

New Penta-ether as the Internal Donor in the MgCl_2 -supported Ziegler-Natta Catalysts for Propylene Polymerization^{*}

Roya Zahedi^a, Faramarz Afshar Taromi^{b**}, Seyed Heidar Mirjahanmardi^c,
Mehdi Nekoomanesh Haghighi^d, Khosrow Jadidi^e and Roghayeh Jamjah^d

^a Department of Chemistry, Amirkabir University of Technology, 15875-4413, Tehran, Iran

^b Department of Polymer Engineering, Amirkabir University of Technology, 15875-4413, Tehran, Iran

^c Department of Polymer Engineering, Amirkabir University of Technology-Mahshahr Campus, 63516-43659, Mahshahr, Iran

^d Iran Polymer and Petrochemical Institute (IPPI), 14977-13115, Tehran, Iran

^e Department of Chemistry, Shahid Beheshti University, 19839-69411, Tehran, Iran

Abstract The penta-ether compound was synthesized by the reaction of di(trimethylolpropane) with sodium hydride as the strong base and methyl iodide as the alkyl halide. This compound was characterized by NMR, FTIR, and GC techniques. The MgCl_2 -supported titanium catalysts were incorporated with varying amounts of penta-ether compound as the internal donor and also the catalysts without the internal donor were synthesized. The synthesized catalysts and the conventional Ziegler-Natta catalyst were characterized. The titanium contents were determined by spectrophotometry, magnesium by complexometric titration and chloride by argentometric titration. The effects of the new internal donor on propylene polymerization with the prepared MgCl_2 -supported Ziegler-Natta catalysts were investigated and then these results were compared to the results obtained using the conventional diisobutyl phthalate-based-Ziegler-Natta catalyst. The highest crystallinity degree, melting temperature, and isotacticity of polypropylene were obtained using the catalyst with a penta-ether/ Mg molar ratio equal to 0.21.

Keywords: Williamson reaction; Internal donor; Ziegler-Natta catalyst; External donor; Propylene polymerization.

INTRODUCTION

Among polyolefin resins, polypropylene is one of the largest in demand in the world market due to its high performance characteristics such as stiffness, impact resistance, transparency, ability to be recycled^[1], light weight, corrosion resistance^[2], high melting temperature (165 to 173 °C^[3]), good processability^[4], and low production cost^[5]. Polypropylene has a variety of application on daily life, from packaging, toys, pipes, tools^[6], and domestic appliances to specialty applications in the electronic, airplane, and automotive industries^[3]. Since the memorial discovery by Karl Ziegler and Giulio Natta in 1953 and 1954^[7], the heterogeneous Ziegler-Natta catalyst has become indispensable catalyst for the industrial production of polyolefins for more than half century^[8].

The last generation of these systems is generally based on TiCl_4 adsorbed on MgCl_2 , with a Lewis base, usually called the donor^[9] and a cocatalyst, and polymerization is carried out in the presence of hydrogen^[10]. In general, a complete Ziegler-Natta catalyst system is required with both an internal donor (ID) added during catalyst preparation and an external donor (ED) added during polymerization simultaneously with

^{*} This work was financially supported by the Marun Petrochemical Co., Mahshahr, Iran.

^{**} Corresponding author: Faramarz Afshar Taromi, E-mail: afshar@aut.ac.ir

Received August 12, 2015; Revised November 12, 2015; Accepted November 15, 2015

doi: 10.1007/s10118-016-1751-2

alkylaluminum cocatalyst^[1, 9]. In contact with alkylaluminum cocatalyst, supported titanium tetrachloride is converted to an active site that equips a coordinative vacancy for incoming olefin monomer and a titanium-carbon bond as a growing chain^[8]. The accepted mechanism for the polymer chain growth reaction (propagation step) is based on that proposed by Cossee-Arlman^[11] in 1964 for the heterogeneous Ziegler-Natta catalysts. The chain growth mechanism basically occurs in two steps: (i) olefin coordination to a vacant site; (ii) olefin insertion into the metal growing chain bond through a *cis*-opening of the olefin double bond^[12]. The oxidation state of titanium species varies from (IV) to (II) during polymerization. Soga *et al.* concluded that both of Ti^{2+} and Ti^{3+} species were active for ethylene polymerization but α -olefins including propylene could polymerize only with Ti^{3+} species^[10, 13].

There is agreement that the activated $MgCl_2$ primary particles are made of a limited number of $Cl-Mg-Cl$ monolayers piled irregularly one on top of the other, which should present (110) and (104) lateral cuts^[9]. The two surfaces differ in coordination of the surface magnesium atoms; the (104) surface features five coordinate magnesium atoms, whereas the (110) surface features four coordinate magnesium atoms. The unsaturated magnesium atoms generate adsorption sites for titanium tetrachloride and electron donors. Coadsorption of titanium tetrachloride and electron donors has been shown to have several effects. Donors present in excessive amounts may lead to effective poisoning of the polymerization active sites *via* direct binding to the titanium atoms, therefore affecting molecular weights of the polymeric products. In addition, donors bound to the magnesium dichloride surfaces in the proximity of the titanium species may alter their steric environment and even improve their stereospecificity^[14]. Electron donor compounds influence the type and distribution of active centers of the catalysts^[15, 16], the stereo- and region-chemistry of the synthesized polypropylene^[9], and properties of polymer produced^[16].

The fifth generation of Ziegler-Natta catalyst systems has been developed^[1] using diethers (as the internal donor) without the need of an external donor to produce polypropylene^[16] also with high isotactic index, because this internal donor strongly coordinates to the support and cannot be extracted by the cocatalyst during polymerization. The development of internal donors with novel structures and functions is the most direct and sensible way to produce a new generation of this catalyst^[1]. By complexing with the magnesium atom through the lone pairs of electrons on its two O atoms, diether assists in enhancing the peripheral electron density of the titanium atom, which is connected to a magnesium atom through the double chloride bridges^[17]. The presence and the structure of electron donors influence the activity, the isospecificity (from a large fraction of almost atactic polymer as in the absence of any electron donor^[18]), the chain transfer with hydrogen of the catalysts (which clearly allows one to control the molecular weights of the produced polymers^[18]), and the molecular weight distribution (that can be rather narrow or rather broad^[18]), and the melting temperature of the corresponding polymers^[19].

It was shown that more effective 1,3-diethers have to possess a short distance between the O atoms of the OR-groups (R: Alkyl) to coordinate preferentially to the same magnesium atom of the (110) face of $MgCl_2$ ^[16]. It was found that certain 2,2-disubstituted-1,3-dimethoxypropanes with branched and bulky hydrocarbon substituents in the 2-position have the best performance^[20, 21]. Bulky substituent on the diether (such as diisobutyl) gives similar isotacticity to the phthalate/silane pair, but twice the productivity. The MWD of the polymer is also narrower. A less hindered substituent on the diether (such as ethyl, butyl) gives similar activity, but a lower isotacticity^[22]. Diethers with linear and less bulky hydrocarbon substituents is reported to be a lower performance electron donor^[20] and these compounds when coordinated on the magnesium adjacent to the active titanium atoms, cannot be able to make the active centers highly stereospecific^[19].

So far, more literatures reported the polymerization of propylene using Ziegler-Natta catalysts containing ether compounds with two methoxy groups as internal donors. For the first time, in this study, a multi-ether compound (penta-ether) intended to be used as a new internal donor for the $MgCl_2$ -supported Ziegler-Natta catalysts was designed, synthesized, and then characterized. The $MgCl_2$ -supported Ziegler-Natta catalysts were synthesized from $MgCl_2$ adduct as a support, $TiCl_4$ as an active site, and this new penta-ether as an internal donor. In order to achieve the optimum molar ratio from the internal donor in Ziegler-Natta catalysts (ID/Mg),

varying amounts of the internal donor were used in the preparation of catalysts. Then, polymerization of propylene was carried out with these catalysts, with and without the external donor. The effects of different amounts of the penta-ether compound as the internal donor on the performance of the Ziegler-Natta catalysts were investigated and then compared to the industrial diisobutyl phthalate-based Ziegler-Natta catalyst.

EXPERIMENTAL

Materials

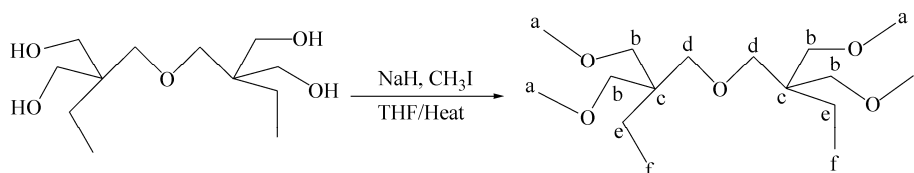
All the materials and operation steps were performed under dry nitrogen atmosphere using a standard glove box and nitrogen line. Ultrahigh purity nitrogen (99.999%, Farafan Gas Co., Iran) after by passing through columns packed with silica gel (with moisture indicator), potassium hydroxide (KOH), and molecular sieves (3 and 4 Å) were used for the synthesis of penta-ether.

Triethylaluminum (TEA, 10% solution in hexane), propylene (99.8%), hydrogen (99.99%), *n*-hexane (99.97%), cyclohexylmethyldimethoxysilane (C-donor), diisobutyl phthalate-based MgCl_2 -supported Ziegler-Natta catalyst, and nitrogen (99.9%, for synthesis of catalysts and polypropylenes) were obtained from Marun Petrochemical Co., Mahshahr, Iran. $\text{MgCl}_2 \cdot 2.7\text{EtOH}$ adduct was obtained from Petrochemical Research & Technology Co., Tehran, Iran.

Tetrahydrofuran (THF, 99%), *O*-xylene ($\geq 99.8\%$), ethyl acetate (99.8%), sodium sulfate, sulfuric acid (95%–97%), potassium hydroxide pellets, methyl iodide ($\geq 99\%$), hydrogen peroxide (30%), sodium rods, molecular sieves (3 and 4 Å), calcium hydride (95%), sodium hydride (NaH, 60 wt%), benzophenone, silica gel (60), silica gel with moisture indicator, and *n*-heptane (99%) were purchased from Merck. Toluene (99%, Acros), diethyl ether (99%, Acros), di(trimethylolpropane) (97%, Aldrich), titanium tetrachloride (99.99%, Tianjin) were purchased. All solvents were dried prior to use.

Penta-ether Synthesis

The 1-(2,2-bis(methoxymethyl)butoxy)-2,2-bis(methoxymethyl)butane penta-ether compound as the internal donor was synthesized according to the literature^[23, 24] as shown in Scheme 1. All the synthesis and reactions were performed under dry nitrogen atmosphere. The di(trimethylolpropane) (0.02 mol, 5.01 g) was dissolved in dry THF (33 mL). Another flask equipped with a stirrer was charged with THF (33 mL) and NaH (0.12 mol, 4.8 g) dispersed therein. The above solution of di(trimethylolpropane) was dropwise added slowly from a dropping funnel into the dispersion liquid at 0 °C. After completion of the dropping, the mixture was stirred at room temperature for 1 h. Then, the mixture was cooled to 0 °C, and methyl iodide (0.16 mol, 9.96 g) was dropped into the mixture. After completion of the dropping, the mixture was stirred at 35 °C for 2 h. The reaction solution was washed with water, and then the reactant was extracted therefrom with diethyl ether. The obtained ether extract was dried with anhydrous sodium sulfate, and was filtrated. After that, the solvent was distilled off, and the residue was purified with silica gel column chromatography (hexane:ethyl acetate; 4.2:0.8) to obtain of 1-(2,2-bis(methoxymethyl)butoxy)-2,2-bis(methoxymethyl)butane (Yield: 93%, purity: 95.76% (GC area percentage), and density: 0.92 g/mL).



Scheme 1 Synthesis of the 1-(2,2-bis(methoxymethyl)butoxy)-2,2-bis(methoxymethyl)butane

Penta-ether Characterization

The FTIR spectrum of the penta-ether compound was applied using a Bruker Tensor 27 FTIR spectrometer, and the ^1H -NMR and ^{13}C -NMR spectra of this ether were recorded using a Bruker Avance III spectrometer operating at 400 MHz.

FTIR (KBr): 2850–2875 (C–H, sp^3), 1465 (CH_2), 1375 (CH_3), 1200 (C–C), 1115 (C–O), and 960 (C–O–C).

^1H -NMR (400 MHz; in CDCl_3): δ H 3.24 (12H, s, CH_3^{a}), 3.16 (8H, s, CH_2^{b}), 3.14 (4H, s, CH_2^{d}), 1.30 (4H, q, CH_2^{c}), and 0.77 (6H, t, CH_3^{f}).

^{13}C -NMR (400 MHz; in CDCl_3): δ C 73.41 (4C, s, CH_3^{a}), 71.14 (4C, s, CH_2^{b}), 59.30 (2C, s, CH_2^{d}), 43.15 (2C, s, C^{c}), 23.06 (2C, s, CH_2^{e}), and 7.60 (2C, s, CH_3^{f}).

Catalysts Preparation

The Ziegler-Natta catalysts were prepared by a general procedure reported in the literature^[23, 25–28] with the following modifications. In the current study, the penta-ether-based Ziegler-Natta catalysts were prepared by a chemical reaction method. The preparation was carried out using a three-necked glass reactor equipped with a mechanical stirrer and all procedures were performed under dry nitrogen atmosphere. In a 500 mL glass reactor, anhydrous magnesium chloride adduct (50 mmol, 4.76 g), *n*-heptane (35 mL), toluene (35 mL), and titanium tetrachloride (400 mmol, 44 mL) were added successively, while the temperature of the suspension was kept at $-20\text{ }^\circ\text{C}$. The mixture was continuously stirred and heated up to $60\text{ }^\circ\text{C}$ to add 1-(2,2-bis(methoxymethyl)butoxy)-2,2-bis(methoxymethyl)butane (ID) and held at $75\text{ }^\circ\text{C}$ for 2 h. The solid catalyst was formed during the procedure. The supernatant (mother liquor) was decanted and the solid part was washed three times with each 50 mL of dry *n*-heptane. Then, titanium tetrachloride (200 mmol, 22 mL) and toluene (75 mL) were added. Next, the reactor temperature was brought to $110\text{ }^\circ\text{C}$ and held for 1 h. After that, the supernatant was decanted and the solid catalyst was washed with toluene and *n*-hexane at $90\text{ }^\circ\text{C}$ three times and then decanted. The solid catalyst was dried under dry nitrogen. The light brown catalyst powder was obtained and then kept under nitrogen atmosphere. The ID/Mg molar ratios were varied in every catalyst synthesis experiment to get varying degree of donor incorporation (Cats A–D). Also, one catalyst was synthesized without any internal donor (Cat-0).

Catalysts Characterization

For quantitative analysis, the catalyst sample (1 g) was weighted under a nitrogen atmosphere and dispersed into *n*-heptane (100 mL) and then the suspension was stirred at room temperature for 1 h.

Most of the examples of chemical analysis demand that the metal content must first be extracted and dissolved (digestion step). Acid digestion procedures were employed for the determination of elements in the solids. Sulfuric acid acted as a dehydrating agent. After reaction with H_2SO_4 , the contents of titanium, magnesium, and chloride in the MgCl_2 -supported Ziegler-Natta catalysts were determined by spectrophotometry, and by complexometric and argentometric titration, respectively^[29]. The characterization results of the prepared solid catalysts are shown in Table 1.

Table 1. The composition of prepared catalysts and diisobutyl phthalate-based catalyst

Cat	ID ^a (mmol)	ID/Mg	Ti (wt%)	Mg (wt%)	Cl (wt%)
Cat-ZN ^b	–	–	3.4	24.4	57.1
Cat-0	0	0	4.3	27.2	63.1
Cat-A	1.5	0.07	3.4	18.2	62.0
Cat-B	3.0	0.13	3.3	18.2	56.7
Cat-C	4.8	0.21	3.2	16.5	55.0
Cat-D	6.6	0.29	3.1	15.8	54.2

^a Internal donor: 1-(2,2-bis(methoxymethyl)butoxy)-2,2-bis(methoxymethyl)butane

^b Industrial Ziegler-Natta catalyst containing diisobutyl phthalate as the internal donor

The content of titanium was determined photometrically^[25, 30, 31]. Titanium was measured by UV-Vis spectrophotometer after the solid catalyst was fully dissolved in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution. The resulting yellow Ti(IV) complex was measured at 410 nm. Sulfuric acid and hydrogen peroxide acted as dehydrating and oxidizing agents, respectively.

The content of magnesium was determined complexometrically after preliminary dissolution of the solid catalyst in a solution of sulfuric acid. In order to precipitate titanium in hydroxide form, the pH was raised to 4.5

with sodium hydroxide. Magnesium was determined by titration with EDTA in the presence of methyl red indicator solution in addition to Eriochrome black T. The sample was titrated with EDTA solution (0.1 N) until the color clearly turned from red to green.

The content of chloride was determined potentiometrically. Chloride was measured by potentiometric titration with an AgNO_3 solution after preliminary dissolution of the solid catalyst in a solution of sulfuric acid in the absence of reducing agents. The end point of the titration occurred when all the chloride ions were precipitated.

Scanning electron microscopy (SEM) was conducted to determine the morphology of the MgCl_2 -supported Ziegler-Natta catalyst obtained with an optimum ID/Mg molar ratio (Cat-C) and the diisobutyl phthalate-based Ziegler-Natta catalyst. The SEM images were performed using a Philips XL30 scanning electron microscopy. The catalyst powders were mounted on aluminum stubs and sputter coated with gold to make them conductive. The SEM images reveal that, unlike the particles of Cat-C, which do not have a definite shape, the diisobutyl phthalate-based Ziegler-Natta catalyst particles are spherical in shape. Also, in both cases, the particles sizes of the catalysts were not uniform. The SEM images of the diisobutyl phthalate-based catalyst and Cat-C are shown in Fig. 1.

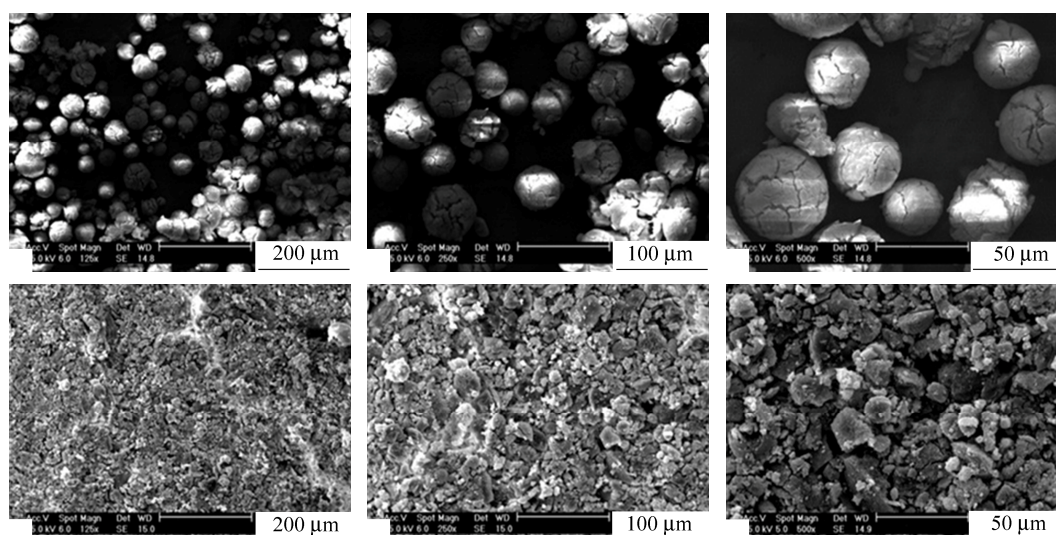


Fig. 1 Scanning electron microscope images of the diisobutyl phthalate-based MgCl_2 -supported Ziegler-Natta catalyst (top) and Cat-C (bottom).

Polymerization

The bulk polymerization of propylene was prepared according to the procedure reported in the literature^[32–35], with the following modifications. Polymerization of propylene was carried out in a 2.5 L stainless steel reactor equipped with a thermocouple, an automatic temperature control unit, and a paddle mechanical stirrer, which was built by Marun Petrochemical Co., Mahshahr, Iran. The reactor was evacuated and purged with nitrogen several times to minimize residual oxygen and moisture. Prior to use, the catalyst powder (10 mg) was suspended in a dry hexane (100 mL) solution containing TEA cocatalyst (10.5 mL, 10 wt% in hexane) with and without cyclohexylmethyldimethoxysilane, under a stream of dry nitrogen at room temperature for 5 min. The TEA/C-donor molar ratio was kept equal to 24.2. The reactor was then charged with the pre-contact mixture, followed by 0.2 MPa hydrogen and 2.3 L of pressurized liquid propylene at 3 MPa. Reaction runs were conducted at 70 °C for 2 h, under stirring of 300 r/min. Reaction runs were halted after reaching the specified batch time through reactor depressurization. The reactor was then cooled down to ambient temperature. The obtained polymer samples were dried in an oven at 60 °C for 1 h. Finally, the polymers were weighted and characterized.

Polymer Characterization

The isotacticity was determined indirectly by measuring the xylene soluble fraction of the polymer^[25]. The xylene solubility (XS) can be used to characterize the crystalline and amorphous fractions of the final polymer^[32]. Polypropylene isotacticity was determined using a procedure based on dissolving a shot of polypropylene in *O*-xylene at 135 °C, cooling the solution to 25 °C under controlled conditions, filtering the solid phase, distilling the *O*-xylene from the solution, and measuring the mass of the dissolved substances. The xylene solubility results of the prepared polypropylenes are shown in Table 2.

Table 2. Results of propylene polymerization ^a

Cat	C-donor ^b (mmol)	$M_w \times 10^4$ ^c (g/mol)	$M_n \times 10^4$ ^c (g/mol)	MWD ^c	MFI ^d (g/10min)	XS ^f (%)	Catalyst activity (kgPP/gCat)
Cat-ZN ^g	–	25.01	3.39	7.4	–	43	14
	0.3	37.07	8.38	4.4	4.1	4.8	15
Cat-0	–	14.78	1.59	9.3	–	47	18.7
	0.3	17.68	2.50	7.1	–	36	16.5
Cat-A	–	28.65	4.40	6.5	4.4	8.7	7.2
	0.3	29.90	4.87	6.1	4.2	4.8	7.0
Cat-B	–	25.84	3.45	7.5	4.8	7.9	9.4
	0.3	26.65	3.86	6.9	4.6	4.4	8.6
Cat-C	–	27.40	4.31	6.4	4.6	4.8	14.7
	0.3	27.82	4.76	5.8	4.4	3.1	12.6
Cat-D	–	27.94	3.92	7.1	4.6	5.1	13.6
	0.3	28.50	4.20	6.8	4.2	3.8	12.2

^a Polymerization condition: 10 mg Cat, propylene = 2.3–l, $P = 3$ MPa, $H_2 = 0.2$ MPa, TEA/C-donor = 24.2, $t = 2$ h, and $T = 70$ °C, ^b Cyclohexylmethyldimethoxysilane, ^c M_n : Number average molecular weight, M_w : Weight average molecular weight, and MWD: Molecular weight distribution, ^d Melt flow index, ^f Xylene solubility, ^g Industrial Ziegler-Natta catalyst containing diisobutyl phthalate as the internal donor

The average molecular weights (M_n and M_w) and molecular weight distribution (MWD) of the polypropylene fractions were measured using Perkin Elmer PL 220 high temperature gel permeation chromatography (GPC) in a nitrogen atmosphere at 160 °C, using 1,2,4-trichlorobenzene as a solvent. The injection volume was 20 μ L. The calibration was made by polypropylene as the standard sample. The GPC results of the prepared polypropylenes are shown in Table 2.

The melt flow index (MFI) is typically expressed in terms of grams of polymer passing through a standardized capillary under a standard load over 10 min. The melt flow index of polypropylene was measured on a Ceast melt flow tester 2000 at 230 °C and a constant load of 2.16 kg over 10 min. The MFI results of the prepared polypropylenes are shown in Table 2.

All differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo 822^e differential scanning calorimeter in a nitrogen atmosphere at a rate of 50 mL/min. Samples of about 2–5 mg were melted in aluminum pans by heating them from 25 °C up to 200 °C at a rate of 10 K/min, and were held at this temperature for 5 min in order to ensure the erasure of previous thermal history, then cooled down to 25 °C, held at 25 °C for 5 min, and then finally heated again to 200 °C. The melting temperature (T_m), enthalpy of fusion (ΔH_m), crystallization temperature (T_c), enthalpy of crystallization (ΔH_c), and crystallinity degree (X_c) were determined. The melting temperature and enthalpy of fusion were determined in the second scan. The DSC results are shown in Table 3.

The control of polypropylene particles morphology is based on the replication phenomenon, that is, the formation of a polymer particle on a catalyst particle with the reproduction of its shape^[36]. Figure 2 shows the SEM images of polypropylenes produced using Cat-ZN (Top) and Cat-C with an optimum ID/Mg molar ratio equal to 0.21 without the external donor (Bottom). The surface morphology of the polypropylene prepared with industrial Cat-ZN exhibits a spherical shape and replicates the catalyst particle morphology. Some particles of polypropylene produced using Cat-C with an ID/Mg molar ratio equal to 0.21 have a central core with spiral strings around it, and the general shape of the polypropylene particles is almost similar to the Cat-C particles.

Table 3. The DSC results of polypropylenes ^a

Cat	C-donor ^b	T_m ^c (°C)	ΔH_m ^c (J/g)	T_c ^c (°C)	ΔH_c ^c (J/g)	X_c ^c (%)
Cat-ZN ^d	–	159.42	41.9	107.46	50.01	20.33
	0.3	164.49	84.29	106.42	95.61	40.61
Cat-0	–	156.63	35.98	105.06	52.47	17.43
	0.3	158.45	50.52	105.41	56.67	24.55
Cat-A	–	160.12	67.51	106.42	75.81	32.60
	0.3	161.43	83.01	107.45	90.78	40.08
Cat-B	–	160.25	68.94	106.66	75.75	33.24
	0.3	161.69	83.56	107.49	91.16	40.35
Cat-C	–	160.99	69.25	106.86	76.11	33.43
	0.3	163.86	85.35	107.67	95.73	41.21
Cat-D	–	160.81	69.12	106.59	75.97	33.32
	0.3	163.47	84.39	107.29	93.18	40.75

^a Polymerization condition: 10 mg Cat, propylene = 2.3–l, $P = 3$ MPa, $H_2 = 0.2$ MPa, TEA/C-donor = 24.2, $t = 2$ h, and $T = 70$ °C, ^b Cyclohexylmethyldimethoxysilane, ^c T_m : Melting temperature, ΔH_m : The enthalpy of fusion, T_c : Crystallization temperature, ΔH_c : The crystallization enthalpy, and X_c : Crystallinity degree, ^d Industrial Ziegler-Natta catalyst containing diisobutyl phthalate as the internal donor

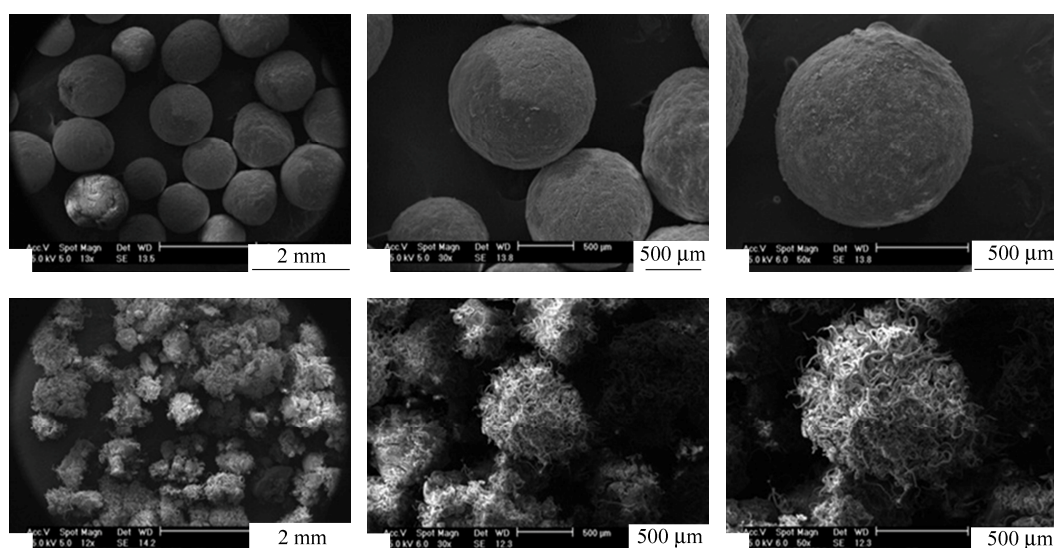


Fig. 2 Scanning electron microscope images of the polypropylenes produced using the diisobutyl phthalate-based $MgCl_2$ -supported Ziegler-Natta catalyst (top) and Cat-C (bottom)

RESULTS AND DISCUSSION

The new Ziegler-Natta catalysts containing different amounts of new synthesized penta-ether compound as the internal donor were used for propylene polymerization with and without the external donor. The effects of different ID/Mg molar ratios in catalysts for propylene polymerization were studied and compared to polypropylenes that were prepared using Cat-ZN and Cat-0. The results of propylene polymerization are shown in Tables 2 and 3.

Composition of the Prepared Catalysts

The different ID/Mg molar ratios of the penta-ether compound as an internal donor were used for synthesis of the new Ziegler-Natta catalysts. Table 1 shows the results of the analysis of the prepared catalysts and Cat-ZN. As shown in Fig. 3, the titanium, magnesium, and chloride contents of Cat-0 were the highest values compared to the other catalysts. By adding an internal donor in the catalyst systems (Cats A–D), these values were decreased. As the internal donor increases, it occupies more coordination sites on which titanium could have

otherwise coordinated. Further, the internal donor forms complexes with magnesium and titanium chlorides; virtually the entire amount of the internal donor enters the composition of the solid product, thus leading to a minor decrease in the content of magnesium and chloride in the solid product^[37]. The contents of titanium in Cats A–D were nearly similar to each other and not significantly different than Cat-ZN, and all titanium contents were in the optimum range. The titanium, magnesium, and chloride contents in Cats A–D were in the ranges 3.1 wt%–3.4 wt%, 15.8 wt%–18.2 wt%, and 54.2 wt%–62.0 wt%, respectively.

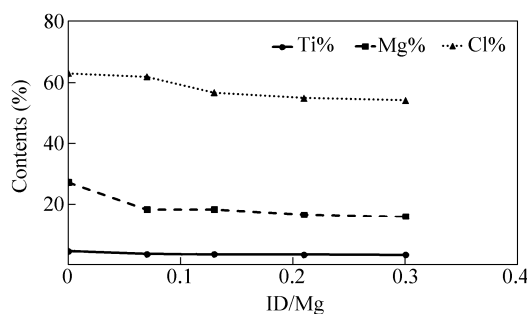


Fig. 3 Ti, Mg, and Cl contents curves for Cat-0 and Cats A–D

Effects of the Penta-ether Internal Donor on the Catalytic Activity of the Ziegler-Natta Catalyst and the Xylene Solubility of Polypropylene

The activity results of the prepared catalysts (Cat-0 and Cats A–D) and Cat-ZN, and also the isotacticity results of the polypropylenes with and without the external donor are given in Table 2. Cat-ZN, without the use of the external donor, in the polymerization step produced polypropylene with low isotacticity (xylene solubility equal to 43%), which significantly increased with the addition of an external donor (xylene solubility equal to 4.8%). These results reveal an essential role of the external donor for propylene polymerization with the diisobutyl phthalate-based Ziegler-Natta catalyst, compared to polymerization with the penta-ether-based Ziegler-Natta catalysts.

The highest activity is related to Cat-0, with and without the use of the external donor. By adding the internal donor during the preparation step of the catalysts, the activity of Cats A–D were decreased, due to the deactivation of some atactic sites in the prepared catalysts. However, the isotacticity of the polypropylenes prepared using these catalysts were increased compared to Cat-0. It is believed that the internal donor blocks particular sites on the MgCl_2 surface which would otherwise, upon coordination with TiCl_4 , generate the precursors of non-stereospecific active sites^[38].

As shown in Fig. 4, Cat-C has the lowest xylene solubility and also the highest isotacticity with and without the external donor, compared to the other catalysts. As shown in Fig. 5, in comparing Cats A–D, it was revealed that the activity of the prepared catalysts with and without the external donor, decreases in the following order: Cat-0 > Cat-C > Cat-D > Cat-B > Cat-A. Thus, after Cat-0, the highest catalyst activity was found in Cat-C with an optimum ID/Mg molar ratio equal to 0.21.

In the presence of the external donor, the isotacticity of the polypropylenes was increased, although the activity was slightly decreased. However, in the propylene polymerization, even without the external donor, the polypropylenes prepared with Cats A–D showed good isotacticity compared to Cat-ZN. These characteristics are typical for catalysts containing an ether compound and are in agreement with those characteristics reported in former studies. In the polymerization of propylene without the external donor, most of the diisobutyl phthalate in Cat-ZN was extracted. Thus, the extracted diisobutyl phthalate cannot continue to play its role as an internal donor, but the ether internal donor, when in the condition of polymerization, cannot be easily extracted from the catalyst.

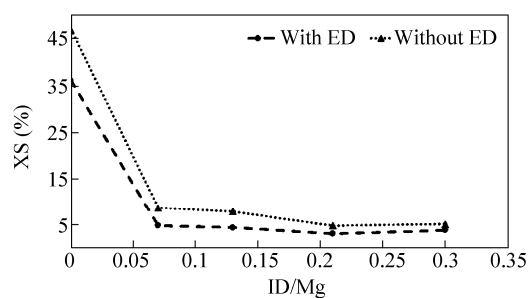


Fig. 4 Xylene solubility curves of Cat-0 and Catsby A-D with various ID/Mg molar ratios

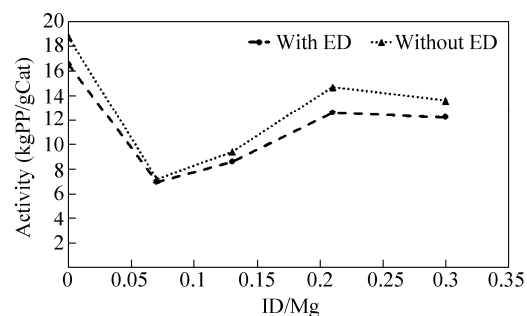


Fig. 5 Activity curves of Cat-0 and Catsby A-D with various ID/Mg molar ratios

Effects of the Penta-ether Internal Donor on Average Molecular Weight and Molecular Weight Distribution of Polypropylene

The hydrogen response abilities of catalysts for propylene polymerization under the same hydrogen content and other polymerization conditions were studied. In the presence of the external donor, the MFI value of polypropylene prepared using Cat-ZN was the lowest, compared to that of polypropylene prepared using Catsby A-D. This means that polypropylene prepared using Cat-ZN containing diisobutyl phthalate as the internal donor has the highest molecular weight compared to Catsby A-D containing penta-ether as the internal donor. Thus, the addition of the penta-ether compound as the internal donor in the preparation of the catalysts increased the hydrogen response of the catalyst in propylene polymerization. The highest hydrogen response, and also the lowest molecular weight of the prepared polypropylene are related to Cat-B, with an ID/Mg molar ratio equal to 0.13. In general, the addition of the external donor in propylene polymerization has led to a reduction of hydrogen response and therefore increased the molecular weight of polypropylene. It should be noted that, due to the adhesive polypropylene particles with high xylene solubility prepared using Cat-ZN (without the external donor) and Cat-0 (with and without the external donor), it was not possible to measure the related polypropylenes MFI values.

The GPC results are given in Table 2. The polypropylene produced using Cat-0 with and without the C-donor, as the external donor, has the lowest M_w and the broadest MWD, although these values slightly increased and narrowed, respectively, by adding the external donor. The addition of the C-donor in the polymerization of propylene with Cat-ZN has led to the production of polypropylene with the highest M_w and the narrowest MWD compared to polypropylene produced using Cat-ZN without the external donor. Also, it is obvious that the C-donor has a significant effect on the M_w and MWD of polypropylene produced using Cat-ZN compared to those produced using catalysts containing penta-ether as the internal donor. In general, it is well known that the addition of the external donor increased M_w and narrowed the MWD of polypropylene.

The M_w of polypropylenes, with and without the use of the external donor, decreases in the following order: Cat-A > Cat-D > Cat-C > Cat-B > Cat-0, while the MWD of the corresponding polypropylenes decreases in the order of: Cat-0 > Cat-B > Cat-D > Cat-A > Cat-C. Among the prepared catalysts containing penta-ether, with and without the external donor, Cat-C produced polypropylene with the narrowest MWD, while Cat-B produced polypropylene with the broadest MWD and the lowest M_w . The M_w value is consistent with the highest MFI value of polypropylene produced using Cat-B. These results concluded that the hydrogen response of Cat-B is the highest. Cat-A without the external donor produced polypropylene with the highest M_w , which is consistent with the lowest polypropylene MFI value. As shown in Table 2, the MFI results, with and without the external donor, are consistent with the GPC results. Therefore, with an increase in polypropylene M_w , the MFI values decrease.

Effects of the Penta-ether Internal Donor on the Thermal Properties of Polypropylene

The DSC results are given in Table 3. From the obtained results it was concluded that Cat-0 produced polypropylene with the lowest thermal properties than any other catalyst. These thermal properties cannot be significantly improved by adding the external donor in the polymerization of propylene, but the thermal

properties were improved by adding the internal donor (penta-ether) in the preparation step of the catalysts (Cats A-D). Thus, it can be concluded that the internal donor plays an important role in the thermal properties of polypropylene, while the external donor is unable to compensate for its absence in the catalyst.

By comparing the thermal properties of polypropylenes produced with and without the external donor, it is obvious that the external donor plays an important role in improving the thermal properties of polypropylenes, especially for Cat-ZN. The polypropylene produced using Cat-ZN without the external donor has undesired thermal properties that were improved with the addition of the external donor in the polymerization of propylene, especially melting temperature and crystallinity degree of polypropylene. The effect of the external donor in polymerization of propylene using Cat-ZN is much greater than in Cats A–D. These results indicate that the penta-ether as the internal donor in the catalysts has an important effect on the thermal properties of polypropylene, compared to diisobutyl phthalate as the internal donor. Thus, it is obvious that the thermal properties of polypropylenes were influenced by the type of internal donor in the solid catalysts and the presence of the external donor in the polymerization of propylene.

The melting temperature, the enthalpy of fusion and the crystallinity degree of the prepared polypropylenes without an external donor decrease in the following order: Cat-C > Cat-D > Cat-B > Cat-A > Cat-ZN > Cat-0. Among the prepared catalysts containing penta-ether, Cat-C with an optimum ID/Mg molar ratio equal to 0.21 has the highest thermal properties. Although the melting temperature (without the external donor), enthalpy of fusion, crystallization temperature (with the external donor), crystallization enthalpy and the crystallinity degree of polypropylene prepared using Cat-C are higher than those of polypropylene prepared using Cat-ZN, the melting temperature (with the external donor) and crystallization temperature (without the external donor) of the polypropylene produced by Cat-ZN are higher.

The melting endotherms and the crystallization exotherms for the polypropylene samples prepared using Cat-ZN, Cat-0, and Cats A-D, with and without the external donor, are shown in Figs. 6 and 7, respectively. It can be seen that the endotherms of the obtained polypropylenes with and without the external donor are unimodal, clearly indicating the presence of one kind of polypropylene crystal with distinct melting temperature values. As shown in Fig. 6, the polypropylenes produced with the external donor have a higher melting

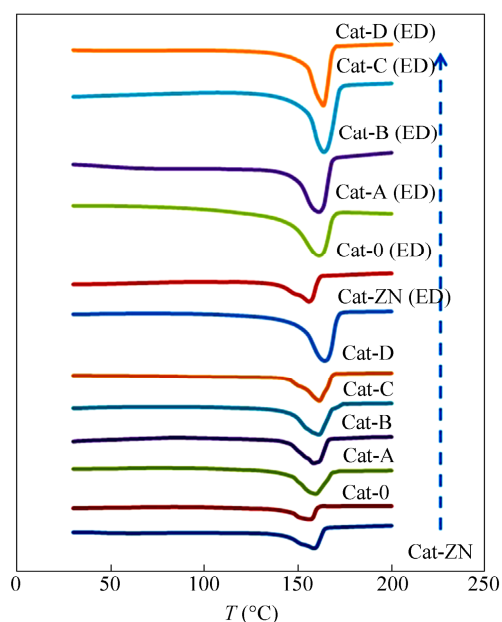


Fig. 6 The DSC melting temperature curves of polypropylenes produced by catalysts bearing different amounts of penta-ether as the internal donor, and Cat-ZN

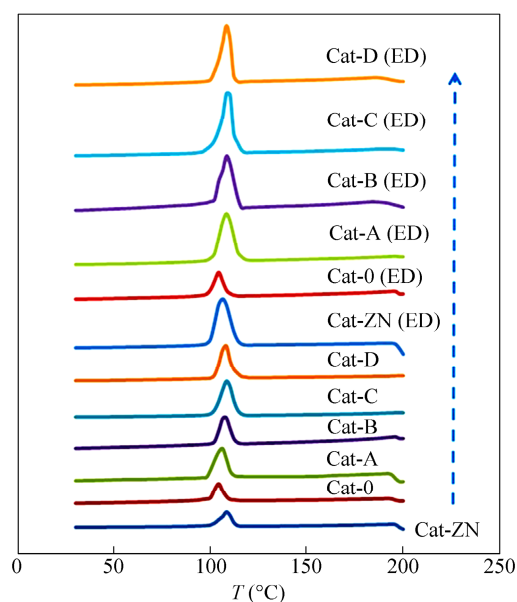


Fig. 7 The DSC crystallization temperature curves of polypropylenes produced by catalysts bearing different amounts of penta-ether as the internal donor, and Cat-ZN

temperature compared to those prepared without the external donor, and the highest enthalpy of fusion is related to polypropylene produced using Cat-C with the external donor.

Figure 7 shows the crystallization curves of polypropylenes and it is obvious that all the curves are unimodal. As shown in Table 3 and Fig. 7, similar to other thermal properties of polypropylenes, the crystallization temperature and crystallization enthalpy were increased by the addition of the C-donor as the external donor in the polymerization of propylene. The highest crystallization temperature (with external donor) and crystallization enthalpy (with and without the external donor) are related to polypropylenes produced using Cat-C.

CONCLUSIONS

A novel penta-ether compound was synthesized using the Williamson reaction and then employed as the internal donor in the synthesis of the MgCl_2 -supported Ziegler-Natta catalysts for propylene polymerization. The composition of the prepared catalysts and Cat-ZN were determined.

The effects of penta-ether as the internal donor on the catalytic activity of the MgCl_2 -supported Ziegler-Natta catalysts, and isotacticity, average molecular weight, molecular weight distribution, crystallinity degree, and thermal properties of polypropylenes were studied. The results indicated that the isotacticity and thermal properties of polypropylenes increased with the addition of the external donor in the polymerization. The optimum ID/Mg molar ratio (equal to 0.21) is related to Cat-C, which has the highest activity and produced polypropylene with the highest isotacticity, compared to other prepared catalysts containing penta-ether (Cats A, B, D). Cat-B with an ID/Mg molar ratio equal to 0.13 has the best hydrogen response compared to the other catalysts. It can be seen that the catalysts containing penta-ether as the internal donor with four methoxy groups have good hydrogen response. It can also be seen that Cat-C, containing penta-ether as the internal donor with an optimum ID/Mg molar ratio equal to 0.21, is a favorable catalyst for the production of polypropylene with the desired properties compared to the conventional 4th generation Ziegler-Natta catalysts (Cat-ZN) containing diisobutyl phthalate as the internal donor, with and without the external donor.

Hydrogen, as well as internal and external donors strongly impacts the properties of the obtained polypropylenes. The broadest polypropylene MWD and the lowest M_w were obtained using Cat-0, with and without the external donor. Cat-ZN in the presence of the C-donor produced the highest M_w and the narrowest MWD. Among the prepared catalysts containing penta-ether as the internal donor, Cat-C with a molar ratio of ID/Mg equal to 0.21, with and without the external donor, has the narrowest MWD.

The DSC results showed that Cat-0 produced polypropylenes with poorer thermal properties, both with and without the external donor, which indicates that the internal donor played a more important role than the external donor in the polymerization of propylene. Polypropylene produced using Cat-ZN in the presence of the external donor has the desired thermal properties. The role of the external donor to effectively improve the polypropylene thermal properties is obvious, especially for Cat-ZN. The prepared polypropylenes using the catalysts containing penta-ether as the internal donor, even without the external donor, have almost all the desired properties. However, these properties are improved with the use of the external donor. Among the penta-ether-based catalysts, Cat-C produced polypropylene with the most desirable thermal properties compared to the others.

Comparing the results of the analysis of polypropylenes prepared with and without the internal and external donors, we found that the internal and external donors played an important role in the polymerization of propylene and in controlling the properties of polypropylene. Of course, the external donor improved the isotacticity, thermal properties, and M_w of polypropylene, but reduced the activity and MFI values. It was also concluded that the external donor influenced the polypropylene M_w via the use of hydrogen as a chain transfer agent.

REFERENCES

- 1 Marques, M.D.F.V., Cardoso, R.D.S. and Da Silva, M.G., *Appl. Catal. A: Gen.*, 2010, 374: 65
- 2 Suhm, J., Heinemann, J., Wörner, C., Müller, P., Stricker, F., Kressler, J., Okuda, J. and Mülhaupt, R., *Macromol. Symp.*, 1998, 129: 1
- 3 Alshaiban, A. and Soares, J.B., *Macromol. React. Eng.*, 2012, 6: 265
- 4 Taniike, T. and Terano, M., in: "Polyolefins: 50 years after Ziegler and Natta I", ed. by Kaminsky, W. and Böhm, L., Springer Press, Heidelberg, 2013, p.81
- 5 Soares, J.B., *Chem. Eng. Sci.*, 2001, 56: 4131
- 6 Kashiwa, N.J., *Polym. Sci., Part A: Polym. Chem.*, 2004, 42: 1
- 7 Corradini, P., Guerra, G. and Cavallo, L., *Acc. Chem. Res.*, 2004, 37: 231
- 8 Chammingkwan, P., Thang, V.Q., Terano, M. and Taniike, T., *Top. Catal.*, 2014, 57: 911
- 9 Credendino, R., Liguori, D., Morini, G. and Cavallo, L., *J. Phys. Chem. C*, 2014, 118: 8050
- 10 Li, P., Tu, S., Xu, T., Fu, Z. and Fan, Z., *J. Appl. Polym. Sci.*, 2015, 132: 41689
- 11 Taniike, T. and Terano, M., *J. Catal.*, 2012, 293: 39
- 12 Groppo, E., Seenivasan, K. and Barzan, C., *Catal. Sci. Technol.*, 2013, 3: 858
- 13 Taniike, T., Wada, T., Kouzai, I., Takahashi, S. and Terano, M., *Macromol. Res.*, 2010, 18: 839
- 14 Bazhenov, A.S., Denifl, P., Leinonen, T., Pakkanen, A., Linnolahti, M. and Pakkanen, T.A., *J. Phys. Chem. C*, 2014, 118: 27878
- 15 Bazhenov, A., Linnolahti, M., Pakkanen, T.A., Denifl, P. and Leinonen, T., *J. Phys. Chem. C*, 2014, 118: 4791
- 16 Potapov, A.G. and Politanskaya, L.V., *J. Mol. Catal. A: Chem.*, 2013, 368–369: 159
- 17 Wang, N., Qin, Y., Huang, Y., Niu, H., Dong, J.Y. and Wang, Y., *Appl. Catal. A: Gen.*, 2012, 435–436: 107
- 18 Correa, A., Piemontesi, F., Morini, G. and Cavallo, L., *Macromolecules*, 2007, 40: 9181
- 19 Morini, G., Albizzati, E., Balbontin, G., Mingozi, I., Sacchi, M.C., Forlini, F. and Tritto, I., *Macromolecules*, 1996, 29: 5770
- 20 Sacchi, M.C., Forlini, F., Tritto, I., Locatelli, P., Morini, G., Noristi, L. and Albizzati, E., *Macromolecules*, 1996, 29: 3341
- 21 Chadwick, J.C., Van Der Burgt, F.P., Rastogi, S., Busico, V., Cipullo, R., Talarico, G. and Heere, J.J., *Macromolecules*, 2004, 37: 9722
- 22 Jenny, C. and Maddox, P., *Curr. Opin. Solid State Mater. Sci.*, 1998, 3: 94
- 23 Song, B.G., Choi, Y.H. and Ihm, S.K., *J. Appl. Polym. Sci.*, 2013, 130: 851
- 24 Hamaki, H., Hirahata, W., Fujiwara, Y., Kimata, S., Hama, H. and Ikeda, K., 2013, U.S. Pat., 0,109,789 A1
- 25 Song, B.G. and Ihm, S.K., *J. Appl. Polym. Sci.*, 2014, 131: 40536
- 26 Cui, N., Ke, Y., Li, H., Zhang, Z., Guo, C., Lv, Z. and Hu, Y., *J. Appl. Polym. Sci.*, 2006, 99: 1399
- 27 Lu, L., Niu, H. and Dong, J.Y., *J. Appl. Polym. Sci.*, 2012, 124: 1265
- 28 Chen, B., Zhang, Q.F., Zhao, L.P., Zhang, X.Q. and Zhang, H.X., *Polym. Bull.*, 2013, 70: 2793
- 29 Bichinho, K.M., Pires, G.P., Dos Santos, J.H.Z., De Camargo Forte, M.M. and Wolf, C.R., *Anal. Chim. Acta.*, 2004, 512: 359
- 30 Taniike, T., Funako, T. and Terano, M., *J. Catal.*, 2014, 311: 33
- 31 Makwana, U.C., Singala, K.J., Patankar, R.B., Singh, S.C. and Gupta, V.K., *J. Appl. Polym. Sci.*, 2012, 125: 896
- 32 Lima, A., Azeredo, A.P., Nele, M., Liberman, S. and Pinto, J.C., *Macromol. Symp.*, 2014, 344: 86
- 33 Ribour, D., Spitz, R. and Monteil, V., *J. Polym. Sci., Part A: Polym. Chem.*, 2010, 48: 2631
- 34 Chang, H., Li, H., Zheng, T., Zhou, Q., Zhang, L. and Hu, Y., *J. Polym. Res.*, 2014, 21: 554
- 35 Zhou, Q., Zheng, T., Li, H., Li, Q., Zhang, Y., Zhang, L. and Hu, Y., *Ind. Eng. Chem. Res.*, 2014, 53: 17929
- 36 Bukatov, G., Sergeev, S., Zakharov, V. and Potapov, A., *Kinet. Catal.*, 2008, 49: 782
- 37 Chumachenko, N., Zakharov, V., Bukatov, G. and Sergeev, S., *Appl. Catal. A: Gen.*, 2014, 469: 512
- 38 Andoni, A., Chadwick, J.C., Niemantsverdriet, J.H. and Thüne, P.C., *Catal. Lett.*, 2009, 130: 278