Polymerization of Olefins through Heterogeneous Catalysis. XV. The Influence of Pressure in the Solution Copolymerization of Ethylene

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SYNOPSIS

The high-temperature solution homopolymerization of ethylene and copolymerization with 1-hexene using highly active $TiCl_4/MgCl_2$-supported catalyst was studied. Experiments with pressure variations in the range 100–400 Psig were carried out at 185°C and for 10 min polymerization time. Both peak initial rate of polymerization and the catalyst productivity in homo- and copolymerization were found to increase steadily with increasing reactor pressure. Higher polymerization rates arose in copolymerization compared to homopolymerization, especially above 200 Psig total pressure. In both cases, the reaction order with respect to ethylene concentration was close to two. The number-average molecular weight was found to be almost independent of pressure, whereas in copolymerization, the weight-average molecular weight was observed to decrease from about 200,000 to 120,000 over the range of pressure studied. The polydispersity index in copolymerization was found to decrease steadily from 8 to about 4 with increasing pressure. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The influence of hydrogen, comonomer, and temperature on the polymerization kinetics and the polymer properties in the solution copolymerization of ethylene have been reported in the first three parts of this study.[1-3] In the present article, the effect of varying the reactor pressure on the homo- and copolymerization of ethylene in solution is discussed. For the analysis of the kinetics in the solution polymerization of ethylene, the effect of varying the ethylene partial pressure is of fundamental importance. Here, we provide data on the effect of reactor pressure on the polymer molecular weight, the reaction order, the decay rate constant, and the copolymerization parameters.

In Ziegler–Natta polymerization systems, it is well established that an increase in the monomer concentration leads to a dramatic increase in the polymerization rate and the catalyst productivity. This observation has been reported in the scientific literature for gas,[4-6] slurry,[7,8] and solution[9,10] polymerization systems. However, because of the fact that different catalysts, materials, and polymerization conditions have been employed, different observations and conclusions have been reported. For example, some reports have observed a linear increase in the productivity with increasing monomer pressure, whereas others have found a nonlinear relationship. Also, the reaction order with respect to the monomer concentration has been variously reported as a first- or a second-order dependency. This again emphasizes the complexity of Ziegler–Natta polymerization systems and the difficulties in formulating a unified understanding of the effect of a particular parameter, e.g., pressure, on the polymerization kinetics. Consequently, caution should be exercised when different results originating from the use of different catalysts and polymerization conditions are compared.

In gas- or slurry-phase ethylene homopolymerization with high-activity $TiCl_3$ or $TiCl_4/MgCl_2/THF$ catalysts impregnated in silica, Karol et al.[4]

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reported a second-order dependency on the ethylene partial pressure. Similarly, a second-order dependency was also reported in gas-phase C_2/C_6 or C_2/C_4 copolymerization with the same type of catalysts. However, in gas-phase ethylene homopolymerization using a $VCl_3/THF/SiO_2$ catalyst, the reaction order was close to two, but unlike the Ti-based catalyst, the kinetic order in C_2/C_6 copolymerization was close to unity.[4] In contrast, a reaction order in the range 1.5–1.6 for gas-phase ethylene homopolymerization using a $TiCl_4/MgCl_2$-based Ziegler catalyst supported on silica was reported by Kissin.[5] In a series of polymerization experiments in which the ethylene partial pressure was varied repeatedly over the range 2.8–13.8 bar, it was found that the ethylene pressure changes produced very large and reversible changes in the polymerization rate.[5]

In the slurry-phase polymerization of ethylene, a similar enhancement of the catalyst productivity with increasing pressure was reported by Wang et al.[7] Using a chromium Phillips-type catalyst, Wang et al. investigated the effect of the ethylene pressure, 2–11 atm, on the polymerization. The monomer pressure was found to affect both the shape of the rate–time profile and the value of the polymerization rate. The authors reported a 5.2-fold increase in the average rate (2 h polymerization time) and a 5.8-fold increase in maximum polymerization rates. However, the plots of R_p (av) and R_p (max) vs. the pressure were not shown to be linear; instead, these values were found to increase up to a limiting constant value when a reactor pressure of 11 atm was reached. Wang et al. suggested that a possible explanation for the observed changes in rate with pressure could be greater fragmentation of the silica support with increasing pressure, which would make available more active surface sites. Determination of the active site concentration by the ^{14}CO-radio-labeling technique revealed an increase in [C^*] from 3.2 to 7.3 mol/mol Cr and an increase in the propagation rate constant value from 1710 to 4490 L/mol s in the pressure range 2–10 atm.[7] Thus, for this system, there appears to be a nonlinear pressure dependence due to changes in the catalyst surface.

Comparing three catalytic systems, $TiCl_3/AlEt_3$, $Mg(OC_2H_5)_2/TiCl_4/AlEt_3$, and bis(triphenyl)-chromate/SiO_2,[11] for the polymerization of ethylene in the slurry phase, Böhm[8] found that the polymerization rate was linear with the pressure increase, 0–10 bar, for the first catalyst system. For the $Mg(OC_2H_5)_2/TiCl_4/AlEt_3$ catalyst, in the pressure range 0–6 bar, the relationship was linear *only* after 2 bars of pressure. Finally, for the Cr-based catalyst system,[11] the plot of R_p vs. ethylene pressure was

linear above a pressure of about 10 bar up to about 35 bar. Böhm[8] interprets these results to mean that in ethylene polymerization with a high-activity catalyst a linear relationship of R_p with monomer exists above a certain level of monomer concentration. The comparison of the high-activity Ti- and Cr-based catalysts given by Böhm emphasize that the range of linearity of the relationship varies from one catalyst system to another.

In solution ethylene/1-butene copolymerization under high pressure with a $TiCl_3/0.33AlCl_3/VCl_3$ catalyst system, Machon[9] found that the catalyst efficiency increased with increasing pressure, up to 1500 bar, but decreased with increasing polymerization temperature. Using high-activity Ti- and Cr-based supported catalysts in the solution polymerization of ethylene, Agapiou and Etherton[10] reported that in the range of pressure, 10–30 bar, the productivity increases linearly with the pressure increase. However, for much higher pressures, 0–1500 bar, the authors found that the productivity was approximately linear with pressure up to 750 bar, and then approximately linear up to 1500 bar, but at a different slope. Agapiou and Etherton[10] concluded that, with the exception of the region around the break in the line, the productivity is first order in ethylene concentration.

In an attempt to explain kinetics orders between one and two, some workers have proposed various mechanisms. Kissin[5] viewed a monomer molecule to convert a potentially reactive center into a completely operational one. Then, a second site was suggested to be used by olefin molecules for chain growth reaction. Alternatively, in a recent report, Ystenes[12] hypothesized a "trigger mechanism" whereby a two-monomer transition state exists. Ystenes suggested that the entering of a new monomer unit triggers the insertion of the already complexed monomer and that the catalytic center is activated through the insertion of the first monomer unit. Such a kinetic model can predict reaction orders between 1.0 and 2.0.

The purpose of the present study was to investigate the influence of the reactor pressure on the polymer properties, on the one hand, and to determine the effect of this parameter on the kinetics of ethylene homo- and copolymerization in a high-temperature solution reactor, on the other. In particular, the effect of varying the pressure in the homopolymerization of ethylene, without H_2, and the copolymerization of ethylene with 1-hexene, in the presence of H_2, was studied. The results were analyzed in terms of the kinetic reaction order with respect to ethylene concentration, the catalyst ac-

tivity decay rate law, and the reactivity ratios r_1 and r_2 for copolymerization.

EXPERIMENTAL

The experiments were carried out in a solution polymerization reactor at 185°C and over a pressure range of 100–400 Psig using isopar-E as solvent. The hydrogen and comonomer (1-hexene) were charged initially and the ethylene metered to the reactor on demand. The heterogeneous catalyst was a $TiCl_4$/$MgCl_2$ system using triethylaluminum as the cocatalyst. The polymerization time was approximately 10 min. The details of the apparatus and experimental procedure are provided in reference 1.

RESULTS

The Effect of Ethylene Partial Pressure on Polymerization Rate

Ethylene homopolymerization in a solution reactor has been carried out at a constant temperature of 185°C for a range of pressures and over a 10 min polymerization period in the absence of hydrogen. The solubility of the ethylene monomer in the isopar-E solvent increases steadily with increasing ethylene pressure, as shown in Figure 1. It can be seen that increasing the pressure by a factor of four, 100–400 Psig, leads to an increase in the ethylene concentration in the solvent by a factor of 7.3.

In the same reactor, ethylene/1-hexene copolymerization using a low concentration of hydrogen was carried out by varying the ethylene pressure. At the time that these experiments were carried out, the exact concentrations of hydrogen, ethylene, and the comonomer dissolved in the solvent were not available. Consequently, the concentrations of 1-hexene and hydrogen were changed in proportion to the change in the ethylene pressure. This produced variations in ethylene concentration, hexene/ethylene, and hydrogen/ethylene molar ratios in the solvent with varying ethylene pressure, as shown in Figure 2. The dissolved H_2/C_2 and C_6/C_2 molar ratios varied significantly only at low reactor pressure; little change in these ratios is observed for reactor pressures above 200 Psig. As can be seen from Figure 2, ethylene concentration in the solvent in copolymerization was essentially the same as that in homopolymerization for a given pressure.

Rate–time profiles for the homopolymerization of ethylene under various reactor pressures are shown in Figure 3. As expected, the initial peak in the polymerization rate is highest at the highest reactor pressure used. As the reactor pressure is decreased, both the drop in the initial peak and also the decrease in the average rate with time are quite dramatic. Similar observations in the case of ethylene/1-hexene copolymerization are also evident in Figure 4. From both plots it is clear that pressure variations do not affect the shape of the rate–time profile to a great extent; however, a remarkably high initial R_p (max) is noticed at the highest pressure
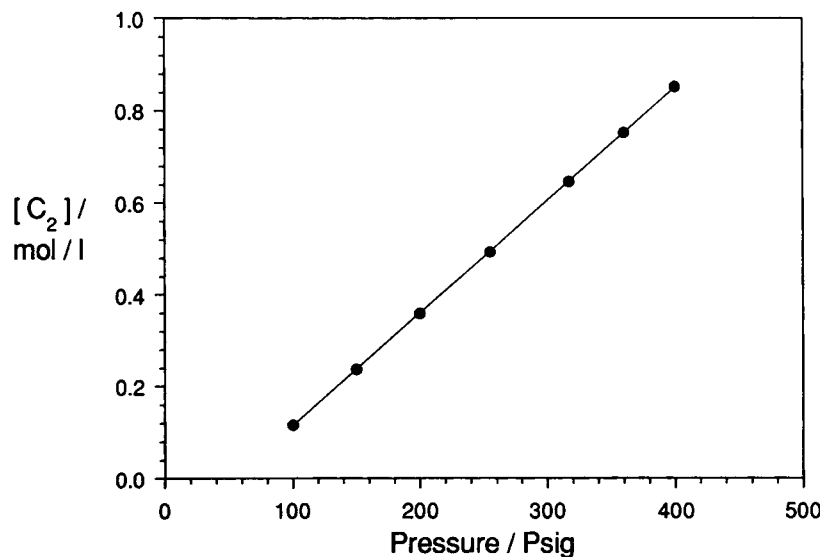

Figure 1   Effect of varying ethylene pressure on ethylene concentration in isopar-E solvent at 185°C (homopolymerization).
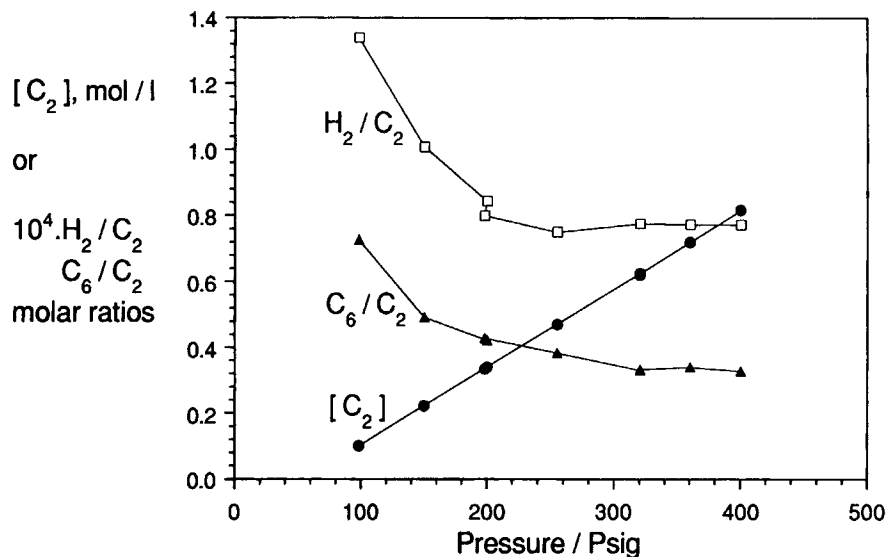
Figure 2 Effect of varying ethylene pressure on ethylene concentration and C_6/C_2 and H_2/C_2 molar ratios in isopar-E solvent at 185°C.

used both in the homo- and the copolymerization of ethylene. Comparing the rate–time profiles in Figures 3 and 4 reveals that at 400 Psig pressure the R_p (max) in copolymerization is higher than that in homopolymerization by a factor of two. In general, for copolymerization, smoother rate–time profiles are obtained when compared to the rate–time pro-

files in homopolymerization. One factor that has great influence here is the absence of hydrogen in homopolymerization and the presence of both the comonomer and the hydrogen in copolymerization. Also, the presence of H_2 and the comonomer give a lower molecular weight polymer. This results in a more homogeneous solvent–polymer mixture com-
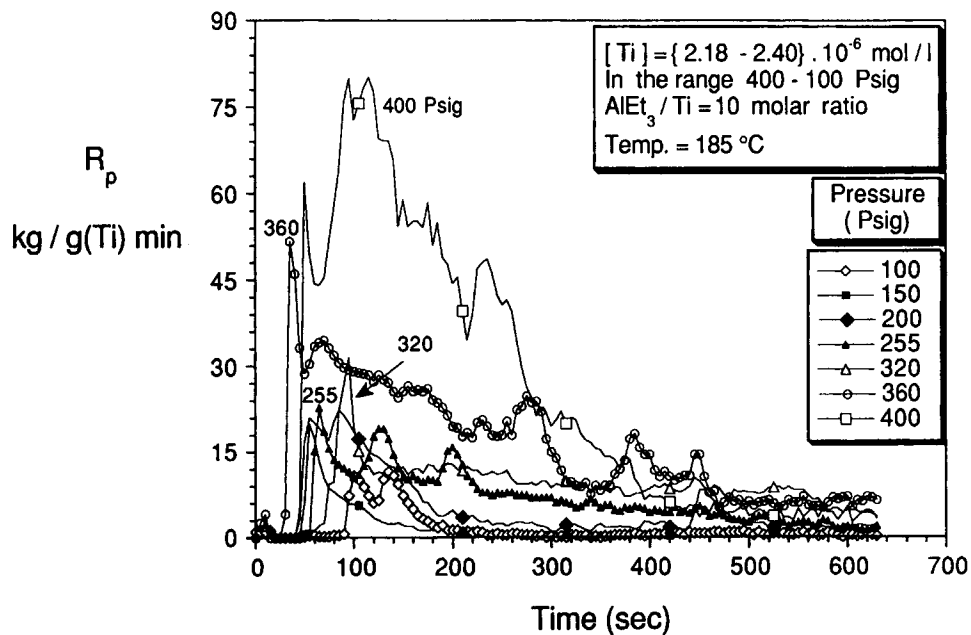
Figure 3 Rate–time profiles for the homopolymerization of ethylene in solution at different ethylene pressures.
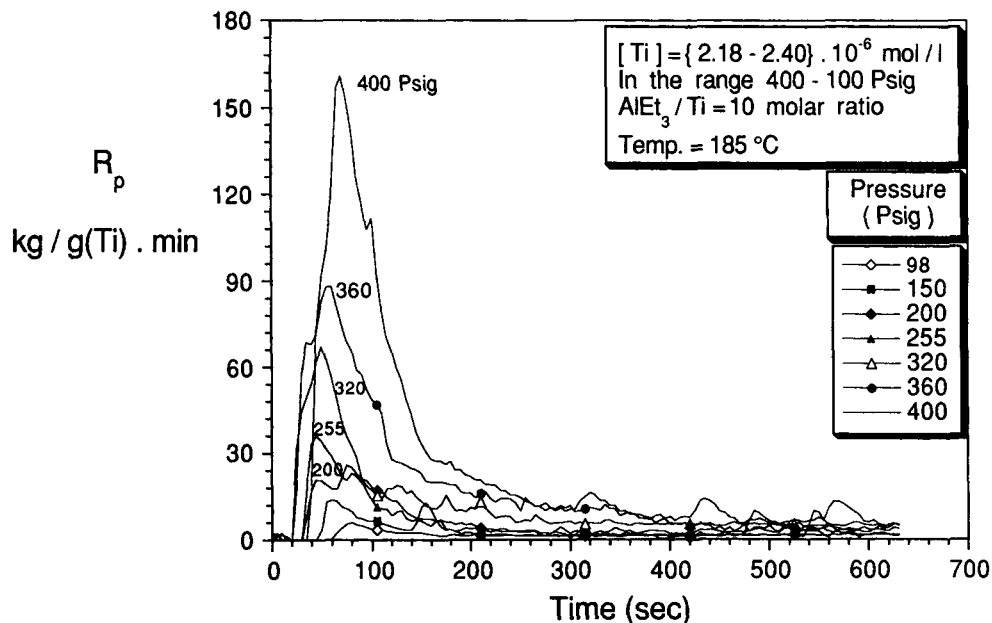
Figure 4   Ethylene consumption rate in C_2/C_6 copolymerization in dependence on the reactor pressure. H_2/C_2 and C_6/C_2 molar ratios as in Figure 2.

pared to the homopolymerization runs where the absence of hydrogen gives a higher molecular weight polymer with lower solubility and a less homogeneous mixture.

The higher rates of ethylene consumption in the case of copolymerization are due to the presence of the comonomer and hydrogen. These two components were reported earlier to boost the initial po-

lymerization rate and thus to increase the catalyst productivity when used in moderate concentrations.[1,2] The higher activity in copolymerization is most pronounced at high reactor pressure; however, the comparison of rate–time profiles in homo- with copolymerization is more difficult at low reactor pressure, due to the lower reactivities in both cases and the fluctuation of the initial polymerization rate
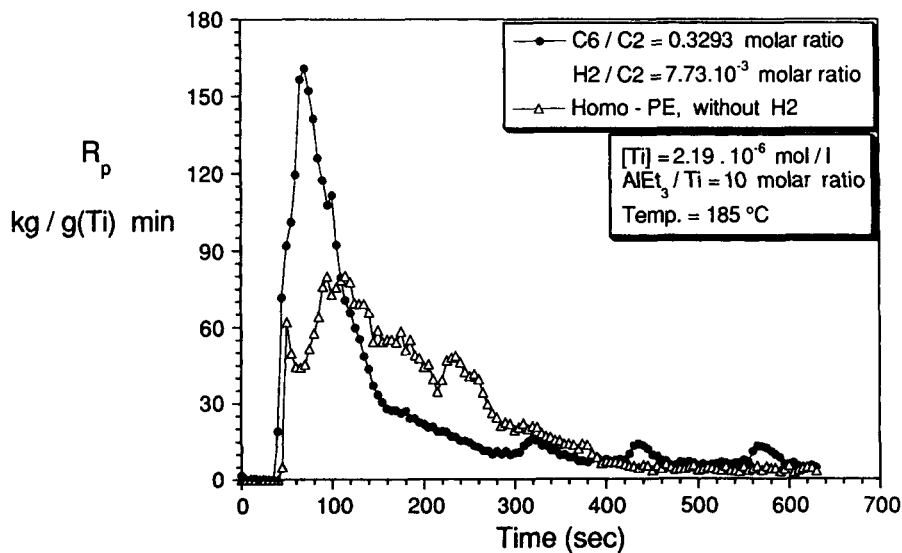

Figure 5   Comparison of the ethylene consumption rate in homopolymerization and in C_2/C_6 copolymerization at 400 Psig total pressure.
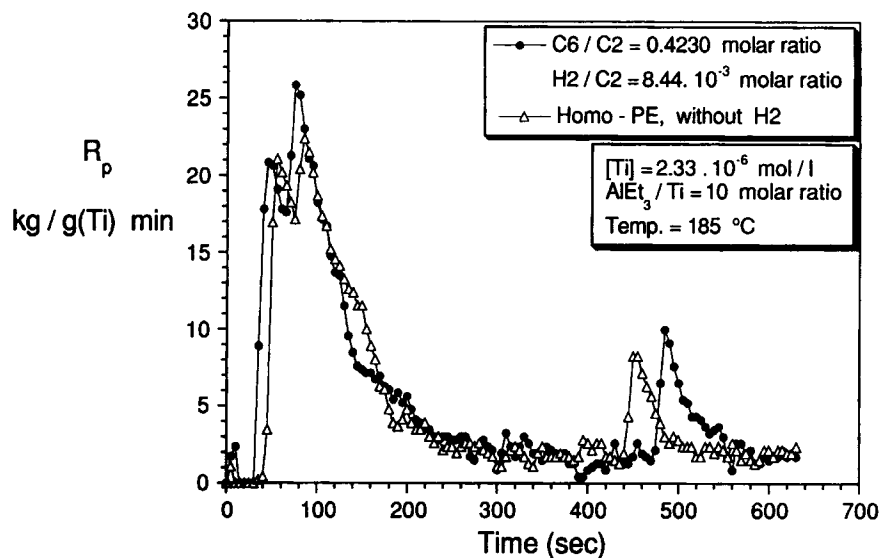
Figure 6   Comparison of the ethylene consumption rate in homopolymerization and in C_2/C_6 copolymerization at 200 Psig total pressure.

especially in the case of homopolymerization. To illustrate these points, comparisons of the homopolymerization rate–time curves with those obtained in copolymerization with 1-hexene at 400 and 200 Psig reactor pressure are shown in Figures 5 and 6, respectively. In both figures, there are one or more small peaks in feed rate at low reaction rates; these are thought to be due to relatively small pressure blips that affect the feed rate more strongly when reaction rate is low.

As mentioned above, catalyst productivity increases dramatically with increasing ethylene partial pressure (and resulting dissolved ethylene concentration; cf. Fig. 1). The increase in catalyst yield and R_p (max) with increasing ethylene partial pressure for homo- and copolymerization is shown in Figures 7 and 8. In both cases, it was found that the yield and R_p (max) increase slowly in the range of low pressure, 100–200 Psig (0.1–0.4 mol/L) and more dramatically when the reactor pressure is in-
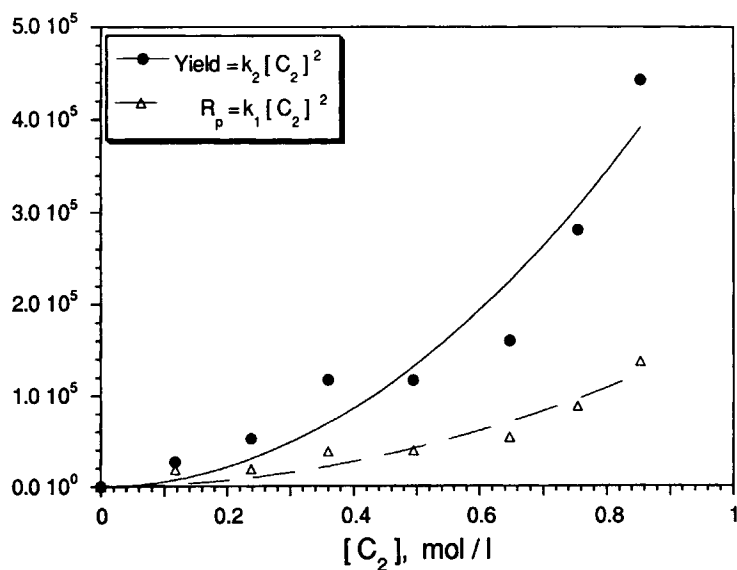

Figure 7   Fit of yield (mol/mol Ti) and R_p (max) (mol/mol Ti min) for second-order dependence on ethylene concentration. Ethylene homopolymerization: conditions as in Figure 3.
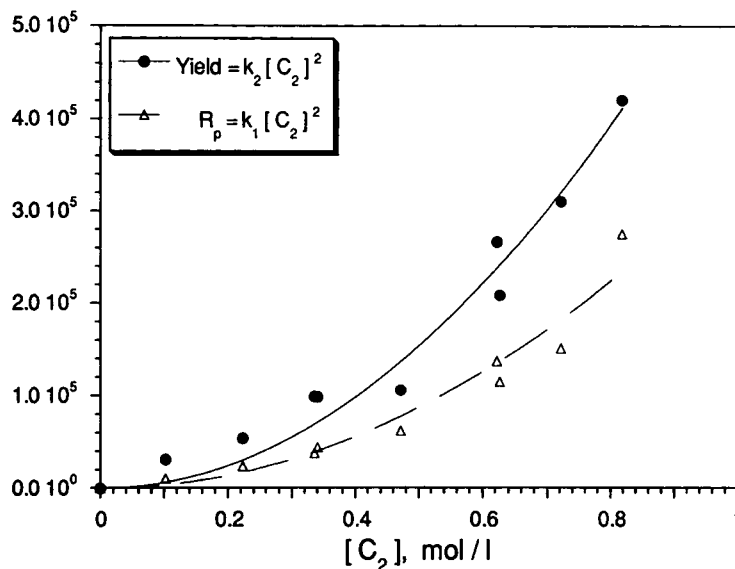
Figure 8 Fit of yield (mol/mol Ti) and R_p (max) (mol/mol Ti min) for second-order dependence on ethylene concentration. C_2/C_6 copolymerization: Conditions as in Figure 4.

creased above 200 Psig (0.4 mol/L). Thus, for both homo- and copolymerization, the increase in catalyst productivity with increasing ethylene partial pressure is nonlinear. Note that at higher reactor pressures variations in dissolved C_6/C_2 and H_2/C_2 molar ratios with pressure are minimal; this suggests that the increase in catalyst productivity and reaction rate is due mainly to increasing ethylene concentration and not to any fundamental change in the comonomer or hydrogen-to-ethylene molar ratios.

Effect of Ethylene Partial Pressure on Polymer Properties

Because of the difficulty in determining homopolyethylene molecular weight by GPC, only the number-average molecular weight, M_n, is available as determined by FTIR,[13] and there is a great deal of scatter in these data. However, the copolymer molecular weight has been determined more precisely by the GPC technique. A comparison of the M_n values in homo- and copolymerization is shown in Figure 9, where it can be seen that M_n values for the homopolyethylenes and ethylene/1-hexene copolymer samples are fairly close, with a tendency toward lower M_n values in the case of homopolymerization. However, caution should be exercised because these values have been obtained by different techniques. For copolymerization, it appears that M_n is essentially constant with pressure.

The weight-average molecular weight for the ethylene/1-hexene copolymer is observed to decrease with increasing reactor pressure, as is seen in Figure 10. Within the range of pressure increase, M_w decreases by about 40%. At the same time, Figure 11 shows that there is a 50% decrease in the polydispersity index, M_w/M_n, of the copolymer when increasing ethylene pressure from 100 to 400 Psig.

Although Figure 2 shows that the dissolved C_6/C_2 molar ratio changed only slightly above a reactor pressure of 200 Psig, the polymer composition shows a linear decrease in comonomer content with pressure increase, (cf. Fig. 12). This suggests that there could be a change in the proportion of the different types of active centers that are selective toward ethylene with increasing pressure. Similarly, as the amount of comonomer incorporated decreases with increasing pressure, the branching degree (expressed as methyl groups per 1000C atoms) also decreases (Fig. 13). The reduction in the $CH_3/1000C$ is observed to be in the same order as the reduction in the mol % 1-hexene incorporated, i.e., about 40% over the pressure range studied.

DISCUSSION

Effect of Ethylene Partial Pressure on Polymer Properties

An increase in the partial pressure of ethylene has resulted in a strongly nonlinear increase in ethylene
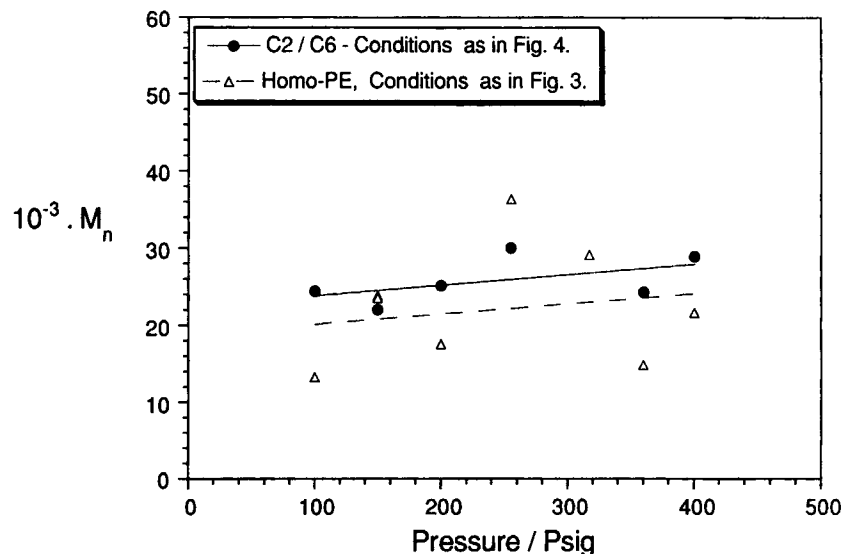
Figure 9 Reactor pressure variation effect on the number-average molecular weight. M_n determined by FTIR for Homo-PE and by GPC for C_2/C_6 copolymer.

consumption rate and in catalyst yield for both homo- and copolymerization. In addition, this increase in reactor pressure is found to decrease the weight-average molecular weight (cf. Fig. 10) and the polydispersity index (cf. Fig. 11) by almost 50%, while the mol % 1-hexene incorporation decreases by about 40%. These polymer molecular weight trends are in contrast to earlier results[1,2] at constant pressure, where it was shown that M_w and the polydispersity index are virtually constant with varying

comonomer/ethylene molar ratios and only decrease 20–30% with a large increase in H_2/C_2 ratio. Thus, the effects of pressure on the polymer molecular weight are difficult to explain qualitatively. Further interpretation is deferred until detailed modeling can be carried out.

Kinetic Reaction Order

Determination of the kinetic reaction order is a fundamental requisite for the understanding of the po-
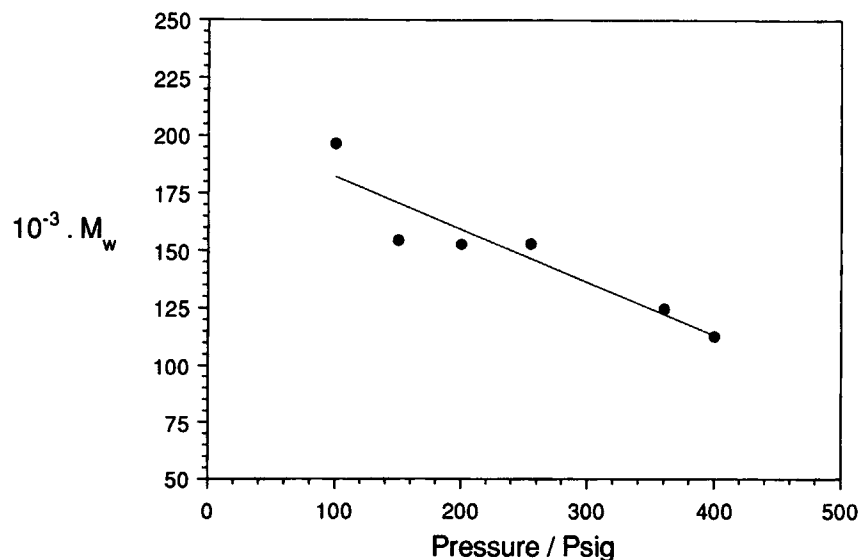

Figure 10 Reactor pressure variation effect on the weight-average molecular weight in C_2/C_6 copolymerization. Conditions as in Figure 4.
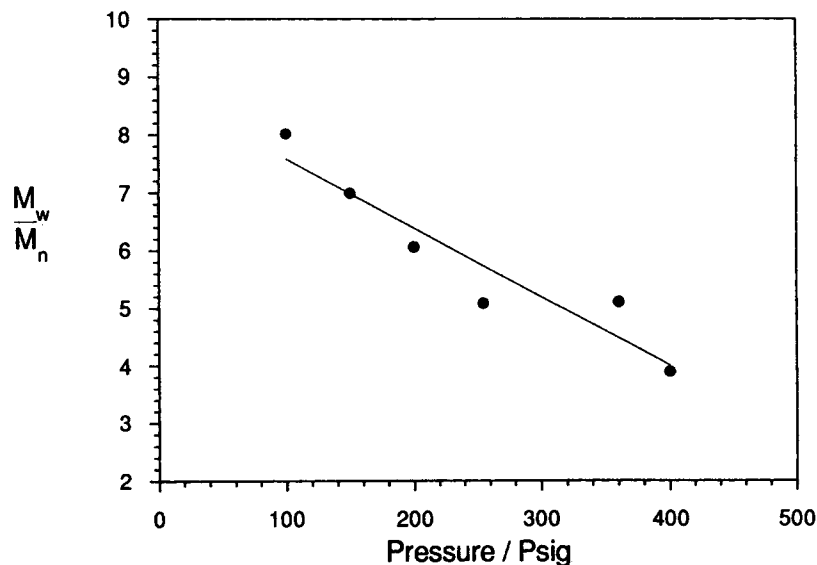
Figure 11   Reactor pressure variation effect on the polydispersity index, M_w/M_n, in $C_2/$ C_6 copolymerization. Conditions as in Figure 4.

lymerization kinetics. With respect to the monomer concentration, Karol et al.[4] reported a second-order dependency on the ethylene pressure in the gas- and slurry-phase ethylene polymerization. Kissin,[5] studying the gas-phase ethylene polymerization, reported values in the range 1.5–1.6. In the solution polymerization of ethylene with high-activity catalysts, Agapiou and Etherton[10] stated that the productivity is first order in ethylene concentration. In the present study, the reaction order with respect to the ethylene concentration is analyzed both for homo- and copolymerization of ethylene. In Figures 7 and 8, it has been shown that both plots of productivity and R_p (max) vs. the reactor pressure were not linear. Initially, it was thought that the influence of H_2 and the comonomer was the cause of the nonlinearity of the plots in the copolymerization case. However, the data obtained in homopolymerization, and in the absence of H_2, confirm the nonlinearity of the plots.
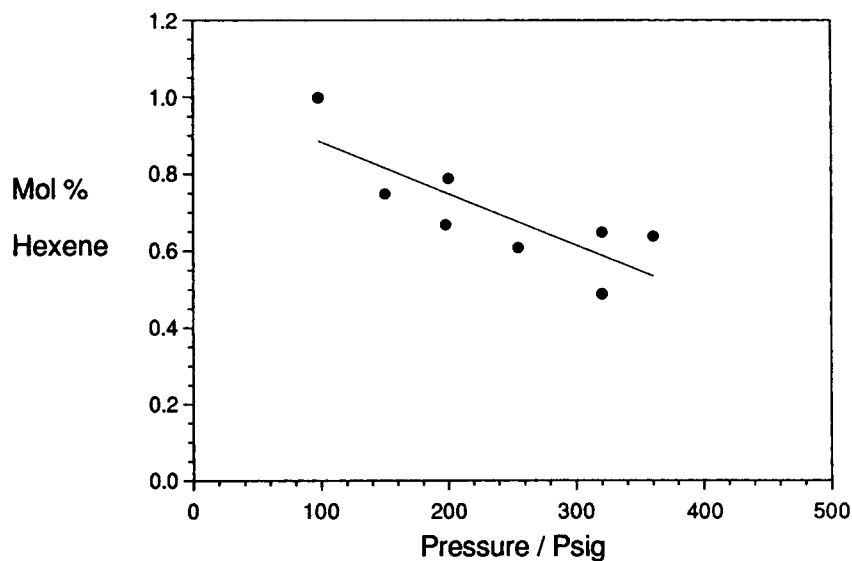

Figure 12   Reactor pressure variation effect on the mol % 1-hexene incorporation and C_2/C_6 copolymerization. Conditions as in Figure 4.
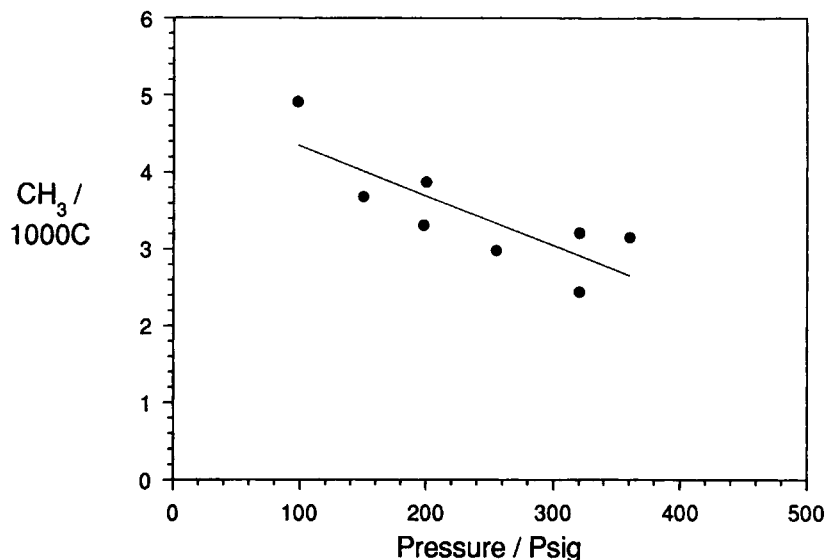
Figure 13   Reactor pressure variation effect on the branching content in C_2/C_6 copolymerization. Conditions as in Figure 4.

To begin the analysis of the reaction order, power-law expressions, $R_p = k_1[C_2]^n$ and yield $= k_2[C_2]^m$ were fit to the homopolymerization and ethylene/1-hexene copolymerization data shown in Figures 7 and 8. In each case, the overall yield and R_p (max) are compared as a function of ethylene concentration. For homopolymerization (Fig. 14), it can be seen that the reaction order is about 2.3 when the yield is used and about 2.0 when R_p (max) is employed. In the case of copolymerization (Fig. 15),

the reaction order is 2.5 for yield and 1.9 for R_p (max). These results, summarized in Table I with error bounds on the parameters, show that a reaction order of 2 provides a good representation for all the data. In fact, the curves shown in Figures 7 and 8 are second-order fits to the data with correlation coefficients between 0.96 and 0.98.

These results add to the conflicting reports on reaction order already discussed above. However, they are consistent with the recent results of Karol
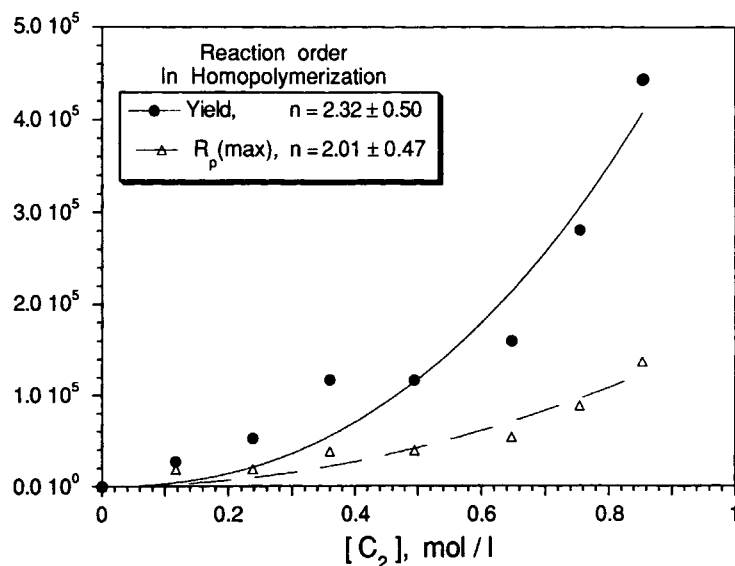

Figure 14   Yield and R_p (max) curve fitting according to the equation Y (or R_p) $= k_i \cdot [C_2]^n$. Ethylene homopolymerization: conditions as in Figure 3.
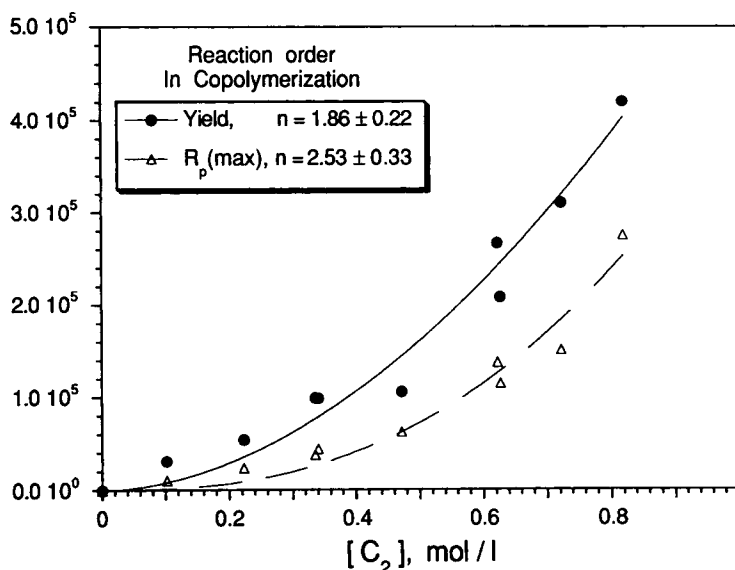
Figure 15 Yield and R_p (max) curve fitting according to the equation Y(or R_p) $= k_i \cdot [C_2]^n$. C_2/C_6 copolymerization: conditions as in Figure 4.

et al.[4] who found second-order kinetics for a $TiCl_4/MgCl_2$ catalyst.

Catalyst Deactivation

Analysis of the decay in the polymerization rate with time obtained under various reactor pressures in the homo- and copolymerization of ethylene has been performed employing a first-order deactivation rate law given by

$$R_p = R_\infty + (R_{max} - R_\infty)\exp\{-k_d(t - t_{max})\} \quad (1)$$

where t_{max} is the time at peak rate, R_{max}.

A sample of the fit for the rate–time profiles in homopolyethylene and ethylene/1-hexene copolymerization are shown in Figures 16 and 17, respectively. In addition, the k_d values estimated from these plots are presented in Table II. It can be seen from

Figures 16 and 17 that the decay in the polymerization rate with time is well represented by the first-order decay rate law. This observation has also been confirmed for other polymerizations performed under various reactor conditions for the system under investigation.[1-3]

Table II   Deactivation Rate Constant Values, k_d, in Homopolyethylene and Ethylene/Hexene Copolymerization Independent of Pressure

	Homo-PE	C_2/C_6 Copolymerization
Pressure (Psig)	k_d (min^{-1})	(k_d (min^{-1})
100	1.9932 ± 0.083	
98		1.9046 ± 0.085
150	1.7919 ± 0.055	1.3780 ± 0.046
150	1.4873 ± 0.097	
200	1.0197 ± 0.034	1.0406 ± 0.024
200	0.7841 ± 0.036	0.8618 ± 0.026
255	0.2325 ± 0.025	1.2445 ± 0.032
320	—	0.7641 ± 0.023
320	—	1.5379 ± 0.058
360	0.2944 ± 0.021	0.9426 ± 0.027
400	0.3333 ± 0.017	1.2182 ± 0.024

Table I   Reaction Kinetic Order with Respect to Ethylene[a]

	Homo-PE (without H_2) (Fig. 14)	C_2/C_6 Copolymerization (with H_2) (Fig. 15)
Yield	2.32 ± 0.50	1.86 ± 0.22
R_p (max)	2.01 ± 0.47	2.53 ± 0.33

[a] Correlation coefficients varied from 0.96 to 0.98 for the estimates.

k_d values from Figures 16 and 17. Polymerization conditions as in Figures 3 and 4.
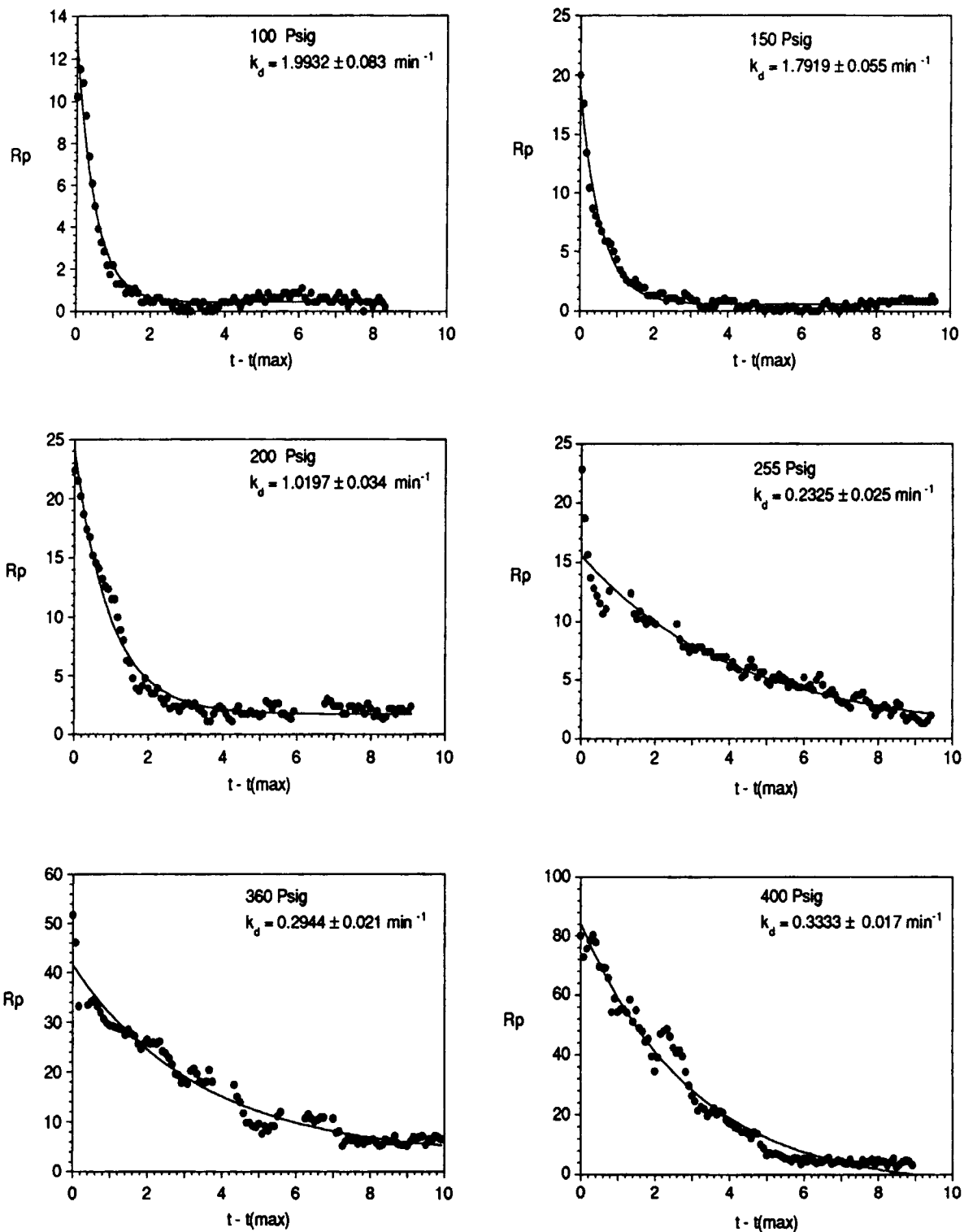
Figure 16 Plots of R_p vs. $t - t_{(max)}$ according to a first-order decay law, eq. (1). Ethylene homopolymerization at different reactor pressures. Conditions as in Figure 3.
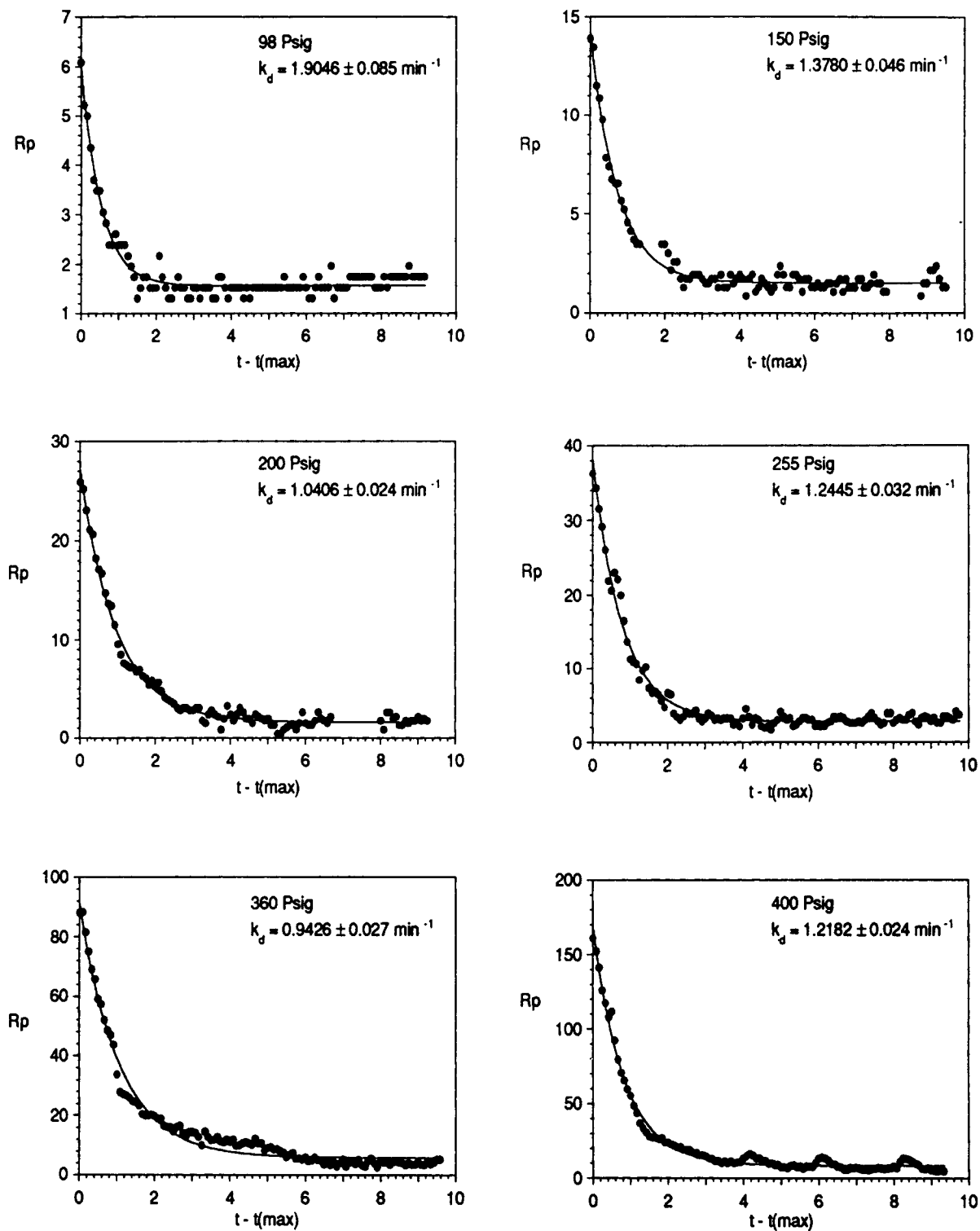
Figure 17   Plots of R_p vs. $t - t_{(\text{max})}$ according to a first-order decay law, eq. (1). Ethylene copolymerization at different reactor pressures. Conditions as in Figure 4.

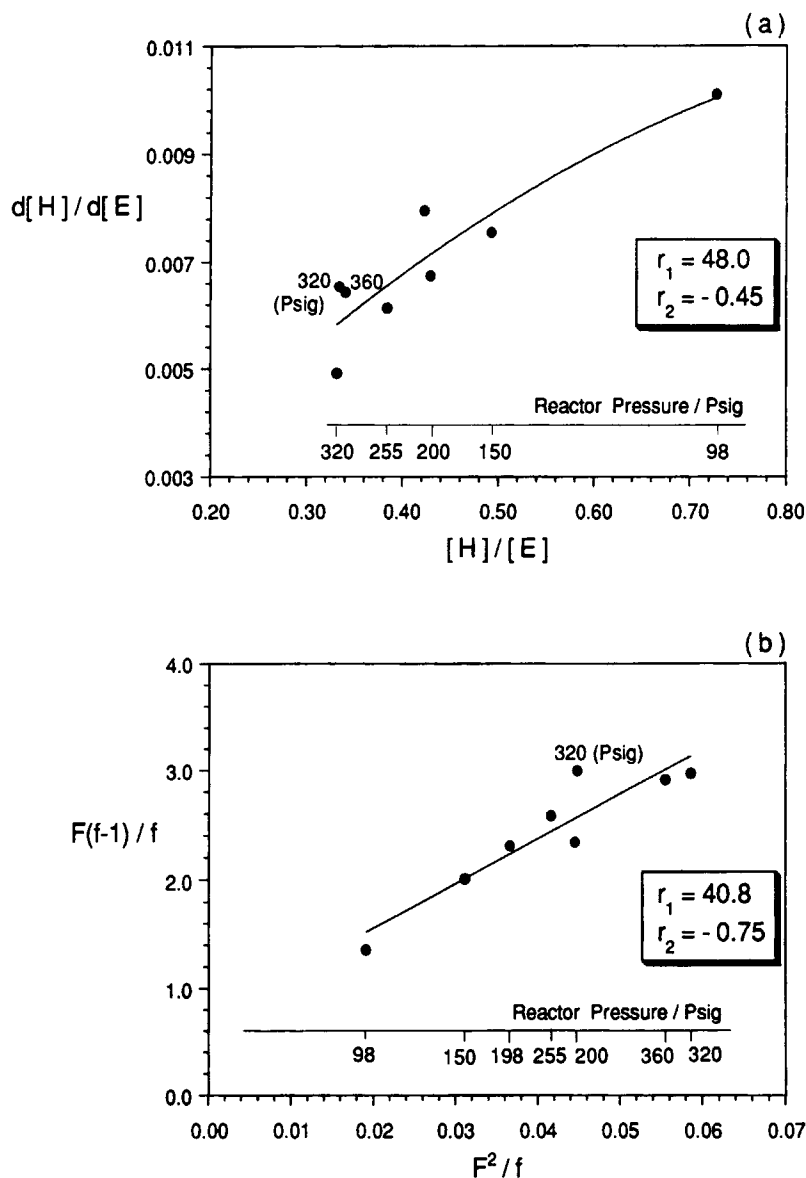**Figure 18** Estimation of r_1 and r_2 parameters in C_2/C_6 copolymerization. (a) Mayo–Lewis (curve fitting); (b) Fineman–Ross: eqs. (1) and (2) in Ref. 2. Conditions as in Figure 4.

The decay rate constant values, k_d, presented in Table II show that in homopolymerization the k_d value decreases quite rapidly with increasing reactor pressure and that the highest k_d value was obtained at the lowest pressure: 100 Psig. The rate–time profiles shown in Figure 3 for homopolymerization show that at high reactor pressure the decay in the rate after attaining R_p (max) is not as severe as in the copolymerization case. In copolymerization, there is some scatter in the k_d values estimated. Even though the data for copolymerization show that k_d tends to

decrease with increasing pressure, the effect is not as clear as in the case of homopolymerization. However, it is very clear that for pressures above 200 Psig the rate of deactivation is much less for homopolymerization.

Copolymerization Parameters

As described in Ref. 2, the Mayo–Lewis[14] and the Fineman–Ross[15] equations may be used for the estimation of the copolymerization parameters. In the

present article, it was attempted to keep the C_6/C_2 molar ratio in the solvent constant when the pressure variation was carried out. Because the exact concentration of ethylene and 1-hexene were not available at the time these experiments were performed, the C_6/C_2 molar ratio was observed to decrease slightly with increasing pressure in the range 100–200 Psig. Above 200 Psig, the C_6/C_2 molar ratio decreased only slightly. The Mayo–Lewis and Fineman–Ross plots are shown in Figure 18.

Note that the two procedures give somewhat different r_1 and r_2 values, but they are consistent and show that r_2 is negative. This is indicative of multiple sites as indicated earlier.[2] The r_1 and r_2 parameters estimated here are at about double those estimated in the preceding publication using the Mayo–Lewis and the Fineman–Ross equations and for the same ethylene/hexene copolymer.[2] However, the very narrow C_6/C_2 range explored in the present experiments adds much greater uncertainty to the present estimates of r_1 and r_2, so that the earlier values of r_1 and r_2 (Ref. 2) should be used.

CONCLUSIONS

In the solution polymerization of ethylene with a highly active supported titanium catalyst, increased ethylene partial pressure has been shown to lead to a nonlinear increase in the polymerization rate and catalyst productivity for both homopolymerization and ethylene/1-hexene copolymerization.

The decay in the rate of ethylene consumption with time is shown to fit a first-order decay rate law. The decay rate constant values are found to be significantly lower for homopolymerization compared to copolymerization, especially at higher reactor pressures.

The observed dependence of polymer yield and R_p (max) on the ethylene concentration show that the reaction order for homo- and copolymerization is about 2. These results and that of MWD dependence on pressure require more sophisticated interpretations. Thus, a subsequent paper in this series will provide detailed quantitative kinetic modeling in order to explain these results.

REFERENCES

1. I. A. Jaber and W. H. Ray, *J. Appl. Polym. Sci.*, to appear.
2. I. A. Jaber and W. H. Ray, *J. Appl. Polym. Sci.*, to appear.
3. I. A. Jaber and W. H. Ray, *J. Appl. Polym. Sci.*, to appear.
4. F. J. Karol, S.-C. Kao, and K. J. Cann, preprint, *AIChE* meeting, New Orleans, April 1992.
5. Y. V. Kissin, *J. Mol. Catal.*, **56**, 220–236 (1989).
6. K. Y. Choi and W. H. Ray, *J. Appl. Polym. Sci.*, **30**, 1065 (1985).
7. S. Wang, P. J. T. Tait, and C. E. Marsden, *J. Mol. Catal.*, **65**, 237–252 (1991).
8. L. L. Böhm, *Angew. Makromol. Chem.*, **89**, 1–32 (1980).
9. J. P. Machon, in *Transition Metal Catalyzed polymerizations: Ziegler–Natta and Metathesis Polymerizations*, R. P. Quirk et al., Eds., Cambridge University Press, New York, 1988, p. 344.
10. A. K. Agapiou and B. P. Etherton, in *Transition Metal Catalyzed Polymerizations: Ziegler–Natta and Metathesis Polymerizations*, R. P. Quirk et al., Eds., Cambridge University Press, New York, 1988, p. 364.
11. W. L. Carrick, R. J. Turbett, F. J. Karol, G. L. Karapinka, A. S. Fox, and R. N. Johnson, *J. Polym. Sci. Part A-1*, **10**, 2609 (1972).
12. M. Ystenes, *J. Catal.*, **129**, 383–401 (1991).
13. ASTM, D-2238 Method B.
14. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
15. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 269 (1950).