

Continuous Polymerization Parameters from Batch Kinetic Data

INTRODUCTION

The performance of commercial, continuous polymerization reactors can often be predicted from laboratory or pilot plant semibatch data. Proper scale-up, however, requires that kinetic parameters for batch systems be modified to account for the distribution of catalyst residence times that are characteristic of continuous operation. This is especially true when catalyst activity varies during polymerization.

The relationships between batch and continuous rate data can be expressed in a rather simple, closed form. The equations have been tested for the gas phase polymerization of propylene using modified TiCl_3 -DEAC catalyst.

DERIVATION OF EQUATIONS

Assume simple, first-order polymerization kinetics where chain propagation is rate-limiting, or

$$\dot{P} = k[C^*][M] \quad (1)$$

Monomer concentration $[M]$ is calculated from monomer density at reaction temperature and pressure. In this model, $[M]$ is considered constant; diffusion effects are included in the value of k .

This model treats monomer diffusion effects in this manner because they cannot be separated from kinetic effects. Where diffusion through polymer particles is rate-limiting and catalyst decay rates are measured experimentally at or near operating temperatures and pressures, any particle diffusion effects show up as apparent catalyst activity decay. For gas phase polymerization,

$$[M] = \pi y z m / RT \quad (2)$$

The amount of active catalyst present $[C^*]$ must be calculated differently for batch and continuous systems.

BATCH KINETICS

In the batch system,

$$[C^*] = fC_0 \quad (3)$$

where measured catalyst activity does not change during a polymerization:

$$w = P/C_0 = \dot{P}\theta/C_0 \quad (4)$$

Substituting eqs. (1)–(3) into eq. (4):

$$w = (kf) (\pi y z m \theta) / (RT) = k_0 (\pi y z m \theta) / (RT) \quad (5)$$

Experimental measurements of monomer uptake rate during semibatch polymerizations show that the rate–time relationship can often be approximated as a simple exponential decay.

Often, rates measured during the first few minutes of a semibatch polymerization will show an initial induction period followed by a short period of higher activity before rate begins falling off exponentially. This complication can be ignored when (1) the time before steady decay is short compared to total polymerization time and (2) integration of the actual rate–time curve gives substantially the same productivity as is obtained by extrapolating the decay portion of the rate–time curve back to zero time.

$$r = r_0 \exp(-n\theta) \quad (6)$$

Average polymerization rate becomes

$$r\theta = \int_0^\theta r d\theta = r_0 \int_0^\theta \exp(-n\theta) d\theta = (r_0/n)[1 - \exp(-n\theta)] \quad (7)$$

or

$$r/r_0 = [1 - \exp(-n\theta)]/(n\theta) \quad (7')$$

Inserting this correction into eq. (5),

$$w = (k_0/n)(\pi yzm/RT)[1 - \exp(-n\theta)] \quad (8)$$

A similar relationship had previously been used by Wisseroth¹ to describe gas phase polymerization of propylene.

CONTINUOUS KINETICS

For a continuous system, on the other hand, catalyst is constantly being added to and removed from the reactor. Catalyst concentration in the reactor can be obtained from the catalyst concentration in exiting polymer, which in steady state exactly equals catalyst concentration in the reactor itself. But in the steady state, rates are constant so that

$$C/P = \dot{C}/\dot{P} = 1/w \quad (9)$$

and

$$[C^*] = f(\dot{C}/\dot{P})(\rho V) \quad (10)$$

But

$$I = \rho V \quad (11)$$

Combining eqs. (1), (2), (10), and (11) and rearranging,

$$\dot{P} = \sqrt{k_0 \dot{C} I (\pi yzm)/(RT)} \quad (12)$$

Equation (12) shows that production rate varies as the square root of catalyst feed rate for continuous systems obeying simple first-order kinetics. This relationship also can be calculated from the data of Taylor for continuous slurry polymerization of propylene.²

This equation offers an alternate explanation of Brockmeier's statement that the yield for a continuous backmixed reactor is always less than for a semibatch reactor.³ Catalyst decay and diffusion effects are not needed to explain the rate differences actually observed.

An alternate expression to eq. (12) substitutes catalyst productivity for catalyst feed rate using eq. (9):

$$\dot{P}w = k_0 I (\pi yzm/RT) \quad (13)$$

Equations (12) and (13), like eq. (5) for batch systems, imply constant catalyst activity. To correct for catalyst activity decay, the distribution for catalyst residence times must be taken into account.

CATALYST ACTIVITY DECAY

For a perfectly mixed single stage continuous reactor, the distribution of catalyst residence times⁴ is given by

$$\phi = (1/\tau) \exp(-\theta/\tau) \quad (14)$$

Instantaneous reaction rates for individual catalyst particles in the reactor are given by

$$r = \int_0^\infty \phi r d\theta \quad (15)$$

Substituting eqs. (6) and (14) into eq. (15), then integrating, yields

$$\begin{aligned} r &= \frac{r_0}{\tau} \int_0^\infty \exp[-(1/\tau + n)\theta] d\theta \\ &= \frac{r_0}{1 + n\tau} \end{aligned} \quad (16)$$

The average activity throughout the reactor bed is obtained by integrating eq. (16):

$$\bar{r}\tau = \int_0^\tau r d\tau = (r_0/n) \ln(1 + n\tau) \quad (17)$$

or

$$\bar{r}/r_0 = (1/n\tau) \ln(1 + n\tau) \quad (17')$$

or

$$\bar{r}/r_0 = (\dot{P}/nI) \ln(1 + nI/\dot{P}) \quad (17'')$$

An equation similar to eq. (17'') can be found in Wisseroth¹ to describe continuous polymerization of propylene.

Equation (17'') can be used to correct eqs. (12) and (13) for the effects of catalyst activity decay to yield, respectively,

$$\dot{P} = (k_0\dot{C}/n)(\pi yzm/RT) \ln(1 + nI/\dot{P}) \quad (18)$$

and

$$w = (k_0/n)(\pi yzm/RT) \ln(1 + nI/\dot{P}) \quad (19)$$

COMPARISON OF METHODS

In practice, k_0 and n can best be determined for various catalyst modifications in semibatch laboratory or pilot plant polymerizations at temperatures and pressures similar to those to be employed in the continuous unit. These values can be used directly to predict plant behavior.

Conversion of these equations to slurry or bulk phase polymerization is obvious. The appropriate monomer concentration from gas-liquid equilibrium data or liquid monomer density are substituted for the gas densities used in this paper.

As noted above, diffusion effects are lumped into the numerical values of k_0 and n . By obtaining these parameters at conditions similar to normal operating conditions, no further separation of diffusion and kinetic parameters is either necessary or possible. While perhaps intellectually unsatisfying, this approach is rather pragmatic.

Agreement between semibatch and continuous unit data is illustrated in the table below for several different TiCl_3 -DEAC catalysts evaluated at approximately 30 atmosphere and 80°C (see Table I).

In these calculations, the catalyst decay parameter n was calculated from monomer uptake rate needed to maintain reactor pressure during batch polymerizations. Typical rate decay curves are given for three representative TiCl_3 -DEAC systems in Figure 1. These data were obtained during semibatch polymerizations in 1-L Parr bombs. As seen in Figure 1, the data can be adequately represented by an exponential decay curve [eq. (6)] with $n = 0.33/\text{h}$.

APPENDIX: NOMENCLATURE

- C catalyst inventory in continuous reactor
 \dot{C} catalyst feed rate to continuous reactor

TABLE I
 Agreement between Semibatch and Continuous Unit Data

Catalyst	k_0 , L/g·h	
	Semibatch, eq. (8)	Continuous, eq. (19)
A	92.0	92.7– 93.1
B	98.7	98.2–106.9
C	103.8	100.5–107.1
D	109.4	115.6–117.9
E	112.4	118.3–121.2
F	115.6	106.7
G	122.6	124.0

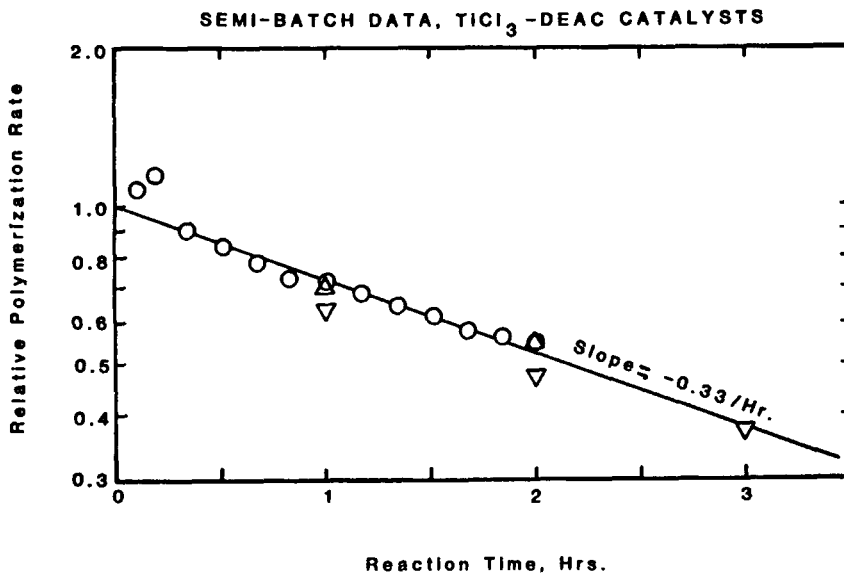


Fig. 1. Typical rate decay relationship.

C_0	weight of catalyst charged to a batch reactor
$[C^*]$	number of active catalyst sites in reactor
f	fraction of catalyst molecules that are active sites
I	polymer inventory in reactor
k	kinetic rate constant
m	monomer molecular weight
$[M]$	monomer concentration (wt/unit vol)
n	apparent catalyst activity decay parameter (reciprocal time)
P	total polymer produced
\dot{P}	polymerization rate
r	instantaneous monomer uptake (polymerization) rate
r_0	rate extrapolated back to zero time
\bar{r}	average reactor rate during polymerization
R	Universal gas constant (consistent units)
T	reactor absolute temperature
V	volume of reactor bed
w	catalyst productivity (wt polymer produced/wt catalyst charged)
y	mol fraction monomer in vapor phase
z	compressibility factor
θ	polymerization time
π	reactor absolute pressure
ρ	bulk density of polymer bed in reactor
τ	nominal average residence time, = I/\dot{P}
ϕ	normalized probability that a catalyst particle has been in the reactor exactly for time θ

References

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JAMES F. ROSS

Northern Petrochemical Company
Morris, Illinois 60450

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