

RESIN DESIGN AND OPTIMIZATION: HIGH-TEMPERATURE (140-200°C) N-BUTYL ACRYLATE POLYMERIZATION

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Abstract: Liquid-phase, free-radical, solution polymerization of n-butyl acrylate (nBA) in the absence of initiators at temperatures 140, 160 and 180°C was carried out, and the polymer chains were characterized structurally. On the basis of the characterized chain structures, detailed reaction mechanisms and rate laws were proposed. The postulated reaction mechanism and rate laws were used to develop a mathematical model for an nBA semi-batch polymerization reactor. Reaction rate constants were estimated from measurements of monomer conversion, polymer average molecular weights, number of terminal double bonds and number of branching points. Qualitative customer specifications were quantified and then expressed in terms of indices used at the plant level, leading to quantitative description of the desired resin in terms of plant product-quality indices such as conversion, polymer average molecular weights, number of terminal double bonds and number of branching points. Once decision was made to produce the desired resin in a semi-batch nBA polymerization reactor, by using the developed model a multi-objective optimization problem was formulated and was solved. Operation of the reactor according to the calculated optimal feed policy led to the production of high-quality resins at lower operating costs (due to the use of less initiator and a shorter batch time).

Keywords: resin design, resin optimization, high-temperature polymerization, n-butyl acrylate, mathematical modeling, spontaneous thermal initiation, polymer characterization

1. INTRODUCTION

In response to stricter environmental regulations on the level of volatile organic contents in paints and coatings, high-temperature solution polymerization has increasingly been used to manufacture low-molecular-weight, acrylic polymer resins for automotive coatings [1].

High-temperature (140–200°C), free-radical polymerization of acrylate and methacrylate monomers involves a number of side reactions that affect the quality of the polymer product significantly. These reactions have little

effect at low temperatures. Because the existing “low-temperature” models do not account for these reactions, they are unable to describe accurately the dynamics of nBA polymerization at the high temperatures. Motivated by the poor accuracy, we studied the kinetics of liquid-phase, high-temperature (140–200°C), free-radical, nBA and n-butyl methacrylate, polymerization reactions. The study showed the significant impact of the side reactions that are usually ignored at low temperatures on the final polymer quality. For example, in nBA polymerization, intra/inter chain-transfer to polymer leading to the occurrence of beta-scission reactions and the formation of short/long chain branching were observed.

Electrospray ionization coupled with mass spectrometry (ESI/MS) results on low molecular weight polymer (less likely to have long chain branching) showed that there are five major types of polymer chains. The presence of these polymer chains explicitly suggested the extensive

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occurrence of reactions such as chain transfer-to-solvent and β -scission. 1 and 2D NMR provided a definitive proof of β -scission and chain branching.

A comprehensive model that accounts for monomer thermal initiation, backbiting, chain transfer to polymer, β -scission of tertiary radicals, and consumption of dead chains with terminal double-bonds, was developed. The reaction rate constants were estimated from measurements of conversion, molecular weight, number of terminal double bonds and number of branching points. By using the developed model, a multi-objective optimization problem was formulated and solved. Operation of the reactor according to the optimal feed policy led to the production of high-quality resins at lower operating costs.

Section 2 describes the development of the reactor model, including the model parameter estimation and the model validation. Section 3 presents the optimization formulation and results.

2. MATHEMATICAL MODELING

2.1 Reaction Mechanisms

Liquid-phase solution free-radical polymerization of n-butyl acrylate in the absence of initiators at temperatures 140, 160 and 180°C was carried out in a RC1e calorimeter over a wide conversion range. Conversion, polymer average molecular weights, number of terminal double bonds and number of branching points were measured by gravimetry, gel permeation chromatography (GPC), and 1 and 2D NMR. nBA polymer-chain end groups and structural characteristics (long/short chain branching) of nBA were characterized to understand the complex reactions occurring at the high temperatures. Electrospray ionization coupled with mass spectrometry (ESI/MS) results on low molecular weight polymer (less likely to have long chain branching) showed that there are five major types of polymer chains. The presence of these polymer chains explicitly suggested the extensive occurrence of reactions such as chain transfer-to-solvent and β -scission. 1 and 2D NMR provided a definitive proof of β -scission and chain branching.

For thermal polymerization of nBA, the following elementary reactions were considered: monomer thermal initiation, chain propagation, intramolecular chain transfer, intermolecular chain transfer to polymer, β -scission of tertiary radicals, chain transfer to monomer and solvent, consumption of dead polymer chains with terminal double bonds, and termination by combination (see Table 1). Tertiary radicals formed by intramolecular chain transfer and intermolecular chain transfer to polymer may propagate and consequently lead to short and long chain branching, respectively. Polymer chains with vinylidene double bond may also react with a propagating radical.

The following assumptions were made:

Table 1. Reaction mechanism for high-temperature nBA polymerization.

Initiation	$2M \xrightarrow{k_{th}} 2R_1$ $I \xrightarrow{fk_d} 2R_1$
Propagation	$R_1 + M \xrightarrow{k_p} R_1$
Chain transfer to polymer	$R_1 + D + TC \xrightarrow{k_{tp}} D + R_2$
Backbiting	$R_1 \xrightarrow{k_{bb}} R_3$
Transfer to monomer	$R + M \xrightarrow{k_{rM}} D + R_1$
Transfer to solvent	$R + S \xrightarrow{k_{rS}} D + R_1$
Long-chain branching	$R_2 + M \xrightarrow{k_{p1}} R_1 + LB$
Short-chain branching	$R_3 + M \xrightarrow{k_{p1}} R_1 + SB$
β_2 -scission	$R_2 \xrightarrow{k_{\beta}} D + R_1 + TDB$
β_3 -scission	$R_3 \xrightarrow{k_{\beta}} D + R_1 + TDB$
Terminal double-bond	$R_1 + D + TDB \xrightarrow{k_{tdb}} R_2$
Termination by combination	$2R \xrightarrow{k_{tc}} D$

- Combination is the major termination mode for polymerization of nBA; termination by disproportionation was ignored.
- Initiation by impurities is negligible, and the monomer self-initiation reaction is 2nd-order.
- The tertiary radicals do not participate in intermolecular chain transfer to polymer, backbiting or terminal double bond reactions.

2.2 Reaction Rate

To derive rate laws for high-temperature free-radical polymerization of nBA, the method of Villerraux and co-workers [2, 3] was used. In this method, instead of considering polymer chains with different characteristic molecular structures, separate rate laws are developed for concentrations of characteristic molecular structures, in addition to the rate laws developed for live and dead polymer chains. The assumptions, quasi-steady-state assumption and long chain hypothesis, were made.

$$\begin{aligned}
 r_M &= 2k_{th}[M]^2 + k_{trM}[M][R] + \{k_p[R_1] + k_{p1}([R_2] + [R_3])\}[M] \\
 r_S &= k_{trS}[S][R] \\
 r_I &= 2fk_d[I] \\
 r_{SB} &= k_{p1}[R_3][M] \\
 r_{LB} &= k_{p1}[R_2][M] \\
 r_{TDB} &= k_{\beta}([R_2] + [R_3]) - k_{tdb}[R_1][TDB] \\
 r_{\mu_0} &= 0.5k_{tc}[R]^2 + (k_{trM}[M] + k_{trS}[S])[R] + k_{\beta}([R_2] + [R_3]) - k_{tdb}[TDB][R_1] \\
 r_{\mu_1} &= (k_{tc}[R]^2 + k_{tp}[TC][R_1] + (k_{trM}[M] + k_{trS}[S])[R] + k_{\beta}[R_3])\lambda'_1 + (0.5k_{\beta}[R_2] - k_{tp}[TC][R_1])\nu_1 - k_{tdb}[TDB][R_1]\mu'_1 \\
 r_{\mu_2} &= k_{tp}[TC][R_1](\lambda'_2 - \nu_2) + \{(k_{trM}[M] + k_{trS}[S])[R] + k_{\beta}[R_3]\}\lambda'_2 + k_{\beta}[R_2](0.5\nu_2 - 0.25\nu_1^2) - k_{tdb}[TDB][R_1]\mu'_2 + k_{tc}[R]^2(\lambda'_2 + \lambda_1^2)
 \end{aligned}$$

where

$$R = \left(\frac{2\{k_{th}[M]^2 + fk_d[I]\}}{k_{tc}} \right)^{0.5}$$

$$\begin{aligned}
[R_1] &= \frac{[R]}{1 + \gamma_2 + \gamma_3}, \quad [R_2] = \gamma_2[R_1], \quad [R_3] = \gamma_3[R_1] \\
\gamma_3 &= \frac{k_{bb}}{k_{p1}[M] + k_{t_{rM}}[M] + k_{t_{rS}}[S] + k_{tc}[R] + k_{\beta}} \\
\gamma_2 &= \frac{k_{tp}[TC] + k_{t_{db}}[TDB]}{k_{p1}[M] + k_{t_{rM}}[M] + k_{t_{rS}}[S] + k_{tc}[R] + k_{\beta}} \\
[TC] &= \mu_1 - [LB] - [SB] - [TDB] \\
\mu'_k &= \mu_k/\mu_0, \quad \lambda'_k = \lambda_k/\lambda_0, \quad k = 1, 2 \\
\nu_1 &= \mu_2/\mu_1
\end{aligned}$$

2.3 Balance Equations

Balances on various species and structural characters led to the following model:

$$\begin{aligned}
\frac{dV}{dt} &= F_m + F_I + F_S \\
\frac{dV[M]}{dt} &= -r_M V + F_m[M]_m \\
\frac{dV[S]}{dt} &= -r_S V + F_I[S]_i + F_S[S]_s \\
\frac{dV[I]}{dt} &= -r_I V + F_I[I]_i \\
\frac{dV\mu_k}{dt} &= r_{\mu_k} V, \quad k = 0, 1, 2 \\
\frac{dV[SB]}{dt} &= r_{SB} V \\
\frac{dV[LB]}{dt} &= r_{LB} V \\
\frac{dV[TDB]}{dt} &= r_{TDB} V
\end{aligned} \tag{1}$$

The reaction mixture density was assumed to be constant. Number-average and weight-average molecular weights of dead polymer chains are obtained from:

$$M_n = M_m \mu'_1, \quad M_w = M_m \frac{\mu'_2}{\mu'_1} \tag{2}$$

where M_m is the molecular weight of the monomer. Polydispersity index:

$$PDI = M_w/M_n$$

2.4 Rate Constant Estimation and Model Validation

Accurate reaction rate constant values are available for those reactions that are dominant at low temperatures. For these reactions, the rate constants taken from the literature are given in Table 2. The rate constants, k_{p1} , $k_{t_{db}}$, k_{bb} , k_{β} , k_{th} , and k_{tp} were estimated from measurements of monomer conversion, weight-average

Table 2. Model parameter values taken from the literature.

$k_p =$	$1.66 \times 10^7 \exp\left(\frac{-11270}{RT}\right), \text{ l mol}^{-1} \text{ s}^{-1}$	[4]
$k_t =$	$2 \times 10^{8.67} \exp\left(\frac{-5390}{RT}\right), \text{ l mol}^{-1} \text{ s}^{-1}$	[5]
$k_{t_{rM}}/k_p =$	$0.016 \exp\left(\frac{-15200}{RT}\right)$	[6]
$k_{t_{rS}}/k_p =$	$19.5 \exp\left(\frac{-32145}{RT}\right)$	[7]

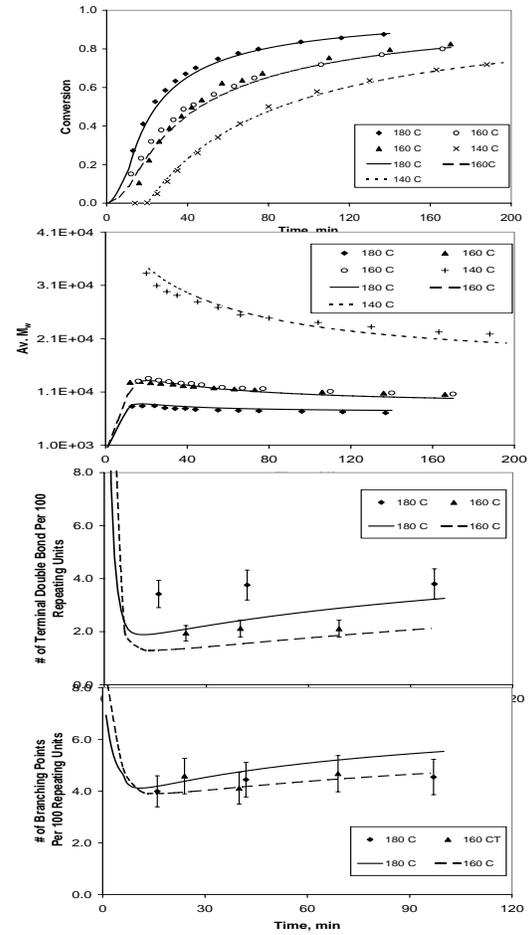


Fig. 1. Model prediction and measurements of monomer conversion, weight-average molecular weight, number of terminal double bonds per 100 monomer units, and number of branching points per 100 monomer units.

molecular weight, number of terminal double bonds, and number of branching points per one hundred monomer-repeating units. A DuPont secrecy agreement does not permit us to report the Arrhenius equations for the estimated model parameters here. Figure 1 compares the model predictions with measurements. One can see that the predictions and experimental data agree reasonably well.

3. REACTOR OPTIMIZATION

Qualitative customer specifications were quantified and then expressed in terms of indices used at the plant level, leading to quantitative description of the desired resin in terms of plant product-quality indices such as conversion, polymer average molecular weights, number of terminal double bonds and number of branching points.

The amount of monomer and solvent to be used in each batch cycle is 7 kg of monomer (nBA) and 3 kg of solvent

Table 3. Optimal nBA-polymerization feed policy.

Batch Time (<i>min</i>)	100	200	300	400
Fraction of monomer added in each time interval	0.11	0.66	0.09	0.00
	0.40	0.33	0.88	0.06
	0.49	0.00	0.00	0.94
	0.00	0.00	0.01	0.00
	0.00	0.00	0.01	0.00
	0.00	0.01	0.02	0.00
Fraction of solvent added in each time interval	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00
	0.68	0.00	0.00	0.00
	0.00	0.00	0.00	0.00
	0.03	0.00	0.00	0.00
Fraction of initiator solution added in each time interval	0.50	0.00	0.00	0.00
	0.00	0.00	0.00	0.00
	0.00	0.00	0.02	0.01
	0.01	0.00	0.00	0.05
	0.01	0.00	0.00	0.03
	0.01	0.00	0.00	0.00
Temperature in each time interval	0.02	0.03	0.03	0.08
	0.00	0.05	0.00	0.01
	448.2	445.7	448.4	411.7
	449.7	445.7	448.1	411.8
	453.2	441.9	452.4	410.9
	453.2	444.3	451.2	415.9
Cost function	453.2	440.7	451.4	414.8
	453.2	441.8	452.2	412.2
	453.2	440.7	452.2	415.8
	453.2	445.7	451.5	413.0
	3.16	0.18	0.12	2.74
	0.99	1.00	1.00	0.95
M_w	8002	7990	7975	7998
PDI	3.8	3.5	3.3	3.9
Total initiator used	0.54	0.08	0.05	0.18

(xylene). Maximum amount of initiator to be used is 1% of the monomer (i.e. 0.07 kg). 1.5 kg of the solvent is loaded initially. 0.35 kg of the solvent is used to dissolve the 0.07 kg initiator in. The initiator solution is added to the reactor according to an optimal feed policy to be calculated. The remaining solvent (1.15 kg) is added as the reaction proceeds. The optimization problem is how to add 7 kg of the monomer, 1.15 kg of the solvent, and at most the 0.42 kg of the initiator solution to the reactor and how to vary the reactor temperature in the range of 120-180°C so that the cost function:

$$10^3(1-x_m)^2 + 10^3\left(\frac{M_w}{8000} - 1\right)^2 + 0.5 * \left(\frac{PDI}{2} - 1\right)^2 + 10 * m_i$$

is minimized. Here m_i is total mass of the initiator added, and x_m is the monomer conversion.

The feed and temperature profiles are time-discretized by dividing the batch time into eight equal time intervals. During each of the time intervals, the temperature and feed flow rates remain constant. The time-discretization converts the dynamic optimization problem into a static optimization problem with (4×8) optimizing variables. The constrained static optimization problem is solved using the Optimization Toolbox of MATLAB. The op-

timal profiles for batch times of 100, 200, 300 and 400 minutes are given in Table 3.

4. NOTATION

D	= dead polymer chain
F_m	= volumetric flow rate of the M feed stream
F_I	= volumetric flow rate of the I feed stream
F_S	= volumetric flow rate of the S feed stream
I	= initiator
$[I]_i$	= molar concentration of I in the I stream
LB	= long branching point
$[M]_m$	= molar density of the monomer
M	= monomer
R	= live polymer chain
R_1	= secondary radical
R_2	= mid-chain tertiary radical
R_3	= near end-chain tertiary radical
S	= solvent
$[S]_i$	= molar concentration of S in the I stream
$[S]_s$	= molar concentration of S in the S stream
SB	= short branching point
TC	= tertiary carbon
TDB	= terminal double bond

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