Reactive Extrusion of Polypropylene II: Degradation Kinetic Modeling

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Synopsis

A kinetic model for the free-radical-initiated molecular weight degradation of polypropylene was further developed. The model has a single variable parameter, the initiator efficiency, f. Assumptions were detailed, new comparisons with experimental data presented, and model sensitivity to the value of f evaluated. The model was found to provide a good description of both molecular weight distribution and molecular weight average data from degradations carried out in a single-screw extruder at 200 and 220°C. Data at 0.04 wt% initiator feed concentration were fit and the resulting f value used to predict results at 0.01 wt% and 0.02 wt%. In accordance with observation, the model predicted that temperature would have no effect on the molecular weight of the extrudate because the comparatively long (≥ 2.8 min) residence time in the extruder permitted degradation reactions to go to completion. The model predictions were found to depend upon the change in molecular weight distribution rather than the absolute value of the distribution data. Predictions were therefore unaffected by concentration correction in size exclusion chromatography interpretation. The model was determined to have a low sensitivity to the value of f. Hence, f was estimated to only $\pm 25\%$ and it is anticipated that attempts to use the model for comparing different initiators would be limited by this characteristic. Also, because the minimum residence time in the extruder was 2.8 min, the model has yet to be tested against data at times less than this value.
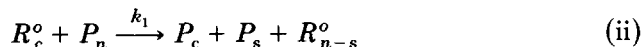
INTRODUCTION

This paper is the second in a series on the degradation of polypropylene by a free radical initiator during extrusion. Part I[1] showed that initiator concentration was of overwhelming importance while temperature apparently had no effect. A review of previous attempts to model polypropylene degradation[2-4] and a new model to explain the above results were recently published[2,3]. This paper extends development of that model. Assumptions are further considered, new comparisons with experimental data are presented, and model sensitivity to the value of its single parameter, the initiator efficiency, is examined.

THEORY

The degradation of polypropylene by a free-radical initiator can be represented by the following model:[2,3]

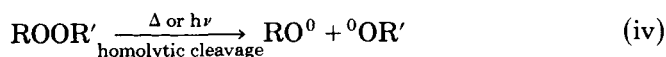*Author to whom correspondence should be addressed.

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Initiation

$$I \xrightarrow{k_d} 2R_c^o \qquad \text{(i)}$$

Hydrogen Abstraction and Chain Scission

$$R_c^o + P_n \xrightarrow{k_1} P_c + P_s + R_{n-s}^o \qquad \text{(ii)}$$

Termination

$$R_r^o + R_s^o \xrightarrow{k_t} P_r + P_s \qquad \text{(iii)}$$

where
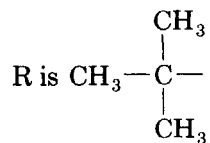
I = free radical initiator;

R_c^o = free radicals produced directly by the initiator (primary free radicals);

R_{n-s}^o = free radicals of length $n - s$ units;

R_r^o, R_s^o = free radicals of length r and s, respectively;

P_n, P_r, P_s = polymer of chain length n, r, and s, respectively;

P_c = molecule resulting from termination of primary free radical by hydrogen abstraction from polymer;

k_d, k_1, k_t = rate constants of initiation, scission, and termination reactions, respectively.
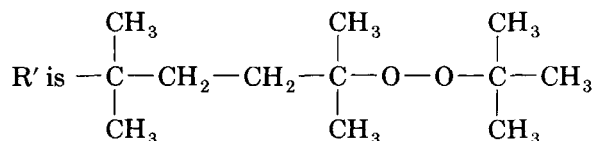
The assumptions inherent in the above model are:

1. The decomposition of the initiator is portrayed as a simple one-step reaction. For the initiator actually used, DHBP (2,5-dimethyl-2,5-bis(t-butyl-peroxy) hexane), the situation is more complicated. The decomposition kinetics in dilute benzene solution and in the polymer matrix was found to be first order.[5,6] Under heat or radiation exposure, dialkyl peroxides decompose homolytically into two free radicals:[6]

$$ROOR' \xrightarrow[\text{homolytic cleavage}]{\Delta \text{ or } h\nu} RO^0 + {}^0OR' \qquad \text{(iv)}$$

where, for DHBP:

$$\text{R is } CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} -$$

and

$$\text{R' is } -\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - O - O - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_3$$
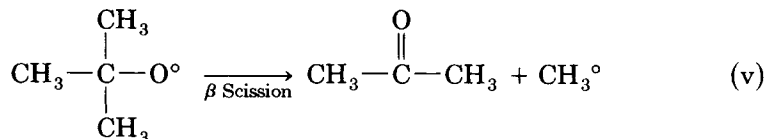
It is assumed here that R' does not further decompose. The observed first-order decomposition for this initiator[6] provides some support for this assumption.

Also, tertiary alkoxy radicals can undergo further fragmentation (e.g., β scission) to form ketones and alkyl radicals:

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O° \quad \xrightarrow{\beta \text{ Scission}} \quad CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3° \qquad (v)$$

Thus, another assumption associated with the initiator is that the secondary reaction is unimportant in the polypropylene degradation.

2. Only R_c^o is considered sufficiently active to degrade polymer. This is reasonable since R_c^o is the tertiary alkoxy radical and is known to be chemically very reactive compared to the polymer free radicals produced by hydrogen abstraction and scission.[7] Furthermore, R_c^o is small and more mobile than polymer free radicals.

3. Termination by combination is negligible. This is a common assumption in polypropylene degradation work and has been shown by many workers to be valid.[8-10]

4. Only polymer free radicals (R_r^o) and no primary free radicals (R_c^o) terminate by disproportionation. This assumption is a consequence of (2) and (3) above.

5. Primary free radicals either terminate by transfer (a consequence of (2) above) or are "wasted" by unspecified side reactions. One source of such side reactions can be proprietary stabilizers contained in the polypropylene fed to the extruder. To account for this "wastage" an initiator efficiency, f, is defined as:

$$f = \frac{\begin{array}{l}\text{Concentration of primary free radicals}\\ \text{which cause chain scission [reaction (ii)]}\\ \text{at time } t\end{array}}{\begin{array}{l}\text{Total concentration of primary free}\\ \text{radicals produced at time } t\end{array}} \qquad (1)$$

Throughout the development it is assumed that f is a constant. Furthermore, as mentioned previously, a single-step initiator decomposition is assumed. If R' in reaction (iv) further decomposes, then the total concentration of primary free radicals produced at time t could be double the value used here.

In this study, f can also help to accommodate such variables as inefficient mixing of the initiator with the polymer in the extruder. The rate equations for the concentrations of each of the reactants and products in the above model were written and a stationary state for all free-radical concentrations present was assumed. Then, in deriving the expression for $[P_r]$, it was found that k_1 and k_t "canceled out" leaving f as the single unknown parameter.[2,3] The following expression for the concentration of polymer of chain length "n" at time t_2, $[P_n]_2$ was obtained:

$$[P_n]_2 = \frac{-\lambda_3}{\lambda_2} + \frac{(\lambda_2[P_n]_1 + \lambda_3)}{\lambda_2} \exp(\lambda_1\lambda_2(t_2 - t_1)) \qquad (2)$$

where

$$\lambda_1 = \frac{2fk_d[I]m_o}{\rho_p} \tag{3}$$

$$\lambda_2 = (1 - n) \tag{4}$$

$$\lambda_3 = 2 \sum_{r=n+1}^{\infty} [P_r] \tag{5}$$

$$[I] = [I]_o \exp(-k_d t) \tag{6}$$

This equation considers only a very small time increment, time t_1 to time t_2. Then, λ_1, λ_2, and λ_3 can be considered constant at the time t_1 value and the above equation can be used to step from the $[P_n]$ at time t_1 (i.e., $[P_n]_1$ to the $[P_n]$ at time t_2 ($[P_n]_2$): That is, it allows us to step from a known $[P_r]$ versus r at time zero to a $[P_r]$ versus r distribution at any other time by proceeding in a series of small time increments. The value of λ_3 is calculated with the aid of the molecular weight distribution calculated at the end of the previous increment. The molecular weight distribution of the feed is supplied to begin the calculation. The summation represented by λ_3 need only use the molecular weight distribution ordinates at chain lengths greater than the chain length of interest. This is advantageous because inaccurate low molecular weight tail ordinates can be avoided.

Before comparing the individual computed polymer concentrations with those obtained from the extruder, the residence time distribution must be considered. This can be done by numerically solving the following equation:[11]

$$\overline{[P_n]} = \int_o^{\infty} [P_n](t)E(t)\,dt \tag{7}$$

where $E(t)$ is the normalized residence time distribution and the bar over the $[P_n]$ on the left-hand side of the equation indicates that it is an average value obtained by summing the contributions from all residence times.

MODEL FITTING AND STATISTICS

Fitting this model to the data requires nonlinear regression. The Fibonacci method is the most efficient single parameter search known. It can be used to search for initiator efficiency, f, until the following "objective function" is minimized:

$$O(f) = \sum_{j=1}^{n} w_j |\Delta_j(y)|^p \tag{8}$$

where f the initiator efficiency, is the parameter to be determined, w_j are weighting factors, $\Delta_j(y)$ is the residual ($\Delta_j(y) = y_j - \hat{y}_j$), y_j is the observed experimental value of the response, $\hat{y}_j$ is the value of the response predicted by the fitted equation and, p is a chosen constant.

Here,

$$\hat{y}_j = [P_r] \text{ obtained from Eq. (2)};$$

$$p = 2 \text{ (i.e., a least-squares analysis)}.$$

In engineering practice, objective functions of the above form are often used. However, it is important to realize that different forms can give dramatically different results. Even when the form is fixed, the value of the weighting factors can be chosen based on one or more criteria: purely statistical considerations centering upon the error in the data; the desire to fit one particular area of the data because it is most important to product performance; the need to properly "scale" the equation in order to ease the work of the nonlinear regression method.

With the use of only statistical considerations and assuming that the error in each individual polymer concentration used is independent of the error in any other, the weighting factors, w_j, are equal to the reciprocal of the error variances (i.e., $w_j = 1/\sigma_j^2$ where σ_j^2 is the error variance of $[P_r]_j$. The initial fitting[3,4] was done by setting $w_j = 1/([P_r]_j)^2$. It was therefore assumed that the error variances were proportional to the square of the magnitude of the response variables.

This assumption can be readily examined by examining the proportionality after calculating the error variances. If incorrect, the actual values of the error variances can be used instead of using the assumption.

In addition to providing a realistic treatment of the data, by decreased weighting of the least precise data, the use of statistics to choose the weighting factors enables us to estimate the precision of the initiator efficiency values obtained. Determining the "95% confidence limits" on "f" is important if the model is to be used in future with data from different initiators in order to determine which has the highest efficiency.

Equation (2) is nonlinear in the parameter "f." Thus the usual procedure is to obtain an approximate confidence interval by using a first-order Taylor series expansion in terms of the parameter. Equation (2) can be written:

$$[P_r] = F(f, r) \tag{9}$$

where f is the parameter, r is the independent variable, and $[P_r]$ is the response.

The approximate $(1 - \alpha)$ 100% confidence interval can then be determined from:

$$\text{confidence}_{\text{limits}} = \pm t_{\nu, \alpha/2}(V(f))^{1/2} \tag{10}$$

where

$t_{\nu, \alpha/2}$ is the $(1 - (\alpha/2))$ 100% point of the

t-distribution with ν degrees of freedom.

$$V(f) = (X'.X)^{-1}\sigma^2, \tag{11}$$

and X and X' are the matrix and transpose matrix (for one independent variable, the matrices become vectors) with the elements

$$X_j = \frac{\delta F(f, r)}{\delta f} \qquad (12)$$

and σ^2 is the error variance of the $[P_r]$ data. In using Eq. (10) it is common practice[12] to consider the value of $t_{\nu, \alpha/2}$ as 2 (since Eq. (10) is only an approximation because the model is nonlinear and since its value is near 2 for larger numbers of observations). Also, an overall estimate of σ^2 can be obtained from:

$$\sigma^2 = \frac{\text{minimum value of the objective function}}{(k - 1)} \qquad (13)$$

where k is the number of observations.

The initial modeling work was done by fitting the $[P_r]$ versus r data at seven selected values of r by searching for f using the Fibonacci Search method to minimize Eq. (8). The values of r used were: 388, 784, 1602, 3405, 7722, 19169, and 53442. The weighting factors in Eq. (8) were the reciprocal of the square of the experimental $[P_r]$ values.

Although $[P_r]$ versus r, the "chain length distribution," is a form of the molecular weight distribution and is directly predicted by the kinetic model, being a "number" distribution, it heavily weights the low molecular weight end. It is possible that detail of the high molecular weight end, the end that was of most interest in this work, could be lost. To examine that possibility, the model can readily be made to predict a form of the distribution which has the logarithm of molecular weight on the abscissa. The ordinate of this distribution is termed W_N (log M) where W_N (log M) d log M is the weight fraction of polymer molecules with molecular weight between log M and log M + d log M. The relationship between this ordinate and $[P_r]$ is:[13-15]

$$[P_r] = \frac{\rho_p}{2.303 \, m_o r^2} W_N(\log M) \qquad (14)$$

where ρ_p is the density of the polymer and m_o is the monomer molecular weight.

W_N (log M) versus log M closely resembles the raw output from the size exclusion chromatograph, the instrument used here to obtain the molecular weight information. The basic reason for this is that separation in size exclusion chromatography (SEC) is often nearly a straight line when plotted as log M versus retention time. Details of the distribution visible on the chromatogram are plainly seen on a plot of W_N (log M) versus log M but are frequently concealed when $[P_r]$ versus r are plotted. In the remainder of this paper, although there is some reference to chain length distribution, most of the discussion will examine W_N (log M) versus log M and refer to it alone as the molecular weight distribution.

Model sensitivity to the value of f is closely related to the precision of the f values. In addition, model sensitivity indicates if there are any values of f which could cause unexpectedly large or small changes in molecular weight distribution. The X_j given by Eq. (12) is sometimes referred to as the sensitivity coefficient.[12] It indicates the change in the value of the polymer concentration $[P_r]$ obtained as a result of a small change in the parameter f. If desired, W_N (log M) can be substituted for $[P_r]$ to show changes in the molecular weight distribution.

It is possible to calculate the X_j and plot them as a function of f. However, for this single-parameter case it is even more straightforward to simply show how molecular weight distributions and molecular weight averages change as f is changed. This type of inspection is something that would normally be done before any regression method is used to see if the model has a chance of fitting the data.

EXPERIMENTAL

Experimental work to obtain the data used here is summarized in Refs. 1, 2, 13–16. All of the kinetic modeling work was done on a PC-XT compatible microcomputer (Ultimate Business Systems Ltd., Toronto, ON).

RESULTS AND DISCUSSION

General Characteristics of the Model

Figure 1 shows the variation of the predicted molecular weight distribution as initiator efficiency is changed from 0 to 1.0 in steps of 0.1 (assuming 0.04 wt% initiator and 220°C). The molecular weight distribution of PD 888 polypropylene was used as the initial condition. The distributions lose their high molecular weight tail and become narrower as the initiator efficiency is increased. Since f and initial initiator concentration appeared as a product in Eq. (3), increasing initiator efficiency had the same effect as increasing initiator concentration. The result appeared very similar to the experimental data presented previously.

Figure 2 shows the effect of increasing initiator efficiency (or initiator concentration) on $\overline{M}_n$ and $\overline{M}_w$ as predicted by the model. $\overline{M}_n$ decreased by a maximum of 17.3% and $\overline{M}_w$ by a maximum of 41.6% as f was changed from 0.00 to 1.0. These percentages bracketed the experimental values of 14.8 and 33.5%, respectively, observed previously.

These predictions were obtained from solving Eq. (2). When Eq. (7) was used with Eq. (2), identical results were obtained regardless of which experimentally determined residence time distribution was employed for $E(t)$. The essential reason for this effect was that all of these residence time distributions included a relatively long (≥ 2.8 min) time delay as part of the curve. The predictions are for extrudate molecular weights and extrudate must reside in the extruder for at least 2.5 min. According to this model, when literature values of rate constants k_d are used (7.08 min^{-1} at 200°C and 39.42 min^{-1} at 220°C)[6] 2.8 min is more than sufficient time for all polymer degradation to be completed.[2,3] For this reason, in all of the results in this paper, only Eq. (2) was used.

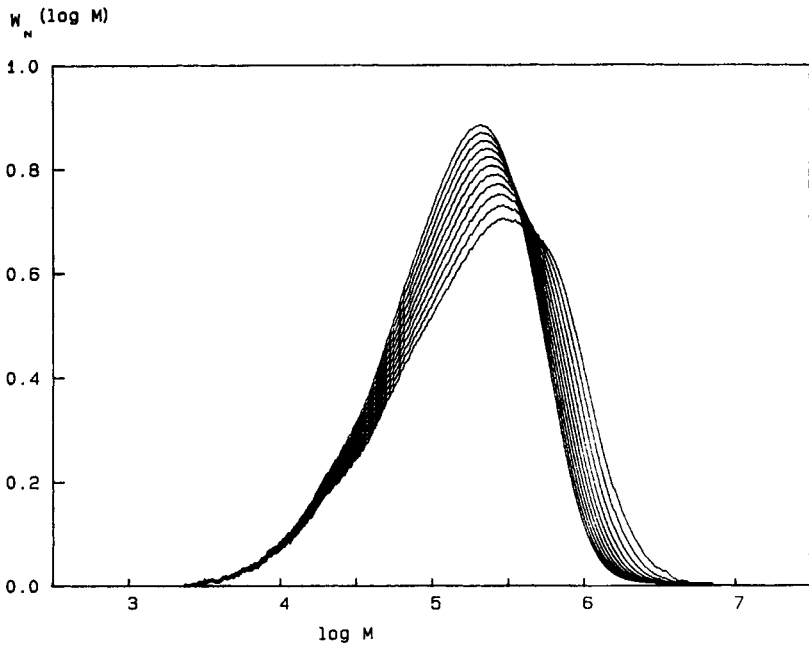Fig. 1. Variation of predicted molecular weight distribution with initiator efficiency, f. The narrowing of the molecular weight distribution is shown as it increases from 0 to 1.0 in steps of 0.1.
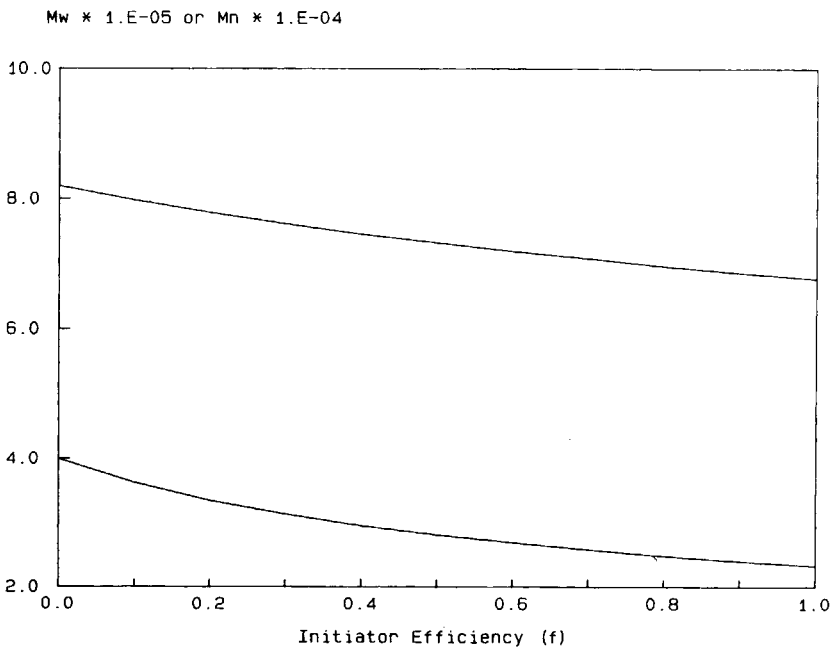

Fig. 2. Variation of molecular weight averages with initiator efficiency, f. Upper curve is $\overline{M}_n$ and lower curve is $\overline{M}_w$.
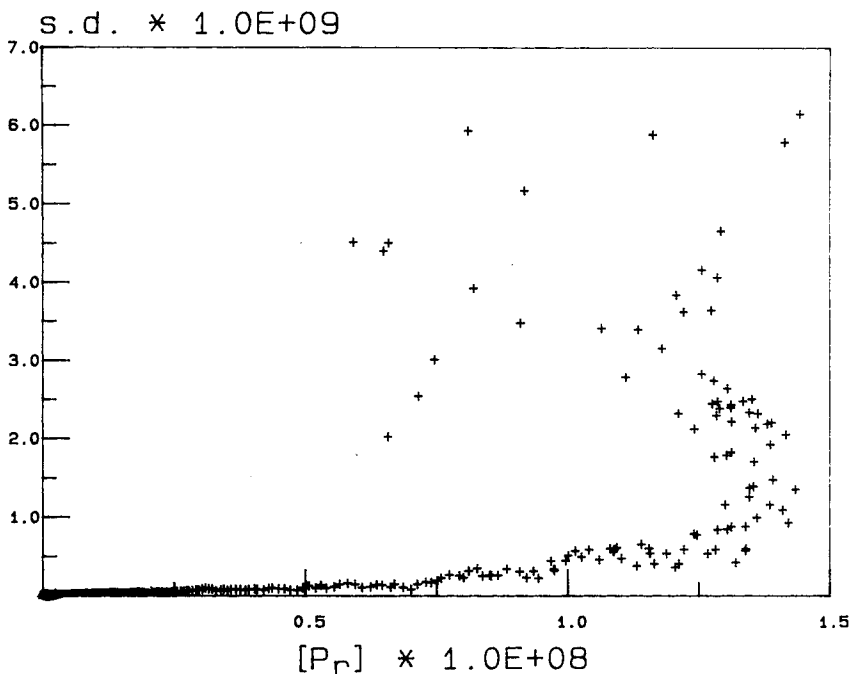
Fig. 3.   Error standard deviation of $[P_r]$ (s.d.) versus $[P_r]$.

Fitting and Predicting the Molecular Weight Data

The model was tested by fitting data at the 0.04 wt% initiator concentration and using the f value so obtained to predict the data at the lower concentrations. In accomplishing this, the weighting factor values used meant that a proportionality between the error variance of the $[P_r]$ and $[P_r]$ was assumed. The assumption was examined by calculation and plotting of the actual variance values in Figure 3. Since it was then evident that the proportionality only holds for the lowest values of r the better alternative of using the reciprocal of the actual error variance values as weighting factors was employed instead. As shown in Table I the resulting estimated f of 0.58 ± .15 is not significantly different from the value of 0.60 previously determined.[2,3]

The result of using W_N (log M) versus log M instead of $[P_r]$ versus r is shown in Table I. Again no significant change in f was found.

Another concern was the possible need for a concentration correction in the SEC interpretation. There was likely an effect of injection concentration on the peak retention times of very high molecular weight polystyrene standards used in calibration. However, the subject of how to correct for this effect remains a subject of research. One popular method, the Rudin Model,[17] was applied to the data and found to significantly change the molecular weight distributions. Figure 4 shows an example. The interesting result however, was that, as shown in Table I, when the corrected data were used, the estimated f values were not significantly different from those of the uncorrected data. The reason for this was attributable to the model being mostly dependent upon the change in the molecular weight distribution rather than the absolute value

TABLE I
Estimation of Initiator Efficiency

T (°C)	Fitted data	$f \pm 2\sigma_f$	Obj. fun. $\times 10^{19}$
220	uncorrected [P_r] vs. r	0.58 ± 0.15	0.266
220	uncorrected W_N vs. log M	0.60 ± 0.15	0.268
220	corrected [P_r] vs. r	0.59 ± 0.13	0.210
200	uncorrected [P_r] vs. r	0.60 ± 0.13	0.142
200	uncorrected W_N vs. log M	0.53 ± 0.14	0.162

of the distribution at any time. Model predictions are based on both a molecular weight distribution at time zero and a single value of f. It is the change in the molecular weight distribution that is important and not the absolute value of the distributions. By subtracting distributions it was demonstrated[14,16] that this change was not significantly different with or without the concentration correction.

Figures 5 to 7 show the results of using a value of f = 0.60 obtained from fitting the molecular weight distribution at 220°C and at 44 rpm. Figure 5 shows that the fit is also good to the 200°C data at the same screw rpm. Furthermore, predictions at both temperatures for lower initiator concentrations (Figs. 6 and 7) are within the experimental error of the data.

Table II shows the results of this fitting/predicting process in terms of molecular weight averages. Results are within experimental error.

Precision of Initiator Efficiency Estimates

The 95% confidence limits for the initiator efficiency values determined by the search are shown in Table I. It can be seen that the confidence interval is quite wide ($\pm 25\%$). Figure 2 and Table III show that the uncertainty in f translates into a 3% uncertainty in $\overline{M}_n$ and a 6% uncertainty in $\overline{M}_w$. These are the same as the estimated uncertainties in experimentally measuring these quantities. Thus, comparatively large variations in f can be tolerated before a significantly different molecular weight average is evident. The consequence of this is that initiator efficiencies from this model likely only provide a coarse gradation of differences in initiators.

Figure 8 shows the effect of the confidence limits of f on the theoretical molecular weight distributions obtained. Again, comparing the results to experimental reproducibility (Fig. 1, Ref. 1) it is evident that the 25% variation in f causes a change which is within the experimental reproducibility of the measured molecular weight distributions.

CONCLUSIONS

It was further demonstrated that a kinetic model having only a single variable parameter, the initiator efficiency, f, adequately fit and predicted
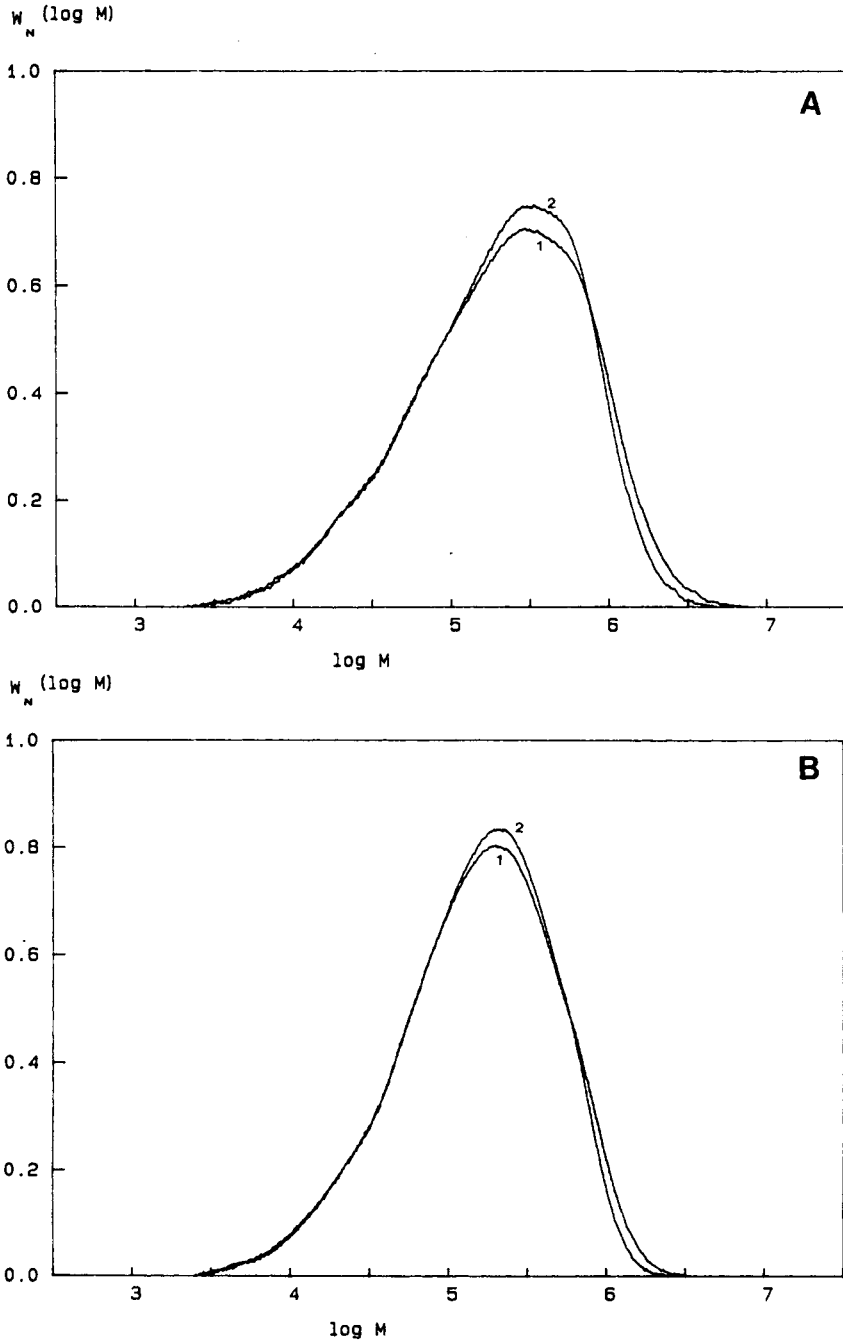
Fig. 4.   The effect of concentration correction on the molecular weight distribution of extruder feed and final product: (A) Feed (PD 888 Polypropylene); (B) product obtained from run at 220°C and 0.04 wt% initiator. 1 = uncorrected; 2 = corrected.
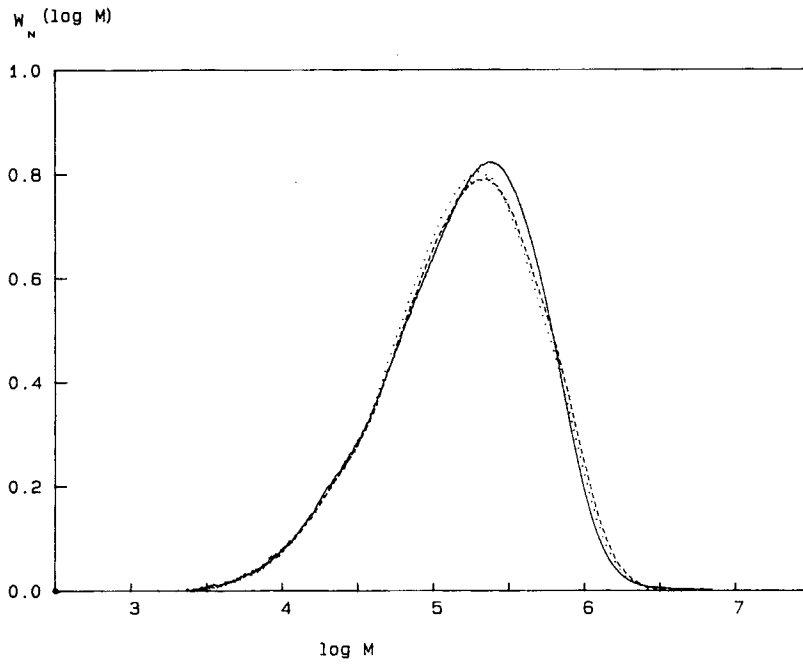
Fig. 5.   Molecular weight distributions of extrudate obtained with 0.04 wt% initiator: (---)200°C; (· · ·)220°C; (—)kinetic model fit.
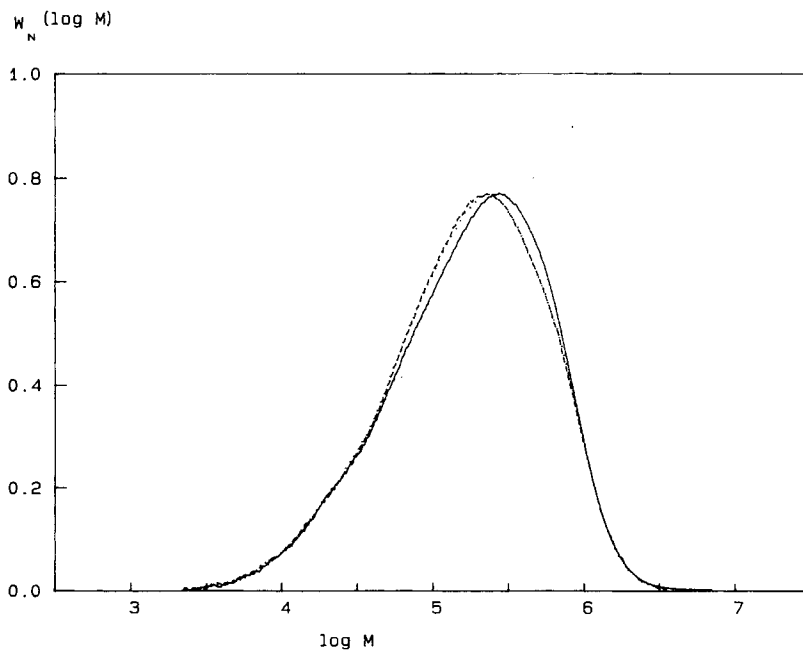

Fig. 6.   Molecular weight distributions of extrudate obtained with 0.02 wt% initiator: (---)200°C; (· · ·)220°C; (—)kinetic model fit.
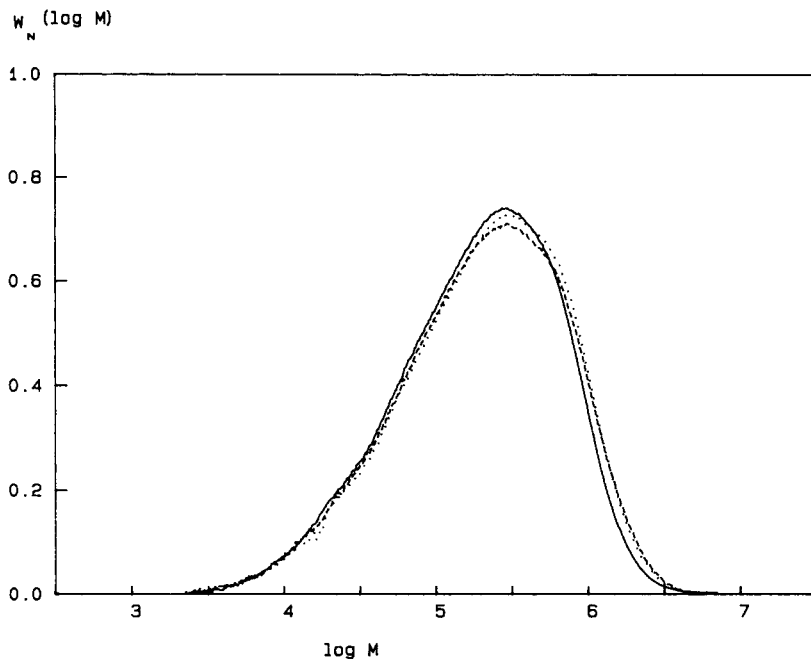
Fig. 7.   Molecular weight distributions of extrudate obtained with 0.01 wt% initiator: (---)200°C; (· · ·)220°C; (—)kinetic model fit.

TABLE II
Molecular Weight Averages: Experimental and Theoretical

$[I]_o$ wt%	$\overline{M}_n \times 10^{-4}$			$\overline{M}_w \times 10^{-5}$		
	200°C	220°C	Model	200°C	220°C	Model
Feed	8.19	8.19	—	4.00	4.00	—
0	8.10	7.89	7.89	4.11	4.06	4.06
0.010	7.66	8.15	7.88	3.78	3.87	3.50
0.020	7.38	7.33	7.62	2.98	2.98	3.15
0.040	7.25	6.98	7.18	2.67	2.66	2.71

TABLE III
Effect of Confidence Interval on Molecular Weight Averages
and Polydispersity (220°C, 0.04 wt%)

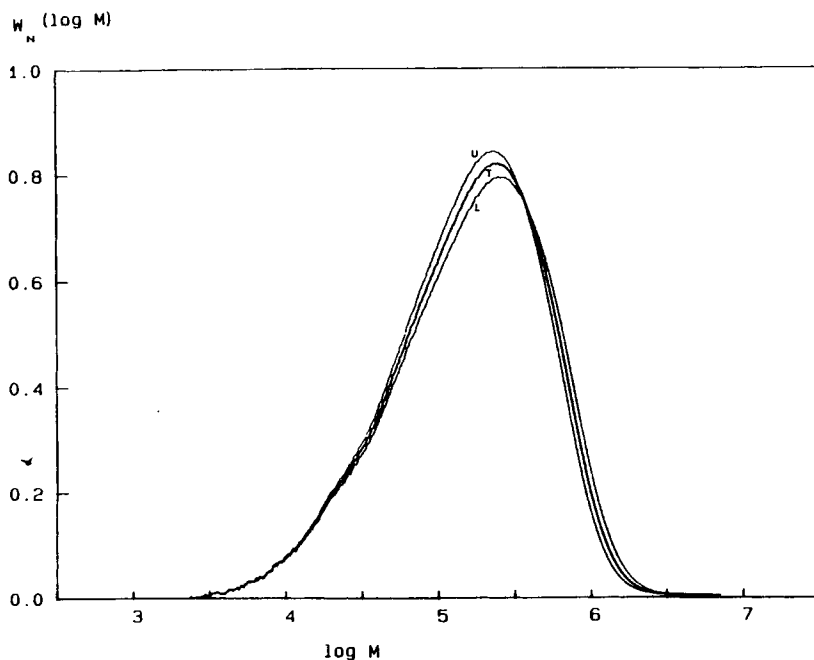| Condition	f value	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
Lower limit	0.43	7.41	2.91	3.92
Estimated value	0.58	7.21	2.71	3.76
Upper limit	0.73	7.04	2.55	3.62

W_N (log M)

Fig. 8. Effect of precision of f on the calculated molecular weight distribution: L for f = (lower 95% confidence limit); T for f = (estimated value); U for f = (upper 95% confidence limit).

molecular weight distribution, $\overline{M}_n$ and $\overline{M}_w$ data over the range of conditions investigated. In particular, the model correctly predicted that no effect of temperature would be evident because of the long "plug flow" residence time in the extruder.

For the range of conditions examined here, this model did not require data which was of absolute accuracy. Since it utilized the measured molecular weight distribution of the feed as its initial condition, change in molecular weight distribution was the important information. The same value of f was found to fit molecular weight distribution data which was concentration-corrected as that which was not so corrected.

Use of the molecular weight distribution based upon a $\log M$ scale gave the same results as use of a chain length distribution.

The model was not very sensitive to the value of f. It was determined that f was estimated to only $\pm 25\%$. This variation in f corresponded to a variation in theoretical molecular weight distribution, $\overline{M}_n$ and $\overline{M}_w$ that was the same as the estimated experimental error in these quantities ($\pm 3\%$ and $\pm 6\%$, respectively). This will limit utility of the model for distinguishing different initiators based upon their initiator efficiency.

Since the minimum residence time in the extruder was 2.8 min, this model has yet to be tested against data obtained at lower reaction times.

NOMENCLATURE

$E(t)$	normalized residence time distribution ordinate
f	initiator efficiency
I	free radical initiator
k_1	transfer and scission rate constant
k_d	decomposition rate constant
k_t	termination rate constant
m_o	monomer molecular weight
$\bar{M}_n$	number-average molecular weight
$\bar{M}_w$	weight-average molecular weight
$[P_r]$	ordinate of polymer chain length distribution or the concentration of polymer of chain length r (mole per unit volume)
P_c, P_n, P_r, P_s	polymer of chain length c, n, r, s, respectively
r	chain length, number of monomer units
R_c^o	primary free-radicals (directly from initiator)
R_{n-s}^o, R_r^o, R_s^o	free-radicals of chain length $n - s$, r, s, respectively
t	time
$W_N (\log M)$	ordinate of the molecular weight distribution ($W_N (\log M)$ d $(\log M)$ is the weight fraction of polymer between $\log M$ and $\log M + d (\log M)$).
w_j	weighting factor
y_j	response variable
λ_1, λ_2, λ_3	parameters in Eq. (2) [defined by Eq. (3), (4), and (5)]
ρ_p	polymer density

Subscripts

o	time zero
t	time, t

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