Polymerization of Olefins through Heterogeneous Catalysis XI: Gas Phase Sequential Polymerization Kinetics

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SYNOPSIS

A unique series of ethylene and propylene sequential polymerization experiments have been carried out in a stirred bed gas phase reactor using unsupported Stauffer AA catalyst ($TiCl_3 \cdot \frac{1}{3} AlCl_3$). Several interesting kinetic results were observed. It was found that propylene causes rate enhancement for a subsequent ethylene polymerization but that ethylene causes a rate reduction for a subsequent propylene polymerization. Furthermore, the rate enhancement/reduction effect increases with the duration of the preceding polymerization. Chemical/kinetic effects were found to be the likely causes of both the rate enhancements and the rate reductions observed during sequential polymerization. It was also shown that enhanced monomer sorption caused by the presence of a more soluble component, such as a heavier comonomer, does contribute to rate enhancement during *simultaneous* copolymerizations, but is not a factor for *sequential* polymerizations. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Olefin copolymers (e.g., linear low density polyethylenes, ethylene–propylene elastomers, and impact-grade polypropylenes) continue to grow in commercial importance. The variety of products and the range of properties that can be achieved has led to a great deal of interest in these copolymers. This study focuses on sequential polymerization kinetics, an area that is important for several reasons. Sequential polymerizations are used in commercial processes in a number of ways: prepolymerizations are often used in controlling catalyst activity and morphology and second-stage polymerizations, such as ethylene–propylene copolymerization after propylene homopolymerization, are frequently used to produce impact-grade polyolefins. Sequential polymerizations also provide a tool by which to study some of the interactions between monomers and the effects on (co)polymerization kinetics. This paper follows up on preliminary results presented earlier.[1]

Sequential Polymerization

It is important to first clarify the terminology used in this paper. Many patents and publications claim the synthesis of olefin block polymers such as P-E, P-EP, or $(EP)_n$, where P, E, and EP represent propylene, ethylene, and ethylene–propylene block segments, respectively. Much effort has gone into finding direct and primarily indirect evidence for the synthesis of true "block copolymer" where clearly defined segments (blocks) of different monomers exist within single polymer chains. Because it is often unclear as to whether true block copolymer has been produced, the terms "sequential polymerization" and "sequential polymers" will generally be used in the remainder of this paper. Instead of referring to the product that is assumed to be produced, these terms refer to the process employed. The idea of sequential polymerization (wherein monomers are polymerized in sequence) is to be contrasted with that of "random" or "statistical" copolymerization (wherein monomers are copolymerized simultaneously).

Commercial interest in sequential polymerization of olefins has largely been fueled by an interest in improving the properties of polyolefins and, es-

pecially, isotactic polypropylene. Because isotactic polypropylene has a glass-transition temperature near 0°C, it becomes brittle at low temperatures. Thus, it is not suitable for applications subjected to low temperatures (such as refrigerated consumer containers). While this deficiency has been partly overcome by blending isotactic polypropylene with 10–20% rubber (e.g., ethylene–propylene random elastomer), the polymer blend, although tougher, shows lower tensile strength and modulus. Many workers have thought that this trade-off in properties is at least partially caused by incompatibility between the rubber and plastic, thus leading to microphase segregation. It is thought that one way of improving compatibility is to chemically bond the rubber and plastic (as in a true P-EP block copolymer) or to at least produce a more intimate mixture of plastic and rubber by producing the rubber *in situ* within the homopolymer matrix. Research and development in sequential polymerization has continued with interest toward further improvements in processes and polymer properties, and the development of "polymer alloys."

Heggs[2] has reviewed the patent literature on sequential polymers; refer to this excellent review of catalysts, monomers, processes, and polymer properties. More recent patents for sequential polymerization processes cover a variety of reactor train configurations. For example, Himont's "Spheripol" process employs a liquid slurry loop homopolymerization reactor followed by a gas-phase fluidized bed copolymerization reactor.[3,4] Both Union Carbide[5] and BP Chemicals[6] have each developed processes using two gas-phase fluidized bed reactors in series while Amoco's polypropylene process consists of two horizontal stirred bed gas-phase reactors in series.[7] The use of many other types of reactors and configurations has also been reported in the patent literature.

A review of sequential polymerizations reported in the scientific, nonpatent literature is presented in Table I.[8–31] Much of the work has focused on detailed synthesis procedures and the estimation of "mean chain lifetime." Kissin[32] defines mean chain lifetime as the time necessary for a given active center to form a polymer chain of the steady-state degree of polymerization. Chain lifetime is critical because "the basis for synthesizing block polymers is that, if it is possible for a polymer chain to remain alive and grow for a long time, it should be possible to form long segments of two or more olefin molecules in the same polymer chain."[33] Heggs[2] has reviewed mean chain lifetimes for unsupported (low-

activity) Ti-based catalysts and concludes that chain lifetimes on the order of 1–10 min can be expected for these catalysts. With modern high-activity supported catalysts, for which the polymerization rate constants are one or more orders of magnitude greater than those of unsupported Ti-based catalysts, the chain lifetimes are expected to be on the order of seconds.

Of the workers[8–31] listed in Table I, those who estimated chain lifetimes usually did so by measuring intrinsic viscosity and the time beyond which this value (which is related to molecular weight) no longer changes. Also, the majority of workers listed in Table I used only indirect physical measurements (i.e., X-ray scattering to measure crystallinity, stress–strain tests, measurements of melt behavior, electron microscopy to study morphology) to conclude that true block copolymer was synthesized. The exception is the work of Prabhu, et al.[13–16] Through a procedure by which the product was complexed with urea, fractionated, and analyzed using C^{13} NMR, Prabhu et al. concluded that they had indeed synthesized true block copolymer. However, Prabhu et al. did not estimate chain lifetimes and instead only estimated *catalyst* lifetimes. Busico et al.[17,18] repeated the experiments of Prabhu et al., but used lower temperatures and lower pressures (0.1 and 1 atm) to give longer chain lifetimes. Busico et al. found evidence that block copolymer was produced at 0.1 atm (for which chain lifetimes were estimated to be 60 s), but not at 1 atm (for which chain lifetimes were estimated to be 6 s).

The lack of conclusive direct evidence, along with the characteristic short-chain lifetimes of Ziegler catalysts at normal temperatures (at least 25°C), led Boor[33] to suggest that most probably the claimed block copolymer products were present in only small concentrations, while the major products were homopolymer and/or (random) copolymer.

Table I also lists examples of some more unusual sequential polymerizations. Doi and Ueki,[20] using the soluble $V(acac)_3$ catalyst at very low temperatures, claim a living coordination polymerization but the process is not yet commercially practical. The last six examples given in Table I involve nonolefin monomers and mixed polymerization mechanisms, such as coordinated Ziegler–Natta polymerization followed by free-radical polymerization. These examples are included here to give the reader an idea of the range of catalyst systems and polymerization mechanisms used in olefin sequential polymerization. Further discussion beyond this point will focus on Ziegler–Natta polymerizations.

Table I   Examples of Sequential Olefin Polymerization in Nonpatent Literature

Reference	Author	Catalyst	Reactor	Temperature (°C)	Monomers	Claimed Product
8	Natta	α-TiCl$_3$/TEA	Slurry (toluene)	15–18	Ethylene, propylene	(P-E)$_{5-7}$
9, 10	Bier et al.	Hoechst aTiCl$_3$/DEAC	Slurry (heptane)	50	Ethylene, propylene	(E-P)$_n$
11	Gandini, Heinen	TiCl$_3$/TEA	Slurry (toluene)	50	Propylene, styrene	(S-SP)$_n$
12	Hagemeyer, Edwards	TiCl$_3$/TEA	Slurry (mineral spirit)	70–80	Ethylene, propylene	P-E
13–16	Prabhu et al.	δ-TiCl$_3$/DEAC	Gas	40–50	Ethylene, propylene	E-P-E; E-EP-E; P-EP-P; (E-P)$_n$
17, 18	Busico et al.	δ-TiCl$_3$/DEAC	Gas	25	Ethylene, propylene	P-E; E-EP
19	Kontos et al.	VCl$_4$ or VOCl$_3$/DEAC or EADC; TiCl$_4$/LiAlR$_4$	Slurry (heptane)	25–35	Ethylene, propylene, butene	(EP-E)$_n$; (EP-P)$_n$; (EB-B)$_n$; (EP-EP')$_n$
20	Doi et al.	V(acac)$_3$/DEAC	Slurry (toluene)	−78	Ethylene, propylene	P-EP-P
21	Lindsey	V(acac)$_3$/DEAC	Slurry (liq. C$_3$H$_6$, n-butane)	0–20	Ethylene, propylene, (methyl- or ethyl-acrylate/AlCl$_3$)	EP-AP
22	Jezl et al.	TiCl$_3$/DEAC + benzoyl peroxide	Slurry (hexane)	70	Polar monomer + ethylene or propylene	(P or E)-polar monomer[a]
23, 24	Agouri et al.	TiCl$_3$/DEAC + cumene peroxide	Slurry (heptane)	45; 60	Ethylene, methyl methacrylate	E-MMA[a]
25	Doi et al.	V(acac)$_3$/DEAC	Slurry (toluene)	−78/25	Propylene, methyl methacrylate	P-MMA[a]
26–29	Fontanille, Siove, et al.	Polystyrene$_{100}$-polybutadiene$_3$-Li + TiCl$_4$	Slurry (toluene)	22	Ethylene, propylene	S-(E or P); S-EP[b]
30	Drzewinski, Cohen	Bu-Li + TiCl$_4$	Slurry (hexane)	50	Propylene, 1,3-butadiene	B-P[b]
31	Doi et al.	MgCl$_2$/TiCl$_4$/ethyl benzoate/TEA	Slurry (heptane)	25	Propylene, methyl vinyl ketone	P-MVK[c]

[a] Coordinated Z-N/free-radical.
[b] Anionic/coordinated Z-N.
[c] Coordinated Z-N/anionic.

Rate Enhancement Effects

Nearly all the literature (both patent and nonpatent) on sequential olefin polymerization deals with catalysts, polymerization procedures, product analysis, and polymer properties. This is not too surprising since the primary motivation for sequential polymerization has been to improve the properties (and in particular the impact properties) of polyolefins. Very little mention is ever made of polymerization kinetics and even less has been reported about either the absence or presence of a "rate enhancement effect" during sequential polymerization. As shown in Table II,[34–42] the enhancement of po-

lymerization rate of a monomer (e.g., ethylene) when in the presence of comonomer (e.g., propylene) has been reported by a number of workers for simultaneous (random) copolymerizations. Figure 1 shows an example of rate enhancement reported by Tait et al.[39] for the copolymerization of ethylene and 4-methyl-1-pentene (4-MP-1) in slurry. Tait et al. observed that increasing the amount of 4-MP-1 comonomer causes an increase in the rate of ethylene polymerization and also a change in the shape of the rate-time profile.

Table II also lists the explanations proposed by the investigators for the observed rate enhancements. The first six workers in Table II[34–39] proposed

Table II   Examples of Copolymerization Rate Enhancement

Reference	Author	Catalyst	Reactor	Product	Proposed Reasons for Observed Enhancement
34	Valvassori et al.	VCl_4/AlR_3	Liquid	Simul. E & P	Active sites that homopolymerize E or copolymerize E & P, but cannot homopolymerize P
35	Soga et al.	Soluble Cr-based/ DEAC	Toluene	Simul. E & P	Same as Valvassori. Proposed P forms stable complex with Cr^{+2} that can be removed by E. No rate enhancement
36	Calabro, Lo	$SiO_2/TiCl_4/$ MgRX/TEA	Hexane	Simul. E & H; E-EH-E	Hexene modifies catalyst sites before and/or during activation period. Speculate stabilization of Ti^{+3} sites
37	Pino et al.	$MgCl_2/TiCl_4/AlR_3$	Heptane	Simul. E & P; E & B	Comonomer increases intrinsic activity by modifiying active sites; may also create new sites
38	Spitz, Duranel, et al.	$MgCl_2/LB/TiCl_4/$ TEA/ethyl paratoluate	Heptane	Simul. E & P; E-EP-E	Some active sites lose ability to initiate P but still initiate E. Propylene causes activation of new sites and therefore higher ethylene rate
39	Tait et al.	δ-$TiCl_3/DEAC$; δ-$TiCl_3/AlR_3$; $MgCl_2/LB/$ $TiCl_4/AlR_3$	Pentamethyl heptane	Simul. E & C_8; E & 4MP1	Measured increased number of active sites with increasing comonomer; suggested: catalyst breakup, diffusion of monomer and alkyl, displacement of adsorbed molecules on sites, activation of new or dormant sites by reactions with comonomer
40	Kashiwa et al.	$MgCl_2/TiCl_4/TEA$	Decane	P-EP-P	Caused by increased propagation rate of ethylene
41	Spitz et al.	$SiO_2/MgCl_2/TiCl_4/$ isoprenyl Al	Gas	Simul. E & B	Enhanced solubility of monomers caused by more amorphous polymer
42	Soga et al.	Solvay-type $TiCl_3$; $(RCp)_2TiMe_2$	Heptane	Simul. E & P	Reduction in diffusion resistance caused by decrease in copolymer crystallinity

Monomer abbreviations: E, ethylene; P, propylene; B, 1-butene; H, 1-hexene; 4MP1, 4-methyl-1-pentene.

kinetic explanations involving the presence or formation of different types of active sites, each of which may show different activities for the various monomers. Kashiwa and Yoshitake[40] attributed their observed rate enhancement to the higher propagation rate constant of ethylene. The last two workers in Table II[41,42] attributed their observed rate enhancement to physical effects, such as enhanced solubility of the monomer or reduced diffusion resistance of the monomer.

Three of the references cited in Table II also report sequential polymerization kinetic experiments. Soga et al.[35] used a soluble $Cr(C_{17}H_{35}COO)_3/$ Et_2AlCl catalyst system that was inactive for propylene polymerization but active for ethylene homopolymerization and somewhat active for ethyl-

ene/propylene simultaneous copolymerization. Soga et al. Polymerized ethylene in toluene at 0°C after first adding to the reactor 1 atm of propylene for 35 min and then evacuating the propylene from the reactor. They observed no difference in activity when compared to a normal run with just ethylene.

Kashiwa and Yoshitake[40] employed a supported $MgCl_2/TiCl_4/AlEt_3$ catalyst system and carried out a P-EP-P-EP-P-EP-P sequence of polymerizations, where P and EP represent propylene homopolymerization and ethylene/propylene simultaneous copolymerization, respectively (Fig. 2). Kashiwa and Yoshitake found that polymerization rate increased during ethylene/propylene copolymerization, but that when the ethylene feed was stopped the rate quickly dropped to the level for propylene
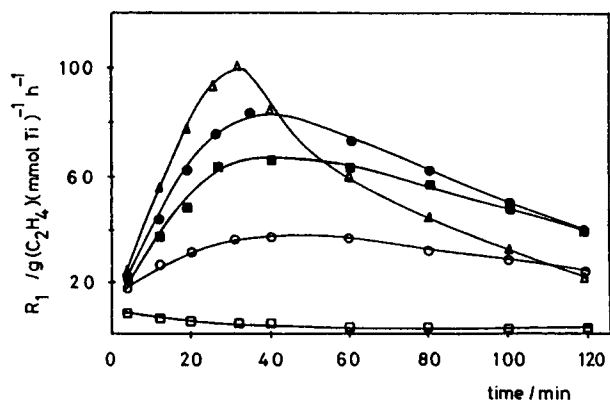
Figure 1 Ethylene polymerization rate for the homopolymerization of ethylene and the copolymerization of ethylene and 4-methyl-1-pentene (4-MP-1) using a δ-TiCl$_3$ · $\frac{1}{3}$AlCl$_3$-Al(i-Bu)$_3$ catalyst system at 60°C. ($\square$) ethylene homopolymerization; (○) copolymerization with 0.16 mol/dm^3 4-MP-1; (■) copolymerization with 0.24 mol/dm^3 4-MP-1; (●) copolymerization with 0.39 mol/dm^3 4-MP-1; (△) copolymerization with 0.55 mol/dm^3 4-MP-1.[39]

homopolymerization. This observation is consistent with their explanation that the increased rate is caused by the higher propagation rate constant of ethylene, and not because of an increase in the number of active sites.

Spitz et al.[38] conducted a number of sequential polymerization experiments in heptane slurry using a supported MgCl$_2$/Lewis base/TiCl$_4$/AlEt$_3$/ethyl
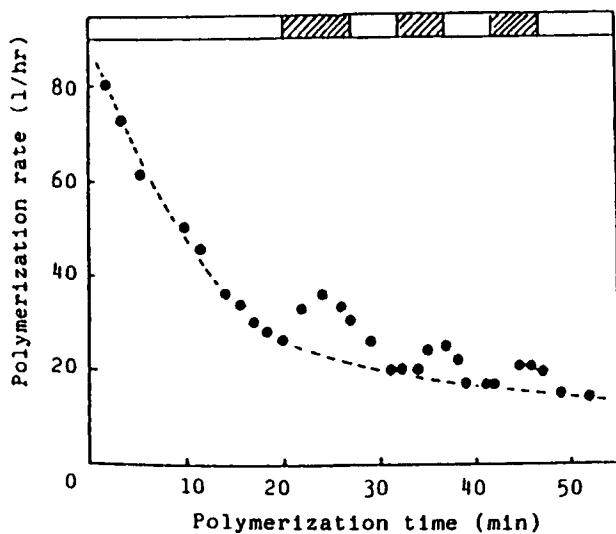
Figure 2 Effect of ethylene addition on polymerization rate for MgCl$_2$/TiCl$_4$/AlEt$_3$ catalyst at 70°C in decane. (Shaded part of bar at top indicates propylene and ethylene mixture; white part indicates propylene only.)[40]
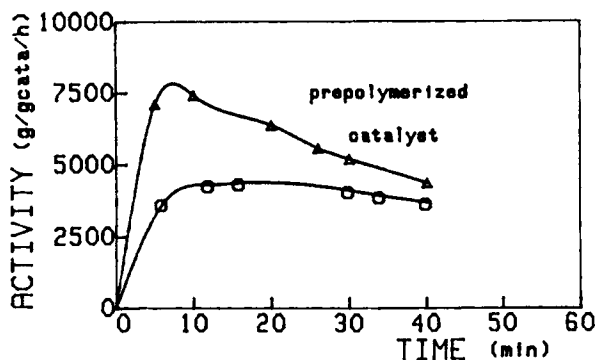

Figure 3 Ethylene polymerization in heptane at 80°C and total pressure of 9 bars using a MgCl$_2$/Lewis base/TiCl$_4$/AlEt$_3$/ethyl paratoluate catalyst. The upper curve indicates ethylene polymerization rate after a propylene prepolymerization (5 g propylene/g catalyst) at 20°C.[38]

paratoluate catalyst system. As shown in Figure 3, prepolymerization with a small amount of propylene caused the maximum ethylene polymerization rate to nearly double. Spitz et al. also carried out an E-EP-E sequential polymerization (Fig. 4). During the middle ethylene/propylene copolymerization step, the polymerization rate gradually increased and during the last ethylene polymerization step the rate remained high. From this experiment Spitz et al. concluded that propylene "induces an irreversible activation of the catalyst." To examine the effect of ethylene on propylene polymerization kinetics, Spitz et al. performed a P-EP-P sequential polymerization. As shown in Figure 5, the activity increased suddenly when "a very small amount of ethylene" was added to the reaction mixture. Spitz et al. observed that the total amount of excess monomer po-
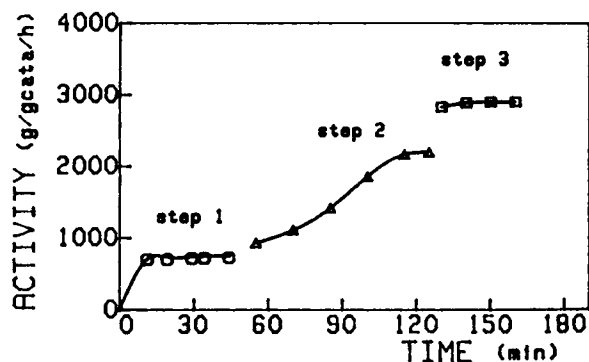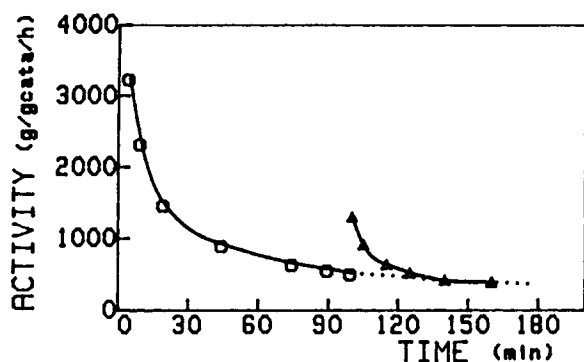

Figure 4 E-EP-E sequential polymerization in heptane at 63°C and total pressure of 3 bars using a MgCl$_2$/Lewis base/TiCl$_4$/AlEt$_3$/ethyl paratoluate catalyst. The middle copolymerization step was performed with 4% propylene in the gas mixture.[38]

Figure 5   P-EP-P sequential polymerization in heptane at 60°C and total pressure of 4 bars using a $MgCl_2$/Lewis base/$TiCl_4$/$AlEt_3$/ethyl paratoluate catalyst. A "very small amount of ethylene" was added at time $\approx$ 100 min.[38]

lymerized during the experiment was approximately 20 times the amount of ethylene added and that "the activation is reversible and certainly restricted to the duration of full ethylene consumption."

To explain their observations, Spitz et al. hypothesized that some of the catalytic sites "deactivate" for propylene polymerization by no longer being able to initiate growing chains with propylene. Because these sites are still able to initiate chains with ethylene, the addition of ethylene causes an increased rate of propylene polymerization by propagation into already initiated chains. Spitz et al. also hypothesize that propylene causes active sites to be created, thereby leading to an increased rate of ethylene polymerization after a propylene prepolymerization or during copolymerization with a "small" amount of propylene.

Objectives

From the literature reviews it is apparent that most of the work on sequential polymerizations has focused on catalysts, polymerization procedures, product analysis, and polymer properties, with few studies of kinetics reported. Also most of the reported experiments showing copolymerization rate enhancement effects have been simultaneous copolymerizations conducted in liquid slurry reactors.

There is a shortage of information on monomer/comonomer rate effects during sequential polymerizations and particularly for gas phase reactors. The objective of this work is to study these effects and to investigate the degree to which physical (e.g., monomer sorption and diffusion) and chemical (e.g., formation of sites and multiple types of sites) phenomena are able to explain the observations.

EXPERIMENTAL

A schematic diagram of the gas phase reactor system used for ethylene and propylene sequential polymerizations is shown in Figure 6.[43] The reactor is a one-liter stainless steel reactor (Parr Instrument Company) and is equipped with a helical stirrer. Gases (Ultra High Purity-grade nitrogen, polymer-grade ethylene, polymer-grade propylene, and hydrogen) are purified over oxidation–reduction and molecular sieve beds before being fed to the reactor. Temperature control of the reactor is effected by controlling the temperature of the oil bath in which the reactor is partially immersed. Pressure inside the reactor is controlled by the gas feed pressure regulators.

Since the reactor is operated in semi-batch mode (continuous gaseous monomer feed; no gas vent or polymer discharge during reaction), monomer is fed on demand in order to keep the reactor pressure constant as determined by the gas feed pressure regulator setting. This feature also means that under quasi-steady state (rate of accumulation of gas in the reactor is negligible if pressure is maintained relatively constant) the rate of monomer flow into the reactor is equal to the rate of monomer consumption by reaction. By measuring the monomer feed flowrates (using Hastings electronic mass flow meters and controllers), the instantaneous rates of polymerization are easily measured.

The reactor is initially loaded with a 300 g bed of small glass beads (1-mm diameter) to help disperse the catalyst. For the sequential polymerization experiments, 0.100 g of catalyst (unsupported Stauffer AA catalyst, $TiCl_3 \cdot \frac{1}{3} AlCl_3$) and 3.2 mL of co-catalyst (25% solution of Et_2AlCl in heptane) are injected into the reactor to give an Al/Ti molar ratio of 10. An additional 10 mL of purified HPLC-grade heptane is used to wash the catalyst into the reactor. After catalyst injection, the reactor is evacuated for 15 min to remove liquid heptane from the system.

The first monomer is then fed to the reactor and the gas flow continues on demand to maintain constant reactor pressure. After the desired period of polymerization, the monomer feed is stopped and the reactor slowly vented and evacuated. The reactor is held at full vacuum for 30 s between monomer feed stages. Then the monomer feed is changed to the next desired monomer and the polymerization process repeated. This cycle is repeated until the desired sequence of polymerizations has been completed. For the sequential polymerization experiments, propylene polymerizations are carried out at 7.0 atm and ethylene polymerizations at 1.3 atm.
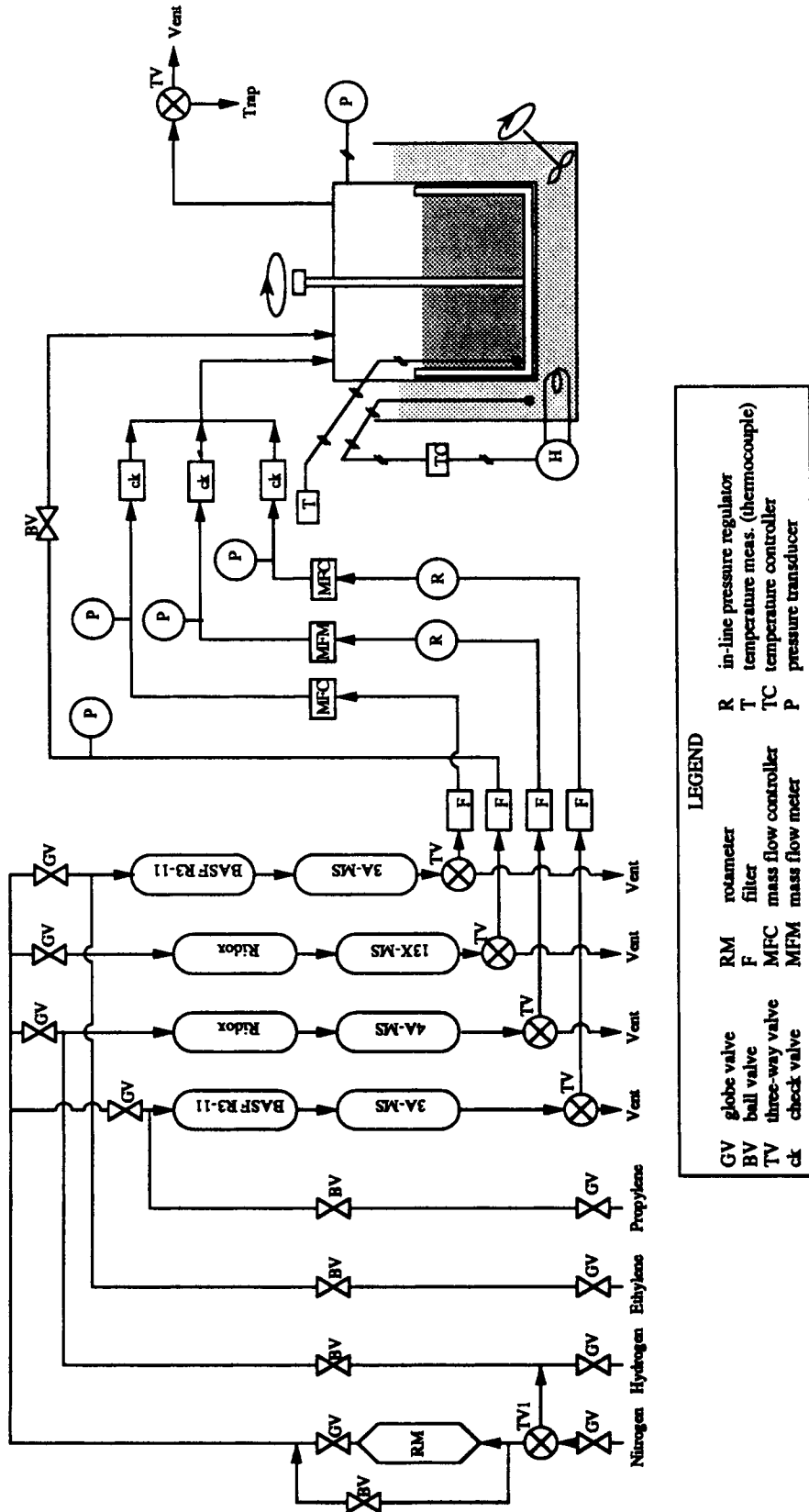
Figure 6 Gas phase stirred bed reactor (vertical) for ethylene and propylene sequential polymerization.

After the experimental run, total polymer yield is determined gravimetrically. Yields are also calculated by integrating the instantaneous monomer feed flow rates. The polymer is separated from the glass bead bed by floating the polymer in water. After washing and filtering the polymer with methanol to remove catalyst residues, the polymer is dried.

This gas phase polymerization process offers particular advantages for studying sequential polymerization kinetics. First, the absence of a liquid phase, which can act as a monomer reservoir, enables rapid changes between monomer feeds (approximately 5 min to change monomer feeds). Second, the semi-batch operation of the reactor allows the measurement of instantaneous rates of polymerization for each monomer.

RESULTS AND DISCUSSION

Effect of Propylene on Ethylene Polymerization Kinetics

Because ethylene generally polymerizes one order of magnitude faster than propylene, removal of the increased amount of heat generated by polymerization was a concern. Heat removal from the reactor was generally adequate. However, heat removal from the growing polymer particles by the surrounding gas was inadequate during early experiments and was seen in the formation of melted polymer around

the glass beads. To reduce the amount of heat generated by polymerization, the ethylene pressure was reduced to nearly the lower limit of operability (5 psig). Heat removal from the particles was improved by increasing the surface area of the growing polymer particles without increasing the size and activity of the catalyst particles. This was accomplished by carrying out a short propylene prepolymerization (to a yield of approximately 20 to 25 g polymer per gram catalyst over a period of 15 min) prior to the ethylene homopolymerization. Admittedly, this propylene prepolymerization may cause an enhancement of ethylene polymerization rate, as found by Spitz et al. for heptane slurry polymerization.[38] However, it was not possible to reproducibly prepolymerize ethylene at pressures below what was already being used during the normal homopolymerization.

Because of run-to-run variations in the rate of polymerization (e.g., caused by variability in catalyst loading, the amount of impurities present in the reactor, or monomer pressure), the polymerization rate curves reported here have been normalized to facilitate comparison. The normalization was carried out so that the initial rate of polymerization, determined by ignoring the initial spike caused by reactor fill-up and extrapolating the rate curve to time zero, was set to a reference value of 100.

It is necessary to first determine whether interrupting the polymerization affects the polymerization kinetics. Figure 7 shows the ethylene polymer-
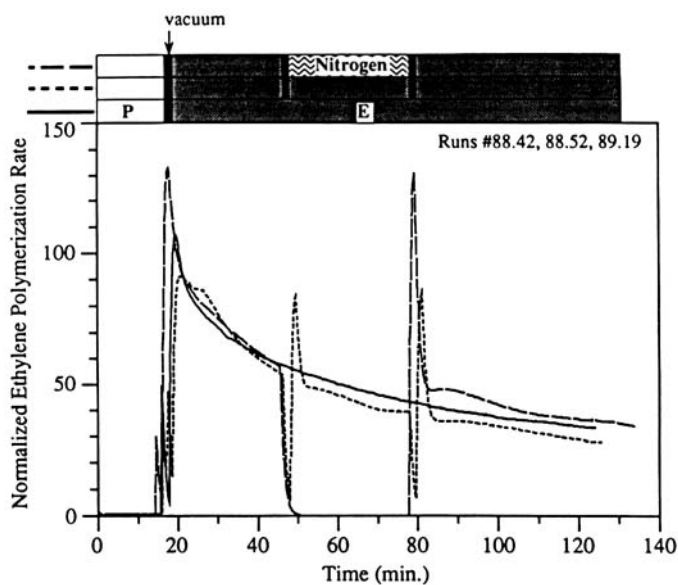

Figure 7   Ethylene polymerization rate (normalized) for interruption experiments: P-E; P-E-E-E; and P-E-nitrogen-E.

ization rate for three different interruption experiments. The basecase ethylene homopolymerization (after a 15-min propylene prepolymerization) shows a deactivating rate profile. The large spikes in the rate curves are due to reactor fill-up and no ethylene polymerization rate is shown for periods during which no ethylene is present in the reactor. Interrupting the polymerization at two times (at approximately 46 and 78 min) by evacuating the reactor and refilling with ethylene (a P-E-E-E sequence) did not produce any significant deviation from the basecase polymerization rate profile. Furthermore, replacement of the ethylene in the third step with the inert gas nitrogen (a P-E-nitrogen-E sequence with nitrogen pressure of 6.4 atm) also did not appreciably alter the rate profile. During the nitrogen step, the catalyst activity continued to decay and the ethylene rate during the fourth step is close to that of the basecase polymerization. This continuation of catalyst deactivation in the absence of polymerization is similar to that reported by Choi and Ray for gas phase propylene homopolymerization with the same catalyst system.[44]

The above set of interruption experiments show that the experimental procedure does not produce any artifacts in the polymerization kinetic data. With this assurance, a set of P-E-P-E sequential polymerizations were performed (Fig. 8). Curve 1 corresponds to the same basecase ethylene poly-

merization shown in Figure 7. Curves 2–5 show the normalized ethylene polymerization rate for four P-E-P-E runs with varying durations (5, 15, 30, and 60 min) of the second propylene step. As seen in Figure 8, the ethylene polymerization rates of the last step show a rate enhancement when compared to the basecase polymerization (curve 1). Furthermore, as the second propylene step increases in duration, the enhancement effect increases both in terms of absolute rate and especially relative to the basecase polymerization rate.

Even though the kinetics of solid catalyzed olefin polymerization are strongly dependent on the catalyst and the reaction medium (i.e., gas or liquid), these results can be compared to the examples of rate enhancement observed by other workers. As shown in Figure 1 for the slurry copolymerization of ethylene and 4-methyl-1-pentene with a δ-$TiCl_3 \cdot \frac{1}{3} AlCl_3$-$Al(i$-$Bu)_3$ catalyst, Tait et al.[39] found that increasing concentrations of comonomer caused the rate enhancement effect during simultaneous copolymerization to increase. It may be possible that increasing concentration of comonomer during simultaneous copolymerization is analogous to increasing duration of propylene polymerization during sequential polymerization.

As shown in Figure 3, Spitz et al.[38] found that ethylene polymerization rate (in heptane at 80°C with a $MgCl_2$-supported Ti catalyst) was increased
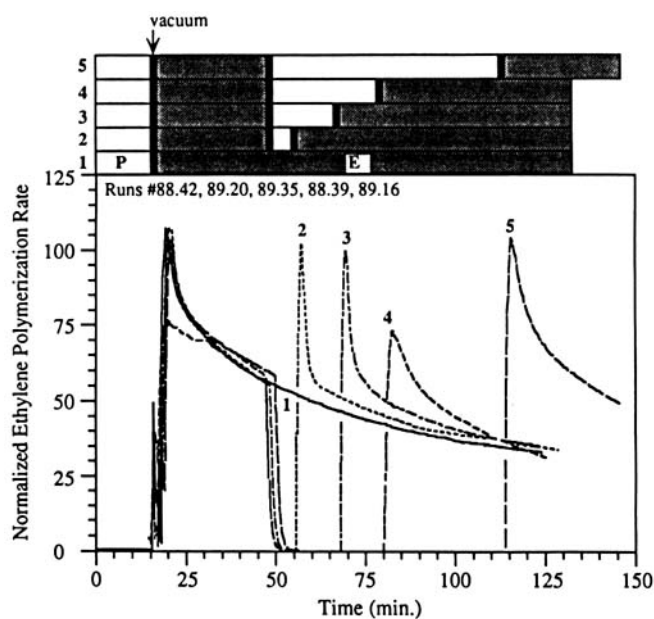

Figure 8 Ethylene polymerization rate (normalized) for sequential polymerization experiments. Curve 1: P-E sequence. Curves 2–5: P-E-P-E sequence with varying durations of the second P step.

after propylene prepolymerization. Spitz et al. also found that ethylene polymerization rate (in heptane at 63°C with a MgCl$_2$ supported Ti catalyst) was increased following an ethylene/propylene copolymerization (Fig. 4).

Most recently, Tait et al.,[45] using a δ-TiCl$_3$ · $\frac{1}{3}$AlCl$_3$ catalyst in slurry polymerization, have reported rate enhancement effects similar to our observations. Tait et al. found rate enhancement of ethylene polymerization following prepolymerizations with a number of different α-olefins (propylene, 4-methyl-1-pentene, butene, and hexene) and also observed an increase in enhancement with increasing duration of the prepolymerization. Tait et al. measured an increase in active site concentration (after propylene prepolymerization) corresponding to the increased rate of polymerization. However, these workers did not investigate the effect of ethylene prepolymerization on propylene polymerization rates.

The proposed explanations for comonomer rate enhancement listed in Table II can be categorized according to two main groups: chemical/kinetic explanations and physical explanations. The chemical explanations generally focus on the active sites and their modification: the activation of new or dormant sites by reactions involving comonomer; the displacement by comonomer of adsorbed or complexed molecules on the sites; and the inability of some types of sites to initiate or homopolymerize a certain monomer. The physical explanations include: the exposure of more active sites by improved catalyst breakup during copolymerization; the reduction of mass transfer resistance caused by the formation of more amorphous copolymer; and the enhanced solubility of monomers caused by amorphous copolymer formed or increased polymer swelling by the heavier comonomer.

Through sequential polymerization experiments, it is possible to further investigate the last physical explanation listed above. In Figure 9, Li and Long[46] plot the solubility of methane and ethylene vapor in low density polyethylene (LDPE). The heavier pure component, ethylene (curve 1), has a higher solubility than the lighter pure component, methane (curve 4). Based upon these independent solubilities, Li and Long calculated the predicted solubility of a 50 : 50 mixture of ethylene and methane (curve 3). However, their experimental results show that the solubility of the mixture is significantly enhanced (curve 2) because of the higher solubility of ethylene. Hutchinson and Ray[47] have suggested that this type of sorption enhancement by a heavier component (such as comonomer) might contribute to copolymerization rate enhancement effects for gas phase polymerization.
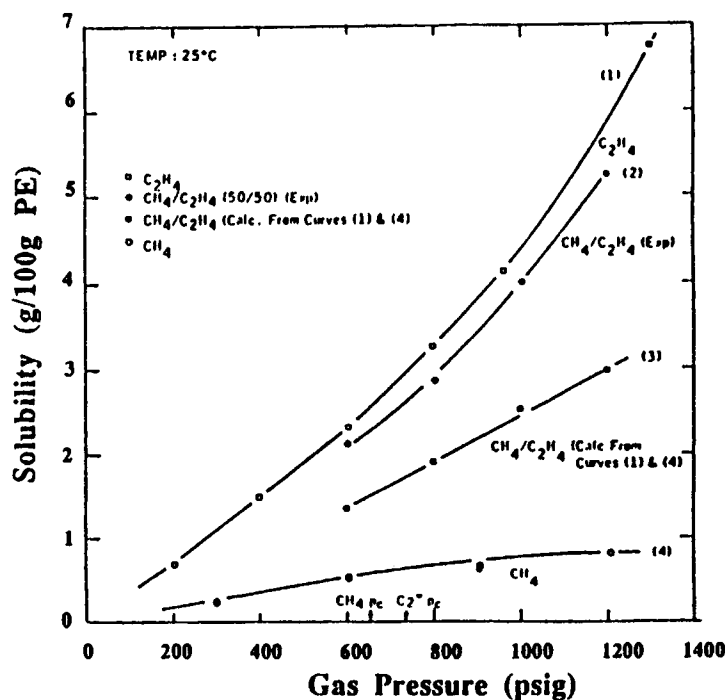

Figure 9   Solubility of methane and ethylene vapors in low density polyethylene at 25°C.[46]

In practice, this enhanced sorption effect should be independent of whether the heavier component can be polymerized. Thus, it is expected that propane and propylene should have approximately the same sorption enhancement effect on ethylene. To examine the influence of propane on ethylene polymerization rate, ethylene was polymerized in the presence of propane (Fig. 10). For the sequence P-E-(ethylene + propane) used for curves 2 and 3, the partial pressure of ethylene was the same during the second and third steps. From curve 3, it appears that the presence of 7 atm of propane increased the solubility of ethylene sufficiently to produce a significant rate enhancement effect, when compared to the basecase P-E polymerization (curve 1). However, the presence of 4 atm of propane did not result in a significant rate enhancement effect.

For the experiments depicted in Figure 10, it was assumed that propane is inert and does not react with the other monomer (ethylene) or with the catalyst. To check this assumption, the P-E-P-E sequence of polymerizations was repeated, except with propane substituted for propylene during the third step (P-E-propane-E). Figure 11 shows that, as before, a 60-min period of propylene in the third step of a P-E-P-E sequence (curve 3) produces a significant rate enhancement. However, an equally long period of propane during the third step of a P-E-propane-E sequence (curve 2) does *not* result in a significant rate enhancement effect. This observation leads to the conclusions that propane is inert

and that the primary cause of the observed ethylene rate enhancements in sequential polymerizations is chemical/kinetic in nature (since it is assumed that propane and propylene behave similarly with regard to physical properties).

Up to this point it has been assumed that the reactor evacuation (a gradual evacuation to "full" vacuum, which is then maintained for 30 s) between sequential polymerization steps has been sufficient to remove the monomer from the reactor. Although this is certainly true for gaseous monomer, it is appropriate to check if this assumption holds for monomer sorbed in the polymer particles. It is reasonable to assume that macroparticle pore diffusion resistance for gas phase olefin polymerization is negligible and that therefore microparticle diffusion resistance would be the primary source of any mass transfer limitation. To conservatively estimate monomer desorption times from the polymer microparticles (i.e., to err on the side of overestimation), the following assumptions are made:

1. neglect macroparticle gas phase mass transfer resistance in the pores of the polymer particle;
2. neglect consumption of monomer by reaction (provides a conservative estimate of desorption time);
3. assume spherical polymer microparticles with initial spatially uniform concentration of sorbed monomer;
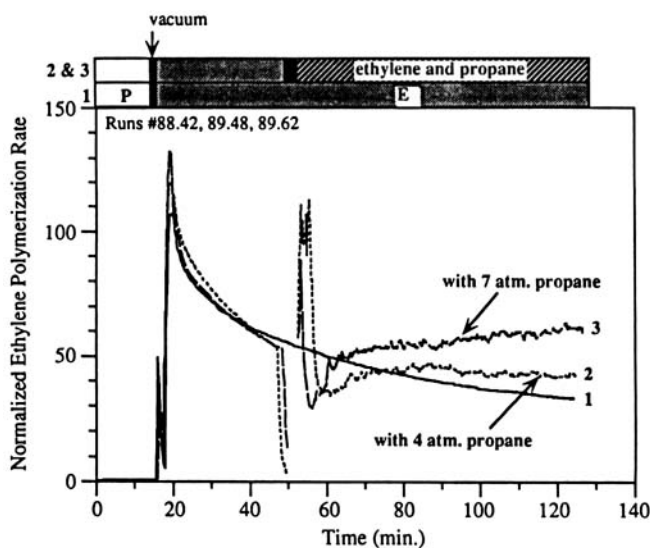

Figure 10   Ethylene polymerization rate (normalized) for ethylene polymerization in the presence of varying amounts of propane. Curve 1: P-E sequence. Curve 2: P-E-(ethylene + 4 atm propane). Curve 3: P-E-(ethylene + 7 atm propane). The ethylene partial pressure of each run was the same for the steps with and without propane.
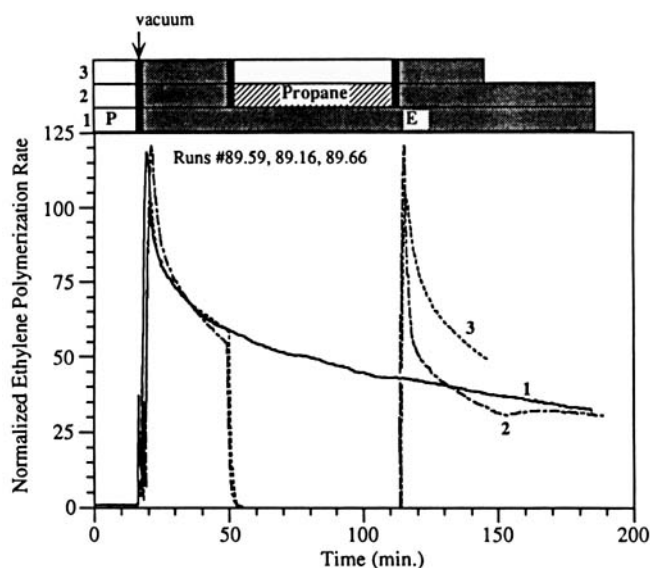
Figure 11   Ethylene polymerization rate (normalized) for ethylene sequential polymerization. Curve 1: P-E sequence. Curve 2: P-E-propane-E sequence. Curve 3: P-E-P-E sequence. Propylene and propane pressures were both 7 atm.

4. neglect particle–particle interactions;
5. assume the particle boundary is subjected to a step change to zero concentration of monomer and no fluid motion.

Because a number of workers have reported the formation of polymer globules that are agglomerates of the polymer microparticles,[48,49] monomer desorption from these agglomerates should also be considered and is assumed to behave in the same manner as desorption from microparticles. By applying a material balance around the polymer microparticle/agglomerate,[50] it is possible to calculate the time needed to achieve a certain degree of desorption from the center of the polymer microparticle or agglomerate. The times needed for monomer desorption to be 95% complete at the center of polymer microparticle/agglomerate are shown in Table III for a range of monomer diffusivities and microparticle/agglomerate diameters. Floyd et al.[51] have reviewed

published data and report that microparticle diffusivities under reaction conditions lie in the range of 10^{-8} to 10^{-6} cm^2/s for diffusion of ethylene and propylene in olefin homopolymers or copolymers.

Assuming a conservative catalyst fragment diameter of 0.1 μm for the Stauffer AA catalyst (TiCl$_3 \cdot \frac{1}{3}$ AlCl$_3$) and a growth factor of 5–8 corresponding to polymer yields in the sequential polymerization experiments, desorption times are only a small fraction of a second, even for the lowest value of monomer diffusivity. Thus, the procedure used during the sequential polymerization experiments should easily allow for complete removal of monomer (as well as nitrogen or propane) between steps. This is confirmed by the P-E-propane-E experiment shown in Figure 11. Since it is known from Figure 10 that propane, if present in sufficient concentration will cause a rate enhancement effect, the amount of propane remaining in the polymer after the evacuation step in Figure 11 is, if not virtually

Table III   Time (s) for Monomer Desorption to Be 95% Complete at Microparticle/Agglomerate Center

Monomer Diffusivity (cm^2/s)	Polymer Microparticle/Agglomerate Diameter (μm)					
	0.10	0.50	1.0	5.0	10	40
1.0E-08	0.0010	0.025	0.10	2.5	10	160
1.0E-07	0.00010	0.0025	0.010	0.25	1.0	16
1.0E-06	0.000010	0.00025	0.0010	0.025	0.10	1.6

zero, at least small enough to not cause a rate enhancement.

If, however, larger microparticle agglomerates were present, monomer desorption times could become longer. For agglomerates approximately 1 μm in diameter, as reported by Kakugo et al.,[48] desorption times are still less than a second; while for 10–40 μm agglomerates, as reported by Bukatov et al.,[49] desorption times are on the order of seconds to a few minutes. However, even in the most extreme case, evacuation times of 2–3 min between monomer sequences would be adequate.

Effect of Ethylene on Propylene Polymerization Kinetics

It has already been shown (cf. Fig. 7) that the interruption experimental procedure did not affect ethylene polymerization rates. To test this for propylene polymerization kinetics, the analogous interruption experiments were performed (Fig. 12). The basecase propylene homopolymerization (P) shows a very slightly deactivating rate profile. As with the ethylene interruption experiments, the large spikes in the rate curves are caused by reactor fill-up and no propylene polymerization rate is shown for periods during which no propylene is present in the reactor. As could be expected from the ethylene interruption experiments, interrupting the polymerization at two times (the P-P-P se-

quence) and replacing the propylene in the second step with nitrogen (the P-N-P sequence) did not produce any significant deviation from the basecase polymerization rate profile. These results are in agreement with those of Choi and Ray.[44]

Once again, having been assured that the experimental procedure does not produce artifacts in the polymerization kinetic data, a set of P-E-P sequential polymerization were performed. The (normalized) rates of polymerization of propylene are shown in Figure 13. Curve 1 corresponds to the basecase propylene homopolymerization, while curves 2–6 correspond to P-E-P runs with varying duration (15, 30, 45, 60, and 75 min) of the middle ethylene step. It is apparent that the middle ethylene polymerization causes a rate *reduction* for the subsequent propylene polymerization and that this reduction increases in severity as the duration of ethylene polymerization increases. It is interesting to note that the propylene polymerization rate profiles during the last step continue to show little or no deactivation.

No examples in the literature were found on the effect of pure ethylene *homo*polymerization on propylene polymerization rate during sequential polymerizations. Figures 2 and 5 show that ethylene/propylene *co*polymerization causes an increase in *overall* polymerization rate only for the time that ethylene is still present in the reactor and that the polymerization activity afterward is unchanged. However, both results are from polymerization in slurry with a $MgCl_2$-supported catalyst and exten-
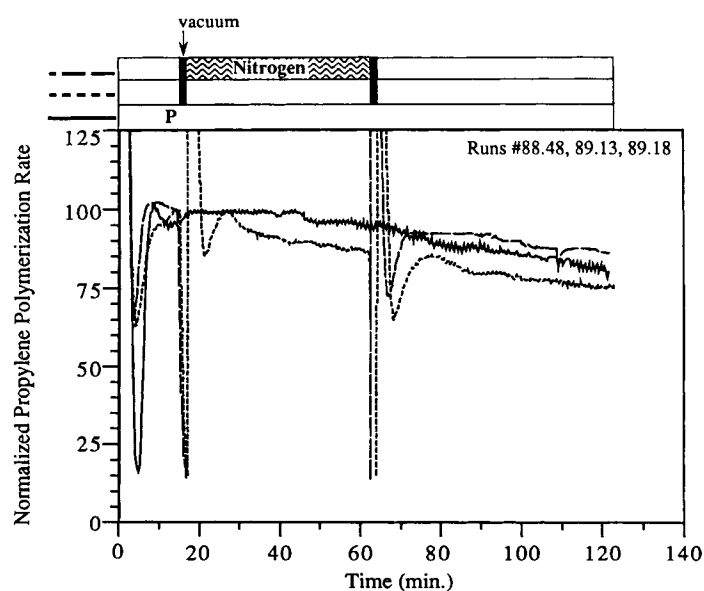

Figure 12   Propylene polymerization rate (normalized) for interruption experiments: P; P-P-P; and P-nitrogen-P.
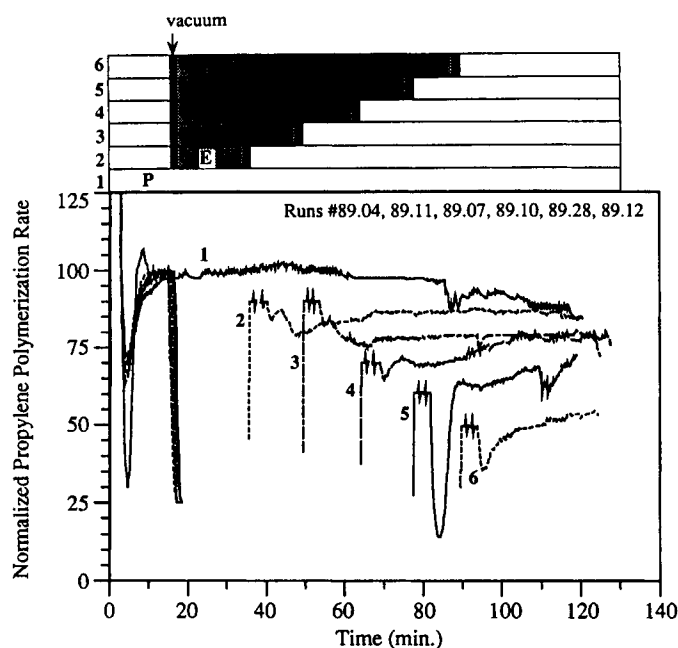
Figure 13   Propylene polymerization rate (normalized) for sequential polymerization experiments. Curve 1: P sequence. Curves 2–6: P-E-P sequence with varying durations of the middle E step.

sion of the results to gas phase polymerization with an unsupported catalyst is not necessarily expected.

Explanations for the observed rate reduction effect may once again be divided into two groups: chemical/kinetic explanations and physical explanations. A possible chemical/kinetic cause would be reactions involving ethylene (but not propylene) that change the active sites to cause a reduction in intrinsic activity and/or a reduction in the number of sites. Supporting evidence for this may be seen in the deactivating rate profile of ethylene homopolymerization (Fig. 7), while propylene polymerization with the same catalyst (Fig. 12) shows only slight deactivation with time.

It is also possible that the formation of a more dense and crystalline polymer (such as high density polyethylene homopolymer) may cause increased mass transfer resistance and a reduction in catalyst activity. To consider this physical explanation further, microparticle diffusion limitations are evaluated. It is assumed that diffusion in the polymer microparticles can be modelled with a single diffusivity coefficient ($\mathcal{D} = 10^{-8}$ cm^2/s for polypropylene and, as a conservative value, 10^{-9} cm^2/s for propylene–ethylene sequential polymer). Following the analysis by Floyd et al. for homopolymerization[51] and assuming a conservative catalyst fragment diameter of 0.1 μm, the microparticle mass transfer

efficiency factor was found to be 1.00 after 15 min of propylene polymerization and 0.95 after an additional 75 min of ethylene polymerization (at the rates measured during the sequential polymerizations). Thus microparticle diffusion resistance is not estimated to contribute significantly to the propylene rate reduction observed in these experiments. However, microparticle diffusion resistance cannot be ruled out for modern high-activity, supported catalysts of larger catalyst fragment sizes.

CONCLUSIONS

A unique series of ethylene and propylene sequential polymerization experiments have been carried out and interesting kinetic results were observed. It was found that propylene causes rate enhancement for a subsequent ethylene polymerization but that ethylene causes a rate reduction for a subsequent propylene polymerization. Furthermore, the rate enhancement/reduction effect increases with the duration of the preceding polymerization. For both rate enhancement and reduction, chemical/kinetic effects are the likely causes of the rate effects observed during sequential polymerization.

It was also shown that enhanced monomer sorption caused by the presence of a more soluble com-

ponent does contribute to rate enhancement during simultaneous polymerizations (e.g., ethylene with propane), but is not a factor for sequential polymerizations.

Some of these ideas have application to industrial processes. Because the order of monomer feeds does influence polymerization rates and polymer properties, it is therefore an important consideration in evaluating reactor operating policies. Also, if unanticipated rate enhancement effects are observed after switching monomer feeds during polymer grade changes, the increased heat generation may cause temperature control difficulties (especially in gas phase reactors).

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