

## 論文の要旨

### 題目 Synthesis and Properties of Tailor-Made Cycloolefin Copolymers Using an *ansa*-Fluorenylamidodimethyltitanium- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ Catalyst System (*ansa*-フルオレニルアミドジメチルチタン- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ 触媒系を用いた精密構造を持つ環状オレフィンコポリマーの合成と性質)

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Norbornene (NB)/ $\alpha$ -olefin copolymers, a kind of cycloolefin copolymers, possess high transparency, low water uptake, excellent thermal stability, and good biocompatibility. These  $\alpha$ -olefins were introduced to reduce the high  $T_g$  of PNB for processability and improve the mechanical properties. NB/ethylene (E) copolymers with different microstructures have been synthesized by various kinds of catalyst systems. However, the copolymerization of NB with propylene (P) is difficult to be achieved because of the steric hindrance of the methyl group of P. The copolymerization of NB and higher  $\alpha$ -olefins is more difficult due to the higher steric hindrance of the side chain of  $\alpha$ -olefins and the catalyst systems for the copolymerization is very limited.

The ( $^i\text{BuNSiMe}_2\text{Flu}$ ) $\text{TiMe}_2$  (I)-modified methylaluminoxane (MMAO)/2,6-di-*tert*-butyl-4-methylphenol (BHT) system was proved to have a living manner for NB/ $\alpha$ -olefin copolymerization. The copolymerization was promoted at moderate speed. When the cocatalyst was changed to  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  with triisobutylaluminum ( $^i\text{Bu}_3\text{Al}$ ) as a scavenger, the catalyst system showed much higher activity. However,  $^i\text{Bu}_3\text{Al}$  caused a chain-transfer reaction which was a problem for achieving living copolymerization.

In this thesis, a mixture of trialkylaluminum ( $\text{R}_3\text{Al}$ ,  $\text{R} = ^i\text{Bu}$  or Oct) with 2 equivalents of BHT in toluene ( $\text{R}_3\text{Al}/\text{BHT}$ ), the average composition formula of  $\text{RAl}(\text{OAr})_2$  ( $\text{Ar} = 2,6\text{-bis}(1,1\text{-dimethylethyl})\text{-4-methylphenyl}$ ), was used as a new scavenger with I- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  for the synthesis of tailor-made NB/ $\alpha$ -olefin copolymers.

In Chapter 2, pseudo-living copolymerization of NB/ $\alpha$ -olefin (1-octene (O), 1-decene (De) or 1-dodecene (Do)) copolymerization was achieved by the I- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{R}_3\text{Al}/\text{BHT}$  ( $\text{R} = ^i\text{Bu}$  or Oct) system at high speed. The quantitatively obtained NB/ $\alpha$ -olefin copolymers with controllable molecular weights were confirmed to have gradient structures.

In Chapter 3, NB/ $\alpha$ -olefin (O or Do) block copolymers with a gradient structure in each isometric block were quantitatively synthesized at high speed through NB/ $\alpha$ -olefin pseudo-living copolymerization by the I- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Oct}_3\text{Al}/\text{BHT}$  system. The strain at break of the NB/ $\alpha$ -olefin block copolymer with moderate block length was massively improved without losing strength compared to the corresponding gradient copolymer.

In Chapter 4, norbornadiene (NBD) homopolymers and NB/NBD/O terpolymers with good solubility were synthesized by different combinations of I or  $[\text{BuNSiMe}_2(2,7\text{-}^i\text{Bu}_2\text{Flu})]\text{TiMe}_2$  (II) with MMAO/BHT or  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/^i\text{Bu}_3\text{Al}/\text{BHT}$ . The II- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/^i\text{Bu}_3\text{Al}/\text{BHT}$  system was found to show the best performance for the synthesis of the homo- and the terpolymers.

In Chapter 5, star polymers with NB/O gradient copolymer arms and cross-linked NBD/E copolymer or cross-linked 1,11-dodecadiene (DoD) polymer core were synthesized by the "arm-first" strategy in one pot using the I- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Oct}_3\text{Al}/\text{BHT}$  system. The NB-rich segments were far from the cores of star polymer, and the O-rich segments were closed to the cores.

In Chapter 6, the results got in this thesis were summarized.