Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article O'toole, J. T.(1968) 'Control of Batch Polymerizations by Continued Feed', Journal of Macromolecular Science, Part A, 2: 1, 183 — 190

To link to this Article: DOI: 10.1080/00222336808053356

URL: http://dx.doi.org/10.1080/00222336808053356

J. MACROMOL. SCI.—CHEM., A2(1), pp. 183-190, Jan., 1968

Control of Batch Polymerizations by Continued Feed

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Summary

The conventional kinetic scheme for a free-radical homopolymerization is modified to incorporate dilution by a feed stream and the effect of propagation on solution density. Neglect of the volume change can result in prediction of erroneously high conversions. The distribution of average molecular weight fractions is evaluated. In the absence of gelation and transfer reactions, the broadening, which is usually thought to arise from varying composition, is found to be small compared to that which is intrinsic to the addition mechanism.

Batchwise free-radical polymerizations are subject to the dual deficiencies of a time-dependent molecular weight and behavior in the late stages which is difficult to predict. It has long been recognized that these factors can be ameliorated by means of continued addition of the primary reactants, and analyses of such schemes have been published [1, 2]. This note is designed to question the importance of the drift which originates with the principal mechanisms and to call attention to certain inadequacies in the previous treatments.

As a framework for discussion, it will be useful to set down rate equations for an addition polymerization allowing for variation in the system volume V and for a specific volume increment v associated with the propagation mechanism:

$$\frac{d}{dt}\,IV = FI_F - k_d IV \tag{1a}$$

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$$\frac{d}{dt} MV = FM_F - k_p{}^2M^2V/\bar{n}k_t \tag{1b}$$

$$\frac{d}{dt} V = F + k_p{}^2M^2Vv/\bar{n}k_t \tag{1c}$$

Here F denotes the volumetric feed rate and $\bar{n} = k_pM/(k_dk_tI)^{1/2}$ the number-average degree of polymerization of the radicals undergoing termination. All other symbols carry the conventional significance. It is important to note that consistent material balances apply only to the <u>total</u> amount of each species. No transfer reactions are considered and the rate constants are assumed to be invariant. Although this model is highly simplified its widespread use justifies an exacting analysis prior to consideration of more complex ones.

MOLECULAR WEIGHT

The two objectives of the control schemes can be treated separately. First, consider the drift in molecular weight which results from consumption of monomer and initiator in proportions which depend on time. It is convenient to delineate systems in terms of a parameter $x = 2k_p(I_0/k_dk_t)^{1/2}$. For slow polymerizations, $x < 1$, and $\bar{n}$ increases monotonically with time in a closed reactor [1]. Fast polymerizations, on the other hand, are characterized by a value of x which is greater than 1 and a minimum molecular weight at some later time. This drift is frequently illustrated by plotting $\bar{n}$ vs. time. This representation, however, fails to emphasize two significant features: (1) equal time increments do not correspond to equivalent contributions to product characteristics as a result of variation of the conversion rate; (2) as long as second-order termination predominates, there are no fractions having less than a certain minimum average degree of polymerization.

A better picture of the dispersion arising from nonstationary concentrations can be obtained by examination of the distribution of whole polymer fractions having a specific value of $\bar{n}$. The unnormalized proportion of each by weight is simply $\bar{n}IV\,dt$. In the absence of continued feed and with the assumption, in the present context, that $v = 0$, the equations (1) can be solved to yield the normalized distribution $w(\bar{n})$. Upon adoption of a dimensionless measure of time, $s^2 = e^{-k_dt}$, the results can be written

$$I/I_0 = s^2 \tag{2a}$$

$$M/M_0 = \exp(xs - x) = s\bar{n}/\bar{n}_0 \tag{2b}$$

$$\bar{n}_0 w(\bar{n})[1 - \exp(xs_1 - 1)] = xs^2/|1 - xs| \tag{2c}$$

where the subscript 0 indicates initial conditions and 1 the final state. When s is a double-valued function of $\bar{n}$ the last expression must be interpreted as the sum of the absolute values of two terms.

The weight distribution of all radicals which existed prior to a given time is given by a weighted integral of $w(\bar{n})$ between the extreme values of the argument. Identification of the instantaneous number distribution as the "most probable," i.e., geometric, yields

$$w(n) = \int d\bar{n}(1 - 1/\bar{n})^n w(\bar{n}) n\bar{n}^{-2} \qquad (3)$$

The function $w(\bar{n})$ is shown in Fig. 1 for representatives of the two

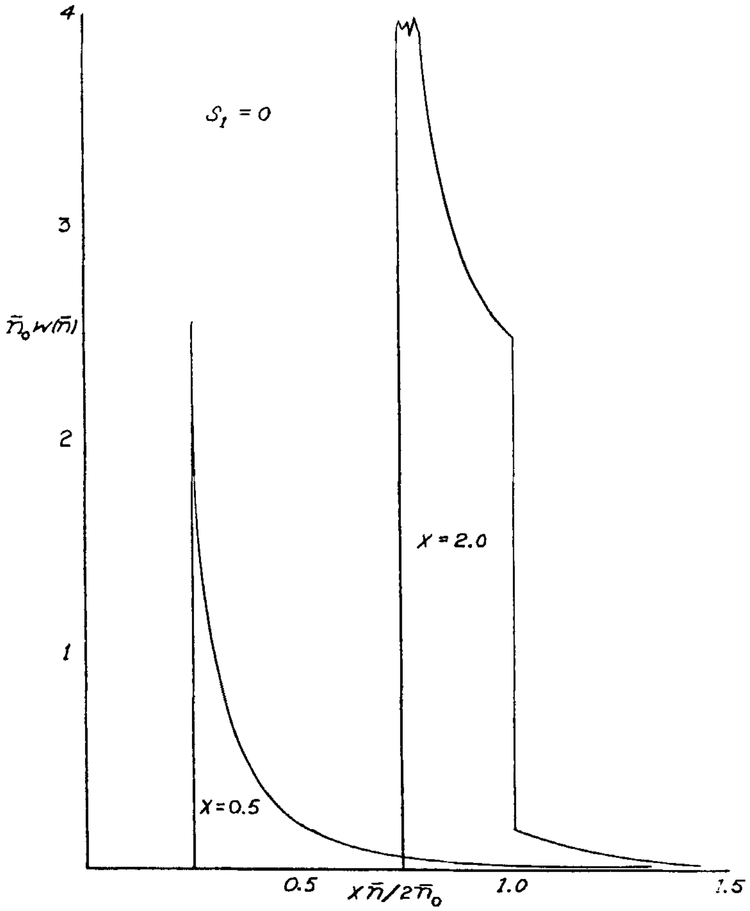

FIG. 1. Weight distribution of average degree of polymerization for unmodified batch reaction.

types of systems. Clearly the fractions themselves are distributed more narrowly than is the material within any given population. All such curves exhibit a finite discontinuity representing the beginning of the reaction. In addition, if $x > 1$, $w(\bar{n})$ becomes infinite at the point corresponding to a minimum molecular weight.

An accepted measure of the width of the distribution is the ratio of weight to the number-average degree of polymerization. The ratio of this parameter for the cumulative material, $\bar{r}$, to that corresponding to the stationary system, r, does not depend on the nature of the termination, i.e., recombination or disproportionation. It is

$$\bar{r}/r = \int d\bar{n}\ \bar{n}^{-1}w(\bar{n}) \int d\bar{n}\ \bar{n}w(\bar{n})$$
$$= \frac{x^2}{2}(1 - s^2)(e^x - e^{xs})^{-2}[\overline{\text{Ei}}(2x) - \overline{\text{Ei}}(2xs)] \quad (4)$$

where $\overline{\text{Ei}}$ is the logarithmic integral [3]. Tabulations of this integral were used to obtain the data listed in Table 1. For all reasonable values of x and of conversion, the predicted additional dispersion is less than the uncertainty in r, which frequently results from lack of knowledge of the mode of termination. If the latter is known, the value of $\bar{r}$ for the polymer product can be obtained upon multiplication by the appropriate numerical factor.

TABLE 1. Relative Heterogeneity $\bar{r}/r$

	x				
s	0.25	0.50	1.0	2.0	4.0
1	1	1	1	1	1
0.8	1.002	1.001	1.000	1.004	1.025
0.6	1.014	1.008	1.001	1.008	1.094
0.4	1.048	1.029	1.006	1.009	1.117
0.2	1.150	1.102	1.039	1.010	1.223
0.1	1.305	1.220	1.099	1.018	1.232
0.01	2.005	1.784	1.415	1.098	1.233
0	∞	∞	∞	∞	∞

It is noteworthy that the logarithmic integral appears in a similar calculation for a model with first-order termination by Chiang and Hermans [4]. They arrived at ratios of the weight to number-average cumulative molecular weight which varied from 1 to 2. On the other hand, an earlier evaluation of the ratio for the case of second-order deactivation by Tobolsky et al. [5] resulted in values of $\bar{r}/r$ between 4 and 5. Their results are believed to be incorrect, as they were based on a modification of Eq. (4) which yielded a divergent integral.

This is not to say that broad molecular weight distributions do not result from transfer reactions, increasing viscosity or variations in temperature. But if these factors are causal, the ideal kinetic scheme represented by Eq. (1) cannot form the basis of a corrective procedure. An indication of the importance of gelation and branching has been given by Nishimura [6], who observed the value of $\bar{r}$ increase by a factor of 2.1 for polystyrene over 80% of the conversion range.

VOLUME EFFECTS AND CONVERSION

The two previous examinations of the semibatch synthesis utilized rate equations which made either no, or only partial, allowance for volume changes. Beste and Hall [2] did so knowingly, apparently having in mind a solution polymerization with addition of relatively concentrated ingredients. This would appear to be a quite reliable approximation for the case of initiator feed only, that is, if $x < 1$. If monomer is to be added, however, the validity of their expressions is not so clear. In addition to this factor, the results of Hoffman et al. [1] are incorrect when $x > 1$, as a consequence of a failure to include the feed term in Eq. (1b). Their expression predicts deceptively high conversions.

The postulated objectives are maximum yield and a value of $\bar{n}$ which does not vary with time. With this point in mind Eqs. (1a–c) can be combined to define an invariant quantity:

$$(I - I_F)V(vM_F + 1) + (M - M_F)(vI_F + 1/\bar{n}) = \text{const.} \tag{5}$$

The remaining integration of the rate equations requires an exact specification of the design of the reaction. As an illustrative example which emphasizes the effect of dilution, consider the case for which monomer is to be fed at the prescribed rate and at the initial concentration level until the quantity $2\bar{n}I/M$ decreases to 1. Afterward, the reaction is to proceed without control. Thus it is assumed that $M_F = M_0$, $I_F = 0$ and, for the sake of clarity, $v = 0$. The complete solution of the rate equations for $(2x - 1)s^2 > 1$ under these conditions is

$$\begin{aligned} 2(M_0/M) &= 2(I_0/I)^{1/2} = 1 + [1 + 2x(s^{-2} - 1)]^{1/2} \\ &= (2/s)(V/V_0)^{1/2} \end{aligned} \tag{6}$$

This result can be compared with that of Beste and Hall by computing the maximum conversion, at $s = 0$, and that at the end of the feed period. If the dilution were neglected, the composition would be given, for $xs > 1$, by

$$M/M_0 = (I/I_0)^{1/2} = s \tag{7a}$$

$$\text{conversion} = (1 - s^2)(2s/x + 1 - s^2)^{-1} \tag{7b}$$

Fractional conversions obtained in this manner, along with that which would result without continued addition, are listed in Table 2. It is evident that for this example modification of the batch reaction produces a decrease in the apparent yield, but the numerical differences are rather small. In contradiction to the statement by Beste and Hall, a terminal period of uncontrolled reaction invariably precludes complete conversion during the period of negligible radical depletion.

TABLE 2. Conversion $1 - M/M_0$: Monomer Feed Only; Steady-State Assumption Invoked

	x		
Conditions	1	2	4
End of feed period, variable volume	0	0.500	0.750
End of feed, constant volume assumed	0	0.600	0.882
Ultimate, variable volume	0.632	0.816	0.908
Ultimate, constant volume	0.632	0.853	0.957
Ultimate, unmodified batch	0.632	0.864	0.982
Ultimate dilution, V/V_0	1	1.333	2.285

In the final stage of polymerization the conventional steady-state assumption is invalid, the rate of generation of radicals becoming insignificant. If termination were entirely by means of a second-order combination the monomer concentration would have the asymptotic form

$$M \sim A(B + k_t t)^{-k_p/k_t} \tag{8}$$

where A and B are constants to be found by matching with the previous approximation. Thus conversion would continue to completion at a very low rate. Because of the relative importance of gelation and transfer reaction, this solution is only suggestive of actual behavior.

In conclusion it might be noted that diagnoses of this sort become meaningful only if the reactor design allows rapid and complete mixing of relatively small quantities of additive. If this is not the case, and it probably is not for most production-scale polymerizations, the predictions are nothing more than mathematical artifacts.

LIST OF SYMBOLS

A, B	undetermined constants; Eq. (8)
$\overline{\mathrm{Ei}}$	exponential integral
F	feed rate
I, I_0, I_F	effective initiator concentration: actual, initial, in feed
k_d, k_p, k_t	rate constants for initiation, propagation, termination
M, M_0, M_F	monomer concentration
$n, \bar{n}, \bar{n}_0$	degree of polymerization: molecular, number average, initial average
$r, \bar{r}$	weight to number average n: instantaneous, cumulative
s, s_1	dimensionless time or conversion: actual, final; Eq. (2a)
t	real time
v	volume increase during propagation
V	system volume
V	reaction volume
w	weight distribution of instantaneous polymer fractions
x	twice the ratio of initial molecular weight to that for complete conversion

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Accepted by editor July 14, 1967
Submitted for publication December 6, 1967

Zusammenfassung

Das konventionelle kinetische Modell einer Radikal-Homopolymerisation wurde modifiziert um auch den Verdünnungseffekt durch Materialzuführung und den Effekt der Kettenfortpflanzung auf die Lösungsdichte zu berücksichtigen. Eine Vernachlässigung der Volumenänderung kann zur Vorausberechnung von irrtümlich hohen Umsatzwerten führen. Ferner wird die Verteilung der Fraktionen mit durchschnittlichem Molekulargewicht behandelt. Bei Abwesenheit von Gelierung und Übertratungsreaktionen war die Streuung, die gewöhnlich auf variierende Zusammensetzung zurückgeführt wurde, klein im Vergleich mit jener die als mit dem Additionmechanismus zusammenhängend angesehen wurde.

Résumé

Le schéma cinétique conventionnel d'une homopolymérisation radicalaire libre est modifié pour y incorporer la dilution par un courrant d'alimentation et l'effet de propagation sur la densité de la solution. Si on néglige le changement du volume on peut obtenir des previsions erronées de conversions elevées. La distribution de fractions de masse moléculaire moyenne est evaluée. Dans l'absence de gelation et de réactions de transfert, on a trouvé, que l'élargissement qu'on supposait provenir de changements de la composition est faible, comparé a celui inhérent au mécanisme d'adition.