

# Thermal Stability of Polymerization Reactors

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## Synopsis

Temperature rises which occur in the early stages of polymerization in batch reactors are discussed. Comparisons between experimental results and a reactor model shows that realistic predictions of temperature rises can be made when the model allows for changes in density and specific heat of the reaction fluid. In the case of styrene polymerization, the neglect of density and specific heat changes leads to the prediction of large temperature increases, which are not found in practice. When allowance for these changes in physical properties is made, agreement between theoretical prediction and experimental results is good.

## INTRODUCTION

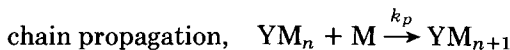
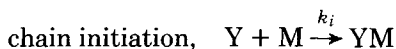
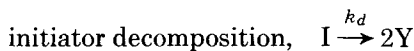
The characteristics of a polymer, which is produced by the free-radical polymerization of a vinyl monomer, depend on reaction conditions. Control of reaction conditions is important but not always easy to achieve. In particular, control of reaction temperature can be difficult because the thermal conductivity of the reaction fluid is low and the heat of reaction is relatively high. The formation of "hot spots" becomes possible. At high conversions, increases in viscosity make mixing more difficult and may lead to thermal instabilities. Even at low conversions, when mixing is relatively easy, it is possible for thermal runaway to occur.

Biesenberger et al.<sup>1</sup> used a computer simulation to determine thermal ignition boundaries for a chain-addition polymerization in a well-mixed batch reactor. They showed that reactor behavior could be very sensitive to small changes in process conditions. Experiments have shown that such sensitivity can be observed in practice.<sup>2</sup> Although trends in thermal behavior have been examined experimentally, accurate correlations between experimental results and the predictions of reactor "models" are relatively rare. Accuracy in such predictions is highly desirable because the safe and successful operation of a polymerization reactor is not possible unless both the existence and location of boundaries are established.

In this paper, it will be shown that small changes in physical properties (which accompany all polymerization reactions) can influence the thermal behavior of a polymerization reactor. This observation has important implications in the design of temperature control procedures. It will also be shown that if these small changes are taken into account, agreement can be obtained between the predictions of a simple reactor model and experimental results. The polymerization of styrene will be used for illustration purposes; the necessary data are available for this reaction.<sup>2</sup>

### THE KINETIC SCHEME

The essential reaction scheme is given below. Free radicals are generated by the thermal decomposition of an initiator I:



In each of these reaction steps, kinetic order corresponds with molecularity. Symbols are listed below.

In the case of styrene polymerization, free radicals can be generated from thermal reaction of the monomer also. This is a second-order reaction which has been characterized previously<sup>3</sup> and is incorporated in the subsequent procedures.

Material balances lead to the following equations:

$$\frac{d(V C_M)}{dt} = -k_p C_M C_Y V$$

$$\frac{d(V C_I)}{dt} = -k_d C_I V$$

$$\frac{d(V C_Y)}{dt} = (2k_d f C_I - k_t C_Y^2 + k_x C_M^2) V$$

$$\frac{d(V \rho S T)}{dt} = -\Delta H k_p C_M C_Y V - UA(T - T_c)$$

The term  $k_x C_M^2$  accounts for thermal generation of radicals from the monomer. Previous work<sup>4</sup> has shown that  $k_x \equiv k_t (k/k_p)^2$ , where  $k$  is the overall rate coefficient for the second-order noncatalyzed polymerization. The density and specific heat of the reaction mixture are given by the following expressions<sup>4</sup>:

$$\rho = a_1 + a_2 C_M + a_3 T$$

$$S = b_1 + b_2 T + b_3 T^2$$

The rate coefficients conform to Arrhenius expressions.<sup>5,6</sup> Values for the activation energies and Arrhenius constants are given below. The values for  $P_d$ ,  $E_d$ , and  $f$  apply to benzoyl peroxide. Over the temperature range used in the illustrations the enthalpy of polymerization will be virtually constant at 73.15 kJ·mol<sup>-1</sup>.<sup>7</sup>

Since the fluid density is a variable, the volume of the reaction mixture will not be constant but is given by

$$V = V_0 \rho_0 / (a_1 + a_2 C_M + a_3 T)$$

Differentiation and subsequent manipulation of the above equations leads to

TABLE I  
Experimental Conditions (2)

Run no.	V/L	$C_{I0}$	$T_R$ ( $^{\circ}C$ )
34	0.0027	0.07	97.5
35	0.0025	0.07	95
43	0.0032	0.07	97.5
85	0.00254	0.10	90

a set of four differential equations which express  $dT/dt$ ,  $dC_M/dt$ ,  $dC_I/dt$ , and  $dC_Y/dt$  as functions of  $T$ ,  $C_M$ ,  $C_I$ , and  $C_Y$ . Once initial conditions have been established, these equations may be solved numerically. In this work, the initial conditions that were chosen were the same as those used in the experimental work of Sebastian and Biesenberger.<sup>2</sup> A fourth-order Runge-Kutta procedure was used for solving the equations. Values for  $U \cdot A$  were obtained from calculations based on the geometry of the experimental reactor and the values for  $U/L$  given by Sebastian and Biesenberger. Their assumption, that the reaction vessel had the heat transport characteristics of an infinite cylinder, is used here also.

Table I shows conditions and run numbers used in the experiments<sup>2</sup>;  $T_R$ , the temperature of the heat exchange fluid, is also the initial temperature of the reaction mixture.

## RESULTS

Solutions to the equations given above are shown in Figures 1 and 2. In all cases, separate solutions have been obtained when density and specific heat are taken as constant. For this latter condition the density and specific heat were

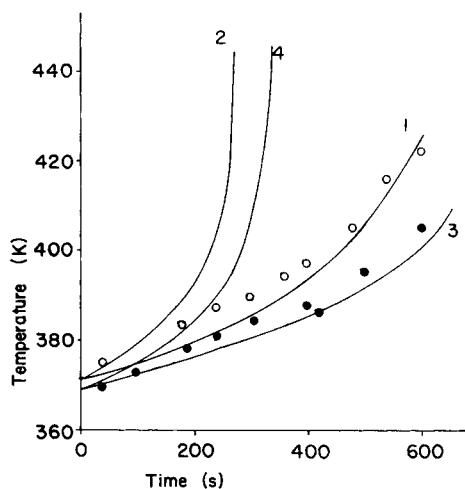


Fig. 1. Changes of reaction temperature with time: (O) experimental results for run 34 (Table I), curve 1 solution of equations for conditions of run 34 and curve 2 solution of equations neglecting changes in density and specific heat; (●) experimental results for run 35, curve 3 solution of equations for conditions of run 35 and curve 4 solution of equations neglecting changes in density and specific heat.

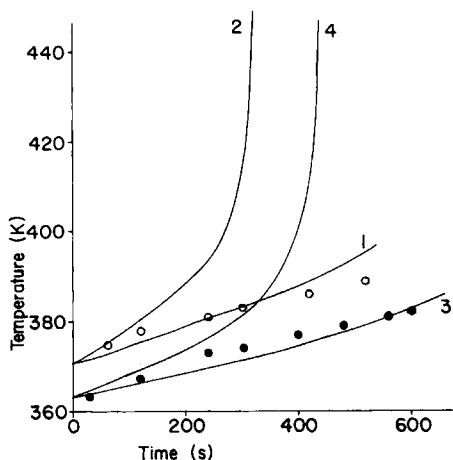


Fig. 2. Changes in reaction temperature with time: (○) experimental results for run 43 (Table I), curve 1 solution of equations for conditions of run 43 and curve 2 solution of equations neglecting changes in density and specific heat; (●) experimental for conditions of run 85, curve 4 solution of equations neglecting changes in density and specific heat.

assumed to remain at values which would have been expected at the start of the reaction.

It can be seen that the experimental results are consistent with the predictions when allowances are made for changes in density and specific heat. However, if these changes are neglected, the solutions to the differential equations deviate markedly from experimental observation. Greater deviations might be encountered if density and specific heat had been assigned their values at 25°C. The changes in these physical properties are not very large, but good agreement between theory and experiment is not obtained unless they are taken into account.

During the course of polymerization, other changes in physical properties will occur also. In the later stages of polymerization increases in viscosity can be expected. This will lead to a reduction in the value of the rate coefficient for chain termination.<sup>8</sup> For the conditions described here, conversions are low enough for viscosity effects to be neglected. Equations which describe the whole range of conversion should take the effects of viscosity into account. This is not a simple matter because the relationships between  $k_t$ , conversion, viscosity, and degree of polymerization are complicated and not understood fully.

In the experiments cited here, thermal runaway was a distinct possibility, even at low conversion. A reactor model which does not take changes in specific heat and density into account will predict temperature rises which are much greater than those which are found in practice (see curves 2 and 4 in Figures 1 and 2). Such a model will fail to discriminate between stable and unstable conditions at reactor startup and is, therefore, of little use in process control.

## NOMENCLATURE

$a_1$	a constant ( $1.3187 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$ )
$a_2$	a constant ( $-0.01769 \text{ kg}\cdot\text{mol}^{-1}$ )

$a_3$	a constant ( $-8.858 \text{ kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$ )
$A$	heat transfer area ( $\text{m}^2$ )
$b_1$	a constant ( $1.938 \text{ kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )
$b_2$	a constant ( $-3.77 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-2}$ )
$b_3$	a constant ( $0.0105 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-3}$ )
$C_I$	concentration of initiator ( $\text{mol}\cdot\text{m}^{-3}$ )
$C_{I_0}$	initial value of $C_I$ ( $\text{mol}\cdot\text{m}^{-3}$ )
$C_M$	concentration of monomer ( $\text{mol}\cdot\text{m}^{-3}$ )
$C_Y$	concentration of radicals ( $\text{mol}\cdot\text{m}^{-3}$ )
$E$	activation energy for thermal polymerization ( $86.0 \text{ kJ}\cdot\text{mol}^{-1}$ )
$E_d$	activation energy for initiator decomposition ( $119.5 \text{ kJ}\cdot\text{mol}^{-1}$ )
$E_p$	activation energy for chain propagation ( $32.6 \text{ kJ}\cdot\text{mol}^{-1}$ )
$E_t$	activation energy for chain termination ( $10.0 \text{ kJ}\cdot\text{mol}^{-1}$ )
$f$	initiation efficiency (0.8)
$\Delta H$	enthalpy of polymerization ( $73.15 \text{ kJ}\cdot\text{mol}^{-1}$ )
$I$	initiator (benzoyl peroxide)
$k$	rate coefficient for thermal polymerization ( $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )
$k_d$	rate coefficient for initiator decomposition ( $\text{s}^{-1}$ )
$k_i$	rate coefficient for chain initiation ( $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )
$k_p$	rate coefficient for chain propagation ( $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )
$k_t$	rate coefficient for chain termination ( $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )
$k_x$	rate coefficient for thermal initiation ( $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )
$M$	monomer (styrene)
$P$	Arrhenius constant for thermal polymerization ( $10^3 \text{ m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )
$P_d$	Arrhenius constant for initiator decomposition ( $10^{13} \text{ s}^{-1}$ )
$P_p$	Arrhenius constant for chain propagation ( $2.2 \times 10^4 \text{ m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )
$P_t$	Arrhenius constant for chain termination ( $2.6 \times 10^6 \text{ m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )
$S$	specific heat ( $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )
$t$	time (s)
$T$	reactor temperature (K)
$T_c$	temperature of heat transfer fluid (K)
$T_R$	initial value of $T$ (K)
$U$	heat transfer coefficient ( $\text{J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$ )
$V$	volume ( $\text{m}^3$ )
$V_0$	initial value of $V$ ( $\text{m}^3$ )
$Y, Y_{M_n}, Y_{M_{n+1}}$	free radicals
$\rho$	density ( $\text{kg}\cdot\text{m}^{-3}$ )
$\rho_0$	initial value of $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )

## References

1. J. A. Biesenberger, R. Capinpin, and J. C. Yang, *Polym. Eng. Sci.*, **16**, 101 (1976).
2. D. H. Sebastian and J. A. Biesenberger, *Polym. Eng. Sci.*, **16**, 117 (1976).
3. B. W. Brooks, *Chem. Eng. Sci.*, **36**, 589 (1981).
4. B. W. Brooks, *Chem. Eng. Sci.*, **34**, 1417 (1979).
5. G. C. Eastman, *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper, Eds., Elsevier, Amsterdam, 1976, Vol. 14A, Chap. 3.
6. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, 1975.
7. *Encyclopedia of Polymer Science and Technology*, Vol. 11, Wiley, New York, 1969.
8. B. W. Brooks, *Proc. Roy. Soc. London, A*, **357**, 183 (1977).

Received December 8, 1981

Accepted August 25, 1982