Influence of Trialkylaluminum Reagents on the Propylene Polymerization Behavior of Bridged and Unbridged 2-Arylindene Metallocene Polymerization Catalysts

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ABSTRACT: Trialkylaluminum reagents such as triisobutylaluminum (TIBA) and trimethylaluminum (TMA) influence the propylene polymerization behavior of methylaluminoxane (MAO)-activated dimethylsilyl[bis(2-phenylindenyl)]zirconium dichloride (**1**). TIBA selectively decreases the productivity of the meso diastereomer of **1** (**1-meso**). This is manifested in an increase in the isotacticity of polypropylene blends prepared from mixtures of **1-rac** and **1-meso** compared to polymer blends prepared in the absence of TIBA. In contrast, added trimethylaluminum decreases the productivity of both **1-rac** and **1-meso**. Similar trends in reactivity with AlR_3 are observed for unbridged bis(2-phenylindenyl)zirconium dichloride (**2**) compared to a mixture of the bridged catalysts containing 57% **1-rac**. Mechanical testing indicates that polypropylene from **2** has superior elastomeric properties to reactor blends prepared from mixtures of **1-rac** and **1-meso** in the presence and absence of trialkylaluminum reagents. Reactor blends prepared without AlR_3 exhibit poorer recovery at 100% and 300% strain than that of the elastomeric polypropylene from **2**. The reactor blends prepared in the presence of TIBA exhibit pronounced yielding and necking during testing, characteristic of a softened plastic.

Introduction

Isotactic polypropylene is a highly crystalline thermoplastic, whereas atactic polypropylene is an amorphous material.[1] Elastomeric forms of polypropylene are also known; Natta et al. were the first to isolate an elastomer of propylene as a heptane-soluble/isopropyl ether-insoluble fraction produced over certain heterogeneous Ti- and V-based catalysts at high temperature.[2−4] Natta et al. attributed the elastomeric properties of this fraction to an isotactic−atactic stereoblock microstructure.[2−4] More recently, Collette and co-workers observed that elastomeric polypropylene could also be obtained using supported tetralkyl group IVB catalysts.[5,6] The elastomeric properties of this material were attributed to the cocrystallization between a low crystallinity, diethyl ether-soluble component and a higher tacticity component. In 1990, Chien and co-workers reported a metallocene system that produces elastomeric polypropylene.[7−9] This catalyst was derived from a stereorigid titanocene that was proposed to alternate between aspecific and isospecific metallocene coordination sites, although other interpretations have been suggested.[10,11] Collins and co-workers reported a 3-methyl-substituted *ansa*-zirconocene that also produces elastomeric polypropylene.[12] Bis(2-arylindenyl)zirconium dichlorides, when activated by methylaluminoxane (MAO), yield a family of elastomeric polypropylenes.[13−21] In this case, the fluxional metallocene catalysts are proposed to interconvert between isospecific and aspecific geometries on the time scale of growth of a single polypropylene chain.

Physical blends of isotactic and atactic polypropylene in general do not exhibit elastomeric properties.[22,23] However, examples have recently appeared that report the preparation of elastomeric blends under certain conditions.[22,24] Collette et al. had proposed that the elastomeric properties of polypropylenes prepared from ZrR_4/Al_2O_3 arose from a high-molecular-weight amorphous fraction that cocrystallized with a more highly isotactic fraction.[5,6] Canich and co-workers reported that blends of low-molecular-weight isotactic polypropylene and high-molecular-weight atactic polypropylene produced from an appropriate combination of metallocene catalysts exhibited elastomeric properties.[24] Chien and co-workers recently observed that a mixture of isospecific and aspecific metallocenes in the presence of a trityl borate activator and a large excess of triisobutylaluminum produced elastomeric polypropylene reactor blends.[22] The elastomeric properties of the latter material were attributed to the presence of a small amount of a stereoblock component.

Trialkylaluminum reagents have a number of effects on homogeneous metallocene mediated α-olefin polymerizations. Such species can alkylate catalyst precursors,[25−28] scavenge trace impurities present in the monomer feed,[25,29,30] and act as chain transfer agents.[25,31] Additionally, trialkylaluminum reagents can be used to activate metallocenes fixed on inorganic supports (methylaluminoxane is not required in this case).[32−36] Complexes between trialkylaluminum species and neutral[37] or cationic[38,39] zirconocenes have been observed. Such heterobimetallic complexes can significantly curb polymerization productivity.

As part of our ongoing investigations on the synthesis of elastomeric polypropylene using unbridged zirconocenes (Scheme 1),[13−21] we report here our studies of the influence of trialkylaluminum reagents on the polymerization behavior of bridged[40] and unbridged 2-arylindene metallocenes as well as selected properties of the resulting polymers.

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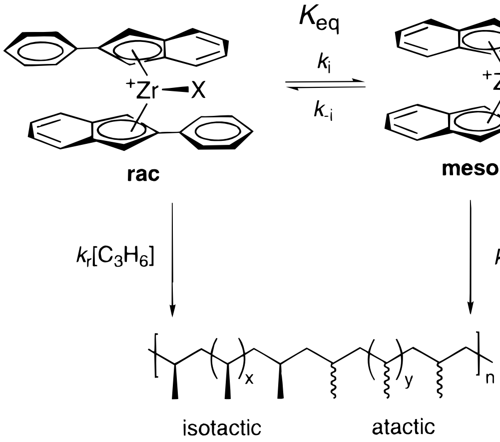
Scheme 1



Results

Propylene polymerizations utilizing *rac*- and *meso*-dimethylsilyl[bis(2-phenylindenyl)]zirconium dichloride (**1**) were run in liquid propylene in the presence of trialkylaluminum reagents. Metallocene stock solutions were prepared for polymerizations using the individual isomers to promote reproducible productivity measurements between runs.[40] When mixtures of **1-rac** and **1-meso** were used in polymerizations, the metallocene was weighed out discretely for each run and added to solid MAO prior to dissolution. This method was used to ensure reproducible characteristics of the polymer blends as measured by ^{13}C NMR, IR, and DSC.[40] The trialkylaluminum compound was added to the stirring metallocene/MAO-activated catalyst solution, and then, polymerization was carried out as described previously.[40]

Propylene polymerizations using **1-rac** or **1-meso** were run in the presence of a large excess of triisobutylaluminum (TIBA, [TIBA]/[Zr] = 1000) and MAO ([MAO]/[Zr] = 1000). The productivity of **1-meso** decreased by a factor of 2, whereas **1-rac** showed comparable productivity under these conditions compared to polymerizations run in the absence of TIBA (Table 1). Polymerizations were also run in the presence of trimethylaluminum (TMA, [TMA]/[Zr] = 100) and MAO ([MAO]/[Zr] = 1000). Productivity decreased markedly for both **1-rac** and **1-meso** compared to polymerizations run in the absence of TMA (Table 1).

The isotacticity of polymers produced by **1-rac** and **1-meso** as indicated by the isotactic pentad content (%mmmm) measured by ^{13}C NMR and IR indices[41] (A_{998}/A_{974}) is comparable for polymers produced in the presence and absence of trialkylaluminum reagents. The melting temperatures and ΔH_f for polymers produced from **1-rac** in the presence and absence of trialkylaluminum reagents are similar (Table 1).

The molecular weights of the polypropylenes produced were measured by gel permeation chromatography (GPC) versus polypropylene standards (Table 1). Both the number-average (M_n) and weight-average (M_w) molecular weights increased by a factor of 2 for polymers prepared with **1-meso** in the presence of TIBA compared to polymers prepared in the absence of TIBA. Polymers produced from **1-rac** showed a slight decrease in M_n and M_w when TIBA was introduced to the polymerization system. When **1-rac** and **1-meso** were utilized in polymerizations with added TMA, the molecular weights of the resulting polymers decreased compared to polymers prepared with no TMA in the reaction mixture.

Mixtures of **1-rac** and **1-meso** were utilized for propylene polymerizations run in the presence of trialkylaluminum reagents (Table 2). At identical catalyst compositions, polymer blends produced in the presence of TIBA exhibited higher isotacticity than that of polymers obtained in the absence of TIBA (Table 2). Polymer blends prepared in the presence of TMA did not exhibit a clear-cut trend in isotacticity when compared to polymers prepared in the absence of TMA (Table 2).

Polypropylene blends prepared from mixtures of **1-rac** and **1-meso** in the presence of TIBA and TMA were fractionated using refluxing hexanes. The hexanes-soluble material was identical to that obtained from polymerizations using **1-meso** alone. The hexanes-insoluble material was the same as polypropylene from **1-rac** alone as determined by ^{13}C NMR and IR.

The DSC profiles of polypropylene blends prepared in the presence and absence of TIBA exhibited similar melting temperatures, although the magnitude of the heat of fusion (ΔH_f) was higher in polymer blends produced in the presence of TIBA (Table 2). The heat of fusion measured for polymer blends prepared in the presence of TMA was consistent with values expected based on the observed %mmmm (Table 2).

In the presence of MAO, unbridged bis(2-phenylindenyl)zirconium dichloride (**2**) yields elastomeric polypropylene.[13] When a mixture of the bridged metallocenes **1-rac** and **1-meso** (%rac = 57) was used for polymerizations, polypropylene blends were produced with isotacticities that matched the polymer from **2** in terms of ^{13}C NMR and IR data as well as the amount of isotactic material present.[40] When TIBA was introduced into the system, both **1** and **2** yielded polypropylenes with higher %mmmm than specimens prepared in the absence of TIBA (Figure 1; Table 2). In the presence of TMA, both **1** and **2** produced polypropylene with lower %mmmm relative to polymers prepared in the absence of TMA (Figure 1; Table 2).

Elastomeric polypropylenes prepared from **2** in the presence and absence of AlR_3 were fractionated using refluxing hexanes (Table 3). The amount of and %mmmm observed for the hexanes-insoluble fraction made in the presence of TIBA was larger than for polymers produced in the absence of TIBA. In contrast, polymers prepared in the presence of TMA were almost entirely hexanes soluble.

The mechanical properties of the polypropylene blends produced from mixtures of **1-rac** and **1-meso** were measured using reported test methods (Table 4).[42,43] The results were compared to values obtained for elastomeric polypropylene from **2** (Table 2, entry 19). Reactor blends prepared in the absence of trialkylaluminum reagents (Table 2, entries 10 and 13) exhibited a lower strain to break than the polypropylene (Table 2, entry 19) from **2** (Table 4; Figure 2). The tensile modulus was considerably higher for these reactor blends than for the elastomeric polypropylenes from **2** (Table 4: 57 and 83 MPa vs 19.8 MPa). These reactor blends exhibited a higher cumulative percentage set[44] (measured after two cycles of 100% strain) than the polypropylene from **2** (%set = 48−49% vs 16%; Table 4; Figure 3). The percent set following the 300% strain test was very high for the reactor blends (set = 115−275%) compared to the material from **2** (set = 45%) (Table 4; Figure 4). After

Table 1. Summary of Polymerization Results Using 1-rac and 1-meso

entry	catalyst	AlR_3	yield (g)	prod.[a]	%mmmm[b]	%m[b]	M_w[c]($\times 10^{-3}$)	M_w/M_n	IR index	T_m (°C)	ΔH_f (J/g)
1	**1-rac**[d]		4.1	2436	87	96	443	3.3	0.9	139	70.0
2	**1-rac**[e]	TIBA[f]	3.5	2063	84	96	338	2.9	0.9	138	61.3
3	**1-rac**[e]	TMA[g]	1.8	1075	88	97	107	2.6	0.9	140	76.3
4	**1-meso**[d]		6.7	4034	6.5	49	156	2.2	0.2		
5	**1-meso**[e]	TIBA	2.9	1730	7.4	50	460	2.4	0.2		
6	**1-meso**	TMA	3.8	2286	6.6	48	74.2	2	nd[h]		

[a] Kilograms of polypropylene per mole Zr per hour. [b] Determined by ^{13}C NMR spectroscopy. [c] Determined by gel permeation chromatography versus polypropylene standards. [d] Values reported are the average of three polymerizations. [e] Values reported are the average of two polymerizations. [f] 1000 equiv. [g] 100 equiv. [h] nd = not determined. Polymer is too sticky to press a film.

Table 2. Summary of Polymerization Results Using Mixtures of 1-rac and 1-meso

entry	% rac	AlR_3	yield (g)	prod.[a]	%mmmm[b]	%m[b]	M_w[c] ($\times 10^{-3}$)	M_w/M_n	IR index	T_m (°C)	ΔH_f (J/g)
7	24		3.5	2082	26	60	304	2.6	0.3	138	13.2
8	24	TIBA[d]	1.7	1038	34	65	388	2.8	0.5	138	15.1
9	24	TMA[e]	2.4	1410	17	57	61.9	2.3	0.3	141	9.4
10	57		5.3	3172	39	69	312	3.3	0.5	138	26.1
11	57	TIBA	4.5	2718	70	86	354	2.7	0.7	139	54.8
12	57	TMA	4.5	1644	24	59	94.2	2.3	0.4	139	32.8
13	61		5.2	3052	45	73	345	3.4	0.6	138	28.7
14	61	TIBA	6.2	3714	72	nd[f]	339	2.9	0.9	138	55.8
15	61	TMA	1.9	1164	44	nd	98.9	2.5	0.6	138	30.7
16	75		4.5	2680	57	nd	374	3.9	0.6	139	49.9
17	75	TIBA	2.8	1662	72	nd	347	2.8	0.9	138	58.5
18	75	TMA	1.8	1050	70	nd	111	3.0	0.8	140	68.3
19	2PhInd[g]		4.6	2756	39	73	502	3.6	0.5	138	14.6
20	2PhInd	TIBA	3.3	1981	47	78	325	5.0	0.5	144	22.3
21	2PhInd	TMA	2.9	1739	19	61	230	2.9	0.5	135	8.4

[a] Kilograms of polypropylene per mole Zr per hour. [b] Determined by ^{13}C NMR spectroscopy. [c] Determined by gel permeation chromatography versus polypropylene standards. [d] 1000 equiv. [e] 100 equiv. [f] nd = not determined. [g] 2PhInd = bis(2-phenylindenyl)zirconium dichloride.

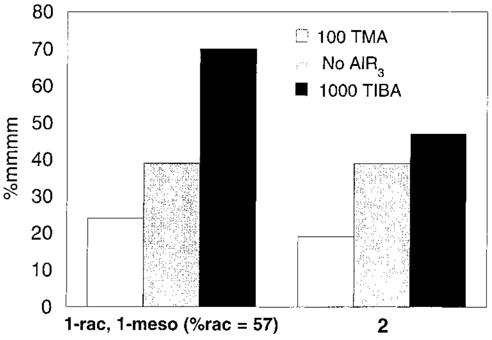


Figure 1. %mmmm of stereoblend polypropylene (from **1** containing 57% **1-rac**) and elastomeric polypropylene (from **2**) in the presence and absence of AlR_3 (R = *i*Bu, CH_3).

Table 3. Summary of Fractionation Studies of Polypropylene Prepared from 2

catalyst	AlR_3	fractions	amount (%)	%mmmm[a]
2PhInd[b]		hexanes soluble	72	25
		hexanes insoluble	28	67
2PhInd	TIBA[c]	hexanes soluble	60	29
		hexanes insoluble	40	74
2PhInd	TMA[d]	hexanes soluble	96	17
		hexanes insoluble	4	55

[a] Determined by ^{13}C NMR spectroscopy. [b] 2PhInd = bis(2-phenylindenyl)zirconium dichloride. [c] 1000 equiv. [d] 100 equiv.

testing, the reactor blend specimens had a "crinkled" set in the gauge area of the specimens, i.e., a wavy shape set in the specimens. This indicates that the samples deformed and recovered nonuniformly.

Reactor blends prepared in the presence of trialkylaluminum reagents were also tested (Table 4). Material prepared in the presence of TMA (Table 2, entry 15) failed at low elongation in tensile tests (5% strain). A reactor blend prepared in the presence of TIBA (Table 2, entry 8) exhibited lower strain to break than those of elastomeric polypropylene from **2** and reactor blends from **1** prepared in the absence of TIBA (Table 4; Figure 2). The tensile modulus measured for this reactor blend was over 5 times that measured for the polypropylene from **2** (Table 4: 262 vs 19.8 MPa). The polymer blend prepared in the presence of TIBA exhibited pronounced yielding and necking during tensile tests (Table 4; Figures 2−4). The cumulative %set[44] measured after two cycles of 100% strain was 82%, a value markedly higher than that observed for the polypropylene from **2** and reactor blends prepared without TIBA.

Discussion

For polymerizations run with **1-rac** or **1-meso** individually in the presence of TIBA, the productivity of **1-meso** is curbed by nearly a factor of 2 and that of **1-rac** is essentially unaffected by the trialkylaluminum reagent (Table 1). This inequivalent effect on **1-rac** and **1-meso** may be due to the geometric placement of the bulky 2-phenyl substituents. For **1-rac**, both sides of the molecule are congested by a phenyl group that hinders TIBA (or species derived from it)[45] from effectively interacting with this isomer. For **1-meso**, both phenyl substituents are localized on one side of the molecule that could allow access to TIBA derived species from the other, more open side. Coordination of TIBA to the cationic zirconocene is expected to slow monomer insertion (by steric blocking of the polymerization active sites), thus giving rise to the observed decrease in productivity in the presence of TIBA. In contrast, TMA appears to reduce the productivity of both **1-rac** and **1-meso** by a similar magnitude. In this case, it appears that TMA can interact with both isomers despite the presence of the 2-phenyl substituent. Polymerizations run with mixtures of **1-rac** and **1-meso** in the presence

Table 4. Mechanical Properties of Polypropylene Samples

sample	EHPP[a]	*i*PP/aPP[b]	*i*PP/aPP/2[b]	*i*PP/aPP + TIBA[c]
%mmmm	39	39	45	34
tensile strength (MPa)	14.4	13.0	14.5	25.2
tensile modulus (MPa)	19.8 ± 1.2	57 ± 12	83 ± 9	262 ± 7
strain to break (%)	890 ± 48	715 ± 65	610 ± 110	437 ± 226
yield stress (MPa)		8.3	11.0	25.2
yield strain (MPa)		48	40	19.0
%set, 300% strain test[d]	45	115–200	275	na[e]
three cycles, 100% strain test:[f] %set, cumulative after first and second cycles	16	48	49	82

[a] Elastomeric polypropylene from **2**. This sample did not exhibit a yield point. [b] Reactor blend of isotactic and atactic polypropylene from a mixture of **1-rac** and **1-meso**. [c] Reactor blend prepared in the presence of triisobutylaluminum. [d] After recovery from 300% elongation; no hold at extension. Set values are based on benchmarks measured on specimen, approximately 30–60 s after beginning of test (immediate set). [e] na = not applicable, due to necking. [f] Three extension cycles to 100% elongation, 30 s hold at extension, 60 s at recovery. Set values are based on strain at which stress exceeds baseline on third extension.

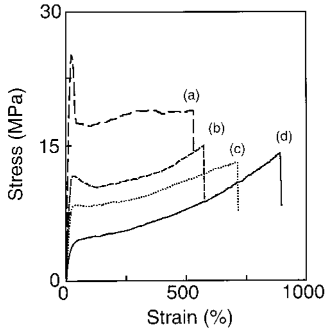


Figure 2. Strain at break for polypropylene reactor blends prepared (a) in the presence of TIBA (%mmmm = 34), (b) in the absence of AlR$_3$ (%mmmm = 45), and (c) in the absence of AlR$_3$ (%mmmm = 39). For comparison, (d) illustrates the behavior of polypropylene prepared with **2** and no AlR$_3$ (%mmmm = 39).

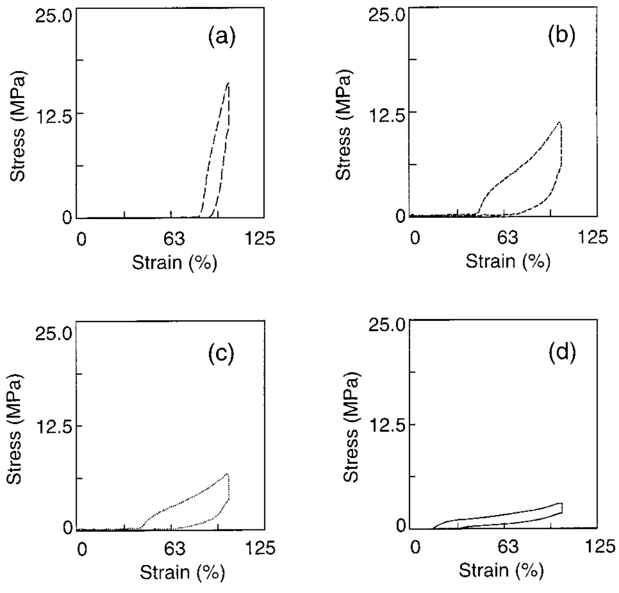


Figure 3. % set in the three-cycle 100% strain test for polypropylene reactor blends prepared (a) in the presence of TIBA (%mmmm = 34), (b) in the absence of AlR$_3$ (%mmmm = 45), and (c) in the absence of AlR$_3$ (%mmmm = 39). For comparison, (d) illustrates the behavior of polypropylene prepared with **2** and no AlR$_3$ (%mmmm = 39).

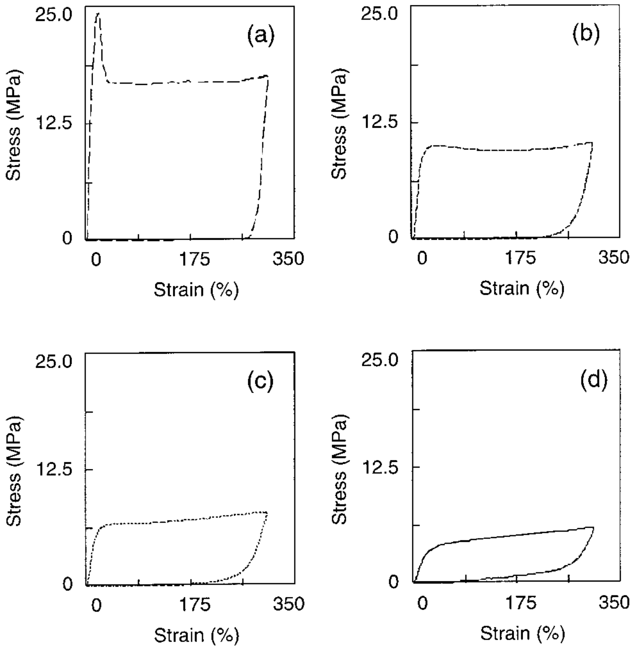


Figure 4. % set in the 300% strain test for polypropylene reactor blends prepared (a) in the presence of TIBA (%mmmm = 34), (b) in the absence of AlR$_3$ (%mmmm = 45), and (c) in the absence of AlR$_3$ (%mmmm = 39). For comparison, (d) illustrates the behavior of polypropylene prepared with **2** and no AlR$_3$ (%mmmm = 39).

of TIBA produce polypropylene blends with higher isotacticities than blends prepared in the absence of TIBA (Table 2), as might be expected from the selective reduction in productivity of **1-meso** relative to **1-rac**. As a result of this effect, reactor blends of similar average structure (Table 2, entries 8 and 10) were produced with either a 24:66 ratio of **1-rac**:**1-meso** in the presence of TIBA or a 57:43 ratio of **1-rac**:**1-meso** without added TIBA (note however that the properties of these blends are different).

Reactor blends prepared from stereorigid catalysts **1-rac** and **1-meso** and the elastomeric polypropylene from unbridged catalyst **2** exhibit different mechanical properties (Table 4; Figures 2–4). In particular, the tensile moduli measured for the reactor blends are higher than those measured for elastomeric polypropylene from **2** (Table 4). This indicates that despite the similar average isotacticity measured by ^{13}C NMR (Table 2), the reactor blends have a much higher content of long isotactic segments capable of crystallization.

Fractionation studies indicate that reactor blends prepared in the presence and absence of AlR$_3$ are both physical mixtures of isotactic and atactic polypropylene. However, the mechanical properties of the blends depend on whether AlR$_3$ was present in the polymerization mixture (Table 4; Figures 2–4). The properties of the blends also depend on the identity of the added trialkylaluminum reagent. The poor mechanical properties of the blend prepared in the presence of TMA is likely due to the low molecular weight of the material (Table 2, entry 15). The molecular weights and molecular weight distributions measured for reactor blends prepared with and without TIBA are similar (Table 2), but the molecular weights of the isotactic (with TIBA: M_w = 338 000; without TIBA: M_w = 443 000) and atactic (with TIBA: M_w = 460 000; without TIBA: M_w = 156 000) components are distinct (Table 1). Collette observed in his investigation of elastomeric polypropylene reactor blends that the molecular weight of the amorphous component plays an important role in determining the mechanical properties of the polymer.[5] He found that the molecular weight of the amorphous, ether-soluble component must be greater than M_w = 250 000 to create an effective elastomeric network when blended with isotactic polypropylene.[5] For the reactor blends studied here, the amorphous component exhibits M_w = 156 000 when no AlR_3 is present.[46] This material exhibits a tensile set in the 300% strain test between 115 and 200% (Table 4). This range is consistent with that observed by Collette et al. for blends with an amorphous component of similar molecular weight.[5] The molecular weights of the amorphous component of the reactor blends appear to increase in the presence of TIBA (Table 1). On the basis of this factor alone, blends prepared in the presence of TIBA are expected to exhibit better recovery properties than blends prepared in the absence of TIBA.[5] However, the recovery properties of the blend prepared with TIBA are clearly worse than those measured for the reactor blends prepared in the absence of AlR_3 (Table 4). The material prepared with TIBA is clearly not elastomeric, indicating that factors other than the molecular weight of the amorphous component must be important in determining the mechanical properties of polypropylene blends.

Polymerizations run with **1** and **2** in the presence of AlR_3 reagents exhibit similar trends in %mmmm (Figure 1). However, the absolute magnitude of the effect differs for **1** and **2**. This could be caused by changes in ligand rotation rate, equilibrium concentration of **2-rac** and **2-meso**, or monomer insertion rates for **2-rac** and **2-meso** due to interaction with the trialkylaluminum reagent (Scheme 1). Similarity in catalyst behavior between the bridged and unbridged complexes supports the hypothesis that the unbridged system operates in both rac and meso modes. These observations also support the use of this *ansa*-metallocene system as a representative model for the polymerization behavior of the unbridged catalyst system.[40]

Conclusions

Trialkylaluminum reagents influence the polymerization behavior of dimethylsilyl[bis(2-phenylindenyl)]-zirconium dichloride (**1**) and unbridged bis(2-phenylindenyl)zirconium dichloride (**2**). Triisobutylaluminum interacts preferentially with **1-meso** to decrease the productivity of this catalyst in MAO-activated propylene polymerizations. Trimethylaluminum curbs the productivity of both **1-meso** and **1-rac**. Polymerizations run using mixtures of **1-rac** and **1-meso** corroborate these trends in productivity as evidenced by modified %mmmm compared to materials prepared without trialkylaluminum reagents. A similar effect on isotacticity is observed when **2** is used in polymerizations in the presence of TIBA and TMA. The similar reactivity patterns of **1** and **2** support the use of these bridged catalysts as models for the polymerization behavior of the unbridged analogue.

Physical tests indicate that the reactor blends exhibit inferior elastomeric properties compared to those of polypropylene derived from the unbridged catalyst **2**. Reactor blends prepared without AlR_3 exhibit recovery properties consistent with those reported by Collette for reactor blends with an amorphous component of similar molecular weight. Reactor blends prepared in the presence of TIBA exhibit clear yielding and necking behavior upon elongation.

Experimental Section

Toluene and liquid propylene were passed over towers containing Q5 and alumina prior to use. **1**[40] and **2**[13] were prepared by procedures described previously. Methylaluminoxane (MMAO Type 4) was obtained from Akzo Nobel as a toluene solution and was dried in vacuo to give a white solid. TIBA and TMA were obtained from Aldrich and were used as received. Polymerizations were carried out in a 300 mL stainless steel Parr reactor equipped with a mechanical stirrer. Temperature was maintained at 20 °C via an ethylene glycol/water cooling loop.

Preparation of Activated Catalysts for Polymerizations Utilizing 1-rac or 1-meso. Metallocene stock solutions were prepared by dissolving 2.5×10^{-5} mol of zirconocene in 25 mL of toluene in an N_2 drybox. Gentle warming was required to bring all the material into solution. After letting the stock solution cool to room temperature, a 5 mL aliquot was added to 294 mg MAO dissolved in toluene. The AlR_3 reagent was added to the stirring metallocene/MAO solution such that the volume of AlR_3 + toluene = 25 mL.

Preparation of Activated Catalysts for Polymerizations Utilizing Mixtures of 1-rac and 1-meso. Batches of solid mixtures (about 50 mg) with a fixed ratio of **1-rac/1-meso** were prepared by adding toluene to an appropriate mixture of **1-rac** and **1-meso**. The solvent was then removed from the stirring mixture in vacuo. The ratio of isomers was confirmed by integration of the $SiMe_2$ proton resonances obtained by ^1H NMR. Only one scan was acquired for each spectrum to ensure accuracy of integral measurement. Catalyst solutions were prepared in an N_2 drybox by dissolving 294 mg of MAO and 5×10^{-6} mol of metallocene in toluene. The AlR_3 reagent was added to the stirring metallocene/MAO solution such that the volume of AlR_3 + toluene = 25 mL.

Propylene Polymerization in Liquid Propylene. The reactor was flushed three times with 50 psig of N_2. Liquid propylene (100 mL) was then introduced. The catalyst solution was injected into the reactor under 200 psig of N_2 to start the reaction. Polymerizations were allowed to proceed for 20 min and then were quenched with 15 mL of methanol injected under N_2 pressure. The reactor was vented, and the polymers were collected and precipitated into acidified methanol (5% HCl). After being stirred overnight, the polymers were washed with methanol and dried in a vacuum oven at 40 °C.

Polymer Characterization. Number- and weight-average molecular weights (M_n and M_w) were obtained using a Waters 150C High-Temperature Chromatograph. Samples were run in 1,2,4-trichlorobenzene at 139 °C using two Polymer Laboratories PL GEL Mixed-B columns at a flow rate of 1 mL/min. %mmmm was determined via ^{13}C NMR spectra recorded at 75.425 MHz on a Varian UI 300 spectrometer at 100 °C using 10 mm sample tubes. Samples were prepared in 1,1,2,2-tetrachloroethane containing about 0.5 mL of d_2-1,1,2,2-tetrachloroethane. IR spectra were obtained from polypropylene films on a Perkin-Elmer 1600 Series FTIR. DSC traces were acquired on a Perkin-Elmer DSC 7. Samples were annealed at 180 °C for 10 min, followed by cooling to 50 °C for polymer blends (−30 °C for block copolymers), and then reheating to 180 °C. The cycle was then repeated. All temperature scans were carried out at 10 °C/min. Two samples of each polymer were run to ensure that the measured numbers were reproducible.

Fractionation Studies. Polypropylene (300−1000 mg) produced from **2** or from mixtures of **1-rac** and **1-meso** was measured into an extraction thimble. The material was extracted into refluxing hexanes under argon for 24 h. The hexanes-soluble material was reprecipitated into methanol. Both fractions were then dried in a vacuum oven at 40 °C.

Mechanical Measurements. Tensile and recovery tests were performed with ASTM D-1708 dumbell specimens (0.9 in. gauge length) die cut from compression-molded sheets. Crosshead separation rate was 25.4 cm/min for the three cycle 100% strain test and 51 cm/min for all other tests. Set after 300% elongation (4× original gauge length) was measured according to the method described by Collette et al.[5] from benchmarks and within about 1 min of recovery (immediate set). No hold time was imposed at extension; crosshead direction was immediately reversed at 300% elongation. The three-cycle 100% strain test was performed by elongating the specimen to twice the original gauge length in three successive cycles of extension and recovery, with 30 s hold at 100% elongation and 60 s hold after crosshead recovery between cycles. In this test, the cumulative set after the first two cycles is measured as the elongation at which stress (or force) exceeds the baseline on the third cycle.

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