Isobutylaluminum aryloxides as metallocene activators in Homo- and copolymerization of olefins

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ABSTRACT: The article describes that sterically hindered isobutylaluminum aryloxides with bulky ^{t}Bu substituents at 2,6- positions of aryl fragment, i.e. $(2,6\text{-di-}{}^t\text{Bu,4-R-C}_6\text{H}_2\text{O})\text{Al}^i\text{Bu}_2$ (R = H (**1-DTBP**), Me (**1-BHT**), ^{t}Bu (**1-TTBP**)) and $(2,6\text{-di-}{}^t\text{Bu,4-R-C}_6\text{H}_2\text{O})_2\text{Al}^i\text{Bu}$ (R=H(**2-DTBP**), Me(**2-BHT**)) can serve as cocatalysts for metallocene complexes. Isobutylaluminum aryloxides have been applied for activation of $rac\text{-Et(2-MeInd)}_2\text{ZrMe}_2$ in homopolymerization of ethylene, propylene, copolymerization of ethylene and propylene, and terpolymerization of ethylene, propylene, and 5-ethylidene-2-norbornene at Al/Zr = 300 mol/mol. The type of R substituent at 4-position has a significant effect on catalyst activity. The catalytic system with **1-TTBP** showed the highest activity in all homo- and copolymerization processes. Diisobutylaluminum aryloxides provide much higher activity to the systems in all polymerization processes and stronger ability for propylene incorporation in copolymer than diaryloxides. The activities of the systems with isobutylaluminum aryloxides are similar or exceed that of the system with MAO as activator as have shown for propylene polymerization. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43276.

INTRODUCTION

Metallocene catalysts are currently considered as the most versatile transition metal catalysts for production of different homo- and copolymers of olefins with tailor-made properties.[1–4] Metallocene catalysts contain two components, a metallocene complex (precatalyst) and a cocatalyst (or activator). The most effective cocatalyst in modern metallocene catalysis is polymethylalumoxane (MAO).[5,6] However the benefits of MAO as activator in practice are compensated by its drawbacks such as high cost at necessity to use it in high molar excess to pre-catalysts (up to 10^3-10^4 mol/mol) and instability under the long-term storage resulting in loss of activating features and irreproducibility of polymer characteristics formed in the presence of aged activator. So, economically it would be extremely advantageous to replace MAO by new effective, stable, and low cost activators.

Sterically hindered phenols $2,6\text{-di-}{}^t\text{Bu,4-Me-C}_6\text{H}_2\text{OH}$ (BHT-H), $2,4,6\text{-tri-}{}^t\text{Bu-C}_6\text{H}_2\text{OH}$ (BHT*-H), and methylaluminum diaryloxides ((BHT)$_2$AlMe and (BHT*)$_2$AlMe) are sometimes used as the component of catalyst system in olefin polymerization. Phenols are applied for binding of free trimethylaluminum

(TMA)[7–15] containing in commercial MAO up to 30 mol % since TMA is capable of blocking the active sites.[16–18] Sterically hindered phenols are inert toward catalytic intermediates even at high excess to metallocene and cause no lowering of the catalytic activity. At the same time, it was demonstrated that adding of phenol to reaction medium enables to control the molecular weight and microstructure of derived (co)polymers.[11,12,14,15] Methylaluminum diaryoxides with tert-butyl substituents in ortho- positions of aryloxy groups simultaneously act as moisture impurities scavenger.[9,10]

Several publications about application of phenols in order to obtain highly effective activators of metallocene complexes should be noted. Pentafluorophenoxy alumoxanes obtained either by reaction of AlMe$_3$ with C$_6$F$_5$OH with following hydrolysis of reaction products or by modification of MAO with phenol were shown to be effective cocatalyst in alkene polymerization reactions.[19] Sterically hindered arylaluminates, oligomeric compounds containing [Al(OPh)-O] units with two ortho-positioned tert-butyl or phenyl groups, obtained by reaction of AlR$_3$ (R=Me, Et, ^{i}Bu, ^{n}Oct) with phenols followed by hydrolysis of reaction products were also shown to be effective

cocatalysts of Cp_2ZrCl_2 and *rac*-EtInd$_2$ZrCl$_2$ in copolymerization of ethylene and hexene-1.[20] These arylaluminates similar to MAO provide high activity to catalytic system at very high molar ratio to precatalysts (10^3-10^4).

Effective activators of *rac*-EtInd$_2$ZrCl$_2$ providing high activity to catalytic system in ethylene polymerization have been obtained by reaction of triisobutylaluminum, triisooctylaluminum, and of their alumoxanes with a number of phenols bearing electron-withdrawing substituents (Ph, F, and Cl) in aryl moiety.[21] These aluminum-based cocatalysts have been generated *in situ* in polymerization medium and used without isolation. The most effective cocatalysts have been obtained with the use of pentafluorophenol. In the case of reactions with trialkylaluminum the cocatalysts formed *in situ* are to be $R_2AlO(C_6F_5)$ as evidenced in Ref. 22 Unlike to cocatalysts reported in[19,20] these compounds effectively activate catalytic system at Al/Zr molar ratio as low as 200/1.

One can find in literature only few examples of alkylaluminum aryloxides usage as activators. Combinatorial methods were used to predict activators based on organoaluminum compounds and compounds containing heteroatom with labile hydrogen atom, including phenols. It was shown that $R_2Al(O(C_6F_5))$ (R=^{i}Bu, ^{i}Oct) proved to be effective activators of heterogeneous titanium-magnesium catalysts in copolymerization of ethylene and octene-1.[23] An effective activation of ethylene polymerization catalyst (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silane-titanium-1,3-pentadiene by isobutylaluminum aryloxide ^{i}BuAl(BHT)(C$_6$F$_5$) derived from interaction of Al(C$_6$F$_5$)$_3$ with corresponding phenol R_2Al(BHT) is claimed in the patent.[24] Multinuclear aluminum cocatalysts have been obtained by the reaction of various phenols, alcohols or diols with trimethylaluminum and were used in situ or as isolated, well-defined species, for the activation of an iminopyridine iron complexes for the oligomerization of ethylene at low Al/Fe molar ratios.[25] These few examples illustrate that alkylaluminum aryloxides can serve as activators of metallocene and post-metallocene complexes and their usage has advantages compared to MAO or alkylaluminates as in[19,20] since they may be synthesized as individual compounds and provide high activity to catalytic system at low Al/precatalysts molar ratios.

Sterically hindered alkylaluminum aryloxides are derived from reaction of AlR$_3$ with corresponding phenols. This method enables formation of mono- and diaryloxides, e.g.,[12,26,27] Alkylaluminum aryloxides without or with not too bulky substituents in O-Ph have a strong tendency to increase the coordination number of aluminum atom leading to formation of dimers via Al-O bridges.[22,28–34] It is only with sufficiently sterically bulky ligands precluding dimerization, such as in BHT, the monomeric 3-coordinated Al species are formed.[12,26,27,35–37] We suggested that these well-known compounds possessing high Lewis acidity could be effective activators of metallocene complexes although they were never tested for the purpose. Dimethylated zirconocene was chosen as precatalysts due to seemingly low alkylating ability of isobutylaluminum aryloxides.

This study show that both isobutylaluminum mono- and diaryloxides with tert-butyl substituents in *ortho*- positions of aryloxy

group(s) can effectively activate dimethylated zirconocene *rac*-Et(2-MeInd)$_2$ZrMe$_2$ in homopolymerization of ethylene, propylene, copolymerization of ethylene and propylene, and terpolymerization of ethylene, propylene and 5-ethylidene-2-norbornene.

EXPERIMENTAL

Reagents

All manipulations with zirconocene and organoaluminum activators were performed in argon atmosphere. Toluene of special grade was distilled over LiAlH$_4$, degassed under reduced pressure, and stored over molecular sieves (4 Å) under argon atmosphere. Toluene-d_8 (Aldrich) used in NMR measurements was dried by multiple distillation over molecular sieves (4 Å). TIBA (Aldrich) as 1M solution in toluene and MAO (Aldrich) as 10 wt % solution in toluene were used as received. Phenols (purity > 98%, Alfa Aesar and Aldrich Chem. Co) were used without prior purification. *rac*-Et(2-MeInd)$_2$ZrMe$_2$ was synthesized by alkylation of starting zirconocene dichloride (Boulder Scientific) using a standard procedure.[38]

NMR Analysis of Isobutylaluminum Aryloxides

The ^{1}H- and ^{13}C-NMR spectra of isobutylaluminum aryloxides as solutions in the mixture of toluene and toluene-d$_8$ were recorded. Signal of resting methyl protons of toluene (2.12 ppm) was used as internal reference.
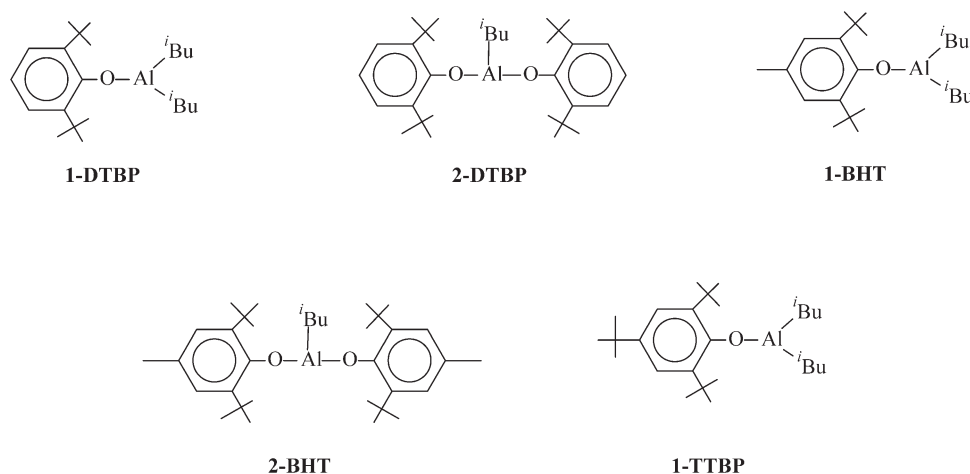
Synthesis of Isobutylaluminum Aryloxides

Phenol (0.015 mol for preparation of monoaryloxides or 0.030 mol for diaryloxides) was dissolved in 4 ml of toluene. The resulting solution was slowly (for ∼30 min) added to 15 mL of TIBA solution in toluene ([Al] = 0.015 mol) under vigorous stirring at room temperature. The reaction was carried to completion which was monitored by ^{1}H NMR spectra of the product. In all the cases the reactions occured selectively with the formation of the desired products. ^{1}H- and ^{13}C-NMR spectra of the products are presented below.

Diisobutylaluminum 2,6-di-tert-Butyl Phenoxide (2,6-di-^{t}Bu-C$_6$H$_3$O)Al^{i}Bu$_2$ (1-DTBP). NMR ^{1}H (toluene-d$_8$, δ, ppm): 0.37 (d., 4H, J=7.1 Hz; CH$_2$, 2 ^{i}Bu),1.01 (d., 12H, J=6.6 Hz; CH$_3$, 2 ^{i}Bu), 1.45 (s. 18H; CH$_3$, 2 ^{t}BuAr), 2.00 (m., 2H; CH, 2 ^{i}Bu), 6.77 (tr., 1H; Ar-H, J=7.8 Hz), 7.16 (d., 2H, J=7.9 Hz; Ar-H); NMR ^{13}C (toluene-d$_8$, δ, ppm): 23.9 (CH$_2$, 2 ^{i}Bu), 25.7 (CH, 2 ^{i}Bu), 28.1 (CH$_3$, 2 ^{i}Bu), 31.9 (CH$_3$, 2 ^{t}BuAr), 34.7 (C, 2 ^{t}BuAr), 119.3, 125.3, 138.3, 156.1 (Ar);

Diisobutylaluminum 2,6-di-Tert-Butyl, 4-Methyl Phenoxide (2,6-di-^{t}Bu,4-Me-C$_6$H$_2$O)Al^{i}Bu$_2$ (1-BHT). NMR ^{1}H (toluene-d$_8$, δ, ppm): 0.38 (d., 4H, J=7.1 Hz; CH$_2$, 2 ^{i}Bu),1.02 (d., 12H, J=6.6 Hz; CH$_3$, 2 ^{i}Bu), 1.46 (s., 18H; CH$_3$, 2 ^{t}BuAr), 2.00 (m., 2H; CH, 2 ^{i}Bu), 2.24 (s., 3H; CH$_3$, MeAr), signal Ar-H is overlapped by toluene-d$_8$; NMR ^{13}C (toluene-d$_8$, δ, ppm): 21.5 (CH$_3$, MeAr), 23.9 (CH$_2$, 2 ^{i}Bu), 25.7 (CH, 2 ^{i}Bu), 28.1 (CH$_3$, 2 ^{i}Bu), 32.0 (CH$_3$, 2 ^{t}BuAr), 34.7 (C, 2 ^{t}BuAr), 125.9, 127.1, 138.0, 153.8 (Ar);

Diisobutylaluminum 2,4,6-tri-tert-Butyl Phenoxide (2,4,6-tri-^{t}Bu-C$_6$H$_2$O)Al^{i}Bu$_2$ (1-TTBP). NMR ^{1}H (toluene-d$_8$, δ, ppm): 0.37 (d., 4H, J=7.1 Hz; CH$_2$, 2 ^{i}Bu),1.00 (d., 12H, J=6.6

Scheme 1. Structures of isobutylaluminum aryloxides.

Hz; CH$_3$, 2 ^{i}Bu), 1.33 (s., 9H; CH$_3$, p-^{t}BuAr), 1.50 (s., 18H; CH$_3$, 2 o-^{t}BuAr), 1.99 (m., 2H; CH, 2 ^{i}Bu), 7.33 (s. 2H; Ar-H); NMR ^{13}C (toluene-d$_8$, δ, ppm): 23.9 (CH$_2$, ^{i}Bu), 25.7 (CH, ^{i}Bu), 28.1 (CH$_3$, ^{i}Bu), 32.0 (CH$_3$, p-^{t}BuAr), 32.1 (CH$_3$, 2 o-^{t}BuAr), 34.6 (C, p-^{t}BuAr), 35.0 (C, 2 o-^{t}BuAr), 121.9, 137.3, 140.3, 153.6 (Ar);

Isobutylaluminum Bis-(2,6-di-tert-Butyl) Phenoxide (2,6-di-^{t}Bu-C$_6$H$_3$O)$_2$Al^{i}Bu (2-DTBP). NMR ^{1}H (toluene-d$_8$, δ, ppm): 0.41 (d., 2H, J=7.2 Hz; CH$_2$, ^{i}Bu), 0.72 (d., 6H, J=6.5 Hz; CH$_3$, ^{i}Bu), 1.55 (s. 36H; CH$_3$, 4 ^{t}BuAr), 1.78 (m., 1H; CH, ^{i}Bu), 6.82 (tr., 2H, J=7.8 Hz; Ar-H), 7.22 (d., 4H, J=7.8 Hz; Ar-H); NMR ^{13}C (toluene-d$_8$, δ, ppm): 23.6 (CH$_2$, ^{i}Bu), 24.9 (CH, ^{i}Bu), 27.4 (CH$_3$, ^{i}Bu), 32.0 (CH$_3$, 4 ^{t}BuAr), 35.2 (C, 4 ^{t}BuAr), 120.0, 125.5, 138.5, 155.0 (Ar);

Isobutylaluminum Bis-(2,6- di-tert-Butyl, 4-Methyl Phenoxide) (2,6-di-^{t}Bu,4-MeC$_6$H$_2$O)$_2$Al^{i}Bu (2-BHT). NMR ^{1}H (toluene-d$_8$, δ, ppm): 0.45 (d., 2H, J=7.2 Hz; CH$_2$, ^{i}Bu), 0.77 (d., 6H, J=6.5 Hz; CH$_3$, ^{i}Bu), 1.59 (s. 36H; CH$_3$, 4 ^{t}BuAr), 1.82 (m., 1H; CH, ^{i}Bu), 2.27 (s., 6H; CH$_3$, 2 MeAr), signal Ar-H is overlapped by toluene-d$_8$; NMR ^{13}C (toluene -d$_8$, δ, ppm): 21.4 (CH$_3$, 2 MeAr), 22.0 (CH$_2$, ^{i}Bu), 25.2 (CH, ^{i}Bu), 27.5 (CH$_3$, ^{i}Bu), 32.0 (CH$_3$, 4 ^{t}BuAr), 35.2 (C, 4 ^{t}BuAr), 126.2, 127.9, 138.1, 152.8 (Ar).

Polymerization

Polymerization was performed in a 200 mL stainless steel reactor equipped with a mechanical stirrer and a temperature-controlled jacket. The reactor was evacuated at 80°C for 3 h and flushed with dry argon. The sealed off ampoule with a specified amount of the catalyst was fixed in the breaker inside of the reactor. The reactor was evacuated at room temperature for 2 h and then sequentially filled with dry toluene (60 mL), required amount of diene (for terpolymerization) and cocatalyst. The solution was then saturated with gaseous monomers at desired monomers pressure and polymerization temperature. Polymerization was started by breaking the glass ampoule with the catalyst. Flow rate of gaseous monomer or comonomers were registered keeping constant pressure inside the reactor. The temperature of the reaction medium within the reactor was

fixed via an internal thermocouple. The reaction was terminated by injection of acidic ethanol containing 5 wt % of HCl. The polymers were multiply washed in the mixture of water with ethanol and then dried in vacuum at 60°C for constant weight.

Characterization of Polymers

MW and MW characteristics of polymers (M_w, M_n, M_w/M_n) were measured by gel permeation chromatography (GPC) using a Waters GPCV-2000 device (PLgel columns, eluent 1,2,4-trichlorobenzene, 135°). GPC columns were calibrated using commercially available polystyrene standards.

Melting point and crystallinity of polymers were determined from the DSC data. Mettler Toledo DSC 822E system with STARe 6.2 software were used for measurements. DSC data consisted of three cycles under argon atmosphere with scan rate of 10 deg/min under following temperature scheme: heating at temperature range from −100 to +170°C, cooling to 10°C, and following reheating to 170°C. Melting points and melting enthalpies are submitted for second heating of the samples.

Copolymers composition was determined by ^{13}C-NMR with broadband ^{1}H decoupling for copolymer solutions in tetrachloroethane-d$_2$ (10 wt %) at 130°C for ethylene/propylene samples and at 110°C for terpolymers with diene. The references of chemical shift of copolymers have been made according to literature data.[39,40] The spectra have been recorded on a "AVANCE II-300" (Bruker) Fourier spectrometer equipped with special Bruker's probe (Probe: 5 mm BB-1H/D S1) operating in temperature range from −130°C to +180°C. Resonance frequency is equal to 75.49 MHz, number of scans 40000.

RESULTS AND DISCUSSION

Aryloxides used as activators (Scheme 1) were (2,6-di-^{t}Bu C$_6$H$_3$O)Al^{i}Bu$_2$ (**1-DTBP**), (2,6-di-^{t}BuC$_6$H$_3$O)$_2$Al^{i}Bu (**2-DTBP**), (2,6-di-^{t}Bu,4-Me-C$_6$H$_2$O)Al^{i}Bu$_2$ (**1-BHT**), (2,6-di-^{t}Bu,4-Me-C$_6$H$_2$O)$_2$Al^{i}Bu (**2-BHT**), (2,4,6-tri-^{t}Bu-C$_6$H$_2$O)Al^{i}Bu$_2$ (**1-TTBP**). Prefix "1-" corresponds to mono- and prefix "2-" corresponds to diaryloxides of isobutylaluminum. Table I illustrates catalytic properties of dimethylated zirconocene rac-Et(2-Me)Ind$_2$ZrMe$_2$ activated by different sterically hindered isobutylaluminum

Table I. Homopolymerizations of Ethylene, Propylene; Copolymerization of Ethylene and Propylene; Terpolymerization of Ethylene, Propylene, and 5-ethylidene-2-norbornene on *rac*-Et(2-MeInd)$_2$ZrMe$_2$ with Isobutylaluminum Aryloxides as Activators (Ethylene Pressure 10.6 atm, Propylene Pressure 4 atm, Toluene, 30°C, Al/Zr = 300 mol/mol)

N	Activator	Monomer(s)[a]	[Zr]·10$^{6, mol}$	t[b], min	Y[c], g	A[d]	M_w	M_n	M_w/M_n	Copolymer composition[e]	T_m[f], °C	χ[g], %
1	1-DTBP	E	6.16	2.9	10.2	450	173,000	49,000	3.5	–	135	70
2	2-DTBP	E	4.19	7.9	4.3	330	171,000	41,000	4.2	–	137	70
3	1-BHT	E	6.16	2.5	8.6	440	162,000	58,000	2.8	–	140	71
4	2-BHT	E	3.94	6.2	3.8	250	n.d.[h]			–	138	62
5	1-TTBP	E	2.46	3.9	8.4	840	n.d.			–	137	63
6	1-DTBP	P	3.45	30.0	2.4	30	179,000	101,000	1.8	–	144	41
7	2-DTBP	P	3.70	30.0	2.1	17	72,000	42,000	1.7	–	143	41
8	1-BHT	P	3.45	6.0	1.8	24	157,000	90,000	1.7	–	142	42
9	2-BHT	P	4.18	9.3	2.0	30	173,000	90,000	1.9	–	140	40
10	1-TTBP	P	2.70	10.3	4.1	210	147,000	66,000	2.2	–	139	42
11	MAO[i]	P	1.50	60.0	4.4	31	93,000	51,000	1.8	–	137	31
12	1-DTBP	E/P	4.68	3.3	12.6	470	92,000	20,400	4.5	86/14	101	22
13	2-DTBP	E/P	6.16	7.0	5.8	130	96,000	30,000	2.2	89/11	99	27
14	1-BHT	E/P	6.16	2.5	12.8	290	108,000	36,000	3.0	82/18	100	18
15	2-BHT	E/P	3.45	10.3	4.7	180	160,000	71,000	2.3	92/8	101	33
16	1-TTBP	E/P	2.46	3.9	6.3	350	143000	61,000	2.3	91/9	102	31
17	1-DTBP	E/P/ENB	6.90	3.3	7.9	130	111,000[j]	43,000	2.6	85/13/2	85, 101	21
18	2-DTBP	E/P/ENB	7.64	5.5	2.7	44	176,000[k]	76,000	2.3	91/7/2	87	20
19	1-BHT	E/P/ENB	6.90	4.0	8.6	140	115,000[l]	38,000	3.0	88/8/4	81, 106	21
20	2-BHT	E/P/ENB	4.19	18.8	1.7	54	181,000	81,000	2.2	91/7/2	82, 99, 122	20
21	1-TTBP	E/P/ENB	2.46	7.0	3.7	156	n.s.[m]			90/8/2	85, 101, 120	20

[a] E, ethylene; P, propylene; ENB, 5-ethylidene-2-norbornene; E/P, 0.7/1 mol/mol; E/P/ENB, 4.7/4.3/1 mol/mol/mol.
[b] Time of polymerization.
[c] Polymer yield in grams.
[d] Specific activity of the system determined by consumption of gaseous monomer in 2 min of reaction time and related to the amount of catalyst and to the concentration of (co)monomers in kg PE/(mol Zr min Σ[comon.]).
[e] Copolymer composition in mol % for E/P and E/P/ENB.
[f] Melting point determined during the second heating of the sample.
[g] The degree of crystallinity of polymer determined from the area of DSC melting endotherms normalized to 293 J/g in the case of polyethylene and copolymers and to 207 J/g in the case of polypropylene.
[h] n.d., not determined.
[i] MAO has been used as activator (toluene, propylene pressure 1.5 atm, Al/Zr = 1000 mol/mol).
[j] GPC curve is bimodal. The values of the peaks maximum and relative areas are indicated in brackets. Pk 1 (4.54, 55%) M_w = 42,000, M_w/M_n = 1.5, Pk(2) (5.15, 45%) M_w = 196,000, M_w/M_n = 1.9.
[k] GPC curve is bimodal: Pk 1 (4.86, 66%) M_w = 92,000, M_w/M_n = 1.6, Pk(2) (5.45, 34%) M_w = 346,000, M_w/M_n = 1.5.
[l] GPC curve is bimodal. Pk 1 (4.42, 31%) M_w = 30,000, M_w/M_n = 1.1, Pk(2) (4.95, 69%) M_w = 152,000, M_w/M_n = 3.0.
[m] Copolymer is not soluble in 1,2,4-trichlorobenzene at 135°C.

aryloxides in reactions of ethylene and propylene homopolymerization, ethylene and propylene copolymerization, ethylene, propylene and 5-ethylidene-2-norbornene terpolymerization, molecular weight characteristics, composition, and thermophysical characteristics of polymers.

All synthesized mono- and disubstituted isobutylaluminum aryloxides are effective activators of *rac*-Et(2-MeInd)$_2$ZrMe$_2$ in homopolymerization of ethylene at molar ratio Al/Zr = 300 mol/mol (Table I, entries 1 − 5). The structural features of each activator are manifested through differences in specific activity of the systems. Under other similar conditions the specific activities of the systems determined as amount of ethylene consumed by the 2'nd minute of polymerization and related to

the catalyst amount and ethylene concentration (kg PE/mol Zr min [E]) corresponds to the row: **1-TTBP** (840) > **1-DTBP** (450) ≈ **1-BHT** (440) > **2-DTBP** (330) > **2-BHT** (250). The systems with bulky disubstituted isobutylaluminum aryloxides showed lesser activity (entries 2,5). The dependencies of ethylene consumption rate on polymerization time for different systems can be illustrated by data on Figure 1. One can see that all the systems display decay-like kinetics so that the maximum value of ethylene consumption rate is observed at the initial stage of the reaction with subsequent considerable decreases over time. Molecular weight of polyethylene samples barely depends on the type of activator ($M_w \sim$ 160000-170000). Their polydispersity indexes are higher (M_w/M_n=3-4) compared to
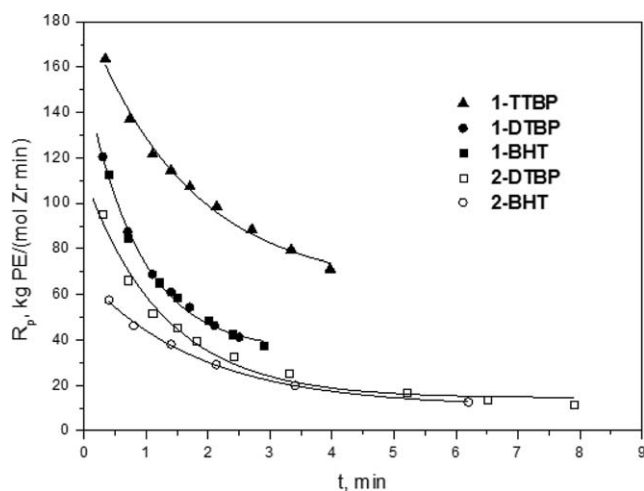
Figure 1. Ethylene consumption rate—polymerization time profiles in ethylene polymerization with catalyst systems *rac*-Et(2-MeInd)$_2$ZrMe$_2$/iso-butylaluminum aryloxides.

Figure 2. Comonomers consumption rate—polymerization time profiles in ethylene/propylene copolymerization with catalyst systems *rac*-Et(2-MeInd)$_2$ZrMe$_2$/isobutylaluminum aryloxides.

polymers formed on single-site catalyst systems (M$_w$/M$_n$~2). It is difficult to say what is the reason of rather high PDI values of ethylene based polymers produced with isobutylaluminum aryloxide activators so far as catalytic systems are formed with participation of two individual compounds (precatalysts and aryloxide). Most probably in the case of homopolymerization of ethylene the increase of PDI may be connected with some overheating of reaction medium in the initial stage of polymerization with such active systems. The increase of temperature up to 70–90°C has been fixed at the polymerization start. However, as will be shown for propylene polymerizations which were passed with considerably lower activities PDI values of polypropylenes are close to two.

Melting points and crystallinity of polyethylene samples obtained with different activators are of about similar values: 137–140°C and 60–70%, correspondingly. These are typical values for linear polyethylene. The absence of branches is also confirmed by the absence of the band at 1378 cm^{-1} in IR spectra of polyethylene films attributing to scissor vibrations of CH$_3$ groups of branches.

The specific activities of the systems with aryloxide activators in propylene polymerization are of significantly lower values than those in polymerization of ethylene (entries 6–10). They are about four times lower for the system with **1-TTBP** and 10–20 times lower for the others. Among the series the system with **1-TTBP** (entry 10) again shows the highest activity of 210 kg PP/ mol Zr min [P] which is 7–12 times higher than those of the systems with other aryloxide activators. Experiment with MAO as the referenced activator (Al/Zr = 1000 mol/mol, entry 11) showed specific activity about seven times lower than in case of **1-TTBP** being at the level of activities of the systems with other aryloxides. Thus, isobutylaluminum aryloxides used for activation at molar ratio Al/Zr = 300 are very effective activators compared or exceeding MAO by their activation ability and the nature of polymerized olefin is important for these systems. Molecular weights of polypropylenes derived with monosubstituted aryloxide activators have close values (M$_w \approx$
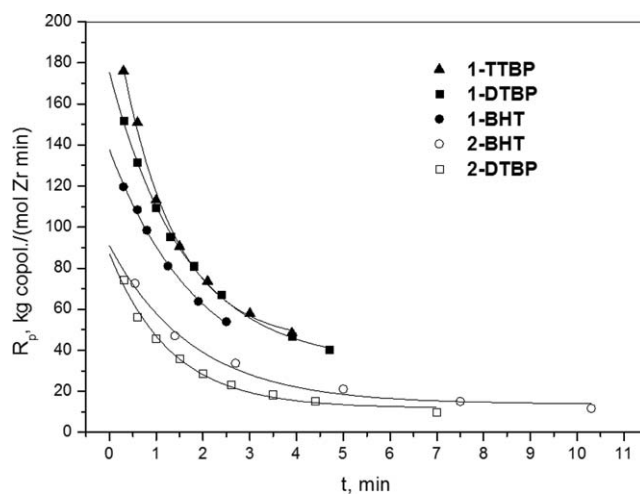
150000–180000) and are much higher than molecular weight of polypropylene obtained with MAO (M$_w$ = 93,000). Molecular weights of polymers derived with disubstituted isobutylaluminum aryloxides are dependent on the type of activator showing approximately two times decrease in the case of **2-DTBP** and some increase for **2-BHT** compared to monosubstituted aryloxides. Polydispersity indexes of polypropylene samples are within the range of M$_w$/M$_n$ = 1.7–2.2 similar to polypropylene derived with MAO as activator (M$_w$/M$_n$ = 1.8). We have mentioned above that the reason of rather high PDI values in the case of polyethylene may be connected with overheating of reaction medium at the first stage of the reaction. This is not the case for propylene polymerization. The temperature of reaction medium remained constant during the reaction. So, the differences in activity values and molecular-weight characteristics of polypropylenes show the formation of various active sites in the reaction of *rac*-Et(2-MeInd)$_2$ZrMe$_2$ with the above activators providing different propagation-termination rates in polymerization process. Isotacticity indexes of polypropylene samples determined as the ratio of areas of the peaks D$_{998}$/D$_{973}$ are in the range of 0.84 and 0.86 which are slightly higher than for the polypropylene produced with MAO D$_{998}$/D$_{973}$ = 0.81. The melting points of polypropylene samples are 140–144°C, crystallinity are 40–42%. Polypropylene produced with MAO has somewhat lower melting point of 139°C but about similar crystallinity of 42%.

Catalyst systems with isobutylaluminum aryloxides are also effective in the synthesis of ethylene/propylene copolymers (entries 12–16). The copolymerizations were conducted at a molar ratio of comonomers in the feed E/P = 0.7/1. Specific activities of the systems are always lower than in the homopolymerization of ethylene. This means that in these systems there is no "effect of the comonomer" which is often observed for Ziegler type heterogeneous catalysts and homogeneous metallocene catalysts. The differences in specific activity are less pronounced in copolymerization than in homopolymerization of ethylene and propylene, but the tendency of reducing activity in
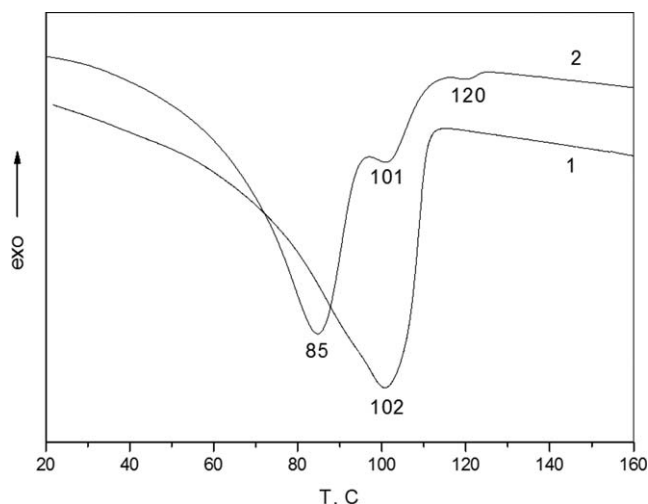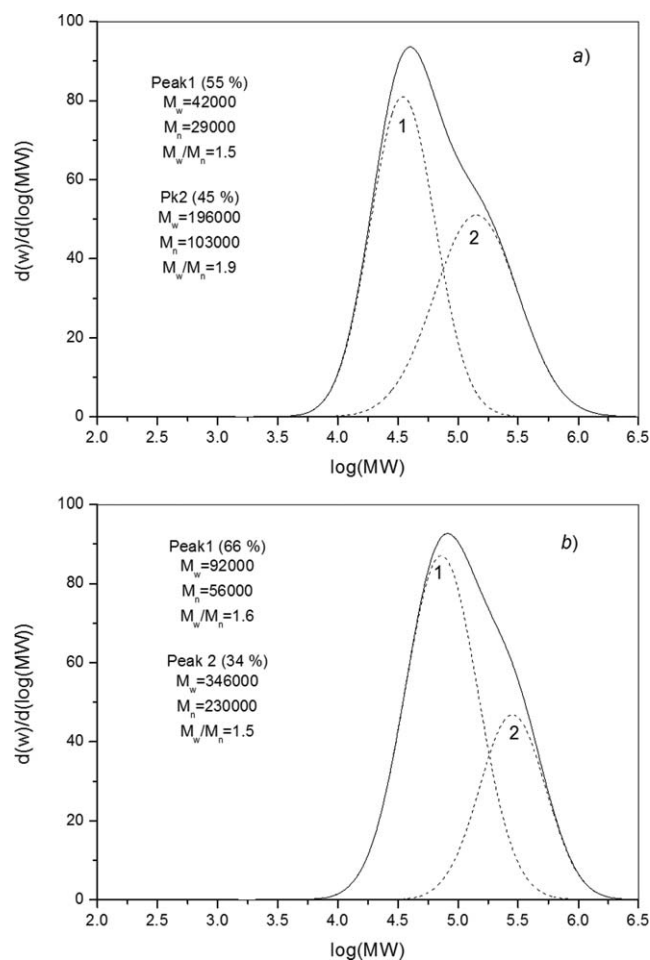
Figure 3. DSC curves of (1) ethylene/propylene copolymer derived with activator **1-TTBP** (entry 16 in Table I) and (2) ethylene/propylene/5-ethylidene-2-norbornene terpolymer derived with activator **1-TTBP** (entry 21 in Table I).

going from monosubstituted to disubstituted activators is also evident (compare entries 12 and 13, 14 and 15). The highest activity of 470 kg of copol./(mol Zr min Σ(comon.)) has been observed for catalytic system with **1-DTBP** activator. Polymerization rate – time profiles (Figure 2) has similar trends as in homopolymerization of ethylene (Figure 1). Molecular weights of copolymers are slightly lower than those of homopolymers of ethylene and propylene. Polydispersity indexes (M_w/M_n) are in a range from 3.0 to 4.2 most probably to some overheating in the beginning of polymerization as in the case of ethylene polymerization. Specific features of activators are manifested through diverse ability to incorporate propylene into copolymer chain. Under other similar conditions the ability to incorporate propylene (mol %) corresponds to the row: **1-BHT** (18) > **1-DTBP** (14) > **2-DTBP** (11) > **1-TTBP** (9) ≈ **2-BHT** (8). Catalyst systems with more crowded disubstituted isobutylaluminum aryloxides allow lower incorporation of propylene compared to monosubstituted ones. Derived copolymers have low melting point (99–102°C) and crystallinity (20–30%). DSC curves are presented as broad peaks (Figure 3, curve 1). The copolymers show low values of glass transition temperatures: −63°C (propylene content 14 mol %, entry 12) and −61°C (propylene content 18 mol %, entry 14).

Catalyst systems with isobutylaluminum aryloxides were also tested in a synthesis of terpolymers of ethylene, propylene, and 5-ethylidene-2-norbornene at a molar ratio of comonomers in the feed E/P/ENB = 4.7/4.3/1 (entries 17–21). Specific activities of the systems with monosubstituted isobutylaluminum aryloxides are within the range of 130-160 kg copol./(mol Zr min Σ[comon.]) (entries 17, 19, 21). Disubstituted activators **2-DTBP** and **2-BHT** (entries 18,20) show about three times lower activity than corresponding monosubstituted analogs (entries 17,19). The highest activity in terpolymerization has been observed with **1-TTBP** similar to the cases of homopolymerization of ethylene and propylene. The type of activator has a sig-

nificant effect on the molecular weight of the resulting copolymers. M_w of copolymers obtained with diaryloxides are of much higher values than those obtained with monoaryloxides (compare entries 17,18 and 19,20). Tercopolymer obtained with **1-TTBP** (entry 21) was insoluble under conditions of GPC measurements probably due to partial crosslinking. Composition of copolymers in terpolymerization is also determined by the type of activator. The highest propylene content was observed in the copolymer derived with **1-DTBP** (13 mol %, entry 17). All other copolymers showed incorporation of propylene at a level of 7–8 mol %. The highest content of diene (4 mol %) was observed in copolymer derived with **1-BHT** (entry 19).

The specific features of terpolymerization with isobutylaluminum aryloxide activators are manifested through compositional inhomogeneity of the derived copolymers that becomes evident in bimodal GPC curves (Figure 4 *a,b*, entries 17,18) and also bi- (entries 17,19) and even trimodal type of DSC curves (entry 21; Figure 3, curve 2). The appearance of a third high temperature peak (120°C) in the terpolymer obtained with **1-TTBP** is probably due to the formation of crosslinked polymeric structures preventing solubility of the copolymer under GPC

Figure 4. GPC curves of ethylene/propylene/5-ethylidene-2-norbornene terpolymers derived on *rac*-Et(2-MeInd)$_2$ZrMe$_2$ with activators (a) **1-DTBP** (entry 17) and (b) **2-DTBP** (entry 18).
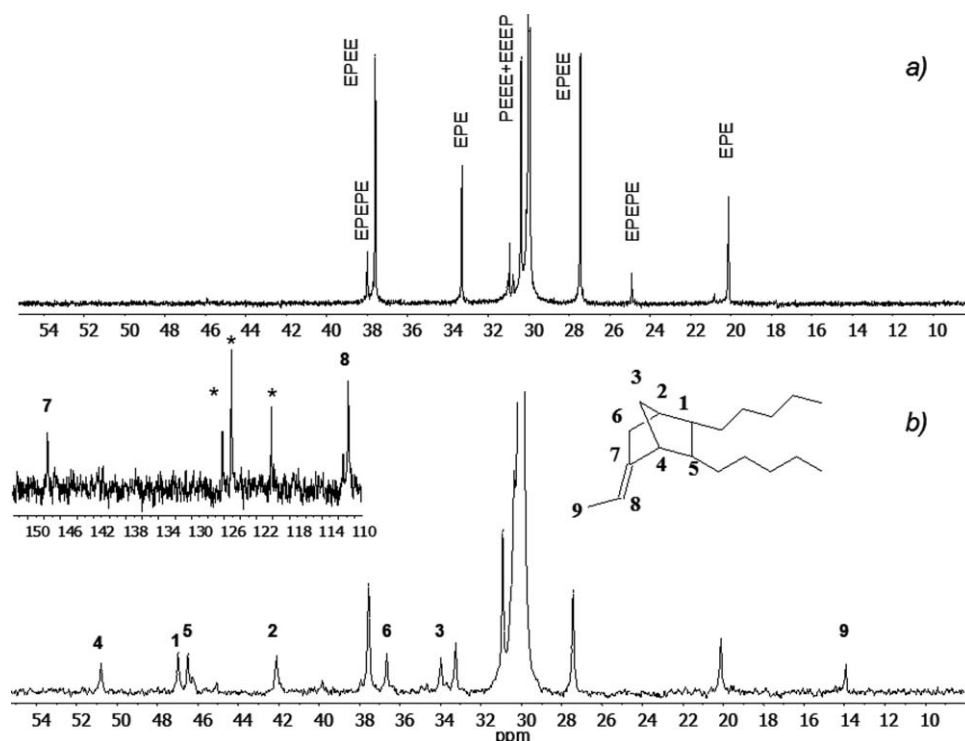
Figure 5. ^{13}C-NMR with broadband proton decoupling spectra of (a) ethylene/propylene copolymer obtained on catalyst system *rac*-Et(2-MeInd)$_2$ZrMe$_2$/**1-DTBP** (entry 13) and (b) ethylene/propylene/5-ethylidene-2-norbornene terpolymer obtained on catalyst system *rac*-Et(2-MeInd)$_2$ZrMe$_2$/**1-BHT** (entry 19). Signals of the remaining phenol are marked with asterisk.

measurements. The reasons of the effects are the subject of further studies. The glass transition temperature is higher for terpolymers (experiments 17 18, 19) than those of ethylene/propylene copolymers being equal to −25, −32, and −18°C, respectively.

Obtaining of ethylene/propylene and ethylene/propylene/diene copolymers with good elastomeric properties is closely related to copolymers composition. The specific feature of catalytic systems based on *rac*-Et(2-MeInd)$_2$ZrMe$_2$ with isobutyl aryloxide activators is their ability to produce alternating copolymers. The ^{13}C-NMR spectra of E/P copolymer [Figure 5(a)] and E/P/ENB terpolymers [Figure 5(b)] do not contain any signals corresponding to PPP sequences (46.0 and 28.3 ppm), while the signals correspondent to PEP sequences (24.9 and 38.0 ppm) have very low intensity in E/P copolymer and are not available in copolymer E/P/ENB. In other words, propylene is incorporated into copolymer macromolecule as isolated units separated by ethylene sequences. That provides formation of low-crystalline copolymers. Exocyclic double bond of diene retains during copolymerization and it can be further used for copolymer functionalization or crosslinking.

Aside from being easy obtainable and effective activators of metallocene complexes in homo- and copolymerization of olefins, isobutylaluminum aryloxides have another practical advantage allowing *in situ* formation of polyolefin stabilizer. The matter is that during washing of the polymer the isobutylaluminum aryloxide cocatalyst is hydrolyzed with formation of

phenol. Phenolic antioxidans such as BHT or MAD are typical stabilizers.[41] The presence of phenol inside of polymer material is recognized by the presence of the narrow absorption band of at 3648–3650 cm^{-1} in FTIR spectra of polymer films. The band is attributed to valence vibrations of phenol OH groups. Sequential washing of polymers with alcohol/water mixture allows regulating the content of phenol in polymers up to zero.

CONCLUSION

It has been shown for the first time that sterically hindered isobutylaluminum aryloxides with tert-butyl groups in 2,6- positions of O-Ph fragment are effective activators of metallocene complexes in olefin polymerization, as shown in examples of homopolymerization of ethylene, propylene; copolymerization of ethylene and propylene and terpolymerization of ethylene, propylene and 5-ethylidene-2-norbornene with zirconocene *rac*-Et(2-MeInd)$_2$ZrMe$_2$. The specific features of activators of different ligand architecture $(2,5-^tBu,4-RC_6H_5O)Al^iBu_2$ (R = H, Me, ^tBu) or $(2,5-^tBu,4-RC_6H_5O)_2Al^iBu$ (R = H, Me) are manifested through significant differences in specific activity of the systems and molecular weight characteristics of resulting polymers. Catalytic systems with these activators show much higher activity in ethylene polymerization than in polymerization of propylene. Monosubstituted isobutylaluminum aryloxides provide much higher activity to the systems in all polymerization processes and stronger ability for propylene incorporation in copolymerization processes than diaryloxides. These observations

indirectly prove the importance of sterical characteristics of activators (counterions) for olefin coordination and insertion. No comonomer effect has been observed in copolymerization of ethylene with propylene and terpolymerization with 5-ethylidene-2-norbornene. Copolymers of ethylene with propylene have low crystallinity (20–30%) and glass transition temperature ($\sim-60°C$). Propylene is incorporated into copolymer macromolecule as isolated units separated by not long ethylene sequences. That provides formation of low-crystalline copolymers. Exocyclic double bond of diene retains during copolymerization and it can be further used for copolymer functionalization or crosslinking. Fractionally inhomogeneous terpolymers of ethylene/propylene/5-ethylidene-2-norbornene are formed with these systems which manifests in polymodality of GPC and DSC curves. Under hydrolysis during washing of polymers isobutylaluminum aryloxide cocatalysts give phenols being typical stabilizers of polyolefins.

ACKNOWLEDGMENTS

REFERENCES

1. Kaminsky, W. *J. Chem. Soc. Dalton Trans.* **1998**, 1413.

2. Brintzinger, H. H.; Fischer, D. *Adv. Polym. Sci.* **2013**, *258*, 29.

3. Razavi, A. *Adv. Polym. Sci.* **2013**, *258*, 43.

4. Boggioni, L.; Tritto, I. *Adv. Polym. Sci.* **2013**, *258*, 117.

5. Chen, E. Y. X.; Marks, T. *Chem. Rev.* **2000**, *100*, 1391.

6. Kaminsky, W.; Sinn, H. *Adv. Polym. Sci.* **2013**, *258*, 1.

7. Reddy, S. S.; Shashidhar, G.; Sivaram, S. *Macromolecules* **1993**, *26*, 1180.

8. Williams, V. C.; Dai, C.; Li, Z.; Collins, S.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Angew. Chem. Int. Ed.* **1999**, *38*, 3695.

9. Stapleton, R. A.; Galan, B. R.; Collins, S.; Simons, R. S.; Garrison, J. C.; Youngs, W. J. *J. Am. Chem. Soc.* **2003**, *125*, 9246.

10. Stapleton, R. A.; Al-Humydi, A.; Chai, J.; Galan, B. R.; Collins, S. *Organometallics* **2006**, *25*, 5083.

11. Tynys, A.; Eilertsen, J. L.; Seppälä, J. V.; Rytter, E. *J. Polym. Sci. Part A, Polym. Chem.* **2007**, *45*, 1364.

12. Descour, C.; Sciarone, T. J. J.; Cavallo, D.; Macko, T.; Keichtermans, M.; Korobkov, I.; Duchateau, R. *Polym. Chem.* **2013**, *4*, 4718.

13. Romano, D.; Andablo-Reyes, E. A.; Ronca, S.; Rastogi, S. *J. Polym. Sci. Part A, Polym. Chem.* **2013**, *51*, 1630.

14. Busico, V.; Cipullo, R.; Cutillo, F.; Friederichs, N.; Ronca, S.; Wang, B. *J. Am. Chem. Soc.* **2003**, *125*, 12402.

15. Manteghi, A.; Arabi, H.; Jahani, Y. *Polym. Int.* **2015**, *64*, 900.

16. Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997**, *30*, 1247.

17. Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **2000**, *201*, 558.

18. Pedeutour, J. N.; Cramail, H.; Deffieux, A. *J. Mol. Catal. Chem.* **2001**, *176*, 87.

19. Kissin, Y. V. *Macromol. Rapid. Commun.* **2004**, *25*, 1554.

20. Kissin, Y. V. *Macromolecules* **2003**, *36*, 7413.

21. Tritto, I.; Boggioni, L.; Sacchi, M. C.; Dall'Occo, T. *J. Mol. Catal. A Chem.* **2003**, *204205*, 305.

22. Hendershot, D. G.; Kumar, R.; Barber, M.; Oliver, J. P. *Organometallics* **1991**, *10*, 1917.

23. US Patent 7683003, **2010** (Inventors: Campbell, R.E.; Desjardins, S.; Hustad, P.D.; Romer, D.R.).

24. US Patent 6528449, **2003** (Inventors: Chen, E.Y.; Kruper, W. J.; Roof, G.R.; Schwartz, D.J.; Storer, J. W.).

25. Boudier, A.; Breuil, P. A. R.; Magna, L.; Olivier-Bourbigou, H.; Braunsteinb, P. *Dalton Trans.* **2015**, *44*, 12995.

26. Shrew, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409.

27. Clegg, W.; Lamb, E.; Liddle, S. T.; Snaith, R.; Wheatley, A. E. H. *J. Organomet. Chem.* **1999**, *573*, 305.

28. Ogrin, D.; Bott, S. G.; Barron, A. R. *J. Chem. Cryst.* **2008**, *38*, 397.

29. Martinez, G.; Pedrosa, S.; Tabernero, V.; Mosquera, M. E. G.; Cuenca, T. *Organometallics* **2008**, *27*, 2300.

30. Giesbrecht, G. R.; Gordon, J. C.; Brady, J. T.; Clark, D. L.; Keogh, D. W.; Michalczyk, R.; Scott, B. L.; Watkin, J. G. *Eur. J. Inorg. Chem.* **2002**, *3*, 723.

31. Firth, A. V.; Stewart, J. C.; Hoskin, A. J.; Stephan, D. W. *J. Organomet. Chem.* **1999**, *591*, 185.

32. Son, A. J. R.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics.* **2003**, *22*, 2318.

33. Dickie, D. A.; MacIntosh, I. S.; Ino, D. D.; He, Q.; Labeodan, O. A.; Jennings, M. C.; Schatte, G.; Walsby, C. J.; Clyburne, J. A. C. *Can. J. Chem.* **2008**, *86*, 20.

34. Yu, T. L.; Huang, C. H.; Yang, L. F.; Ko, B. T.; Lin, C. C. *J. Chin. Chem. Soc. (Taipei)* **2000**, *47*, 1185.

35. Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics.* **1988**, *7*, 2543.

36. Petrie, M. A.; Olmstead, M. M.; Power, P. P. *J Am. Chem. Soc.* **1991**, *113*, 8704.

37. Healy, M. D.; Ziller, J. W.; Barron, A. R. *Organometallics* **1991**, *10*, 597.

38. Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263.

39. Randall, J. C. *JMS – Rev. Macromol. Chem. Phys.* **1989**, *29*, 201.

40. Kolbert, A. C.; Didier, J. C. *J. Appl. Polym. Sci.* **1999**, *71*, 523.

41. Andrews, S. M. In Encyclopedia of Polymer Science and Technology; 4th ed.; Wiley: New York, **2012**; Vol. *1*, p 209.