Transient Response of Continuous-Flow Stirred-Tank Polymerization Reactors

The transient behavior of polymer properties following a step change in feed conditions during copolymerization in a continuous-flow stirred-tank reactor has been investigated by both modeling and experiment. For kinetics appropriate to Ziegler catalyzed olefin polymerization, the dynamic response of polymer molecular weight and composition is predicted to be relatively slow; four to six reactor turnovers could be required to reach steady state. In addition, response time depends on the direction and magnitude of change and is generally shorter when a property value is decreased. These model predictions were confirmed by measurement of the transient response of copolymer composition and molecular weight for ethylene-propylene-ethylidene norbornene terpolymerization.

The model equations also were used to simulate reactor startups, and it was found that steady state following a startup can be reached in about three reactor turnovers. The initial absence of polymer in the reactor causes the dynamic response to be faster for a startup than for reactor control.

Charles Cozewith
Exxon Chemical Co.
Linden, NJ 07036

Introduction

This paper investigates the transient behavior of continuous-flow stirred-tank reactors (CFSTR) used for polymerization with Ziegler catalysts. In particular, we examine the dynamic response of polymer molecular weight and composition for ethylene-propylene copolymerization following a step change in reactor feed conditions. Ethylene-propylene rubbers, which are designated EPM for copolymers and EPDM for diene-containing terpolymers, are available in a wide variety of grades that differ in composition, molecular weight (MW), molecular weight distribution (MWD), compositional distribution, and long chain branching content. In view of the multiplicity of polymer characteristics that must be manipulated to maintain the product on specification and the need to make frequent grade transitions in a multigrade plant, reactor control in this process can be complex.

On-line analyzers for all copolymer properties are not yet a commercial reality. Consequently, reactor control is often open loop, involving laboratory analysis of a sample followed by a step change in the appropriate control parameter to adjust polymer quality. For ethylene-propylene solution polymerization in liquid-filled reactors ranging from pilot to commercial scale in size, we have found that the time to reach steady state in polymer quality following a step change in reactor feed rates could be quite long—five to seven reactor turnovers in some cases. The length and variability of reactor response to control changes leads to difficulty in obtaining the desired quality of control. Although there is a good deal of literature concerning the dynamic behavior of polymerization reactors, much of which has been recently reviewed by MacGregor et al. (1984), there appears to be little information on reactor response to a step change for polymerizations with kinetics appropriate to Ziegler catalysts. Consequently, we have investigated the behavior of polymer properties in ethylene-propylene co- and terpolymerization during unsteady state reactor operation for several control situations of practical interest. We believe these results are also applicable to other polymerizations having kinetics characterized by rapid initiation.

In this paper, equations are derived to predict the dynamic response of number-average molecular weight M_n and of the weight-average to number-average ratio M_w/M_n to a step change in chain transfer agent feed rate for polymerization in a CFSTR. The equations show that the time to reach steady state depends on the direction and magnitude of the change, and M_n lines out faster if it is decreased rather than increased. Polymer MWD broadens during the transient period, with the extent of broadening dependent upon the initial and final M_n levels.

Experimental data were obtained that confirmed the general predictions of the model equations and showed that three to four reactor turnovers are needed to reach steady state upon an M_n decrease, while four to five turnovers are needed if M_n is increased. We have also explored the transient behavior of polymer properties for step changes in monomer feed rate. In this case, numerical integration of the equations representing the polymerization kinetics is required to predict dynamic response. Once again, experimental data and model predictions were in good agreement. Three to four reactor turnovers were required to reach steady state in polymer composition.

Simulation of reactor startup showed that steady state is reached in about three reactor turnovers after initiation of polymerization. The generally shorter transient period for a startup as compared to a step change from one operating point to another is due to the initial absence of polymer in the reactor in the former case. We show that adding the least reactive monomer to the reactor prior to the start of polymerization is a preferred procedure for minimizing polymer composition fluctuations during the startup period.

Experimental Method

Polymerization

Solution polymerizations in Phillips *n*-hexane solvent were carried out in a 12 L continuous-flow stirred-tank reactor agitated by dual, flat-blade disc turbine impellers of standard design. The reactor operates liquid-full. Feed streams were purified to remove potential Ziegler catalyst poisons and to insure maximum catalyst activity and reproducible results. Solvent was passed through silica gel and molecular sieve beds to remove polar impurities and water, while the ethylene and propylene were treated in hot copper oxide and molecular sieve columns for oxygen and water elimination. Ethylidene norbornene was dried over molecular sieves. Ethylene, propylene, and hydrogen feed were added to the solvent flow as gases, and the combined flow was passed through a feed heat exchanger that lowered the temperature to typically −15°C and provided sufficient residence time for the gases to dissolve. Diene was added to this stream as a dilute solution in the solvent. The residence time between the feed injection point and reactor inlet was equivalent to 0.3 reactor turnovers, and this was assumed to be a pure lag for correcting measured transient response. Vanadium catalyst and aluminum cocatalyst were fed separately to the reactor as dilute solutions in the solvent. All feed streams entered the reactor in a well-mixed region near an impeller. Reactor temperature was controlled to ±0.5°C by circulating water through a cooling jacket. Reactor pressure was kept high enough to prevent the formation of a vapor phase.

For the data in Tables 2 and 3, the polymerization was quenched by injecting water into the reactor effluent through a tee mixer. Water was replaced by an isopropanol/hexane solution for the experiments in Table 4 to avoid having to combine immiscible fluids.

Transient experiments were carried out by first bringing the reactor to an initial steady state operating point. Step changes in the appropriate feed rates were then made, and samples of the reactor product were taken at intervals to follow the approach to the new steady state. When steady state was reached, step changes were again made in the feeds to return them to their original levels, and the sampling procedure was repeated as the reactor returned to the initial steady state condition. Transient samples were collected for 0.077 reactor turnovers to provide enough polymer for analysis, and our results thus represent an average value over this period, rather than point values at the stated sample times. Larger samples obtained at steady state were used for determining polymerization rates. Effluent monomer concentrations were obtained by material balances based on feed rates, polymerization rates, and polymer composition.

Polymer was recovered from solution by solvent evaporation followed by drying to constant weight. Number-average molecular weight M_n and weight-average molecular weight M_w were determined at 135°C in 1,2,4-trichlorobenzene solvent with a Waters 150 gel permeation chromatograph equipped with Shodex polystyrene gel columns 802, 803, 804, and 805. Molecular weight values were obtained from the chromatogram with software provided by Computer Inquiry Systems, Inc. The 3σ limits for M_w and M_w/M_n were determined to be 0.24×10^5 and 0.15, respectively, based on replicate determinations of a copolymer with $M_w/M_n = 2.0$ and $M_w = 1.47 \times 10^5$. Mooney viscosity was measured in a Monsanto Mooney viscometer by ASTM D1646. Polymer ethylene content was determined by infrared analysis according to ASTM D3900 with a 3σ value of 0.6 wt. % ethylene. For ethylidene norbornene measurement, the refractive index of polymer films at 90°C was utilized according to the method described by Gardner and Ver Strate (1973). The 3σ value for this technique is 0.19 wt. % diene.

Tracer tests

Reactor mixing was characterized by tracer tests to ascertain whether the assumption of perfect mixing inherent in the solution of the modeling equations was justified. At steady state operating conditions a pulse of xylene tracer was rapidly added into the feed entering the bottom of the reactor. The xylene was injected from a small bomb pressurized with nitrogen, and valved into the feed line. The solution exiting from the top of the reactor was sampled frequently and analyzed for xylene content by UV to determine the time dependence of tracer concentration. Tracer tests were performed with a pure solvent feed in the absence of reaction and during polymerizations conducted over a range of solution viscosities up to a maximum of 1,500 cp [mPa · s] (at zero shear). To characterize the mixing Reynolds number in this non-Newtonian system, a viscosity was calculated according to Metzner et al. (1961) from data obtained with a Brookfield LVT viscometer. The agitator was 10.2 cm in diameter and operated between 145 and 900 rpm for the mixing studies.

For perfect mixing and a pulse tracer injection, the decay of tracer concentration in the reactor outlet is given by the relationship:

$$X/X_i = e^{-\tau} \tag{1}$$

where

X = outlet concentration

X_i = initial concentration in reactor

Data in agreement with this equation should give a straight line with a slope of −1 when log (X/X_i) is plotted vs. τ. Measured tracer response curves at Reynolds number N_{Re} greater than 150

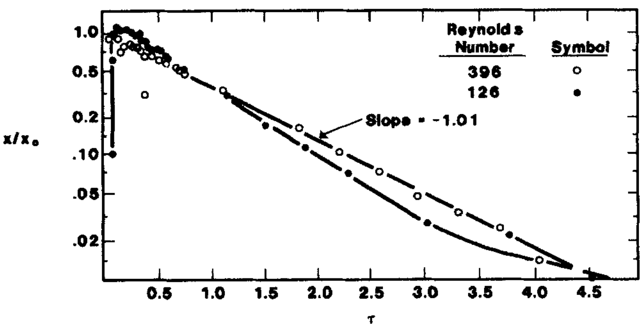

Figure 1. Reactor residence time distribution curves from xylene tracer test.

gave results as indicated in Figure 1 at a Reynolds number equal to 396. The outlet tracer concentration rapidly rises to a maximum and then declines with the time dependence predicted by Eq. 1.

We interpret the initial delay in reaching the maximum tracer concentration as the time needed for the tracer to be thoroughly mixed throughout the reactor contents. It was 0.06 reactor turnovers for this set of data. The exponential decay of tracer concentration following the maximum is indicative of a well-mixed vessel with no stagnant volume. In our tracer experiments the delay time ranged from 0.02 turnovers with pure solvent at N_{Re} = 300,000 to 0.11 turnovers at N_{Re} = 126, which is the second set of data shown in Figure 1. Note in these results that the initial outlet tracer concentration exceeds 1.0; the linear portion of the decay curve has a slope significantly greater than -1; and the evolution of tracer from the reactor persists for a long time. All of these features are characteristic of poor mixing and stagnant zones in the reactor.

We conclude from this study that at $N_{Re} > 400$, which was the lower limit reached in the polymer transient response experiments, perfect mixing is a reasonable approximation to the residence time distribution for the reactor.

Transient Response Equations

The dynamic behavior of a perfectly mixed CFSTR following a step change in operating conditions is modeled by solving the unsteady state material balance equations for a reactant Z

$$dZ/d\tau = R_z\theta - Z + Z_o \qquad (2)$$

for each of the components of the reaction system. The rate of reaction term R_z is obtained from the kinetics of the polymerization. For ethylene-propylene solution copolymerization with soluble vanadium catalysts, the kinetics are characterized by very rapid chain initiation and rapid catalyst decay leading to a loss of catalyst activity in typically 20–30 min. Chain lifetimes are estimated to be on the order of tens of seconds, much longer than in most free radical polymerizations. Thus, the quasi-steady state assumption of constant growing chain concentration is not valid for this system. Cozewith (1980) deduced the copolymerization kinetic scheme shown in Table 1 from data obtained in a CFSTR to account for these reaction characteristics. The reaction rate expressions corresponding to this model were used to examine transient behavior.

Equation 2 was written for each of the reactants in the polymerization scheme and for the first three moments of the molecular weight distribution (MWD). Moment equations were derived from the expressions for chain concentration by standard techniques, and molecular weight averages were obtained from the appropriate moment ratios. The large majority of Ziegler catalysts produce multiple active sites yielding copolymers with broad molecular weight and compositional distributions (Cozewith and Ver Strate, 1971). Detailed kinetic modeling in these circumstances is very difficult because of the large number of rate constants needed to describe the system. In the model discussed here it was assumed that the catalyst produces only one active catalyst species. The resulting 22 simultaneous equations were solved numerically by a computer program utilizing the differential equation algorithm LSODE developed by the Lawrence Livermore Laboratory. Transient behavior could be calculated with this program for either reactor startups, in which no polymer is present initially, or for transitions from one steady state operating point to another following a step change in feed conditions.

Control of polymer molecular weight is an important and frequent requirement in EPDM production. This is most often accomplished by adjusting the flow rate of hydrogen chain transfer agent. When only hydrogen feed is altered, this presents a special case for which an analytical expression for the dynamic response of polymer molecular weight can be obtained. Because of rapid chain reinitiation following chain transfer, hydrogen affects only molecular weight and not polymerization rate or polymer composition. Consequently, the transient response to a hydrogen feed step change requires solution of only three differential equations for hydrogen concentration and the zeroth and second moments of the MWD. The first moment, which equals the moles of monomer reacted, remains unaffected by the H_2 change. First, we derive the transient equation for M_n and M_w for a homopolymerization with instantaneous initiation as given

Table 1. EPDM Kinetic Model

Reaction		Rate Constant	Rate
Catalyst deactivation	$C_1 \rightarrow D$	k_x	k_xC_1
Catalyst deactivation with diene	$C_1 + M_3 \rightarrow D$	k_{x3}	$k_{x3}C_1M_3$
Catalyst activation	$C_1 \rightarrow C_2$	k_a	k_aC_1
Chain initiation	$C_2 + M_1 \rightarrow P_1$	k_{i1}	$k_{i1}C_2M_1$
	$C_2 + M_2 \rightarrow Q_1$	k_{i2}	$k_{i2}C_2M_2$
Chain propagation	$P_i + M_1 \rightarrow P_{i+1}$	k_{11}	$k_{11}M_1P_i$
	$P_i + M_2 \rightarrow Q_{i+1}$	k_{12}	$k_{12}M_2P_i$
	$P_i + M_3 \rightarrow R_{i+1}$	k_{13}	$k_{13}M_3P_i$
	$Q_i + M_1 \rightarrow P_{i+1}$	k_{21}	$k_{21}M_1Q_i$
	$Q_i + M_2 \rightarrow Q_{i+1}$	k_{22}	$k_{22}M_2Q_i$
	$R_i + M_1 \rightarrow P_{i+1}$	k_{31}	$k_{31}M_1R_i$
Chain Termination*			
Spontaneous	$P_i \rightarrow U_i$	k_t	k_tP_i
With propylene	$P_i + M_2 \rightarrow U_i$	k_{t2}	$k_{t2}P_iM_2$
With diene	$P_i + M_3 \rightarrow U_i$	k_{t3}	$k_{t3}P_iM_3$
Chain Transfer*			
With hydrogen	$P_i + H \rightarrow U_i + C_2$	k_{tr1}	$k_{tr1}P_iH$
With aluminum alkyl	$P_i + \text{Al} \rightarrow U_i + P_1$	k_{tr}	$k_{tr}P_i(\text{Al/V-1})$**
With propylene	$P_i + M_2 \rightarrow U_i + Q_1$	k_{trM2}	$k_{trM2}P_iM_2$

*Identical reactions occur with growing chains Q_i and R_i to produce dead chains V_i and W_i. Termination and transfer constants are assumed to be the same regardless of the chain end type.

**Al/V = Aluminum/vanadium molar ratio in reactor by the simplified mechanism:

$$P_i + M_1 \xrightarrow{k_p} P_{i+1} \qquad \text{propagation}$$

$$P_i + H \xrightarrow{k_{tr1}} U_i + P_1 \qquad \text{transfer}$$

$$P_i \xrightarrow{k_t} U_i \qquad \text{termination}$$

since this closely approximates the essential steps that generate the MWD in copolymerization also. Defining the moments

$$F_n = \sum_{i=1}^{\infty} i^n P_i \tag{3}$$

$$G_n = \sum_{i=1}^{\infty} i^n U_i \tag{4}$$

$$Y_n = F_n + G_n \tag{5}$$

gives the degree of polymerization as

$$DP_n = (Y_1/Y_o) \tag{6}$$

$$DP_w = (Y_2/Y_1) \tag{7}$$

For a step change in H_2 feed, the material balance equations are:

$$dH_d/d\tau = -(1 + k_{tr1}F_o\theta)H_d \tag{8}$$

$$d(Y_{od})/d\tau = H_d \tag{9}$$

$$d(Y_{1d})/d\tau = 0 \tag{10}$$

$$d(Y_{2d})/d\tau = F_{1d} \tag{11}$$

$$d(F_{1d})/d\tau = -\gamma[(H_d + \alpha)F_{1d} + H_d\beta] - F_{1d}\delta \tag{12}$$

where

$$\alpha = H_f/(H_i - H_f)$$

$$\beta = F_{1f}/(F_{1i} - F_{1f})$$

$$\gamma = k_{tr1}\theta(H_i - H_f)$$

$$\delta = 1 + k_t\theta$$

The subscript d is used to denote that a variable has been converted to the dimensionless fraction of unaccomplished change: $(Z - Z_f)/(Z_i - Z_f)$, where the subscripts i and f indicate the value of Z at the initial and final steady states. This parameter is 1 at $\tau = 0$ and 0 at $\tau = \infty$.

Equations 8 and 9 can be integrated readily to give:

$$H_d = e^{-A\tau} \tag{13}$$

$$Y_{od} = (Ae^{-\tau} - e^{-A\tau})/(A - 1) \tag{14}$$

where

$$A = (1 + k_{tr1}F_o\theta).$$

Note that Eqs. 8 and 9 and thus Eqs. 13 and 14 are independent of the termination mechanism. The second moment equation is, however, dependent on the termination mechanism and must be integrated numerically. As stated earlier, Y_1, which is equal to the moles of monomer reacted, is not affected by transfer agent concentration. Thus dividing the numerator and denominator of Y_{od} by Y_1 yields

$$\frac{(1/DP_n) - (1/DP_n)_f}{(1/DP_n)_i - (1/DP_n)_f} = (Ae^{-\tau} - e^{-A\tau})/(A - 1) \tag{15}$$

which is the final result describing the transient behavior of DP_n. Since $(1/DP_n)_d = (1/M_n)_d$, Eq. 15 also describes the dynamic response of M_n.

Several conclusions are immediately apparent from Eqs. 13 and 15. In the limit of very fast chain transfer ($A \gg 1$), the fraction of unaccomplished change in $1/M_n$ approaches steady state with the exponential response $e^{-\tau}$, which also describes outlet concentration dynamics for a step change in the absence of reaction. At the limit of very slow transfer ($A = 1$), L'Hospital's rule applied to Eq. 15 indicates that the response function becomes equal to:

$$(1/M_n)_d = (1 + \tau)e^{-\tau} \tag{16}$$

Thus $1/M_n$ always reaches steady state more slowly than an exponential response, and more than three turnovers will be required to line out the polymer molecular weight. Furthermore, it is apparent from Eq. 15 that the fraction of unaccomplished change in $1/M_n$ does not depend on the initial and final values, M_{ni} and M_{nf}, but the fraction of unaccomplished change in M_n itself does. Consequently, the dynamic response of M_n will be a function of both the magnitude and direction of the change.

For example, with the illustrative homopolymerization constants shown in Figure 2, an eightfold step change in H_2 feed concentration causes DP_n to vary from 0.46×10^4 to 1.2×10^4. If a step change H_2 decrease is made, Eq. 13 predicts that 5.5 reactor turnovers are needed to reduce the fraction of unaccomplished change, $(DP_n)_d$, to 0.05, but only 3.5 turnovers are required for a step increase. MWD broadening also occurs during the transient period since the new polymer being formed mixes with the polymer of the initial molecular weight not yet purged from the vessel. As indicated by the calculated curves in

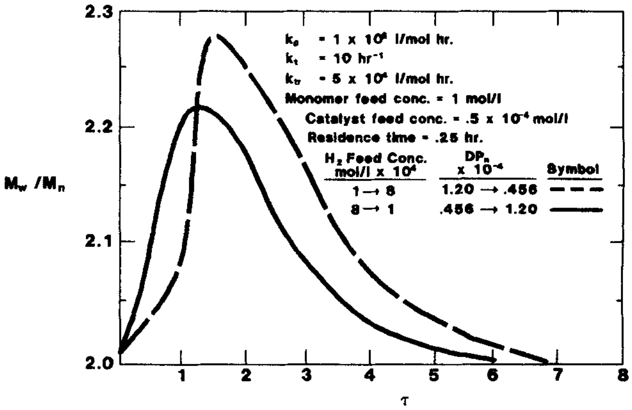

Figure 2. MWD broadening during transient period.

Figure 2, DP_w/DP_n rises from the steady state value of 2.0, which is characteristic for polymerizations in a CFSTR according to the kinetics in Table 1, passes through a maximum after one to two turnovers, and then returns to a value of 2.0. The extent of MWD broadening is primarily dependent on the difference between the initial and final DP_n at steady state. For less than a factor of two difference in DP_n, DP_w/DP_n increases to about 2.1 at most. Consequently, relatively large changes in DP_n are needed to produce appreciable broadening of MWD during unsteady state.

From Eq. 13 it is apparent that the hydrogen concentration in the reactor always reaches steady state more quickly than the exponential response. At the limits of very fast and very slow chain transfer, hydrogen attains its steady state concentration almost instantly for $A \gg 1$ and follows the exponential response $e^{-\tau}$ for $A = 1$.

The identical relationships hold for copolymerization with instantaneous initiation except that the growing chain concentration, F_o, in the parameter A now must be calculated from the sum of the growing chain ends with monomers M_1, M_2, and M_3 as the last added unit.

Polymer Transient Response Measurements

The response of polymer properties to step changes in hydrogen and propylene feed rate was investigated during ethylene-propylene copolymerization with the $VOCl_3/Et_3Al_2Cl_3$ catalyst system. At moderate polymerization temperatures (<50°C) and Al/V ratios greater than about 5, this catalyst is known to produce a polymer with M_w/M_n of 2.0, indicative of the presence of a single active catalyst species, which was assumed in deriving the kinetic equations.

Details of the hydrogen step change experiment are given in Table 2. In the initial steady state H_2 was fed to the reactor at a rate of 3.34 mol/mol $VOCl_3$. The H_2 flow was then terminated and the reactor was allowed to reach a new steady state in polymer molecular weight. Finally, the H_2 flow was restored to the initial value to return the polymerization to the starting conditions. From the M_w/M_n data in Table 2 it can be seen that M_w/M_n is equal to 2.0 within experimental accuracy for M_w less than 140,000, but rises significantly above 2.0 at higher values. Note especially that the sample obtained at steady state in condition B has M_w/M_n equal to 2.73, and a much lower M_n than the sample obtained immediately before it, 0.2 turnovers earlier.

We believe that the broadened MWD for the higher M_w polymers was caused by inadequate short-stopping of the reaction at the reactor outlet due to poor mixing of the quench agent with the viscous polymer solution. Consequently, a small amount of polymerization continued to occur in the sample, forming low molecular weight polymer, which depressed M_n but had no substantial effect on M_w.

To estimate the true M_n at the reactor outlet for the polymers of broadened MWD, we have assumed that M_w was unchanged by the post-reactor polymerization, and that M_w/M_n in the reactor is 1.99, the average value for the twelve polymers analyzed with $M_w < 140{,}000$. The corrected M_n values, equal to $M_w/1.99$, are also given in Table 2. This calculation is only valid if the H_2 step change does not altar M_w/M_n appreciably. The constant value of M_w/M_n for $0 < \tau < 2$ in condition B and for $3 < \tau < 8$ in condition C indicates that this is indeed the case. Also, modeling calculations indicate that M_w/M_n would increase to a maximum of about 2.1 in this experiment, which is in agreement with the data.

From the plot of corrected M_n vs. τ in Figure 3, it can be seen that line-out time strongly depends on the direction of the change in M_n, and four to five reactor turnovers were required to reach steady state when M_n was increased. Replotting the data as the fraction of unaccomplished change in the reciprocal of M_n, Figure 4, $(1/M_n)d$, brings both sets of data onto a single curve, in agreement with the predictions of Eq. 15. The applicability of Eq. 15 can be tested by modeling the transient response with the value of the parameter A in the equation determined

Table 2. Hydrogen Feed Step Change Experiment

Condition	H_2 Feed mol/mol V	Catalyst Efficiency g EPM/mol V	Time, τ* t/θ	M_n $\times 10^{-3}$	M_w $\times 10^{-3}$	M_w/M_n	$M_w/1.99$ $\times 10^{-3}$
A	3.34	119,000	0	41.3	90.8	2.20	45.4
B	0		0.2	48.9	96.4	1.97	48.2
			0.7	50.9	104.8	2.06	52.4
			1.2	56.7	113.6	2.00	56.8
			1.7	67.2	135.8	2.02	67.9
			2.7	71.7	166.7	2.33	83.3
			3.7	87.5	179.6	2.05	89.8
			5.7	97.1	212.2	2.19	106.1
			7.7	103.8	235.0	2.26	117.5
			7.9	85.7	233.5	2.73	116.8
B	0	108,000	0	85.7	233.5	2.73	116.8
C	3.34		0.2	87.0	215.7	2.48	107.9
			0.7	74.8	187.2	2.50	93.6
			1.2	68.3	164.7	2.41	82.4
			1.7	55.4	139.1	2.51	69.6
			2.7	61.7	124.1	2.01	62.1
			3.7	54.6	110.5	2.02	52.5
			5.7	50.0	96.9	1.92	48.5
			7.7	51.6	96.9	1.88	48.5
C	3.34	116,300	7.9	47.2	96.0	2.03	48.0

*Time from H_2 step change

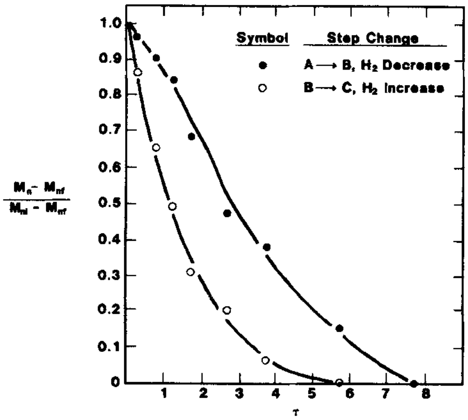

Figure 3. Transient response of M_n to hydrogen step change.

from the steady state operating data for M_n with and without H_2 feed.

The corrected value of M_n for condition B in the absence of H_2 is 116,800. If each mole of vanadium fed to the reactor initiates a chain and there is no chain transfer, then M_n is equal to the weight of polymer produced per mole of vanadium, which is defined as the catalyst efficiency. As shown in Table 2, the three measurements of catalyst efficiency over the course of the experiment are in good agreement and average 114,600 g polymer/mol vanadium. This value is very close to the measured M_n and thus indicates that no chain transfer was occurring in the absence of H_2 if the assumption is correct that each mole of vanadium initiates a chain. With a hydrogen feed of 3.34 mol/mol V, M_n is reduced from 116,800 to 46,700 (average of M_n in conditions A and C). Thus an additional 1.5 moles of chain per mole of vanadium are generated in the presence of hydrogen. Consequently, the fractional conversion of H_2 via chain transfer is 1.5/3.34 or 0.449. According to the kinetics assumed for H_2 transfer in Table 1, steady state conversion for a H_2 feed concentration of H_o is given by

$$(H_o - H)/H_o = k_{tr1}F_o\theta/(1 + k_{tr1}F_o\theta)$$

Consequently, $k_{tr1}F_o\theta$ is equal to 0.815 and A in Eq. 15 is equal to 1.815.

Table 3. Propylene Feed Step Change Experiment

Condition	Propylene/ Ethylene Feed Ratio mol/mol	Catalyst Efficiency g EPM/mol V	Time, τ* t/θ	Polymer Ethylene Content, wt. %
D**	1.25	116,300	0	41.2
E	0.775		0.2	41.3
			0.7	42.2
			1.2	43.2
			1.7	43.3
			2.7	45.5
			3.7	46.1
			5.7	46.8
			7.7	46.8
			7.9	46.8
E†	0.775	105,700	0	46.8
F	1.25		0.2	45.5
			0.7	43.8
			1.2	42.9
			1.7	42.6
			2.7	41.8
			3.7	41.1
			5.7	41.2
			7.7	41.0
F	1.25	113,834	7.9	41.1

*Time from propylene feed step change
**$M_n = 39.2 \times 10^{-3}$; $M_w = 71.9 \times 10^{-3}$; $M_w/M_n = 1.84$
†$M_n = 45.9 \times 10^{-3}$; $M_w = 89.8 \times 10^{-3}$; $M_w/M_n = 1.96$

The measured transient data in Figure 4 lie to the right of the curve calculated from Eq. 15 for $A = 1.815$ and agree much better with the curve calculated for the slow transfer limit of $k_{tr1} = 0$. The explanation of this discrepancy is not apparent. We believe that possible errors in the hydrogen conversion calculated above are not large enough to change transient response appreciably. It is conceivable that the hydrogen reaction kinetics are really much more complicated than assumed, which alters the unsteady state reactor behavior, or that the reactor mixing has not been adequately described in the model. The available data are insufficient to come to any firm conclusions in this regard.

The results of a step change in propylene feed rate, with all other reactor conditions held constant, are presented in Table 3, and the dimensionless polymer ethylene content $(EP)_d$ is shown as a function of time τ in Figure 5. In this series of experiments,

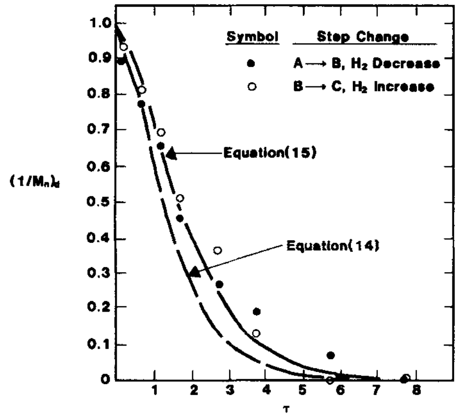

Figure 4. Transient response of $1/M_n$ to hydrogen step change.

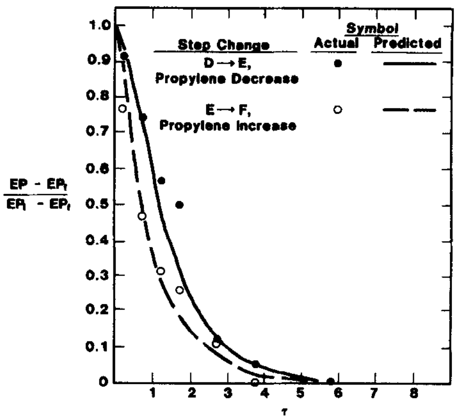

Figure 5. Transient response of ethylene content to propylene feed step change.

Table 4. EPDM Rate Constants, mol/L/h

	$VOCl_3/Al_2Et_3Cl_3$		$VOCl_2(OEt)/AlEt_2Cl$
	Podolyni et al. (1974)	This Work	Cozewith (1980)
k_x	—	—	—
k_{x3}	—	—	1.2×10^6
k_a	∞	1.0×10^4	1.0×10^4
k_{i1}	1.2×10^3	0.5×10^3	5.0×10^3
k_{i2}	—	0.5×10^3	—
k_{11}	7.9×10^6	1.4×10^6	9.7×10^5
k_{12}	7.9×10^5	6.0×10^5	1.9×10^5
k_{13}	—	—	2.3×10^6
k_{21}	6.5×10^5	8.5×10^5	2.3×10^5
k_{22}	1.9×10^4	8.0×10^4	3.8×10^3
k_{31}	—	—	2.5×10^5
k_t	19	2.1	9.8
k_{t2}	0	88.0	1.5
k_{t3}	—	—	0
k_{tr}	—	—	0.059
k_{tr1}	—	7.2×10^4	2.0×10^5
k_{trM2}	—	8.0	15

catalyst efficiency is reduced in condition E because the polymerization rate drops at reduced propylene feed rate. The transient composition data show the same general trends as the M_n results in Figure 3: a longer time is required to reach steady state when ethylene content is increased, and four reactor turnovers are required to reduce $(EP)_d$ to less than 0.05.

In order to model the response to a propylene step change, the full set of kinetic model transient equations must be solved, which requires that all of the kinetic rate constants for the $VOCl_3/Et_3Al_2Cl_3$ catalyst system be known. Rate constants have been published by Podolnyi et al. (1974) based on semibatch polymerizations at 20°C; however, more recent work by Pronyayev et al. (1985) with the same experimental technique gave quite different values for the propagation constants. We found that neither set of rate constants correlated our CFSTR results at 30°C very well. This may be due to the difference in polymerization temperature. In addition, the reaction environment for active catalyst formation is not equivalent in batch and continuous-flow reactors. In the CFSTR the initiation reaction between the vanadium and aluminum catalyst components takes place in the presence of various other soluble vanadium and aluminum compounds already in the reactor. Interactions among these various species can influence the nature of the active catalyst formed. On the other hand, no such interactions occur in the batch or semibatch reactor where active catalyst is initiated in pure solvent or solvent/monomer solutions.

With Podolnyi's constants as a starting point, Table 4, trial and error adjustments in values were made until a reasonable fit to the data we had available at five different reactor operating conditions was obtained. The modified constants, which are also shown in Table 4, predict ethylene contents of 41.0 and 49.0 wt. % at conditions D and E vs. measured values of 41.1 and 46.8%, and catalyst efficiencies of 119,400 and 104,700 g EPM/mol V at conditions D and E vs. measured values of 113,800 and 105,700. In view of the limited data, all at the same reactor residence time, these constants should be regarded as empirical. However, they do serve to correlate observed polymerization rates so that transient response can be predicted by the kinetic model. The unsteady state behavior of polymer composition calculated from the model equations is compared to the measured data in Figure 5, and it can be seen that good agreement is obtained.

In a final experiment to examine the length of time required to reach steady state, propylene, diene, and hydrogen feed rates were changed simultaneously during terpolymerization to alter both polymer composition and molecular weight. These polymerizations were carried out with the $VOCl_2$ (OEt)/diethyl aluminum chloride catalyst system that was the subject of a previous kinetic study (Cozewith, 1980) that generated the rate constants shown in Table 4. This catalyst produces multiple species, and the rate constants represent average values over the population of active sites. Also, the constants are tuned to predict M_n; but since the MWD is broad, with M_w/M_n greater than

Table 5. Terpolymerization Step Change Experiment

Condition	Propylene/Monomer Feed Ratio mol/mol	ENB/Monomer Feed Ratio mol/mol	H_2/Catalyst Feed Ratio mol/mol V	Time, τ* t/θ	Polymer Analysis		
					wt. % Ethylene	wt. % ENB	Mooney Visc.**
G	0.627	0.00641	3.28	0	51.1	4.00	31
H	0.493	0.0135	1.09	0.5	53.9	4.47	34
				1.5	56.3	5.88	48
				2.5	57.9	6.32	63
				3.5	60.8	6.65	79.5
				5.5	61.8	6.97	84.5
				7.5	62.4	6.99	84.5
				9.5	61.8	7.08	85.5
H	0.493	0.0135	1.09	0	61.8	7.08	85.5
I	0.627	0.00641	3.28	0.5	61.2	6.21	64
				1.5	57.5	4.58	42
				2.5	55.5	4.25	34
				3.5	54.3	3.92	32
				5.5	53.9	3.92	30
				7.5	54.0	3.92	30
				9.5	53.8	3.92	30

*Time from step change
**Mooney viscosity at 163°C

2.0, the model does not correctly calculate M_w. As in the previous experiments, after steady state was reached following the first step change in feeds, the feeds were restored to their original values and the reactor allowed to return to the initial steady state. The series of step changes in the experiments, Table 5, caused the diene and ethylene content of the polymer and the molecular weight to increase at first and then to decrease.

Polymer molecular weight in these experiments was measured by Mooney viscosity, which is the most commonly used specification for the molecular weight of commercial elastomers. For polymers of varying MW from the same MWD, Mooney viscosity is well correlated to M_n by the empirical relationship $M_n = bM^a$. Thus the dimensionless parameter

$$[M^a - (M^a)_f]/[(M^a)_i - (M^a)_f]$$

which we abbreviate by $(M)_d$, has the same value as $(M_n)_d$. For terpolymers made with $VOCl_2(OEt)/AlEt_2Cl$ catalyst used in this study the value of the exponent a was found to be 0.41.

Figures 6 to 8 show the measured transient behavior of polymer composition and molecular weight in comparison to the transient response predicted from the kinetic model with the rate constants in Table 4. The agreement between model calculations and experimental results is generally very good, except for the sample obtained at $\tau = 2.5$, which deviates further than the other data points from the predicted response curves.

The data used to generate the rate constants in Table 4 produce values in the correct relative ratio, but the absolute magnitude of the constants is difficult to determine accurately because the active catalyst concentration in the reactor cannot be measured. The calculated $(EP)_d$ transient response is not appreciably changed if the propagation and termination rate constants are either multiplied or divided by a factor of five. Thus discrepancies between calculated and measured results seem to be due to causes other than rate constant uncertainty.

Obviously, more work is desirable to improve the predictive capability of this reactor model based on the simplified kinetics in Table 1 and the assumption of perfect mixing. However, the current model certainly gives reasonable estimates of the lineout times required to reach steady state after a feed step change, and should provide an improved basis for reactor control.

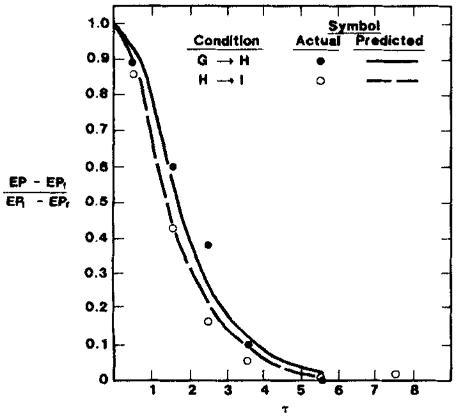

Figure 6. Transient response of polymer ethylene content during terpolymerization.

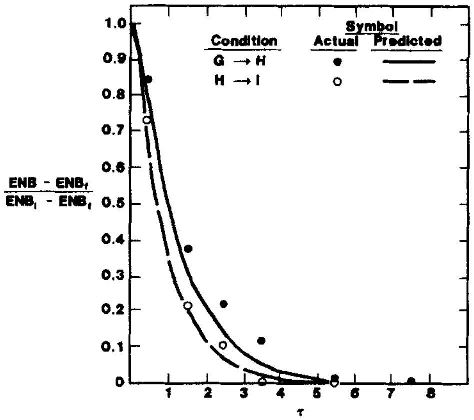

Figure 7. Transient response of polymer diene content during terpolymerization.

Reactor Startup

For EPDM reactor startups, not only is it important to obtain on-specification polymer in the minimum time, but also the production of polymer compositions that could cause operating difficulties must be avoided. Undesirable polymers have low molecular weight, which is difficult to handle in downstream polymer recovery, high ethylene content, which could lead to polymer insolubility and reactor fouling, or high diene content, which could result in polymer crosslinking and gelation. There have been a number of publications that deal with optimization of polymer reactor startup by solving appropriate reactor model equations subject to optimal policy constraints (MacGregor et al., 1984). We have examined the effect of startup procedure by solving the reactor modeling equations for a variety of initial feed concentrations to see if a clearly preferred strategy exists. Calculations were made with the $VOCl_2(OEt)/AlEt_2Cl$ rate constants in Table 4 at reactor conditions that produce an EPDM with 54.8 wt. % ethylene, 4.7 wt. % diene, and an M_n of 7.5×10^4, at a polymer concentration of 12.8 wt. % polymer (based on solvent). In these calculations a constant reactor temperature was assumed throughout the unsteady state startup period.

If the solvent flow to the reactor is established, and then all of

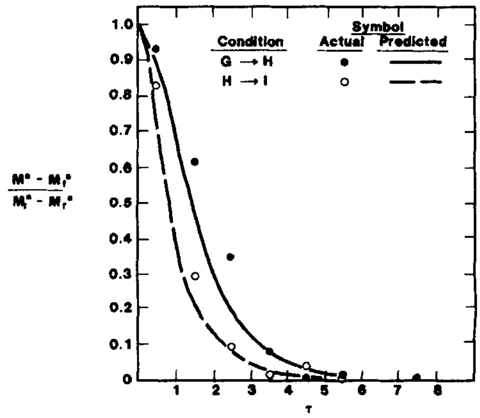

Figure 8. Transient response of Mooney viscosity during terpolymerization.

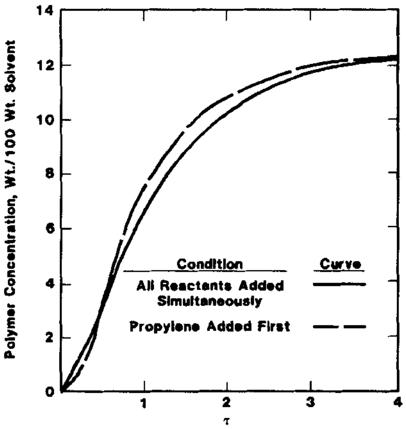

Figure 9. Polymer concentration during reactor startup.

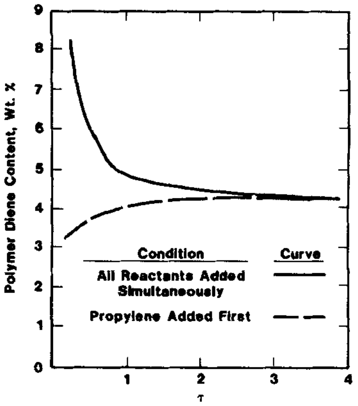

Figure 11. Polymer diene content during reactor startup.

the reactant flows are begun simultaneously in the amount required to produce the desired polymer at steady state, the startup behavior shown by the solid curves in Figures 9 to 12 is obtained. Polymer concentration rises smoothly from zero to the steady state value in about three reactor turnovers, Figure 9. Composition and molecular weight are also lined out at the same time, but the initial polymer formed is high in ethylene and ENB content and low in molecular weight. Low molecular weight is not a serious problem since it persists for a short time (M_n reaches 5×10^4 in about 0.15 reactor turnovers). However, the high ethylene and diene content of the initial polymer could potentially lead to reactor fouling. For a single active catalyst species, the polymer MWD during startup, as measured by M_w/M_n, is narrower than the most probable distribution initially, but M_w/M_n rises rapidly, reaching a value of 2.0 within about one reactor turnover following startup. The narrowed MWD is a consequence of the considerable batch reactor characteristics of the polymerization until appreciable amounts of polymer begin to leave the reactor in the outflow. The fast initiation characteristics of EP kinetics lead to narrower MWD in a batch reactor than in a CFSTR reactor.

To eliminate the large polymer composition variation at startup, we examined the effect of starting the solvent and propylene flow initially, with the propylene feed set at the steady state rate. Then with the reactor propylene concentration already established, all the other reactant feeds were begun to initiate polymerization. The course of the unsteady state period with this startup procedure is shown by the dashed lines in Figures 9 to 12. The presence of propylene prior to the start of polymerization has little effect on polymer concentration or molecular weight, but greatly reduces the initial level of ethylene and diene in the polymer, and steady state in composition is reached much more rapidly. Propylene concentration in the reactor for these two different startup methods approaches steady state monotonically, Figure 13, but the ethylene concentration, Figure 14, and the ENB concentration, exhibit complex dynamic behavior.

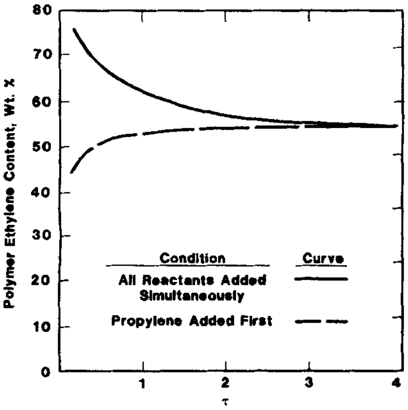

Figure 10. Polymer ethylene content during reactor startup.

Finally, to test whether delayed hydrogen addition would result in a quicker approach to steady state molecular weight, the calculations just described were repeated, except that the hydrogen addition was delayed until 0.167 reactor turnovers after the start of polymerization. With this procedure, M_n increases at about the same rate over the period from 0 to 0.167 reactor turnovers in the presence and absence of hydrogen, but with no hydrogen present, M_n overshoots before attaining the steady state value. Thus there appears to be no advantage in postponing hydrogen addition.

Conclusions

Solution of the unsteady state kinetic equations for Ziegler catalyzed copolymerizations in a CFSTR indicates that lengthy

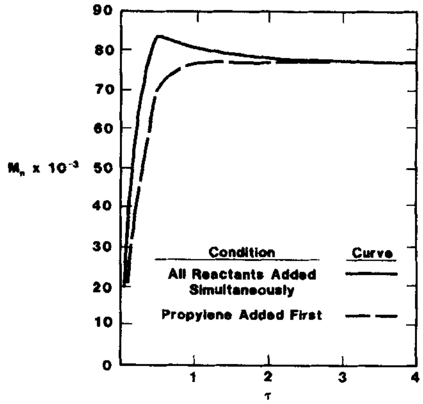

Figure 12. M_n during reactor startup.

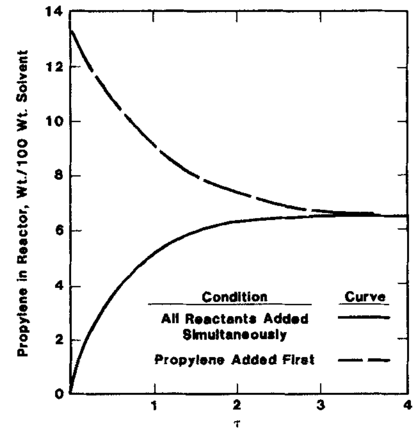

Figure 13. Propylene concentration during reactor startup.

line-out times could be required to reach steady state in polymer properties following a step change in reactor operating conditions. Also, the line-out time will depend on the direction and magnitude of a change, and steady state is reached more rapidly if a property value is decreased rather than increased. This is especially true for molecular weight. Attempts to confirm model predictions experimentally gave reasonably good agreement between predicted and observed results, and the need for long line-out times was confirmed. However, for a step change in hydrogen feed rate polymer M_n took longer to reach steady state than predicted for reasons that are not apparent. Possible causes for the discrepancy are oversimplified kinetics for the polymerization or an inappropriate assumption of perfect mixing in the reactor. Additional studies will be required to resolve the differences between model calculations and experimental results.

Simulations of reactor startup indicated that steady state is reached in about three reactor turnovers simply by starting all the feeds to the reactor at steady state rates. This is considerably quicker than the transient response to a step change, and is due to the initial absence of any polymer in the reactor. Although this procedure leads to a rapid approach to steady state, the initial polymer formed has a very high content of the most reactive monomers, which could cause reactor fouling or gel in EPDM polymerization. This potential problem can be avoided by starting the feed of the least reactive monomer before the other reactants are added to initiate polymerization.

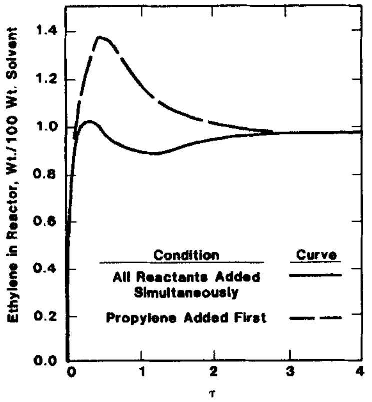

Figure 14. Ethylene concentration during reactor startup.

Acknowledgment

We are grateful to A. Bogard of Exxon Chemical Co. for providing some of the data discussed in this paper.

Notation

a, b = constants in Mooney viscosity/M_n relationship
C_1 = unactivated catalyst concentration, mol/L
C_2 = activated catalyst concentration, mol/L
ENB = ethylidene norbornene content of polymer, wt. %
EP = ethylene content of polymer, wt. %
F_n = nth moment of P_i distribution
G_n = nth moment of U_i distribution
DP_n = number-average degree of polymerization
DP_w = weight-average degree of polymerization
H = hydrogen concentration, mol/L
k = rate constant, Table 1
M = Mooney viscosity
M_1 = monomer 1 (ethylene) concentration, mol/L
M_2 = monomer 2 (propylene) concentration, mol/L
M_3 = monomer 3 (diene) concentration, mol/L
M_n = number-average molecular weight
M_w = weight-average molecular weight
P_i = concentration of growing chains, i units long, ending in monomer 1, mol/L
Q_i = concentration of growing chains, i units long, ending in monomer 2, mol/L
R_i = concentration of growing chains, i units long, ending in monomer 3, mol/L
U_i = concentration of dead chains, i units long, ending in monomer 1, mol/L
V_i = concentration of dead chains, i units long, ending in monomer 2, mol/L
W_i = concentration of dead chains, i units long, ending in monomer 3, mol/L
t = time
X = xylene tracer concentration, g/L
Y_n = nth moment of molecular weight distribution

Greek letters

θ = reactor residence time
τ = dimensionless time, t/θ

Subscripts

d = nondimensional fraction of unaccomplished change, $(Z - Z_f)/(Z_i - Z_f)$
i = initial state, $\tau = 0$
f = final state, $\tau = \infty$
o = reactor feed concentration

Literature Cited

Cozewith, C., "Reactor Modeling in Ethylene/Propylene/Diene Terpolymerization," *73rd AIChE Ann. Meet.* (1980).

Cozewith, C., and G. W. Ver Strate, "Ethylene-Propylene Copolymers: Reactivity Ratios, Evaluation, and Significance," *Macromolecules*, **4**, 482 (1971).

Gardner, I. J., and G. W. Ver Strate, "Determination of Ethylidene Norbornene in EPDM Terpolymers," *Rub. Chem. Tech.*, **46**, 1019 (1973).

MacGregor, J. F., A. Penlidis, and A. E. Hamielec, "Control of Polymerization Reactors: A Review," *Poly. Process Eng.*, **2**, 179 (1984).

Metzner, A. B., R. H. Feehs, H. L. Ramos, R. E. Otto, and J. D. Tuthill, "Agitation of Viscous Newtonian and Non-Newtonian Fluids," *AIChE J.* 7, 3 (1961).

Podolnyi, Y. B., G. V. Solovyeva, and Y. G. Kamenev, "Effect of Ethylidene Norbornene on Elementary Reaction Constants of Copolymerization of Ethylene and Propylene in the Presence of $VOCl_3$—$Al_2Et_3Cl_3$ Catalytic System," *Poly. Sci. USSR,* **16,** 3224 (1974).

Pronyayev, V. N., I. D. Afansev, and G. A. Kovaleva, "The Kinetics of Ethylene-Propylene Copolymerization by the Catalytic System $VOCl_3$—$Al(C_2H_5)_{1.5}Cl_{1.5}$," *Poly. Sci. USSR,* **27,** 1448 (1985).

Manuscript received May 28, 1987 and revision received Sept. 4, 1987.