

Prediction of Molecular Weight Distribution of High-Density Polyethylene Made in a Continuous Reactor from Fixed Ethylene Concentration Batch Reactor Data

R. E. HOFF and M. SHIDA, *Chemplex Company, Rolling Meadows, Illinois, 60008*

Synopsis

The polydispersity index, M_w/M_n , of the product of an ideal continuous stirred tank reactor can be predicted from batch reactor data. A method for the prediction, in the case of high-density polyethylene synthesis, comes from finding the effect of catalyst age upon yield, M_w , and M_n in a batch reactor operated at constant pressure. These catalyst age effects are combined with the catalyst age distribution in the continuous reactor, and integration over all ages gives the yield and the polydispersity index for the continuous reactor product. This scheme for prediction was applied to a particular catalyst system, and the calculated values have been found to agree with observations.

INTRODUCTION

Small-scale laboratory polymerization experiments are frequently done in batch reactors. In the case of ethylene polymerization, the pressure may be held constant by supplying monomer gas as it is consumed. Many industrial processes are operated continuously. The differences between the continuous processes and the batch-type reactors, with respect to product properties, have been analyzed, but all factors have not been taken into account.¹ Denbigh² has compared the molecular weight distributions of continuous and batch reactors in respect to the relation between polymer chain growth time and the time of passage in the continuous stirred tank reactor (CSTR). When the growth time is short compared to the time of passage, the CSTR gives the more narrow molecular weight distribution because of the constant monomer concentration. When the growth time is long compared to the time of passage, the CSTR gives a broader distribution due to the spectrum of residence times. Ethylene polymerization, with supported catalysts, is a reaction in which the polymer growth time is very short.³ Consequently, if the batch reactors are operated at constant monomer concentration, the distinctions between the product of the batch reactor and the CSTR in Denbigh's description become uncertain.

There is, however, a factor not considered by Denbigh² and other investigators,¹ namely, that the catalyst characteristics and the instantaneous molecular weight distribution can be time dependent. Whitaker and Wills⁴ found such a time dependence. The existence of the time dependence is confirmed by our study, although we have found a different kind.

The purpose here is to describe a method of predicting the molecular weight distribution, represented by the commonly used polydispersity index M_w/M_n of the product of a CSTR from batch reactor data. The method is exemplified with the polymerization of ethylene on a supported catalyst, but it should be applicable in any case in which the polymer growth reaction is very short in duration compared to the residence time, and the instantaneous polymer properties change with time at constant monomer concentration.

EXPERIMENTAL

Materials

The catalyst used in this study was of the Phillips type.⁵ It consisted of 2% CrO₃ on 98% SiO₂. Its particle size range was 40–150 microns. It was activated in dry air at 800°C for 5 hr and upon cooling was kept under an atmosphere of dry nitrogen. Ethylene and isobutane were obtained from the Chemplex plant and dried by passage through columns of molecular sieves.

Reaction Vessel

Polymerization experiments were conducted in a 1300-ml stainless steel vessel equipped with an updraft, three-blade marine propeller operated at 420 rpm. Temperature control was provided by refluxing liquid in a surrounding jacket. By variation of the confining pressure, the temperature could be kept within $\pm 2^\circ\text{C}$ of the desired temperature.

Polymerization Rate

Polymerization rate was determined by means of a calibrated flowmeter as described by Hogan.^{3,6} When experimental reactions were completed, the yields were checked by weighing the polymer (Table II).

Reaction Conditions

Catalyst was charged to the ethylene-purged pressure vessel kept at the desired operating temperature, 102°C, the valve was closed, 500 ml of isobutane was forced in with ethylene pressure, and then ethylene was supplied to give 550 psig. The pressure was kept constant by means of a Hoke Model 920 regulator.

Molecular Weight Distribution

A Water Associates Model 200 gel permeation chromatograph was used to determine the molecular weight distributions. Four columns of Styra-

gel of pore sizes 10^6 , 10^5 , 10^4 , and 10^3 Å were used. The operating temperature was 135°C , and 1,2,4-trichlorobenzene was used as the solvent. The flow rate was 1.0 ml/min; 2.0 ml of a 0.25% polymer solution was injected after filtering at 135°C .

THEORETICAL CONSIDERATIONS

The continuous polymerization process takes place under conditions that result in the formation of solid particles of polyethylene maintained in suspension by the mixing devices. The mixing is assumed to be ideal, so that at each instant the product removed is representative of the polymer contained in the reactor vessel. Fragmentation of the particles occurs sufficiently to eliminate the need to consider segregation.^{7,8} Catalyst is removed with the polymer product, either embedded in or attached to the surface of the particles. The process is operated under steady conditions so that the production rate, the amount of polyethylene, and the amount of catalyst in the reactor remain constant.

Under these conditions, the residence time distribution of the catalyst can be expressed in terms of the polymer mean residence time. This residence time distribution serves to produce equations for the yield and the M_w/M_n of the continuous reactor when combined with batch reactor data.

The catalyst residence time distribution is derived as follows: q = feed rate of catalyst, in g/min; N = mass of polyethylene in the reactor; p = production rate, in g/min; C_T = total mass of catalyst in the reactor; C_A = mass of catalyst in the reactor with age less than t ; C_B = mass of catalyst in the reactor with age greater than t ; $\phi'(t)$ = the fraction of the catalyst which remains in the reactor for a period of time between t and $t + dt$; and $x(t)$ = mass of polyethylene produced per gram of catalyst, a function of age (t).

When the reactor is operating at a steady state, a zero time is arbitrarily selected. All of the catalyst that enters the reactor after this instant is new catalyst, and its mass at any clock time t' is defined to be C_A . Three factors control the rate at which new catalyst is removed. The first factor is the production rate, and the second factor is the fraction of the total polyethylene mass originating from the new catalyst. The third factor is the amount of catalyst contained per gram of that polyethylene. The factors causing the decrease in old catalyst are similar, and the mathematical form of these considerations gives eqs. (1) and (2):

$$\frac{dC_A}{dt'} = q - p \frac{\int_0^{t'} x(t)\phi'(t)C_T dt}{N} \frac{C_A}{\int_0^{t'} x(t)\phi'(t)C_T dt} \quad (1)$$

$$\frac{dC_B}{dt'} = -p \frac{\int_{t'}^{\infty} x(t)\phi'(t)C_T dt}{N} \frac{C_B}{\int_{t'}^{\infty} x(t)\phi'(t)C_T dt} \quad (2)$$

Integration of eq. (1) and eq. (2) yields eqs. (3) and (4), respectively:

$$\frac{C_A}{q} = \frac{N}{p} (1 - e^{-pt'/N}) \quad (3)$$

$$\frac{C_B}{C_T} = e^{-pt'/N}. \quad (4)$$

Because the catalyst content of the reactor, C_T , is constant, eq. (4) leads to eq. (5):

$$\frac{C_A}{C_T} = (1 - e^{-pt'/N}). \quad (5)$$

Combining eq. (5) and eq. (3) shows that the mean residence time of the catalyst is equal to the mean residence time of the polyethylene:

$$\frac{C_T}{q} = \frac{N}{p} = \theta. \quad (6)$$

The residence time distribution of the catalyst is the time derivative of eq. (5), specifically

$$\frac{d(C_A/C_T)}{dt} = \frac{e^{-t/\theta}}{\theta}. \quad (7)$$

Equations (5) and (7) have been derived for catalysts under different conditions^{9,10} and for inert tracers.^{1,2}

The catalyst age distribution multiplied by the yield as a function of age from batch reactor data, and integrated over all ages, provides the yield for the continuous reactor. We find that the batch reactor data, as shown in Figure 1, can be approximated by the relations

$$x = \frac{at^2}{2} + bt \quad 0 < t < t_1 \quad (8)$$

$$x = c(t - t_1) + \frac{at_1^2}{2} + bt_1 \quad t > t_1. \quad (9)$$

Consequently, the yield per gram of catalyst in the continuous reactor is

$$\bar{x}_\theta = \int_0^{t_1} \left(\frac{at^2}{2} + bt \right) \frac{e^{-t/\theta}}{\theta} dt + \int_{t_1}^{\infty} \left[c(t - t_1) + \frac{at_1^2}{2} + bt_1 \right] \frac{e^{-t/\theta}}{\theta} dt. \quad (10)$$

Other than by the constants a , b , c , and t_1 , which are fixed by the reactivity of the catalyst, the yield is determined by the residence time of the polymer. This kind of equation has been previously used to predict yield for continuous reactors based upon model reactivities.⁹

However, the purpose of this paper is to predict the molecular weight distribution of the product of a continuous reactor from batch reactor data. This can be accomplished in the following way. Equations (11) and (12) provide M_w and M_n for a mixture of characterized resin samples, and the

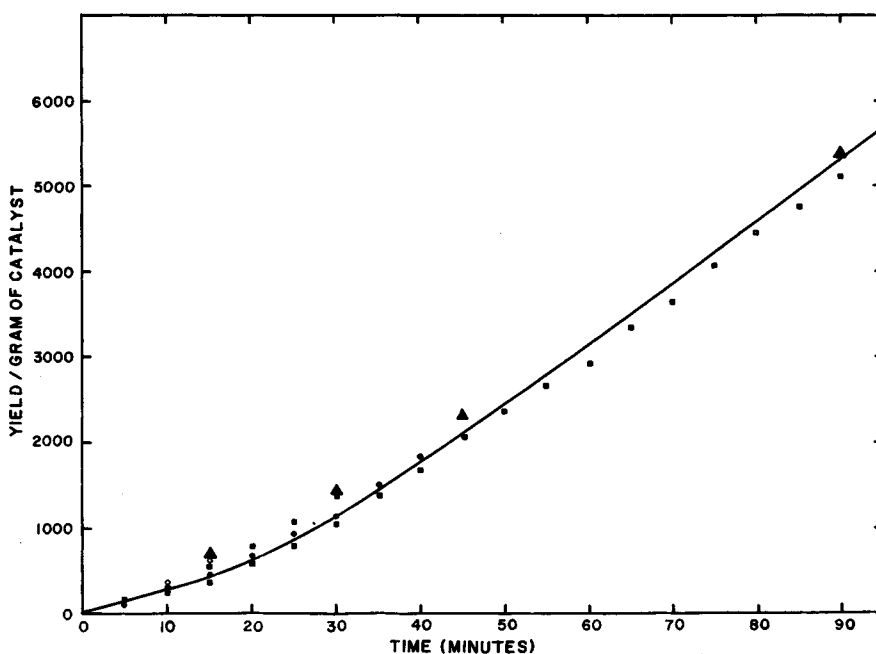


Fig. 1. Effect of time on polymer yield. Actual yield for the batch reactor determined by weighing the polymer (\blacktriangle), and the yields from flowmeter readings, each as grams/gram of catalyst, compared to calculated yield. The symbols (\circ \square \blacksquare \bullet) distinguish flowmeter yields for the four experiments.

equations can be used in the integral form if the number of components is very large. To evaluate the integrals, it is necessary to express the weight fraction, or dw , and $M_w(w)$ and $M_n(w)$ in terms of the same variable in this case catalyst age. Batch reactor data and the yield of the continuous reactor previously obtained allow this to be done:

$$M_w = \sum M_w i W_i = \int M_w(w) dw \quad (11)$$

$$1/M_n = \sum W_i / M_{ni} = \int 1/M_n(w) dw. \quad (12)$$

Since x is the batch reactor yield,

$$dw = (x/\bar{x}_\theta) (e^{-t/\theta} / \theta) dt. \quad (13)$$

The batch reactor data make it easier to approximate M_w/M_n than M_w itself by an equation with catalyst age as the independent variable. Equation (14) is such an approximation, with $g(t)$ representing the age dependence of M_w/M_n . The line through the data points of Figure 2 is a plot of eq. (14) with appropriate values for the constants α and β :

$$g(t) = \alpha/t + \beta. \quad (14)$$

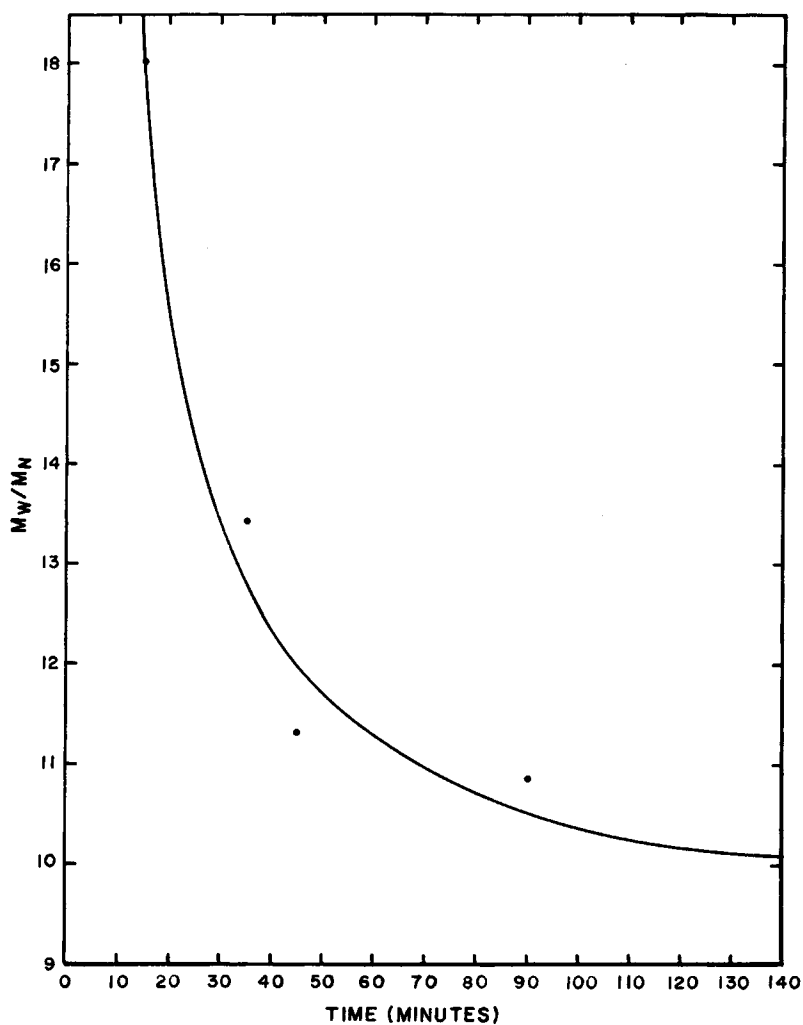


Fig. 2. Effect of time on M_w/M_n . Comparison of M_w/M_n from GPC with a plot of the function used to estimate the effect of time (or catalyst age) on M_w/M_n .

Similarly, Figure 3 shows the way in which eq. (15) approximates the batch reactor data for M_n :

$$H(t) = (B + Kt)^{1/2}. \quad (15)$$

Equations (13), (14), and (15) combined with eqs. (11) and (12) give the desired predicted values of M_n and M_w for the product of a continuous reactor:

$$M_w = (1/\bar{x}_0\theta) \int_0^\infty g(t)h(t)x(t)e^{-t/\theta} dt \quad (16)$$

$$1/M_n = (1/\bar{x}_0\theta) \int_0^\infty [e^{-t/\theta}/h(t)] dt. \quad (17)$$

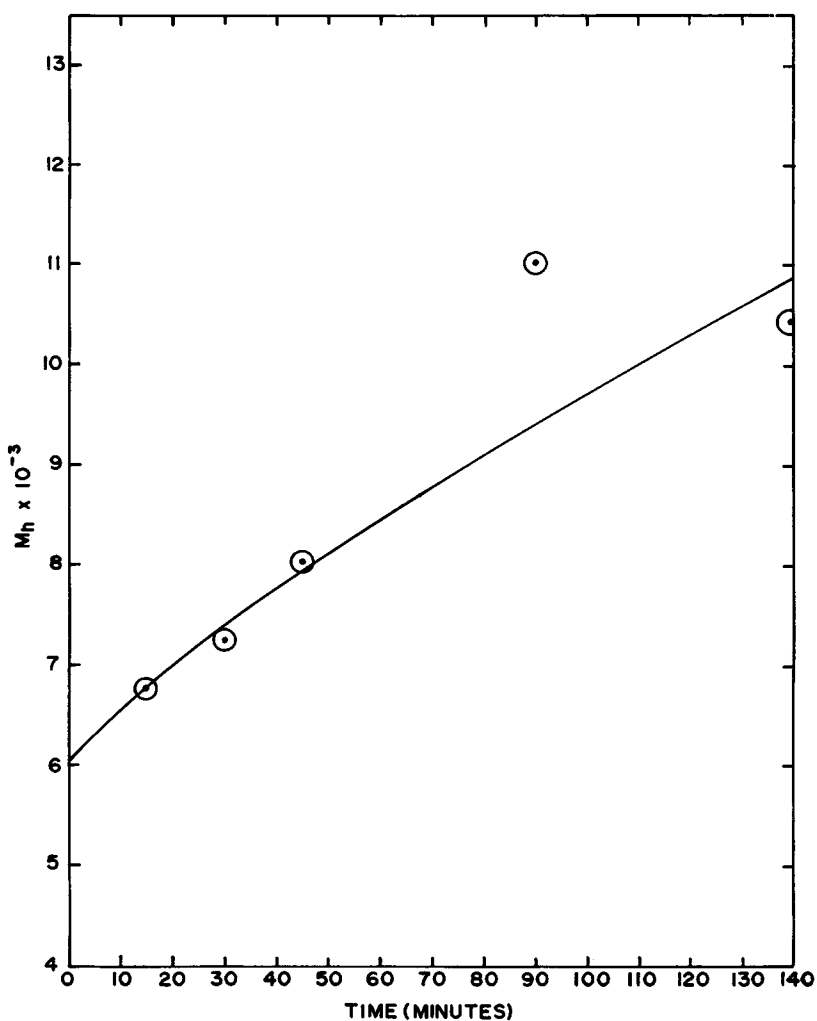


Fig. 3. Effect of time on M_n . M_n values from GPC are shown as data points. The line represents the function used to estimate the effect of time (or catalyst age) on M_n .

Of course, multiplication of eqs. (16) and (17) gives the polydispersity ratio, M_w/M_n .

RESULTS AND DISCUSSION

Figure 1 shows the yield of polyethylene as affected by reaction time for the particular catalyst used in these experiments. The figure contains data points from flowmeter readings as well as polymer weights, and the yields based on flowmeter readings are also given in Table I. The line associated with the data points is a plot of eqs. (8) and (9) with the constants $a = 1.246$, $b = 20$, $c = 70$, and $t_1 = 40$ min. In our opinion, the fit of the equa-

TABLE I
Yield per Gram of Catalyst in Ethylene Polymerization at 550 psig and 102°C

Reaction time, min	Yield, g/g catalyst			
	No. 41	No. 43	No. 45	No. 47
5	99	101	148	142
10	243	228	356	300
15	444	377	602	517
20	675	559		777
25	912	783		1080
30	1165	1060		1382
35	1508	1341		
40	1824	1646		
45	2077	2052		
50		2366		
55		2638		
60		2925		
65		3331		
70		3630		
75		4053		
80		4460		
85		4759		
90		5076		

tions to the data, when these constants are used, is satisfactory for our purpose. The rate of polymerization, which can be obtained from eqs. (8) and (9), shows an increase during the first 40 min and then remains constant at 70 g/g catalyst per min. Similar rate patterns, that is, an initial increase followed by a period of constant polymerization, have been reported by Zakharov and Ermakov.¹¹

The broad molecular weight distributions indicated in Figure 2 are characteristic of Phillips¹² and Ziegler polyethylene.^{13,14} The dramatic effect of reaction time, or catalyst age, upon molecular weight distribution, also shown in Figure 2, has not been observed previously, although Whitaker and Wills⁴ found an increase in the fraction of high molecular weight components with conversion. Their somewhat different observations may have been due to the relatively low reactivities and consequent small yields reported by them, or to differences in catalyst. In any case, the reason for the time effect upon the molecular weight distribution shown by our catalyst is not known. It may, however, be related to the creation of new active sites during the early stages of polymerization.¹¹ The line drawn through the data points of Figure 2 is a plot of the equation $M_w/M_n = (135/t) + 9$, which is eq. (11) with $\alpha = 135$ and $\beta = 9$.

Equation (15) with $B = 37.55 \times 10^6$ and $K = 5.70 \times 10^6$ is plotted in Figure 3.

The integrations indicated by eqs. (15) and (16) have been done by the trapezoid rule using an interval of 0.20 min for the first 40.0 min of age and an interval of $(8\theta - 40)/300$ min for the ages greater than 40 min. The upper limit of the integration was set at 8θ , where θ is the mean residence

time. The calculations were done by Honeywell computer from a Fortran program which also produced calculated values of M_w , M_n , yield, and M_w/M_n for batch and continuous reactors. The adequacy of the 8θ upper limit is shown by the fact that analytic integration of the continuous reactor yield at four values of θ to infinite age agrees with the computer output. Table III is the final result.

The lower M_w/M_n compared to the batch reactor at the shorter residence times is a consequence of the dramatic effect of catalyst age on M_w/M_n and

TABLE II
Yield of Polyethylene per Gram of Catalyst and M_w/M_n at Different Reaction Times

Exp. no.	Reaction time, min	Actual yield, g	Yield from flowmeter, g	Yield from equation, g	M_w/M_n
45	15	697	600	440	18.05
47	30	1455	1370	1160	14.44
41	45	2320	2080	2145	11.66
43	90	5280	5050	5295	10.87

TABLE III
Comparison of Calculated Values of the Polydispersity Ratio for Batch and Continuous Reactors

Batch reaction time or mean residence time, min	Batch		Continuous	
	Yield, g/g	M_w/M_n	Yield, g/g	M_w/M_n
10	262	22.50	320	21.85
15	439	18.00	558	17.21
20	648	15.75	828	14.97
25	887	14.40	1120	13.69
30	1158	13.50	1426	12.87
35	1459	12.86	1742	12.32
40	1792	12.38	2064	11.93
45	2142	12.00	2391	11.64
50	2492	11.70	2722	11.42
55	2842	11.45	3055	11.24
60	3192	11.25	3391	11.10
65	3542	11.08	3729	10.99
70	3892	10.93	4068	10.89
75	4242	10.80	4408	10.81
80	4592	10.69	4749	10.74
85	4942	10.59	5091	10.69
90	5292	10.50	5434	10.64
95	5642	10.42	5778	10.60
100	5992	10.35	6122	10.56
105	6342	10.29	6466	10.53
110	6692	10.23	6812	10.50
115	7042	10.17	7156	10.48

the way the rate of polymerization changes with age. On the other hand, the slightly higher M_w/M_n compared to the batch reactor at longer residence times is due to the contributions of young catalyst to M_n . These relations depend upon the distribution of product with catalyst age as shown in Figure 4.

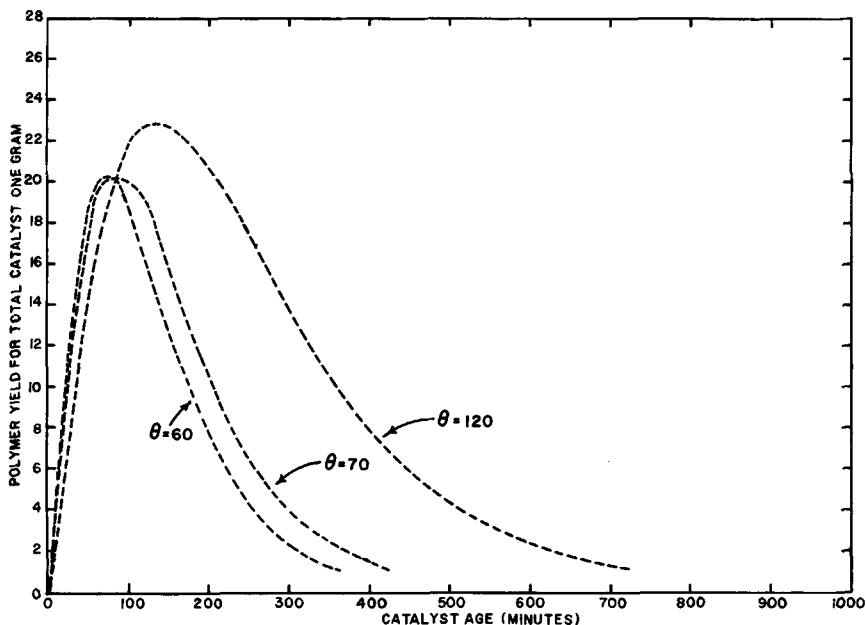


Fig. 4. Polymer distribution with respect to catalyst age. The curve heights represent the amount of polymer made by catalyst with age between t and $t + \Delta t$; Δt is 1 minute. The areas under the curve are the yields for 1 g of catalyst in a perfectly mixed, continuous reactor, for different mean residence times (θ).

In order for Figure 4 to be a true picture, it is obviously necessary for the yield data to be correct. In particular, any decline in reactivity at long times would diminish the amount of skew in Figure 4, and this, in our case, would act to broaden the molecular weight distribution of the continuous reactor product. As a matter of fact, Clark¹⁵ mentions a loss in reaction rate after the period of constant reactivity. However, we have conducted a reaction for 140 min and to a yield of 7600 grams per gram without observing a fall in rate. It is not clear whether any loss which would be observed would be due to the intrinsic properties of the catalyst or to the introduction of poisons with the constantly supplied ethylene, if a small catalyst charge is used; or to choking the reactor vessel, if a larger catalyst charge is used.

From what has already been said, it is clear that an exact prediction from batch reactor data of the molecular weight distribution of the product of a continuous reactor depends upon maintaining all feed materials free of poisons and modifiers. In the case of a particular poison, it might be possi-

ble to study the effect in the batch reactor and apply the results using the principle of the method described in this paper.

Finally, it should be possible to employ this method with experimentally determined residence time distributions.

References

1. E. B. Nauman, *Polymer Reactor Engineering Symposium Preprints*, 55th Chemical Conference and Exhibition of the Chemical Institute of Canada, Quebec City, June 4-7, 1972, pp. 183-229.
2. K. Denbigh, *Chemical Reactor Theory*, Cambridge University Press, Cambridge, 1965, pp. 104-107, 81.
3. J. P. Hogan, *J. Polym. Sci. A-1*, **8**, 2637 (1970).
4. H. L. Whitaker and G. B. Wills, *J. Appl. Polym. Sci.*, **13**, 1921 (1969).
5. J. P. Hogan and L. Banks, U.S. Pat. 2,825,721 (1958).
6. J. P. Hogan, B. E. Nasser, and R. T. Werkman, XXIII, International Congress of Pure and Applied Chemistry, Boston, 1971, *Macromolecular Preprints*, Vol. II, pp. 703-710.
7. Z. Tadmor and J. A. Biesenberger, *Ind. Eng. Chem., Fundam.*, **5**, 336 (1966).
8. *Ibid.*, **5**, 336 (1966).
9. W. Resnick, *Ind. Eng. Chem.*, **52**, 865 (1960).
10. S. L. Andersen and P. H. Matthias, *Ind. Eng. Chem.*, **46**, 1296 (1954).
11. V. A. Zakharov and Yu. I. Ermakov, *J. Polym. Sci. A-1*, **9**, 3129 (1971).
12. A. Clark and G. C. Bailey, *J. Catal.*, **2**, 241 (1963).
13. L. Reich and A. Schindler, *Polymerization by Organometallic Compounds*, Interscience, New York, 1966, p. 338.
14. M. N. Berger, G. Boocock, and R. N. Haward, *Advan. Catal. Relat. Subj.*, **19**, 211 (1969).
15. A. Clark, *Catal. Rev.*, **3**, 145 (1969).

Received January 29, 1973

Revised March 2, 1973