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ORIGINAL PAPER

Preparation of ultra high molecular weight polyethylene with $MgCl_2/TiCl_4$ catalyst: effect of internal and external donor on molecular weight and molecular weight distribution

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Abstract Ultra high molecular weight polyethylene (UHMWPE) was prepared by using $MgCl_2$-supported $TiCl_4$ catalyst in conjunction with triethylaluminium (TEA) cocatalyst. The effects of internal and external donor on polydispersity index (PDI) of UHMWPE were investigated. The catalyst activity with various kinds of internal donor decreased in the following order: none > succinate > phthalate > diether, while the catalyst activity was less influenced by the structure of external donor. The PDI of UHMWPE was examined by using gel permeation chromatography (GPC) analysis and/or rheometry measurements. The PDI obtained by rheometer was matched with the results obtained by GPC within an error of max. 20%. The highest molecular weight and PDI of UHMWPE were obtained by the catalyst of succinate as internal donor. It was also observed that the molecular weight and PDI of UHMWPE were less affected by the introduction of external donor.

Keywords UHMWPE · Internal donor · External donor · Molecular weight distribution

Introduction

Ultra high molecular weight polyethylene (UHMWPE) was a class of linear polyethylene (PE) with a molecular weight numbering in the millions and was also known as high modulus PE or high performance PE [1]. UHMWPE have wide applications, such as bearings, pulleys, lining of trucks or dock guards, furthermore,

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used in biomedical applications [2–5]. The widely application of UHMWPE depended on the considerable mechanical properties of this material: high strength, low creep, low friction coefficient, low abrasion, reduced wear, and good corrosion resistance to fatigue [6–8].

As reported by Kashiwa [9], more than 50% world production of PE was produced by $MgCl_2$-supported Ti-based catalyst. With respect to $MgCl_2$-supported Ti-based catalysts, various kinds of Lewis bases were used as internal donor at catalyst systems and also external donor in the polymerization system [10]. During polymerization, internal donor was removed from catalyst due to complex formation with the alkyl-aluminium cocatalyst, so that external donor was needed to supply for high isotacticity [11]. It was also observed that electro donor (internal and external donor) has a large effect not only on the isospecificity but also on the catalyst activity, molecular weight, and molecular weight distribution for α-olefin polymerization [12, 13]. As reported by Proto [14], the catalyst activity was reduced by the introduction of external donor for propylene polymerization, while the isospecity, molecular weight, and polydispersity index (PDI) were improved significantly. The effect of external donor structure on propylene polymerization with $MgCl_2$-supported $TiCl_4$ catalyst has been studied intensively by many researchers [14–16]. However, the effect of electron donor on ethylene polymerization was less mentioned in the literature.

The aim of the present work was to study the effects of internal and external donor on catalyst activity, thermal property, molecular weight, and molecular weight distribution of UHMWPE produced using $MgCl_2$-supported Ti-based catalyst system.

Experimental

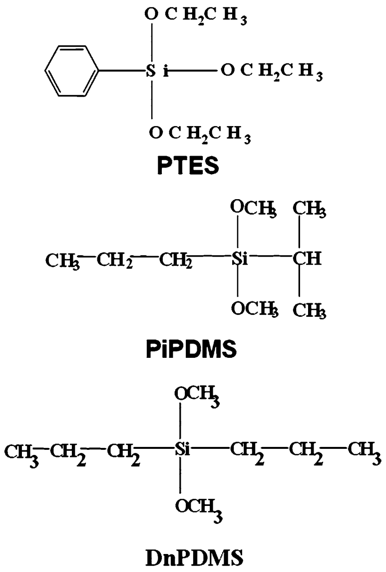
Materials

The $MgCl_2$-supported Ti-based catalyst (Cat A-D), triethylaluminium (TEA) (1.0 M solution in *n*-hexane), and external donor (Phenyltriethoxysilane (PTES), propyl-*i*-propyldimethoxysilane (PiPDMS), di-*n*-propyldimethoxysilane (DnPDMS)) were provided by Korea Petrochemical Ind. Co., Ltd., Korea. The catalyst contents were given in Table 1 and the structure of external donor were shown in Scheme 1. *n*-Hexane was distilled from sodium/benzophenone under nitrogen prior to use.

Table 1 Catalyst composition

	Internal donor	Ti content (wt%)
Cat-A	None	6.0
Cat-B	Di-*n*-butyl-phthalate	1.8
Cat-C	Di-*sec*-butyl-succinate	2.7
Cat-D	1,3-Diether	3.8

Scheme 1 Structure of external donor



Polymerization procedure

The polymerization was carried out in a 300 mL glass reactor equipped with a magnetic stirring bar. The reactor was back-filled three times with nitrogen and charged with the required amount of *n*-hexane. At the stipulated temperature of 40 °C the reaction solution was vigorously stirred under 1 atm of ethylene for the desired period of time after which the cocatalyst (TEA) was added to the reactor. After cocatalyst was added, the external donor and a catalyst solution were injected, respectively, and then the polymerization started with a continuous feed of ethylene. The polymerization temperature was controlled using a water bath. After 2 h, the polymerization was terminated by adding 10% HCl–methanol solution and then the mixture was poured into 500 mL of methanol to precipitate the polymer and followed by drying under vacuum at 60 °C to its constant weight. Based on the weight of the obtained polymer, the catalyst activity (kg polymer/mol Ti h) was estimated.

Polymer characterization

The melting temperature (T_m) and crystallinity (X_c) were determined by differential scanning calorimetry (DSC, DuPont TA 4000, TA Instruments) operating at a heating rate of 10 °C/min. The obtained polymers were cooled down from melt (200 °C) to 30 °C at a rate of 10 °C/min, and the T_m and heat of fusion (ΔH) were determined in the second scan. The X_c calculated with 100% crystalline PE ($\Delta H = 293$ J/g) [17].

The viscosity average molecular weight (M_v) of the polymer was measured in decalin at 135 °C according to the literature [18]. The M_v was calculated according to the following formula;

$$M_v = 5.34 \times 10^4 [\eta]^{1.49}$$

gel permeation chromatography (GPC) measurement was conducted on a PL-220 (Polymer Laboratories) equipped with a refractive-index detector at 135 °C, using 1,2,4-trichlorobenzene as solvent.

Dynamic rheometry measurements were made on a Haake Mars rheometer at 260 °C in parallel plate geometry. Disks (1.0 mm thick, 20 mm diameter) were compression molded at 220 °C, approximately 1000 psi. Dynamic melt rheological properties were obtained from a frequency-sweep test within 0.1–300 rad/s under nitrogen atmosphere to reduce the oxidative degradation. The PDI value of obtained UHMWPE was calculated from rheometry measurements of polymer melts [19, 20].

Results and discussion

Effect of internal donor

The polymerization of ethylene was carried out by using four types of catalysts and their mixtures as containing different internal donor, to investigate the effect of internal donor on molecular weight and molecular weight distribution. The experimental results were given in Table 2.

With regards to the polymerization among the experimental results, Cat-A without internal donor has the highest catalyst activity as well known. The catalyst activity decreased with the incorporation of electron donor at catalyst systems, due to the poisoning of the non-stereospecific active sites [21–23]. The catalyst activity of Cat-C with succinate as internal donor was higher than that of Cat-B with phthalate or Cat-D with diether as internal donor. The activity of catalyst with

Table 2 Effect of internal donor on ethylene polymerization

Catalyst	Activity	T_m (°C)	X_c (%)	M_v[a]	M_w[a]	PDI (GPC)	PDI (Rheometer)
Cat-A	8.1	131.7	45.3	1.3	2.1	4.4	4.4
Cat-B	4.1	131.4	46.6	2.4	3.2	7.1	6.2
Cat-C	6.3	130.8	46.3	3.7	4.2	7.6	8.1
Cat-D	2.1	131.6	45.6	2.0	3.1	6.7	5.6
Cat-A + Cat-B[b]	5.6	130.3	46.5	2.2	2.6	5.4	4.6
Cat-A + Cat-C[b]	6.8	129.2	45.7	2.9	–	–	5.7
Cat-A + Cat-D[b]	4.7	131.5	44.0	2.4	–	–	4.5
Cat-B + Cat-C[b]	4.8	129.4	44.5	3.6	–	–	9.1
Cat-B + Cat-D[b]	2.6	130.0	44.4	2.5	–	–	8.4
Cat-C + Cat-D[b]	3.2	129.9	44.7	3.4	–	–	8.8

Polymerization condition: [Ti] = 1.2×10^{-4} mol/L, [Al]/[Ti] = 400, atmosphere pressure, 40 °C, 2 h

Activity: kg polymer/(g Ti h)

[a] $\times 10^{-6}$ g/mol

[b] Cat-1:Cat-2 = 1:1(mol:mol)

different internal donor decreases in the following order: none > succinate > phthalate > diether. In addition, the effect of catalyst mixtures on ethylene polymerization was examined. It was seen that the catalyst activity of catalyst mixtures had influenced between the lower activities of catalyst.

The T_m and X_c of UHMWPE were determined by DSC. It was found that the T_m and X_c of UHMWPE were less affected by the internal donor of catalyst. The T_m of UHMWPE was in the range from 129.2 to 131.7 °C and X_c was in the range from 44.0 to 46.6%.

The dilute solution viscometry was performed for the viscosity average molecular weight (M_v) measurement. As given in Table 2, the internal donor of $MgCl_2$-supported $TiCl_4$ catalyst has a marked effect on M_v of obtained UHMWPE. The M_v of UHMWPE obtained by polymerization with an internal donor was three times higher than polymerization without internal donor. This phenomenon may be ascribed to the active center for producing low molecular weight polymer was destroyed by the internal donor and/or the decreased chain transfer reaction to TEA due to the complex formation of TEA and internal donor [16]. The M_v of higher than 1.0×10^6 g/mol was obtained in the whole range of this study. The highest M_v (3.7×10^6 g/mol) of UHMWPE was obtained with Cat-C in presence of succinate as internal donor and the lowest M_v (1.3×10^6 g/mol) was obtained with Cat-A in the absence of internal donor. And the M_v of UHMWPE decreases in the following order: succinate > phthalate > diether > none.

It was very difficult to obtain the PDI value of UHMWPE by GPC, the molecular weight distribution of UHMWPE was analyzed through GPC analysis and/or rheometry measurements in this study. The effect of internal donor on molecular weight distribution of the obtained UHMWPE was given in Table 2 and the GPC curve was shown in Fig. 1.

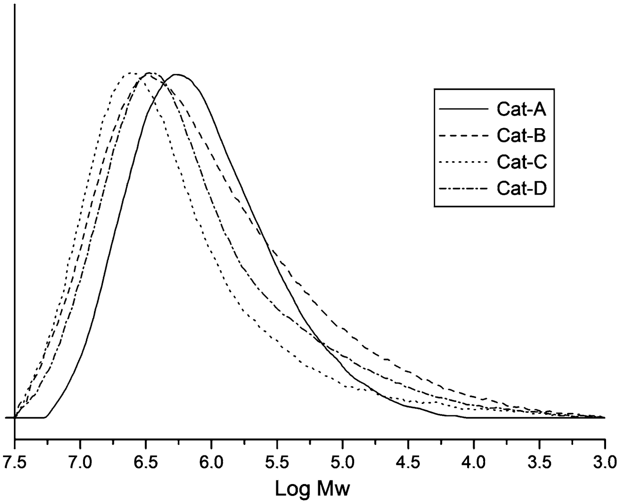


Fig. 1 GPC curves of UHMWPE obtained by Cat-A, Cat-B, Cat-C, and Cat-D

The GPC curve of Cat-A to Cat-D were unimodal and the curve peak was in the order of Cat-C > Cat-B ≈ Cat-D > Cat-A relate to the decreasing order of molecular weight. However, the log M_w was less than 7.5 due to the limit of the GPC analysis. As can be seen in Table 2, the PDI values of UHMWPE obtained by rheometer were matched with the results obtained by GPC within an error of max. 20%. The molecular weight distribution of UHMWPE obtained by catalyst containing internal donor was broader than that obtained without internal donor. The results could correspond to the catalyst with an internal donor have more activity site than the internal donor free catalyst for ethylene polymerization with common $MgCl_2$-supported $TiCl_4$ catalyst system. The PDI value of UHMWPE decreases in the following order: succinate > phthalate > diether > none. With regards to the polymerization with catalyst mixture, the highest PDI value was obtained by Cat-B and Cat-C mixture system. Additionally, the PDI value was improved by the introduction of second catalyst except Cat-A. The increase of PDI value could be explained by the mix of two catalyst's activity site lead to produce more dispersed molecular weight polymer. However, the PDI value of UHMWPE obtained by polymerization with Cat-A mixed with the second catalyst was dependent on highly active catalyst. The results could be due to the higher activity of Cat-A lead to produce more polymers in the catalyst mixture system. It was showed that PDI of obtained UHMWPE could be controlled from 4.4 to 9.1 by changing the internal donor of catalyst and/or their mixtures.

Effect of external donor

External donor plays a fundamental role in modern Ziegler–Natta catalyst systems for olefin polymerization [11, 16]. During polymerization, internal donor was removed from catalyst due to complex formation with the alkyl-aluminium cocatalyst, so that external donor was to supply for high isotacticity [10]. Even if the main function of external donor was to control the catalyst stereospecificity, it was well known that external donor strongly affect the catalyst activity, molecular weight, and the molecular weight distribution of the polyolefins [12, 13]. However, the effect of external donor on ethylene polymerization was less mentioned previously. The polymerization of ethylene was carried out with $MgCl_2$-supported $TiCl_4$ catalyst in the presence and absence of external donor. The polymerization behavior was examined for various kinds of external donor such as PTES, PiPDMS, and DnPDMS. The effect of external donor on ethylene polymerization was given in Table 3.

There was no doubt that silane compounds used as external donors function as deactivators of active sites in propylene polymerization [21, 24]. There exist two types of active Ti^{3+} species at $MgCl_2$-supported $TiCl_4$ catalysts, one having two Cl vacancies and the other having only one Cl vacancy and that external donor selectively block one of the former vacancies. And then, the decrease of catalyst activity could be explained in terms of the poison of catalyst active site (Ti^{3+} species having two Cl vacancies) by the introduction of external donor in propylene polymerization [25]. However, the catalyst activity was almost the same with

Table 3 Effect of external donor on ethylene polymerization

Catalyst	External donor	Activity	T_m (°C)	X_c (%)	M_v[a]	PDI
Cat-A	None	8.1	131.7	45.3	1.3	4.4
	PTES	7.5	130.7	48.5	1.4	4.9
	PiPDMS	6.5	130.4	46.2	1.5	5.4
	DnPDMS	7.4	130.4	48.6	1.4	4.4
Cat-B	None	4.1	131.4	46.6	2.4	6.2
	PTES	3.7	130.9	51.2	2.0	–
	PiPDMS	4.0	131.1	50.1	2.4	–
	DnPDMS	3.9	131.2	51.4	2.0	–
Cat-C	None	6.3	130.8	46.3	3.7	8.1
	PTES	6.1	129.0	50.2	3.7	8.1
	PiPDMS	5.7	131.7	47.3	3.2	8.2
	DnPDMS	5.5	131.0	50.2	3.2	7.8
Cat-D	None	2.1	131.6	45.6	2.0	5.6
	PTES	2.1	131.9	46.7	1.7	–
	PiPDMS	2.0	131.6	49.8	1.7	–
	DnPDMS	1.9	131.7	50.8	1.7	–

Polymerization Condition: [Ti] = 1.2×10^{-4} mol/L, [Al]/[Ti] = 400, [external donor]/[Al] = 0.1, atmosphere pressure, 40 °C, 2 h

Activity: kg polymer/(g Ti h)

[a] $\times 10^{-6}$ g/mol

external donor. It was ascribed that the external donor was less affected on catalyst activity for ethylene polymerization.

The T_m and X_c of UHMWPE were determined by DSC and the results were also given in Table 3. It was found that the T_m of UHMWPE was less affected by the structure of external donor, while the X_c was slightly improved by introduction of external donor. The T_m of UHMWPE was in the range from 129.0 to 131.9 °C and X_c of UHMWPE was in the range from 45.3 to 51.4%.

As can be seen in Table 3, the external donor less affected the M_v of the obtained UHMWPE, although some fluctuations could be observed. The highest M_v (3.7×10^6 g/mol) of UHMWPE was obtained with Cat-C in the presence of PTES as external donor and the lowest M_v (1.3×10^6 g/mol) was obtained with Cat-A in the absence of electron donor.

The effect of external donor on molecular weight distribution of the obtained UHMWPE were carried out by using dynamic measurements for polymerization with Cat-A, Cat-C in the presence and absence of external donor. The PDI value was less influenced by the addition of the external donor, although some fluctuation could be observed. In addition, the PDI value of UHMWPE obtained by Cat-C was larger than that obtained without electron donor, significantly. It was showed that PDI value of obtained UHMWPE was around 5.0 for Cat-A and 8.0 for Cat-B by changing the structure of external donor.

Conclusions

The UHMWPE had prepared by commercial $MgCl_2$-supported Ti-based catalyst activated by TEA cocatalyst. The catalyst activity decreased with the introduction of internal donor at catalyst systems, while the T_m and X_c of obtained UHMWPE were less changed. The molecular weight and PDI value of UHMWPE obtained by catalyst with different internal donor decreased in the following order: succinate > phthalate > diether > none. As regards the catalyst mixture system, the PDI value was improved by the catalyst mixtures. However, the catalyst activity and molecular weight, as well as PDI value of UHMWPE were less affected by the introduction of external donor. The T_m was not changed with the addition of external donor, while the X_c was improved slightly. It was shown that by carefully selection of internal donor and their mixture or structure of external donor in Ziegler–Natta catalyst system for ethylene polymerization, both the molecular weight and PDI value could be controlled. The M_v could be controlled from 1.3×10^6 to 3.7×10^6 g/mol and the PDI was in the range from 4.4 to 9.1.

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