

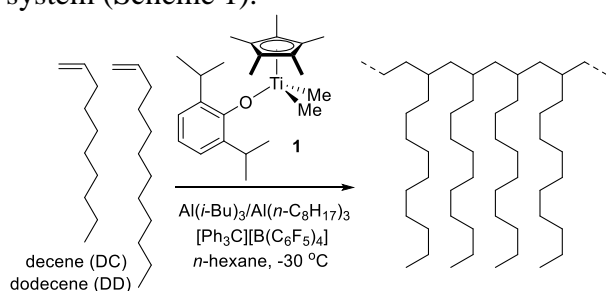
Synthesis of Ultrahigh Molecular Weight Poly(α -olefin)s by Half Titanocene Catalysts

Sarntamon Pengoubol, Kotohiro Nomura
Tokyo Metropolitan University, Tokyo, Japan

*E-mail: ktnomura@tmu.ac.jp

Polyolefins produced by metal catalyzed olefin polymerization are important synthetic polymers in industry and our daily life. Certain poly(α -olefin)s are used in hot melt adhesive application; the ultrahigh molecular weight polymers are expected to exhibit unique properties owing to their cylindrical structures. However, ordinarily metallocene catalysts afford low molecular weight oligomers.

We reported that Cp*TiCl₂(O-2,6-*i*Pr₂C₆H₃) - MAO catalyst exhibited remarkable catalytic activities not only for 1-hexene polymerization [1], but also polymerization of long chain α -olefins such as 1-decene (DC), 1-dodecene (DD), 1-hexadecene and 1-octadecene affording high molecular weight polymers [2]. Since Cp*TiMe₂(O-2,6-*i*Pr₂C₆H₃) (**1**) - borate catalyst also afforded ultrahigh molecular weight poly(1-hexene) when the polymerization was conducted at -30 °C [3], we explored a possibility of synthesis of ultrahigh molecular weight long chain poly(α -olefins) by using this (modified) catalyst system (Scheme 1).



Scheme 1. Polymerization of poly(α -olefin)s.

It turned out that polymerization of 1-decene (DC) and 1-dodecene (DD) afforded ultrahigh molecular weight polymers with low PDI (M_w/M_n) values, when a catalyst system consisting of **1**, [Ph₃C][B(C₆F₅)₄] and Al(*i*-Bu)₃/Al(*n*-C₈H₁₇)₃ was employed. Selected results are summarized in Table 1. Optimization of Al(*i*-Bu)₃/Al(*n*-C₈H₁₇)₃ molar ratio should be necessary for obtainment of polymers with low

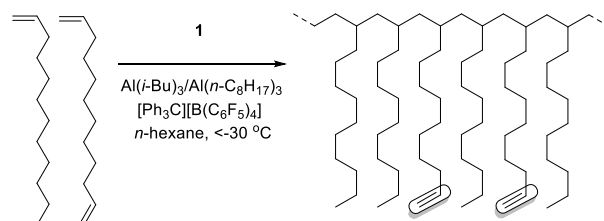
PDI values; the catalytic activity was affected by the ratio. Under the optimized conditions, the resultant polymers possess ultrahigh molecular weights with rather low PDI values; the M_n value increased upon increasing the monomer conversion, suggesting a possibility of (quasi) living polymerization. The PDI values became low when these polymerizations were conducted at -40, -50 °C.

Table 1. Polymerization of 1-decene (DC), 1-dodecene (DD) by Cp*TiMe₂(O-2,6-*i*Pr₂C₆H₃) (**1**) – borate catalyst system.^a

| olefin | Al(<i>i</i> -Bu) ₃ / Al(<i>n</i> -C ₈ H ₁₇) ₃ / 1 | activity ^b | M_n^c ×10 ⁻⁴ | M_w/M_n^c |
|--------|--|-----------------------|------------------------------|-------------|
| DC | 500/-/1.0 | 6972 | 58.2 | 1.57 |
| DD | 500/-/1.0 | 7416 | 48.0 | 1.66 |
| DC | 300/200/1.0 | 6780 | 61.3 | 1.43 |
| DD | 300/200/1.0 | 5580 | 41.2 | 1.53 |
| DC | 100/400/1.0 | 4512 | 58.0 | 1.36 |
| DD | 100/400/1.0 | 4008 | 45.4 | 1.52 |

^aConditions: total volume α -olefin and *n*-hexane 60 mL, -30 °C, 10 min; ^bActivity = kg-polymer/mol-Ti·h; ^cGPC data in THF vs polystyrene standards.

Based on the results in polymerization of long chain α -olefins, described above, we conducted copolymerization of 1-decene with 1,9-decadiene and 1-dodecene with 1,11-dodecadiene using the above borate system. Note that synthesis ultrahigh molecular weight copolymers, containing olefinic double bond in the side chain, has been achieved for the first time by adopting this polymerization technique. More detailed results will be introduced in the symposium.



Scheme 2. Copolymerization of 1-dodecene with 1,11-dodecadiene.

REFERENCES

- [1] K. Nomura, T. Komatsu, M. Nakamura, Y. Imanishi, J.Mol.Catal., 159(2000) 127.
- [2] K. Nomura, S. Pengoubol, W. Apisuk, RSC Adv., 6 (2016) 16203.
- [3] K. Nomura, A. Fudo, J. Mol. Catal. A, 209 (2004) 9.