2Z_d M_L} f(j_0) \quad (4)$$

$$\mu(1 + \theta_L) = u(M_L - M_b) \quad (5)$$

Using  $M_b$  and  $M_L$  from Eqs. (1) and (4), respectively in Eq. (5), we obtain

$$1 + \sqrt{1 + 4\beta} = \frac{k_d(\theta_L)(1 + \delta\theta_L)^2 f(j_0)(1 - e^{-j_0})}{Z_d u^2(1 + \theta_L)}. \quad (4.10)$$

Substitution of  $e^L$  from Eq. (3) into Eq. (2) yields

$$\left( \frac{1 + \theta_{ig}}{1 + \theta_L} \right)^{\frac{A_r}{\mu u}} = 1 - M_L. \quad (4.11)$$

Taking the natural logarithm, we get

$$\frac{A_r}{\mu u} \ln \left( \frac{1 + \theta_{ig}}{1 + \theta_L} \right) = \ln (1 - M_L) \sim -M_L - \frac{1}{2} M_L^2 + O \left( M_L^3 \right). \quad (4.12)$$

Using only the leading order term of the expansion where  $M_L$  is taken from Eq. (4), we get

$$1 + \sqrt{1 + 4\beta} = -\frac{4Z_d A_r \ln \left( \frac{1 + \theta_{ig}}{1 + \theta_L} \right)}{k_d(\theta_L)(1 + \delta\theta_L)^2 f(j_0)}. \quad (4.13)$$

Setting Eqs. (4.10) and (4.13) equal to one another gives us the velocity of the wave as a function of  $\theta_L$ .

$$u^2 = -\frac{k_d^2(\theta_L) (1 + \delta\theta_L)^4 f^2(j_0)(1 - e^{-j_0})}{4A_r Z_d^2 \ln \left( \frac{1 + \theta_{ig}}{1 + \theta_L} \right) (1 + \theta_L)}$$

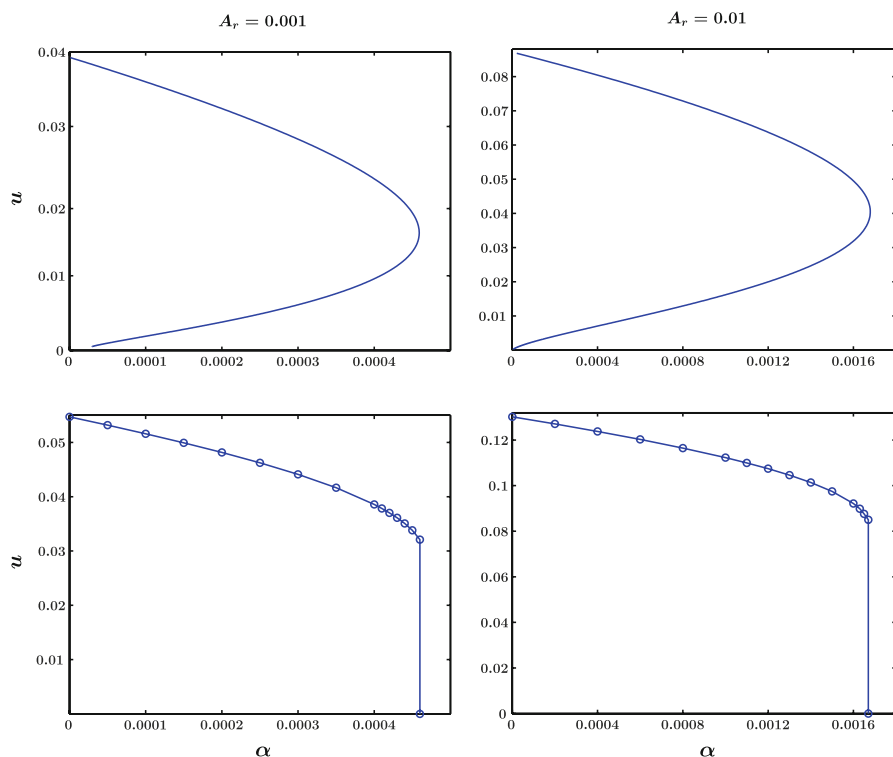
To derive the equation for  $\alpha$  as a function of  $\theta_L$ , the  $O(M_L^2)$  is kept in Eq. (4.12). Solving directly, we obtain

$$\alpha = u^2 B (1 + B)$$

where

$$B \equiv -\frac{2A_r Z_d \ln \left( \frac{1 + \theta_{ig}}{1 + \theta_L} \right) (1 - e^{-j_0})}{A_r Z_d \ln \left( \frac{1 + \theta_{ig}}{1 + \theta_L} \right) (1 + \theta_L) - k_d(\theta_L) (1 + \delta\theta_L)^2 f(j_0) (1 - e^{-j_0})}.$$

Both  $\alpha$  and  $u$  are parametric equations with  $\theta_L$  as the parameter. The parametric curve is given by the solid line shown in Fig. 3. The extinction limit is given by the maximum value of  $\alpha$ . In Fig. 3, the analytical results are shown on the top while the numerical results are shown on the bottom for  $A_r = 0.001$  and  $A_r = 0.01$ . There is good agreement between these two values. The differences in velocity are caused by an inaccuracy in the analysis of the standard FP model. This however, does not cause an inaccuracy in the extinction limits. Without performing a linear stability analysis, we can deduce that the lower branch of the curve where  $du/d\alpha > 0$  in the  $(\alpha, u)$ -plane is unstable. This can be justified physically. Increasing the amount of heat lost in the system increases the velocity of the wave. The results shown in Fig. 3 can be explained physically. When  $A_r$  is very small, there is less available monomer to participate in polymerization reactions and therefore, less heat is released due to the exothermicity of reactions (3) and (4). As a result, the wave is not very resistant against extinction and a small amount of heat lost can extinguish the wave. The opposite is also true. When  $A_r$  increases, there is more available monomer, more heat is released, and the wave becomes more resistant to extinction. As a result, a larger amount of heat lost (a greater value for  $\alpha$ ) is required to extinguish the wave. It is reasonable to conclude that



**Fig. 3** Analytical (*top*) and numerical (*bottom*) extinction limits of the wave for  $A_r = 0.001$  and  $A_r = 0.01$ . For  $A_r = 0.001$ , the analytical and numerical extinction limits are  $\alpha_{cr} \approx 0.00046$  and  $\alpha_{cr} \approx 0.00046$ , respectively while for  $A_r = 0.01$ , the analytical and numerical extinction limits are  $\alpha_{cr} \approx 0.0017$  and  $\alpha_{cr} \approx 0.00167$ , respectively

as  $A_r$  increases even further, the extinction limit will remain the same since essentially the same amount of monomer is present.

## 5 Conclusion

The goal of encapsulating the monomer in free-radical frontal polymerization experiments is to extend the pot life of the system thus preventing SP. SP can interfere with and even prevent normal FP. To be effective, the polymerization system should be almost inert at low temperatures and highly reactive when heated. This is achieved through microencapsulation. Microencapsulation works because free radicals formed by initiator decomposition cannot react with encapsulated monomer molecules.

The starting point of the formulation of the standard model for FP was given by reactions (1), and (3)–(5). We then modeled the monomer release as a first order reaction thereby introducing a new element, reaction (2), into the chemical equations. We considered two cases—one where reaction (2) is temperature dependent and another when it is temperature independent. For the temperature dependent case, we considered the conditions in which the model in Sect. 2 reduced to the standard FP model.

We found that if the release reaction zone and the polymerization reaction zone were sufficiently separated in space, the model would reduce. This happens if  $A_r$  increases like  $O\left(Z_r e^{Z_r}\right)$ .

In Sect. 4, we took reaction (2) to be temperature independent and were able to derive analytically an extinction limit for the traveling wave. This was done by means of an asymptotic analysis of the reaction zone in the limit as the reaction zone shrinks to an interface. The issue of heat losses is important since an insufficient amount of monomer available to participate in polymerization reactions may result in a chemical process so slow that heat losses will extinguish the wave. The capsule shells can also act as a filler and remove heat from the reaction front resulting in extinction.

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