Triple Tandem Catalyst Mixtures for the Synthesis of Polyethylenes with Varying Structures

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Abstract: Tandem catalysis in a single medium presents challenges and opportunities for creating novel synthetic protocols. Thus far, only two homogeneous catalysts have been used in tandem. Herein, we report that it is possible to coordinate the action of three well-defined homogeneous catalysts to produce a wide range of branched polyethylenes from a single monomer. Thus, $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)]\text{-}TiMe\}\{MeB(C_6F_5)_3\}$ (**1**), $[(C_6H_5)_2PC_6H_4C(OB(C_6F_5)_3)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2C_6H_5)$ (**2**), and $\{(H_3C)C[N(C_6H_5)]C\text{-}[O\text{-}B(C_6F_5)_3][N(C_6H_5)]\text{-}\kappa^2N,N\}Ni(\eta^3\text{-}CH_2C_6H_5)$ (**3**) react with ethylene to produce branched polyethylene with structures that cannot be obtained using a single- or a two-component catalyst combination. The properties of the polyethylene depend on the ratio of the three catalysts. High-throughput screening techniques proved essential for optimizing reaction conditions and for probing how the catalyst composition influences the polymer properties.

Introduction

Tandem catalysis, the action of multiple catalysts within the same medium to obtain a desired product from simpler starting materials, constitutes a significant challenge in synthetic chemistry. Multiple catalysts operating simultaneously could circumvent the time and yield losses associated with the isolation and purification of intermediates in multiple step sequences. The generation of harmful chemicals in situ, followed by incorporation into larger molecular structures, would eliminate the inherent dangers associated with transportation from one chemical site to another over long distances. One can even envision the emergence of systems whereby the starting materials are kept constant, while the nature of the product is determined and fine-tuned by the composition of the tandem catalyst mixture.

The motivations given above have generated recent reports that demonstrate the success of tandem catalysis in areas such as organic chemistry[1] and polymer synthesis.[2,3] Thus far, the coordination of only *two* catalysts has been reported. For example, our labs recently reported that solutions of $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)]TiMe\}\{MeB(C_6F_5)_3\}$ (**1**) and $[(C_6H_5)_2\text{-}PC_6H_4C(OB(C_6F_5)_3)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2C_6H_5)$ (**2**) in the same

reactor generate branched polyethylene from ethylene alone.[4] The catalyst from **2** dimerizes ethylene to 1-butene, while that from **1** incorporates the 1-butene into a growing polyethylene chain. For comparison, production of polyethylene copolymers currently involves the generation of 1-alkenes in a separate reaction, followed by addition to a reactor containing ethylene and a copolymerization catalyst.[5]
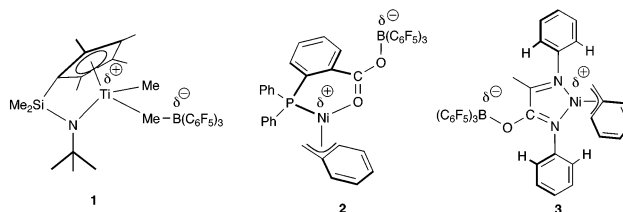
The diversification of catalysts for ethylene oligomerization and copolymerization, together with the improved understanding of the mechanism of action of these catalysts,[6] invite the examination of more complex catalyst mixtures. While this work is highly pertinent to polyolefin manufacturing, one of the largest metal-mediated processes in chemical industry,[7] overcoming the challenges for successful implementation of multiple catalysts

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Scheme 1
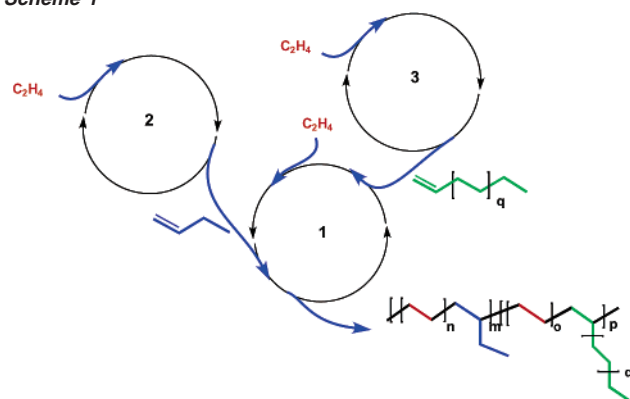
should facilitate development of catalytic schemes in other areas of chemical synthesis.

In this contribution, we show that it is possible to find conditions such that *three* catalysts can be coordinated to provide a branched polyethylene structure from ethylene alone, which is not possible to attain using tandem cooperation of two catalysts (Scheme 1). The method generates polyethylene with a wide range of properties. Furthermore, we emphasize the value of modern high-throughput screening technology in simplifying the optimization of reaction conditions.[8] The three catalysts chosen for this study are **1**, **2**, and $\{(H_3C)C[N(C_6H_5)]C[O-B(C_6F_5)_3][N(C_6H_5)]-\kappa^2N,N\}Ni(\eta^3-CH_2C_6H_5)$ (**3**).[9] Compound **3** generates a Schultz−Flory distribution of 1-alkenes (shown in green in Scheme 1). Controlling the action of **1**, **2**, and **3**, such that the 1-butene generated by use of **2** and the distribution of 1-alkenes from **3** are incorporated by the titanium site into a polyethylene backbone, provides polymers with varying ratios of ethyl branches and longer branches. Because the amount and type of branching influence important properties,[10] such as melting temperature and crystallinity, a well-behaved triple tandem process such as that in Scheme 1 might be used to generate a wide variety of polymer materials more simply and cheaply than with current technology.

Results and Discussion

Sequential Approach. Two-component polymerizations consisting of $1/2/C_2H_4$ or $1/3/C_2H_4$ were initially adjusted to give copolymers that could be characterized by ^{13}C NMR spectroscopy (Table 1).[11] Ethylene gas was introduced into a sealed reactor with the two catalysts, and the consumption of monomer was monitored by a mass flow controller inline with the ethylene feed. To estimate the precatalyst molar ratios, we initially

Table 1. Polymerization by **1/2/3**[a]

| entry | 1:2:3 | branching (%)[b] | | |
		ethyl	butyl	long chain
1	200:0:0	0	0	0
2	200:1:0	0.53	0	0
3	200:0:40	0.27	0.12	0.2
4	200:0:80	0.37	0.13	0.2
5	200:1:40	1.26	0.14	0.1
6	200:1:40	1.40	0.12	0.1
7	200:1:80	2.46	0.50	0.2
8	200:1:80	2.74	0.54	0.2

[a] Conditions: 15 μmol of **1**, 30 mL of toluene, 20 °C, 100 psi C_2H_4, 10 min. [b] Determined by ^{13}C NMR spectroscopy.[11a]

measured the ethylene consumption rate of the individual catalyst systems, that is, $1/C_2H_4$, $2/C_2H_4$, and $3/C_2H_4$, and considered the fact that the consumption of ethylene by the titanium site decreases with increasing 1-alkene concentration. The products were examined by ^1H and ^{13}C NMR spectroscopy, as well as DSC and GPC methods. In Table 1, the % branching corresponds to the number of branched carbons per 100 carbons of the polymer backbone.[12] Only ethyl branches are observed in the $1/2/C_2H_4$ combination (Table 1, entry 2), consistent with the structure of polyethylene-*co*-1-butene.[13] Entries 3 and 4 of Table 1 show that $1/3/C_2H_4$ produces branched polyethylene. The polymer structure, determined by ^{13}C NMR spectroscopy,[11a] is consistent with that shown in Scheme 1, where ethyl (C_2), butyl (C_4), and longer chain branches (C_n, that is, greater than and including hexyl) are observed.[14] The amount of each branch type increases upon increasing the loading of **3** relative to **1** (entries 3 and 4, Table 1). For all of the experiments in Table 1, the total mass of the purified polyethylene product corresponded to at least 95% of the ethylene flow to the reactor measured by the flow meter, demonstrating that the majority of the ethylene was incorporated into the polymer material. There is no evidence (<0.5%) by ^1H or ^{13}C NMR spectroscopy of unreacted olefins in the isolated polymer product.

Three-component polymerizations were first designed on the basis of linear combinations of the two-component systems (Table 1, entries 5−8). Consider entries 5 and 6, which correspond to the combination of entries 2 and 3. The polymer structure contains a $C_2:C_4:C_n$ ratio that cannot be obtained by either of the two-component combinations and shows how a triple component catalyst system can be used to generate novel materials. Entries 7 and 8 demonstrate that increasing the fraction of **3** can substantially increase the presence of C_4 and C_n branches.

A linear combination of two-component catalyst systems does not result in a linear combination of the branching fraction in

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(12) For polymers with branches longer than C_6, there is an overlap of some branch and backbone resonances, which results in an artificially low value for the branch number, see ref 11a.
(13) Ethyl branches give rise to three unique ^{13}C NMR resonances at 26.51, 33.83, and 39.44 ppm corresponding to the ethyl branch methylene ($2B_2$), methylenes α- to the branch (αB_2), and the branch methine (brB_2), respectively.[11a] Integration of these signals as well as the methylene backbone resonance (30.00 ppm) allows for quantitative determination of ethyl branches.
(14) As with ethyl branches, C_4 and C_n branches also give rise to unique resonances in the ^{13}C NMR spectrum. Butyl branches exhibit two unique signals at 23.37 and 33.94 ppm corresponding to branch methylenes next to methine ($4B_4$) and methyl ($2B_2$), respectively.[11a] C_n branches only exhibit one usable resonance from the branch methylene β to the terminal methyl ($3B_n$) at 32.16 ppm. Because only one signal (and therefore one integral) is usable for the quantitation of C_n branches, the errors of the determined values are large, and branching is only reported to one decimal place.
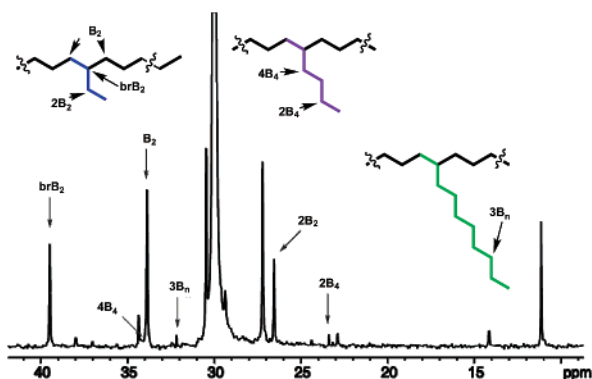
Figure 1. Typical ^{13}C NMR spectrum of a branched polymer produced by action of multiple catalysts.
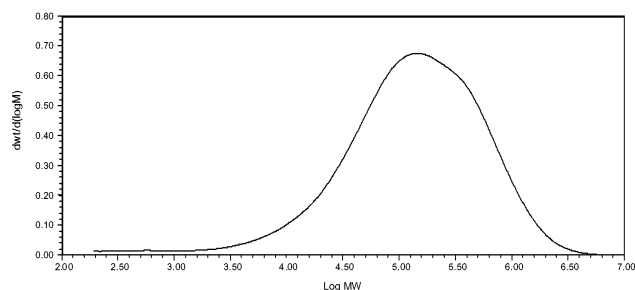
Figure 2. GPC trace of the polymer obtained from the conditions in Table 1, entry 8.

the polymer structure. For example, the sum of the C_2 branches in entries 2 (**1**:**2** = 200:1, 0.53%) and 3 (**1**:**3** = 200:40, 0.27%) is less than the linear combination of the two polymerizations in entry 5 (**1**:**2**:**3** = 200:1:40, 1.26%). Discrepancies of this type may reflect the dependence of the rates of ethylene insertion at the titanium site on the concentration of 1-alkenes, the complex equilibria that exists between the active transition metal and the borate ions,[15] the different rates of initiation at each metal site, differences in rates of insertion of ethylene and α-olefins depending on the identity of the last inserted monomer unit, and the non-steady-state concentration of the monomers.[4]

Practical limitations with the ^{13}C NMR technique are significant. Measuring the number of C_n branches by ^{13}C NMR (Figure 1) is inconvenienced by signal-to-noise problems, even after a prolonged acquisition time (minimum of 12 h). To get the C_n % fraction, one measures the ratio of the backbone peak at 30.00 ppm, relative to the peak labeled $3B_n$ (Figure 1). Correspondingly, there are large standard errors for the value for C_n. Note that small changes in ethyl and butyl branch content can be seen in separate polymerizations under identical conditions, but the lower precision measurement of long chain branches obscures variations in C_n branching (Table 1, entries 5 versus 6 and 7 versus 8).

The GPC trace corresponding to the sample in entry 8 of Table 1 is shown in Figure 2. A broad molecular weight distribution is observed (MWD ≈ 10), together with a small fraction of higher molecular weight polymer. While polymer blends of this type are desirable in some industrial processes,[16] the lack of a single polymer distribution indicates that the cooperative action of the three catalysts is not optimized to generate polymer with a homogeneous structure. It is likely that

at the moment which ethylene enters the reaction cycle the titanium site produces a strictly linear polymer. With increasing reaction time, the concentration of 1-alkenes produced by **2**/C_2H_4 and **3**/C_2H_4 increases, and 1-alkenes begin to incorporate into a growing polymer chain at Ti, until a steady state is reached. Inefficient mixing (limiting the gas uptake rate) exacerbated by the formation of solid polymer, and the inability to inject the catalyst solutions into a preequilibrated system at the desired temperature and pressure, may also contribute to the nonuniform reaction conditions and broad MWD in these experiments.

Ultimately, it proved difficult to design reaction conditions from first principles, primarily because the different precatalysts have different initiation rates. Additionally, the rate of ethylene insertion at the Ti site depends on the substitution of the growing chain in the vicinity of the metal. Different 1-alkenes also display different insertion reactivities, depending on size. The matrix of variables associated with insertion/propagation and relative insertion rates, in conjunction with the time required for ^{13}C NMR analysis, indicated that a different approach, one which would generate a large number of polymerization experiments and resultant polymer structures, was required to attain optimum conditions.

High-Throughput Screening Approach. High-throughput screening techniques in chemistry and biochemistry are widely applied in drug discovery.[17] More recently, they have contributed to developing new organic reactions and novel materials.[18] Reactor technology and software control of reaction conditions continue to improve, and these advances have allowed for tandem polymerizations to be examined using a parallel pressure reactor (PPR).[19] Furthermore, high-throughput polymer characterization (GPC and IR spectroscopy) is now available by robotic assistance.[20] It is possible with this technology to survey very quickly how reaction conditions affect polymer structure. Within one week, it is possible to generate data that would take several months using the linear approach.

The conditions used for the high-throughput screening study were chosen for producing monomodal polymers. Most impor-

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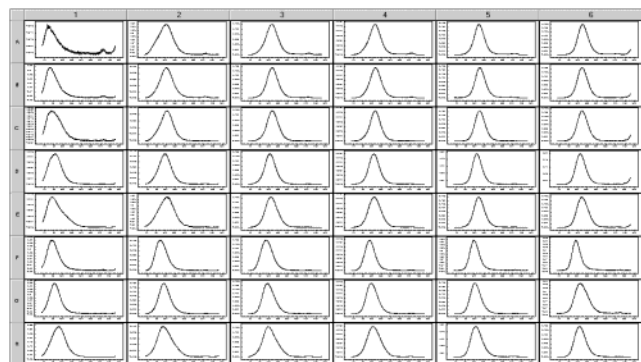
Figure 3. GPC traces from a library of polymers obtained using PPR (*x* axis is retention time; shorter retention time corresponds to higher MW).

tantly, the ability to inject the polymerization catalyst into an equilibrated reactor at high temperature and pressure essentially eliminates the initial production of ethylene homopolymer. High temperature was chosen to improve polymer solubility and minimize biphasic media, which together with a high stirring rate (800 rpm) was chosen to avoid ethylene uptake/diffusion limitations. A small amount of polymethylaluminoxane (PMAO-IP) was used as a scavenging agent for trace (ppm) oxygen and water.[21] Each polymerization reaction was automatically quenched by addition of carbon dioxide once a predetermined ethylene uptake total had been reached, so that stirring would not be obstructed by large quantities of polymer. Conditions with low loadings of **2** and **3** would give a polymer with low comonomer incorporation and therefore low solubility; consequently, the total ethylene uptake limit was set relatively low. Additionally, some polymerizations were carried out after the oligomerization component (**3**) was given more time to build up olefin concentration before injecting **2** and **1**.

On the basis of the measured ethylene consumption rates for **1**, **2**, and **3** under conditions described above, two libraries of polymerizations were carried out covering a range of 50−200 nmol of **1**, 0−10 nmol of **2**, and 0−400 nmol of **3**. Some redundancy was built into the library matrix to determine reproducibility. Two six-by-eight array libraries were obtained in this manner to give a total of 96 polymerizations. Polymers were analyzed by GPC, IR spectroscopy, and DSC. As shown in Figure 3, a large number of the reactions gave monomodal molecular weight distributions. In further discussion, the reactions that gave bimodal distributions and materials with poorly defined melting points will be excluded. Table 2 contains the data for 41 successful triple tandem polymerization reactions. Entries 9 versus 10 and 37 versus 38 show that under identical conditions, separate polymerizations can produce materials that are within 10% difference in the measured properties.

Table 2 also shows that a wide range of materials, with different molecular weights, branching content, and melting

(20) After removal from the reactor, the polymer products were dried to constant weight and characterized using the Symyx Rapid◊GPC system for molecular weight determination, and the Symyx Rapid◊FT-IR technique for a determination of branching content. The Rapid◊GPC technique provided molecular weight data at a rate of 6 min per polymer sample. To ascertain branching content of ethylene-α-olefin copolymers produced in the PPR, we relied on the Rapid◊FT-IR technique, which operates with a throughput of 2 min per sample. Polymer samples were prepared for analysis using liquid handling robots driven by the Symyx Impressionist software.

(21) The presence of the PMAO-IP at such low concentrations did not affect significantly the activities or product distributions of the dimerization (**2**) and oligomerization (**3**) components.

Table 2. High-Throughput Screening Polymerizations Carried out with **1/2/3/**C_2H_4[a]

entry	1 (nmol)	2 (nmol)	3 (nmol)	T (°C)	yield (mg)	activity[b]	T_m (°C)	comonomer % (IR)[c]	MW (/1000)	PDI
1	50	0.00	200	90	85	1690	103	3	1522	3.8
2	50	1.25	100	90	135	13 600	108	6	730	6.0
3	50	2.50	50	90	175	31 400	99	15	326	8.3
4	50	2.50	100	90	138	15 800	102	10	462	6.3
5	50	2.50	200	90	87	3120	67	12	653	5.1
6	50	3.75	0	90	182	56 700	102	19	348	7.5
7	50	3.75	100	90	194	18 300	98	15	470	6.7
8	50	5.00	0	90	216	72 100	104	24	183	7.2
9	50	5.00	50	90	218	38 100	99	40	137	5.7
10	50	5.00	50	90	215	35 800	100	36	135	5.9
11	50	5.00	100	90	232	23 000	95	27	255	5.6
12	50	5.00	200	90	104	4360	71	19	398	6.0
13	100	0.00	200	90	160	5190	116	3	1115	4.0
14	100	1.25	200	90	57	1280	98	8	646	5.5
15	100	1.25	300	90	76	1980	99	7	984	3.7
16	100	2.50	200	90	212	9700	83	13	372	6.9
17	100	3.75	200	90	132	3830	82	15	562	7.1
18	100	5.00	100	90	243	20 000	99	28	183	6.9
19	100	5.00	200	90	240	10 100	79	27	270	6.0
20	100	10.00	100	90	298	24 600	91	46	99	5.2
21	150	1.25	400	90	57	700	95	14	386	6.9
22	200	1.25	300	90	73	1210	96	9	514	6.7
23	200	3.75	300	90	220	3760	84	20	439	7.8
24	200	3.75	400	90	93	1070	80	23	389	7.9
25[d]	50	1.25	100	90	82	4230	88	9	429	5.6
26[d]	50	2.50	100	90	170	10 600	97	19	274	5.9
27[d]	50	3.75	0	90	188	29 100	111	14	344	8.9
28[d]	50	3.75	50	90	97	7630	67	21	422	4.0
29[d]	50	5.00	0	90	225	39 400	103	28	187	6.5
30[d]	50	5.00	50	90	228	21 500	97	42	146	4.9
31[d]	100	1.25	300	90	122	1700	89	11	691	7.3
32[d]	100	2.50	200	90	186	5350	101	15	341	7.8
33[d]	100	2.50	300	90	153	2470	89	15	509	8.5
34[d]	100	5.00	100	90	265	12 000	105	29	169	6.2
35[d]	200	1.25	300	90	210	3440	97	14	467	6.6
36[d]	200	1.25	400	90	166	1880	85	13	576	6.9
37	50	5.00	50	110	192	35 400	96	25	75	4.0
38	50	5.00	50	110	185	32 700	98	23	78	3.9
39	50	5.00	100	110	193	20 800	82	20	111	3.4
40	100	5.00	100	110	223	20 000	100	17	101	4.6
41	100	5.00	200	110	185	9060	89	19	199	5.0

[a] Polymerization conditions: 100 psig C_2H_4, 90 °C, 5.9 mL of toluene. Injection sequence: **3**, delay 25 s, **2**, delay 100 s, **1**. [b] Kg polymer produced per total moles of catalysts per hour of total reaction time. [c] Average total comonomer incorporation in the polymer sample. Measured by IR calibrated against known branch numbers for polyethylene-*co*-1-octene samples. [d] 200 s delay between injection of **3** and **2**.
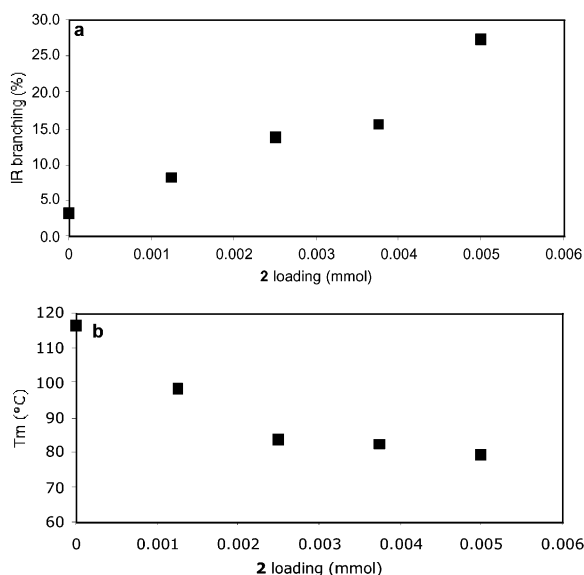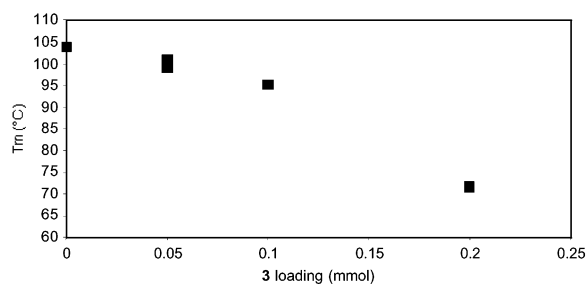
points, can be obtained *directly from ethylene* by simple variations in catalyst combinations. It is possible to extract trends within this data set. Figure 4 (Table 2, entries 2, 4, 7, and 11) shows that increasing [**2**], while keeping [**1**] and [**3**] constant, produces (a) polymers with higher comonomer incorporation and (b) lower melting points. Similar observations are made at higher initial [**1**] and [**3**] (Figure 5 a and b; Table 2, entries 13, 14, 16, 17, and 19). When examining a set of reactions in which [**3**] is increased with constant [**1**] and [**2**] values, one sees a very fast decline in the melting temperature of the material (Figure 6; Table 2, entries 8, 9, 10, 11, and 12). Figure 7 shows the stirrers from a parallel reactor experiment wherein the branching content of the polymer was varied along the vertical direction of the photograph. The polymer becomes more viscous and adheres to the surface as the branching decreases (toward the top of the photograph). Altogether, these observations confirm that the three catalysts act together in a predictable manner and give a single polymer product.

Figure 4. (a) Polymer branching content and (b) melting point versus [**2**]. Loading of **1** = 50 nmol, **3** = 100 nmol. Total volume = 5.9 mL.

Figure 5. (a) Polymer branching content and (b) melting point versus [**2**]. Loading of **1** = 100 nmol, **3** = 200 nmol. Total volume = 5.9 mL.

Figure 6. Polymer melting point versus loading of oligomerization component (**3**). Loading of **1** = 50 nmol, **2** = 5.00 nmol. Total volume of solution = 5.9 mL.

Summary Discussion

In summary, it is possible to combine three homogeneous catalysts to produce products with complex molecular structures from a simple starting material. The composition of the catalyst mixture influences the properties of the polyethylene produced in a reproducible manner. It should be possible with this

Figure 7. Photograph of the stirrers from a parallel reactor which shows the difference in solubility of different polymers produced as the percentage branching increases, as the loading of the oligomerization catalyst (**3**) is increased from zero (top reactor) to 400 nmol (bottom reactor). The photograph was taken after the reactors were cooled and vented.

approach to generate many branched polyethylenes with properties that are tailored for specific applications by simply adjusting the composition of the catalyst mixture. High-throughput reaction and characterization techniques facilitate substantially the search for optimum reaction conditions, to the point where they are essential for the successful implementation of the tandem catalysis concept.

Experimental Section

General Details. All manipulations were carried out in an inert atmosphere of argon or nitrogen using standard glovebox and Schlenk techniques.[22] Compounds **1**,[23] **2**,[4] and **3**[9] were prepared according to literature procedures. Tris(pentafluorophenyl)borane was purchased from Aldrich Chemical Co., Milwaukee, WI, and was sublimed under high vacuum prior to use, or was purchased from Boulder Scientific Co., Mead, CO, and was used without further purification. Toluene was distilled from sodium/potassium alloy or passed over purification columns to remove traces of oxygen and water.

Typical Polymerization Reaction. Polymerizations were typically carried out by charging a Fisher-Porter bottle with toluene and the desired amounts of each catalyst in a glovebox under an inert atmosphere. The reaction vessel would then be sealed, brought out of the glovebox, and placed in a water bath. Ethylene gas was introduced to the reaction, and the consumption of monomer was monitored by a mass flow controller inline with the ethylene feed. At the end of the reaction, the ethylene feed was removed, the vessel was vented, and the reaction was quenched with acetone. The polymers produced were isolated by filtration and washed several times with acetone. This helps to precipitate any soluble polymer as well as wash out the less volatile toluene solvent. Polymers were dried overnight under vacuum, and the polymerization activities were calculated from the mass of product obtained and compared to the values measured by the mass flow controller. The polymer structures were probed by ^{1}H and ^{13}C NMR as well as DSC and GPC. To estimate suitable precatalyst molar ratios, we initially measured the ethylene consumption rate of the individual catalyst systems, that is, $\mathbf{1}/C_2H_4$, $\mathbf{2}/C_2H_4$, and $\mathbf{3}/C_2H_4$, and considered the fact that the consumption of ethylene by the titanium site decreases with increasing 1-alkene concentration.

(22) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society, Washington, D.C., 1987.
(23) Lai, S.-Y.; Wilson, S. R.; Knight, G. W.; Stevens, J. C.; Chun, P.-W. S. U.S. Patent 5,272,236, 1993.

Description of Software for High-Throughput Screening. The successful implementation of a high-throughput synthesis and screening program requires the development of sophisticated software tools. The process begins at the library design phase, where the amounts of each reagent used in the formulation of the 48-well-array have to be calculated on the basis of information that is stored in a database (such as molecular weight, concentrations, etc.). This tool allows the chemist to visualize the amounts of each reagent to be added to the vials to readily visualize the design of the library. Symyx Technologies has developed a powerful library design tool (Library Studio) for this purpose. A recipe file exported from the library design software is read by Symyx's in-house designed robot-control software (Impressionist) and translated into a series of instructions to the liquid-dispense robot for catalyst component mixing and injection into the Parallel Pressure Reactor.

High-Throughput GPC and FT-IR Analysis. After being removed from the reactor, the polymer products were dried to constant weight and characterized using the Symyx Rapid◊GPC system for molecular weight determination, and the Symyx Rapid◊FT-IR technique for a determination of branching content.

High-temperature size exclusion chromatography (also known as gel permeation chromatography, "GPC") was performed using an automated Symyx Rapid◊GPC system as described in U.S. patents 6,175,409, 6,260,407, and 6,294,388. A series of two 30 cm × 7.5 mm linear columns were used, with one column containing PLgel 10 μm, MixB and the other column containing PLgel 5 μm, MixC (available from Polymer Labs). The GPC system was calibrated using narrow polystyrene standards. The system was operated at an eluent flow rate of 1.5 mL/min and an oven temperature of 160 °C. *o*-Dichlorobenzene was used as the eluent. The polymer samples were dissolved in 1,2,4-trichlorobenzene at a concentration of about 1 mg/mL. Between 40 and 200 μL of a polymer solution was injected into the system. The concentration of the polymer in the eluent was monitored using an evaporative light scattering detector. All of the molecular weight results obtained are relative to linear polystyrene standards. The Rapid◊GPC technique provided molecular weight data at a rate of 6 min per polymer sample.

To ascertain branching content of ethylene-α-olefin copolymers produced in the PPR, we relied on the Rapid◊FT-IR technique, which operates with a throughput of 2 min per sample. Polymer samples were prepared for analysis using liquid handling robots driven by the Symyx Impressionist software. An estimate of the comonomer incorporation is based on comparing the ratio of band heights at 4330 cm^{-1} (third overtone of CH bending mode of methylene groups) and 1378 cm^{-1} (methyl deformation mode) to the ratios obtained using a training set of polymer standards with known branch quantities.

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