

# Influence of reaction conditions on catalytic properties of *rac*-Et(2-MeInd)<sub>2</sub>ZrMe<sub>2</sub>/(2,6-<sup>t</sup>Bu<sub>2</sub>PhO-)Al<sup>i</sup>Bu<sub>2</sub> in ethylene-propylene copolymerization

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## ABSTRACT

Ethylene-propylene copolymerization reactions were carried out using *rac*-Et(2-MeInd)<sub>2</sub>ZrMe<sub>2</sub> catalyst and (2,6-<sup>t</sup>Bu<sub>2</sub>PhO-)Al<sup>i</sup>Bu<sub>2</sub> as activator under varying reaction conditions. We demonstrate that reaction conditions such as monomer concentration, Al/Zr molar ratio and solvent type (toluene and heptane) all have significant effect on activity of the system and copolymers composition. The decrease in reaction pressure from 11 to 3 atm leads to: a) 1.6-fold increase in specific activity (from 3030 to 4840 kg copolymer/(mol Zr•h•atm)), b) increase of M<sub>n</sub> value from 38 to 89 kg/mol, and c) increase of ethylene content in copolymer from 87 to 92 mol %. The increase of ethylene/propylene molar ratio from 0.7 to 2 does not significantly affect activity but leads to the rise in the ethylene content in copolymer from 92 to 97 mol % and, correspondingly, to the increase of copolymer crystallinity from 43 to 48%. As a result, thermal and mechanical properties of the obtained polymers also change, according to the shifts in copolymers composition. The change in Al/Zr molar ratio is confirmed to have great effect on the catalytic activity of our systems. In a row of Al/Zr= 100, 150, 200, 300 mol/mol, the lowest activity of 80 and the highest one of 8550 kg copolymer/(mol Zr•h•atm) are observed at 100 and 150 molar ratios correspondingly. We have also demonstrated the ability of catalytic systems with isobutylaluminum aryloxide activators to operate in aliphatic medium (heptane). On another note, during the reaction quenching, aryloxide activator hydrolyzes the polymer infused with 2,6-di-tert-butylphenol antioxidant. This results in the increased resistance of copolymers to the thermal-oxidative degradation. The presence of 4 wt.% phenol in the copolymer leads to an increase in the 5% mass loss temperature by 67°C. Moreover, increasing the residual phenol content from 2 to 4 wt.% affects the mechanical properties of the copolymers: the elongation-at-break increases from 500 to 600%, and the tensile strength decreases from 10 to 8 MPa. **Polyolefins J (2023) 10: 205-210**

**Keywords:** Metallocene; alkylaluminum aryloxide; ethylene-propylene copolymerization; properties.

## INTRODUCTION

Catalytic systems based on metallocene complexes with transition metals of group 4 are effective catalysts for homo- and copolymerization of olefins. They are used to produce a large variety of polymeric materials that are unique in their properties: linear low-density polyethylene (LLDPE), copolymers of ethylene with  $\alpha$ -olefins with widely variable content of the comonomer, isotactic polypropylene, syndiotactic polypropylene, copolymers of ethylene with cyclic olefins, etc. [1-8]. Metallocene and post-metallocene catalysts are used

for copolymerization of ethylene with propylene with specified characteristics [6,9]. Thermal and physical-mechanical properties of copolymers, determined by their microstructure, molecular-mass characteristics, etc., depend on the type of catalyst, methods of its activation and synthesis conditions [9,10].

Previously, we have found out that isobutylaluminum aryloxides are effective activators of metallocene complexes in synthesis of ethylene homopolymerization and synthesis of EPM EPDM copolymers [11-14]. In

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our experiments, aryloxy activators show activity comparable to that of conventionally used MAO and provide some benefits of both evidently practical and as possibly studied objects. Using aryloxy activators with different architecture of aryloxy group containing ligands and different bis-indenyl complexes we have obtained a wide set of polymer samples with a wide range of properties [11,12].

In this new contribution, we study two aspects of ethylene/propylene copolymerizations in such systems. The first one is the question on how the reaction conditions such as reaction pressure, monomer (E/P) molar ratio, activator/catalyst (Al/Zr) molar ratio, and type of solvent affect the copolymerization results. The second one is that how sterically hindered phenol formed *in situ* in the course of polymer washing acts as antioxidant preventing thermal oxidative destruction of copolymers and affects their mechanical properties as compared to free phenol copolymer. Copolymerization reactions were carried out with on the *rac*-Et(2-MeInd)<sub>2</sub>ZrMe<sub>2</sub>/(2,6-<sup>t</sup>Bu<sub>2</sub>PhO-)Al<sup>i</sup>Bu<sub>2</sub> (1-DTBP) catalytic system.

## EXPERIMENTAL

### Reagents

High purity toluene was distilled over LiAlH<sub>4</sub> and kept over molecular sieves (4A) in argon atmosphere (99.999% purity). *rac*-EtInd<sub>2</sub>ZrMe<sub>2</sub> was synthesized by alkylation of corresponding metallocene dichloride (Boulder Scientific) according to the standard technique [15]. Isobutylaluminum aryloxy (2,6-<sup>t</sup>Bu<sub>2</sub>PhO-)Al<sup>i</sup>Bu<sub>2</sub> was obtained by the reaction of Al<sup>i</sup>Bu<sub>3</sub> (Aldrich Chem. Co.) with the corresponding phenol according to the procedures described in our works [11]. All manipulations with *rac*-Et(2-MeInd)<sub>2</sub>ZrMe<sub>2</sub> and isobutylaluminum aryloxides were performed in an argon atmosphere.

### Copolymerization of ethylene and propylene

Polymerization was carried out in a 200 ml stainless steel reactor equipped with a mechanical stirrer and a temperature-controlled jacket. The reactor was vacuumed for 1 hour at 50°C, filled with argon and cooled down to room temperature. The ampule with *rac*-Et(2-MeInd)<sub>2</sub>ZrMe<sub>2</sub> was placed in the reactor in an argon counterflow. The reactor was vacuumed and then charged with a toluene solution of (2,6-<sup>t</sup>Bu<sub>2</sub>PhO-)Al<sup>i</sup>Bu<sub>2</sub> (60 ml of desired concentration providing molar ratio Al/M=300). The reactor was heated to

30°C, and the reaction mixture was saturated with a mixture of ethylene and propylene with a set molar ratio. Polymerization was initiated by the introduction of a catalyst into solution by breaking the ampoule with zirconocene.

The total ethylene/propylene pressure was maintained constant through all polymerization process. The process was stopped by adding 5% solution of hydrochloric acid in ethanol to the reactor. The polymer was washed in water/ethanol mixture, recovered by filtration and dried in vacuum at 60°C.

The E/P copolymer obtained on the *rac*-Et(2-MeInd)<sub>2</sub>ZrMe<sub>2</sub>/isobutylaluminumoxane (IBAO) catalyst system was used as a reference sample in assessing the resistance of copolymers to thermal oxidative degradation. IBAO was synthesized by controlled hydrolysis on ice according to the procedure described in [16, 17]. E/P copolymer characteristics: M<sub>w</sub>=115000, M<sub>w</sub>/M<sub>n</sub>=3.1, E/P composition=91/9.

### Polymer analysis

Molecular weight and molecular weight distributions were measured on a PL-220 high-temperature liquid gel-chromatograph with PL Gel Olexis columns and a refractometer detector, by using solvent 1,2,4-trichlorobenzene at 160°C, and a flow speed of 1 cm<sup>3</sup>/min. Calibration curves were based on polyethylene and polystyrene standards.

Differential scanning calorimetry (DSC) analysis was performed using a DSC 822 Metler Toledo device with STARe 15.0 software with a scanning rate of 10°C/min under an inert atmosphere in the -100 to 170°C temperature range. Melting heats and temperatures were determined at the second heating cycle.

Simultaneous evaluation of mass changes (TGA) and thermal effects occurring in the samples was performed using TGA/SDTA851e Mettler Toledo in the 25-500°C temperature range at a scanning rate of 10°C/min in the air atmosphere.

Powder X-ray diffraction copolymer film patterns were obtained on an ARL X'TRA diffractometer (THERMOFISHER SCIENTIFIC, Switzerland) equipped with a solid-state detector using  $\theta$ - $\theta$  geometry in the 5-50° range with a scan step of 0.02°; exposure time per frame was 1 s.

Monomer content in copolymers and the residual content of phenols in the samples were determined from FTIR spectroscopy of polymer films according to the method described in [18-20]. IR spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer.

### Polymer mechanical tests

Mechanical tests of copolymers were carried out on a 2166 P-5 stretch-breaking machine at room temperature according to the standard ISO 37 technique (Die type 1). The results were averaged out of 5 samples. Stretch speed was 10 mm/min.

## RESULTS AND DISCUSSION

Table 1 summarizes the effects of the above copolymerization conditions on both catalyst specific activity and the properties of copolymers obtained. Catalyst specific activity was determined in terms of kg of copolymer formed/(mol Zr·h·atm). Properties of copolymers are presented by molecular weight characteristics, copolymer composition, crystallinity, phenol content in copolymers, and mechanical characteristics (strain-stress measurements).

The decrease in reaction pressure from 11 to 3 atm (entries 1,2) leads to a 1.6-fold increase in specific activity and significantly affects molecular weight, composition, and properties of the resulting E/P copolymers. At lower pressure, the product shows the increased molecular weight ( $M_n$ ): 89 kg/mol at 3 atm compared to 38 kg/mol obtained at 11 atm. Ethylene content is also higher, 92 mol% at 3 atm vs 87 mol% at 11 atm. These results can be explained by the variable composition of the comonomers fed into the reaction mixture in the course of copolymerization under compared conditions. The fact is that the total reactor pressure is maintained only by feeding extra ethylene. When both monomers are consumed according to their reactivity and only ethylene is

supplied, the E/P ratio gradually rises compared to the initial load (0.7 mol/mol). Since ethylene has higher reactivity than propylene, an increase in both specific activity and ethylene content is observed. The copolymer with higher ethylene content shows higher molecular weight, since chain transfer with ethylene is slower than that with propylene. Melting points, crystallinity and mechanical properties are increased as expected from the difference in ethylene content. DSC thermograms have broad melting peaks with maximums at 99 (sample 1, 11 atm) and 124°C (sample 2, 3 atm). Tensile strength increases significantly from 5 to 10 MPa, and elongation-at-break decreases from 670 to 500%.

The similar, but less pronounced changes such as higher specific activity, higher molecular weight of the copolymer at higher ethylene content in the copolymer are also observed with an increase in E/P ratio in the initial load, other conditions being equal (Table 1, entries 2,3). Melting point, crystallinity and tensile strength of the polymer sample increase, and elongation-at-break decreases.

Entries 2, 4-6 represent the screening of response of activity to Al/Zr molar ratio. The Al/Zr = 100 – 300 ratio was used. At molar ratio Al/Zr = 100 (entry 6), the activity is very low, indicating an insufficient amount of 1-DTBP as activator. The system exhibits the highest activity (8550 kg copolym./(mol Zr h atm)) when the molar ratio Al/Zr = 150 (entry 5). Further increase of the molar ratio to 200 and 300 leads to a significant decrease in the specific activity to 5400 and 4840 kg/(mol Zr h atm), which may be associated with some possible deactivation reactions of zirconocene in the presence of 1-DTBP. These possible pathways should be further analyzed. It should be noted that effective

**Table 1.** Copolymerization of ethylene and propylene on *rac*-Et(2-MeInd)<sub>2</sub>ZrMe<sub>2</sub>/1-DTBP; characteristics, thermal and mechanical properties of E/P copolymers.

No.	P <sup>(a)</sup> atm	E/P molar ratio, % <sup>(b)</sup>	Al/Zr <sup>(c)</sup>	A <sup>(d)</sup>	M <sub>n</sub> kg/mol	M <sub>w</sub> /M <sub>n</sub>	Ethylene content <sup>(e)</sup> , mol. %	T <sub>m</sub> <sup>(f)</sup> °C	χ <sup>(g)</sup> , %	DTBP <sup>(h)</sup> , wt. %	σ <sub>r</sub> <sup>(i)</sup> , MPa	ε <sup>(j)</sup> , %
1	11	0.7/1	300	3030	38	2.7	87	99	39	2	5.0	670
2	3	0.7/1	300	4840	89	3.5	92	124	43	4	10	500
3	3	2/1	300	5400	93	3.0	97	130	48	3	16	125
4	3	0.7/1	200	5400	-	-	89	127	53	2	-	-
5	3	0.7/1	150	8550	-	-	90	122,129	-	2	9	560
6	3	0.7/1	100	80	-	-	88	94	-	1	-	-
7 <sup>(k)</sup>	3	0.7/1	300	5500	91	2.2	89	90	-	4	8	600
8 <sup>(l)</sup>	3	0.7/1	300	4840	89	3.5	92	127	37	2	14	420

Copolymerization conditions: [Zr]≈8·10<sup>-5</sup> mol/l, toluene – 60 ml (unless other solvent is specified), 30°C;

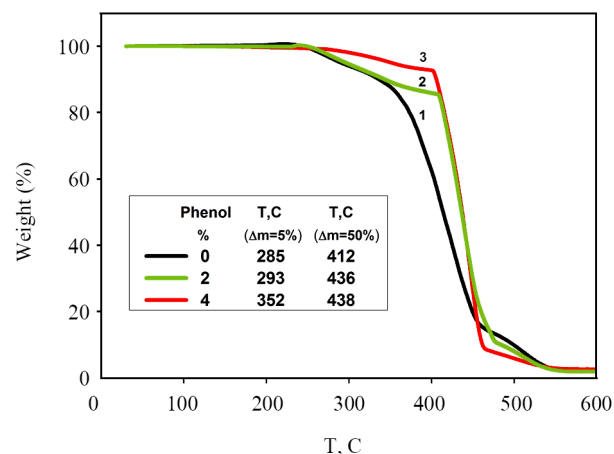
<sup>(a)</sup> Reactor pressure, <sup>(b)</sup> E/P molar ratio, E - ethylene, P – propylene; <sup>(c)</sup> Al/Zr molar ratio, <sup>(d)</sup> Catalyst specific activity in kg copolymer/(mol Zr·h·atm); <sup>(e)</sup> Ethylene content in E/P copolymer; <sup>(f)</sup> Melting temperature determined as maximum peak at DSC curve at second heating of the sample; <sup>(g)</sup> Crystallinity determined by X-ray powder diffraction (XRD) analysis; <sup>(h)</sup> 2,6-*i*-Bu<sub>2</sub>PhOH (DTBP) content in copolymer formed after copolymer washing; <sup>(i)</sup> Tensile strength; <sup>(j)</sup> Elongation-at-break (average of five measurements); <sup>(k)</sup> Solvent—heptane (60 ml); <sup>(l)</sup> Sample 2 was washed with methylene chloride due to the higher solubility of phenol.

activation of this zirconocene by methylalumoxane (MAO) for homo- and copolymerization reactions requires a tenfold excess of the activator [8-10].

Another important variation that has practical implications is aromatic vs. aliphatic solvent as reaction medium. The comparison is presented by entry 2 (toluene) and entry 7 (heptane). The activity of the catalytic system in heptane is higher by  $\sim 14\%$  than that in toluene. The copolymerization in heptane yields a copolymer with a higher propylene content of 11 mol % versus 8 mol % in the case of toluene. Accordingly, the copolymer obtained in heptane has a lower melting point ( $90^\circ\text{C}$  vs.  $124^\circ\text{C}$ ) and lower crystallinity (37 % vs. 47 % by XRD). The molecular weight ( $M_n$ ) of the copolymers obtained in both cases is close to 91 and 89 kg/mol, respectively. The ability of catalytic systems with isobutylaluminum aryloxide activators to work effectively in aliphatic hydrocarbons opens up an opportunity for their application in industry.

In general, for all copolymers obtained with this catalytic system, an increase in the content of ethylene in the copolymers (from 87 to 97 mol %) is accompanied by an increase in the values of tensile strength (from 5 to 16 MPa) and a decrease in the values of elongation-at-break (from 670 to 125 %).

Nascent ethylene-propylene copolymers produced on aryloxide catalytic systems contain sterically crowded phenols in polymer matrix formed during the hydrolysis of activators in the course of copolymers washing [14]. These phenols are structurally similar to traditional phenolic antioxidants used as polyolefin stabilizers [21,22]. In this work, the washed copolymers contain 2,6-di-tert-butylphenol in amounts of 1 to 4 weight %. We evaluated the effect of phenol content on the resistance of copolymers to thermal oxidative degradation and mechanical characteristics of copolymers. As a phenol-free reference, we employed the sample produced by  $rac\text{-Et(2-MeInd)}_2\text{ZrMe}_2$ /isobutylaluminumoxane catalytic system [17]. TGA thermograms of copolymers with content of 2,6-di-tert-butylphenol of 0 (reference sample), 4, and 2 wt.% (samples 2 and 8 in Table 1) are shown in Figure 1. The sample with 2 % of phenol was obtained by additional extraction of sample 2 with methylene chloride. TGA measurements were carried out in the air. From Figure 1 and the weight loss at 5 and 50 weight percent as indicated in the Table embedded in the Figure 1, one can see that the temperature of thermo-oxidative degradation increases significantly with increasing



**Figure 1.** Influence of 2,6-di-tert-butylphenol on the thermal-oxidative degradation of E/P copolymers. TGA of polymers obtained on  $rac\text{-Et(2-MeInd)}_2\text{ZrMe}_2$ /activator catalytic systems where the activators are isobutylaluminumoxane (curve 1, E/P copolymer characteristics in the Experimental) and  $(2,6\text{-}^i\text{Bu}_2\text{PhO-})\text{Al}^i\text{Bu}_2$  (curves 2 and 3, samples 8 and 2 from Table 1).

phenol content.

The physical and mechanical tests showed a higher tensile strength and lower elongation-at-break for the washed sample with 2% phenol content compared to the original copolymer (14 and 10 MPa, 420 and 500%, respectively, samples 8 and 2, Table 1). Reducing the phenol content probably changes the ratio of amorphous and crystalline phases in the copolymer in the direction of increasing the latter.

## CONCLUSION

We demonstrated the influence of the conditions of ethylene with propylene copolymerization process with catalytic system  $rac\text{-Et(2-MeInd)}_2\text{ZrMe}_2/1\text{-DTBP}$  such as monomer concentration, the molar ratio Al/Zr, the type of solvent on the activity of the catalytic system, the composition of the formed copolymers, and their thermal and mechanical properties. It has been shown that the increase in content of 2,6-di-tert-butylphenol in copolymer increases material resistance to thermal-oxidative degradation but may significantly influence the mechanical properties of copolymer.

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## CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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