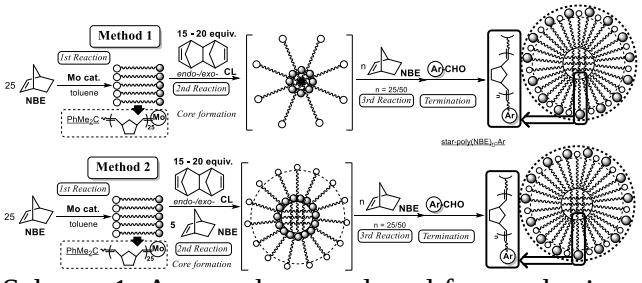
Precise Synthesis of Star-shaped Polymers by Living Ring-Opening Metathesis Polymerization

Zelin Sun, Kotohiro Nomura*
Department of Chemistry, Tokyo Metropolitan University, Tokyo, Japan
...
*E-mail: ktnomura@tmu.ac.jp

Star-shaped polymers, containing multiple linear arms connected at a central branched core, attract considerable attention due to their unique chemical and physical properties. We recently demonstrated a controlled synthesis of star polymers by the living ring-opening metathesis polymerization (ROMP) technique using a Mo-alkylidene initiator by simple sequential addition of norbornene and the cross-linker (Method 1, Scheme 1).[1] The exclusive introduction of functionality into the chain end can easily be achieved by adopting this method. The resultant polymers exhibited unique characteristics as supported catalyst,[2] as well as fluorescent materials.[3] Synthesis of star polymers with more branching should offer new carriers possible for providing more integration of functionalities.

We herein demonstrate that the synthesis can be achieved by increasing amount of cross-linking reagent (CL) with control of the reaction time in the core formation step (2nd reaction), or conducting core formation in the co-presence of NBE (Method 2, Scheme 1). Optimization of reaction conditions (conc. etc.) is also a crucial factor for obtainment of the polymer with narrow PDI (M_w/M_n) values. It turned out that method 2 afforded high molecular weight polymers with more branching compared to Method 1.



Scheme 1. Approaches employed for synthesis of star-shaped polymers with more side arms.

Unique characteristics by integration of functional groups introduced onto the star-surface in the polymers prepared by adopting this method can be highly expected. In particular, the introduction of two different catalysts (catalyst and cocatalyst) exist on the same surface (Chart 1) would provide unique characteristics (concerted effect) that cannot be achieved by the ordinary catalysis. 4-Pyridine carboxaldehyde and 4-formyl-2,6-diisopropyl phenol were thus used to terminate the polymerization for introduction of two different end groups on the same surface.

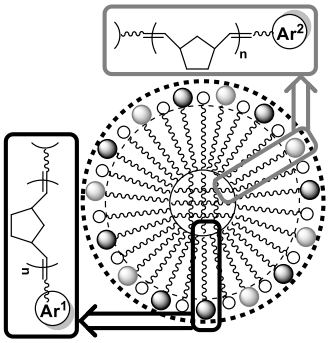


Chart 1. Synthesis of star-shape polymers containing different end groups.

Synthesis of star-shaped polymers with two different functionalities were explored by using Method 1, and the selected results are summarized in Table 1. Introduction of the end groups were confirmed by ^{1}H NMR. More detailed results will be introduced in the symposium.

Table 1. Synthesis of star-shaped polymers by Method 1. [a]

run	2nd time/min	M_n[b]×10^{-4}	M_w/M_n[b]	yield[c] / %
1	50	12.1	1.49	94
2	50	12.4	1.54	93
3	70	13.2	1.39	95
4	70	13.1	1.21	95

[a]Conditions: toluene (total 20.0 g) at 25°C, Mo-cat. 2.0×10^{-5} mol, CL 3.0×10^{-4} mol, NBE (3rd) 25 equiv to Mo. [b]GPC data in THF *vs* polystyrene standards. [c]Isolated yields.

REFERENCES

[1] K. Nomura, Y. Watanabe, S. Fujita, M. Fujiki and H. Otani, Macromolecules, 42 (2009) 899.
[2] K. Nomura, K. Tanaka and S. Fujita, Organometallics, 31 (2012) 5074.
[3] K. Takamizu and K. Nomura, J. Am. Chem. Soc., 134 (2012) 7892.