

Article

Propylene Polymerization Performance with Ziegler-Natta Catalysts Combined with U-Donor and T01 Donor as External Donor

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Abstract: In propylene (C3) polymerization with Ziegler-Natta catalyst, not only internal donor but also external donor is very important to make isotactic polypropylene (PP) with higher yield. Most propylene-based polymers have been commercially produced with Ziegler-Natta catalysts combined with dialkyl-dialkoxy silane compounds ($R_2Si(OR)_2$) such as C-donor, P-donor, and D-donor as external donors. In this paper, we will introduce the propylene polymerization performance with aminosilane compounds, i.e., diethylamino triethoxy silane (U-donor) and bis(ethylamino) di-cyclopentyl silane (T01 donor), as external donor in Ziegler-Natta catalyst. The polymerization screening experiments were conducted using some triethoxyalkylsilanes compounds (1–7) and performances were compared with U-donor. The polymerization results of the binary donor system show improvement in stereoregularity. These aminosilane compounds exhibit high hydrogen response in propylene polymerization and high copolymerization performance of propylene (C3) and ethylene (C2) in ICP production compared with dialkyl-dialkoxy silane compounds. While using methanol as an additive along with external electron donor, as a serendipitous, the copolymerization activity, block ratio, EPR (ethylene-propylene rubber) content improve significantly for U-donor as compared with T01 donor and C-donor.

Keywords: Ziegler-Natta catalysts; aminosilane external donor; U-donor; T01 donor; propylene polymerization; hydrogen response and impact copolymer (ICP)



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1. Introduction

Polypropylene (PP) is widely used in many applications such as injection molding, film, non-woven fabric, and so on [1,2]. In industrial production, most of the PP is produced with Ziegler-Natta catalyst (ZN catalyst), with $MgCl_2$ support, $TiCl_4$ as active sites, and Lewis base compound (typically named internal electron donor, ID) [3–9], combined with alkyl compound and another class of Lewis base compound (named external electron donor, ED) [10].

The main roles of the internal and external donors in propylene (C3) polymerization are improvement of catalyst activity and formation of isospecific active species [7,8]. The internal donor is added during catalyst preparation and directly supported on $MgCl_2$ surface, which suggested that internal donor could control the $TiCl_4$ distribution and form highly isospecific sites on $MgCl_2$ surface [7,8].

Many ZN catalysts used in industry contain phthalate compounds as internal donors [2,11]. In addition to phthalates, diether [12], succinic acid esters [13], diol diesters [14,15], etc., are used, and catalysts using these internal donors are spreading worldwide due to the influence of REACH regulation in Europe [2].

The polymerization performance of the ZN catalyst varies depending on the choice of internal donor, but is also affected by the external donor to be combined. In general, dicyclopentyl dimethoxy silane (DCPDMSi; DCP; D-donor), diisopropyl dimethoxy

silane (DIPDMSi; DIP; P-donor), and cyclohexyl methyl dimethoxy silane (CMDMSi; CM; C-donor) have been used in both of academic and industrial fields so far and exhibit different isospecificity and chain transfer reactivity with hydrogen. Accordingly, the combination of internal and external donors is very important to obtain polypropylene showing the desired physical properties [16–18].

On the other hand, the performance improvement of electric injection molding machines has a great impact on the performance of the catalyst. In other words, innovation of thin wall injection molded technology was born by combination of this molding machine with high flow and high crystalline PP, and the products are utilized for food packaging. Therefore, there is a demand for a catalyst system of high H₂ response (chain transfer reaction under low H₂ concentration) which gives high flow PP. Unfortunately, the current external donors mentioned before cannot meet this requirement.

From such a point of view, we propose two kinds of amino silane compound as external donor; diethylamino tri-ethoxy silane (U-donor) [19–21], and bis(ethylamino) di cyclopentyl silane (T01 donor) [22,23] commercial product of Toho Titanium Co., Ltd. These aminosilane compounds exhibit higher H₂ response than those of dialkoxy silane compounds in propylene polymerization. Moreover, we found that these aminosilane compounds show unique performance in the production of impact copolymer (ICP), which is block copolymerization of polypropylene and ethylene-propylene copolymer.

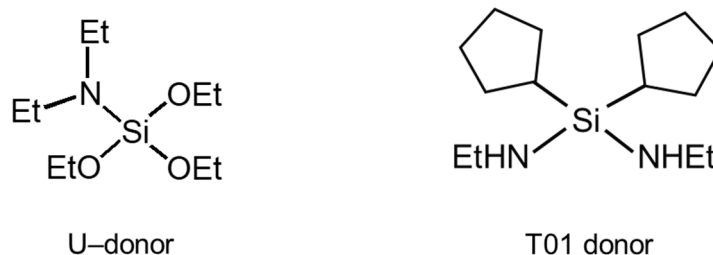
In this paper, we describe the fundamental polymerization performance with U-donor and T01 donor in combination with phthalate-based ZN catalyst.

2. Results and Discussions

2.1. Homo Polymerization (Homo-PP)

2.1.1. Propylene Polymerization with ZN Catalyst with U-Donor and T01 Donor

The two commercial products of alkoxy aminosilane compounds (U-donor and T01 donor) were used as external electron donor (ED) for propylene polymerization (Scheme 1). These external electron donors (U-donor and T01 donor) were used for propylene homo polymerization (homo-PP) and impact copolymerization (ICP-PP). The results were compared with other external electron donors such as C-donor and D-donor, which are most commonly industrially used external electron donors. The polymerization screening experiments were carried out using various triethoxysilane compounds and the results were compared with U-donor.



Scheme 1. Structure of external electron donors (U and T01).

2.1.2. Propylene Polymerization with U-Donor vs. C-Donor

The propylene polymerization experiments were carried out in the presence of ZN catalyst with U-donor and C-donor as external electron donors with different hydrogen concentrations. The obtained polymerization results are compiled in Table 1. The U-donor-based polymers (run 1–3) show very high hydrogen response (Figure 1) with high stereoregularity as compared with C-donor (run 4–5). The high hydrogen response and high stereoregularity play a very important factor in industrial polypropylene (PP) production, where consumption of hydrogen amounts is relatively low using U-donor with high rigidity polymer production as compared with C-donor. However, the catalyst activity for U-donor-based polymers was slightly lower than the C-donor-based polymers, where U-

donor can use only for special application PP grades such as high rigidity PP for automotive applications, high MFR PP (high melt flow rate PP) for fiber grade applications, etc.

Table 1. Propylene polymerization results by U- and C-donors under various hydrogen concentrations.

Run No. *	External Donor	H ₂	Activity	MFR	XS
		[NL]	[g-PP/g-cat h]	[g/10 min]	[wt%]
1	U-donor	1.5	44,000	13	0.8
2	U-donor	4.0	56,300	89	0.8
3	U-donor	6.0	55,600	160	1.1
4	C-donor	1.5	55,900	4	1.0
5	C-donor	4.0	66,500	23	1.1

* Polymerization conditions: Al/ED/Ti = 500/50/1, C₃ = 12.6 mol, pre-contact at 20 °C for 5 min, main polymerization at 70 °C for 60 min.

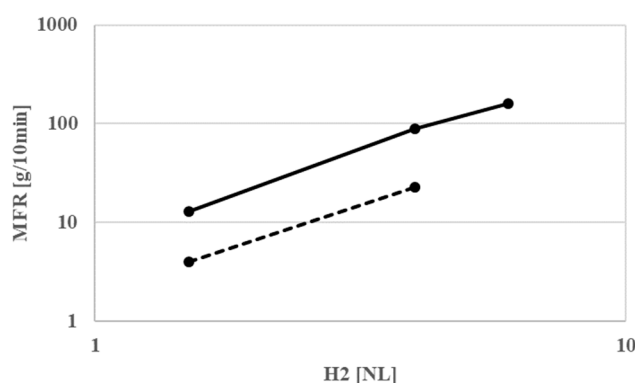
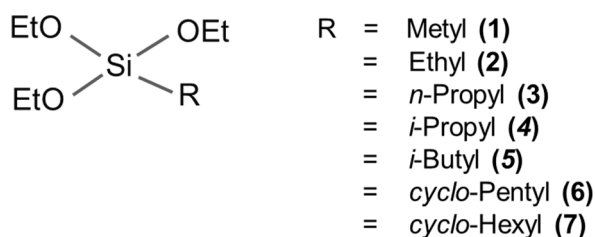


Figure 1. H₂ response on MFR; **Solid line:** U-donor, **Dotted line:** C-donor.

2.1.3. External Electron Donor Screening against U-Donor

The trialkoxyalkylsilane compounds are known as external donors with high H₂ response [24]. The polymerization screening experiments were conducted and performance comparisons were made between some triethoxyalkylsilanes (Scheme 2; 1–7) and U-donor along with ZN catalyst. The obtained results are summarized in Table 2.



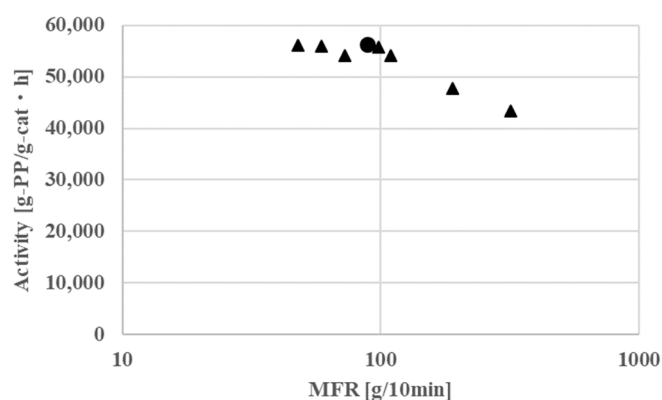
Scheme 2. Structure of triethoxyalkylsilane compounds (1–7) as external donors.

The compounds 4–6 (run 9–11) achieved high catalyst activity, which is similar to U-donor catalyst activity (run 2). However, the hydrogen response for compound 5 (run 19) appears slightly higher than the U-donor and or slightly lower for compounds 4 and 6 as compared with U-donor. The compounds 1 and 2 (run 6 and 7) show lower catalyst activity as compared with U-donor. However, high hydrogen responses are observed for both the compounds (1 and 2). The catalyst activity for compound 3 and 7 (run 8 and 12) appears very similar, which are slightly lower than the U-donor activity. On the other hand, hydrogen response for compound 3 appears higher than U-donor and slightly lower hydrogen response was observed for compound 7 as compared with U-donor. The relationship between catalyst activity and MFR (melt flow rate) for compound 1–7 and U-donor are shown in Figure 2.

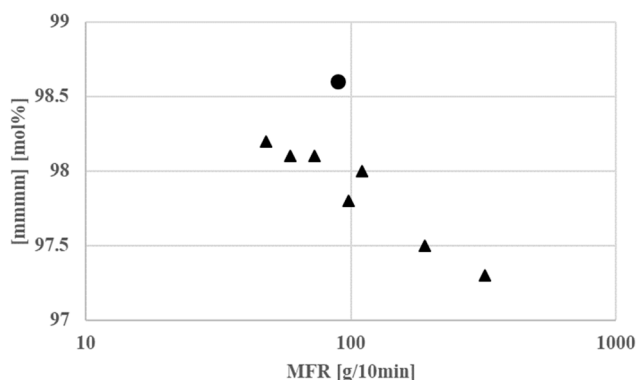
Table 2. External donors of triethoxyalkylsilanes (1–7) propylene polymerization screening against U-donor.

Run No. *	External Donor	Activity	MFR	XS	[mmmm]
		[g-PP/g-cat h]	[g/10 min]	[wt%]	[mol%]
6	Methyl-Si(OEt) ₃ (1)	43,300	320	1.2	97.3
7	Ethyl-Si(OEt) ₃ (2)	47,800	190	1.1	97.5
8	<i>n</i> -Propyl-Si(OEt) ₃ (3)	54,200	110	1.3	98.0
9	<i>i</i> -Propyl-Si(OEt) ₃ (4)	55,900	59	1.2	98.1
10	<i>i</i> -Butyl-Si(OEt) ₃ (5)	55,800	98	1.1	97.8
11	<i>cyclo</i> -Pentyl-Si(OEt) ₃ (6)	56,100	48	1.2	98.2
12	<i>cyclo</i> -Hexyl-Si(OEt) ₃ (7)	54,100	73	1.3	98.1
2	U-donor	56,300	89	0.8	98.6

* Polymerization conditions: Al/ED/Ti = 500/50/1, C₃ = 12.6 mol, H₂ = 179 mmol, pre-contact at 20 °C for 5 min, main polymerization at 70 °C for 60 min.

**Figure 2.** Relationship between MFR vs Activity; ●: U-donor, ▲: Alkyl triethoxyalkylsilanes (1–7).

The xylene soluble and stereoregularity appears for compounds 1–7 in the range of 1.1–1.3 wt% and 97.3–98.2 mol% respectively, which are lower than U-donor performances. The relationship between MFR and stereoregularity (pentad isotacticity; mmmm) is shown in Figure 3, where U-donor appears better for both hydrogen response and stereoregularity. Overall, the polymerization screening performance for triethoxysilane compounds (1–7) appears much lower as compared with U-donor performances.

**Figure 3.** Relationship between MFR vs [mmmm]; ●: U-donor, ▲: alkyl triethoxy silane compounds.

2.1.4. Effect of Binary Use of U and D Donor for Propylene Polymerization

The polymerization screening experiments were carried out with binary donors (U + D donors; run 13–14 and 17) keeping MFR around 35 g/10 min and the results were compared

with single donor systems U and D respectively (run 15 and 16). The polymerization experiments with U-donor and subsequent addition of D-donor, mix of U- and D- donors, D-donor with subsequent addition of U-donor and only with D-donor results are summarized in Table 3.

Table 3. Effect of binary use of U- and D- donor for propylene polymerization *.

Run No. *	1st ED	2nd ED ²	H ₂	Activity	MFR	XS	Mw/Mn
			[NL]	[g-PP/g-cat h]	[g/10 min]	[wt%]	
13	U-donor	D-donor	4.0	40,200	34	0.8	6.3
14	U- + D-donors	—	9.0	63,500	37	0.6	5.9
15	U-donor	—	2.6	46,100	36	0.8	4.8
16	D-donor	—	9.0	68,600	32	0.8	6.2
17	D-donor	U-donor	9.0	66,000	34	0.7	6.1

* Polymerization conditions: Al/ED/Ti = 500/50/1, ED = external donor, C₃ = 17.6 mol, pre-contact at 20 °C for 5 min, main polymerization at 70 °C for 60 min. ² ED (external donor; 0.2 mmol) was added after 15 min from the start of the polymerization (run 13 and 17). U-donor: diethylamino triethoxy silane; D-donor: dicyclopentyl dimethoxy silane.

The target MFR was around 35 min/10 min using U-donor and the required hydrogen amount is 2.6 NL (run 15) and the polymerization experiment with U-donor and subsequent addition of D-donor, the required amount of hydrogen was 4 NL (run 13). For the similar polymerization using D-donor and subsequent addition of U-donor, the required amount of hydrogen was 9.0 NL (run 17). In addition, using only D-donor (run 16) very similar hydrogen (run 17) was achieved. The polymerization using only U-donor achieved a very high hydrogen response (run 15). On the other hand, mix donor (U and D, run 14), sequence donor additions (run 13 and 17) show that the hydrogen responses decreased significantly. The catalyst activity for U-donor (run 15) and sequence donor addition (U and D, run 13) show lower than the other polymerization experiments (run 14, 16–17). For the mix donor (U + D, run 14), slightly higher stereoregularity was observed (XS: 0.6%) as compared with other cases, which are in the range of 0.7–0.8%. The gel permeation chromatography (GPC) shows slightly lower molecular weight distribution for only using U-donor (*Mw/Mn* = 4.8, run 15) and mix donor (U + D, run 14) *Mw/Mn* appears 5.9. The molecular weight distribution (*Mw/Mn*) for run 13, 16–17 appears in the range of 6.1–6.3. The lower molecular weight distribution (*Mw/Mn*) using U-donor (run 15), could be due to very low amount of hydrogen consumption and generated optimum range of polymer chains.

2.1.5. Propylene Polymerization with T01 Donor and U-Donor

The propylene polymerization experiments were carried out using ZN catalyst with T01 donor and the results were compared with U-donor results. The obtained polymerization results are compiled in Table 4. The T01 donor-based polymers (run 18–19) achieved a very high hydrogen response as compared with U-donor based polymers (run 3). However, lower stereoregularity was observed under identical external donor concentration (Si/Ti = 50 mol/mol). On the other hand, while increasing the donor concentration (Si/Ti = 100 mol/mol, run 19) the stereoregularity improved significantly (run 19) and high hydrogen response still remained intact for T01 donor as compared with U donor.

In addition, with a higher amount of donor concentration for T01 donor the catalyst activity marginally decreased (run 19). It is possible to achieve much higher hydrogen response using T01 donor and required to use a high amount of T01 donor for maintaining similar stereoregularity. As per the polypropylene, targeted applications both U-donor and T01 donor can be applied as per the requirement of high MFR and polymer rigidity.

Table 4. Propylene polymerization results by T01 donor as external donor.

Run No. *	External Donor	H ₂	Si/Ti	Activity	MFR	XS
		[NL]	[mol/mol]	[g-PP/g-cat h]	[g/10 min]	[wt%]
18	T01 donor	6	50	55,000	380	1.5
19	T01 donor	6	100	49,300	330	0.9
3	U-donor	6	50	55,600	160	1.1

* Polymerization conditions: Al/ED/Ti = 500/100 or 50/1, C₃ = 17.6 mol, pre-contact at 20 °C for 5 min, main polymerization at 70 °C for 60 min.

2.2. Impact Copolymerization (ICP-PP)

Propylene Copolymerization with ZN Catalyst with U-, T01 and C-Donors

The impact copolymerization experiments were carried out in the presence of ZN catalyst with U-, T01, and C-external electron donors and with the effectiveness of additive. The obtained copolymerization results are summarized in Table 5. In this case, methanol (MeOH) was used as an additive during copolymerization.

Table 5. Additive effect in impact copolymer production with ZN catalyst combined with U-donor.

Run No. *	External Donor	Additive **	Homo Polymerization Activity	Copolymerization Activity	Block Ratio	EPR Content	C2 Content in EPR
			[g-PP/g-cat h]	[g-ICP/g-cat h]	[wt%]	[wt%]	[wt%]
20	U-donor	—	41,600	7,300	14.9	12.7	49.4
21	U-donor	MeOH	43,300	12,800	22.8	17.5	49.8
22	T01 donor	—	44,400	18,300	29.1	25.0	42.5
23	T01 donor	MeOH	36,700	12,200	24.9	22.2	42.1
24	C-donor	—	57,000	9,700	14.5	12.0	40.2
25	C-donor	MeOH	56,300	10,300	15.5	11.8	40.3

* Copolymerization conditions: 1st hPP; Al/ED/Ti = 1200/120/1, C₃ = 12.6 mol, pre-contact at 20 °C for 5 min, main polymerization at 70 °C for 60 min. 2nd ICP; C₂/C₃ gas polymerization at 70 °C for 60 min. C₂/C₃/H₂ = 1.7/2.3/0.086 mL/min (Total pressure 1.2 MPa). ** Additive amount: MeOH/Al = 0.31 mol/mol.

The homo polymerization appears almost similar catalyst activity for U and T01 donors (run 20 and 22), which are lower than using C-donor (run 24). The copolymerization activity, block ratio, and EPR content appear very similar for both U- and C- donors (run 20 and 24). On the other hand, with the introduction of methanol as an additive along with U-donor, as a serendipitous, the copolymerization activity, block ratio, and EPR content improve significantly (run 21). This could be due to the effect of reaction between AlEt₃ (TEAL) with methanol along with U-donor. For example, the triethylaluminum (TEAL) reacts with methanol and produces AlEt₂(OMe) (Al/MeOH = 0.31). The catalyst active species of U-donor is deactivated by AlEt₃. At the same time, addition of methanol prevented the deactivation of the active species and as a result copolymerization activity improved for U-donor. For T01 donor, very high ICP performance was showed as compared with U- and C- donors, however, with addition of methanol the ICP performance decreased significantly (run 22 and 23). The poor ICP performance for T01 donor with methanol as an additive could be due to the steric hindrance between AlEt₂(OMe) (Al/MeOH = 0.31) and T01 donor. However, for C-donor no change in polymerization performances (run 24 and 25) was observed under identical polymerization conditions using methanol as an additive.

3. Materials and Methods

3.1. General Remarks

The phthalate-containing ZN catalyst used in this paper was a highly isospecific THC catalyst, commercially manufactured by Toho Titanium Co., Ltd., Kanagawa, Japan. The Ti content of the catalyst was determined by the absorbance at 410 nm of Ti-H₂O₂ complex in

acidic aqueous solution with a UV-vis spectrometer (JASCO, V-550, Tokyo, Japan), after the catalyst was dissolved and stirred in hydrochloric acid aqueous solution for 20 min. To determine phthalate content, the catalyst was decomposed by hydrochloric acid aqueous solution, and organic compounds were extracted with toluene. Phthalate content was determined by a gas-chromatography (GC-2014, Shimadzu, Kyoto, Japan). The contents of Ti and di-n-butyl phthalate (DNBP) in catalyst were 1.9 wt% and 6.1 wt%, respectively. Diethyl amino tri-ethoxy silane (U-donor) and bis(ethylamino) di cyclopentyl silane (T01 donor) commercial external electron donor sold by Toho Titanium were used as such. The purity of U-donor, T01 donor, and C-donor were >98%. The triethoxyalkylsilanes compounds (1–7) were commercially obtained and used without further purification.

3.2. Characterization

3.2.1. Melt Flow Rate (MFR) of Polymer

MFR, which indicates the melt flow property of polymer, was measured according to ASTM D 1238, JIS K 7210.

3.2.2. Xylene-Soluble (XS) Content in Polypropylene

4 g of PP and 200 mL of p-xylene were charged into a 200 mL volume round bottom flask. The polymer was dissolved under boiling temperature of p-xylene for 2 h. After cooling of the solution for 1 h at 23 °C, the precipitated PP was filtrated. p-Xylene solvent of the filtrate was evaporated and the fraction of p-xylene solution was determined from the amount of polymer remaining.

3.2.3. XS Content in ICP (Ethylene-Propylene Rubber (EPR) Content)

5 g of ICP and 250 mL of p-xylene were charged into a 500 mL volume round bottom flask. The polymer was dissolved under boiling temperature of p-xylene for 2 h. The liquid temperature was cooled to 23 °C for 1 h, and the undissolved component and the dissolved component were separated by filtration. The solution of the dissolved component was collected, and p-xylene was distilled off by heating and drying under reduced pressure. The weight of the obtained residue was determined, and its relative weight ratio to the ICP used was calculated and used as an EPR content.

3.2.4. Ethylene Content in XS of ICP

A small amount of the obtained EPR was sampled and formed into a film with a hot press. Ethylene content in EPR was calculated from the thickness of the film and absorbance was measured using FT-IR (Nicolet 7600, Thermo Fisher Scientific, Tokyo, Japan) on the basis of a calibration curve prepared by plurality of sample having a known ethylene content.

3.2.5. Ethylene Content in Xylene-Insoluble (XI) of ICP

A small amount of a xylene-insoluble fraction obtained by xylene extraction of ICP was sampled and formed into a film with a hot press. Ethylene content in the xylene-insoluble fraction was calculated in the same manner as in the ethylene content in XS of ICP.

3.2.6. ¹³C-NMR Measurement

The ¹³C-NMR (JNM-ECA400, JEOL, Tokyo, Japan) spectra was recorded at 125 °C to measure the tacticity of homo PP. Deuterated benzene bromide (Br-Ph-d₅) was used as NMR solvent mixed with o-dicholobenzene (Br-Ph-d₅:ODCB = 3:7, in *v/v*). 0.2 g of polymer sample was placed into a 10 mm NMR tube followed by 3 mL of the mixed solvent, and nitrogen was purged. The tube was capped and placed in a block heater at 145 °C to dissolve hPP sample. The mixture was stirred by a vortex mixer time to time and again heated in the block heater until it became a homogeneous clear solution. Acquisition parameters were the time 10 s with a 90-degree flip angle, the plus interval 18 s, and 6000 scans.

3.2.7. Molecular Weight Distribution

Gel permeation chromatography (GPC: HLC-8321, Tosoh, Tokyo, Japan, Colum: TSKgel, Shodex, Tokyo, Japan) was carried out at 140 °C to determine the molecular weight distributions of obtained hPP. About 4.0 mg of hPP sample and ODCB with BHT were placed into a vial bottle with a Teflon cap. The vial bottle was inserted to a block heater, setting the temperature at 140 °C, and stirred time to time until the mixture became a homogenous clear solution.

3.3. Bulk Polymerization of Propylene

To 2000 mL volume stainless steel auto clave, 20 mL of n-heptane, 1.32 mmol of triethyl aluminum, and 0.132 mmol of silane compound as the external donor, and the catalyst as 0.00264 mmol of Ti were charged. Liquid propylene (1.0 L) and H₂ (1.5 NL) were fed to the reactor. After 5 min of pre-polymerization at 20 °C, the temperature rose quickly to the polymerization temperature. Polymerization reaction was performed for 1 h. The polymerization was terminated by cooling the temperature to room temperature and purging of propylene gas. The produced polypropylene powder was collected from the reactor.

3.4. Production of Impact Copolymer Polypropylene (ICP-PP)

To 2000 mL volume stainless steel auto clave, 20 mL of n-heptane, 1.32 mmol of triethyl aluminum, and 0.132 mmol of silane compound as the external donor, and the catalyst as 0.00264 mmol of Ti were charged. Liquid propylene (1.0 L) and H₂ (1.5 NL) were fed to the reactor. After 5 min of pre-polymerization at 20 °C the temperature rose quickly to the polymerization temperature. Polymerization reaction was performed at 65 °C for 45 min. After the completion of polymerization, propylene gas was purged while the temperature of the reactor was lowered to room temperature. Then, the total weight of autoclave was measured, and the amount of the polymer obtained was determined from the difference between the total weight and a weight weighted in advance before the start of polymerization. A portion of the polymer was sampled for MFR measurement under nitrogen. A monomer supply line and the like were connected again to the autoclave, and ethylene, propylene, and hydrogen were added at an C₂H₄/C₃H₆/H₂ molar ratio of 1.7/2.3/0.086 to the reactor with a stirrer, which was then warmed to 70 °C. While ethylene, propylene, and hydrogen were introduced thereto at an C₂H₄/C₃H₆/H₂ ratio of 1.7/2.3/0.086 in terms of L/min. Copolymerization reaction was performed under conditions of 1.2 MPa, 70 °C and 60 min to obtain impact copolymer (ICP).

4. Conclusions

We have carried out propylene polymerization experiments in the presence of ZN catalyst with U-donor as an external electron donor with various hydrogen concentrations and the results were compared with C-donor. The U-donor-based PP polymers show high hydrogen response with high stereoregularity as compared with C-donor, which are an industrially important parameter for PP production. However, PP-polymer yield is lower for U-donor than using C-donor. The external electron donor screening experiments were carried out using various triethoxyalkylsilane compounds (1–7) against U-donor. The catalyst activity and hydrogen response including stereoregularity (pentad isotacticity, mmmm) were high for U-donor-based PP-polymers as compared with triethoxyalkylsilane compounds (1–7).

The polymerization screening experiments were carried out using binary donors (U + D) keeping MFR around 35 g/10 min. The target MFR (~35 g/10 min) could be achieved with very low hydrogen using U-donor (run 15). However, the catalyst activity was low as compared with using D-donor with the same stereoregularity (run16). In addition, in the binary donor system (combination of U and D) the catalyst activity and stereoregularity improve significantly (run 14) with moderate molecular weight distribution ($M_w/M_n = 5.9$).

The propylene polymerization using T01 donor show a very high hydrogen response as compared with U-donor. However, under the same Si/Ti ratio low stereoregularity was observed for T01 donor as compared with U-donor. On the other hand, with an increased amount of Si/Ti ratio the stereoregularity improves significantly and keeps high hydrogen response intact.

The impact copolymerization experiments were carried out using U, T01, and C donors in the presence of ZN catalyst and their effect on introducing methanol as an additive. The introduction of methanol as an additive copolymerization activity, block ratio, and EPR content improved significantly for U-donor. In case of T01 donor polymerization, block ratio and EPR content decreased including homo polymerization activity. However, as such using T01 donor very high copolymerization performance was observed. In addition, in the case of C-donor no methanol effect was observed.

In conclusion, both U and T01 donors show polypropylene special applications as compared with conventional external donors (C and D). Especially, using U-donor high MFR grade homo PP, such as fiber grade applications, was achieved. The U-donor can be useful for producing ICP-PP having high MFR and high stiffness with low to medium EPR contents. On the other hand, T01 donor can be suitable for producing high MFR and high EPR such as RTPO (reactor made thermoplastic polyolefin) grade applications.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal12080864/s1>. Figure S1: Molecular weight distribution of homo-PP (run 13–17). Figure S2: NMR Spectrum of homo-PP (run 2). Figure S3: NMR Spectrum of homo-PP (run 6). Figure S4: NMR Spectrum of homo-PP (run 7). Figure S5: NMR Spectrum of homo-PP (run 8). Figure S6: NMR Spectrum of homo-PP (run 9). Figure S7: NMR Spectrum of homo-PP (run 10). Figure S8: NMR Spectrum of homo-PP (run 11). Figure S9: NMR Spectrum of homo-PP (run 12). Table S1: IR analysis results of impact copolymer PP (ICP-PP) C2 content present in ethylene propylene rubber (EPR) run 20–25).

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