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ORIGINAL PAPER

Tailoring polypropylene properties by package of internal/external donor in Ziegler-Natta catalysts

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ABSTRACT

Insights have been developed into the influence of different structures, including bismethoxymethylfluorene (B) and 2,2-diisopropyl succinate (I), on both internal donor (ID) and external donor (ED) roles on the performance of $MgCl_2$/ID/$TiCl_4$. Catalyst performance including activity, hydrogen response, molecular weight distribution and thermal properties is explained through the coordination nature of external donors and its correlation with the internal donor. Replacement of the typical alkoxysilane ED with B and I leads to an overall decrease in activity, which is more pronounced (average 1.4 times) in systems with similar structures as ID and ED. However, these compounds significantly enhance hydrogen response. The use of B as ED leads to an average 1.5-fold increase in MFI and usage of I as ED results in an average 1.1 times increase in MFI. Changing the ED influenced the thermal properties so that in the catalyst with the succinate structure as ID, altering the ED from alkoxysilane to I, leads to an increase in crystallinity from 43.86% to 48.12%. These findings suggest that the choice of package of internal and external donor can significantly influence the resulting polymer characteristics. **Polyolefins J (2024) 11: 255-263**

Keywords: External donor; fifth generation catalyst; molecular weight.

INTRODUCTION

Until now, the industrial development of the Ziegler-Natta propylene polymerization process has involved five generation of catalysts in which electron donors play a crucial rule [1]. In recent decades, the most commonly catalyst used in the polypropylene production contains phthalate as an internal donor (ID) and alkoxysilane as an external donor (ED). The current interest in tailoring the final polymer properties has made lines in introducing new structures as donors and disclosing the mechanism of their reactions [2-3]. But the point that less noticed is the interdependence of ID and ED which can deprioritize the introduction of new structures and make it possible to design catalyst systems by well-known dononrs. It has been suggested that ED selectively poisons aspecific centers and generate new centers, having different stereo specificity. This role was always influenced by ID and varied by changing the ID structure [4]. Nevertheless, removing the large extent of internal donors from the support by alkylation and complexation reactions with the cocatalyst makes it difficult to have conclusive

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findings on internal/external donor interdependence [5].

A fifth class of internal donors, including diether and succinate, remains strongly coordinated to the support when the catalyst brought into contact with the cocatalyst. On the other hand, using typical alkoxysilane structures as ED leads to the worsening of the hydrogen response that limits final polymer application [6]. Therefore, in an approach to get evidence of internal/external donor interdependence, replacing both common internal and external donors with diether and succinate structures could be considered.

Our group has studied $MgCl_2$/Mixed-ID/$TiCl_4$ catalyst systems incorporated with fifth generation electron donors containing mixture of bis-methoxy methyl fluorene (B) and 2,2-diisopropyl succinate (I) as internal donors. The results provided proper connection among coordination nature of electron donors and final polymer properties including MWD [7]. Meanwhile, in these systems the impact of alternative external donors on the catalysts performance was also thoroughly examined. The results indicated that diether and succinate as ED have a great impact on hydrogen response and molecular weight [8].

It has been reported that typical external donors namely, alkylalkoxysilane, leads to a worsening of the hydrogen response, which limits the use of these catalysts for certain applications such as thin wall injection molding (TWIN) [6], therefore, it would be necessary to select a specific type of catalyst system to solve this problem. Regarding the results of our previous works, we extended our research to study the polymerization performance of $MgCl_2$/ID(diether or succinate)/$TiCl_4$ catalyst systems using the same structures (diether or succinate) as external donor and comparing it with alkoxysilane one. This facilitates the development of internal and external donor package for fifth generation Ziegler-Natta catalyst, taking into account the desired polymer characteristics.

EXPERIMENTAL

Materials

Propylene (polymerization grade) was supplied by Arak Petrochemical Co (Iran). Nitrogen and hydrogen (99.99%) were supplied by Arkan Gas Company (Iran). The triethylaluminum (TEAl), titanium tetrachloride ($TiCl_4$), and cyclohexyl methyl dimethoxy silane (C) were supplied from Arak Petrochemical Co (Iran). n-Heptane (97%, Dijung) and n-hexane (97%, Dijung) were refluxed over calcium hydride for 48 h and distilled before use. Ortho xylene (98%, Merck) was used as received. The methods that have been reported in the literature were modified and used for the synthesis of 9, 9-bis methoxy methyl fluorene (B) and diethyl-2, 3-diisopropyl succinate (I) [9-10].
Regarding the effect of the alcohol content of the adducts on the related Ziegler-Natta catalyst performance [11], microspherical $MgCl_2.n(C_2H_5OH)$ with n = 2 to 2.2 and average particle size of 28.72 µm was prepared by the method described in the literature [12] and then proceeded by successive alcohol extraction using the thermal route to prepare adduct with n = 2 to 2.1.

Catalyst synthesis

The catalysts were prepared according to the procedure reported in the literature [13] with minor modifications. The preparation was carried out using a 1-L stainless steel Buchi reactor and all experiments were performed under nitrogen atmosphere. 145 mL of $TiCl_4$ was introduced at 0°C to the reactor and then 6 g of the $MgCl_2.2.1(C_2H_5OH)$ adduct was added and the temperature was raised to 40°C. The electron donor was added at an Mg/ID molar ratio of 10 and stirred at 110°C for 1 h, after which the stirring was stopped and the supernatant was removed by siphoning and 90 mL of fresh $TiCl_4$ was added and reacted at 110°C for 30 min. Next, the stirring was stopped and the supernatant was siphoned off and the solid catalyst was washed at 60°C for seven times. Two catalysts were synthesized in the same procedure: Catalyst B (9, 9-bis (methoxymethyl)-fluorene (B) as internal donor) and catalyst S with diethyl-2, 3-diisopropyl succinate (I) as internal donor.

Propylene polymerization

Polymerization was carried out in a 1L stainless steel Buchi reactor. The reactor was purged with N_2 and evacuated four times successively. 400 mL *n*-heptane, along with a desired amount of cocatalyst, catalyst, and external donor were added in the order. In the pre-polymerization step, the calculated volume of hydrogen and propylene monomer was introduced and the total pressure was kept at 2 bar for 20 min. Then the temperature was raised to 70°C and the polymerization maintained at 6-bar propylene for 2 h. In the final step, the polymerization was terminated by venting the unreacted monomer and drying the polymer for 2 h under vacuum at 60°C.

Characterization

The content of titanium (Ti) and magnesium (Mg) in the solid catalysts was studied by Atomic Absorption Spectroscopy (AAS). The content of chloride in the catalysts was determined by microwave digestion and potentiometric titration, UOP 291c test method.

The Thermal Gravimetric Analysis (TGA) of the adduct was performed by a TGS-2 Perkin Elmer. The Isotactic Index was reported by the xylene-soluble fraction of the polymers according to standard test methods D5492-98.

The molecular weight and dispersity (Đ) were determined by Gel Permeation Chromatography (GPC) measurement with 1, 2, 4-trichlorobenzene as a solvent and linear polystyrene as a standard sample using PL 220 high-temperature (Agilent Company). The molecular weight distribution curve of the catalysts was deconvoluted to Flory components by MATLAB R2014a software. The Melt Flow Index (MFI) is the mass of polymer (in grams) that passes through a standard capillary under a standard load during 10 min. The MFI of polypropylene was measured by MFI-4 (Gottfert Company) at 230°C, under a 2.16 kg load over 10 min.

Differential Scanning Calorimetery (DSC) thermograms were recorded using a METTLER TOLEDO. The samples were cooled down from 200°C to 50°C at a rate of 10°C/min and the melting temperature (T_m) and enthalpy of fusion (ΔH_m) were determined in the second scan. The degree of crystallinity (X_c) was calculated with using 100% crystalline PP (ΔH_m= 209 J/g) [14].

RESULTS AND DISCUSSION

Catalyst composition and elemental distribution in particles

Two kind of catalysts were prepared with varying internal donor types. Table 1 presents the results of compositional analysis of the prepared catalysts. The Ti content of both catalysts is high, which may be attributed to the low quantity of internal donor used (Mg/ID=10) that increases the possibility of occupation of adsorption sites with $TiCl_4$ [15]. Both catalysts exhibit significant donor content; however, there is a notable difference in the donor content between them. The succinate content in catalyst S is higher, approximately twice that of the diether content in catalyst D. It could be attributed to the higher adsorption energy of interaction of succinate with $MgCl_2$ surface that increases the possibility of occupation of $MgCl_2$ surface sites in comparison to diether and even $TiCl_4$ [16,17].

Table 1. Elemental composition of sunthesized catalysts.

Sample	Elemental composition (wt.%)				
	B	I	Ti	Mg	Cl
Catalyst D	7.4	---	7.4	11.8	47.7
Catalyst S	---	12.28	4.7	12.4	45.9

B: 9, 9-bis methoxy methyl fluorene, I: diethyl-2, 3-diisopropyl succinate, catalyst D: including diether internal donor
catalyst S: succinate internal donor

The distribution of elements in the catalyst particles was analyzed using an energy dispersive spectrometer (EDS) on the SEM microscope (Figure 1). The results indicate an even distribution of elements in both catalysts. Given that the uniform distribution of titanium sites in catalyst particles significantly influences the control of stresses induced during polymerization, it is reasonable to anticipate that these catalysts would exhibit good performance in polymerization.

Polymerization

The results of propylene polymerization for the prepared catalysts with different internal donors (B and I) in the presence of different types of external donors (C, B, I) are given in Table 2.

Effect of external donor structure on catalyst performance

Both catalysts in the presence of C exhibit maximum activity. Regarding the other two structures, it is noteworthy that the use of an external donor with the same structure as internal donor results in a significant decrease in activity, which is approximately 1.4 times lower on average for both catalysts D and S (Table 2). Several interactions could be considered regarding the reaction of external donor with the catalyst surface, which makes it complicated. It is inevitable that a group of active centers would be deactivated by ED [18]. It could also replace internal donors or have selective coordination on vacant sites on the lateral cuts of $MgCl_2$, meanwhile there is the possibility of its interaction with cocatalyst [19] (Scheme 1).

To explain the activity trend observed in Table 2, it is necessary to consider the difference in coordination modes between diether and succinate, regardless of their usage as internal or external donor. In general, rigid and bulky diether structures resulting from short oxygen-oxygen bond length usually result in selective

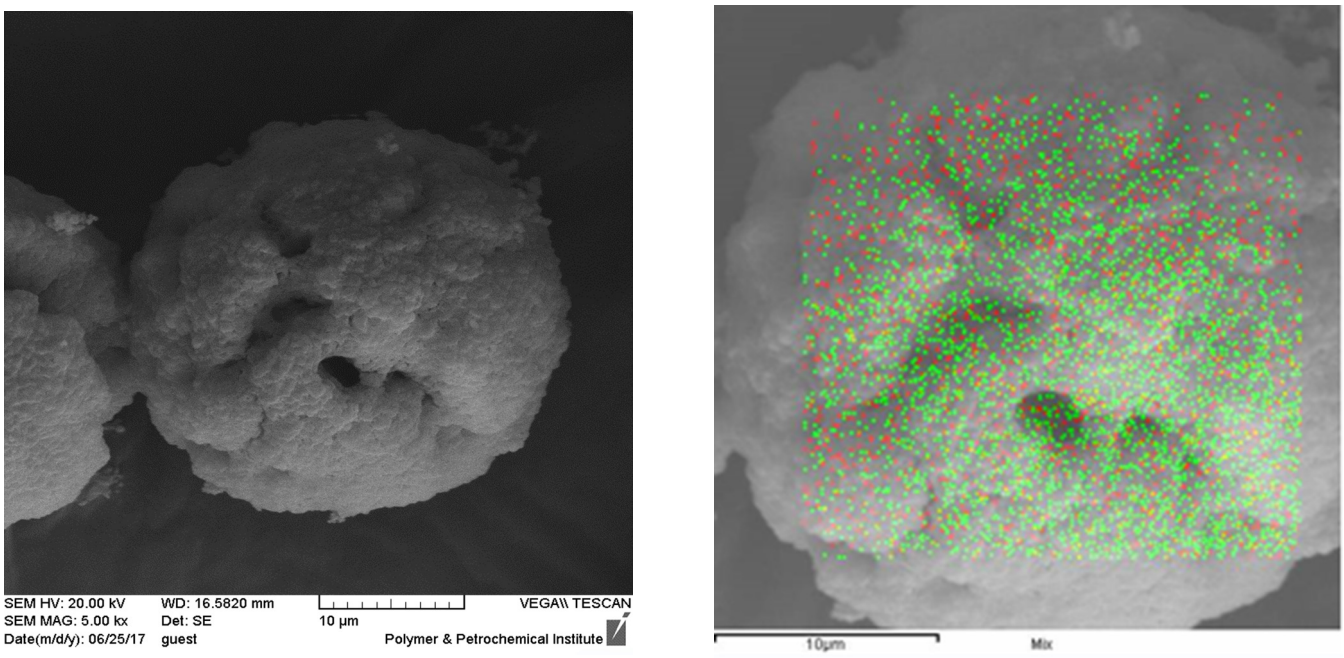
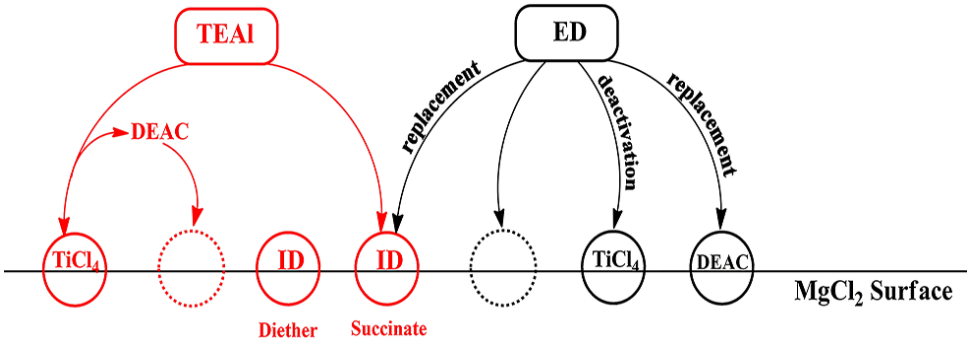


Figure 1. SEM images of catalyst particles and element distribution (titanium and magnesium as red and green spots, respectively): (a) Catalyst D, and (b) Catalyst S.

bidentate coordination (chelate) on (110) lateral cut of $MgCl_2$. Consequently, as an internal donor they are less susceptible to replacement by TEAL or ED. In contrast, more flexible structures such as succinate with a longer spacer between the coordinating oxygen atoms could be adsorbed on (100) and (110) lateral cuts with bridge, chelate, or inter-layer bridging (zip) coordination modes [20]. This structural flexibility provides the potential for diverse interactions of succinate with TEAL or ED.

In catalyst D, the use of B as an external donor does not induce any new potential positions for increasing the active sites. However, in the presence of I, there exists the possibility of competitive interaction between succinate and Mg atoms adjacent to the central Ti centers [18], which may enhance its activity.



Scheme 1. Possible interactions of ED with $MgCl_2$ surface.

In catalyst S, the use of B as external donor provides new stable active sites, while in the presence of I, there is no apparent change in the nature of coordination sites.

According to Scheme 1, diethylaluminum chloride (DEAC), formed by the reaction of titanium species and aluminum trialkyls, coordinates on the $MgCl_2$ surface adjacent to the Ti active centers [21]. In this condition, ED because of its more stable coordination with $MgCl_2$, replace the DEAC and improve the stereo selectivity of active centers. Therefore, regardless of what type of ED is used, the isotacticity index (I.I) is higher than 98.70%.

For both catalysts, the use of a diether or succinate external donor leads to an increase in MFI compared to the conventional alkoxysilane external donor (C). These data confirm the capability of non-alkoxy silane structure, as ED, to improve hydrogen response of these systems. Meanwhile, no matter which structures used as ED, the hydrogen response of catalyst D is higher than that of S. It could be explained through the role of internal donors on the formation of region-defects. In systems with diether internal donors, there is a high incidence of regio-defects (2, 1-defect and 1, 3-defect) [22]. On the other hand, these systems contain the narrower distribution of active species, for which the effects of the regio-defects became more effective. Therefore, the reduction in regioselectivity leads to a high probability of chain transfer and a decrease in molecular weight (M_w), as reported in catalyst D (Table 2).

According to Table 2, the use of an external donor with the same structure as internal donor leads to the increase in M_w. It is well known that M_w is affected by chain propagation and chain transfer rate, mainly hydrogen transfer, and in most cases is influenced by region-selectivity of active centers [23,24]. Therefore, it could be concluded that in systems with the same structure as both internal and external donors, active centers with higher regio-selectivity are formed.
Meanwhile, Table 2 depicts that the change of ED has a slight effect on Đ and as we expected, the S catalyst showed higher Đ.

Active center study by deconvolution of polymer molecular weight

It is known that $TiCl_4$/ID/$MgCl_2$ type supported Ziegler-Natta catalysts contain multiple types of active centers [25,26] whose distribution on the catalyst surface could be effectively obtained by deconvolution of polymer MW, and it should be noted that it can be fitted by multiple Flory functions [27,28]. In this work, molecular weight distribution curves of all prepared polymers were deconvoluted into four most probable distribution peaks. Each resolved curve corresponds to a certain type of active center with a characteristic

Table 2. Effect of different EDs on the performance of different catalysts in propylene polymerization.

Catalyst	ED	Activity (Kg PP/gcat)	Isotacticty Index(I.I)	MFI	$M_w \times 10^{-4}$ (g/mol)	$M_n \times 10^{-4}$ (g/mol)	*Đ
Catalyst D	C	9.36	99.60	33.03	204.7	79.3	2.60
	B	5.61	99.98	57.82	190.6	190.6	2.58
	I	8.60	99.90	39.73	155.5	1545.5	2.80
Catalyst S	C	7.22	98.92	11.82	301.0	911.9	4.13
	B	7.17	99.98	16.90	243.70	702.4	3.76
	I	5.98	98.70	12.90	291.20	928.0	4.45

C:Cyclohexyl methyl dimethoxy silane, TEAl/Cat: 54, TEAl/ED: 15,H_2: 4.5 mmol,*Đ was calculated by M_w/M_n.

Table 3. Result of deconvolution of the MWD curve of catalyst D.

	Site 1		Site 2		Site 3		Site 4	
Catalyst D	F_r [a]	M_w [b]	F_r	M_w	F_r	M_w	F_r	M_w
ED:C	10.17	17.85	45.46	57.66	32.89	124.22	11.48	245.3
ED:B	4.22	12.50	56.44	46.83	31.43	105.9	7.91	212.12
ED: I	8.68	15.16	51.06	54.9	32.57	127.44	7.68	292.5

Table 4. Result of deconvolution of the MWD curve of catalyst S.

	Site 1		Site 2		Site 3		Site 4	
Catalyst S	F_r [a]	M_w [b]	F_r	M_w	F_r	M_w	F_r	M_w
ED:C	15.77	22.38	41.64	71.57	32.65	189.5	9.94	535.25
ED:B	11.76	16.10	43.34	56.48	34.41	148.07	10.49	391.42
ED: I	15.66	17.01	37.96	60.97	35.72	174.71	10.66	479.47

molar mass and a certain mass fraction (Fr, %) [29]. According to the results, which have been depicted in Tables 3 and 4, the active centers could be divided into two kinds: $C_1^*+C_2^*$ representing the active center producing low molecular weight polymer, and $C_3^*+C_4^*$ representing the high molecular weight polymer.

Effect of external donor type on active center characteristics

The molar mass of all four active centers in the presence of donor C is higher than two other external donors in both catalysts D and C. In catalyst D, the replacement of C with B or I leads to the increase of the mass fraction value (Fr%) of ($C_1^*+C_2^*$) and decrease of ($C_3^*+C_4^*$), while no remarkable change was observed by changing external donor from B to I (Table 3). In other words, in this catalyst, the use of dither or succinate as external donor has no effect on the Fr% value of the active centers, and it does not matter whether the centers with low or high molecular weight are responsible for this.

In catalyst S, from external donor C to I, a specific decrease in the Fr% value of ($C_1^*+C_2^*$) and an increase in ($C_3^*+C_4^*$) were observed, respectively (Table 4). It reveals that in this system, succinate structure has a profound role in converting low molar mass active centers to higher ones. It could be concluded that the use of succinate structure, as both internal and external donors, is responsible for directing mass fraction of active centers to higher ones, which is in line with our previous report [7-8].

Thermal properties of polypropylene samples

The thermal properties of samples were studied by DSC (Table 5). The results show that the crystallinity of the polymer samples in both catalysts was clearly influenced by the type of external donor and that replacing the typical alkoxysilane structures with

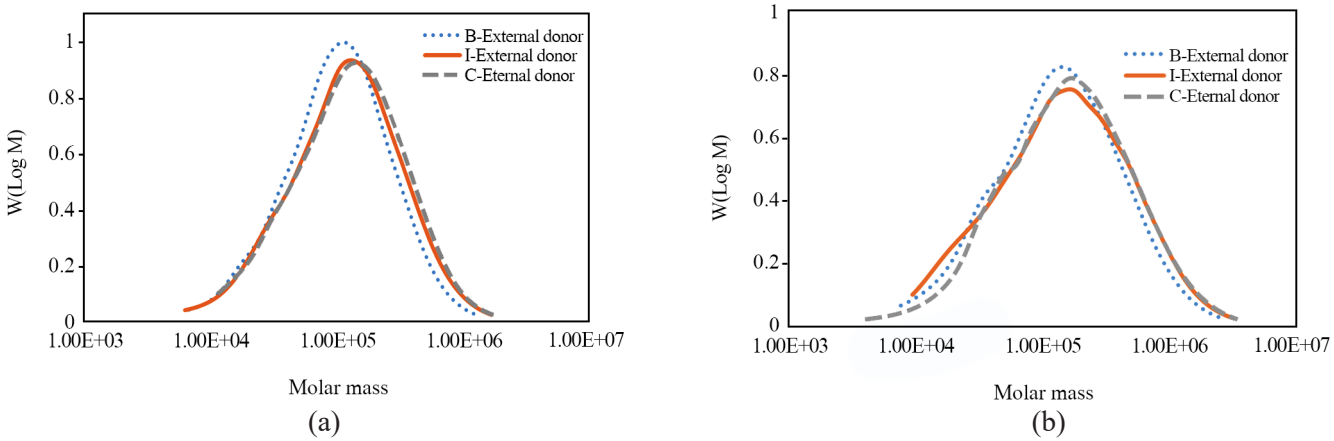


Figure 2. Molecular weight distribution curves of the samples in the presence of different external donors: (a) Catalyst D, and (b) Catalyst S.

Table 5. Thermal properties of samples in the presence of different external donors.

Catalyst	ED	Tm (°C)	Tc(°C)	X_c%	ΔH_m(J/g)	ΔH_c(J/g)
Catalyst D	C	158.2	111.76	44.54	92.25	91.33
	B	158.81	114.00	47.01	97.37	96.08
	I	159.81	113.38	45.42	94.06	94.2
Catalyst S	C	160.44	113.08	43.86	90.84	94.39
	B	160.95	115.15	45.19	93.58	97.80
	I	158.95	113.02	48.12	99.66	96.64

diether or succinate leads to an increase in crystallinity. This is more noticeable in catalyst S, and replacing C with the external succinate (I) donor leads to an increase in X_c from 43.86% to 48.12%. In addition, the trend in Table 4 shows that the use of a structure as both internal and external donors has a certain effect on the final thermal properties. These data state that the external donor structure has more profound effect in stereo regularity of polymers chains than the internal donor one.

CONCLUSIONS

The performance of diether and succinate as EDs was studied in $TiCl_4$/ID/$MgCl_2$ systems (ID: diether/succinate). Given the similarity between the structures of internal and external donors, an opportunity was provided to examine their interdependence and their impact on catalyst performance. The results indicated that catalyst performance could be controlled by choosing the appropriate choice of electron donor package. Major findings are described as follows:

- Replacement of alkoxysilane structure with other EDs leads to a decrease in activity but the amount of this reduction is greater in the systems with the same structure in both roles. In addition, the isotacticity index does not change sharply based on the type of external donor.
- The main range of MFI is controlled by the type of ID, but in each category the effect of ED on MFI is undeniable and increases with the use of non-alkoxysilane structures.
- ED structure does not affect the distribution of active centers but in the systems with the same structure as both internal and external donors, active centers with higher regio-selectivity are formed.
- The molar mass of all four active centers in the presence of donor C is higher than those in the presence of two other external donors in both catalysts D and C. The results show that in catalyst S, the external succinate donor is more efficient in converting low molar mass centers to higher ones compared to the other two external donors.
- The data revealed that the external donor structure has a more profound effect on the stereoregularity of polymers chains than the internal donor structure.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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