Novel polyolefin-supported Ziegler catalysts system for olefin polymerization

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Abstract

Chapter 1: General Introduction

In world production of synthetic materials, polyolefins hold first place (55 %) because of their specific properties, such as high chemical and mechanical resistance, easy processibility, low specific gravity, and low cost. The industrial polyolefin market is still growing, and new grades of polyolefins with high performance are eagerly awaited. Thus, much interest has been devoted to the design and synthesis of new grades of polyolefins. One of the methods to achieve the new-grade polyolefins with high performance is the synthesis of new composite materials, in which the properties of polyolefins can be improved by adding other polymers. The control of the crystalline and amorphous components in the composite is practically important both in the development of new polymers or tailor-made polyolefins and in the control of the polymer properties. Since the development of highly active supported Ziegler catalyst, a great deal of attention has been focused on the improvement of the effectiveness of the catalyst supports. Recently, the use of polymer as a support has appeared. The main aim of using the catalysts is the improvement of the catalyst abilities. In this dissertation, it was used the Ziegler catalyst on the polymer supports as a component of the crystalline or amorphous part of the new polyolefin-supported Ziegler catalyst systems. The purpose is to present properties of novel Ziegler catalyst systems, and to focus an ethylene polymerization with polyolefin-supported Ziegler catalyst. The fundamentals of the Ziegler catalyst and the history of polyolefins produced with Ziegler catalyst are presented as a general introduction in the first chapter. Chapter 2 deals with the results of ethylene polymerization including unique property of the modified-polypropylene-supported Ziegler catalyst. The next two chapters, Chapters 3 and 4 give the control of the molecular weight and molecular weight distribution using two types of polyolefin-supported Ziegler catalysts. Chapter 5 is concerned with the results of ethylene and 1-hexene copolymerization with the modified-polypropylene-supported Ziegler catalyst system. The last chapter summarizes the conclusive items of this dissertation.

From the standpoint of polyolefin industries, a part of this work relating polymerization experiments under the specific conditions has been conducted the possibilities of novel catalyst designs.

Chapter 2: Ethylene polymerization by modified-polypropylene-supported highly stable Ziegler catalyst

A modified-polypropylene-supported Ziegler catalyst was prepared using polypropylene containing a small amount of poly(7-methyl-1,6-octadiene) as a starting polymer for bromination, lithiation, and reaction with $TiCl_4$. Ti content of the catalyst measured by inductive-coupled-plasma spectrometry was 2.5 wt.-%.The polymerization of ethylene was carried out using the catalyst with triethylaluminum (TEA) in toluene at 60 ℃ up to 100 h. The yield increased linearly with the polymerization time, indicating that the active sites of the modified-polypropylene supported Ziegler catalyst are practically stable without deactivation even for 100 h.

Chapter 3: Multiplicity of molecular weight distribution of polyethylene produced with modified-polypropylene-supported Ziegler catalyst systems

The molecular weight and molecular weight distribution of polyethylene prepared with the modified-polypropylene-supported Ziegler catalyst were investigated in terms of the variation of the polymerization conditions, such as a kind of co-catalyst, its concentration, and polymerization temperature. The polymerization of ethylene was conducted with the modified-polypropylene supported Ziegler catalyst in the presence of TEA in toluene at 60 ℃. The polymerization with TEA afforded a polyethylene showing a symmetrical GPC curve with extremely broad molecular weight distribution (Mw/Mn $>$ 100). The GPC curve of a polyethylene obtained with diethylaluminum chloride showed a characteristic shape, which was comprised of an extremely sharp peak at low-molecular weight region and a broad peak with quite small intensity in the range of 10^4 to 10^7 molecular weight region. The result was completely changed by replacing the triethylaluminium into other alkylaluminiums, such as diethylaluminium chloride. It was found that polyethylenes with very broad, narrow, bimodal, and multimodal molecular weight distributions could be obtained by simply varying the co-catalyst. The molecular weight distributions of polyethylenes obtained were also very much sensitive to the difference of the co-catalyst concentration and the polymerization temperature. From the results obtained in this study, it is suggested that the modified-polypropylene-supported Ziegler catalyst can be feasible as a novel candidate for the catalyst system giving polyethylenes with controlled molecular weight distributions in the wide range of molecular weight.

Chapter 4: Polyolefin-supported soluble titanium based Ziegler catalyst for the production of polyethylene with narrow molecular weight distribution

A novel polyolefin-supported homogeneous Ziegler catalyst prepared from ethylene-

propylene-diene monomer elastomer (EPDM) was successfully developed for the production of polyethylene with narrow molecular weight distribution. EPDM-supported Ziegler catalyst was prepared from polypropylene containing a small amount of poly(ethylene-*co*-propylene-*co*-1,4-hexadiene) by bromination, lithiation, and reaction with $TiCl_4$. Ti contents of the catalyst measured by inductive-coupled-plasma spectrometry was 0.38 wt.-%. Ethylene polymerization with the EPDM-supported catalyst was investigated in terms of the stability of the active sites on the catalyst and variation of molecular weight distribution arising from the change of co-catalyst. Activity of the catalyst was practically stable without deactivation at 60 ℃ for 25 h, regardless of the kinds of the co-catalyst and the polyolefin support. Whereas, the variation of molecular weight distribution of polyethylene arising from the change of co-catalyst was found to be affected by the properties of the support. High molecular weight polyethylene having narrow molecular weight distribution (Mw/Mn = 2.2), was obtained by the EPDM-supported catalyst with triethylaluminium at appropriate conditions. The extraction experiment of the resulting polymer was also performed to elucidate whether the chain growth occurs via ethylene insertion into (1) a Ti-carbon bond formed by alkylation of the titanium species during the activation reaction with co-catalyst, or (2) a bond between Ti species and polymer support produced during the catalyst preparation procedure. The ethylene insertion into a Ti-carbon bond formed by alkylation with co-catalyst [(route (1)] was confirmed by the fractionation.

Chapter 5: Heterogeneous modified-polypropylene-supported Ziegler catalyst / MMAO system for producing ultrahigh molecular weight polyethylene and poly(ethylene-*co*-1-hexene) with a homogeneous comonomer distribution

Heterogeneous and homogeneous modified-polyolefin-supported Ziegler catalysts were prepared using amorphous and crystalline polyolefins containing a small amount of reactive vinyl groups. Olefin polymerization with these catalysts were investigated in terms of the stability of the active sites on the catalysts and variation of molecular weight and its distribution arising from the change of polyolefin support and co-catalyst. As the results, it was demonstrated that the active sites of the modified-polyolefin supported Ziegler catalysts are practically stable without deactivation at 60 ℃ for 25 h regardless of the kinds of the polyolefin supports. Whereas, the variation of molecular weight and its distribution of polyethylene arising from the change of co-catalyst was found to be strongly affected by the nature of the support.

Chapter 6: General Conclusions

Chapter 2 is concerned with the stability of the modified-polypropylene-supported Ziegler catalyst for ethylene polymerization. The next two chapters, Chapters 3 and 4 show the multiplicity of the molecular weight and its distribution using two types of polyolefin-supported Ziegler catalyst. Chapter 5 relates to the results of ethylene and 1-hexene copolymerization with the modified-polypropylene-supported Ziegler catalyst and

modified-polymethylalumoxane system. Chapters 2-5 provided the following findings:

(1) The modified-polypropylene-supported Ziegler catalyst used in this study has the special characteristic property that the active sites in the catalyst are extremely stable without deactivation even after 100 h.

(2) The molecular weight and molecular weight distribution of the polyethylene obtained with the modified-polypropylene-supported Ziegler catalyst were very sensitive to the various factors like the kind of co-catalyst, its concentration, and the polymerization temperature.

(3) The EPDM-supported catalyst with TEA was found to afford a high molecular weight polyethylene having narrow molecular weight distribution. The comparison of the catalyst performance between the heterogeneous and homogeneous polyolefin-supported Ziegler catalysts indicated that the persistency of the active sites against time and temperature was almost the same, but the influence of the kinds of co-catalysts and their concentration on the molecular weight distribution was dependent upon the properties of the polyolefin supports.

(4) The ultra-high molecular weight of the polyethylene and ethylene/1-hexene copolymer was obtained with the modified-polypropylene-supported Ziegler catalyst and MMAO system. Furthermore, high molecular weight ethylene/1-hexene copolymer having a homogeneous distribution of 1-hexene was obtained by the heterogeneous modified-PP supported catalyst and MMAO system.

Conclusively, the novel polyolefin-supported Zielger catalyst systems exhibited various unique properties, highly stable catalytic activity, and drastic change of activity by the kinds of co-catalysts. Furthermore, the molecular weight and its distribution of the polyethylenes were remarkably changed by polymerization conditions such as polyolefin support (crystalline and amorphous) and the kinds of co-catalysts. The findings of this dissertation will have great significance for olefin polymerization using industrial Ziegler catalyst systems.

Publication list

Oridinal Articles

[1] H. Mori, K. Ohnishi, and M. Terano: "Ethene polymerization with modified-polyolefin-supported highly stable Ziegler catalyst" *Macromol. Rapid Commun.* **17**,25 (1996).

[2] H. Mori, K. Ohnishi, and M.Terano: "Multiplicity of molecular weight distribution of polyethene produced with modified-polypropene-supported Ziegler catalyst systems" *Macromol. Chem. Phys.* **199**, 393 (1998).

[3] K. Ohnishi, H. Mori, and M.Terano: "Polyolefin-supported homogeneous titanium based Ziegler catalyst for the production of polyethene with narrow molecular weight distribution" *Macromol. Chem.Phys.* **199**, 1765 (1998).

[4] K. Ohnishi, H. Mori, and M.Terano: "Heterogeneous modified-polypropene-supported Ziegler catalyst / MMAO system for producing ultrahigh molecular weight polyethene

and poly(ethene-*co*-hexene-1) with a homogeneous comonomer distribution" *Macromol. Chem. Phys.* submitted.

Patent Application

[1] *JP7-224224* (Application Number) K. Ohnishi, H. Mori,M. Terano (Patent right for Mitsubishi Chemical)

[2] *JP8-314605* (Application Number) K. Ohnishi, H. Mori, M. Terano (Patent right for Mitsubishi Chemical)

[3] *JP10-341942* (Application Number) K. Ohnishi, H. Mori, M. Terano (Patent right for Mitsubishi Chemical)

Other Articles

[1] H. Mori, M. Yamahiro, K. Tashino, K. Ohnishi, K. Nitta, M. Terano: "Synthesis of polypropene-*block*-poly(ethene-*co*-propene) by short-period polymerization with $MgCl_2$-supported Ziegler catalyst" *Macromol. Rapid Commun.* **16**, 247 (1995).

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