Polymerization of Olefins through Heterogeneous Catalysis. XIII. The Influence of Comonomer in the Solution Copolymerization of Ethylene

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SYNOPSIS

The copolymerization of ethylene with highly active $TiCl_4/MgCl_2$-supported catalysts in solution reactors at 185°C and 400 Psig pressure is presented. The performance of these highly active supported catalysts at high reaction temperature is characterized by a high initial rate that decays rapidly within the 10 min polymerization time period. In the presence of hydrogen and a comonomer, catalyst yields up to about 300 kg/g (Ti) are achieved. Kinetic data obtained on the influence of a comonomer, e.g., 1-octene or 1-hexene, indicate rate enhancement when used in moderate concentrations. Higher concentrations of comonomer result in a decreasing rate of ethylene consumption. Comonomer/ethylene molar ratios in the range 0–0.827 resulted in comonomer incorporation up to about 2.6 mol % and a small reduction in the polymer molecular weight. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the first paper of this series,[1] the essential features of solution ethylene copolymerization processes were reviewed and extensive experimental results presented showing the effect of hydrogen concentration on the rate profile and polymer properties. In this paper, we report the results of a study using the same experimental system in which we vary the amount and type of comonomer for the case of two different solvents.

Copolymers of ethylene with higher linear α-olefins continue to be of increasing importance to industry. Thus, it is important to develop a fundamental understanding of this copolymerization process. In Ziegler–Natta polymerizations, it is normally observed that the addition of a small amount of a comonomer, e.g., 1-octene, to an ethylene polymerization system results in enhancing the rate of ethylene consumption relative to homopolymerization. The magnitude of this enhancement effect is dependent on the catalytic system and to a large extent on the length of the carbon chain of the α-olefin comonomer. The comonomer not only affects the polymerization kinetics but also induces some fundamental changes to the polymer structure. In copolymerization, the chain microstructure of the polymer depends on the type of the comonomer used, the distribution of the comonomer units along the molecules, and the molecular weight of the polymer. These properties ultimately influence the physical properties of the polymer, i.e., viscolastic, mechanical, and melting behavior.[2]

The comonomer effect on the kinetics of olefin polymerization has been investigated by many authors in this field. The majority of these investigations were conducted in slurry polymerizations,[3-6] and much fewer in gas-[7-9] or solution-phase polymerizations.[10,11] Tait et al.[3] investigated ethylene copolymerization in the slurry phase with a number of α-olefins. An enhancement effect was observed upon introduction of a small amount of the comonomer. The authors[3] attributed such enhancement effects to different chemical and physical factors and suggested that no single explanation may be adequate to describe the behavior of a variety of different catalytic systems. In gas-phase ethylene/butene copolymerization, Spitz et al.[7] found that the polymerization rate is faster at the beginning of the

reaction but decreases continuously with time. The stability of the catalyst was found to decrease when the H_2 pressure is increased or when aluminum alkyls with a reducing power greater than isoprenyl aluminum, like trihexyl or trioctyl aluminum, are used. Spitz et al.[7] therefore suggested that the deactivation is due to a chemical effect rather than to a physical one. Kashiwa et al. investigated the copolymerization of ethylene in solution reactors using a homogeneous vanadium catalyst[11] and a heterogeneous $TiCl_4/MgCl_2$-supported catalyst.[10] The polymerization activity was reported to be much higher using the $TiCl_4/MgCl_2$-supported catalyst. Moreover, comparing the activity of different comonomers, Kashiwa et al. reported that the molar ratios of comonomer incorporated into the comonomer in the reactor were higher in the order of propylene > 1-butene > 4-methyl-1-pentene. The increase in the M_w/M_n value with an increase of comonomer content was attributed to the diversity of active centers rather than to a diffusion phenomena.[10]

Thus, our aim is to shed more light on this rarely studied solution copolymerization process. The present article is the second in a series of our investigation of the kinetics and the polymer properties synthesized in solution reactors. Here, the effect of the comonomer on the polymerization rate and resulting polymer properties is investigated for the case of two different solvents.

EXPERIMENTAL

The experiments were carried out in a solution polymerization reactor at 185°C and 400 Psig pressure using either isooctane or isopar-E as solvent. The hydrogen and comonomer (1-octene or 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 Ref. 1.

RESULTS

Effect of Comonomer on the Polymerization Rate

In the present investigation, the copolymerization of ethylene with 1-octene or 1-hexene in the presence of H_2 is investigated. As shown in Figure 1, keeping all polymerization conditions constant, the C_8/C_2 molar ratio was varied in the range 0.139–0.827. The highest initial maximum was observed at the lowest C_8/C_2 used. With increasing 1-octene amount added, a drop in the initial maximum and a faster decay in the polymerization rate was evident.

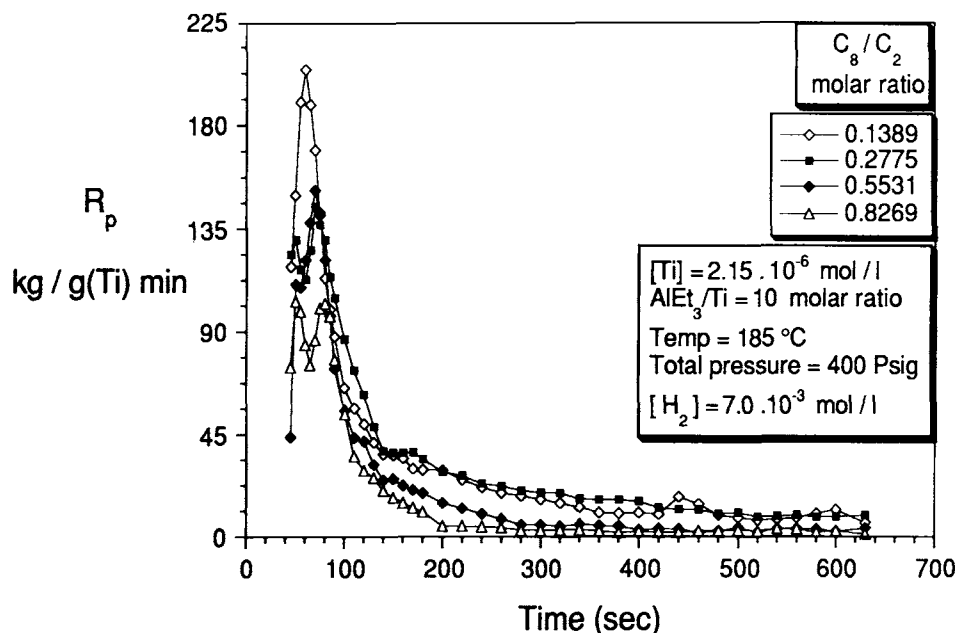Rate–time profiles for the ethylene/1-hexene copolymerizations are shown in Figure 2. When no 1-

Figure 1   Effect of C_8/C_2 molar ratio ([C_8] variation) on the ethylene consumption rate. Solvent = isooctane.
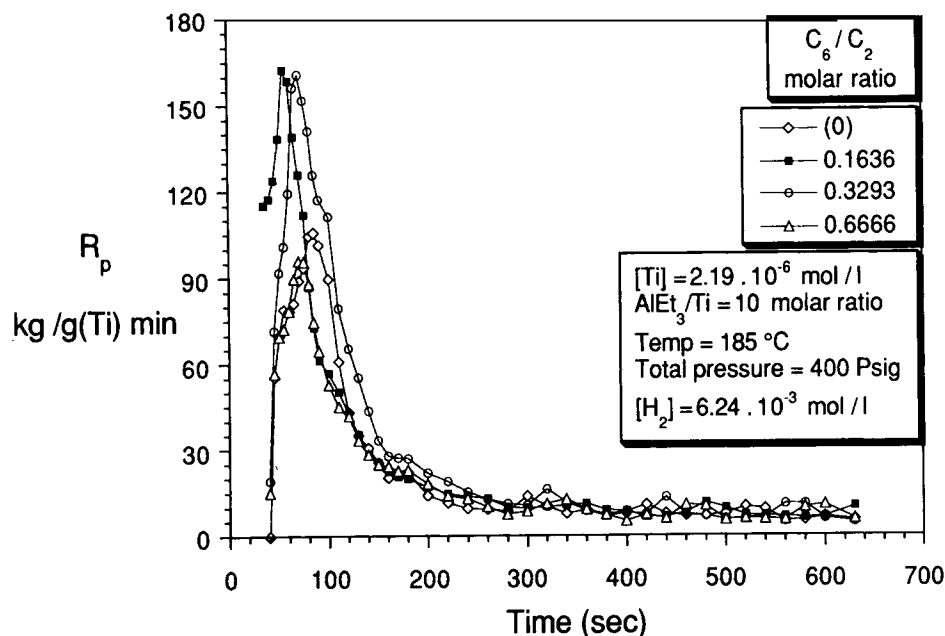
Figure 2 Effect of C_6/C_2 molar ratio ([C_6] variation) on the ethylene consumption rate. Solvent = isopar-E.

hexene is used, a low initial maximum is obtained. Immediately upon using a small amount of 1-hexene (C_6/C_2 molar ratio = 0.1636), a very high initial rate of polymerization is attained. At high C_6/C_2 molar ratios, it is observed that $R_{p\,(max)}$ is depressed, as in the case of ethylene/1-octene copolymerization (Fig. 1). From these results, it is clear that when a moderate comonomer concentration is used a rate enhancement effect is observed at the very early stage of the polymerization.

A rather surprising observation, however, is that when Figures 1 and 2 are compared it is noticed that the rate of ethylene consumption is much higher when 1-octene is used rather than 1-hexene as the comonomer. This is quite unlikely in Ziegler–Natta polymerizations, since it is well established that polymerization activity tends to decrease with an increase in the carbon atom number of the comonomer. In other words, the activity in copolymerization should be in the order $C_2/C_6 > C_2/C_8$ and not the other way around.

Figure 3 summarizes the catalyst yields in the experiments shown in Figures 1 and 2 for the two comonomers employed and shows two distinct trends. At a low comonomer/ethylene molar ratio, the yield tends to increase, then decreases upon increasing the comonomer/ethylene ratio further. A strange observation, however, is that the catalyst yield is much higher, at low comonomer/ethylene ratio, when 1-octene rather than 1-hexene is used.

This unusual trend was investigated further and was found to be due to the use of different solvents in the two sets of polymerizations reported. Isooctane solvent was used in the case of ethylene/1-octene copolymerization (Fig. 1), whereas the isopar-E solvent was used in the case of ethylene/1-hexene copolymerization (Fig. 2).

To verify that the behavior observed in Figure 3 is due to different solvents, ethylene/1-octene copolymerizations were repeated using the isopar-E solvent. The rate–time profiles obtained are shown in Figure 4. It is clear that, particularly, the initial polymerization rate is much lower in isopar-E as compared to isooctane. Now, when the catalyst yield is plotted against the comonomer/ethylene ratio for the two comonomers using the same solvent, isopar-E, a more realistic picture is seen (Fig. 5). As expected, copolymerization with 1-hexene produces much higher rates than does copolymerization with 1-octene (cf. Figs. 6 and 7).

The question of the effect of two different solvents is a complex one related to their relative solubilities for H_2, monomers, and polymer. First, there is strong evidence that isopar-E is a significantly better solvent for polymer than is isooctane. For example, when isooctane was employed as the solvent, serious problems were encountered in flushing the polymer solution at the end of the 10 min polymerization period. A large proportion of the polymer came out of solution and the polymer remained in the reactor
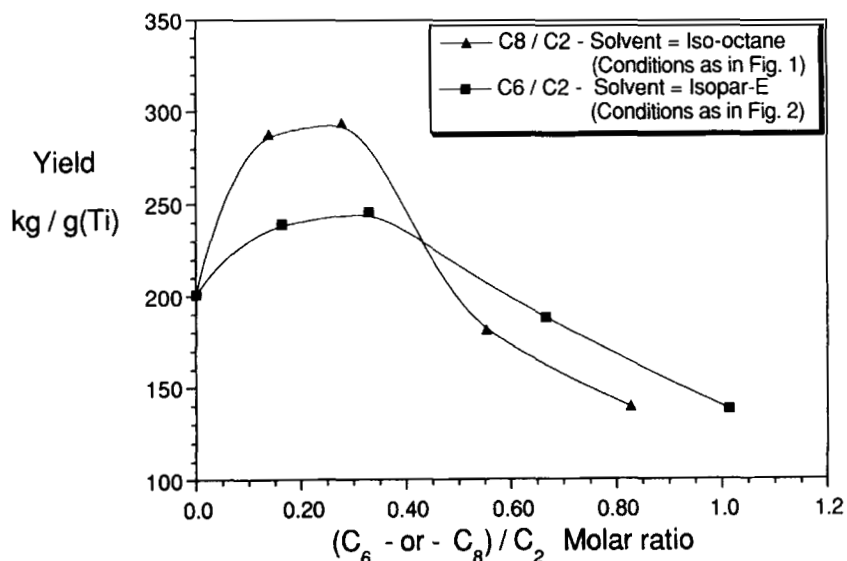
Figure 3   Effect of comonomer/ethylene molar ratio on the polymerization yield. C_2/C_6 and C_2/C_8 copolymerization in different solvents.

as clumps and the solvent contained only a small fraction of the polymer. This caused serious problems in recovering the polymer from the reactor. By contrast, when isopar-E (mixture of C_8—C_9 isoparaffinic hydrocarbons) was used as the solvent, the results were extremely satisfactory in terms of polymer solution flushing. The polymer remained in solution and could be easily removed from the reactor as a viscous liquid.

However, there are other properties of the two solvents that also contribute to the increase in polymerization rate in isooctane compared to isopar-E (cf. Figs. 8 and 9). This will be discussed in more detail in the next section.
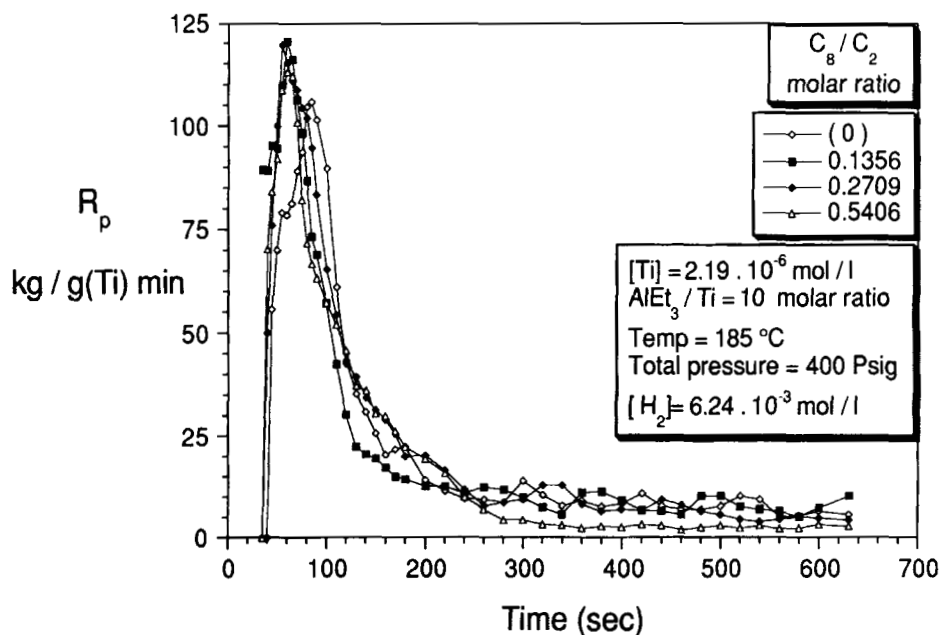

Figure 4   Effect of C_8/C_2 molar ratio ([C_8] variation) on the ethylene consumption rate. Solvent = isopar-E.
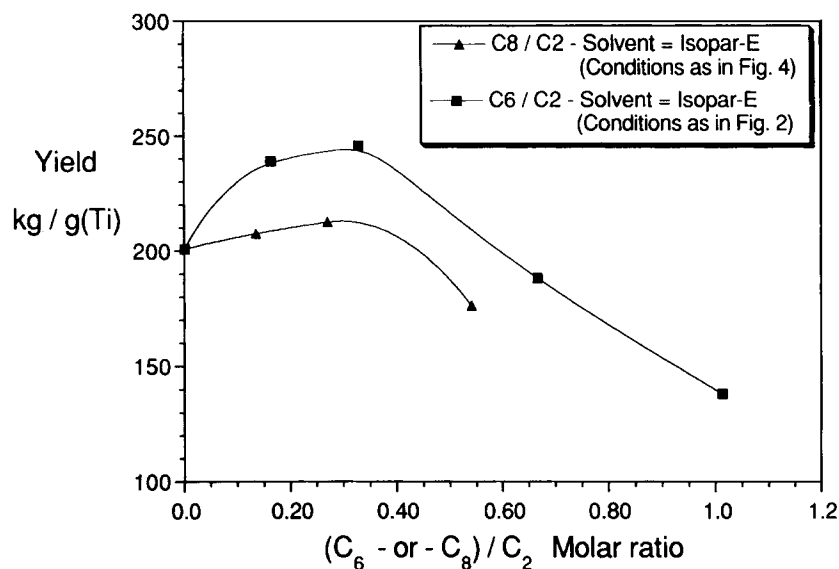
Figure 5   Effect of comonomer/ethylene molar ratio on the polymerization yield. C_2/C_6 and C_2/C_8 copolymerization in the same solvent (i.e., isopar-E).

Effect of Comonomer on Polymer Properties

It is known that the presence of comonomer tends to decrease the polymer molecular weight due to chain transfer reactions and to the reduced reactivity of the comonomer. In the present study, the effect of 1-octene and 1-hexene on the number- and weight-average molecular weight is presented in Figures 10 and 11, respectively. It can be seen from both plots that both comonomers tend to decrease M_n and M_w over the homopolymerization case. In both figures it is observed that the molecular weight for the case of C_2/C_8 copolymers in isooctane is significantly lower than for polymerization in isopar-E. The reason for this can be seen in Table I where the relative solubilities of small molecules in the two solvents are tabulated. Note that the H_2/C_2 ratio, under the same conditions, is always higher when
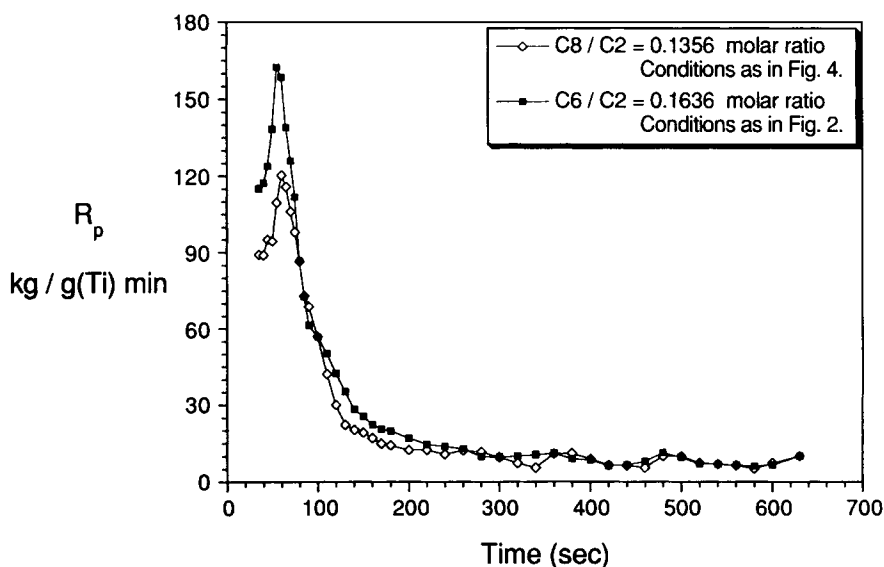

Figure 6   Comparison of the ethylene consumptions rate in C_2/C_6 and C_2/C_8 copolymerization in the same solvent, isopar-E.
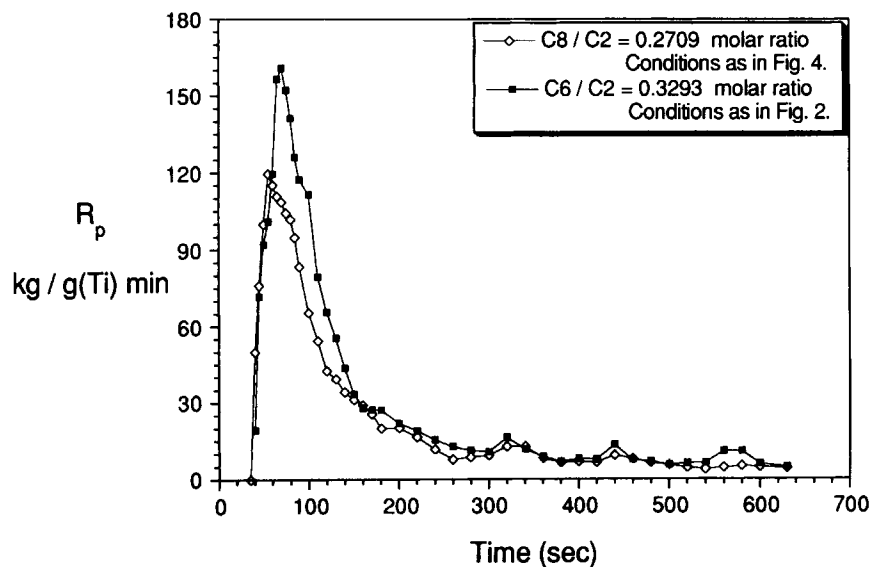
Figure 7   Comparison of the ethylene consumption rate in C_2/C_6 and C_2/C_8 copolymerization in the same solvent, isopar-E.

the isooctane solvent is used. This is the reason why we have a lower molecular weight polymer in this solvent.

Similar data are obtained for the polydispersity index, M_w/M_n (Fig. 12), where it is seen that the polydispersity is not strongly affected by the comonomer concentration. However, when the isopar-E solvent is used, the polydispersity index for both copolymers is about 5–6, whereas when the isooctane

solvent is employed in C_2/C_8 copolymerization, the polydispersity is about 3–4.

Kashiwa et al.[10] found that the polydispersity index increased with increasing comonomer content for ethylene copolymerization in solution with propylene, 1-butene, or 4-methyl-1-pentene. The highest polydispersity values were obtained for C_2/C_3 copolymerization. Kashiwa et al. attributed the observed increase to the presence of different types of
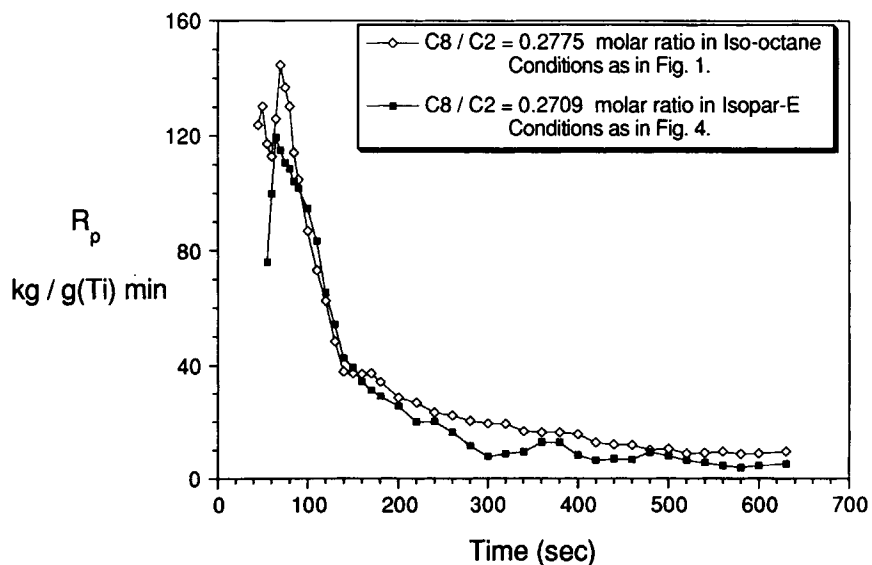

Figure 8   Rate of ethylene consumption in C_2/C_8 copolymerization in different solvents: isooctane or isopar-E.
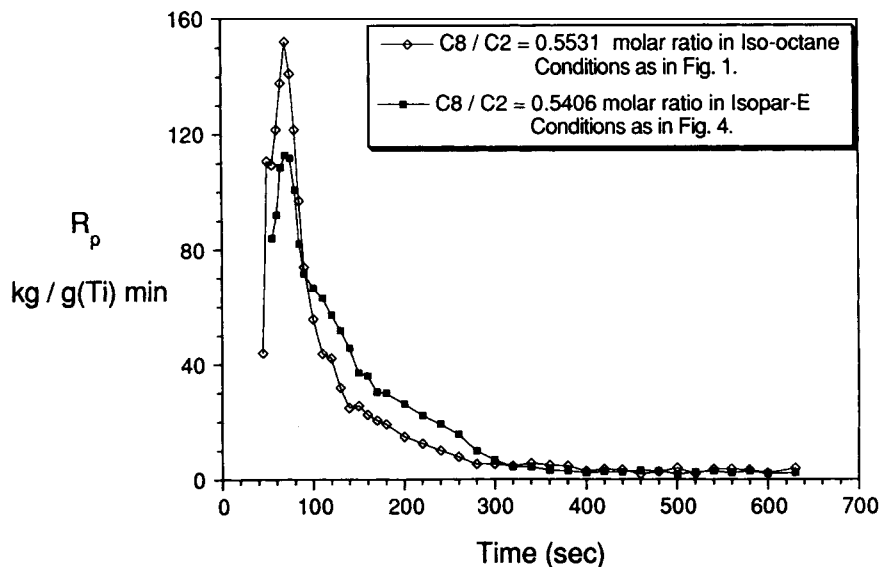
Figure 9 Rate of ethylene consumption in C_2/C_8 copolymerization in different solvents: isooctane or isopar-E.

active centers, and not to a diffusion problem. The difference in the polydispersity trends with results reported in the present study could be because Kashiwa et al. used higher reactive comonomers, compared to 1-hexene and 1-octene in this investigation. In addition, Kashiwa et al. employed a longer polymerization time, 40 min, and used the comonomers in batch. This would be expected to lead to an

increase in the polydispersity as was observed by Kashiwa et al.[10] Because of the high reactivity of propylene and butene, their concentration will certainly deplete very fast during the 40 min polymerization time; consequently, this will lead to a large deviation in the ethylene/comonomer ratio during the 40 min polymerization time. The relatively constant polydispersity values obtained in this study
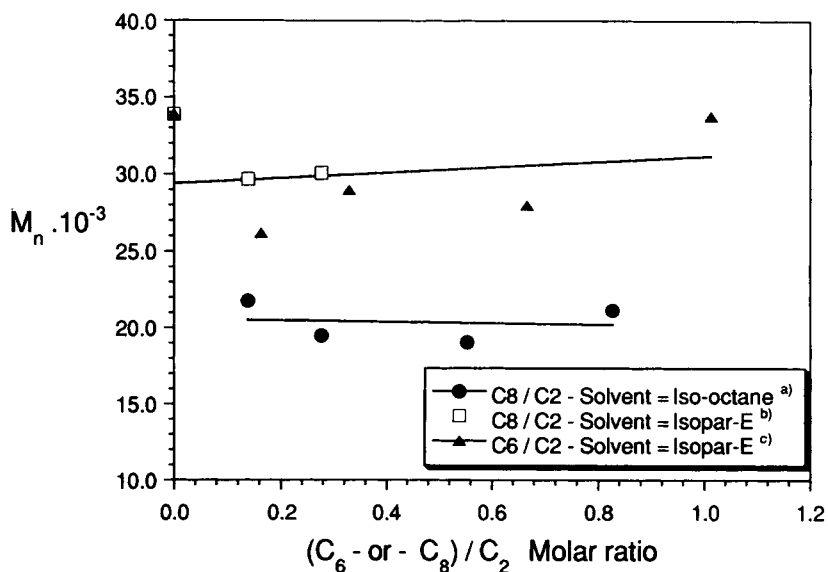

Figure 10 Effect of the comonomer/ethylene molar ratio on the number-average molecular weight: (a) conditions as in Figure 1; (b) conditions as in Figure 4; (c) conditions as in Figure 2.
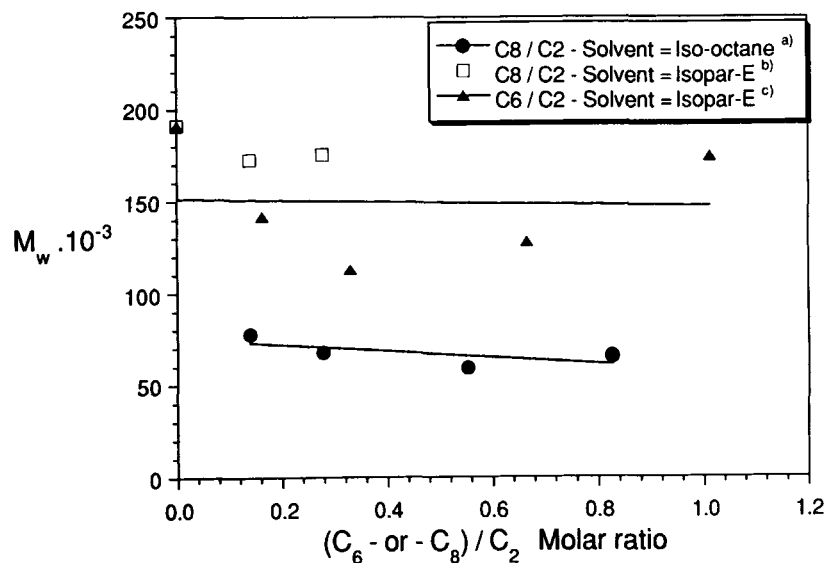
Figure 11 Effect of the comonomer/ethylene molar ratio on the weight-average molecular weight; (a), (b), and (c) as in Figure 10.

are comparative for much lower reactive comonomers and, at the same time, for only the 10 min polymerization period.

Naturally, as the comonomer concentration increases, the amount of comonomer incorporated, expressed as mol %, also increases. This is shown in Figure 13 for both C_2/C_6 and C_2/C_8 copolymerization. Again, it is expected that the mol % incorporation in the case of C_2/C_6 copolymerization would be higher than in the case of C_2/C_8 copolymerization because of the higher activity of 1-hexene, and this is true when the same solvent type is used. However, when isooctane was the solvent, significantly greater incorporation of the comonomer was found. The branching degree, expressed as the number of methyl groups per 1000 C, is directly pro-

portional to the amount of the commoner incorporated. Figure 14 presents the branching content for the copolymers synthesized vs. the comonomer/ethylene molar ratio. From these figures, it is seen that under the conditions used the amount of the comonomer incorporated is somewhat low, about 2.5 mol %.

Combined Effects of Hydrogen and Comonomer

The effect of hydrogen on the copolymerization is reported in detail in Ref. 1. Hydrogen and the comonomer have been observed to increase the initial maximum polymerization rate when used in moderate concentrations. In these experiments, constant [H_2] was used when the comonomer concentration

Table I Solubility Comparison of Ethylene, Hydrogen, and 1-Octene at Exactly the Same Initial Concentration in Isooctane or Isopar-E Solvents: Reactor Temperature 185°C and Pressure 400 Psig[a]

Solubilities in Isooctane Solvent					Solubilities in Isopar-E Solvent				
[C_2] (mol/L)	$10^3 \cdot$ [H_2] (mol/L)	[C_8] (mol/L)	$10^3 \cdot H_2/C_2$ Molar Ratio	C_8/C_2 Molar Ratio	[C_2] (mol/L)	$10^3 \cdot$ [H_2] (mol/L)	[C_8] (mol/L)	$10^3 \cdot H_2/C_2$ Molar Ratio	C_8/C_2 Molar Ratio
0.7928	7.039	0.1102	8.8786	0.1390	0.8306	6.235	—	7.5069	—
0.7940	7.017	0.2203	8.8376	0.2775	0.8309	6.238	0.1126	7.5082	0.1356
0.7964	6.974	0.4405	8.7574	0.5531	0.8312	6.242	0.2251	7.5100	0.2709
0.7987	6.931	0.6604	8.6776	0.8269	0.8316	6.248	0.4495	7.5133	0.5406

[a] Solubility determination based on the Soave–Redlich–Kwong equation, Ref. 25, in the first part of this series.[1]
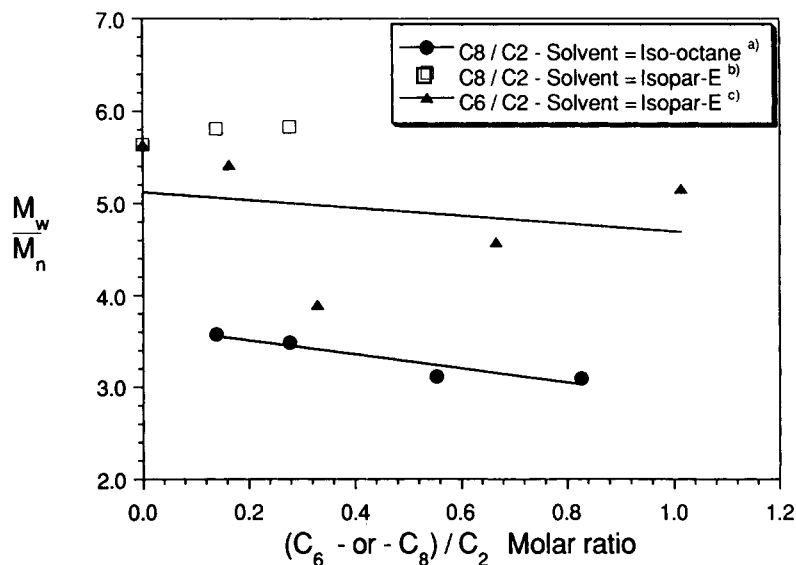
Figure 12 Effect of the comonomer/ethylene molar ratio on the polydispersity index, M_w/M_n; (a), (b), and (c) as in Figure 10.

was varied. To clarify and better understand the influence of H_2 or the comonomer separately on the polymerization rate and the polymer properties other polymerizations were carried out whereby a homopolymerization run without H_2 was conducted; then, the same experiment was repeated in the presence of either hydrogen or comonomer or both. The rate–time profiles for these polymerizations are shown in Figure 15. In addition, Table II presents the values of the maximum polymerization rates,

yields, and polymer properties obtained under these conditions.

The lowest initial polymerization rate is obtained when neither H_2 nor the 1-hexene comonomer was used. The decay in the polymerization rate of ethylene in the absence of H_2 and the comonomer is observed to be the least significant of all. When either H_2 or the comonomer is present in the polymerization medium, a higher initial polymerization rate is observed; however, the decay now becomes
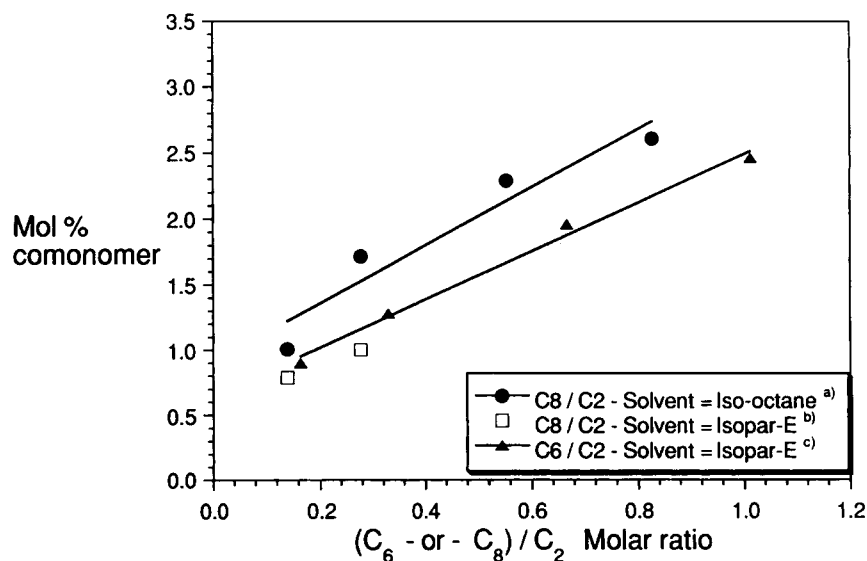

Figure 13 Effect of the comonomer/ethylene molar ratio on the mol % comonomer incorporation; (a), (b), and (c) as in Figure 10.
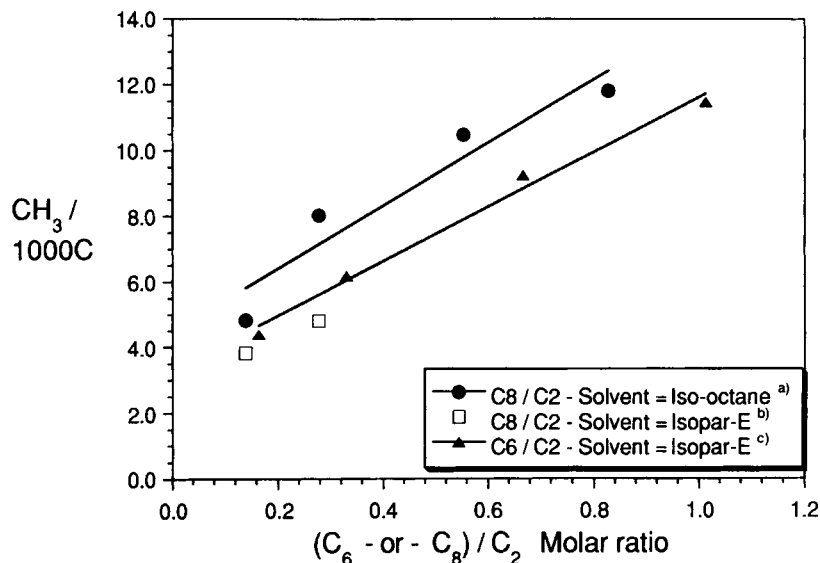
Figure 14 Effect of the comonomer/ethylene molar ratio on the branching content; (a), (b), and (c) as in Figure 10.

much faster. A remarkable increase in the initial rate of polymerization is obtained when both H_2 and the comonomer are present, and the decay in this case is similar to that when only H_2 or the comonomer is present. The data in Table II show that similar polymerization yields are attained when both H_2 and the comonomer or none of these are present. This can be attributed to the striking difference in the rate–time profile shape. The lowest polymeriza-

tion yields were obtained when only one component was used (i.e., H_2 or 1-hexene), basically because of the relatively low initial maximum and fast decay.

The results in Figure 15 and Table II confirm the overall trend for the data presented in our studies, i.e., when H_2 or the comonomer are used in moderate quantities, they can contribute to an activation mechanism and therefore induce higher initial activity. Even though both H_2 and the comonomer
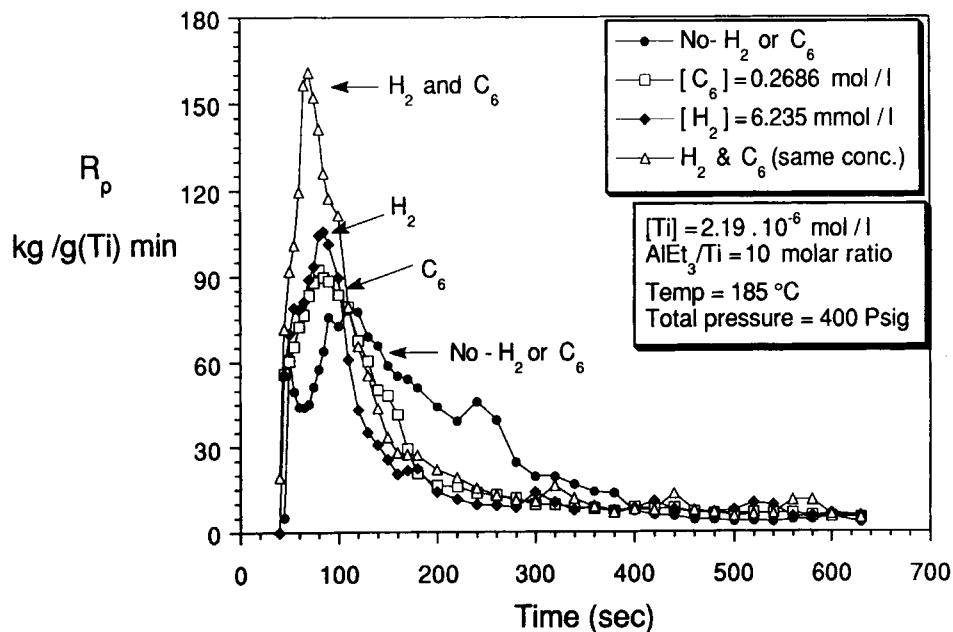

Figure 15 Effect of the presence of hydrogen and/or 1-hexene on the consumption rate of ethylene. Solvent = isopar-E.

Table II   Effect of Hydrogen and/or 1-Hexene on the Polymerization of Ethylene in the Solution Phase

$10^3 \cdot [H_2]$ (mol/L)	$[C_6]$ (mol/L)	Yield [kg/g (Ti)]	$R_{p(max)}$ [kg/g Ti min]	$10^{-3} \cdot M_w$	$10^{-3} \cdot M_n$	M_w/M_n	C_6 (mol %)	$CH_3/1000$ C
—	—	259	78	—	21.7	—	—	—
—	0.2686	217	92	211.2	29.9	7.06	0.53	2.6
6.235	—	200	106	191.3	33.9	5.64	—	—
6.325	0.2694	246	161	113.0	29.0	3.90	1.28	6.17

Conditions as in Figure 15.

contribute to a faster initial rate of polymerization, they simultaneously increase the deactivation in the rate of polymerization when used in excess. This shows the dynamic character as well as the complexity of the system under investigation.

DISCUSSION

Rate Enhancement due to the Comonomer

Many studies have reported on the ability of an α-olefin comonomer in increasing the reaction rate of ethylene. Most of these investigations have been carried out in slurry[3-6] and fewer in gas-phase polymerizations.[7-9] Rate-enhancement effects in olefin copolymerizations have been discussed by many authors in this field. There are two main types of explanations that have been put forward to explain rate enhancement of ethylene consumption as a result of the comonomer addition: chemical and/or physical factors. Using mathematical modeling, the importance of monomer mass transfer resistance has been emphasized and it was concluded that the degree of monomer mass transfer limitations is strongly dependent upon both the catalyst particle size and size of the primary crystallites.[12] Furthermore, it has been suggested that lower crystallinities, in copolymerization, will result in increased diffusion rates and, consequently, in higher polymerization rates if the reaction is diffusion-controlled.[13] Tait et al.[3] suggested a number of physical and chemical factors that could possibly account for the increase in the polymerization activity. The authors[3] further emphasized that no single explanation may be adequate to account for the behavior of a variety of different catalytic systems.

In the present study, rate enhancement due to the presence of a small amount of the comonomer is particularly interesting because this emphasizes that such rate-enhancement effects induced by the comonomer are not only observed in slurry[3,4] or gas-phase[8,9] polymerizations, but also in the solution copolymerization of ethylene.

Because of the fact that the polymer is in solution at the high temperatures employed, the enhancement effects observed by the presence of the comonomer are more likely due to chemical factors rather than to physical ones. Although the diffusion of ethylene is easier at lower polymer crystallinities in gas- or slurry-phase polymerizations, in solution polymerization the diffusion of ethylene to reach the catalyst active center does not depend on diffusion through the semicrystalline polymer. Thus, it is difficult to explain the observation from physical considerations. The results reported in the present study also indicate that the comonomer plays an important role in the deactivation process. Excess comonomer concentration can result in increased adsorption and competition in reactions with ethylene and the aluminum alkyl compound. In addition, the new sites that are activated or modified by the comonomer seem to be more unstable and deactivate rather rapidly within the short 10 min polymerization time.

From the data, it is possible to fit a first-order deactivation rate constant as explained in Ref. 1, and a sample of the application of this law to some of the rate–time profiles reported in this paper is shown in Figure 16. To indicate the effect of comonomer type and concentration on the rate of deactivation, the deactivation rate constants were determined for all runs and are summarized in Table III. These clearly indicate that the presence of H_2 or the comonomer accelerate the rate of deactivation over the cases where neither H_2 nor the comonomer are present. However, if H_2 is present, the addition of comonomer seems to have only a minor effect on the rate of deactivation.

Effect of Solvent

We saw in the previous section that the polymer is much less soluble in isooctane than in isopar-E. Thus, for isooctane, lean and rich polymer phases may coexist, thus giving rise to what is known as phase separation[14,15] during the polymerization. As this problem was encountered under various H_2 and
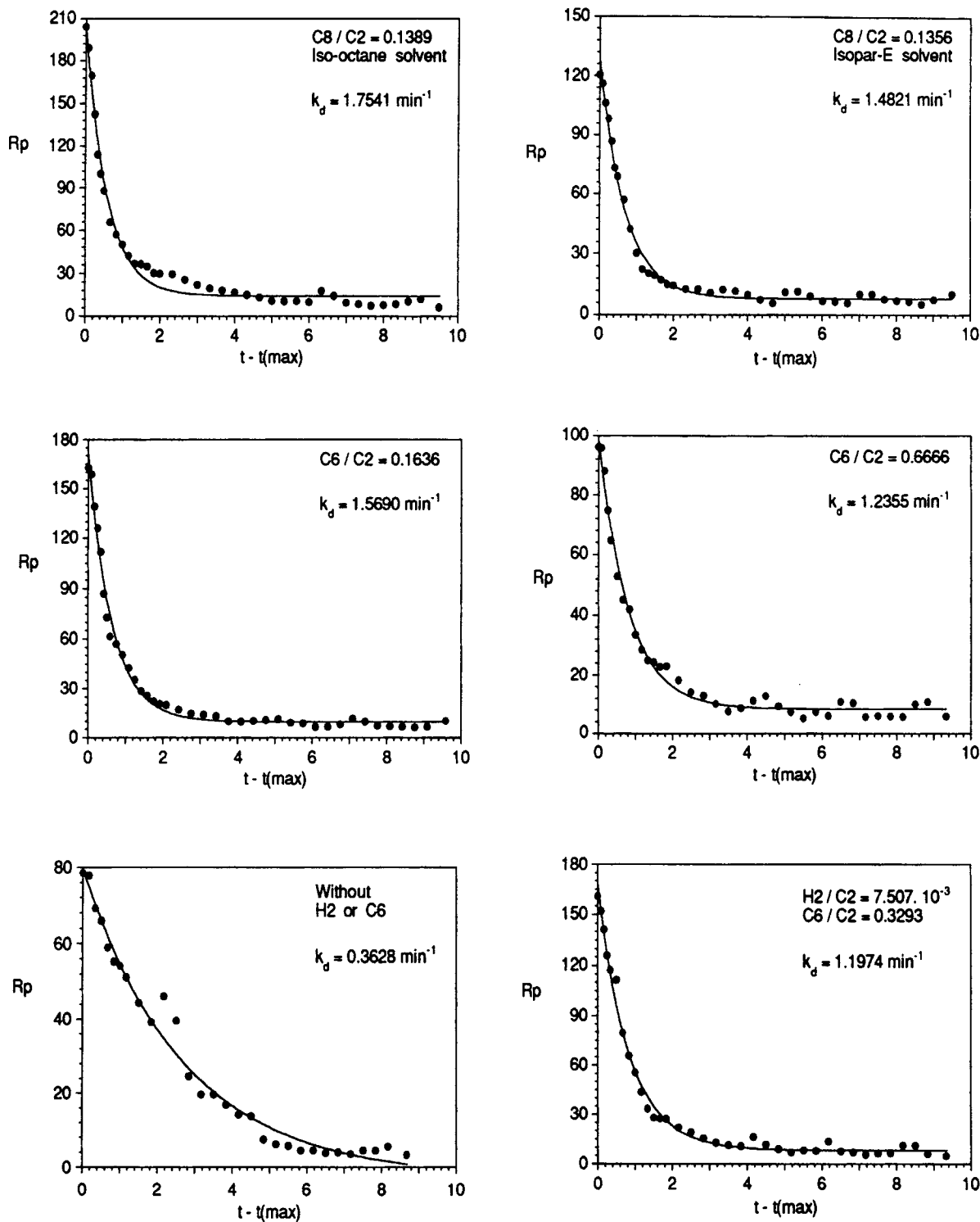
Figure 16 Plots of R_p vs. $t - t_{(max)}$ according to a first-order decay law: eq. (1), Ref 1. k_d values are tabulated in Table III.

comonomer concentrations, it seems clear that polymer solubility must be responsible.

The question now is how can the observed dif-

ferences in the polymerization activity be explained when different solvents are employed under exactly the same reactor conditions. Two main factors may

Table III   First-order Deactivation Rate Constant Values (k_d)

$C_8/C_2{}^a$ Molar Ratio	k_d (min^{-1})	$C_8/C_2{}^b$ Molar Ratio	k_d (min^{-1})
0.1389	1.7541	—	1.5897
0.2775	1.1830	0.1356	1.4821
0.5531	1.8160	0.2709	0.9404
0.8269	1.8940	0.5406	0.9407

$C_6/C_2{}^c$ Molar Ratio	k_d (min^{-1})	$10^3 \cdot H_2/C_2{}^d$ Molar Ratio	$C_6/C_2{}^d$ Molar Ratio	k_d (min^{-1})
—	1.5897	—	—	0.3628
0.1636	1.5690	—	0.3193	0.7889
0.3293	1.1975	7.507	—	1.5897
0.6666	1.2355	7.620	0.3293	1.1974

[a] C_2/C_8 copolymerization in isooctane solvent. Conditions as in Figure 1.
[b] C_2/C_8 copolymerization in isopar-E solvent. Conditions as in Figure 4.
[c] C_2/C_6 copolymerization in isopar-E solvent. Conditions as in Figure 2.
[d] Polymerization conditions as in Figure 15.

be the cause for the higher activity observed in the case when isooctane is used as the solvent. The first is that mass transfer of ethylene could be better in isooctane as compared to isopar-E. Second, in the above cases, two monomers and hydrogen were used, even though the same pressure of ethylene and same initial [H_2] and [1-octene] were employed; still, if the solubility of ethylene and hydrogen are different in the two solvents, then the molar ratios of H_2/C_2 and C_2/C_8 would be different. This surely can lead to different activities in the two solvents. To verify this, Table I presents a comparison of the concentrations of the components used and their ratios in the two solvents utilized. Note that both the H_2 concentration and the H_2/C_2 molar ratio are found to be always higher in the isooctane solvent compared to isopar-E. This finding explains, on the one hand, the higher activity observed in isooctane relative to isopar-E (recall from Ref. 1 that it was found that moderate [H_2] levels can increase the activity) and, on the other hand, the lower polymer molecular weight obtained in isooctane as shown in Figures 10 and 11.

Mass transfer between the gas and liquid phases may also play a role. For example, Hsu et al.,[16] using a high-activity $TiCl_4/MgCl_2$-supported catalyst in slurry polymerization of propylene, showed that because of the high initial activity in these systems, and limited gas–liquid mass transfer, the propylene monomer concentration falls significantly (~25%) during the early stages of polymerization. If this is the case, then this drop of monomer concentration

should be much more severe in the solution copolymerization of ethylene. To illustrate this phenomenon, Figure 17 presents a comparison of a real ethylene copolymerization experiment in solution [where the catalyst yield of about 200 kg/g (Ti) is obtained in 10 min] to a slurry experiment producing the same yield of polymer where polymerization lasts normally for more than 1 h. It is quite obvious that most of the polymer formed in the solution process is actually obtained in the very first few minutes where a remarkably high initial rate is obtained. As shown by Hsu et al.,[16] if the propylene monomer depletes by about 25% during the very first few minutes of slurry polymerization, then by simply comparing the curves in Figure 17 it can be concluded that such mass transfer limitations of the ethylene monomer in the present system should be much more dramatic.

On the other hand, due to the very high initial rate of polymerization, it is anticipated that the viscosity of the polymer solution would rise rather sharply during the very start of the polymerization. This would certainly lead to difficulty in the mass transfer of ethylene in the liquid phase. Apart from thermal deactivation, which also should be very significant, mass transfer of ethylene is believed to play a major role in causing the very fast rate of deactivation observed in the solution copolymerization of ethylene.

Finally, observe that if, as suspected, isooctane does allow a phase separation during polymerization, then the viscosity of the reactor liquid would be
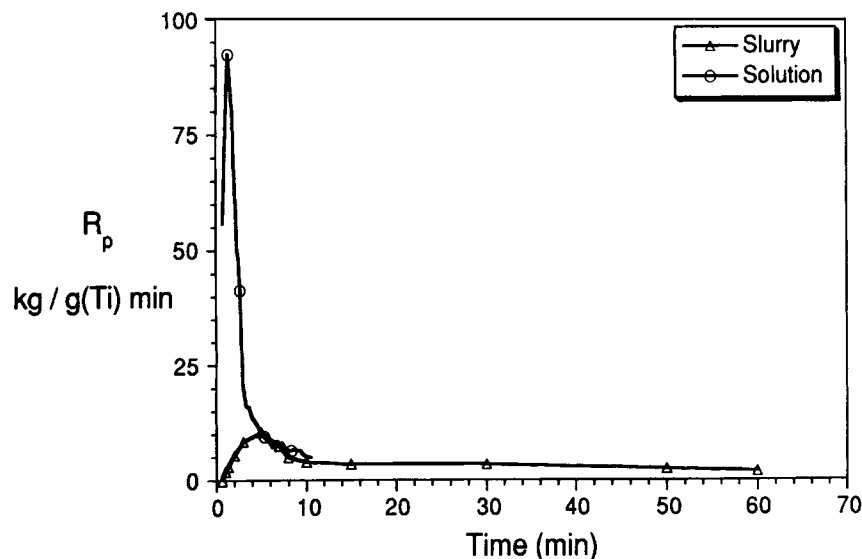
Figure 17   Comparison of rate–time profile of a real copolymerization of ethylene in the solution phase with a slurry-phase polymerization to obtain same activity.

much less than in the case when isopar-E is used. This would promote gas–liquid mass transfer of ethylene and further enhance the rate of polymerization in isooctane.

Copolymer Composition

The Mayo–Lewis[17] or the Fineman–Ross[18] equations are used frequently for the estimation of the copolymerization parameters r_1 and r_2 in Ziegler–Natta-catalyzed polymerizations. Because there can be several types of active sites, these approaches lead to average r_1, r_2 values. However, these averages can be meaningless (and even negative) in predicting sequence length distributions. In fact, the diversity of active centers is one of the main reasons for the nonuniformity or the heterogeneous distribution of the comonomer units in the resulting copolymer.

For the evaluation of the true reactivity ratios for each type of site, it is necessary to analyze the resulting copolymer and know the concentration and the distribution of the comonomer units. The most common approach is to use NMR techniques for the evaluation of the comonomer content and units distribution along the polymer chain.[6,19]

The polymer composition data available in the present study permits the use of the Mayo–Lewis or the Fineman–Ross formulations for the evaluation of only average copolymerization parameter values. Using the Mayo–Lewis equation [eq. (1)], Böhm[20] suggested that for low comonomer content in the polymer a simplification can be employed for

the estimation of the r_1 parameter. However, we found that this approach did not work reliably for our data and, thus, the full Mayo–Lewis and Fineman–Ross approaches were used. For the Mayo–Lewis approach, the relation between polymer composition and monomer composition is given by

$$d[O]/d[E] = [O]/[E] \cdot \frac{r_2 \cdot [O]/[E] + 1}{[O]/[E] + r_1} \quad (1)$$

where $d[O]/d[E]$ = octene/ethylene molar ratio in the copolymer; $[O]/[E]$ = octene/ethylene initial molar ratio in the solvent; and $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$.

Alternatively, the Fineman–Ross equation is given by

$$\frac{F(f-1)}{f} = \frac{F^2}{f} \cdot r_1 - r_2 \quad (2)$$

where $F = [E]/[O]$ is the ethylene/octene initial molar ratio in the solvent, and $f = [E]/[O]$, the ethylene/octene molar ratio in the copolymer.

The application of eqs. (1) and (2) to the results obtained in this work is shown in Figures 18 and 19 for C_2/C_8 and C_2/C_6 copolymerization, respectively. The two approaches give slightly different values for r_1 and r_2, but r_2 is negative in both fits. The differences in the values of the copolymerization parameters obtained using the above equations and the fact that r_2 is negative indicate that caution

should be considered before making any conclusions. Floyd[21] also found a negative value for r_2 when the Fineman–Ross equation was applied to the ethylene/propylene copolymerization data. Floyd emphasized that when the polymers are compositionally heterogeneous, the reactivity ratios derived from kinetic measurements are not meaningful. Further experiments capable of defining multiple sites would be necessary for something more than average values.

CONCLUSIONS

Ethylene copolymerization in solution has been shown to yield very high rates of polymerization. The rate–time profiles are characterized by a remarkably fast and high initial rise and very rapid decay within the 10 min polymerization time. The
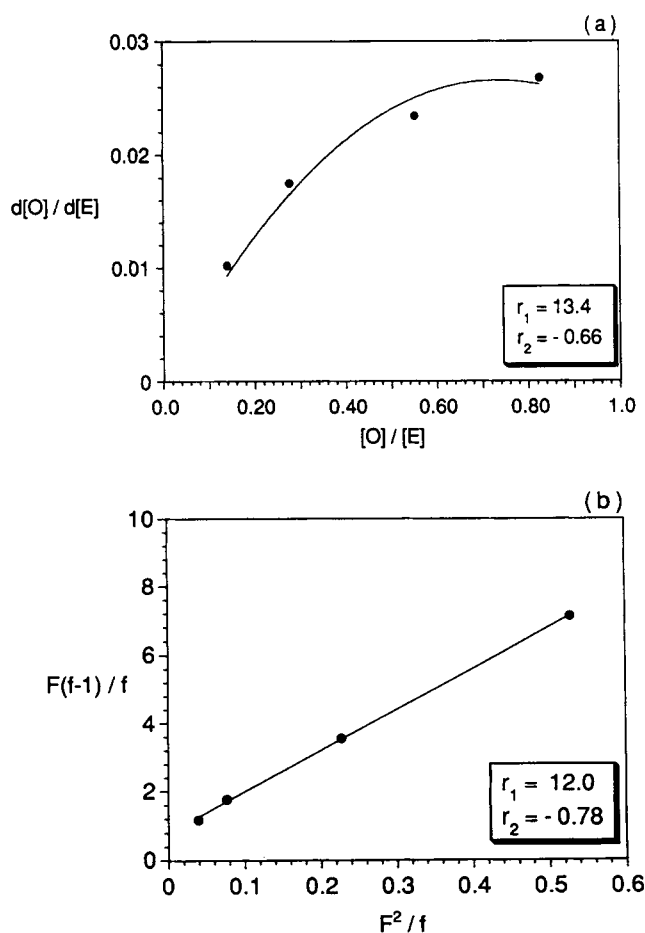

(a)

$r_1 = 13.4$
$r_2 = -0.66$

(b)

$r_1 = 12.0$
$r_2 = -0.78$

Figure 18   Estimation of r_1 and r_2 parameters in C_2/C_8 copolymerization: (a) Mayo–Lewis (curve fitting); (b) Fineman–Ross: eqs. (1) and (2) in text. Conditions as in Figure 1.
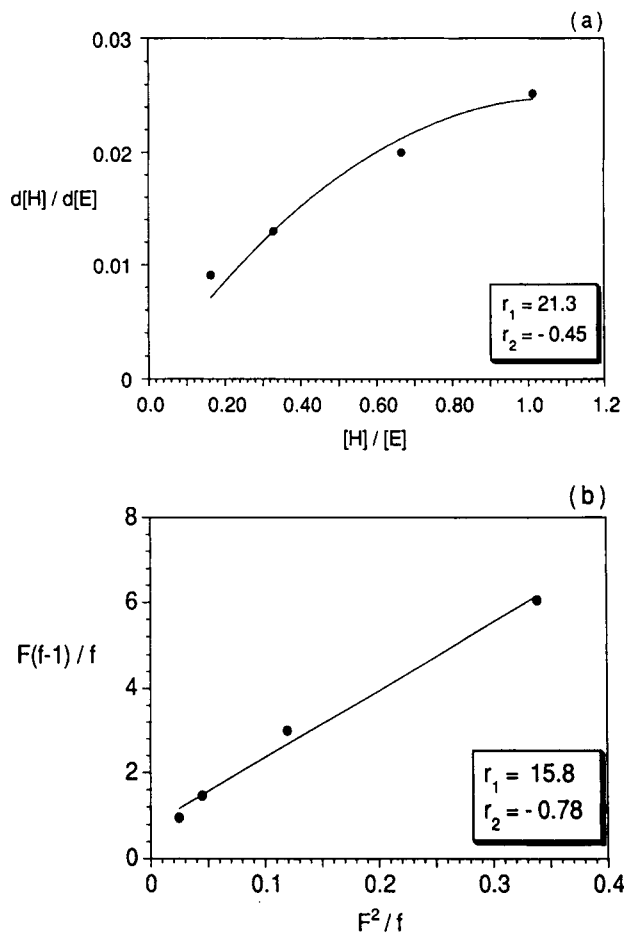

(a)

$r_1 = 21.3$
$r_2 = -0.45$

(b)

$r_1 = 15.8$
$r_2 = -0.78$

Figure 19   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 text. Conditions as in Figure 2.

high maximum in R_p and the fast decay are the result of employing a high-activity Ti-supported catalyst and a high polymerization temperature. The severe reactor conditions, e.g., temperature and solution viscosity, are believed to contribute to the fast decay.

The results in Table II and Figure 15 confirm the overall trend for the data presented in this article, i.e., when used in moderate quantities, the comonomer can contribute to an activation mechanism and therefore induce higher initial activity. Even though both H_2 and the comonomer contribute to a faster initial rate of polymerization, they simultaneously increase the deactivation in the rate of polymerization when used in excess. This shows a dynamic character, as well as the complexity of the system under investigation.

The creation of new sites and the modification of the active site environment is thought to be the reason for the initial higher activity observed when low

comonomer concentration is used. However, excess comonomer results in a deactivation process. This can result from adsorption and competition in reactions with ethylene and the aluminum alkyl compound. In addition, higher α-olefins have stronger donation ability compared with ethylene; this can result in overreducing the titanium to low inactive oxidation states. Karol et al.[8] stated that the initially most active sites activated by the comonomer are highly acidic; these sites deactivate rather rapidly by interacting with Lewis bases (electron donors and α-olefins). Transfer reactions also with the comonomer should play an important role in reducing catalyst activity when such reactions are pronounced at high comonomer concentration.

Subsequent papers in this series will be concerned with the effects of temperature and pressure variations on the kinetics and polymer properties. Other future papers will discuss a comprehensive model embodying both chemical and physical mechanisms for a more detailed interpretation of these results.

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