# A Kinetic Investigation of Butyl Acrylate Polymerization

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## SYNOPSIS

An experimental investigation of the kinetics of the bulk free radical polymerization of butyl acrylate initiated with 2,2'-azobisisobutyronitrile (AIBN) was conducted at 50° and 60°C using two initiator concentrations. Conversion levels were measured by gravimetry and were independently confirmed using replicate runs. The experiments, conducted in glass ampoules, were performed over the full conversion range. A mathematical model for process simulation purposes was developed. The model was able to predict conversion at the two temperatures and initiator concentrations, thus providing a better understanding of the butyl acrylate homopolymerization kinetics.

## INTRODUCTION AND LITERATURE REVIEW

In the study of copolymerization kinetics of systems having butyl acrylate (BA) as one of the comonomers, a significant lack of knowledge of the homopolymerization rate constants for BA has been noted.[1] The use of the terminal as well as the penultimate unit model to describe the rate of copolymerization necessitates the knowledge of reliable values for the homopolymerization rate constants.

This study represents an effort to add to the existing knowledge of butyl acrylate homopolymerization.

Work performed on the homopolymerization kinetics of butyl acrylate is scarce. The *Polymer Handbook*[2] contains some reports of propagation and termination rate constants for this system where, in general, researchers have concentrated on experiments using different temperatures and solvents at low conversion levels only. Reported values of rate constants for bulk, solution, or emulsion polymerizations can be found in Gladyshev and Rafikov,[3] Yokawa et al.,[4] Kamachi et al.,[5] Kaszás et al.,[6] and Maxwell et al.[7] Full conversion range experiments have been reported by Scott and Senogles[8,9] and Wunderlich.[10] The latter investigated the solution homopolymerization at various temperatures and initiator/monomer concentrations in what seems to be the first attempt toward a more thorough study of butyl acrylate kinetics.
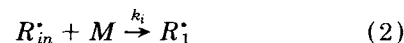
## THEORETICAL BACKGROUND

### Polymerization Rate

#### Initiation

The initiator, $I$, decomposes into two free radicals, $R^{\bullet}$, via the following scheme:

$$I \xrightarrow{k_d} 2R^{\bullet} \tag{1}$$

$k_d$ is a temperature dependent rate constant for initiator decomposition. The decomposition proceeds with an efficiency, $f$. The radicals, also known as primary radicals, add to monomer $M$ as follows:
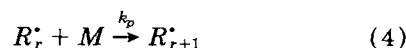
$$R_{in}^{\bullet} + M \xrightarrow{k_i} R_1^{\bullet} \tag{2}$$

If $k_d$ and $f$ are known, $k_i$ is not required. The rate of initiation is then given by:

$$R_I = 2f k_d [I] \tag{3}$$

#### Propagation

In the propagation step, a monomer unit adds to an active site on a growing radical chain and the active site is transferred to the terminal unit on the chain.

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$$R_r^{\bullet} + M \xrightarrow{k_p} R_{r+1}^{\bullet} \tag{4}$$

The rate of polymerization is defined as

$$R_p = k_p[R^{\bullet}][M] \tag{5}$$

### Chain Transfer to Small Molecules (T)

The growing radical may, at some point in the reaction, transfer its active center to a small molecule ($T$), such as solvent, monomer, initiator, impurity, or chain transfer agent (CTA). Thus, the polymerization is terminated prematurely, creating a shorter (dead) polymer molecule of length $r$ ($P_r$). The transferred radical may or may not continue to react. This is shown below:

$$R_r^{\bullet} + T \xrightarrow{k_{fT}} P_r + T^{\bullet} \tag{6}$$

$$T^{\bullet} + M \xrightarrow{k_p^1} R_1^{\bullet} \tag{7}$$
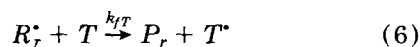
### Chain Transfer to Polymer

In a way analogous to the transfer of the active center to small molecules, the active center may transfer to a dead polymer chain, thus creating branched instead of linear polymers. The reaction proceeds as follows:

$$R_r^{\bullet} + P_s \xrightarrow{k_{fp}} P_r + R_s^{\bullet} \tag{8}$$

### Terminal and Internal Double-Bond Reactions

Another cause of long chain branching (trifunctional or tetrafunctional) is the reaction of a growing polymeric radical with a dead polymer molecule containing a terminal or internal double-bond, as shown below:

$$R_r^{\bullet} + P_s \xrightarrow{k_p^*} R_{r+s}^{\bullet} \tag{9}$$
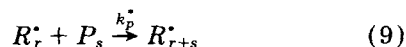
### Termination

Should a growing radical chain not undergo any transfer reactions, it will eventually terminate when it encounters another growing radical chain end. The active centers coming together may terminate either by combining to form a larger polymer molecule, or disproportionating to form two separate dead polymer molecules. The reactions are shown below:

$$R_r^{\bullet} + R_s^{\bullet} \xrightarrow{k_{tc}} P_{r+s} \tag{10}$$

$$R_r^{\bullet} + R_s^{\bullet} \xrightarrow{k_{td}} P_r + P_s \tag{11}$$
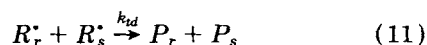
The termination rate $R_t$ is defined as

$$R_t = k_t[R^{\bullet}]^2 \tag{12}$$

A steady-state hypothesis can be applied, stating that $R_I \simeq R_t$, or that the total radical concentration is as follows:

$$[R^{\bullet}] = (R_I/k_t)^{1/2} \tag{13}$$

The termination rate constant, $k_t$, is not really a constant, but changes with the viscosity of the reaction medium. In other words, $k_t$ is diffusion-controlled. In order to explain the diffusion-control phenomenon, it is best to briefly review how two free radical chains meet and terminate. The first step, known as translational diffusion, involves the approach of the two macroradical chains toward each other. The next step, segmental diffusion, involves the diffusion of the chain segments containing the active center toward each other. Finally, the third step, chemical reaction, takes place. With this in mind, one can envision three diffusion-control intervals. The first, where the mixture has a low viscosity, is segmental diffusion-control. This stage may occur anywhere from 0 to 15% conversion. Of course, the ranges of conversions for each interval depend on the particular polymerization system and conditions. The next interval, translational diffusion-control, occurs up to very high conversions ($\sim$ 85–90%). The final stage is known as the reaction–diffusion control interval. At this stage, the viscosity is so high that the polymer chains barely move and the approach of two active centers can only be accomplished by the addition of monomer. This final step is extremely slow. The point at which reaction–diffusion significantly contributes to the slowing of the reaction and the point at which translational diffusion becomes unimportant are, and may continue to be, unclear. In other words, what is happening at very high conversions is still a matter of active research. Recent work by Zhu et al.[11] using electron spin resonance techniques seems quite promising in offering a better understanding of very high conversion kinetics, as does the work by Russell et al.[12]

Throughout the first two termination diffusion-control intervals, the propagation rate "constant" remains constant. However, in the reaction–diffusion regime, it too becomes diffusion controlled. The points at which the diffusion-control intervals change have been represented by a function of molecular weight and conversion, in a way analogous to a viscosity change in the reaction mixture.[13-15]

Using elements from the free volume theory, one can describe the diffusion-control regime for the polymerization of butyl acrylate. In the first interval, the segmental diffusion-controlled termination rate constant is described after Mahabadi and O'Driscoll[16] as

$$k_t = k_{tseg} = k_{to}(1 + \delta c) \qquad (14)$$

where $k_{to}$ is the initial termination rate constant, $\delta$ is a parameter dependent on the molecular weight of the polymer radicals and solvent quality, and $c$ is the mass concentration of accumulated polymer in the reaction mixture.

The point at which translational diffusion becomes the rate determining step is identified by a parameter $K_3$, which has been found to have an Arrhenius-type temperature dependence, and has been defined by Marten and Hamielec[13] as

$$K_3 = \bar{M}_{wcr1}^m \exp(A/V_{Fcr1}) \qquad (15)$$

where $A$ and $m$ are adjustable parameters, and $\bar{M}_{wcr1}$ is the accumulated weight-average molecular weight at the monomer conversion at which the termination rate is translational diffusion-controlled. $V_{Fcr1}$ is the critical free volume corresponding to that conversion.

The free volume in a polymerization is given by

$$V_F = \sum_i (0.025 + \alpha_i(T - T_{gi})) \frac{V_i}{V_T} \qquad (16)$$

where, in the bulk polymerization case, $i$ represents the monomer and the polymer and $\alpha_i$ is the difference in the thermal expansion coefficients for component $i$ above and below its glass transition temperature, $T_{gi}$. $T$ is the polymerization temperature, $V_i$ is the volume of each component, and $V_T$, the volume of the reaction mixture, is described as

$$V_T = V_0(1 + \epsilon x), \qquad (17)$$

where $V_0$ is the initial volume of the reaction mixture, $x$ is the molar monomer conversion, and $\epsilon$ is the shrinkage factor given by

$$\epsilon = \frac{\rho_p - \rho_m}{\rho_p} \qquad (18)$$

where $\rho_p$ is the polymer density and $\rho_m$ is the density of monomer.

The translational diffusion-controlled termination rate constant, $k_T$ is given by:

$$k_T = k_t^* \left(\frac{\bar{M}_{wcr1}}{\bar{M}_w}\right)^n \exp\left(-A\left(\frac{1}{V_F} - \frac{1}{V_{Fcr1}}\right)\right) \qquad (19)$$

where $k_t^*$ is the value of $k_t$ when eq. (15) is satisfied. $n$ is an adjustable parameter.

The reaction–diffusion controlled termination rate constant, $k_{trd}$, is given by:

$$k_{trd} = \frac{8\pi N_A \delta D}{1000} \qquad (20)$$

where

$$\delta = \left(\frac{6V_m}{\pi N_A}\right)^{1/3} \qquad (21)$$

$$D = \frac{n_s l_0^2}{6} k_p[M] \qquad (22)$$

and $N_A$ is Avogadro's number, $\delta$ is the reaction radius, $D$ is the reaction diffusion coefficient, $V_m$ is the monomer molar volume, $n_s$ is the number of monomer units in one polymer chain segment and $l_0$ is the length of the monomer unit.

When the polymerization temperature is less than the glass transition temperature of the polymer being synthesized, the propagation reaction rate becomes diffusion-controlled. The propagation rate constant is then given by

$$k_p = (k_p)_0 \exp\left(-B\left(\frac{1}{V_F} - \frac{1}{V_{Fcr2}}\right)\right) \qquad (23)$$

where $(k_p)_0$ is the chemically-controlled propagation rate constant, $B$ is an adjustable parameter and $V_{Fcr2}$ is the critical free volume where the propagation reaction becomes diffusion-controlled.

In many modelling cases, the initiator efficiency has been assumed constant over the full conversion range. Hamielec et al.[17] state that the efficiency begins to decrease at almost the same point at which the propagation reaction becomes diffusion-controlled. They expressed the efficiency decrease in a form similar to that for the diffusion-controlled propagation rate constant in eq. (23). Kinetic experiments concerning the initiator efficiency by Garcia-Rubio and Mehta[18] showed a slow decrease in the initiator efficiency at high conversions. A more recent investigation by Russell et al.[19] suggested that the initiator efficiency drops off even more dramat-

ically than was previously assumed. They argued that for a homopolymerization, the efficiency, $f$, will begin to drop off at a critical conversion at which the following relation holds

$$\sigma = [6D_m(w_p)/(k_{pt}C_m)]^{1/2} \qquad (24)$$

where $\sigma$ is the radius of interaction of the reactants, $D_m$ is the diffusion coefficient for monomer, $w_p$ is the weight fraction of polymer, $k_{pt}$ is the rate coefficient for addition of a monomer unit to an initiator free radical and $C_m$ is the concentration of monomer. The initiator efficiency decrease is then described as

$$f = \left(\frac{dx/dt}{k_p(1-x)}\right)^2 \frac{k_t}{k_d[I]} \qquad (25)$$

The propagation and termination rate constants in eq. (25) are assumed to be well known. This, however, may not be the case for many polymer systems and hence, empirical or semiempirical approaches may still be of practical use.

## Molecular Weight

The number–average $(\bar{M}_n)$ and weight–average $(\bar{M}_w)$ molecular weight of the polymer can be calculated by two different methods. Both methods are briefly developed below for the case of a batch reactor. The reader is strongly encouraged to see Hamielec et al.[17] for more details on the derivation of the molecular weight equations.

### Instantaneous Method

The instantaneous method of molecular weight calculations is restricted to linear polymer chains.[20,21] The instantaneous number– and weight–average molecular weights are given by:

$$M_n = M_o \frac{2}{2\tau + \beta} \qquad (26)$$

$$M_w = M_o \frac{2\tau + 3\beta}{(\tau + \beta)^2} \qquad (27)$$

where

$$\beta = \frac{k_{tc}R_I^{1/2}}{k_p[M]k_t^{1/2}} \qquad (28)$$

$$\tau = \frac{k_{td}R_I^{1/2}}{k_p[M]k_t^{1/2}} + C_m + \frac{k_{fT}[T]}{k_p[M]} \qquad (29)$$

$C_m$ is the chain transfer to monomer constant, defined as:

$$C_m = \frac{k_{fm}}{k_p} \qquad (30)$$

$M_o$ is the molecular weight of a repeat unit in the polymer chain.

The cumulative number– and weight–average molecular weights are given by:

$$\bar{M}_n = \frac{x}{\int_0^x dx/M_n} \qquad (31)$$

$$\bar{M}_w = \frac{1}{x} \int_0^x M_w dx \qquad (32)$$

where $x$ is the total monomer conversion on a weight basis.

## Method of Moments

If long chain branching reactions such as transfer to polymer and internal or terminal double-bond polymerization are important, one must resort to the method of moments calculation. The moments $(Q_0, Q_1, Q_2)$ of the molecular weight distribution are expressed in differential equation form as:

$$\frac{d(VQ_0)}{dt} = \left(C_m + C_T \frac{[T]}{[M]} - C_k \frac{Q_1}{[M]} - K \frac{Q_0}{[M]} \right.$$
$$\left. + \frac{(k_{td} + k_{tc}/2)[R^\bullet]}{k_p[M]} \right) k_p[M][R^\bullet]V \qquad (33)$$

where the constant for internal double-bond polymerization is:

$$C_k = \frac{k_p^{**}}{k_p} \qquad (34)$$

and the constant for terminal double-bond polymerization is:

$$K = \frac{k_p^*}{k_p} \qquad (35)$$

$$\frac{d(VQ_1)}{dt}$$

$$= k_p[M][R^\bullet]V\left(1 + C_m + C_T \frac{[T]}{[M]}\right) \qquad (36)$$

$$\frac{d(V Q_2)}{dt} = k_p[M][R^\cdot] V\left(2 \times BRACKET\right.$$

$$\times \frac{1 + KQ_1/[M] + C_k Q_2/[M]}{DENOM}\bigg)$$

$$\times \left(FACTOR + \frac{k_{tc}[R^\cdot]}{k_p[M]} \times \frac{BRACKET^2}{DENOM^2}\right) \quad (37)$$

where

FACTOR

$$= \frac{R_I}{k_p[M][R^\cdot]} + 1 + C_m + C_T \frac{[T]}{[M]} \quad (38)$$

$$BRACKET = 1 + C_m + (C_p + C_k)\frac{Q_2}{[M]}$$

$$+ \frac{R_I}{k_p[M][R^\cdot]} + K \frac{Q_1}{[M]} + C_T \frac{[T]}{[M]} \quad (39)$$

$$DENOM = C_m + C_p \frac{Q_1}{[M]}$$

$$+ \frac{(k_{tc} + k_{td})[R^\cdot]}{k_p[M]} + C_T \frac{[T]}{[M]} \quad (40)$$

In the above equations, $C_T \dfrac{[T]}{[M]}$ represents the contribution of all transfer to small molecules reactions such as transfer to solvent, initiator, chain transfer agent, and impurities.

The cumulative molecular weight averages can now be calculated as:

$$\bar{M}_n = M_o \frac{Q_1}{Q_0} \quad (41)$$

$$\bar{M}_w = M_o \frac{Q_2}{Q_1} \quad (42)$$

Finally, the average number of branches per molecule can be calculated by:

$$\frac{d(V Q_0 \bar{B}_{N3})}{dt} = k_p[R^\cdot] V (C_p Q_1 + KQ_0) \quad (43)$$

$$\frac{d(V Q_0 \bar{B}_{N4})}{dt} = k_p[R^\cdot] V C_k Q_1 \quad (44)$$

where $\bar{B}_{N3}$ and $\bar{B}_{N4}$ are the average number of trifunctional and tetrafunctional branches per molecule, respectively.

## EXPERIMENTAL METHODS AND DESIGN

### Purification of Reagents

Purification of reagents was performed by classical methods described by Stickler.[22] The initiator, 2,2′-azobisisobutyronitrile (AIBN) (Polysciences Inc.), was recrystallized three times from absolute methanol. The monomer, butyl acrylate (Aldrich Chemical Co. Inc.), was washed three times with a 10% sodium hydroxide solution, washed three times with distilled water, dried over calcium chloride, and freshly distilled under vacuum at, at most, 48 h before use, and stored at −10°C. All of the solvents used over the course of the experiments (toluene, ethanol) were used as packaged without further purification.

### Experimental Design

The experiments were carried out in borosilicate glass ampoules of length 10 cm and outer diameter 1.7 cm. The monomer and initiator were weighed and then pipetted into numbered ampoules. The ampoules were degassed by several vacuum freeze–thaw cycles, were flame-sealed and subsequently submerged in a 50° or 60°C water bath for a recorded time interval. The ampoules were removed from the water bath at appropriate intervals to ensure a well-defined conversion vs. time plot. Due to the fact that the samples were in a gel-like state, the extraction of residual monomer from them was not possible using conventional methods. Upon removing the ampoules from the water bath, the ampoules were frozen, broken, and the frozen polymer/monomer mixture was weighed. These samples were then placed in toluene at −10°C in order to remove residual monomer, and were then precipitated with a 10-fold excess of ethanol and dried in a vacuum oven at 40°C until a constant weight was reached.

The reaction temperature and the initial initiator concentration were the factors in a $2^2$ factorial design as shown in Table I. Replicate runs were performed at $T = 50°C$, $[I]_o = 0.00025$ mol/L and $T = 60°C$, $[I]_o = 0.001$ mol/L.

The isolated polymers were analyzed for conversion by gravimetry. Attempts to analyze the samples for molecular weight proved unsuccessful. It was practically impossible to dissolve fully the polymer in common gel-permeation chromatography solvents (e.g., toluene, tetrahydrofuran, etc.). The polymer had not dissolved even a month after the polymerization runs.
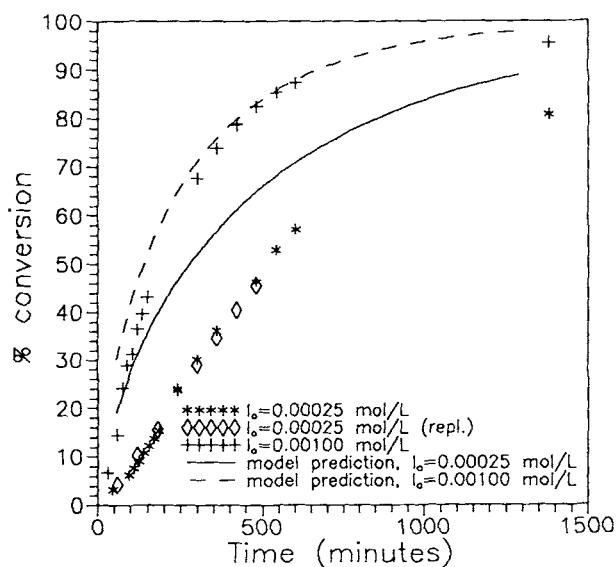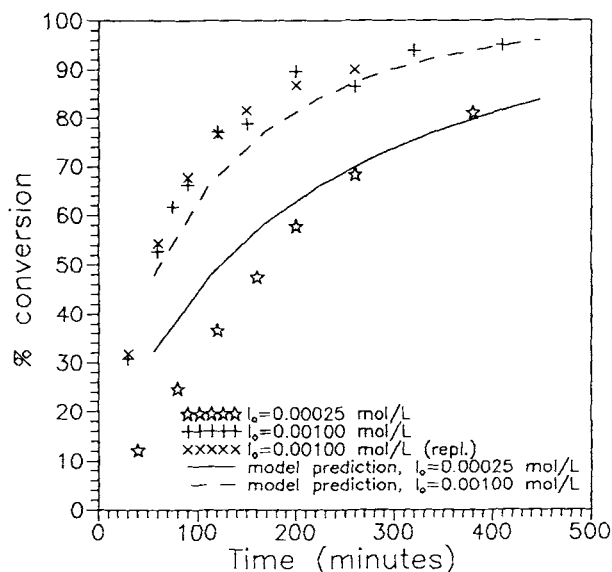
**Table I   $2^2$ Factorial Design**

| Run | $[I_o]$ mol/L | Temperature (°C) |
|-----|---------------|------------------|
| 1 | 0.00025 | 50 |
| 2 | 0.001 | 50 |
| 3 | 0.00025 | 60 |
| 4 | 0.001 | 60 |

## EXPERIMENTAL RESULTS AND DISCUSSION

The gravimetric results are in the form of percent monomer converted to polymer on a mass basis, and are plotted in Figures 1 and 2. Figure 1 shows the conversion vs. time data for the lower temperature, while Figure 2 shows those for the higher temperature. The solid or dashed lines on both graphs represent predictions from the computer simulation (see Mathematical Modelling section).

The reproducibility of the experiments was ensured by the replication of runs at two of the experimental design points, namely, $T = 50°C$, $[I]_o = 0.00025$ mol/L, and $T = 60°C$, $[I]_o = 0.001$ mol/ L. Looking at the relevant data points on Figures 1 and 2, one can see no significant difference between the replicate runs and the original ones.

Looking at the conversion–time data, one sees a curved profile. That is, the gel-effect seems to be present at the very onset of polymerization. As well, there appears to be a limiting conversion for all

**Figure 2**   Conversion vs. time results, $T = 60°C$.

cases. This limiting conversion is well demonstrated in Figure 1, where polymerizations were carried out for almost 24 h. As mentioned earlier, attempts at fully extracting the residual monomer from the polymer were quite tedious and required leaving the polymer in toluene at $-10°C$ for periods of 24 h or more.

A valid concern with ampoule experiments is whether the runs are, in fact, isothermal. It has been shown by Armitage et al.[23] that use of ampoules can lead to nonisothermal behavior when polymerizations are run to high conversion. They polymerized methyl methacrylate monomer at 70°C with 0.057 mol/L of AIBN initiator. Temperature excursions of up to 80°C were measured. It was in the interest of maintaining isothermal conditions in the ampoules that the size of the ampoules for the experiments for this work was chosen, as noted earlier. This size was approximately the same as in the work of Armitage et al.[23] The most notable differences between this work and theirs was that in this work, the temperature was 10 to 20 degrees lower, the initiator concentration was 50 to 200 times lower, and the polymerization times were significantly longer (their polymerizations ran for only 1 h). Because of these differences, it is likely that we had isothermal polymerizations (see Dubé[24]).

As mentioned earlier, it was practically impossible to dissolve fully the polymer in order to perform gel-permeation chromatography (GPC) for molecular weight calculations. This finding is in agreement with earlier observations by Wunderlich.[10] The fact

**Figure 1**   Conversion vs. time results, $T = 50°C$.

that one can not fully dissolve the polymer is an indication that the polymer produced is highly branched, and probably has a molecular weight of around $10^7$ or $10^8$. Butyl acrylate is known to be a "hot" monomer. One can additionally postulate that both transfer to monomer (leading to terminal double-bond polymerization) and transfer to polymer reactions are important, leading to very high molecular weights and branching levels.

## MATHEMATICAL MODELLING

### Simulation Model

Developing a model for this system involved the use of the theoretical expressions shown earlier and the use of kinetic constants, either from the literature, or estimated from results of this work. The model consists of a set of differential equations that describe material balances on the reaction mixture.

Material balances are written for monomer, polymer, and initiator in a batch reactor to yield:

$$\frac{dN(t)}{dt} = -R_p(t)V_T(t) \qquad (45)$$

$$\frac{dP(t)}{dt} = R_p(t)V_T(t) \qquad (46)$$

$$\frac{dN_I(t)}{dt} = -k_d N_I(t) \qquad (47)$$

where $N(t)$ is the number of moles of monomer, $P(t)$ is the number of moles of monomer bound in the polymer, $N_I(t)$ is the number of moles of initiator, and $R_p(t)$ is the rate of polymerization as defined earlier in eq. (5). The total volume of the reaction mixture, $V_T(t)$, can be expressed either as a differential equation or, equivalently, as an algebraic equation, as shown in eq. (17).

The mass conversion $x$ can be expressed in differential equation form as:

$$\frac{dx}{dt} = M_o dN(t)/dt \qquad (48)$$

Finally, the expressions for the molecular weight part are as shown in eqs. (33) to (44).

Several assumptions were made in order to simplify the mathematical model to some extent. These were: (a) No impurities are present in the reaction mixture, (b) The reaction is homogeneous, (c) The decomposition of the initiator occurs by thermal

methods and not by ultraviolet light, (d) The volume contribution by the initiator is negligible, (e) The volume shrinkage factor, $\epsilon$, is not a function of conversion, (f) Long polymer chains are formed, (g) The radicals are at steady-state, and (h) There are no heat losses to the surroundings from the temperature bath. These assumptions are quite common in the modelling literature and are valid, given the experimental procedures described earlier.

### Parameter Estimation and Discussion

Several constants appear within all of the model differential equations. Most are known or have been previously estimated in the literature. Others were found by making calculated guesses from intuition and known correlations, or through comparison with other homopolymer systems. These values, used in the computer program, are given in Table II.

Values for the ratio of the propagation and termination rate constants of butyl acrylate were obtained using the experimental results and the modelling efforts presented herein. These values are also cited in Table II.

From perusal of various literature references, and the *Polymer Handbook*,[2] it is suspected that butyl acrylate terminates primarily by way of combination, although some disproportionation may take place at elevated temperatures. Hence, for the modelling runs, termination was assumed to occur entirely by combination. By employing the parameters

**Table II    Model Constants and Their Values**

| Model Constant | Value |
| --- | --- |
| $A$ | 1.5 |
| $B$ | 1.0 |
| $c_m$ | $3.0 \times 10^{-2} \exp(-1000/RT)$ |
| $f$ | 0.65 |
| $K_3$ | 0.0009 |
| $k_d$ | $0.652 \times 10^{17} \exp(-30719.02/RT)$ $(\mathrm{min}^{-1})$ |
| $k_p/k_t$ (50°C) | 0.00377 |
| $k_p/k_t$ (60°C) | 0.00342 |
| $l_o$ | $25 \times 10^{-9}$ m |
| $m$ | 0.5 |
| $n$ | 1.75 |
| $n_s$ | 10.0 |
| $T_{gm}$ | 185.15 K |
| $T_{gp}$ | 218.0 K |
| $V_{Fcr2}$ | 0.040 |
| $\alpha_m$ | $1.189 \times 10^{-3}$ K$^{-1}$ |
| $\alpha_p$ | $0.48 \times 10^{-3}$ K$^{-1}$ |
| $\delta$ [eq. (14)] | 0.031 L/g |

shown in Table II, the model predictions appeared as previously shown in Figures 1 and 2. The agreement between model and experimental results is quite satisfactory, except for the low initiator concentration in Figure 1. Also, in Figure 2, a discrepancy appears at the portion of the conversion curve below 55%, again for the low initiator concentration. This may suggest that for the low initiator concentration, the initiator efficiency employed (see Table II) may not reflect the true picture. Another possible effect that might be responsible for the discrepancies at low initiator concentrations is the one alluded to by Scott and Senogles,[9] namely that the propagation rate of butyl acrylate might be affected by dimerization of monomer. Worth noting, however, is the fact that in this work no further parameter fit was attempted, since such a fit would not be justified by the information content of the data collected herein. This certainly suggests that further experiments and modelling efforts are needed, if one is to extrapolate to conditions outside the range of experiments of the present work.

## SUMMARY

The use of a model in conjunction with experimental data for the polymerization of butyl acrylate has revealed that termination can be regarded as primarily occurring by combination. Also, the effects of chain transfer to monomer, terminal double-bond polymerization, and chain transfer to polymer may all be significant for the reaction conditions at which the experiments were performed. Clearly, branching reactions are important.

## NOMENCLATURE

| | |
|---|---|
| $C_p$ | ratio of $k_{fp}$ to $k_p$ |
| $[I]$ | concentration of initiator (mol/L) |
| $[I]_0$ | initial concentration of initiator (mol/L) |
| $k_{fm}$ | rate constant for transfer to monomer (L/mol min) |
| $k_{fp}$ | rate constant for transfer to polymer (L/mol min) |
| $k_{fT}$ | rate constant for transfer to a small molecule $T$ (L/mol min); $T$ denotes solvent, |

| | |
|---|---|
| | monomer, initiator, impurity, or chain transfer agent |
| $k_i$ | rate constant of addition of primary radical to monomer (L/mol min) |
| $k_p$ | propagation rate constant (L/mol min) |
| $k_p^*$ | rate constant for terminal double-bond polymerization (L/mol min) |
| $k_p^{**}$ | rate constant for internal double-bond polymerization (L/mol min) |
| $k_p^1$ | propagation rate constant of transferred radical species (L/mol min) |
| $k_t$ | overall termination rate constant (L/mol min) |
| $k_{tc}$ | termination by combination rate constant (L/mol min) |
| $k_{td}$ | termination by disproportionation rate constant (L/mol min) |
| $[M]$ | monomer concentration (mol/L) |
| $\bar{M}_n, \bar{M}_w$ | accumulated number- and weight-average molecular weight, respectively |
| $[R^\bullet]$ | total concentration of radicals (mol/L) |
| $R_{in}^\bullet$ | denotes primary radicals |
| $R_r^\bullet$ | growing radical of chain length $r$ |
| $t$ | time |
| $V, V_T$ | total volume of reaction mixture (L) |

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