

# Polymerization of Olefins through Heterogeneous Catalysis. XIV. The Influence of Temperature in the Solution Copolymerization of Ethylene

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## SYNOPSIS

The influence of temperature variation on the kinetics and the polymer properties in the homo- and copolymerization of ethylene in a solution reactor is discussed. The polymerization is conducted in a semibatch mode at 320 Psig total reactor pressure for 10 min polymerization time. Temperature variations in the range 145–200°C in both homo- and copolymerization of ethylene with 1-octene shows that the highest catalyst yield was obtained at temperature of 165–175°C. At the optimal temperature, a high initial maximum in the rate of ethylene consumption is attained in a few seconds followed by a relatively slow decay when compared with polymerization conducted at higher temperatures. Polymerization at temperatures  $\geq 185^\circ\text{C}$  resulted in a lower peak in the consumption rate of ethylene accompanied by a rapid decay with time. In the case of ethylene/1-octene copolymerization, a rather low comonomer incorporation level is obtained at the conditions employed; the 1-octene incorporated was only 0.2–0.7 mol %. Higher  $M_w$  values, of about 350,000 at 145°C, are obtained in homopolymerization in comparison to  $M_w$  values obtained in copolymerization, of about 195,000 at the same temperature. Over the temperature range of 145–200°C, both  $M_w$  and  $M_n$  values vary by about 40%. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

In the first two parts of the present investigation,<sup>1,2</sup> the catalytic polymerization of ethylene in solution at 185°C and 400 Psig reactor pressure was investigated. Through the use of the same apparatus and experimental procedure, the present article discusses the effect of temperature variations in the range 145–200°C at reactor pressure of 320 Psig, on the polymerization kinetics and the polymer properties. Knowledge of temperature effects is important to our understanding and such data for high-temperature polymerization in Ziegler–Natta-catalyzed polymerizations are rather scarce. Most reported studies are limited to the temperature range 20–100°C. From previous studies, the apparent effect of an increase in the polymerization temperature is a dramatic increase in the catalyst activity up to a

certain optimal temperature, beyond which a further increase in the reactor temperature leads to a reduction in the activity. Thus, all site activation, chain propagation, and site deactivation steps vary significantly with temperature.

The polymerization of  $\alpha$ -olefins is carried out at high temperature in solution and relatively high-pressure processes. In reported studies on the effects of high temperature in Ziegler–Natta-catalyzed polymerization,<sup>3–10</sup> it is normally observed that higher initial polymerization rates are obtained at higher reaction temperatures and that catalyst deactivation is also significant. Thus, catalysts used at low temperatures, 20–100°C, are not necessarily suitable for high-temperature polymerizations, e.g.,  $\geq 150^\circ\text{C}$ . Kissin and Beach<sup>5</sup> investigated different catalyst systems at high reaction temperatures and reported that the most stable are the  $\text{TiCl}_4/\text{AlEt}_2\text{Cl}$  system and the least stable are the  $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4/\text{AlEt}_2\text{Cl}$  and  $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$  catalyst systems. In the present study, we used a  $\text{TiCl}_4/\text{MgCl}_2/\text{AlEt}_3$  catalyst system.

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One important requisite of catalysts employed at high polymerization temperature is that they should be able to withstand high temperature and to achieve maximum activity immediately upon injection in the reactor. Because rates of deactivation are rather high in these systems, high initial activity is crucial in high-temperature polymerizations. An advantage that results from this is that the residence time for these polymerizations is quite short, on the order of minutes. At high pressure, e.g., 15,000 Psig, the residence time can only be 1–2 min, whereas at medium-to-low pressure, e.g., 500 Psig, a residence time of 5–30 min can be employed. Longer polymerization times cannot be tolerated because of fast catalyst deactivation. Finally, because these catalysts are usually used for the production of LLDPE, they must be capable of high comonomer incorporation levels. At the high temperatures of solution processes, relatively high rates of chain-transfer reactions result in lower molecular weight resins. In addition, the reactivity ratios for copolymerization can be significantly different from those found in low-temperature copolymerization.

## EXPERIMENTAL

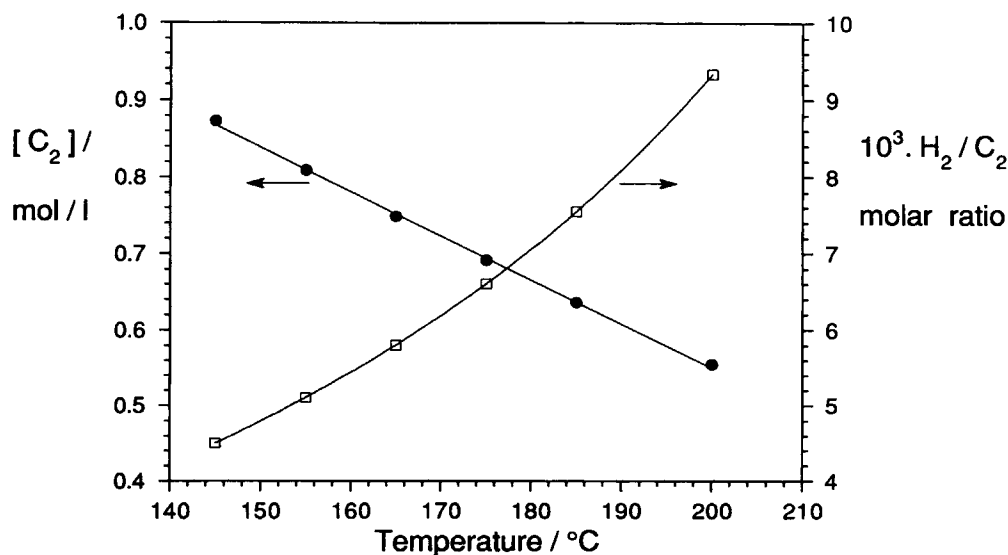
The experiments were carried out in a solution polymerization reactor over a temperature range of 145–200°C and at 320 Psig pressure using isopar-E as solvent. The hydrogen and comonomer (1-octene) were charged initially and the ethylene metered to

the reactor on demand. The heterogeneous catalyst was a  $\text{TiCl}_4/\text{MgCl}_2$  system using triethylaluminum as the cocatalyst. The polymerization time was approximately 10 min. The details of the apparatus and experimental procedure are provided in Ref. 1.

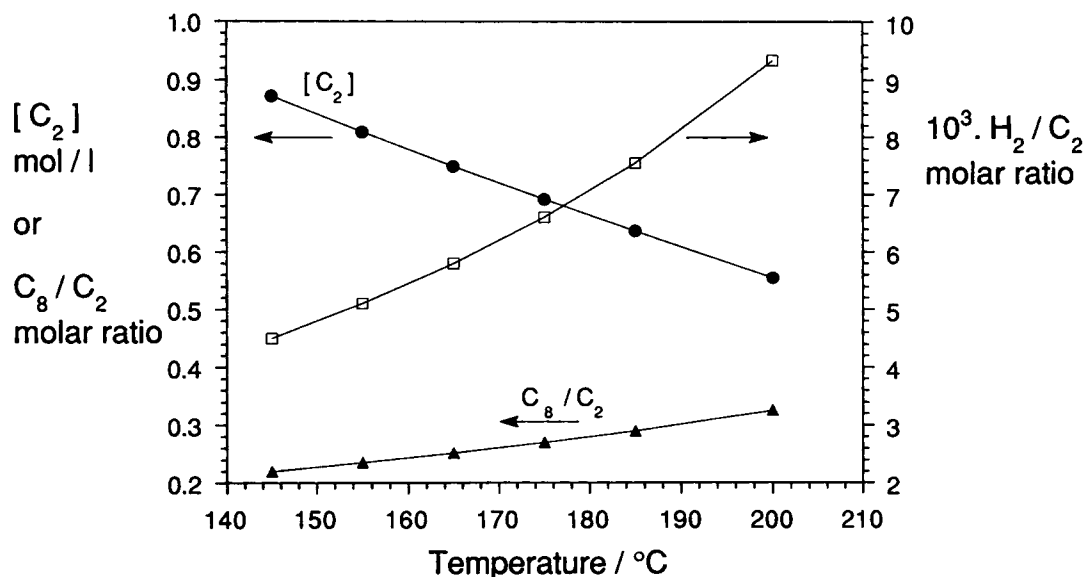
## RESULTS

### Temperature Effects on Reaction Kinetics

In the homopolymerization of ethylene at 320 Psig total reactor pressure, the initial  $\text{H}_2$  concentration was maintained constant. However, because ethylene solubility in the solvent phase decreases with increasing reactor temperature, the dissolved  $\text{H}_2/\text{C}_2$  molar ratio was observed to increase with increasing temperature. The variation of ethylene concentration and the  $\text{H}_2/\text{C}_2$  molar ratio within the temperature range studied are shown in Figure 1. Similarly, in ethylene/1-octene copolymerization, the initial  $\text{H}_2$  and the comonomer 1-octene concentrations were maintained constant; nevertheless, by changing the reactor temperature, ethylene solubility diminishes, thus resulting in an increase in both the dissolved  $\text{H}_2/\text{C}_2$  and the  $\text{C}_8/\text{C}_2$  molar ratios. This is shown in Figure 2. It would have been advantageous to maintain the dissolved  $\text{H}_2/\text{C}_2$  and  $\text{C}_8/\text{C}_2$  molar ratios constant when varying the reactor temperature so that the observed effects could be related directly to the kinetic effects of changing the reaction temperature rather than also including solubility effects. However, at the time these experi-



**Figure 1** Effect of varying the temperature on the ethylene concentration and the  $\text{H}_2/\text{C}_2$  molar ratio. Homopolymerization: 320 Psig pressure, isopar-E solvent.

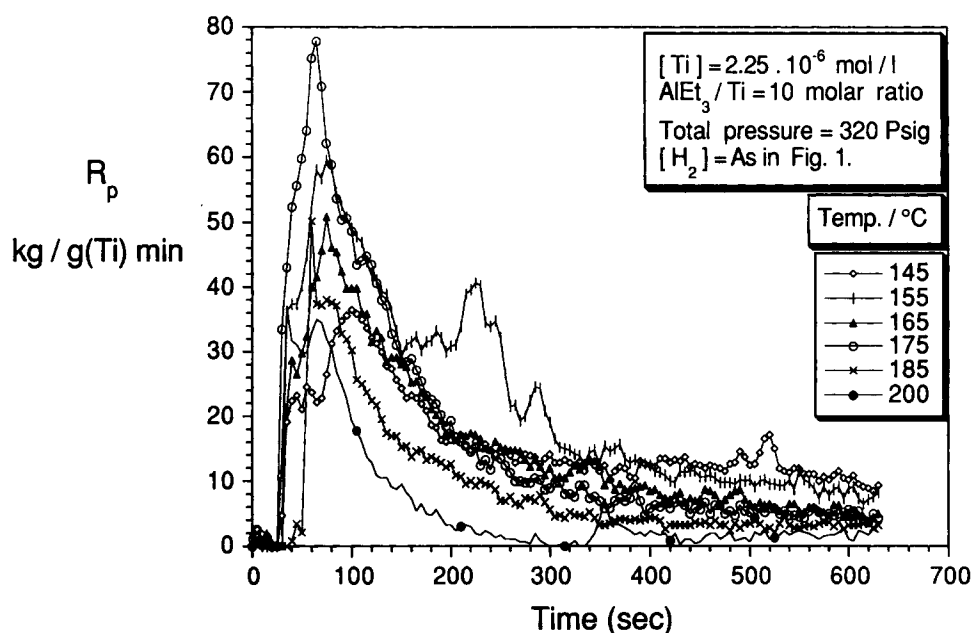


**Figure 2** Effect of varying the temperature on the ethylene concentration and the  $H_2/C_2$  and  $C_8/C_2$  molar ratios. Copolymerization: 320 Psig pressure, isopar-E solvent.

ments were performed, the very precise vapor-liquid equilibria data necessary to compensate the gas-phase composition were not available to us. Thus, we analyzed all of the effects of temperature changes.

Rate-time profiles for ethylene homopolymerization in solution at 320 Psig total reactor pressure and in the temperature range 145–200°C are shown in Figure 3. Keeping all other polymerization con-

ditions constant, the highest initial maximum accompanied by a relatively slow decay in the rate of ethylene consumption was observed at the polymerization temperature of 175°C. Above or below 175°C, a lower initial peak was found. The lowest initial peak was at 145 or 200°C. In the temperature range 145–155°C, a low initial peak combined with minimal decay in the polymerization rate was ob-



**Figure 3** Effect of varying the reactor temperature on the ethylene consumption rate in homopolymerization.

tained. As expected, the decay in the consumption rate of ethylene with time was most significant at 200°C. In homopolymerization, these observations emphasize that the optimal temperature is about 175°C.

Similar effects of reactor temperature variation in ethylene/1-octene copolymerization are shown in Figure 4. The highest initial peak in the ethylene consumption rate in copolymerization is observed at 165°C rather than at 175°C in the case of homopolymerization (cf. Fig. 3). Again, at 145–155°C, lower initial peaks in the polymerization rate are observed with minimal decay with time. Copolymerization carried at 200°C resulted in the lowest initial maximum and the fastest decay in the rate of ethylene consumption with time.

In both the cases of homopolymerization or ethylene/1-octene copolymerization, the decay in the polymerization rate with time is believed to result from thermal deactivation rather than from the increase in the  $H_2/C_2$  or the  $C_8/C_2$  molar ratios. This point will be discussed in more detail below.

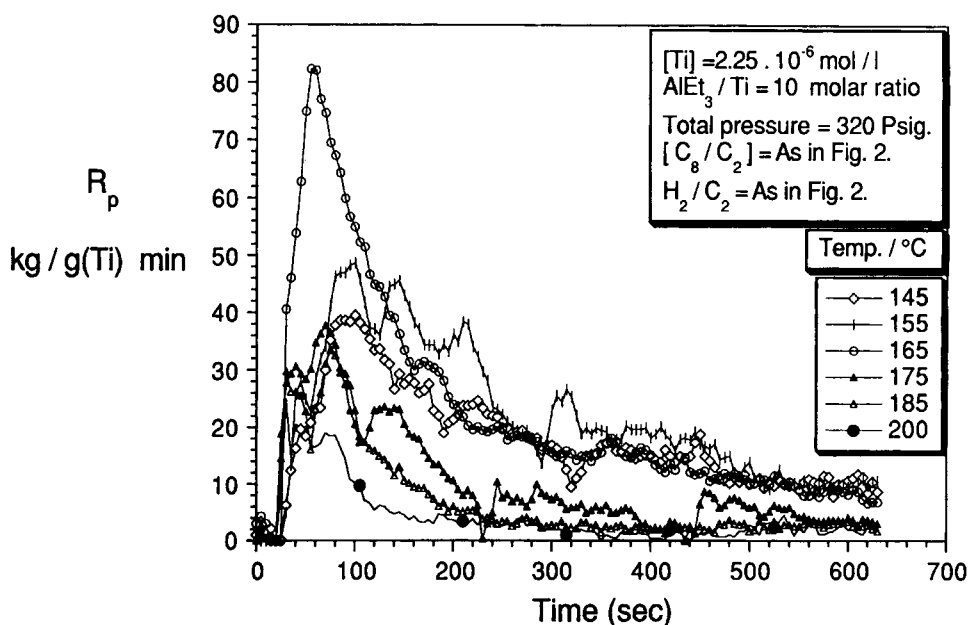
A comparison of rate-time profiles in homo- and copolymerization reveals that the rate-time profiles are very similar. Figures 5 and 6 show a comparison at 165 and 200°C, respectively. The results show that the initial polymerization rate tends to be higher in copolymerization at 165°C. In contrast, when a reactor temperature of 200°C is employed, the initial

polymerization rate is higher in the case of homopolymerization.

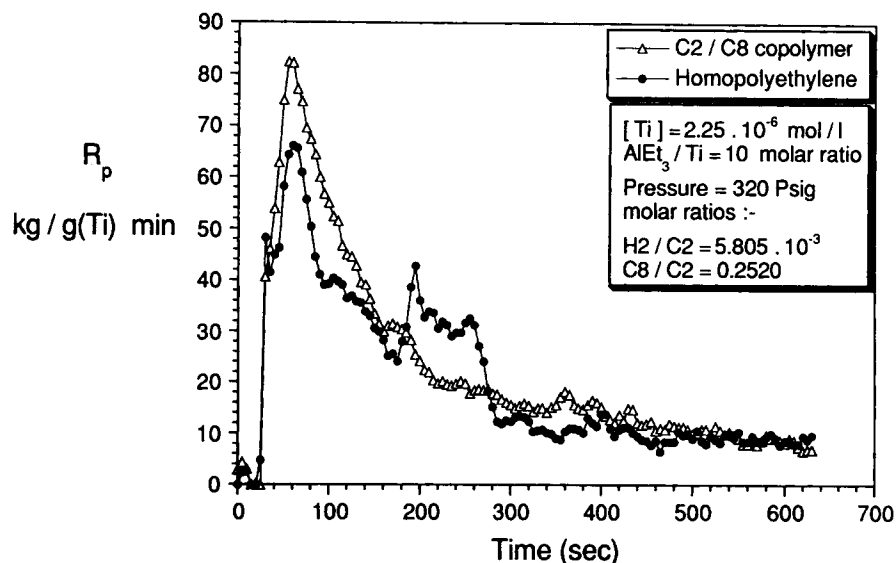
The yields from the two types of polymerizations are compared as a function of temperature in Figure 7. In both cases, the catalyst yield increases slowly with increasing temperature and reaches a maximum for a temperature in the range 155–165°C. A dramatic drop in the catalyst yield is evident in both cases at temperatures  $\geq 175^\circ\text{C}$ . Note that at lower temperatures the yields are slightly higher in the case of copolymerization, while this trend is reversed when higher reactor temperatures are used. The reduction in the catalyst yield at temperatures  $\geq 175^\circ\text{C}$  is due to relatively lower peaks in rate and to fast deactivation, as is evident from Figures 3 and 4.

### Temperature Effects on Polymer Properties

In Ziegler-Natta polymerization systems, chain-transfer reactions tend to increase with increasing polymerization temperature. In the present system, the most pronounced chain-transfer reactions are believed to be with hydrogen and with ethylene and the 1-octene comonomer. With increasing temperature, increased rates of chain-transfer reactions result in lowering the polymer molecular weight. In this section, a comparison of the effect of the reactor temperature on the polymer molecular weight in the



**Figure 4** Effect varying the reactor temperature on the ethylene consumption rate in  $C_2/C_8$  copolymerization.

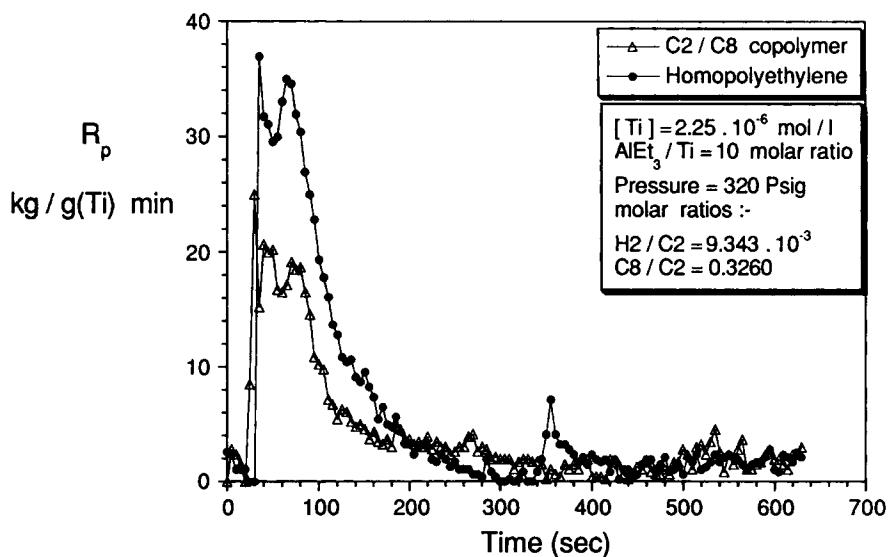


**Figure 5** Comparison of the ethylene consumption rate in  $C_2/C_8$  copolymerization and in ethylene homopolymerization at  $165^\circ\text{C}$ .

homo- and copolymerization of ethylene is presented. Figure 8 compares the values of number-average molecular weight for homopolyethylene and ethylene/1-octene copolymer. Note that about 20% higher  $M_n$  values are obtained in the case of homopolymerization. Since in homo- and in copolymerization the same  $H_2$  concentration was used, then the lower  $M_n$  values obtained in copolymerization must be due to the presence of the comonomer. In addition, with temperature varying from 145 to

$200^\circ\text{C}$ , the  $M_n$  values in homo- and in copolymerization decreased by about 40%.

The influence of temperature on the weight-average molecular weight for both homopolyethylene and  $C_2/C_8$  copolymer is shown in Figure 9. Similar to the trend observed in  $M_n$ , higher  $M_w$  values are obtained in the case of homopolyethylene in the temperature range  $145\text{--}175^\circ\text{C}$ . The difference between the  $M_w$  of the homopolyethylene and copolymer at low reactor temperatures of  $145\text{--}155^\circ\text{C}$  is



**Figure 6** Comparison of the ethylene consumption rate in  $C_2/C_8$  copolymerization and in ethylene homopolymerization at  $200^\circ\text{C}$ .

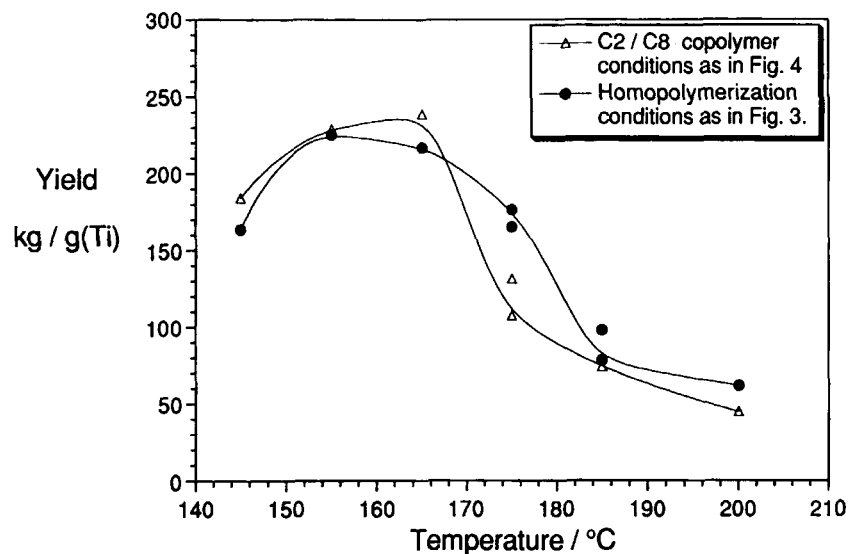


Figure 7 Effect of the reactor temperature variation on the polymer yield.

very large compared to the difference at temperature of 200°C. In summary, in the temperature range 145–200°C, the  $M_w$  in homopolyethylene is between 356,000 and 120,000, whereas in copolymerization,  $M_w$  is in the range 240,000 to 158,000. On the other hand, values obtained on the polydispersity index,  $M_w/M_n$ , indicate some scatter, as shown in Figure 10. This is due to the well-known inherent difficulties with the precision of high-temperature GPC for highly crystalline, high molecular weight polyolefins. The data indicate that the polydispersity of the ethylene/octene copolymer synthesized at tempera-

tures 145–200°C and at 320 Psig total pressure is in the range 4–6. These values are in good agreement with those obtained previously at 185°C and 400 Psig.<sup>1,2</sup> On the other hand, the polydispersity values in the case of homopolymerization are observed to decrease from about 6 to 2.9. Thus, in general, the results obtained in this study show that the polydispersity for the homo- and copolymerization of ethylene synthesized at 145–200°C are in the range 3–6. These results are in contrast to those reported by Machon<sup>4</sup> who found higher polydispersity values in the polymerization of ethylene at 1500 bars using

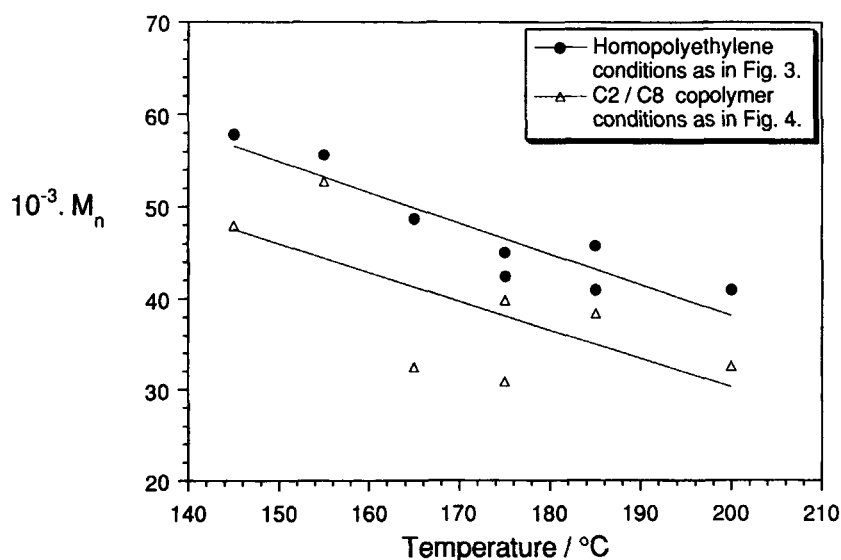


Figure 8 Temperature variation effect on the number-average molecular weight.

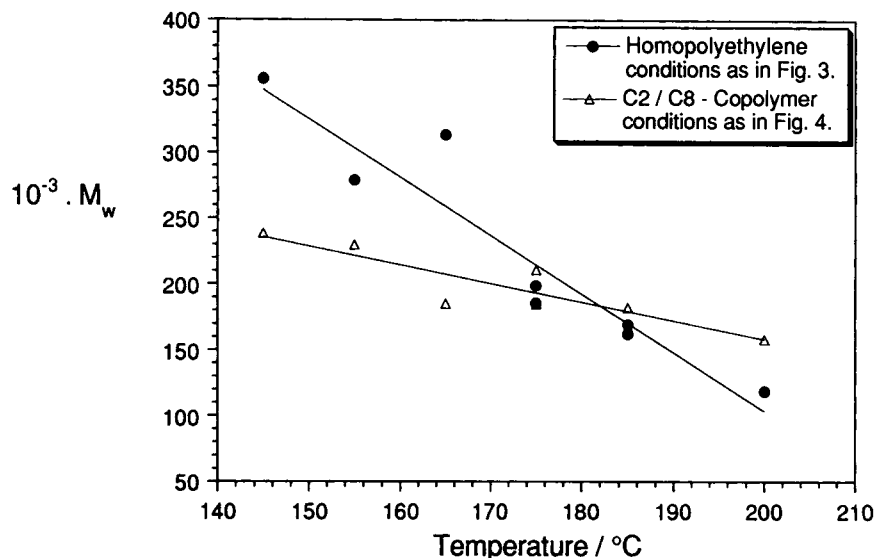


Figure 9 Temperature variation effect on the weight-average molecular weight.

a  $\text{TiCl}_3 \cdot \frac{1}{3} \text{AlEt}_2\text{Cl}$  catalyst system. In that work, the polydispersity index was reported to increase from 4.8 to 10.8 in the temperature range 210–270°C.

In addition to the kinetic influence of temperature in reducing the polymer molecular weight, Figures 1 and 2 also show that the dissolved  $\text{H}_2/\text{C}_2$  and the  $\text{C}_8/\text{C}_2$  molar ratios increase dramatically with increasing polymerization temperature. This also contributes significantly to the observed reduction in the molecular weight by increasing the rates of chain-transfer reactions with the hydrogen and the comonomer. Thus, the influence of temperature on

molecular weight is a combination of kinetic and physical solubility effects.

The incorporation level of 1-octene in the polymer chain with increasing temperature is shown in Figure 11, where it can be observed that the mol % of 1-octene incorporation increased by a factor of three within the temperature range employed. Even so, the maximum incorporation of 1-octene is somewhat low under the experimental conditions used. Because the threefold increase in the mol % 1-octene incorporation with increasing temperature (cf. Fig. 11) is much larger than the 50% increase in the dissolved

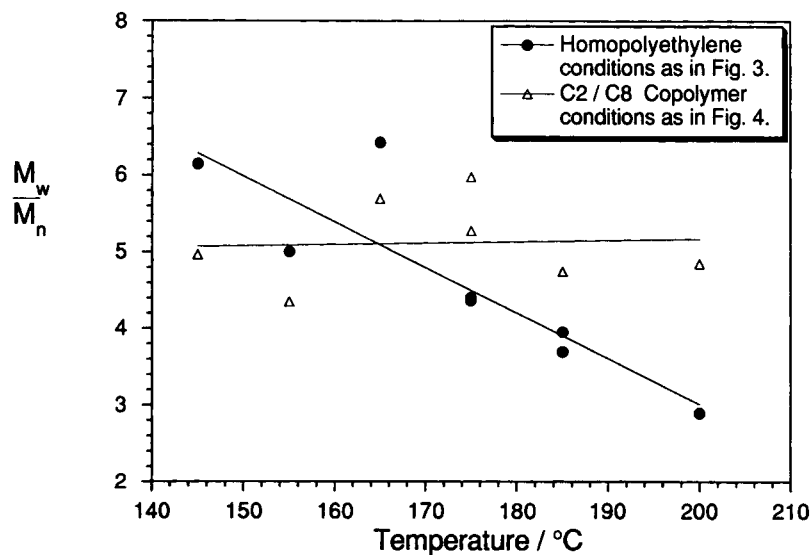
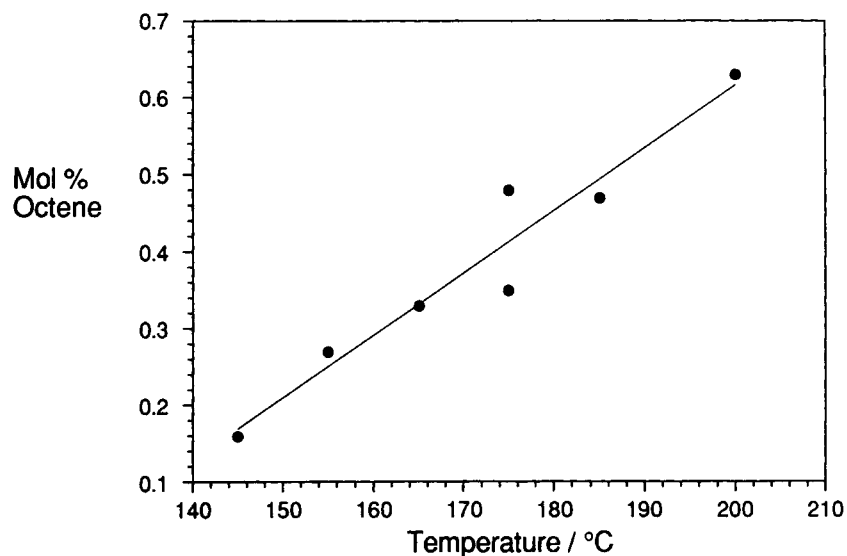


Figure 10 Temperature variation effect on the polydispersity index,  $M_w/M_n$ , of homopolyethylene and  $\text{C}_2/\text{C}_8$  copolymer.

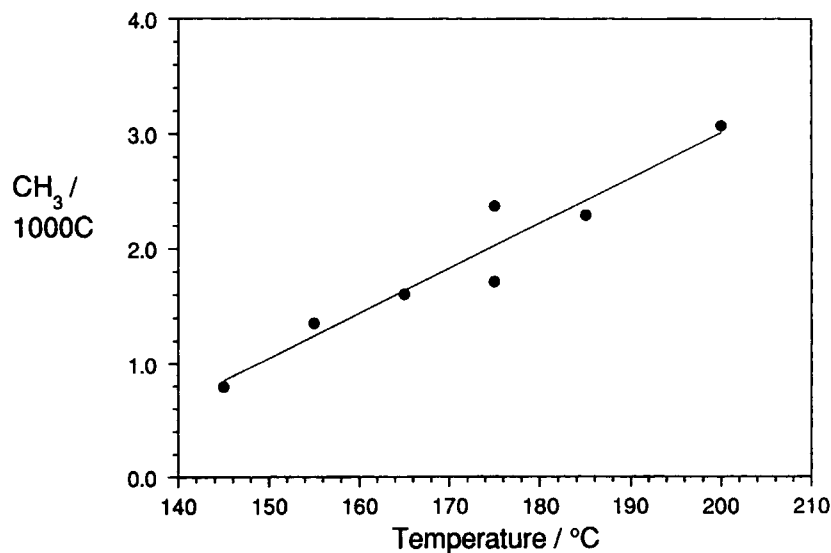


**Figure 11** Temperature variation effect on the mol % 1-octene incorporation. Conditions as in Figure 4.

$C_8/C_2$  molar ratio, the reactivity ratios must also be strong functions of temperature so as to allow accelerated rates of 1-octene insertion with increasing polymerization temperature. This observation has also been reported by other workers in this field.<sup>8-10</sup> As a consequence of increasing comonomer incorporation with temperature, the branching degree (given as  $CH_3/1000C$ ) increases similarly with reactor temperature increase (Fig. 12).

#### Experiments with Controlled Activity and Comonomer Incorporation Level

In the preceding section it was shown that for all the experiments so far that the comonomer incorporation level is quite low, i.e., < 0.7 mol %. Thus, further experiments were carried out to show the simultaneous control of activity and comonomer incorporation and to increase the amount of octene



**Figure 12** Temperature variation effect on the branching content of  $C_2/C_8$  copolymerizations. Conditions as in Figure 4.



**Table I Effect of Varying [Ti], Temperature, and 1-Octene Concentration on the Solution Polymerization of Ethylene**

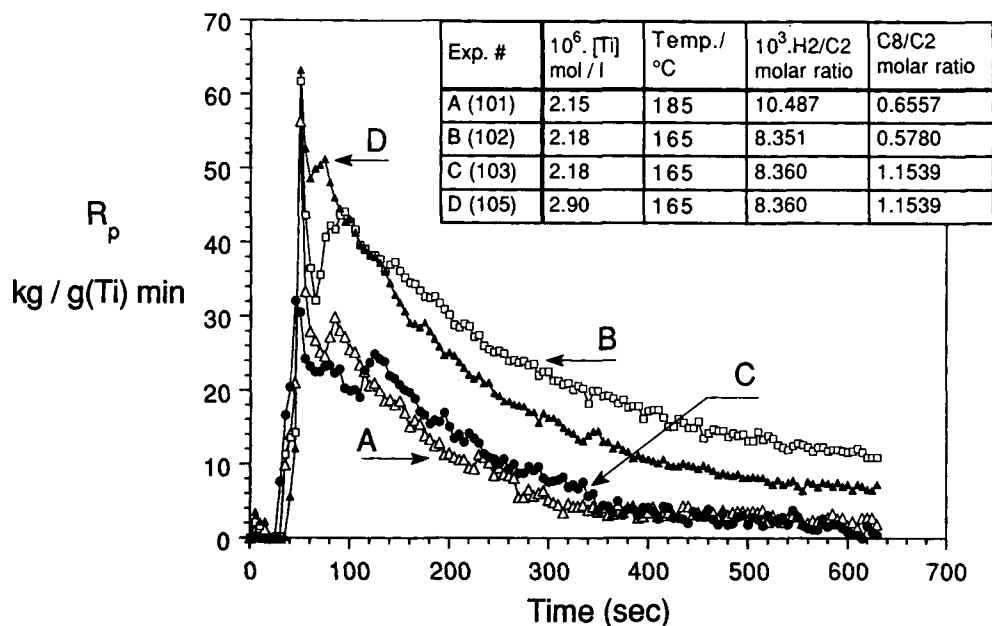
Exp. No.	$10^6 \cdot [\text{Ti}]$ (mol/L)	Temp (°C)	Yield [kg/g (Ti)]	$[\text{C}_2]$ (mol/L)	$10^3 \cdot \text{H}_2/\text{C}_2$ (Molar Ratio)	$\text{C}_8/\text{C}_2$ (Molar Ratio)	$\text{CH}_3/1000\text{C}$	Mol % $\text{C}_8$
A	2.15	185	92.7	0.8234	10.487	0.6557	4.4	0.91
B	2.18	165	226.9	0.9502	8.351	0.5780	3.3	0.67
C	2.18	165	96.7	0.9515	8.360	1.1539	6.7	1.41
D	2.90	165	187.0	0.9515	8.360	1.1539	9.2	1.94

Reactor total pressure = 400 Psig; initial total solvent volume = 500 mL isopar-E (including comonomer); polymerization time = 10 min;  $\text{AlEt}_3/\text{Ti}$  = 10 molar ratio.

built into the polymer chain. A total reactor pressure of 400 Psig was used. Moreover, to achieve high overall yield and high comonomer incorporation, it was necessary to introduce three main changes in the polymerization conditions: first, to increase the total initial solvent volume from 400 to 500 mL (including comonomer); second, to decrease the polymerization temperature from 185 to 165°C to decrease the rate of deactivation; and, finally, to increase the Ti catalyst concentration by about 25%. The data obtained are presented in Table I and Figure 13. The first comparison is made between two runs performed at 185 or 165°C; all other conditions being constant, the data for these two runs (denoted A and B) show that the catalyst yield is much lower at 185°C due to fast deactivation and that the comonomer incorporation for both A and B is still

below 1%. To maintain high yield and at the same time increase the comonomer content, experiment C was performed at 165°C using double the initial concentration of 1-octene compared to run B. This resulted in increasing the comonomer content from 0.67 to 1.41 mol %; however, we see from the rate-time profiles for experiments B and C that about 50% of the overall rate was lost by doubling the amount of 1-octene. Consequently, to maintain high activity and at the same time high comonomer content, experiment D was carried out using higher [Ti] catalyst levels, but keeping all other conditions the same as for run C. The rate-time profiles in Figure 13 show that the rate has almost doubled, and at the same time we now have a comonomer content of about 2%.

This type of manipulation of the experimental



**Figure 13** Rate-time profiles for ethylene consumption in  $\text{C}_2/\text{C}_8$  copolymerization with controlled activity and comonomer incorporation level (cf. Table I).

conditions emphasizes the great flexibility of the ethylene solution polymerization process in controlling the polymerization rate, on the one hand, and simultaneously designing the polymer properties, on the other.

## DISCUSSION

From our experiments, we saw that the activity and catalyst yield can be slightly higher in copolymerization compared to homopolymerization at low temperatures. This trend reverses when reaction temperatures above 175°C are utilized. The presence of the comonomer at high temperature produces somewhat lower yields that are manifested by lower peak rate and enhanced catalyst decay. One might suspect this to be due to higher dissolved  $H_2/C_2$  and  $C_8/C_2$  ratios at higher temperatures (cf. Figs. 1 and 2). However, it is believed that the major reason for the lower activities observed at higher temperatures are due to thermal deactivation and faster destruction of the active centers.

The above argument is supported by the fact that increasing the  $H_2/C_2$  ratio in earlier experiments<sup>1</sup> up to the highest dissolved  $H_2/C_2$  ratio used here led to an increase in the polymerization activity. Similarly, in copolymerization, the increase in the dissolved  $C_8/C_2$  molar ratio is found to be in the range 0.220–0.326 (cf. Fig. 2). This is considered to be too small to cause any significant reduction in the catalyst activity based on the results reported in Ref. 2. Thus, the observed reduction in the initial polymerization rate and the catalyst yield occurring at high polymerization temperatures are believed to be primarily due to thermal deactivation by destruction active polymerization centers.

Having said this, we believe that the presence of the comonomer has two opposing effects: First, as shown in Ref. 2, the presence of comonomer increases the yield at moderate temperatures. However, the results both here and in Ref. 2 show that the rate of catalyst deactivation in the presence of comonomer is enhanced. Thus, those catalyst sites coordinated with the comonomer may be of higher activity but are less stable than are the other sites. This could explain the experimental results.

In the first part of this series on the solution copolymerization of ethylene,<sup>1</sup> it was shown that the decay in the polymerization rate with time is quite severe for the system under investigation due to the severe reactor conditions employed. For these earlier polymerizations at 185°C and 400 Psig total pres-

sure,<sup>1,2</sup> the decay in  $R_p$  with time has been shown to fit an exponential form of the first-order decay rate law of the form

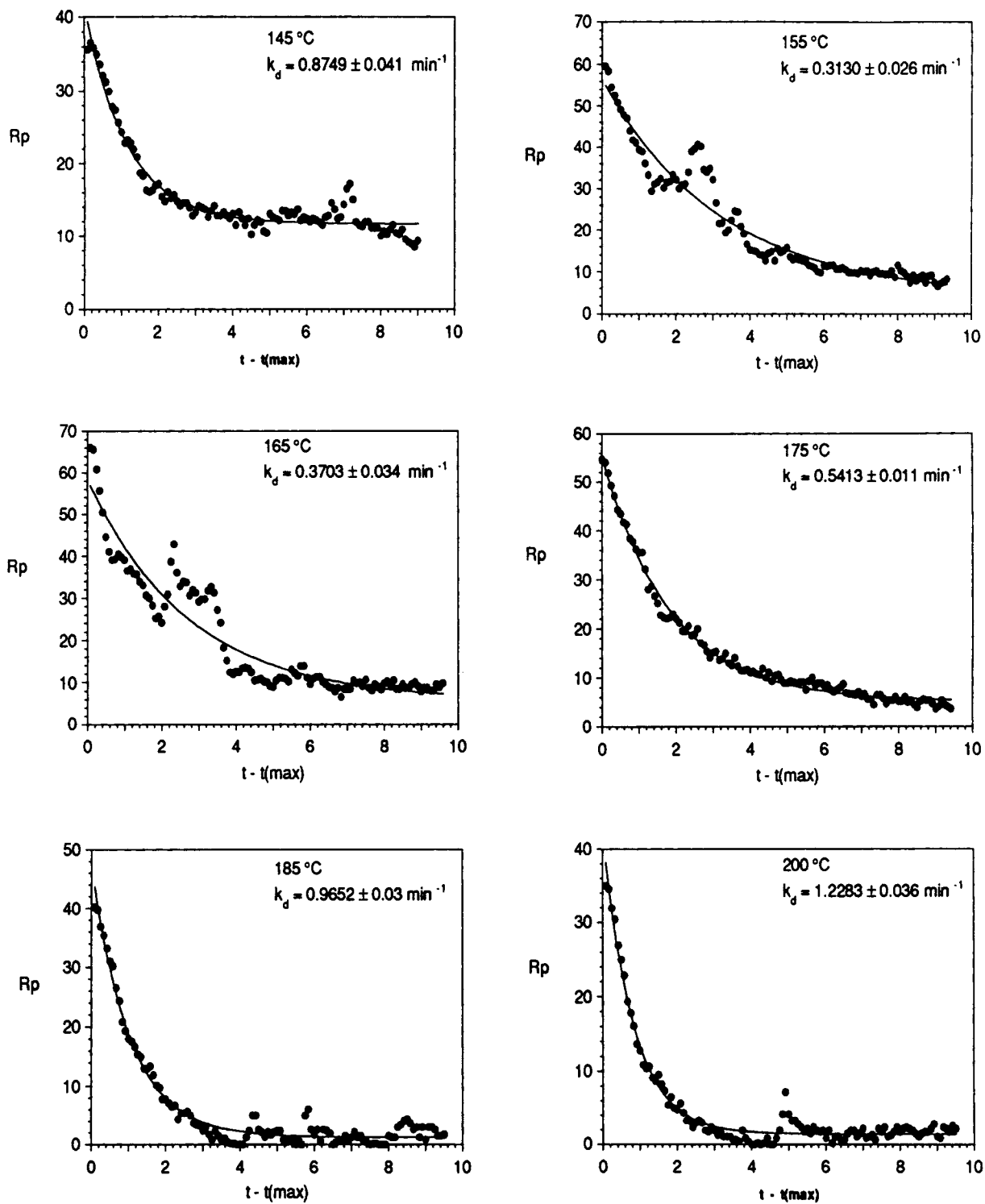
$$R_p = R_\infty + (R_{\max} - R_\infty)e\{-k_d(t - t_{\max})\} \quad (1)$$

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

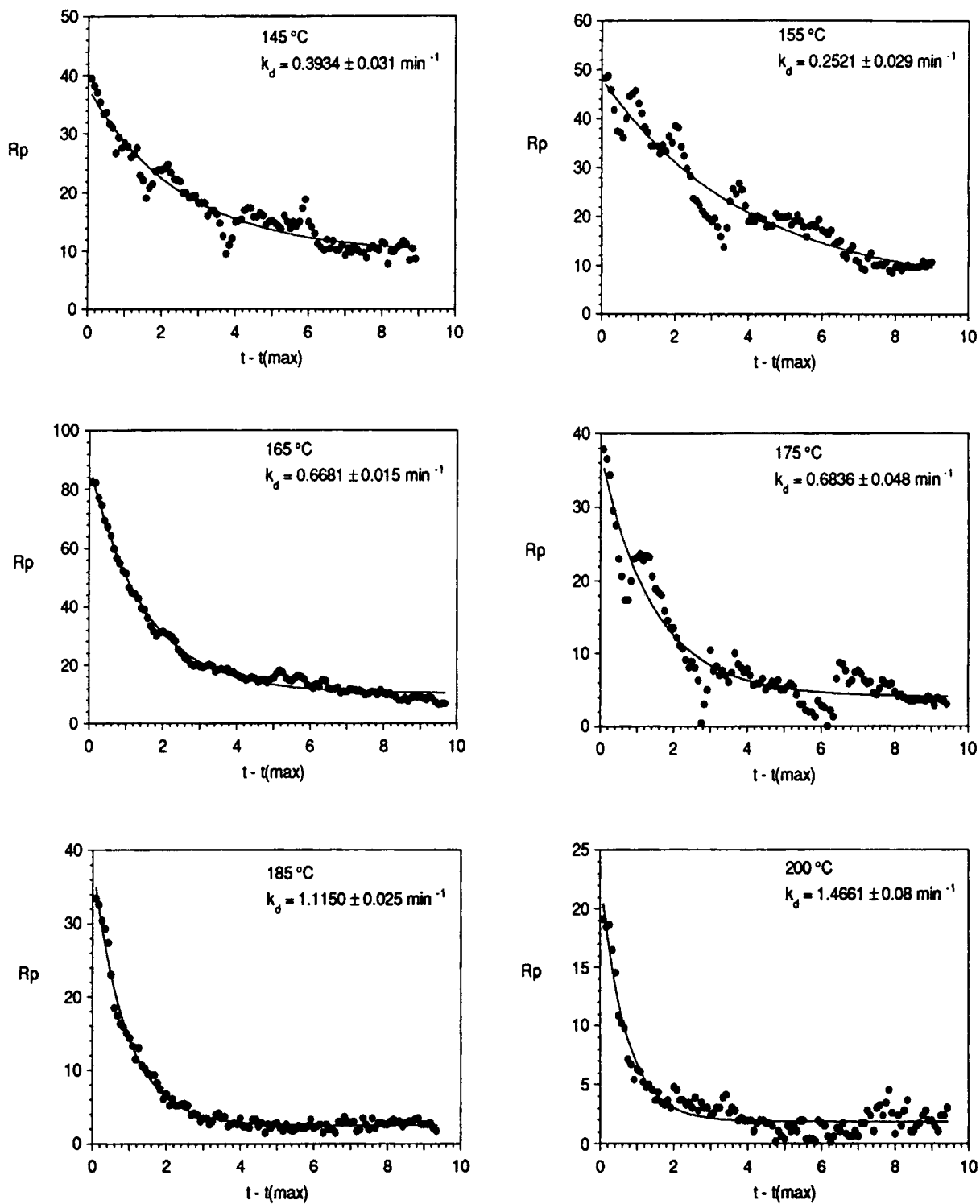
The data from the present study will also be analyzed in the same way. A sample of plots of  $R_p$  vs.  $t - t_{\max}$  according to eq. (1) is presented in Figure 14 for homopolymerization and in Figure 15 for copolymerization. It is also evident here that the first-order decay rate law fits the data obtained rather well. The slight scatter in the  $k_d$  values reported in Table II originate from some fluctuation in the consumption rate of ethylene with time (see Figs. 3 and 4) and not from the decay rate law. In general, the  $k_d$  values show the tendency to increase with increasing temperature, as is expected. Furthermore, the  $k_d$  values for both homo- and copolymerization are fairly close, with somewhat higher values obtained for copolymerization in the region 185–200°C.

Many authors in the field of Ziegler–Natta polymerizations have reported apparent activation energy values for olefin polymerizations. Some of the reported values for propylene or ethylene in slurry- or gas-phase polymerizations are collected in Table III. It seems that apparent activation energy values in the gas phase are slightly lower than those in the slurry-phase polymerization. The reports in the literature using the Arrhenius type of plot generally show that  $\log \{R_p/[M]\}$  against  $1/T$  is not completely linear over a wide range of temperature. The plot is usually linear in the region of low temperatures; then, a break in the line is observed when high polymerization temperatures are employed.

An Arrhenius type of plot using  $\log \{\text{yield}/[M]\}$  vs.  $1/T$  for the homo- and the copolymerization with 1-octene experiments carried out in this work is shown in Figure 16. Here, the yield is taken as (mol/mol Ti). It is evident that plots of the data obtained in the homo- and copolymerization are very similar and have the same break in the line when polymerization temperatures  $\geq 165^\circ\text{C}$  are used. The lines in Figure 16 consist of two linear parts: one in the region 145–165°C and the other in the range 165–200°C. The apparent overall activation energy,  $E_a$ , for ethylene polymerization estimated from the two linear parts are presented in Table IV. Because the octene content was so small, the  $\log \{\text{yield (mol/mol Ti)}/[M]\}$  term used in the case of copolymerization was employed by substituting only the eth-



**Figure 14** Plots of  $R_p$  vs.  $t - t_{(max)}$  according to a first-order decay law, eq. (1). Ethylene homopolymerization at different temperatures.



**Figure 15** Plots of  $R_p$  vs.  $t - t_{(max)}$  according to a first-order decay law, eq. (1).  $C_2/C_8$  copolymerization at different temperatures.

**Table II** Deactivation Rate Constant,  $k_d$ , Values in Homopolyethylene and Ethylene/Octene Copolymerization in Solution

Temp (°C)	Homo-PE $k_d$ (min <sup>-1</sup> )	$C_2/C_8$ Copolymerization $k_d$ (min <sup>-1</sup> )
145	0.8749 ± 0.041	0.3934 ± 0.031
155	0.3130 ± 0.026	0.2521 ± 0.029
165	0.3703 ± 0.034	0.6681 ± 0.041
175	0.7073 ± 0.013	0.6836 ± 0.048
175	0.5413 ± 0.011	
185	0.9652 ± 0.030	1.1150 ± 0.0025
185	0.7287 ± 0.018	
200	1.2283 ± 0.036	1.4661 ± 0.080

$k_d$  values from plots in Figures 14 and 15.

ylene concentration for  $[M]$ . Note that the slope of the Arrhenius curve in the higher-temperature range is slightly steeper when comonomer is present, reflecting slightly enhanced deactivation rates in this case.

There are serious problems in interpreting the apparent activation energy data reported in Table III and Figure 16. First of all, the monomer concentration used is quite different in all cases. For the slurry- and gas-phase results in Table III, it is usually the fluid-phase concentration, rather than the proper polymer sorbed concentration, that is used to calculate  $E_a$ , so that it contains thermodynamic phase equilibria effects. Similar phase equilibria problems exist for the data in Figure 16, as we have discussed above. Hutchinson and Ray<sup>25</sup> showed the

proper way to separate out phase equilibria effects. Second, the observed rate is a complex function of site activation, propagation, and deactivation kinetics. Thus, at low temperatures, site activation and propagation will dominate, and at high temperatures, site deactivation controls the rate. This is seen clearly in Figure 16.

To separate deactivation effects, the  $k_d$  values estimated in the homo- and copolymerization of ethylene in Table II may be used to evaluate the deactivation energy,  $E_d$ , in the temperature range 145–200°C. Figure 17 presents a plot of  $\log k_d$  against  $1/T$  using the values of  $k_d$  from Table II. The results given in Table IV show that the deactivation energies,  $E_d$ , for homopolymerization are higher than for ethylene/octene copolymerization under the same experimental conditions. This supports our hypothesis that comonomer coordinated sites are less stable than are other sites.

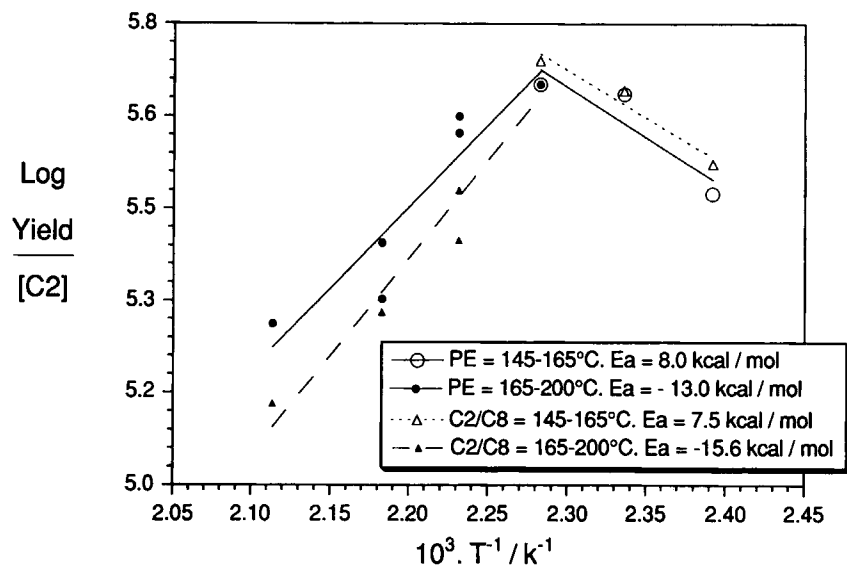
As a final point, it is well known that the degree of gas-liquid mass transfer resistance will increase with increasing temperature. Thus, it is possible that some of the molecular weight decrease and comonomer incorporation increase with increasing temperature may be due to these mass-transfer effects. A further paper in this series will analyze this aspect of the data.

## CONCLUSIONS

High-temperature investigations of the solution polymerization of ethylene have shown that the optimal polymerization temperature, at 320 Psig reactor

**Table III** Apparent  $E_a$  (kcal/mol) Values Reported in the Literature for Propylene Polymerization Unless Otherwise Stated

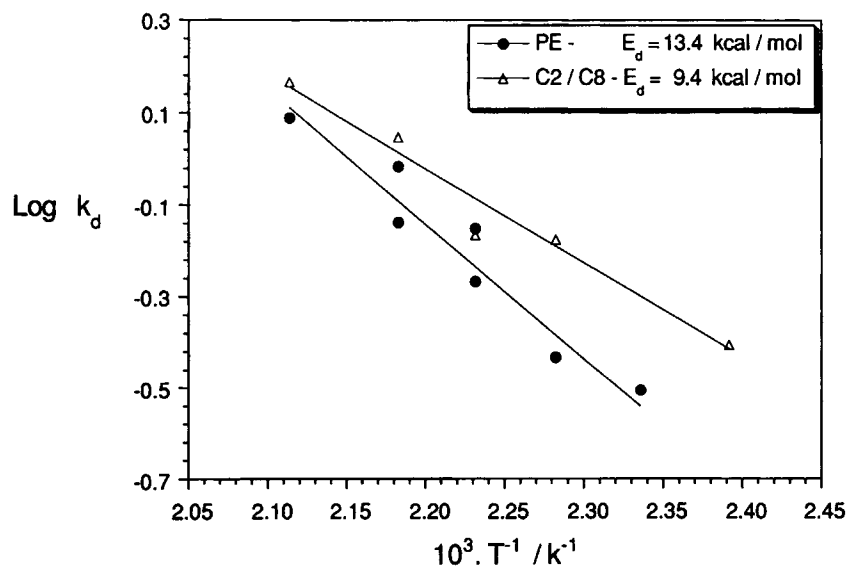
Catalyst System	Slurry	Gas	Ref.
TiCl <sub>3</sub> /AlEt <sub>3</sub>	—	14.5	11
MgCl <sub>2</sub> /TiCl <sub>4</sub> /AlEt <sub>3</sub> /EB	—	5.3	12
$\delta$ -TiCl <sub>3</sub> · $\frac{1}{3}$ AlCl <sub>3</sub> /AlEt <sub>2</sub> Cl	—	4.0–10.0	13
TiCl <sub>3</sub> /AlEt <sub>2</sub> Cl	13.5	12.0	14, 15
TiCl <sub>3</sub> /AlEt <sub>3</sub>	—		
TiCl <sub>3</sub> /AlEt <sub>3</sub>	11.5–12.5	4.9–5.7	16
$\alpha$ -TiCl <sub>3</sub> /AlEt <sub>3</sub>	10.0	—	17
$\delta$ -TiCl <sub>3</sub> · $\frac{1}{3}$ AlCl <sub>3</sub> /AlEt <sub>2</sub> Cl	11.2	—	19
MgCl <sub>2</sub> /EB/TiCl <sub>4</sub> /AlEt <sub>3</sub>	12.0	—	20
MgCl <sub>2</sub> /EB/ <i>p</i> -cresol/AlEt <sub>3</sub> /TiCl <sub>4</sub>	12.0	—	21
MgCl <sub>2</sub> /EB/TiCl <sub>4</sub> /Al( <i>i</i> -Bu) <sub>3</sub>	12.3	—	22
MgH <sub>2</sub> /TiCl <sub>4</sub> /AlEt <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> polymerization)	11.5	—	23
SiO <sub>2</sub> /MgCl <sub>2</sub> /TiCl <sub>4</sub> (C <sub>2</sub> H <sub>4</sub> polymerization)	11.8	—	24



**Figure 16** Arrhenius plot of  $\log\{\text{yield}/[C_2]\}$  vs.  $1/T$  in ethylene homopolymerization and in C<sub>2</sub>/C<sub>8</sub> copolymerization. Conditions as in Figures 3 and 4.

pressure, is in the range 165–175°C. A high initial rate of polymerization and reasonable decay rates are realized at these temperatures both in the homo- and copolymerization with 1-octene. Below or above the optimal temperature, a lower initial peak rate is obtained. At 145°C, the initial rate of polymerization is low and the decay in the polymerization rate is minimal. At high reaction temperatures, there are low initial peak rates and very fast decay. It is very likely that there is a continual increase in the gen-

eration of active centers with increasing temperature in the low region, 145–175°C. However, higher reaction temperatures are evidently destabilizing and destroy some highly active centers, thus resulting in lower peak rates, lower overall yield, and fast decay. It is believed that thermal deactivation is the principal factor in the lower activities obtained at high temperatures. This is supported by the data obtained for the  $k_d$  constant. The data obtained in this investigation also show that the presence of the



**Figure 17** Arrhenius plot of  $\log k_d$  against  $1/T$ .

**Table IV Overall Activation and Deactivation Energy Values for Ethylene Homo- and Copolymerization in the Solution Phase**

Temp Range (°C)	Homo-PE (kcal/mol)	C <sub>2</sub> /C <sub>8</sub> Copolymer (kcal/mol)
Activation energy ( $E_a$ )		
145–165	8.0	7.5
165–200	–13.0	–15.6
Deactivation energy ( $E_d$ )		
145–200	13.4	9.4

comonomer enhances the decay in the polymerization rate, possibly due to the decay of less stable sites activated by comonomer.

Comonomer incorporation and branching degree have been observed to increase with increasing temperature due to increasing dissolved C<sub>8</sub>/C<sub>2</sub> molar ratio at higher temperatures and temperature effects on reactivity ratios. The possible effects of gas–liquid mass-transfer limitations on comonomer incorporation will be the subject of a further paper in this series.

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