Kinetics of NBMA Polymerization in a Starved Feed Reactor

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ABSTRACT: A starved feed reactor (SFR) is a semibatch polymerization reactor in which initiator and monomer are fed slowly into a fixed amount of solvent. The polymerization is carried out isothermally at elevated temperatures. The added initiator decomposes instantaneously, and the added monomer polymerizes immediately. The monomer concentration in the SFR is very low, ideally approaching zero. The reactor is in a starved status for reactants. The molecular weight of the product polymer can be effectively controlled by the feed ratio of monomer to initiator. This article presents a study on the kinetics of NBMA polymerization in an SFR. The model parameters were regressed with the experimental data. Although the mass fraction of polymer in the SFR was high (higher than 50%), viscosity was not high and the "gel effect" was weak because of the low molecular weight of the products. It was found that the termination rate constant is a power function of polymer concentration, and the lumped rate constant, $k_p/(k_t^0)^{1/2}$, can be modeled by the Arrhenius equation. The initiator efficiency, f, remained constant at a temperature less than 120°C, and increased with the temperature increasing at temperatures greater 120°C. The other parameters remained constant in the experiment range. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2068–2075, 2001

Key words: kinetics model; radical polymerization; starved feed reactor; *n*-butyl methacrylate

INTRODUCTION

A starved feed reactor (SFR) is a semibatch polymerization reactor into which initiator and monomer are fed continuously. The molecular weights of the products in the reactor can be controlled effectively by the ratio of the flow rates of monomer and initiator. The low-molecular-weight polymer thus can be used directly in high-solids fraction coatings. In an SFR the flow rates of the reactants are very low, and the amount of initiator used is greater than usual. The reaction temperature is so high that the initiator fed into the reactor decomposes instantaneously and the monomer reacts immediately. In an ideal case the concentrations of the initiator and the monomer in the reactor should be very low, ideally approaching zero. And because the reactor is in a "starved" status for reactants, the molecular weight is very low (the degree of polymerization is usually 30–100).

The kinetics of *n*-butyl methacrylate (NBMA) polymerization in an SFR is not the same as that produced in a normal reactor. Literature on polymerization kinetics is abundant, but only a few articles have concerned SFR performance.[1–4] This article presents a study on the kinetics of NBMA polymerization in an SFR, which had previously been unavailable.

Kinetics Model for NBMA Polymerization in an SFR

In a radical polymerization, the initiator decomposes into primary radicals

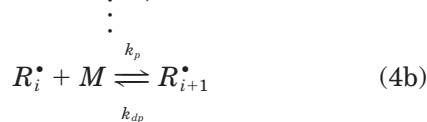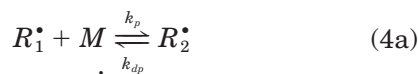$$\text{Initiator initiation } I \xrightarrow{k_d} 2R_0^\bullet \qquad (1)$$

At the same time the monomer may also form a primary radical at high temperatures[5]:

$$\text{Thermal initiation } 3M \xrightarrow{\bar{k}_i} 2R_0^\bullet \qquad (2)$$

Primary radical reacts with monomer to form monomer radicals

$$R_0^\bullet + M \;\rightarrow\; R_1^\bullet \qquad (3)$$
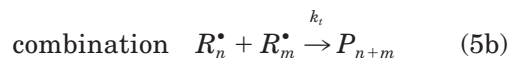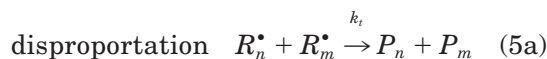
The radical species then attack the monomer to form a growing radical chain; meanwhile, the growing radicals may depropagate at elevated temperatures. Propagation and depropagation are shown as

$$R_1^\bullet + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} R_2^\bullet \qquad (4a)$$

$$\vdots$$

$$R_i^\bullet + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} R_{i+1}^\bullet \qquad (4b)$$

Two propagating radicals can terminate forming polymers in disproportionation and combination:

Termination:

$$\text{disproportation } R_n^\bullet + R_m^\bullet \xrightarrow{k_t} P_n + P_m \quad (5a)$$

$$\text{combination } R_n^\bullet + R_m^\bullet \xrightarrow{k_t} P_{n+m} \qquad (5b)$$

Meanwhile, the primary radical, $R_0^\bullet$, may terminate with the propagation radicals, $R_n^\bullet$

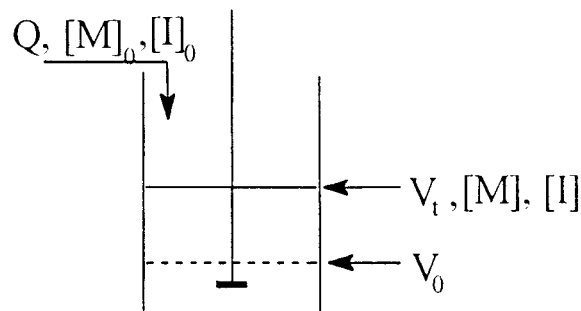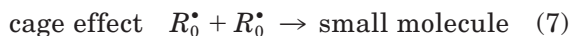$$R_0^\bullet + R_n^\bullet \xrightarrow{k_{tpr}} P_n \qquad (6)$$

Figure 1 Chart of a starved feed reactor.

For a propagation radical, eq. (6) is a termination to produce a dead polymer with chain length n, but for a primary radical, eq. (6) is a co-reaction to reduce the initiation efficiency, two other co-reactions, for cage effect and induced decompose, for the primary radical follow

$$\text{cage effect } R_0^\bullet + R_0^\bullet \rightarrow \text{small molecule} \quad (7)$$

induced decompose

$$R_0^\bullet + I \rightarrow \text{small molecule} \quad (8)$$

For a typical polymerization in this reactor, the relative contribution of chain transfer reaction to the initiator, solvent, and monomer, as well as to the polymers, is negligible. In addition, thermal initiation is negligible though reaction temperatures are high (normally 100°C–170°C),[4] so the initiation rate may be written in the form

$$r_I = r_{I,I} + r_{I,T} = 2fk_d[I] + 2\bar{k}_i[M]^3 \qquad (9)$$

where $\bar{k}_i$ is the thermal initiating rate constant and k_d is the decomposition rate constant of initiator for 2,2′-azobisisobutyronitrile (AIBN)

$$k_d = 1.6248 \times 10^{15}\exp(-1.551 \times 10^4/RT), \, T/K \qquad (10)$$

Figure 1 shows a chart of an SFR. V_0 is the initial solvent charged into the reactor is, Q is the constant flow rate of the initiator solution and monomer fed into the reactor, and $[I]_0$ and $[M]_0$, respectively, are their concentrations in the feed stream.

In an SFR the initiator is fed to the reactor very slowly, the concentration of initiator is typically very low, and the concentration of initiator is 0.0003 mol/L, much more lower than that in a normal polymerization reactor, so the concentra-

tion of primary radical in an SFR is also lower. On the other hand, the propagation rate is more rapid than the termination rate, normally r_p/r_t, which is equal to 10^3–10^5; so, eq.(6) is negligible in the total reactions and does not contribute to overall termination. The material balance for the initiator is

$$\frac{d\{V_t[I]\}}{dt} = [I]_0 Q - k_d[I]V_t \qquad (11)$$

Integration of eq. (11) yields

$$[I] = \frac{Q[I]_0}{V_t} \cdot \frac{1}{k_d} \cdot \{1 - \exp(-k_d t)\} \qquad (12)$$

If it is assumed that the numbers of radicals in the reactor are constant, then

$$\frac{d\{V_t[R_1^{\bullet}]\}}{dt} = \left\{ r_I + k_{dp}[R_2^{\bullet}] - k_p[M][R_1^{\bullet}] \right.$$
$$\left. - k_t[R_1^{\bullet}]\left(\frac{r_I}{k_t}\right)^{1/2} \right\} V_t = 0 \quad (13a)$$

$$\frac{d\{V_t[R_i^{\bullet}]\}}{dt} = \left\{ k_p[M][R_{i-1}^{\bullet}] + k_{dp}[R_{i+1}^{\bullet}] - k_p[M][R_i^{\bullet}] \right.$$
$$\left. - k_{dp}[R_i^{\bullet}] - k_t[R_i^{\bullet}]\left(\frac{r_I}{k_t}\right)^{1/2} \right\} V_t = 0 \quad (13b)$$

In eqs. (13a) and (13b), the depropagation of growing radicals is considered. When propagation and depropagation reach equilibrium, there is

$$k_p[R_{i-1}^{\bullet}][M]_e = k_{dp}[R_i^{\bullet}] \qquad (14)$$

where $[M]_e$ is the equilibrium monomer concentration. Eq. (14) can be rewritten as

$$k_{dp} = k_p[M]_e/([R_i^{\bullet}]/[R_{i-1}^{\bullet}]) \qquad (15)$$

Noting that $J = [R_{i+1}^{\bullet}]/[R_i^{\bullet}]$, Eq. (15) gives

$$k_{dp} = k_p[M]_e/J \qquad (16)$$

Substituting eq. (16) for eqs. (13a) and (13b) gives

$$J = \frac{(k_p/\sqrt{k_t})([M] - [M]_e)}{(k_p/\sqrt{k_t})([M] - [M]_e) + \sqrt{r_I}} \qquad (17)$$

$$[R_1^{\bullet}] = \left(\frac{r_I}{k_t}\right)^{1/2}(1 - J) \qquad (18a)$$

$$[R_i^{\bullet}] = \left(\frac{r_I}{k_t}\right)^{1/2}(1 - J)J^{i-1} \qquad (18b)$$

The monomer balance in the system is

$$\frac{d\{V_t[M]\}}{dt} = Q[M]_0 - r_{POL}V_t \qquad (19)$$

where r_{POL} is the rate of monomer consumption in the reaction with the primary radicals in the initiation step and with macroradicals in the propagation step and the rate of monomer produced in depropagation. r_{POL} can be written as

$$r_{POL} = r_I + r_p - r_{dp} \qquad (20)$$

where r_p is the propagation rate

$$r_p = k_p[M] \sum_{i=1}^{\infty} [R_i^{\bullet}] = k_p[M]\left(\frac{r_I}{k_t}\right)^{1/2} \qquad (21)$$

And r_{dp} represents the depropagation rate

$$r_{dp} = k_{dp} \sum_{i=2}^{\infty} [R_i^{\bullet}] = k_p[M]_e \sum_{i=1}^{\infty} [R_i^{\bullet}]$$
$$= k_p[M]_e(r_I/k_t)^{1/2} \quad (22)$$

Substituting eqs. (21) and (22) for eq. (20) gives

$$r_{POL} = \sqrt{r_I}\{\sqrt{r_I} + (k_p/\sqrt{k_t})([M] - [M]_e)\} \quad (23)$$

Substituting eq. (17) for eq. (23) gives

$$r_{POL} = \frac{1}{1 - J} \cdot r_I \qquad (24)$$

So the material balance for the monomer is

$$\frac{d\{V_t[M]\}}{dt} = Q[M]_0 - \frac{1}{1 - J} \cdot r_I \cdot V_t \quad (25a)$$

And eq. (25a) can be rewritten as

$$\frac{dn_m}{dt} = \dot{n}_m - \frac{1}{1 - J} \cdot r_I \cdot V_t \qquad (25b)$$

Either eq. (25a) or eq. (25b) is the kinetics model of NBMA polymerization in an SFR. The monomer concentration in an SFR can be calculated from the kinetics model. The model involves the following parameters:

- initiator efficiency f
- lump rate constant $k_p/(k_t)^{1/2}$

The propagation rate constant keeps constant with a wide range of viscosities,[6] but the termination rate constant has a relation to the viscosity in the system and to the polymer chain length. This effect was first reported by O'Dricoll et al.[7] and later confirmed and modeled by other researchers.[8–11] Models of this type take the following form

$$\frac{k_t}{k_t^0} = \left(\frac{C_p^0}{C_p}\right)^{\alpha} \left\{ \begin{array}{cc} C_p \leq C_p^0 & \alpha = 0 \\ C_p > C_p^0 & \alpha = \alpha \end{array} \right\} \qquad (26)$$

Substituting eq. (26) to $k_p/(k_t)^{1/2}$ gives

$$k_p/(k_t)^{1/2} = (k_p/(k_t^0)^{1/2})(C_p/C_p^0)^{\alpha/2} \qquad (27)$$

So the model parameters are

- initiator efficiency f
- lump rate constant $k_p/(k_t^0)^{1/2}$
- critical polymer concentration C_p^0
- correction constant α

EXPERIMENTAL

Purification of Reactants

Monomer (NBMA) and solvent (2-heptanone, also known as methyl amyl ketone) were washed with 5% aqueous NaOH to remove inhibitors, antioxidants, and impurities The organic phases were then washed with deionized water to a neutral pH (pH = 7) and dried overnight with calcium anhydride. They were then distilled at reduced pressure at a reflux temperature of <25°C, the head and tail fractions were excluded, and the middle fractions were stored in sealed flasks under refrigeration (−10°C) and used within 24 h.

The initiator (AIBN) was double-recrystallized from ethanol using standard procedures, dried under high vacuum, and refrigerated (−10°C) until use.
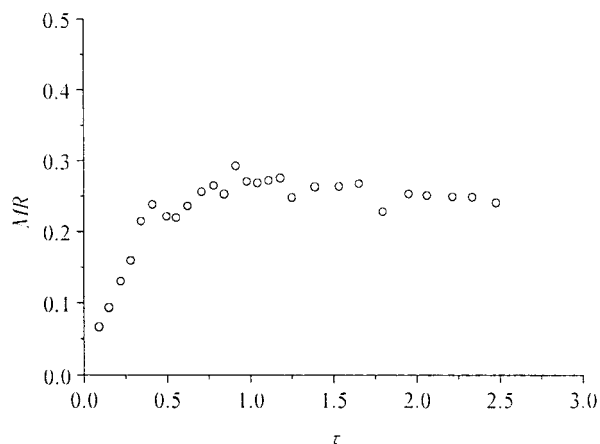

Figure 2   Mass ratio of NBMA to solvent versus reaction time ($T = 150$°C, $\theta = 4362.53$ s).

Experimental Procedures

The initiator solution (0.3) was made and kept at room temperature (23°C–25°C). The monomer was stored in a bath of ice water. The initiator and the monomer were pumped in that order into the reactor into which an aliquot (0.2 L) of solvent (the mass was measured and recorded) was initially charged. The reaction temperatures were 100°C, 110°C, 120°C, 130°C, 150°C, and 170°C. Over the course of the run, samples were withdrawn at intervals and placed in a vial where a measured quantity of inhibitor had been deposited to terminate the reaction. The samples were then analyzed for the mass ratio of monomer to solvent (*MR*), solids fraction (*sf*), and molecular weight (MW).

Samples Analysis

The *MR* was determined via gas chromatography (Model 1002 GC, Shanghai Analysis Instrument Co. Ltd.), the *sf* was determined through gravimetry, and the MW was determined with a WATERS 150C GPC/ALC.

RESULTS AND DISCUSSION

Analysis of Experimental Data

Figures 2–4 present the experimental results of mass ratio, solid fraction, and molecular weight versus reaction time at one of the reaction temperatures, in which the reaction time is dimensionless time and is defined as
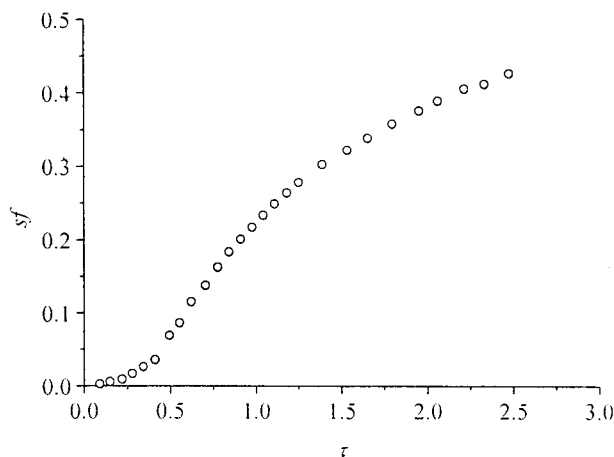
Figure 3 Solids fraction versus reaction time (T = 150° C, θ = 4362.53 s).

$$\tau = t/\theta, \quad \theta = V_0/Q \tag{28}$$

As the volume of the reaction mixture is expected to change with temperature and the volume decreases with monomers polymerizing to polymers, the volume in the system at time t can be accurately calculated as

$$V_t = m_s/\rho_s + m_m/\rho_m + m_p/\rho_p$$

The densities of 2-heptanone, NBMA, and PNBMA at any temperature are as follows:

$$\rho_s = A - BT - C/(D-T)$$
$$A = 1.0823, B = 0.68128 \times 10^{-3}, C = 28.077, D = 711.81, T/K$$

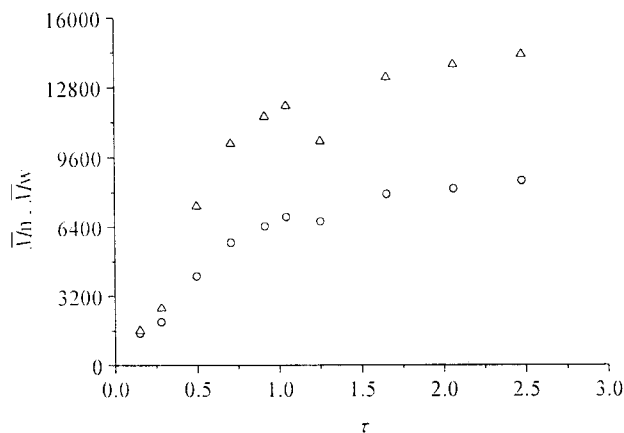**Figure 4** Number-average molecular and weight-average molecular weight versus reaction time (T = 150°C, θ = 4362.53 s): ($\bigcirc$) number-average molecular weight; ($\triangle$) weight-average molecular weight.
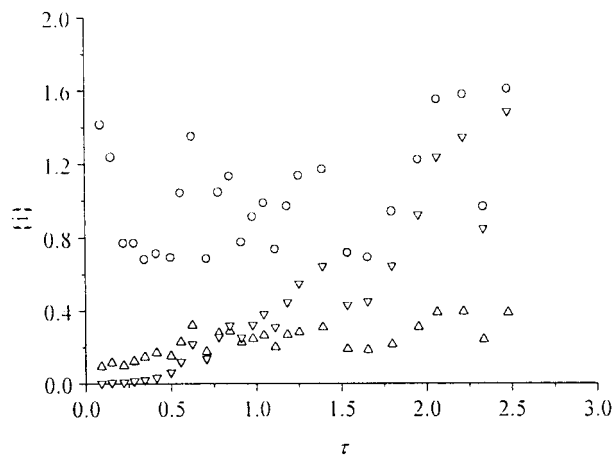
Figure 5 Mass of monomer, solvent, and polymer in sample removed from SFR run: ($\bigcirc$) mass of solvent in sample; ($\triangledown$) mass of monomer in sample; ($\triangle$) mass of polymer in sample.

$$\rho_m = 924.0 - 0.918 \, (T - 273.15), \text{g/cm}^3$$
$$\rho = 1080.8 - 0.605 \, (T - 273.15), \text{g/cm}^3$$

The mass of a sample (commonly 1.5–3 g) is far less than that of the contents in the reactor at any time, but the feeding rates of reactants are small (commonly 1.5 g/min). Figure 5 shows the mass of solvent, monomer, and polymer in a sample removed from an SFR run. If samples are taken every 5 min over the course of a run, the mass of material fed into the reactor is 7.5 g during the 5 min, and the mass ratio of a sample to the material fed into the reactor during the 5 min is 20%–40%. Such an amount is comparatively large, such that corrections must be made for the contents of the reactor, taking into that account the masses of solvent, monomer and polymer in the system at time t can be calculated with the following equations

$$(m_s)_i = (m_s^0 + \dot{m}_s t_i) - \sum_{j=1}^{i-1} m_{sj}'$$

$$(m_m)_i = MR_i(m_s)_i$$

$$(m_p)_i = sf_i\{[m_s^0 + (\dot{m}_s + \dot{m}_m)t_i]$$

$$- \sum_{j=1}^{i-1} (m_{sj}' + m_{mj}' + m_{pj}')\} \quad (i \geq 2, j \geq 1) \tag{29}$$

Regression of Model Parameters

In the regression of model parameters, the objective function used in this article is

$$s = \ln \sum_{i=1}^{N_{MR}} (MR_c - MR_e)_i^2 + \ln \sum_{i=1}^{N_{sf}} (sf_c - sf_e)_i^2 \quad (30)$$

where MR_e and sf_e are the experimental results and MR_c and sf_c are the model values calculated from eq. (25) as follows:

$$MR_{c,i} = \frac{m_{m,c,i}}{m_s^0 + \dot{m}_s t_i}, \quad i = 1$$

$$MR_{c,i} = \frac{m_{m,c,i} - \sum_{j=1}^{i-1} m'_{mj}}{m_s^0 + \dot{m}_s t_i - \sum_{j=1}^{i-1} m'_{sj}}, \quad i \geq 2$$

$$sf_{c,i} = \frac{\dot{m}_m t_i - m_{m,c,i}}{m_s^0 + \dot{m}_s t_i + \dot{m}_m t_i}, \quad i = 1$$

$$sf_{c,i} = \frac{\dot{m}_m t_i - m_{m,c,i} - \sum_{j=1}^{i-1} m'_{pj}}{m_s^0 + \dot{m}_s t_i + \dot{m}_m t_i - \sum_{j=1}^{i-1} (m'_{sj} + m'_{mj} + m'_{pj})}, \quad = i \geq 2 \quad (31)$$

where $m_{m,c,i}$ is the result of integration of the kinetics model.

Discussion

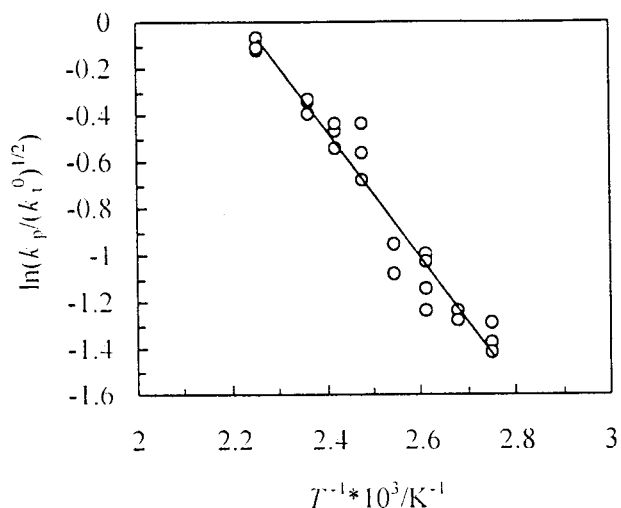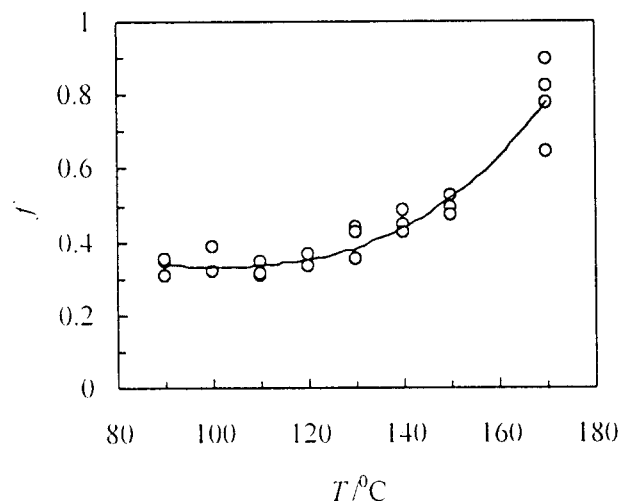The model parameters were calculated as discussed above. The relationship between the lump

Figure 7 The relationship of initiation efficiency and temperature.

rate constant, $k_p/(k_t^0)^{1/2}$, and temperature is as follows:

$$k_p/(k_t^0)^{1/2} = 432.68 \exp(-2726.1/T) \quad (32)$$

Figure 6 shows this relationship. Other parameters are shown in Figures 7–9.

CONCLUSIONS

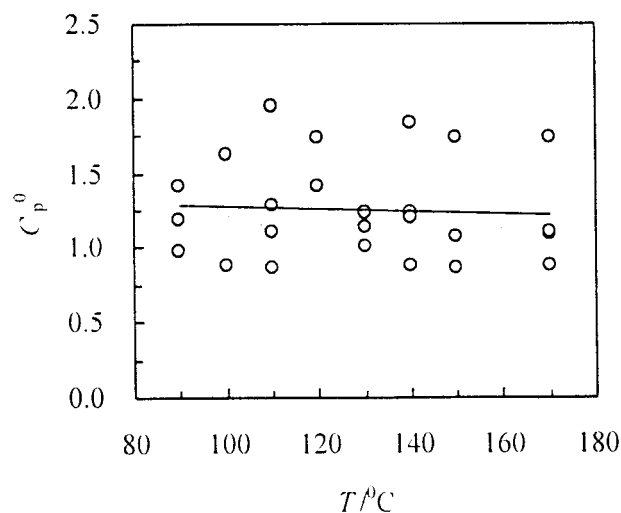In a starved feed reactor the molecular weight of the resulting polymer is effectively controlled by

Figure 6 Rate constant $[k_p/(k_t^0)^{1/2}]$ versus temperature.

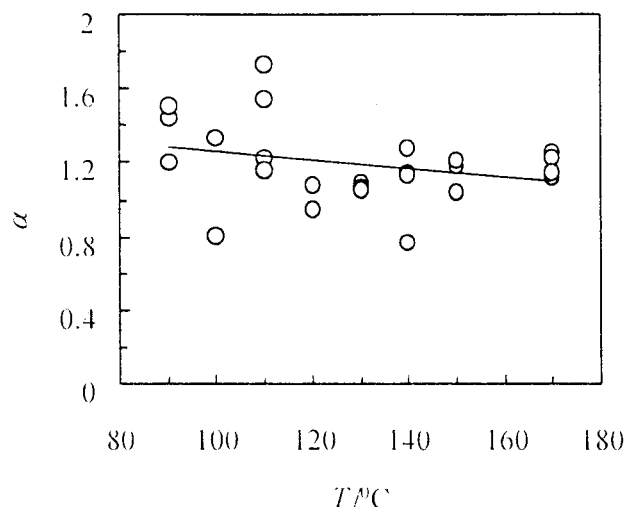**Figure 8** The relationship of critical polymer concentration and temperature.

Figure 9 The relationship of correction constant α and temperature.

the feed rates of the monomer and initiator. The degree of polymerization in an SFR is 30–100. In this article a kinetics model was set up, and the model parameters were regressed with the experimental data. The relationship between the lump rate constant and temperature can be represented via an Arrhenius equation.

Although the solid fraction in the SFR is rather high, viscosity is not high and the "gel effect" is weak because of the lower molecular weight of the products. The termination rate constant was found to be a power function of the polymer concentration. The initiator efficiency, f, was about 0.36 when the reaction temperature was lower than 120°C, but it increased with the temperature when the temperature was higher than 120°C. The critical polymer concentration and the correction constant kept constant at the experimental range.

NOMENCLATURE

C_p^0 critical polymer concentration (mol/L)
C_p polymer concentration (mol/L)
f initiator efficiency
I initiator molecule
$[I]_0$ initiator concentration in the SFR feed stream (mol/L)
k_d initiator decomposition rate constant (s)
J a constant
$\bar{k}_i$ thermal initiation rate constant (L^2 mol^{-2} s^{-1})

k_p propagation rate constant (L mol^{-1} s^{-1})
k_t termination rate constant(L mol^{-1} s^{-1})
M monomer
$\bar{M}_n$ number-average molecular weight
$\bar{M}_w$ weight-average molecular weight
MR   mass ratio of monomer to solvent
$[M]_0$ monomer concentration in the SFR feed stream (mol/L)
m_m mass of monomer in SFR (g)
m_p mass of polymer in SFR (g)
m_s mass of solvent in SFR (g)
m_s^0 mass of initial solvent charged to SFR (g)
$\dot{m}_m$ mass flow rate of monomer into SFR (g/s)
$\dot{m}_s$ mass flow rate of solvent into SFR (g/s)
m'_m mass of monomer in SFR samples (g)
m'_s mass of solvent in SFR samples (g)
m'_p mass of polymer in SFR samples (g)
N_i number of samples of type i (i represents MR, sf, $\bar{M}_n$, $\bar{M}_w$)
n_m moles of monomer in SFR (mol)
$\dot{n}_m$ molar flow rate of monomer into SFR (mol/s)
Q volume feed rate of the SFR feed stream (L/s)
R gas constant
$R_0^\bullet$ primary radicals
$R_i^\bullet$ a radical that has i monomer units incorporated
r_I initiation rate (mol L^{-1} s^{-1})
$r_{I,I}$ initiator initiation rate (mol L^{-1} s^{-1})
$r_{I,T}$ thermal initiation rate (mol L^{-1} s^{-1})
r_P propagation rate (mol L^{-1} s^{-1})
r_{POL} rate of monomer consumption in polymerization (mol L^{-1} s^{-1})
s objective function
sf solids fraction
T reaction temperature (K)
t time (s)
V_0 volume of initial solvent charged to reactor (L)
V_t volume of reaction mixture in SFR at time t (L)
α a constant
θ replacement time of the reactor, s
ρ density (g/L)
τ dimensionless time

Subscripts

c calculated value from models
e experimental value
m monomer

p polymer
r chain length
s solvent

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