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Isospecific polymerization of propylene with titanium diamide complexes

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In olefin polymerizations, the development of novel highly functionalized polymers has been desired and tried for long time. To achieve it, a stereospecific living polymerization is believed to be effective and have advantage with the syntheses of terminally functionalized polymer as well as block copolymer. However, the limited catalyst systems can exhibit the stereospecific living polymerization at low polymerization temperature, since the chain transfer and termination reactions frequently occur in the polymerization with usual catalyst system.

For the purpose of finding out a new catalyst system for the stereospecific living polymerization, the following three methods can be considered; 1) synthesis of a new catalyst designed, 2) living polymerization with stereospecific catalyst by controlling polymerization conditions, and 3) modification of non-stereospecific catalyst having a property of living polymerization into stereospecific one. In the case of 1), it is, however, very difficult to design the catalyst suitable for the living polymerization. The possibility of the case 2) has been already provided by using metallocene catalysts. On the other hand, McConville reported the living polymerization of 1-hexene with $[ArN(CH_2)_3NAr]TiMe_2$ ($Ar=2,6\text{-}^iPr_2C_6H_3$) $-B(C_6F_5)_3$ catalyst system, but did not mention about the stereospecificity of this catalyst system.

From such a viewpoint, I tried to evaluate the case 3) using this titanium diamide complex in this thesis.

Propylene polymerizations were performed with the titanium diamide complexes under various polymerization conditions. It was found that $[ArN(CH_2)_3NAr]TiCl_2$ ($Ar=2,6\text{-}^iPr_2C_6H_3$) activated by $Ph_3CB(C_6F_5)_4$ and TIBA affords isotactic polypropylene (iso-PP) with high molecular weight having narrow molecular mass distributions in high yield. From ^{13}C NMR analysis of the resulting polymer, it was obvious that the propylene monomer is inserted into the metal-carbon bond via 1,2-addition and the polymerization proceeds with an enantiomorphic-site control mechanism to produce iso-PP. The activity for iso-PP exhibited the second order dependence on the propylene concentration, indicating that two propylene monomers coordinate at the Ti metal center in the transition state. To check this point, the propylene polymerization was conducted in the presence of cyclohexene, which will be able to coordinate at the active center in place of propylene. As a consequence, iso-PP could be obtained even under low propylene pressure by adding a substantial amount of cyclohexene in the feed.

On the other hand, it was also observed that the molecular weight of iso-PP gradually increase as the polymerization time passes, in spite of the chain transfer reaction by alkylaluminium. This result suggests that appreciable amounts of the active species connecting a polymer chain exist in the polymerization system. Accordingly, the synthesis of block copolymer of propylene and 1-hexene was attempted by the propylene polymerization followed by the addition of 1-hexene in the feed. The analytical results of the resulting polymer showed that the isotactic poly(propylene-*block*-1-hexene) is produced.

In this thesis, I could achieve to obtain the isospecific titanium diamide catalyst and show the possibility for the isospecific living polymerization with this catalyst system. In addition, it could be demonstrated that this catalyst system is available for the preparation of terminally functionalized iso-PPs as well as block copolymers containing iso-PP sequence.