Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Chao, Chariya , Praserthdam, Piyasan , Khorbunsongserm, Supaporn and Rempel, Garry L.(2003) 'Effects of TMA and MAO on Ethylene-Propylene Copolymer Using Supported Zirconocene Catalysts', Journal of Macromolecular Science, Part A, 40: 2, 181 — 192

To link to this Article: DOI: 10.1081/MA-120017259

URL: http://dx.doi.org/10.1081/MA-120017259

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. 40, No. 2, pp. 181–192, 2003

Effects of TMA and MAO on Ethylene–Propylene Copolymer Using Supported Zirconocene Catalysts

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ABSTRACT

Copolymerization of ethylene and propylene was carried out in the presence of rac-ethylenebis(indenyl)zirconium dichloride ($Et[Ind]_2ZrCl_2$) with SiO_2 as the support for the catalyst. The effect of trimethylaluminum (TMA) and methylaluminoxane (MAO) was investigated using two methods of providing a supported system i.e., *in situ* supported system and a preformed supported system. Catalyst activity increased with increasing the $[Al]_{TMA}/[Zr]$ ratio to a maxima whereafter an adverse effect was observed in both the *in situ* and preformed supported system, while activity continuously increased with the increase of the $[Al]_{MAO}/[Zr]$ ratio. With respect to the molecular weight of the copolymers, an increase of TMA in the system reduced Mw only slightly, while an increase in MAO appeared to have no effect. This suggested that chain transfer to alkylaluminum is not the major chain transfer reaction for this copolymerization system. The molecular weight distribution of copolymer obtained for these supported systems is higher than for the copolymer normally produced from the corresponding homogeneous system. These supported systems might yield plural active species. Copolymers produced have ethylene incorporation close to the ethylene molar

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DOI: 10.1081/MA-120017259
1060-1325 (Print); 1520-5738 (Online)

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feed ratio with random distribution of comonomer insertion. A very low level of the PPP triad was observed. The amount of Al loaded on silica depended linearly with $[Al]_{MAO}$ added, whereas almost all the loaded Zr were immobilized on the support. From SEM-EDX analysis, Al was well dispersed on the silica support, no effect of zirconocene catalyst loaded on the Al distribution was observed at the reaction condition used. In ethylene/propylene copolymer produced, Al was detected throughout the particles supporting the possibility of catalyst fragmentation mechanism.

Key Words: Supported metallocene; Metallocene catalyst; Ethylene–propylene copolymerization; Trimethylaluminum.

INTRODUCTION

Group 4 metallocenes with methylaluminoxane (MAO) as cocatalyst form well defined active species for olefin polymerization. Their single site character combined with their potential to vary their polymerization behavior by tuning the ligand structure has caused an enormous interest in the scientific community as well as in the industry.[1] These catalysts permit a strong control of the regio- and stereo-regularities and of the molecular weight distribution (MWD) of homopolymers, as well as the synthesis of random copolymers with narrow MWDs, and narrow chemical composition distribution (CCD), with higher activities. It is desirable to immobilize metallocene catalysts on supports to replace the conventional Ziegler–Natta catalysts used in industrial slurry and gas phase processes. Methods for immobilizing metallocenes fall largely into two categories: (1) MAO-mediated systems, in which impregnation of the support with MAO is followed by the addition of a metallocene catalyst, and (2) directly impregnated metallocene onto the support.[2–5] In general, supported metallocenes have a lower catalytic activity than their corresponding homogeneous metallocene systems. Soga et al. reported that TMA can act as a cocatalyst in ethylene polymerization without MAO present when *in situ* supported Cp_2ZrCl_2 with $Cl_2Si(CH_3)_2$ modified silica was used.[6] Chu et al. carried out ethylene polymerization with an *in situ* supported metallocene catalyst. In the absence of trimethyl aluminum (TMA), *in situ* supported $Et[Ind]_2ZrCl_2$ was not active, while $Et[Ind]_2Zr(CH_3)_2$ was active. The addition of TMA during polymerization activated the catalyst.[7]

The $Et[Ind]_2ZrCl_2$ catalyst is by far the most studied metallocene system in the open literature for the production of polyethylene, polypropylene, as well as EP copolymers. In EP copolymerizations, this ansa-metallocene catalyst incorporates larger amounts of propylene than do nonbridged systems and leads to the production of lower molecular weight materials. Haag et al. studied the effect of MAO in ethylene/propylene copolymerization using SiO_2/MAO supported $Et[Ind]_2ZrCl_2$ with an external addition of MAO. The copolymer produced gave plural CCD. The copolymer produced at higher $[Al]_{MAO}/[Zr]$ was found to have higher ethylene content, higher melting temperature and higher molecular weight.[8]

This study also examined the effect of TMA and MAO on ethylene–propylene copolymerization with different supporting procedures: SiO_2/MAO supported $Et[Ind]_2ZrCl_2$, and *in situ* SiO_2/MAO supported $Et[Ind]_2ZrCl_2$.

EXPERIMENTAL

Chemicals

Rac-ethylenebis(indenyl)zirconium dichloride (Et[Ind]$_2$ZrCl$_2$) was obtained from Aldrich Chemical Company, Inc. and used as received. Ethylene and propylene used in this investigation were polymerization grade obtained from National Petrochemical Co., Ltd., Thailand. Methylaluminoxane (MAO) 2.857 M in toluene was donated by Tosoh Akzo, Japan. Silica gel from Fuji Silasia Chemical Ltd., (Cariact P-10, surface area 300 m^2/g) was calcined under vacuum at 400°C for 6 h. Toluene was donated by Exxon Chemical Thailand Ltd. It was dried over dehydrated CaCl$_2$ and distilled over sodium/benzophenone under argon atmosphere prior to use. Trimethylaluminum [Al(CH$_3$)$_3$] 2.0 M in toluene was supplied from Nippon Aluminum Alkyls, Ltd., Japan. Ultra high purity argon (99.999%) was purchased from Thai Industrial Gas Co., Ltd and further purified by passing through a molecular sieve 3 A, BASF catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentaoxide (P$_2$O$_5$) to remove traces of oxygen and moisture.

All the chemicals were manipulated under inert atmosphere using a Vacuum Atmospheres glove box and/or Schlenk techniques.

Supporting Procedures

Preparation of SiO$_2$/MAO

Silica gel was calcined under vacuum at 400°C for 6 h. Calcined silica 1 g was reacted with the desired amount of MAO in 10 mL of toluene at room temperature for 30 min. The solid part was separated and washed 5 times with 20 mL of toluene, followed by drying *in vacuo* at room temperature to obtain the catalyst support precursor SiO$_2$/MAO.

Supported SiO$_2$/MAO/Et(Ind)$_2$ZrCl$_2$

The catalyst support precursor was stirred at room temperature with the desired amount of Et(Ind)$_2$ZrCl$_2$ solution in toluene for 30 min. The solid part was washed with toluene and then dried *in vacuo* at room temperature.

Polymerization Reactions

Ethylene and propylene were mixed in a gas cylinder at a 70/30 molar ratio with quantities of the two gases small enough to prevent their condensation. The glass reactor is first connected to the gas handling part of the system and then it is evacuated and filled with the mixed ethylene/propylene gas. The mixture of gas is continuously fed through a reactor at a flowrate of 0.3 L/min to maintain the gas composition in the reactor. Gas chromatography was used to confirm the constant ratio of ethylene to propylene in the reactor throughout the polymerization time. Xu et al. showed that the system with a continuous flow of monomer gas (purge mode) provides better results for a kinetic study of ethylene homopolymerization and ethylene/propylene copolymerization than a no-purge mode. An increase in activity and improvement in reproducibility was also observed.[9]

Using Schlenk techniques, the catalyst support precursor was suspended in toluene and the desired amount of TMA was injected into the reactor. Once the solvent is saturated with the monomer at the atmospheric pressure and at the desired temperature (40°C), a solution of $Et[Ind]_2ZrCl_2$ in toluene was added to initiate the reaction. The reaction was terminated by stopping the feed of monomer and pouring the reaction solution into an excess amount of methanol. The copolymer produced was dried *in vacuo* at room temperature overnight.

Polymer Characterization

Molecular weight and molecular weight distributions of the produced ethylene–propylene copolymer were investigated with a high-temperature Gel Permeation Chromatography (GPC) instrument (Waters 150-C) equipped with a viscometric detector, differential optical refractometer and four styragel HT type columns (HT3, HT4, HT5 and HT6) with a 1×10^7 exclusion limit for polystyrene. The analyses were performed at 135°C using 1,2,4-trichlorobenzene as solvent. The columns were calibrated with standard narrow molar mass distribution polystyrene and linear low density polyethylene.

^{13}C-NMR spectroscopy was used to determine propylene incorporation and polymer microstructure. Chemical shifts were referenced internally to the major backbone methylene resonance (taken as 30 ppm from Me_4Si) and calculated according to the method of Randall.[10] Sample solutions were prepared in o-dichlorobenzene and benzene-d_6 (20 vol%) for internal lock signal. The ^{13}C-NMR spectra were obtained at 80°C using JEOL JNM-A500 operating at 125 MHz. Spectra were taken with a 70° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s.[8,11]

Al distribution on the catalyst support precursor and polymer particles were investigated by Scanning Electron Microscope (SEM) with Energy Dispersive X-ray analysis (EDX).

RESULTS AND DISCUSSION

Ethylene/propylene copolymerization was carried out with various amounts of TMA and MAO. Table 1 shows catalytic activity and copolymer properties synthesized with different $[Al]_{TMA}/[Zr]$ mole ratio using the SiO_2/MAO *in situ* supported system. When no TMA was present, some activity was observed. However, the activity was found to increase further with an increase of TMA up to a $[Al]_{TMA}/[Zr]$ mole ratio as high as 1000. As the $[Al]_{TMA}/[Zr]$ mole ratio was increased further, the activity was found to decrease to some extent. TMA is a scavenger, which may help in reducing the amount of impurities in the system thereby leading to an increase in activity. TMA is also able to inhibit certain functions of MAO. Several explanations for this are possible. Since TMA is a stronger alkylating and reducing agent than MAO, TMA could cause the reduction of

Table 1. Activity and properties of copolymer produced with a different amount of TMA in SiO_2/MAO *in situ* supported system using catalyst concentration = 60 μM, $[Al]_{MAO}/[Zr]$ mole ratio = 215, reaction temperature 40°C, and reaction time 30 min.

Run	$[Al]_{TMA}/[Zr]$ (mole ratio)	Activity (kgpolymer/molZr hr)	Mw	MWD	Ethylene in copolymer (%)
EP1	0	2364	51000	3.2	70.5
EP2	500	3301	44000	3.0	
EP3	1000	3404	43000	2.8	
EP4	1500	3246	66000	5.0	75.1
EP5	2000	2879	59000	4.9	
EP6	2500	3016	57000	4.8	
EP7	3000	2732	55000	4.7	
EP8	3500	2591	59000	4.8	72.4

the zirconocene compound resulting in an inactive species. It may also compete with MAO as a complexing ligand leading to a catalyst of lower polymerization activity. Furthermore, the addition of TMA can lower the degree of oligomerization of MAO and its overall effectiveness. Therefore, the addition of TMA has both advantages and disadvantages to activity.[12]

Molecular weight slightly decreased when more TMA was added. This might result from increasing the chance of the chain transfer to alkylaluminum reaction leading to termination of the growing chain. However, chain transfer to TMA might not be the major chain transfer reaction in this system since only a small change in Mw resulted even when a high excess of TMA was added. MWD broadening likely resulted from the interactions between the metallocene and the support, which leads to the formation of active sites differing in electronic and steric character. Ethylene incorporation in copolymers was found to be close to the ratio of the ethylene to propylene feed ratio. No significant effect of TMA on ethylene incorporation was observed. All the copolymers produced were amorphous with no melting temperature.

MAO has many possible functions in metallocene catalyst systems, such as scavenging of impurities, alkylation, ionization and/or reduction of the transition element, stabilization of cationic metallocene alkyl and/or the counter ion, and perhaps others. One important role of MAO is apparently to prevent the formation of a $ZrCH_2CH_2Zr$ species (bimolecular processes). This is one of the reasons why a very large amount of MAO is needed to realize the maximum catalytic activity of the ansa-metallocene complexes in solution polymerization. One way to lower this requirement is to immobilize the complex on a support. With increased amounts of MAO used in the catalyst precursor, catalytic activity was continuously increased with increase of MAO while no significant effect on molecular weight was observed (Table 2). The increase in activity did not linearly depend on the amount of MAO used but the activity increased more when using a high level of MAO.

Chien and He investigated the $SiO_2/MAO/Et(Ind)_2ZrCl_2$ supported system at the [Al]/[Zr] ratio of 50 on the silica with various amounts of additional MAO added in the solution. At the total [Al]/[Zr] ratio in the range of 4390 to 670, the activity was the same

Table 2. Activity and properties of copolymer produced with different amounts of MAO in SiO_2/MAO *in situ* supported system using catalyst concentration 60 μM, $[Al]_{TMA}/[Zr]$ mole ratio = 2500, reaction temperature 40°C, and reaction time 90 min.

Run	$[Al]_{MAO}/[Zr]$ (mole ratio)	Activity (kgpolymer/molZr hr)	Mw	MWD	Ethylene in copolymer (%)
EP9	98	158	23000	3.5	77.8
EP10	118	199	27000	4.4	79.6
EP11	157	507	28000	3.9	
EP12	184	915	25000	3.9	77.7
EP13	215	2075	33000	2.5	

but markedly higher than the supported system without an additional MAO. The copolymers produced had compositions close to the comonomer feed ratio but when the [Al]/[Zr] molar ratio was reduced to 130, copolymer with higher ethylene incorporation was obtained.[13] It seems that a high level of MAO impregnated on silica is still necessary to obtain the high activity in ethylene/propylene copolymerization with this supported system, while additional MAO in solution had less effect.

The molecular weight of the copolymer produced, when different amounts of MAO were used in the precursor preparation, did not change significantly under the condition used in this work. However, for the homogeneous catalyst system, it was found that the Mw increased slightly by lowering $[Al]_{MAO}/[Zr]$ ratio.[12]

When $Et[Ind]_2ZrCl_2$ was supported on SiO_2/MAO instead of being injected separately into the reactor, TMA showed more adverse effect on the catalytic activity at higher $[Al]_{TMA}/[Zr]$ ratios. In general, the activity of the in-situ system was a little higher than for the preformed supported system. This might have resulted from the exposure and activation of new sites formed after catalyst fragmentation, which could be reached easier by monomer in the case of *in situ* supported system compared to the preformed active sites covered by the polymer layer in a preformed supported system. There was no significant change in molecular weight and molecular weight distribution of the copolymer obtained from the *in situ* or preformed supported system. Molecular weight of copolymers produced with this supported system also decreased when higher amounts of TMA were used in

Table 3. Activity and properties of copolymer produced with different amounts of TMA in $SiO_2/MAO/Et(Ind)_2ZrCl_2$ supported system using catalyst concentration = 47.5 μM, $[Al]_{MAO}/[Zr]$ mole ratio = 272, reaction temperature 40°C, and reaction time 30 min.

Run	$[Al]_{TMA}/[Zr]$ (mole ratio)	Activity (kgpolymer/molZr hr)	Mw	MWD	Ethylene in copolymer (%)
EP14	0	1873	83000	4.0	65.4
EP15	500	2540	57000	3.3	
EP16	1500	3093	59000	5.3	73.5
EP17	2500	2464	51000	4.4	
EP18	3500	1448	49000	4.8	78.4

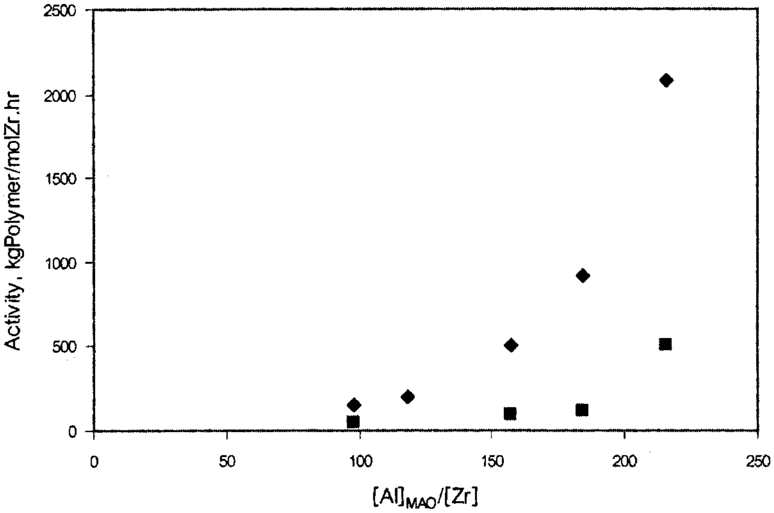

Figure 1. Effect of MAO on activity of different supporting systems: (◆) *in situ*; (■) supported.

the same manner as that of *in situ* system (Table 3). Chu et al. compared homogeneous, supported and, *in situ* supported $Et[Ind]_2ZrCl_2$ on SiO_2 for ethylene and 1-hexene copolymerization. They found that the *in situ* supported system showed higher activity than the supported system. The amount of 1-hexene incorporated in the copolymer of the preformed supported system is similar to the *in situ* supported system but less than the homogeneous catalyst system. Molecular weight of the copolymer produced did not depend on the supporting procedure while the MWD of the *in situ* supported system is broader. They proposed the existence of at least two different active species in the case of the *in situ* supported system.[14]

When the amount of MAO used was varied with the preformed supported system, the activity continuously increased similar to that of the *in situ* system (Fig. 1). However, the increase in activity according to MAO added was more pronounced in the *in situ* system. Molecular weight of copolymer increased when $[Al]_{MAO}/[Zr]$ was increased for the preformed supported system (Table 4). This effect was not observed with the *in situ*

Table 4. Activity and properties of copolymer produced with different amounts of MAO in $SiO_2/MAO/Et(Ind)_2ZrCl_2$ supported system using catalyst concentration 120 μM, $[Al]_{TMA}/[Zr]$ mole ratio = 2500, reaction temperature 40°C, and reaction time 90 min.

Run	$[Al]_{MAO}/[Zr]$ (mole ratio)	Activity (kgpolymer/molZr hr)	Mw	MWD	Ethylene in copolymer (%)
EP19	98	46	30000	2.9	78.2
EP20	157	92	39000	2.9	78.4
EP21	184	115	41000	2.9	78.8
EP22	215	505	47000	2.9	

Table 5. Triad sequence distribution of ethylene (E)/propylene (P) copolymers. Triad sequences were calculated from ^{13}C-NMR by the Randall method.[10]

Run	Support	$[Al]_{TMA}/[Zr]$ (mole ratio)	$[Al]_{MAO}/[Zr]$ (mole ratio)	E	P	EEE	PEE + EEP	PEP	EPE	PPE + EPP	PPP
EP1	SiO_2/MAO	0	215	0.705	0.295	0.312	0.330	0.063	0.173	0.108	0.014
EP4	SiO_2/MAO	1500	215	0.751	0.249	0.392	0.309	0.051	0.169	0.072	0.007
EP8	SiO_2/MAO	3500	215	0.724	0.276	0.336	0.332	0.056	0.170	0.103	0.003
EP9	SiO_2/MAO	2500	98	0.778	0.222	0.449	0.291	0.038	0.149	0.069	0.003
EP10	SiO_2/MAO	2500	118	0.796	0.204	0.486	0.273	0.037	0.147	0.052	0.005
EP12	SiO_2/MAO	2500	184	0.777	0.223	0.446	0.286	0.045	0.157	0.063	0.004
EP14	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	0	272	0.654	0.346	0.226	0.345	0.083	0.192	0.126	0.027
EP16	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	1500	272	0.735	0.265	0.356	0.331	0.049	0.170	0.089	0.006
EP18	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	3500	272	0.784	0.216	0.456	0.290	0.038	0.152	0.062	0.002
EP19	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	2500	98	0.782	0.218	0.465	0.270	0.046	0.149	0.065	0.004
EP20	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	2500	157	0.784	0.216	0.464	0.278	0.042	0.152	0.059	0.005
EP21	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	2500	184	0.788	0.212	0.463	0.287	0.038	0.154	0.055	0.003

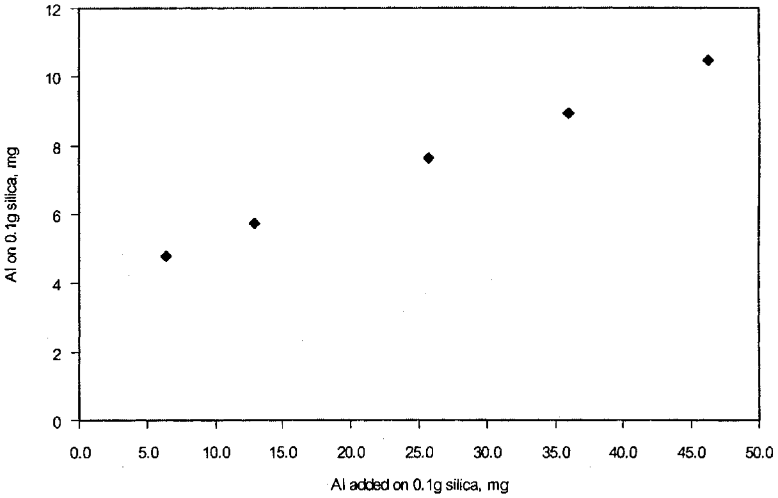

Figure 2. Amount of Al impregnated on the silica measured by ICP at various amounts of MAO added.

system. Haag et al. used a SiO_2/MAO/Et(Ind)$_2$ZrCl_2 supported system with external MAO added. They found that the optimum $[Al]_{MAO}/[Zr]$ molar ratio to the activity was about 1300. An increase of $[Al]_{MAO}/[Zr]$ resulted in an increase in %ethylene in copolymer, Tm, and Mw.[8]

The results obtained for the triad sequence distribution shown in Table 5, indicate a very small amount of [PPP], [PPE], [EPP] triads occur suggesting the more chance of having isolated propylene [P] in the polymer chain. These catalyst systems seem to

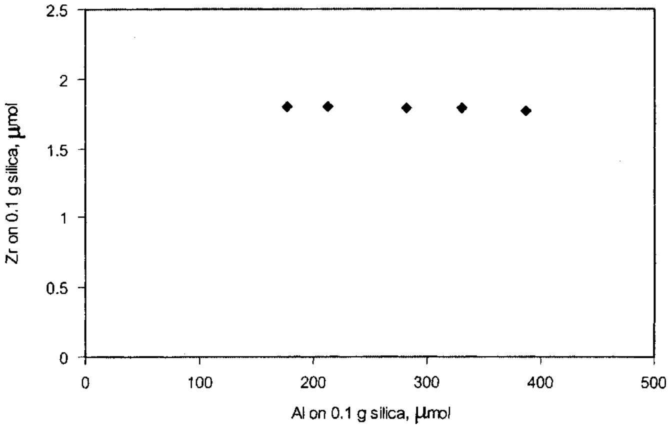

Figure 3. Amount of Zr on support measured by ICP at various ratio of Al on silica surface at Zr loading of 18.02 μmol per gram silica.

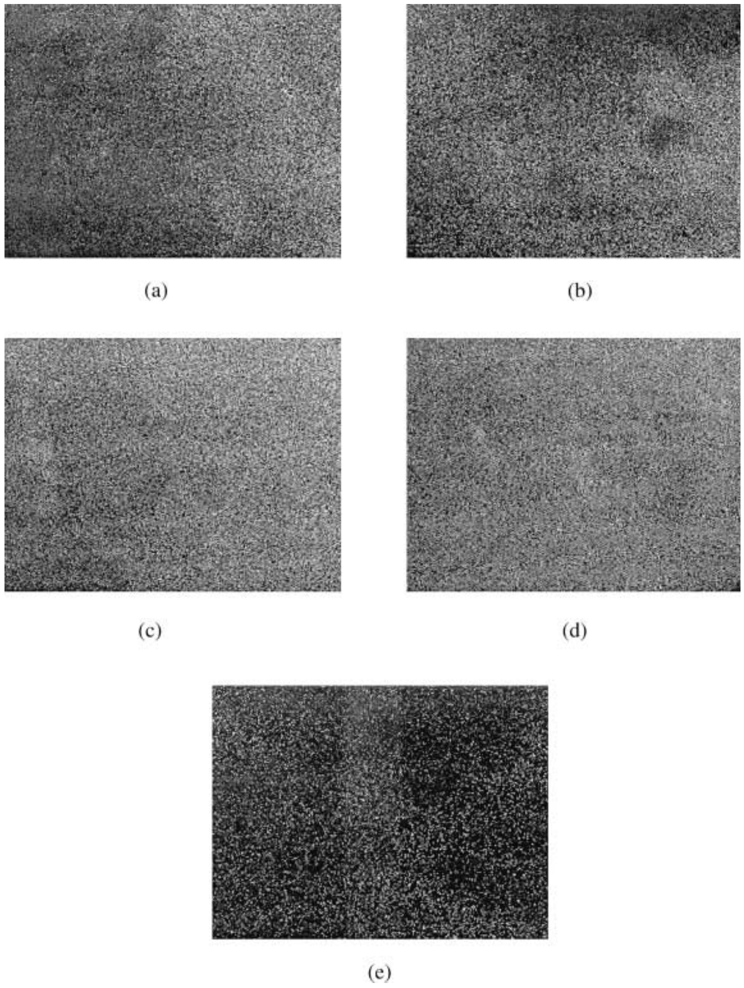

Figure 4. Al distribution from Scanning Electron Micrographs of the catalyst precursor and ethylene/propylene copolymer [3000 ×] (a) SiO2/MAO at [Al]/[Zr] = 98, EP9 (b) SiO2/MAO/Et(Ind)2ZrCh at [AI]/[Zr] = 98, EP19 (c) SiO2/MAO at [Al]/[Zr] = 215, EP13 (d) SiO2/MAO/Et(Ind)2ZrCh at [AI]/[Zr] = 215, EP22 (e) ethylene/propylene copolymer produced.

provide alternating polymer chains and do not produce blocks of each monomer, which is similar to the nature of this catalyst in the soluble system reported.[15] Immobilization apparently did not alter its polymerization behavior.

Considering the correlation between the amount of MAO added to silica in the impregnation step and the aluminum content of SiO_2/MAO precursor obtained, Al on silica increased linearly with Al weight added (Fig. 2). And when the SiO_2/MAO with a different amount of MAO impregnated was further treated with the $Et[Ind]_2ZrCl_2$, Zr content on the support was investigated. It can be seen from Fig. 3that almost all the loaded Zr were immobilized on the support. The blank reaction was carried out by passing Argon through the reactor instead of comonomer feed. After 30 min, the reaction solution was taken for evaluating the Zr concentration. In the *in situ* case, 0.00416 mg of Zr was found in the solution compared to 0.164 mg added to reactor suggesting that most of the Zr remained bound to the support. For the preformed supported case, 0.00296 mg of Zr was found in the solution, while 0.13 mg of Zr was initially bound to the support; thus, it can be concluded that no significant leaching occurred during the copolymerization reaction.

From EDX analysis in Fig. 4, Al is well dispersed throughout the catalyst support precursor. No significant difference of Al distribution can be observed between the catalyst support precursor prior and after metallocene loaded (compared Fig. 4(a) with 4(b) and Fig. 4(c) with 4(d)). Unfortunately, Zr distribution cannot be taken with this method because of the very low Zr amount loaded and too low intensity detected. In ethylene/propylene copolymer produced (Fig. 4(e)), Al was detected constantly throughout the polymer particles. This suggested that the catalyst support precursor was fragmented during the polymerization proceeded.

CONCLUSION

TMA may provide both an advantage or a disadvantage with respect to copolymerization activity depending on the amount used. Furthermore, for the reaction conditions investigated herein, the addition of TMA only slightly affected molecular weight of the copolymer produced, suggesting that chain transfer to alkylaluminum is not the major chain transfer reaction. Molecular weight distribution of these systems were higher than for the analogous homogeneous system so there might be different active species occurring in the system. The effect on the activity of MAO was more obvious than TMA; increase in MAO impregnated on silica significantly increased the activity. The correlation of MAO amount on silica and activity is not linear; the activity increased exponentially with increased level of MAO added and this was more pronounced with the in-situ system. The ethylene incorporation of copolymer produced was close to the feed ratio. TMA and MAO amount did not show any significant effect on copolymer sequence distribution. The copolymer had a random distribution of propylene insertion with very low amount of PPP triad in the polymer chain. Rate profile of the polymerization or the activity as a function of polymerization time will be useful to clarify the mechanism of the copolymerization with this supported system. The reaction system that can provide the data of comonomer consumption with time would be set in the future work.

ACKNOWLEDGMENTS

Thanks are due to Ms. Wanna Saririnnuth for NMR analysis. We are grateful to the Thailand Research Fund (TRF) for financial support of this work.

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Received May 5, 2002
Revised September 11, 2002