Synthesis and Microstructural Study of Stereoblock Elastomeric Polypropylenes from Metallocene Catalyst (2-PhInd)$_2$ZrCl$_2$ Activated with Cocatalyst Mixtures

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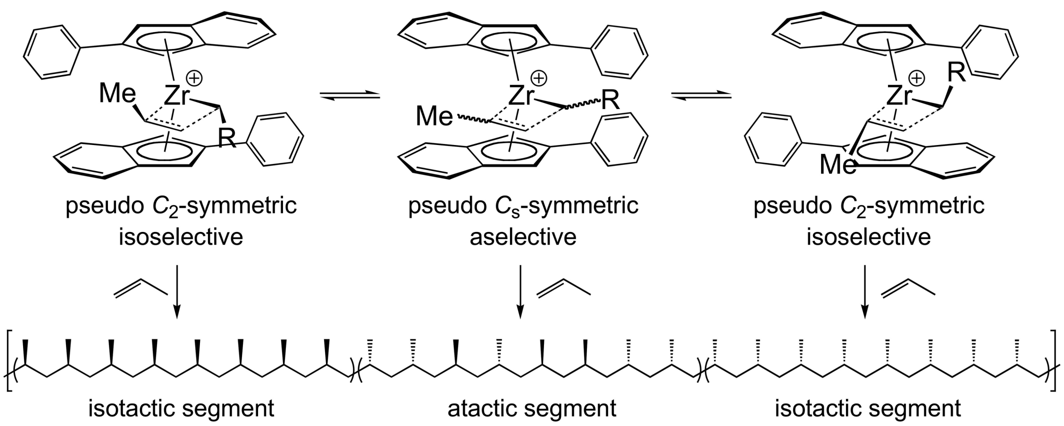
ABSTRACT: Various elastomeric polypropylenes (PPs) are synthesized through homogeneous propylene polymerization with metallocene catalyst (2-PhInd)$_2$ZrCl$_2$ in the presence of different cocatalyst mixtures: triethylaluminum (TEA)/methylaluminoxane (MAO) or triisobutylaluminum (TIBA)/MAO in the range of Al$_{AlR3}$/Al$_{MAO}$ = 0.0–0.9. The cocatalyst formulation impacts the resultant polymer microstructure and the thermal and dynamic mechanical properties of the produced PPs. ^{13}C NMR analysis of the polymers reveals essentially atactic PP, with *mmmm* = 7.9%, when Al$_{AlR3}$/Al$_{MAO}$ = 0.0. The *mmmm* pentad content is maximized when Al$_{AlR3}$/Al$_{MAO}$ = 0.8; for TIBA, *mmmm* = 23.5%; and for TEA, *mmmm* = 17.6%. Differential scanning calorimetry analysis and dynamic mechanical thermal analysis corroborate these findings. Specifically, T_m, ΔH_m, and T_g are essentially maximized under these conditions, and the minimum damping is observed for Al$_{AlR3}$/Al$_{MAO}$ = 0.6–0.8. ^{1}H NMR analysis of the mixtures of catalyst and cocatalysts (without monomer) shows very minor differences for [Zr]:Al$_{AlR3}$ in the range of 1:1–1:5. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 724–731

KEYWORDS: catalysts; elastomers; metallocene catalysts; polyolefins; poly(propylene) (PP)

INTRODUCTION En route toward producing polyolefins with novel characteristics and properties, researchers moved toward designing new types of polymerization catalysts. Catalyst alloys, hybrid catalysts, and multicatalyst systems can be considered among the newly innovated strategies toward the diversification of polyolefins.[1–5] The interactions of catalysts, cocatalysts, active species, and other agents present in the polymerization media are often quite interesting and are still under debate.[6] The interactions between catalyst and cocatalysts often impact catalyst performance and allow control of the polymer microstructure,[7–15] and these interactions seem to become increasingly interesting when catalysts are activated by cocatalyst mixtures.[15,16]

Different approaches may be implemented when activating Ziegler–Natta/metallocene catalyst alloys. Methylaluminoxane (MAO) can be used as the sole cocatalyst to activate both of the precatalysts, or two activators, such as MAO and triethylaluminum (TEA), may be added in two different stages.[17–19] The former strategy is not economically optimal because of the greater consumption of expensive MAO, and the latter strategy is often inconvenient to perform. Therefore, the simultaneous injection of two activators seems to be economically and procedurally ideal.[20] Substantial literature evidence can be found regarding various effects of mixtures of cocatalysts on the performance of metallocene catalysts as well as ZN catalysts in the polymerization of ethylene and α-olefins.[6,7,15,16]

MAO is a strong Lewis acid that is not accompanied by any nucleophilic components and is the most common activator used for metallocene catalysts. On the other hand, TEA and triisobutylaluminum (TIBA) are used to activate Ziegler–Natta catalysts by transferring an alkyl group to the transition metal center.[21] Although MAO is commonly used to activate metallocenes,[5] it should be noted that in some cases, TIBA alone also has the ability to activate metallocene catalysts.[13,14] However, it should be emphasized that TEA and TIBA generally function better in combination with MAO. Furthermore, trimethylaluminum (TMA) is another alkyl aluminum—present in common commercial MAO—which is a potential chain transfer agent that undoubtedly affects



SCHEME 1 Stereoblock isotactic/atactic polypropylene formation is possible with (2-PhInd)$_2$ZrCl$_2$/MAO via configurational oscillation of the metallocene.

polymerization characteristics such as molecular weight, microstructure, and catalyst activity.[22,23]

Another type of cocatalyst used in polymerization with metallocene catalysts is modified methylaluminoxane (MMAO), which is the usual MAO wherein some of the methyl groups are replaced by other alkyl groups—usually isobutyl or *n*-octyl.[21] These types of cocatalysts contain more than 65% methyl groups and therefore remain predominantly MAO. A variety of MMAOs are commercially available.[21] Olefin polymerization with metallocene catalysts/MMAOs is widely studied, and the cocatalyst effect on polymer microstructure has been investigated. It is clear that MMAOs can dictate different microstructures in comparison with the polymerizations for which MAO is used as the sole cocatalyst.[7,15]

In the case of using cocatalyst alloys, various catalytic effects may be encountered—especially with the performance of the metallocene component. So far, several different effects have been reported for the inclusion of alkyl aluminums during the polymerization with metallocene catalysts in the presence of MAO. They may act as alkylating agents for the metallocene catalysts,[6,7,14,24–26] scavengers of impurities present in the feed or reaction media,[6,15,21,27–30] chain transfer reagents,[6,21,23,30–33] reactivation agents for the metal sites,[6] traps for TMA present in MAO through alkyl group exchange,[6,22] and finally, a very important effect is their impact on the microstructure of the produced polymers[6,7,15]—which typically has a considerable effect on the physical/mechanical properties of the polymers.

One of the best-known unbridged metallocene catalysts is (2-PhInd)$_2$ZrCl$_2$, which has been widely studied by Waymouth and coworkers for its production of stereoblock/elastomeric polypropylene (PP), as described in Scheme 1.[34–38] Various articles have been published on the mechanism of the production of these kinds of polymers.[39] These PPs were first introduced by Natta using conventional Ziegler–Natta catalysts, and it was proposed that the formation of the polymer is governed by a kinetic factor, which was the ratio between the growth rate and the rate of configurational inversion at the metal site.[40]

In this article, elastomeric PPs are produced with the (2-PhInd)$_2$ZrCl$_2$ metallocene catalyst in the presence of TEA/MAO and TIBA/MAO cocatalyst mixtures. The produced polymers were characterized using ^{13}C NMR, differential scanning calorimetry (DSC), and dynamic mechanical thermal analysis (DMTA). The catalyst/cocatalyst mixtures were also studied using ^{1}H NMR analysis to assess the effects of cocatalyst mixtures on the structure of the catalyst.

EXPERIMENTAL

Materials

2-Phenylindene and MAO (10 wt % solution in toluene) were obtained from Aldrich Chemical Company (Munich, Germany). TEA was provided by Maroon Petrochemical Company (Mahshahr, Iran). Methyl lithium and TIBA were purchased from Merck Chemical Company (Germany). Ethereal hydrochloric acid (2 N) was purchased from Acros Chemical Company (USA). Toluene was provided by Bandar Imam Petrochemical Company (Bandar Imam, Iran) and was refluxed and distilled over sodium before use and kept over 4 Å/13× activated molecular sieves. Propylene was obtained from Maroon Petrochemical Company (Mahshahr, Iran). All manipulations involving air-sensitive compounds were performed under an atmosphere of dried nitrogen in a glove box.

Metallocene Synthesis

(2-PhInd)$_2$ZrCl$_2$ was synthesized using a modified version of the literature method.[36,41–43] The final product was obtained by removing the solvent under reduced pressure. A fine yellow powder was obtained and characterized by ^{1}H NMR (CDCl$_3$): δ 7.59 (d, 4H), 7.39 (m, 4H), 7.27 (m, 2H), 7.19 (dd, 4H), 7.02 (dd, 4H), 6.55 (s, 4H). The ^{1}H NMR spectrum of (2-PhInd)$_2$ZrCl$_2$ in benzene-d_6 is shown in Figure 6(a).

Polymerization

Polymerization reactions were performed in a 1-L Büchi reactor (Büchi Glas Uster bmd300) equipped with controlling systems for temperature, stirring speed, and reaction pressure. A total of 500 mL of dried toluene was injected into the reactor. The desired amount of AlR$_3$ (R = Et or *i*-Bu) was injected and then MAO was introduced. The amounts were prescribed such that Al_{MAO}/Zr was constant at 500; the amount of AlR_3 varied so that its molar fraction was equal to 0.2, 0.4, 0.6, 0.8, or 0.9, relative to MAO. A measured amount of metallocene catalyst was injected (dissolved in a small volume of toluene) and then the polymerization reaction was conducted at 6 bar of propylene, 35 °C, and 800 rpm stirring for 60 min. The obtained polymers were poured into acidified methanol, collected by filtration, dried, and weighed.

Polymer Characterization

Fractionation of all polymers was performed in boiling heptane. Most of the polymers were completely heptane-soluble; those that were not provided an insignificantly small heptane-insoluble fraction—small enough generally to limit characterization to DSC. ^{13}C NMR analysis of the polymers was performed on an INOVA 500 NMR Instrument, and ^1H NMR analyses of the catalysts were recorded using a BRUKER 400 AVANCE NMR Instrument. DSC analysis of the polymers was performed on a NETZCH DSC 200 F3; heating and cooling scan rates were both 10 °C/min. DMTA of the samples was performed using a DMTA–Triton, Tritec 2000, DMA, Air Oven Instrument in bending mode at 1 Hz. The intrinsic viscosities were determined in decahydronaphthalene at 135 ± 1 °C using a SOFICA-CINEVISCO viscometer, serial V04/1CE. For calculation of M_v, the Mark–Houwink–Sakurada equation was used. The requisite constants a and K were not available for isotactic/atactic elastomeric PP; hence, the constants for atactic PP were used ($a = 0.77$ and $K = 15.8 \times 10^{-3}$ mL/g).[44]

RESULTS AND DISCUSSION

Before performing any analysis on the polymers, they were fractionated in boiling heptane. The polymers produced by TEA/MAO or MAO alone were separated into two fractions—heptane-soluble and heptane-insoluble—and the insoluble fraction increased as the TEA concentration increased. However, the polymers produced by TIBA/MAO were completely soluble in boiling heptane and therefore just one fraction was obtained. Figure 1 shows the ^{13}C NMR spectra of the heptane-soluble PP fraction obtained through polymerization of propylene using $(2\text{-PhInd})_2ZrCl_2$ as the catalyst in the presence of cocatalyst mixtures. The stereochemical pentad distributions are summarized in Table 1. It is apparent from Figure 1 and Table 1 that as the TIBA concentration increased, the *mmmm* pentad fraction increased, reached a maximum at $Al_{TIBA}/Al_{MAO} = 0.8$ (*mmmm* = 23.5%), and then began to decrease. In the case of increasing TEA concentration, an increasing *mmmm* pentad trend was also apparent, but less dramatic; the *mmmm* pentad fraction reached a maximum at $Al_{TEA}/Al_{MAO} = 0.8$ (*mmmm* = 17.6%).

Furthermore, Table 1 tracks the average length of isotactic blocks having four or more monomer units, according to the equation $<B_i>(\geq 4) = 4 + 2[mmmm]/[mmmr]$ developed by Randall, which is applicable to all PP microstructures.[45,46] This block length parameter increased with added TIBA (from 5.4 to 7.0) and added TEA (from 5.4 to 6.4) and maximized with $Al_{AlR3}/Al_{MAO} = 0.8$. This analysis further confirms the impact of added trialkylaluminum on the catalytic behavior and polymer tacticity.

Table 2 correlates the results obtained from DSC and the % *mmmm* pentad content obtained from ^{13}C NMR analysis of the PPs. With the TIBA/MAO system, there seems to be a proportional correlation between the *mmmm* pentad content and melting temperature (T_m). The relationships between % *mmmm* and heat of melt (ΔH_m) and between % *mmmm* and the glass transition temperature (T_g) are considerably clearer. These relationships suggest the presence of crystalline physical crosslinks made by the isotactic segments within the elastomeric PPs. As the concentration and length of isotactic stereoblocks increase,[47] the concentration of the crystalline domains (Fig. 2) increases correspondingly and T_m and ΔH_m increase, as expected. The other pentads do not contribute significantly to long-range conformational order and, therefore, do not influence T_m and ΔH_m. Very similar observations are made for the TEA/MAO system. Molecular weights—as measured here by the viscosity-average molecular weight M_v—do not exhibit an obvious correlation with the obtained thermal data and play a secondary role at best.

As is clear from Table 2, GPC analysis of the heptane-soluble fractions of the samples provided valuable information. The polymers produced with the TIBA/MAO systems afforded broader molecular weight distributions (polydispersity index, PDI = 2.20–3.16) compared with the TEA/MAO systems (1.97–2.00); this is an important difference between TIBA and TEA not previously recognized. The PDI values near 2.0 for added TEA corroborate the proposed single-site behavior (producing isotactic segments and atactic segments from different conformations of the same catalyst) and discount the possibility that stereoisomeric polymer blends might be present to account for the observed pentad distributions found for the heptane-soluble fraction. It seems that when TEA is added to the polymerization medium, two catalysts are generated and they dictate two different microstructures (one heptane-insoluble), albeit with very different activities. This behavior was altered with use of TIBA, which completely curtailed the formation of heptane-insoluble polymer, but did result in heptane-soluble material with a somewhat broader molecular weigh distribution—pointing toward some multisite behavior.

The smaller heptane-insoluble fractions obtained from the MAO and TEA/MAO systems were also characterized through DSC analysis; these all exhibited high melting temperatures near 160 °C, indicative of isotacticity. This heptane-insoluble component is likely made by an active species quite different from the species responsible for the heptane-soluble fraction. This isotactic fraction is apparently formed when small alkyl aluminums TMA or TEA are present. However, when TIBA is added, alkyl exchange reactions with the TMA already present in the MAO seem to convert the TMA to bulkier alkyl aluminums and the species responsible for the heptane-insoluble fractions are not generated.

Another observation is the relationship between polymerization activities and *mmmm* pentad content (isotacticity) of the

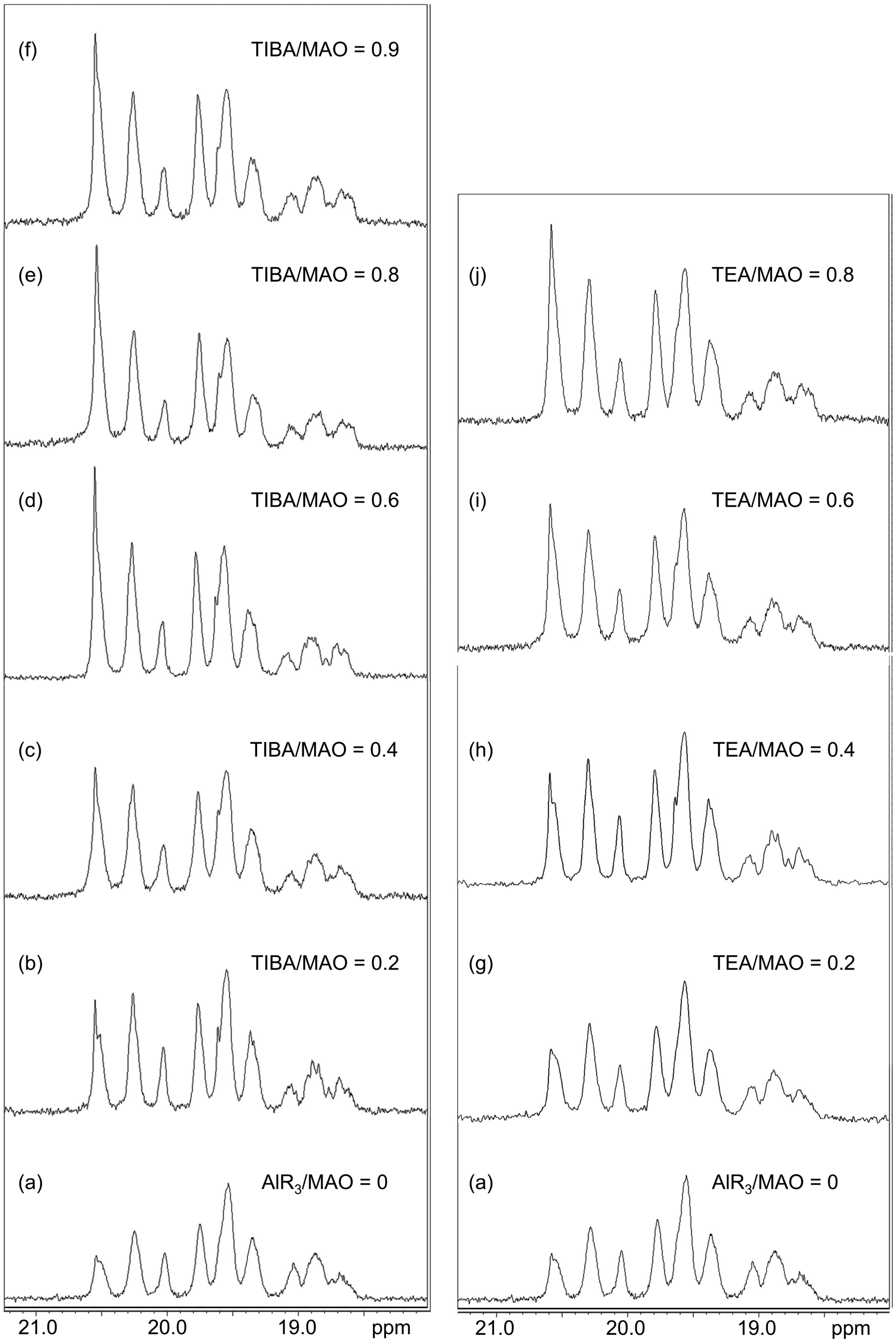


FIGURE 1 ^{13}C NMR analysis of elastomeric polypropylenes produced with different AlR_3/MAO molar ratios.

polymers. As illustrated in Figure 3, addition of TIBA [Fig. 3(a)] or TEA [Fig. 3(b)] initially lowers polymerization activities as the *mmmm* fractional content increases. Thereafter, increasing activity is observed for increased TIBA or TEA concentration (as *mmmm* follows upward), although this trend is slight with TEA. Polymer molecular weight mostly exhibited the opposite response. Initial amounts of added TIBA affected an increase in M_v, but additional amounts caused a progressive decrease in the molecular weight [Fig. 3(a)]. For added TEA, M_v showed a continuously decreasing response [Fig. 3(b)]. The added trialkylaluminum likely provides an additional chain termination pathway via alkyl exchange, thereby lowering molecular weight.

TABLE 1 Pentad Distribution of Elastomeric Polypropylenes Obtained from (2-PhInd)$_2$ZrCl$_2$ with MAO alone, TIBA/MAO, and TEA/MAO[a]

Entry	AlR$_3$/MAO	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mmrm* + *rrmr*	*mrmr*	*rrrr*	*rrrm*	*mrrm*	$<B_i>(\geq 4)$[b]
1	0.0	7.9	11.6	6.5	11.6	23.9	13.2	6.3	11.8	7.1	5.4
2	TIBA 0.2	12.2	13.9	6.5	12.0	22.5	12.3	4.3	9.2	7.0	5.8
3	TIBA 0.4	15.4	14.1	6.5	12.8	20.9	11.4	4.1	8.1	6.6	6.2
4	TIBA 0.6	18.9	15.0	5.5	12.3	20.0	10.5	3.5	7.6	6.6	6.5
5	TIBA 0.8	23.5	15.8	5.1	13.1	18.7	8.9	3.0	6.9	5.3	7.0
6	TIBA 0.9	19.0	14.7	5.8	12.9	19.2	9.7	4.2	7.9	6.6	6.6
7	TEA 0.2	11.4	13.4	6.5	12.6	23.8	12.2	4.9	9.5	5.7	5.7
8	TEA 0.4	12.8	14.6	6.4	12.5	22.6	11.8	3.9	8.8	6.5	5.8
9	TEA 0.6	15.8	13.9	6.4	12.4	20.7	11.2	4.6	8.33	6.6	6.3
10	TEA 0.8	17.6	14.9	4.9	11.6	21.4	11.4	3.3	8.8	6.2	6.4

[a] In all cases, the Al$_{\text{MAO}}$:Zr molar ratio is 500:1 and the pentad assignments are made according to Ref. 39.

[b] The average lengths of isotactic blocks greater or equal to four are calculated according to Randall by $<B_i>(\geq 4) = 4 + 2[mmmm]/[mmmr]$.[45,46]

Figure 4 records the damping ability of the produced PPs, as measured by DMTA. This variable-temperature analysis was conducted for samples with no added AlR$_3$ (Table 1, entry 1, MAO only), TIBA/MAO = 0.2, 0.6, and 0.9 (Table 1, entries 2, 4, and 6), and TEA/MAO = 0.4, 0.6, and 0.8 (Table 1, entries 8, 9, and 10). In the added TIBA series, the minimum damping (minimum tan δ) was obtained for entry 4 with an intermediate TIBA/MAO value of 0.6. In the added TEA series, the minimum damping was observed for entry 10, which used the highest TEA/MAO value of 0.8. Generally, the PPs made in the presence of TIBA exhibit greater damping than those made in the presence of TEA. A contributing explanation for this is the presumed isobutyl endgroup that initiates many of the chains in the presence of TIBA; this sterically demanding endgroup (compared with ethyl from TEA) results in a greater free volume for the polymers from the TIBA series and the damping ability tracks accordingly.

The damping ability of the polymers is related to both the isotacticity and the polymer molecular weight. High fractions of *mmmm* and high molecular weights contribute to poor damping, whereas low fractions of *mmmm* and low molecular weights lead to effective damping. As the glass transition temperature also correlates with % *mmmm* and molecular weight, it is not surprising that the damping ability (tan δ) is inversely proportional to the measured T_gs; this relationship is shown for added TIBA [Fig. 5(a)] and added TEA [Fig. 5(b)].

To better understand the role of the aluminum cocatalysts in the polymerization process, changes in the catalyst structure were studied in the presence of different catalyst/cocatalyst mixtures by ^{1}H NMR. The physical properties of the catalyst changed in response to added cocatalyst. Addition of MAO resulted in orange oils; addition of pure TIBA or TEA gave yellow solids akin to the original material; addition of MAO/TIBA or MAO/TEA afforded brown oils. The ^{1}H NMR spectra of the catalyst and cocatalyst mixtures (in benzene-d_6) are depicted in Figure 6. As is clear from the figure, when the catalyst is reacted with all types of cocatalysts including MAO, TIBA, TEA, MAO/TIBA, and MAO/TEA, the indenyl-H peak at 6.55 ppm mostly or completely disappears. The fine structure of the ligands is reorganized, but mostly retained upon addition of MAO alone [Fig. 6(b)]. However, the

TABLE 2 Results Obtained from ^{13}C NMR, Viscometric, GPC, and Thermal Analyses of Heptane-Soluble PP Fractions

Entry	% *mmmm*	M_v (g/mol)	M_n (g/mol)	M_w (g/mol)	PDI	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_g (°C)
1	7.9	49,000	90,000	168,000	1.87	127.0	0.46	114.2	0.53	−13.0
2 (TIBA)	12.2	72,000	27,800	76,300	2.75	127.3	0.73	114.3	0.80	−6.1
3 (TIBA)	15.4	65,000	48,300	152,500	3.16	127.5	1.05	114.4	1.23	−2.5
4 (TIBA)	18.9	59,000				128.0	1.70	114.5	1.42	−3.0
5 (TIBA)	23.5	42,000	28,300	62,100	2.20	127.5	1.49	114.5	1.28	−6.6
6 (TIBA)	19.0	41,000				127.3	0.53	114.6	0.56	−9.2
7 (TEA)	11.4	42,000				127.0	0.42	114.5	0.48	−8.2
8 (TEA)	12.8	36,000				127.3	0.56	114.7	0.63	−7.0
9 (TEA)	15.8	28,000	24,000	47,200	1.97	127.5	0.67	115.2	0.73	−6.8
10 (TEA)	17.6	17,000	21,700	43,500	2.00	128.3	0.90	115.8	0.96	−6.5

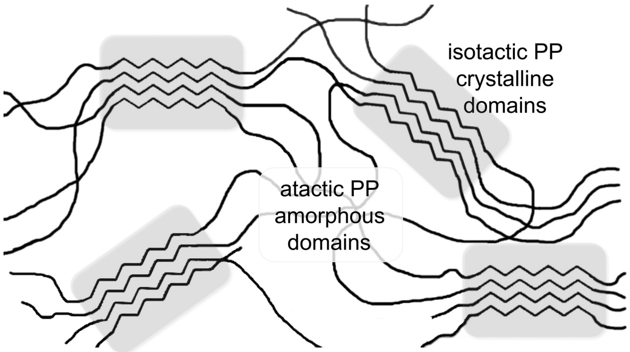


FIGURE 2 Representation of isotactic/atactic stereoblock polypropylene bearing isotactic PP blocks that crystallize and physically crosslink amorphous atactic PP segments. The concentration and length of these isotactic domains are the primary determinants for T_m and ΔH_m.

remaining spectra [Fig. 6(c–h)] include addition of TIBA or TEA and uniformly exhibit very broad NMR features in the aromatic region. It can be noted that all cocatalyst combinations—including TIBA alone or TEA alone—resulted in

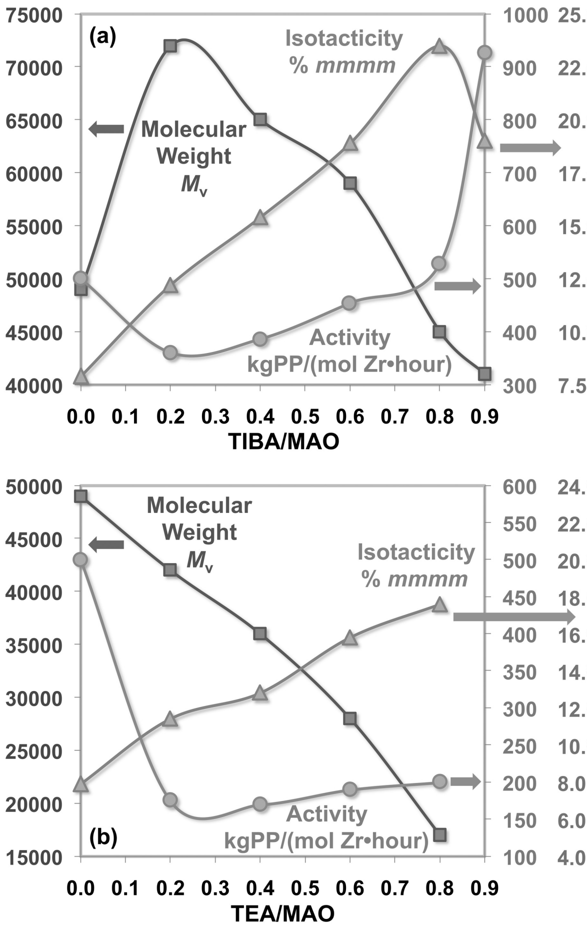


FIGURE 3 The dependence of polymerization activity, *mmmm* pentad content, and viscosity-average molecular weight (M_v) on added TIBA (a) and added TEA (b).

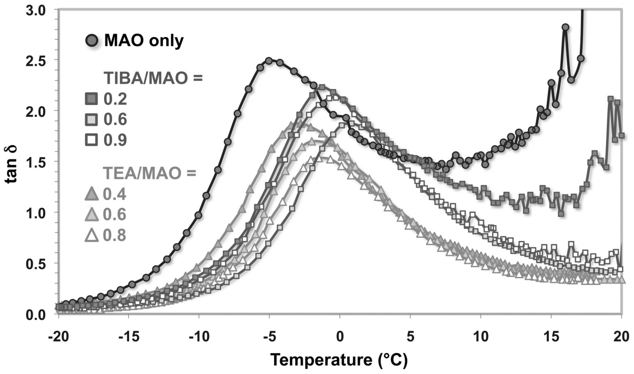


FIGURE 4 Dynamic mechanical thermal analysis of the heptane-soluble fractions of synthesized elastomeric polypropylenes from MAO only, TIBA/MAO (=0.2, 0.6, and 0.9), and TEA/MAO (=0.4, 0.6, and 0.8).

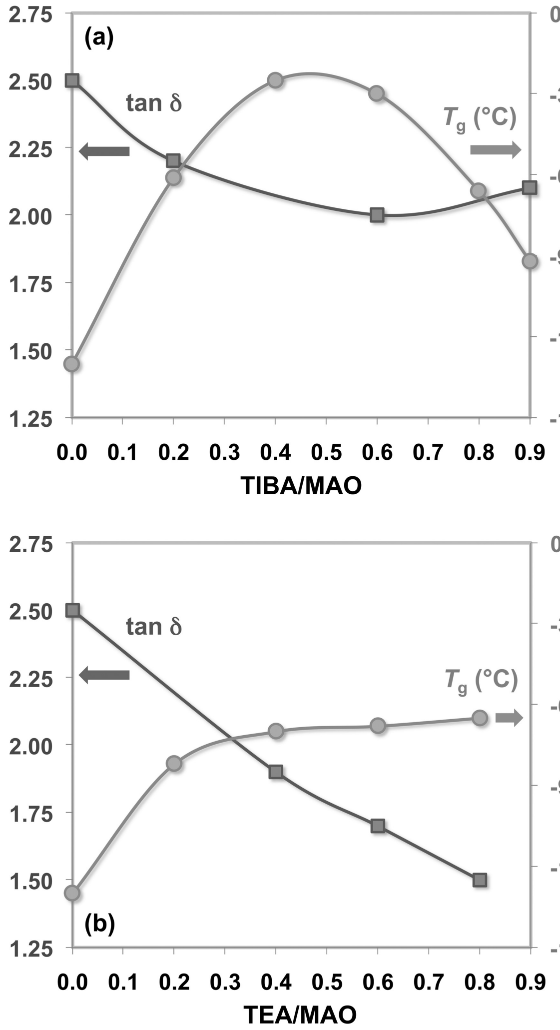


FIGURE 5 The inverse relationship between damping ability (tan δ) and glass transition temperature (T_g) for the synthesized elastomeric polypropylenes with added TIBA (a) and TEA (b).

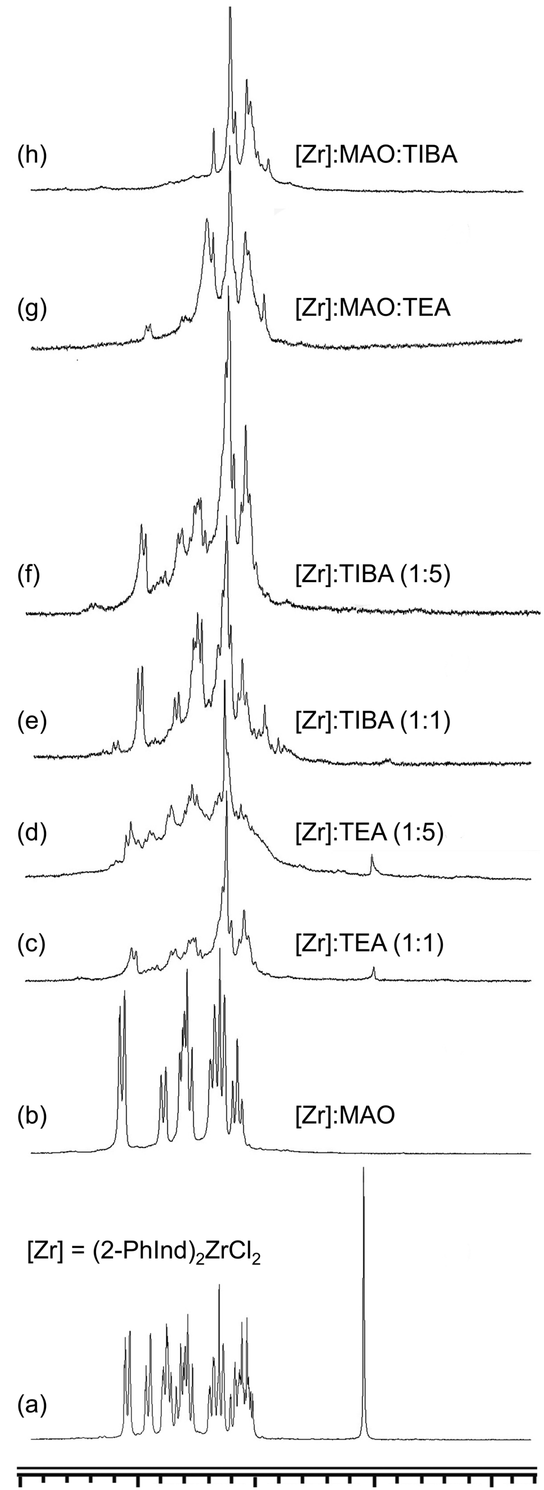


FIGURE 6 ^{1}H NMR analysis (in benzene-d_6)of the catalyst/cocatalyst mixtures: (a) pure (2-PhInd)$_2$ZrCl$_2$; (b) (2-PhInd)$_2$ZrCl$_2$/MAO; (c) (2-PhInd)$_2$ZrCl$_2$/TEA (1:1); (d) (2-PhInd)$_2$ZrCl$_2$/TEA (1:5); (e) (2-PhInd)$_2$ZrCl$_2$/TIBA (1:1); (f) (2-PhInd)$_2$ZrCl$_2$/TIBA (1:5); (g) (2-PhInd)$_2$ZrCl$_2$/(MAO/TEA); and (h) (2-PhInd)$_2$ZrCl$_2$/(MAO/TIBA). The peak at 6.55 ppm originates with the indenyl-H protons and the peak at 7.15 ppm is from residual protons in the benzene-d_6 solvent.

catalyst systems competent for ethylene polymerization. However, only those that included MAO were capable of polymerizing propylene.

CONCLUSIONS

Elastomeric PPs were produced using (2-PhInd)$_2$ZrCl$_2$ in the presence of various cocatalysts and cocatalyst mixtures, including MAO, TIBA/MAO, and TEA/MAO. The inclusion of trialkylaluminum can have a striking effect on the catalytic behavior. For example, with MAO alone, essentially atactic PP (*mmmm* = 7.9%) is obtained. However, with added TIBA (Al_{TIBA}/Al_{MAO} = 0.8) the *mmmm* pentad content rises to 23.5% and stereoblock isotactic/atactic PP is obtained. Multiple investigations of the polymers and catalyst/cocatalyst mixtures resulted in the following principal findings:

(1) MAO as the sole cocatalyst produced PPs that fractionated into two fractions: a heptane-soluble part and a heptane-insoluble part. Our investigations suggested that the TMA present in MAO caused the variable catalytic behavior. (2) TIBA/MAO activators produced polymers that were completely soluble in heptane. TIBA apparently functioned as a scavenger for the TMA present in MAO at low concentrations. As the TIBA/MAO quotient increased, *mmmm*, T_g, T_m, T_c, ΔH_m, ΔH_c, and the damping ability of the polymers increased, reached a maximum, and then decreased. These observations were related to a combination of polymer tacticity and molecular weight (as measured by M_v), which impacted the free volume present. (3) TEA/MAO activators produced polymers having a major heptane-soluble fraction and a minor heptane-insoluble fraction; as the TEA content increased, the heptane-insoluble fraction also increased. For the heptane-soluble fractions, increased TEA correlated with increased *mmmm*, T_g, T_m, T_c, ΔH_m, ΔH_c, and the damping ability of the polymers. (4) DSC and ^{13}C NMR analysis of the polymers showed that T_m, T_c, ΔH_m, and ΔH_c are directly determined by the isotacticity content, parameterized by % *mmmm*; the molecular weight (M_v) plays a minor role within the range occupied by the present samples. (5) Investigations of catalyst/cocatalyst interactions showed that MAO, TIBA, and TEA affect a drastic shift of the catalyst indenyl-H proton in the ^{1}H NMR spectrum, indicating fluxional behavior. Test reactions showed that TIBA or TEA alone can activate the catalyst for ethylene polymerization, but not for propylene polymerization. MAO is required to polymerize the α-olefin. (6) DMTA analysis of the heptane-soluble polymer fractions indicated that T_g and tan δ (the damping ability) are directly correlated to the *mmmm* pentad fraction and molecular weight M_v, which, in turn, impacts the free volume present in the polymers.

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