Sixth-generation of ziegler-natta catalyst for homopolymer polypropylene polymerization: Effect to product properties and regulation

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Abstract. The development of catalysts for polypropylene (PP) polymerization has begun since Ziegler-Natta (Z-N) discovered the catalyst for polyethylene polymerization. However, the first-generation catalyst which was a combination of TiCl3-AlEt2Cl (catalyst-co-catalyst) has low productivity and isotacticity. The modifications continue to be made to increase the productivity and isotacticity by combining the Z-N catalyst with MgCl2, internal donors, and external donors. The fourth-generation Z-N catalyst, TiCl3/Phthalate/MgCl2–AlEt3/Silane, has given satisfactory results with high productivity and isotacticity. Another concern arose when phthalate derivatives turned out to be able to initiate cancer formation. This problem has led catalyst development to the sixth-generation Z-N catalyst with a phthalate-free internal donor. This research intends to study the effects of sixth-generation catalysts to polypropylene properties when compared to the fourth-generation catalysts. We produced homopolymer polypropylene (HPP) by fourth- and sixth-generation of Z-N catalyst with the same polymerization technology. Then, the effects on product properties, namely melt flow rate (MFR), xylene soluble, residual catalyst, physical properties, optical properties, and rheological properties were observed. Sixth-generation catalyst exhibited a better stereoregularity and it made a better flexural modulus. The rheological properties showed the sixth-generation catalyst products have lower molecular weight and it generates fewer gels and lower impact strength. Sixth-generation catalyst also exhibited lower catalyst residue which allows lower dosage of an acid scavenger with comparable color performance. With increasingly strict restrictions on the use of phthalates, the sixth-generation catalyst is more convenient to use. In terms of the effect on the polypropylene properties, fourth- and sixth-generation catalysts have their respective advantages.

Keywords: PP Homopolymer, fourth-generation Z-N, sixth-generation Z-N, phthalate

1. Introduction
Polypropylene polymerization has evolved from the past few decades. It started by using the first-generation Z-N catalyst, the catalyst/co-catalyst system, TiCl3/Al(C2H5)3. This first-generation catalyst is only able to achieve the productivity of 0.8–1.2 kgPP/gCat and isotacticity index of 90–94 % (polymerization in hexane slurry, no data for bulk polymerization) [1]. The second-generation was developed by Solvay where the TiCl3 catalyst enhancements involved the reduction of TiCl3 using diethyl aluminum chloride and followed by ether treatment to remove triethyl aluminum and TiCl3 treatment to change the β-TiCl3 to δ-TiCl3 [2]. Solvay claims that his method can produce catalysts with spherical shape and narrow particle size distribution (PSD) resulting in a microporous sponge-like...
structure. The performance of this catalyst can achieve the productivity of 10–15 kgPP/gCat and isotacticity 94–97% (in bulk polymerization) [1]. Therefore, this second-generation catalyst can be called a porous TiCl3–DEAC system.

In terms of increasing the productivity of the Z-N catalyst for polypropylene polymerization, it was found that MgCl2 supported catalyst gave a higher productivity [3, 4]. However, this catalyst has a low stereospecificity (isotacticity < 50%) [1]. Answering the problem, Lewis bases were introduced in this catalyst system with the TiCl4, MgCl2, and Lewis base. Lewis base usually has one or more oxygen atoms that can donate a pair of free electrons to the Mg atom in MgCl2. The donors will eventually be bound to the surface of MgCl2 and increase the steric environment so that propylene can only enter on certain sides of the Ti atom [5, 6]. These Lewis bases are differentiated as first Lewis base which is put together with the catalyst, so it is called internal donor (Di). The second Lewis base is added separately and called external donor (De). Ziegler-Natta catalyst systems and its performances are presented in table 1.

Research on the comparison of productivity and stereospecificity of various generations of Ziegler-Natta catalysts has been carried out [1, 7-9]. However, the effect of these catalyst types on polypropylene properties has not been much studied. Therefore, this research focuses on comparing the effect of fourth- and sixth-generation catalysts on polypropylene product.

The consideration of the use of a sixth-generation catalyst began after it was discovered that a phthalate derivative in a fourth-generation catalyst system could initiate breast cancer [10]. The restriction on the use of phthalates has been carried out in the European region with the inclusion of 6 phthalate derivative compounds in the REACH Annex XVII restricted substances list. The compounds in question include Bis (2-Ethylhexyl) phthalate (DEHP), Dibutyl phthalate (DBP), Benzyl butyl phthalate (BBP), Di-isononyl phthalate (DINP), Di-isodecyl phthalate (DIDP), and Di-n-octyl phthalate (DNOP). On 4 June 2015, EU RoHS2 (Directive 2011/65/EU) was also revised by the publication of new Directive (EU) 2105/863 to add 4 phthalate-derived compounds including DEHP, BBP, DBP, and DIBP. In the EU RoHS2 document, all phthalate derivatives that have been mentioned are limited to less than 0.1% and this prohibition is effective from 22 July 2019 for all electrical and electronic equipment irrespectively from Category 8 and Category 9 [11].

2. Experimental

All experiments have been carried out using homopolymer polypropylene MFR 2, 3, 7, 8 and 10 for biaxially oriented polypropylene (BOPP), thermoforming, yarn, cast film, tubular quenching film, and injection molding application produced by PT Chandra Asri Petrochemical. All the products were produced by two types of catalyst, fourth-generation of Z-N catalyst and sixth-generation of Z-N catalyst with the same reactor and polymerization process (gas phase polymerization).

| Table 1. Ziegler-Natta catalyst composition and performance in different generations. |
|---------------------------------|--------------------------|----------------|-----------------|
| Generation                     | Composition              | Productivity<sup>11</sup> (kgPP/g Cat) | Isotacticity index<sup>11</sup> (%) |
| 1<sup>st</sup> Gen.            | TiCl3 + Al(C2H5)2        | N/A            | 90–94           |
| 2<sup>nd</sup> Gen.            | Porous TiCl3 + Al(C2H5)3 | 10–15          | 94–97           |
| 3<sup>rd</sup> Gen.            | TiCl4/EB/MgCl2 + Al(C2H5)3/MPT | 15–30          | 90–95           |
| 4<sup>th</sup> Gen.            | TiCl4/Phthalate/MgCl2 + Al(C2H5)3/Silane | 30–60          | 95–99           |
| 5<sup>th</sup> Gen.            | TiCl4/Dieter/MgCl2 + Al(C2H5)3 | 70–120         | 95–99           |
| 6<sup>th</sup> Gen.            | TiCl4/p-Ethoxy Ester/MgCl2 + Al(C2H5)3/Dexe | N/A            | N/A             |
2.1. Rheological analysis

The rheological analysis was conducted to see the flow behavior of polymer produced by fourth-generation and sixth-generation of Z-N catalyst. The flow behavior was used as an approach to compare the molecular weight of polymers [12]. It was performed in a twin-bore capillary rheometer (Bagley correction) using die with L/D 16 at temperature 230 °C with total of 9 min of preheating time. The method is in accordance with ASTM D3835. The result was shown as shear viscosity (Pa.s) of polymer melt [13].

2.2. Melt flow rate analysis

Melt flow analysis was performed using an extrusion plastometer according to ASTM D1238. The temperature was set at 230 °C and used a load of 2.16 kg. After the temperature was stable, 4 g of polypropylene pellets were filled into the bore and testing was started after preheating time has been completed (7 ± 0.5 min). The result was shown as the weight of the polymer in grams per 10 min (g/10 min).

2.3. Xylene soluble

Xylene soluble is a method to determine the number of atactic in the polypropylene matrix. The analysis was carried out using NMR equipment because it is more convenience compared to the reflux method in terms of time and steps [14]. Pellet samples were filled into the NMR tube (maximum until 2 cm from the top) and then it was placed into the NMR [14].

2.4. Fines

The analysis was conducted using a sieve shaker apparatus with 125 μ sieve. Polymer resins were weighed and then placed in sieve shaker. The result was shown in % weight.

2.5. Colorimeter

Polypropylene pellet color was rated as Yellowness Index (YI). This parameter was measured by Colorimeter equipment following ASTM D6290. Polypropylene pellet was filled into the transparent sample cup and placed on the scanning area of the instrument [15]. The cup must be covered with a black cap to minimize interference from outside light.

2.6. Gels performance

Gel counting analysis was intended for film grade application following ASTM D3351. It included cast film and inflated film. Before conducting the gel counting, polymer samples were converted to film using a cast film machine (± 40 μm thickness) or tubular quenching machine (± 25 μm thickness). The area of the film being analyzed was 4 × 4 in. with 5 repetitions. The film sample was then placed on the OHP with a 5 times magnification [16]. Gels were categorized as large if it was larger than 4 mm and small if it was between 2–4 mm.

2.7. Catalyst metal residue

The residue of the metal compound of catalyst (Ti) can be measured quantitatively by X-ray fluorescence (XRF) [17]. Polypropylene plaque was prepared by hot press molding using a mold with a thickness of 3 mm and a diameter of 40 mm. The hot press temperature was set at 230 °C.

2.8. Physical properties

Physical properties are included in flexural modulus and Izod impact performance. The test was conducted according to ASTM D790 for flexural modulus and ASTM D256 for Izod impact strength [18]. Polypropylene pellets were first formed into plaques (type I) using injection molding. The plaques were then conditioned according to ASTM D618.

2.9. Film optical properties

Film optical properties are included haze, gloss, and clarity each of which following ASTM D1003, D2457 and D1746. All those ASTM standards are applicable for plastics film and sheet. The method
has also been done by Oas for haze, clarity, and gloss analysis of polypropylene bottle samples. Before optical analysis was conducted, fabricated films must first be conditioned at a temperature of 23 ± 2 °C and a humidity of 50 ± 5 %RH for a minimum of 40 h. The films were then made into a specimen 50 mm × 50 mm.

3. Results and discussion

Figure 1a shows the comparison of xylene soluble between polypropylene produced with the fourth-generation of Z-N catalyst and those produced using the sixth-generation Z-N catalyst in several MFR ranges. In all MFR ranges, the sixth-generation shows comparable results towards the fourth-generation even with less catalyst consumption (less internal donor consumption). It means that for the same amount of catalyst consumption, the sixth-generation gives lower xylene soluble values (more isotactic). This also proves that the internal donor of sixth-generation catalysts can match the performance of phthalate [8]. When comparing the external donor consumption, the sixth-generation can save more than 50 % by weight.

Xylene soluble describes the atactic content in polymers. The higher the atactic content, the lower the isotacticity of the polymer. Stereoregularity is very closely related to the physical properties of polypropylene, especially flexural modulus which describes the rigidity of the final product [19]. Figure 1b shows the relationship between xylene soluble and flexural modulus in several grades of PP. As xylene soluble increases, the flexural modulus decreases. This happens to both products produced by fourth-generation and sixth-generation catalysts. The interesting thing is, significantly, the sixth-generation products have a flexural modulus that is higher than the fourth-generation consistently at all grades.

On the contrary to flexural modulus, the impact properties are more influenced by molecular weight [20]. The smaller molecular weight causes the impact strength decreases [18]. The impact energy not only causes deformation/strain but the required energy to cause a fracture. The intermolecular force of the polymer is not enough to hold this energy so that intramolecular interactions are more dominant in this case. The longer the molecular chain (high molecular weight), the higher the intramolecular interactions within it so that the impact strength is greater [21]. On the contrary to low molecular weight polymers with more intermolecular interactions exhibits lower impact strength.

![Figure 1](image-url)

**Figure 1.** Analysis result for several PP grades, (a) Xylene soluble (% atactic) as a function of MFR, and (b) Flexural modulus as a function of XS.
In figure 2 HPP MFR 10 has lower shear viscosity (less viscous) which means it has lower molecular weight [12]. This proves that with increasing MFR the molecular weight will decrease. This happens during the polymerization process, precisely in the hydrogen termination process. High MFR can be achieved with more hydrogen feeds, meaning that the termination process is more numerous and results in shorter polymer chains (lower molecular weight) [22]. Another fact, in both MFRs, the products produced by the sixth-generation catalyst always have lower viscosity. It means that at the same MFR, the sixth-generation catalyst produces a lower molecular weight.

The relationship between Izod impact and MFR can be seen in figure 3a. In general, the impact strength decreases with the increasing MFR. The data also show that HPP grades produced by sixth-generation catalysts have a lower impact strength than those produced from the fourth-generation catalysts due to lower molecular weight and this is consistent with the results discussed in Kirk-Othmer encyclopedia of Chemical Technology [8]. These characteristics apply to all MFR ranges.

![Figure 2. Rheological analysis (shear viscosity) of HPP MFR 3 and MFR 10.](image1)

![Figure 3. Analysis result for several PP grades. (a) Izod impact strength as a function of MFR, and (b) Fines content of resin as a function of MFR.](image2)
Low molecular weight also affects the physical form of polymer resins as shown in figure 3b. Low molecular weight polymer will act as plasticizer and soften the polymer material [23]. The content of fines increases with the increasing MFR due to lower molecular weight. As well as the performance of two different catalysts where the sixth-generation catalysts produce more fines in polymer resins compared to the fourth-generation catalysts.

Polypropylene pellets contain metal residues such as calcium from additives, aluminum from co-catalyst, titanium and magnesium from the catalyst, and other metals from impurities. The metal content can be detected quantitatively by XRF. Metal residue analysis is focused on catalyst residue, Ti, because of its contribution to the polypropylene oxidation process. The results will be displayed in percent by weight of Ti in polypropylene samples. The results of a quantitative XRF analysis of several HPP samples are shown in figure 4a. As the productivity of the sixth-generation catalyst is much higher, this leaves less catalyst residue in the polymer. Catalyst residues (metal compounds) can accelerate the initiation of the oxidation process [25]. One of the parameters that indicates the oxidation in a polymer is discoloration (generally becomes yellowish). In order to neutralize the catalyst residue in the polymer, acid neutralizer/acid scavenger is added which in this case can be from the metal-soap group (calcium stearate, zinc stearate, etc.), metal oxide (CaO, ZnO, etc.), or hydrotalcite compounds [24]. Low catalyst residue can be a reason to reduce the dosage of acid scavenger to reduce costs. In figure 4b, the sixth-generation catalyst product has a typical color similar to a fourth-generation product with a note that the dosage of acid scavenger is lower.

In the case of film properties, especially the clarity and gloss performance, they do not show differences as shown in table 2. However, in gel count properties, the sixth-generation catalyst product shows a better performance than the fourth-generation catalyst. This is related to the molecular weight.
of the polymer produced. Gels have visual defects and it can be caused by higher-molecular-weight material or contamination [25]. Since sixth-generation catalyst produces lower molecular weight polymer, it can reduce the probability of gel phenomenon.

4. Conclusion
Sixth-generation Z-N catalyst gives a better performance in terms of productivity and stereoregularity. Higher polymer’s isotacticity of sixth-generation Z-N catalyst affects physical properties, especially flexural modulus (stiffness). While other physical properties, in this case, the impact strength, are not directly related to stereoregularity. Izod impact is more influenced by the weight of the molecule polymer. From the rheology approach, the sixth-generation catalysts produce polymers with lower molecular weight compared to fourth-generation and it affects to smaller Izod impact of HPP grades. The different catalyst shows an insignificant correlation to clarity and gloss performance but it highly affects the gel performance. Sixth-generation Z-N catalyst shows a better gel performance in terms of lower molecular weight polymer. Higher productivity of sixth-generation Z-N catalyst also affects to the lower metal residue (Ti) so the acid scavenger dosage can be adjusted to lower value with comparable color performance. Thus, with increasingly strict restrictions on the use of phthalates, the sixth-generation catalysts are more convenient to use. In terms of performance, fourth- and sixth-generation catalysts have their respective advantages.

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