Synthesis of Soluble Star-Shaped Polymers via In and Out Approach by Ring-Opening Metathesis Polymerization (ROMP) of Norbornene: Factors Affecting the Synthesis

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Abstract: The methods for one-pot synthesis of 'soluble' star-shaped polymers by sequential living ring-opening metathesis polymerization (ROMP) of norbornene (NBE) and cross-linking (CL) reagent using $Mo(CHCMe_2Ph)(N-2,6-^iPr_2C_6H_3)(O^tBu)_2$ have been explored. The method (called the "in and out" or core-first approach) basically consists of (i) the living ROMP of NBE (formation of arm), (ii) reaction with CL (formation of core), (iii) additional living ROMP of NBE (propagating arms from the core, formation of star), (iv) end-modification via Wittig-type cleavage of metal–carbon double bonds containing polymer chain with aldehyde. Two different approaches in the core formation step (reaction with CL mixed with/without NBE) for synthesis of the high molecular weight star-shaped ROMP polymers with more branching, unimodal molecular weight distributions have been explored in detail. The method (reacting CL with NBE in the core formation step) under highly diluted conditions afforded the high molecular weight polymers with unimodal molecular weight distributions.

Keywords: metathesis; living polymerization; molybdenum; star-shaped polymers; ring-opening metathesis polymerization

1. Introduction

Star-shaped polymers consisting of linear arms connected at a central branched core are one of the simplest nonlinear polymers, and study for the precise synthesis by living polymerization technique attracts considerable attention [1–7]. Synthesis by adopting ring-opening metathesis polymerization (ROMP) [8–16] has been employed by sequential addition of monomers/cross linkers (CLs) [12,17–30], and the resultant polymers (soluble in organic solvent, such as toluene, chloroform, dichloromethane, etc.) were applied as fluorescent materials [19], supported catalysts [20], and as controlled release and drug delivery systems [24,26,27]. In this method, related examples for synthesis of cross-linked ROMP polymers (insoluble in common organic solvents) were also known [31–35], especially in terms of application as monolith materials. Two major approaches shown in Scheme 1, such as the "in and out" (core first) approach using a molybdenum–alkylidene catalyst [17–21], and arm (brush) first approach using a ruthenium–carbene catalyst [23–28], have been known for synthesis of 'soluble' star-shaped ROMP polymers. As observed in the synthesis by adopting other methods, such as controlled radical polymerization (atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain-transfer polymerization (RAFT) techniques), the arm first approaches using a (commercially available) ruthenium–carbene catalyst generally require chromatographic purifications (including macromonomer (arm) purifications,

as viscous oil) [29]. By contrast, the one-pot approach using a molybdenum catalyst (in and out approach) [17–21], Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (**Mo cat.**), does not require tedious purification steps, and enables an introduction of a functionality to the polymer chain ends (star surface) via a Wittig-type reaction of metal–carbon double bond containing a polymer chain with certain aldehyde [12,16–21,36–38].
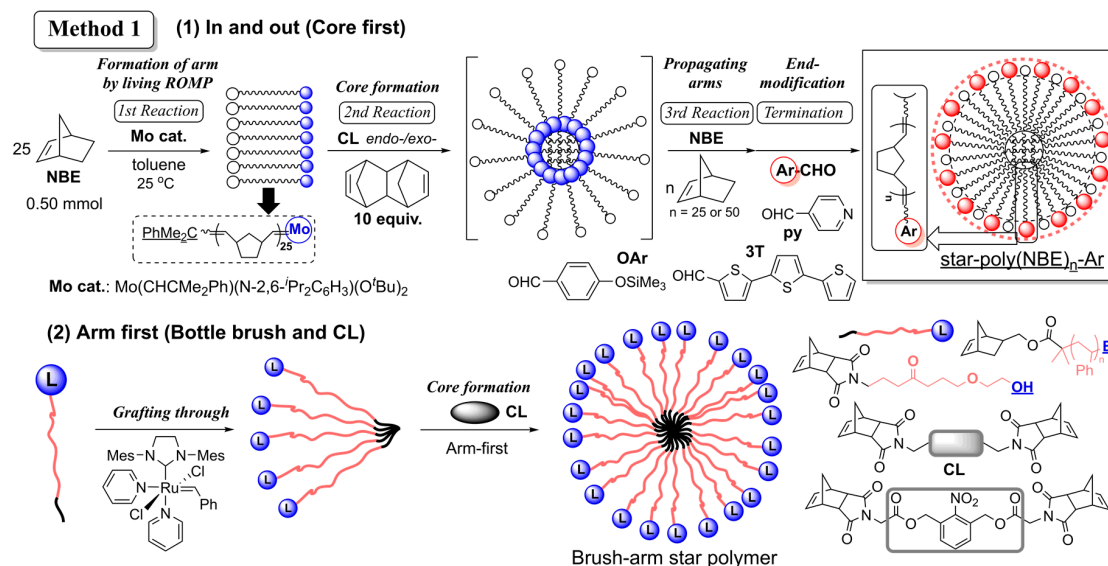
Scheme 1. Two approaches employed for synthesis of star-shaped polymers by living ring-opening metathesis polymerization (ROMP) of cyclic olefins by molybdenum, ruthenium catalysts. NBE = Norbornene, CL= Cross-linking.

For example, as shown in Scheme 2, pyridine modified 'soluble' star-shaped polymers, **star-poly(NBE)$_n$-Py** (n = 25, 50), were used as the effective ligand for ruthenium catalyzed chemoselective hydrogen transfer reduction of various ketones, such as 5-hexen-2-one, 2-allyl-cyclohexanone, 5-isopropenyl-2-methylcyclohexanone (dihydrocarvone), and the activity by RuCl$_2$(PPh$_3$)$_4$ increased with addition of the star polymer ligand [20]. The catalyst could be recovered quantitatively by pouring the reaction mixture into methanol and could be reused without further purification; both the activity and the selectivity did not decrease in the several recycle runs [20]. Moreover, the observed catalytic activities were close to those using the supported catalysts with linear poly(NBE) containing pyridine at the chain end, suggesting that unique characteristics observed in the linear ROMP polymers could be preserved by placing the pyridine moiety on the star surface (and the star polymer supported catalysts showed better efficiency in the catalyst recycle) [20].
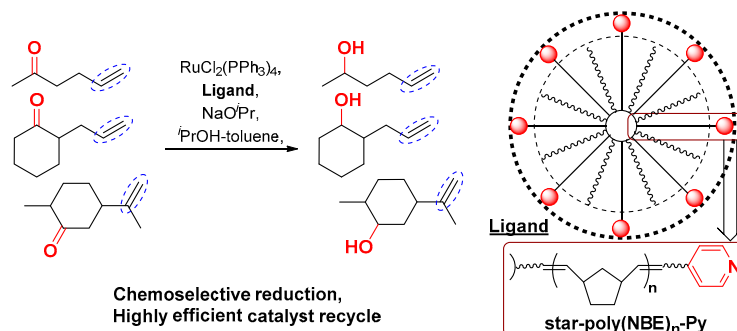
Scheme 2. Chemoselective hydrogen transfer reactions of ketones by efficient recyclable ruthenium catalyst supported by star–polymer ligand [20].

Since it was demonstrated that, as also described above, these ring-opened polymers, poly(NBE), possessed a rather linear nature compared to ordinary polymers prepared by vinyl additions exemplified by poly(acrylamide) due to the cyclic structure in the main chain [39], it is thus highly expected that these "surface-modified" star polymers can be used as advanced materials that cannot be achieved by ordinary end-modified linear and bottle brush polymers. However, previous reports [17–20], by adopting so-called Method 1 (shown in Scheme 1), only demonstrated synthesis of the 'soluble' polymers with a limited number of arms under limited conditions (5 or 10 equivalent of CL [17], shown below in Table 1) due to a difficulty of the molecular weight control, as also described below. Therefore, the development of a controlled synthesis of 'soluble' star-shaped ROMP polymers having more arms has been an important subject in terms of application of these star-shaped polymers as functional materials.

Table 1. Synthesis of star-shaped polymers by living ring-opening metathesis polymerization (ROMP) using Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (Method 2) [a].

| Run	Toluene [b]/g	2nd				3rd	M_n [e]	M_w/M_n [e]	Yield [f]
	x/y/z	CL [c] /equiv	NBE [c] /equiv	conc. [d] /×10^{-2} M	time /min	NBE [c] /equiv	/×10^{-5}		/%
1 [g]	3.0/4.0/4.0	10	–	8.67	50	25	0.88	1.19	96
2 [g]	3.0/4.0/4.0	15	–	9.91	50	25	1.34	1.30	96
3 [g]	3.0/4.0/4.0	15	–	9.91	70	25	2.08	2.88 [h]	94
4	3.0/4.0/4.0	15	5	11.1	50	25	1.75	1.97 [h]	95
5	3.0/4.0/4.0	15	5	11.1	70	25	2.13	2.22 [h]	90
6	3.0/4.0/4.0	15	5	11.1	90	25	3.10	6.96 [h]	99
7	3.0/4.0/4.0	15	5	11.1	120	25	3.45	4.74 [h]	94
8	3.0/4.0/4.0	15	5	11.1	120	25	3.66	5.56 [h]	90
9 [g]	5.0/4.0/6.0	15	–	7.71	50	25	1.37	1.44	97
10 [g]	5.0/4.0/6.0	15	–	7.71	70	25	1.44	1.46	99
11	5.0/4.0/6.0	15	5	8.67	50	25	1.45	1.73 [h]	93
12	5.0/4.0/6.0	15	5	8.67	70	25	1.57	1.57 [h]	95
13	5.0/4.0/6.0	15	5	8.67	90	25	1.93	2.05 [h]	93
14	5.0/4.0/6.0	15	5	8.67	120	25	2.40	2.22 [h]	93
15 [g]	11.0/4.0/5.0	15	–	4.62	50	25	1.37	1.22	90
16 [g]	11.0/4.0/5.0	15	5	5.20	50	25	1.45	1.28	91
17 [g]	11.0/4.0/5.0	15	–	4.62	50	50	1.56	1.17 [h]	96
18 [g]	11.0/4.0/5.0	15	5	5.20	50	50	1.91	1.36 [h]	98
19 [g]	11.0/4.0/5.0	15	–	4.62	70	25	1.49	1.37	94
20 [g]	11.0/4.0/5.0	15	5	5.20	70	25	1.53	1.39	96
21 [g]	11.0/4.0/5.0	15	–	4.62	70	50	1.64	1.28 [h]	94
22 [g]	11.0/4.0/5.0	15	5	5.20	70	50	2.02	1.45 [h]	99

[a] Conditions: Toluene at 25 °C (detailed procedure, see Scheme 3, Method 2), 4-pyridine carboxaldehyde was used for termination. [b] Amount of toluene (in gram) in each step (shown in Scheme 3). [c] Equivalent to Mo. [d] Calculated concentration of NBE + CL charged (mmol/L) at the second stage (core formation). [e] Gel–permeation chromatography (GPC) data in tetrahydrofuran (THF) vs. polystyrene standards (g/mol). [f] Isolated yield (%) as MeOH insoluble fraction. [g] Cited from Reference [21]. [h] Bimodal (or multimodal) molecular weight distributions observed on GPC trace.

Recently, we reported an improved protocol for controlled synthesis of 'soluble' star-shaped polymers with more arms (branching) by the living ROMP technique using the Mo–alkylidene initiator by sequential additions of norbornene (NBE) and the cross-linker (CL), expressed as Method 1 in Schemes 1 and 3 (shown below), upon addition of CL (15 and 20 equivalent to Mo) [21]. It turned out that the polydispersity index (PDI, M_w/M_n) values became low with decreasing the monomer concentration (under diluted conditions) in the core formation step (reaction with CL), shown in Scheme 1 (introduced as Method 1) [21]. It also turned out that the M_n values in the resultant polymers increased upon increasing the amount of NBE in the third step (3rd reaction in Method 1) consisting of unimodal molecular weight distributions (M_w/M_n = 1.17, 1.28, shown below in Table 1).

In this paper, we have explored two modified approaches (Methods 2 and 3, shown in Scheme 3) in the core formation step (varying cross-linking density, core size) for preparation of the polymers

with different core sizes upon increasing the amount of CL and/or by mixing CL and NBE. We thus herein introduce factors affecting the precise synthesis of star-shaped ROMP polymers with (relatively) unimodal molecular weight distributions, by adopting the living ROMP technique. Since most methods (controlled radical, ROMP, etc.) face a difficulty of preparation of the polymers with "unimodal" molecular weight distributions and require separation for the obtainment of the desired star-shaped polymers with relatively controlled molecular weights [12,29], the report should be helpful for precise synthesis under optimized conditions.
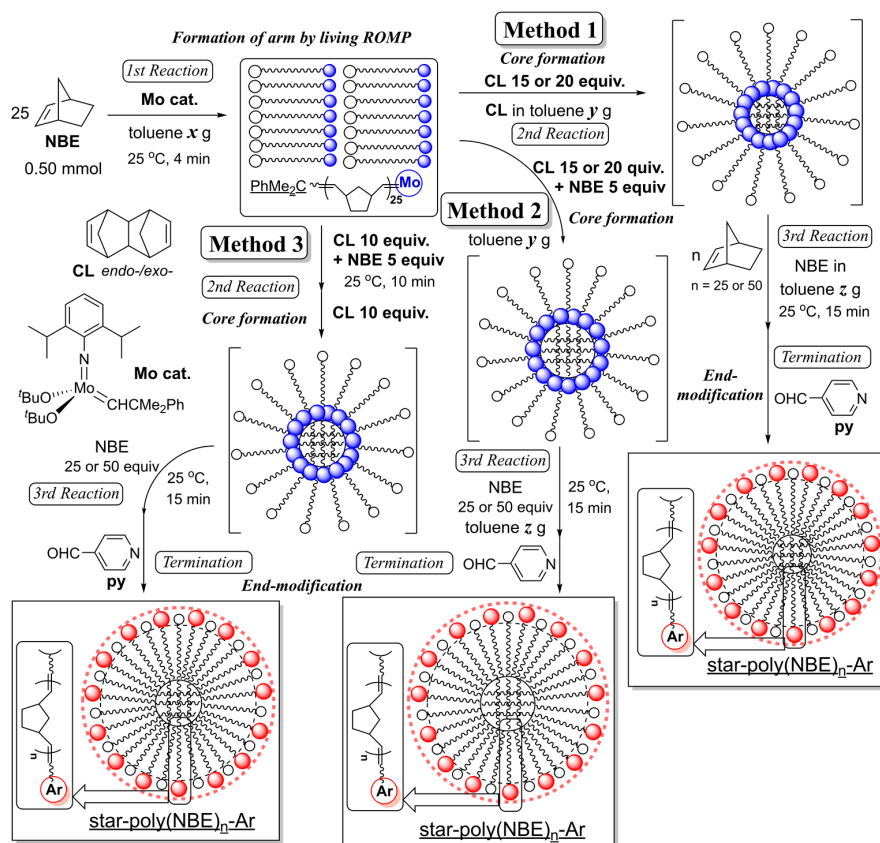
Scheme 3. Approaches explored for one-pot synthesis end-functionalized star-shaped ROMP polymers using molybdenum–alkylidene catalyst (**Mo cat.**).

2. Results and Discussion

Synthesis of Pyridine Modified Star-Shaped Ring-Opened Poly(norbornene)

As described in the introductory section, the method for synthesis of the titled star-shaped polymers using a molybdenum–alkylidene catalyst (**Mo cat.**), the so-called in and out (core first) approach, consists of (i) the living ROMP of norbornene (NBE, formation of arm), (ii) reaction with CL (formation of core), (iii) additional living ROMP of NBE (propagating arms from the core, formation of star), and (iv) end-modification via Wittig-type cleavage of metal–carbon double bonds containing polymer chain with aldehyde. In this method, an exclusive introduction of functionality into the ROMP polymer chain end can be easily achieved through a cleavage of the ROMP polymer–metal double bonds (of Schrock type Mo–alkylidene) with aldehyde, yielding a carbon–carbon double bond via a Wittig-like reaction [8–10,12,16]. Three modified approaches shown in Scheme 3 have thus been considered, because the approaches would prepare the polymers with different core sizes upon increasing the amount of CL (Method 1, Scheme 1) [21] and/or by mixing CL and NBE in the core formation step (varying cross-linking density, core size), as widely employed by the ATRP technique [5].

It has been known in the synthesis of star-shaped polymers using vinyl monomer and divinyl monomer (CL) by controlled radical polymerization that the degree of cross-linking or density of cross-linking (network structure, core size and density) can be tuned in the core formation step by combination of propagation and cross-linking (timing of adding CL during propagation) [5]. In this sense, the core size in the star-shaped ROMP polymers would be controlled (modified) by adopting combined ROMP of CL and NBE in the core formation step (2nd reaction, Methods 2 and 3, Scheme 3). Table 1 summarizes the results with the addition of NBE (5.0 equivalent) in the core formation step (Method 2, CL/Mo = 15, Scheme 3).

It turned out that, as observed previously (runs 2, 3) [21], the M_n values in the resultant polymers increased over the reaction time (50–120 min, runs 4–8, 11–14, CL/Mo = 15), and the PDI values became large when the ROMPs were conducted under rather high CL/NBE concentration conditions (M_w/M_n = 1.97–6.96 (runs 4–7) vs. 1.57–2.22 (runs 11–14)). Under high dilution conditions (as conducted by Method 1, runs 15, 19), the resultant polymers became unimodal molecular weight distributions (M_w/M_n = 1.28, 1.39, runs 16, 20, gel–permeation chromatography (GPC) traces are shown in Figure 1c,f), and the M_n values increased with the increase of NBE in the 3rd reaction (from 25 equivalent to 50 equivalent) with rather low PDIs (runs 18, 22) [21]. The observed increases in the M_n values (e.g., M_n = 145,000 (run 16) or 153,000 (run 20) vs. 191,000 (run 18) or 202,000 (run 22)) were apparently larger than that with the increase of the linear poly(NBE) (2354, from 25 mer (M_n = 2354) to 50 mer (M_n = 4708)), clearly indicating that the resultant polymers are star-shaped ROMP polymers consisting of core and poly(NBE) arms. It also turned out that the M_n values in the resultant polymers were higher than those prepared by Method 1 in most cases. Moreover, the observed increases in the M_n value by Method 2 (e.g., 46,000 from 145,000 (runs 16, 25 equivalent NBE in the third step) to 191,000 (runs 18, 50 equivalent of NBE in the third step); 49,000 from 153,000 (runs 20, 25 equivalent of NBE in the third step) to 202,000 (runs 22, 50 equivalent of NBE in the third step)) are apparently larger than those by Method 1 (e.g., 19,000 from 137,000 (runs 15, 25 equivalent of NBE in the third step) to 156,000 (runs 17, 50 equivalent of NBE in the third step); 15,000 from 149,000 (runs 19, 25 equivalent of NBE in the third step) to 164,000 (runs 21, 50 equivalent of NBE in the third step)). It is thus strongly suggested that the resultant star-shaped ROMP polymers possess more branching (arms) than those prepared by Method 1. The resultant polymers prepared by Method 2 are soluble in toluene, tetrahydrofuran (THF), chloroform, and dichloromethane at room temperature.

Figure 1 shows selected GPC traces in the resultant polymers under different monomer concentrations in the 2nd reaction (in Scheme 3, Method 2, CL/Mo = 15). The resultant polymers prepared under rather high concentration conditions (Figure 1a,d; runs 4, 5) showed bimodal molecular weight distributions (consisting of high and low molecular weights), and the extent in the high molecular weight trace decreased when the ROMPs were conducted under diluted conditions (Figure 1b,e; runs 11, 12). By contrast, the GPC traces became unimodal distributions when the ROMPs were conducted under high diluted conditions (Figure 1c,f; runs 16, 18). It seems that the extent of a higher molecular GPC trace was decreased upon increasing the amount of toluene (or decreasing the monomer concentration); we speculate that this would probably be in order to avoid so-called star–star coupling (further intermolecular metathesis of the core molecules). Therefore, as observed in Method 1, control of monomer concentration in the 2nd step (core formation step) plays an important role for the obtainment of star-shaped ROMP polymers with unimodal molecular weight distributions.

Table 2 summarizes the results for the preparation of the star ROMP polymers by Method 2 under a high CL/Mo ratio (CL/Mo = 20). The results also showed that the M_n values in the resultant ROMP polymers increased over the reaction time in the core formation (2nd step, runs 26–31, 34–37), and the PDI values became low when the ROMPs were conducted under diluted conditions (M_w/M_n = 1.58–2.22, runs 34–37). However, the resultant polymers still possessed bimodal molecular weight distributions (runs 34–37). It should be noted that the PDI values became low when the ROMPs (especially in the first and the second steps) were conducted under high diluted conditions. Moreover, as demonstrated in runs 38 and 40, a certain optimization of reaction time in the second step

(50 min) also seems important for the obtainment of the star-shaped ROMP polymers with unimodal molecular weight distributions (M_w/M_n = 1.52 (run 38), 1.43 (run 40)). It thus becomes clear that precise optimization of the conditions (dilution at the 2nd reaction) should be necessary for obtainment the polymers with rather low PDI values.
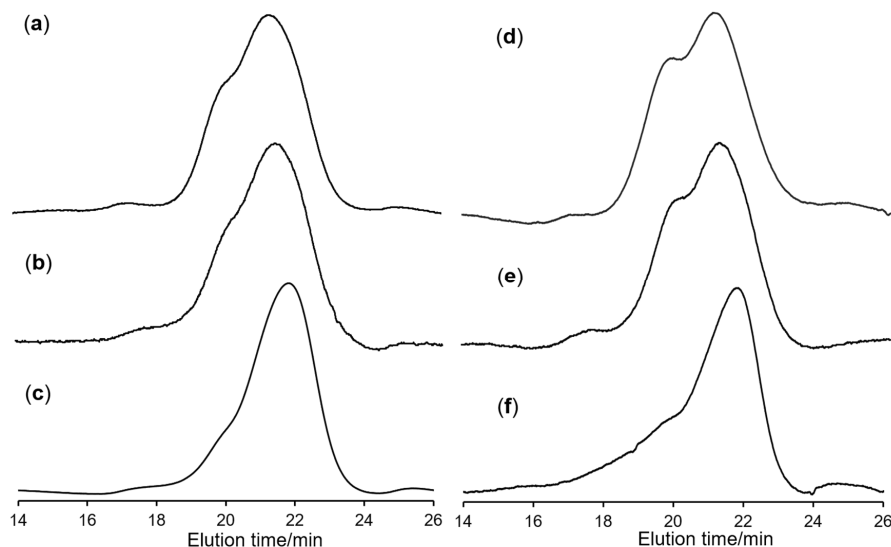
Figure 1. Selected GPC traces in the resultant polymers prepared by Method 2 (shown in Scheme 3, CL/Mo = 15). Reaction time at the second stage (core formation) = 50 min (**a**–**c**), 70 min (**d**–**f**). Calculated concentration for NBE + CL = 11.1 × 10^{-2} M ((**a**) run 4, (**d**) run 5), 8.67 × 10^{-2} M ((**b**) run 11, (**e**) run 12), and 5.20 × 10^{-2} M ((**c**) run 16, M_n = 1.45 × 10^5, M_w/M_n = 1.28; (**f**) run 20, M_n = 1.53 × 10^5, M_w/M_n = 1.39). Detailed data are shown in Table 1.

Table 2. Synthesis of star-shaped polymers by living ring-opening metathesis polymerization (ROMP) using Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (Method 2) [a].

Run	Toluene [b]/g	2nd				3rd	M_n [e]	M_w/M_n [e]	Yield [f]
	x/y/z	CL [c] /equiv	NBE [c] /equiv	conc. [d] /×10^{-2} M	time /min	NBE [c] /equiv	/×10^{-5}		/%
23 [g]	3.0/4.0/4.0	20	–	11.1	50	25	2.86	2.51 [h]	95
24 [g]	3.0/4.0/4.0	20	–	11.1	70	25	3.49	4.31 [h]	98
25 [g]	3.0/4.0/4.0	20	–	11.1	90	25	2.86	2.19 [h]	90
26	3.0/4.0/4.0	20	5	12.4	50	25	2.98	5.91 [h]	94
27	3.0/4.0/4.0	20	5	12.4	90	25	2.99	2.29 [h]	98
28	5.0/4.0/6.0	20	5	9.63	50	25	2.36	2.26 [h]	99
29	5.0/4.0/6.0	20	5	9.63	70	25	2.93	2.56 [h]	94
30	5.0/4.0/6.0	20	5	9.63	90	25	2.64	2.34 [h]	99
31	5.0/4.0/6.0	20	5	9.63	120	25	2.74	2.04 [h]	99
32 [g]	11.0/4.0/5.0	20	–	5.20	50	25	1.49	1.44 [h]	90
33 [g]	11.0/4.0/5.0	20	–	5.20	70	25	1.78	1.54 [h]	91
34	11.0/4.0/5.0	20	5	5.78	50	25	1.40	1.58 [h]	99
35	11.0/4.0/5.0	20	5	5.78	70	25	1.64	1.91 [h]	98
36	11.0/4.0/5.0	20	5	5.78	90	25	1.81	2.20 [h]	98
37	11.0/4.0/5.0	20	5	5.78	120	25	2.14	2.22 [h]	94
38	11.0/8.0/5.0	20	5	4.56	50	25	1.53	1.52	99
39	11.0/8.0/5.0	20	5	4.56	70	25	1.68	1.51 [h]	97
40	15.0/8.0/5.0	20	5	3.77	50	25	1.52	1.43	99
41	15.0/8.0/5.0	20	5	3.77	70	25	1.64	1.46 [h]	98

[a] Conditions: Toluene at 25 °C (detailed procedure, see Scheme 3, Method 2), 4-pyridine carboxaldehyde was used for termination. [b] Amount of toluene (in gram) in each step (shown in Scheme 3). [c] Equivalent to Mo. [d] Calculated concentration of NBE + CL charged (mmol/L) at the second stage (core formation). [e] GPC data in THF vs. polystyrene standards (g/mol). [f] Isolated yield (%) as MeOH insoluble fraction. [g] Cited from Reference [21]. [h] Bimodal (or multimodal) molecular weight distributions observed on GPC trace.

In order to obtain the higher molecular weight polymers (with more branching) with unimodal molecular weight distributions, two step reactions were attempted in the core formation step (Method 3, Scheme 3). In this method, 10 equivalent of CL and 5.0 equivalent of NBE were added into a solution of the initial ROMP with NBE (1st step), and the solution was stirred for 10 min (expecting formation of the initial core), and 10 equivalent of CL was then further added into the solution and stirring of the mixture was continued for a certain period in the 2nd step. The results are summarized in Table 3.

Table 3. Synthesis of star-shaped polymers by living ring-opening metathesis polymerization (ROMP) using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)(O^tBu)_2$ (Method 3) [a].

Run	Toluene [b]/g	2nd					3rd	M_n [f]	M_w/M_n [f]	Yield [g]
	x/y/z	CL(1) [c] /equiv	NBE [c] /equiv	CL(2) [c] /equiv	conc. [d] /$\times 10^{-2}$ M	Time [e] /min	NBE [c] /equiv	/$\times 10^{-5}$		/%
10 [h]	5.0/4.0/6.0	15	–	–	7.71	70	25	1.44	1.46	99
12	5.0/4.0/6.0	15	5	–	8.67	70	25	1.57	1.57	95
13	5.0/4.0/6.0	15	5	–	8.67	90	25	1.93	2.05	93
28	5.0/4.0/6.0	20	5	–	9.63	50	25	2.36	2.26 [i]	99
29	5.0/4.0/6.0	20	5	–	9.63	70	25	2.93	2.56 [i]	94
30	5.0/4.0/6.0	20	5	–	9.63	90	25	2.64	2.34 [i]	99
31	5.0/4.0/6.0	20	5	–	9.63	120	25	2.74	2.04 [i]	99
42	5.0/6.0/4.0	10	5	10	7.88	40	25	1.15	1.88 [i]	91
43	5.0/6.0/4.0	10	5	10	7.88	60	25	1.43	4.42 [i]	92
44	5.0/6.0/4.0	10	5	10	7.88	80	25	1.44	2.11 [i]	91
45	5.0/6.0/4.0	10	5	10	7.88	110	25	3.01	3.42 [i]	94
46	5.0/6.0/4.0	10	5	10	7.88	60	50	2.41	2.83 [i]	94
47	5.0/6.0/4.0	10	5	10	7.88	80	50	2.63	2.35 [i]	92
48	5.0/6.0/4.0	10	5	10	7.88	110	50	3.66	2.81 [i]	93

[a] Conditions: Toluene at 25 °C (detailed procedure, see Scheme 3, Method 3), 4-pyridine carboxaldehyde was used for termination. [b] Amount of toluene (in gram) in each step (shown in Scheme 3). [c] Equivalent to Mo. [d] Calculated concentration of NBE + CL charged (mmol/L) at the second stage (core formation). [e] Reaction time after adding CL(2). [f] GPC data in THF vs. polystyrene standards (g/mol). [g] Isolated yield (%) as MeOH insoluble fraction. [h] Cited from Reference [21]. [i] Bimodal (or multimodal) molecular weight distributions observed on GPC trace.

It turned out that, as observed in Table 2 as well as in Method 1 [21], the M_n values in the resultant polymers increased over the reaction time in the 2nd step (40–110 min, runs 42–45). However, the PDI values (in the polymers prepared by Method 3) were larger (M_w/M_n = 1.88–4.42) than those prepared by Method 2 (M_w/M_n = 2.04–2.56); the PDI values did not improve upon increasing the amount of NBE in the 3rd step (runs 46–48). We thus speculate that this would be due to enhanced star–star coupling (intermolecular metathesis with the initial cores), and the approach in Method 3 is not suitable for this purpose.

3. Concluding Remarks

In this paper, two methods, which are different in the core formation step (2nd reaction), shown in Scheme 3, have been explored for one-pot synthesis of star-shaped ROMP polymers with more branching (arms). Although these reactions required conditions with high dilution for the obtainment of polymers with unimodal molecular weight distributions, as reported previously [21], the number of the poly(NBE) arms can be increased upon increasing the CL (higher CL/Mo ratio, 15, 20, Method 1, Scheme 3). Moreover, the core size can also be controlled upon copresence of NBE (use of CL and NBE in the 2nd step, Method 2, Scheme 3). It is thus possible to prepare high molecular weight star-shaped ROMP polymers with unimodal molecular weight distributions by adopting these approaches, especially by Methods 1 and 2. An introduction of a functional group into the ROMP polymer chain ends (star polymer surface) can also be attained by adopting these methods using molybdenum catalyst [12,16–21], as described in the introduction. We thus believe that the method should be applied for controlled synthesis of functional materials as surface modified star-shaped polymers.

4. Experimental Section

4.1. General Procedure

All experiments were carried out under a nitrogen atmosphere in a vacuum atmospheres dry-box or using standard Schlenk techniques. All chemicals used were of reagent grades and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto Chemical Co., Inc., Tokyo, Japan) was transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the dry-box, and was stored over sodium/potassium alloy, and was used after passing through an alumina short column under nitrogen flow prior to use. Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ [40] and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphtalene (CL, *exo:endo* = 0.15:1.00) [41] were prepared according to the literature, while 4-Pyridinecarboxaldehyde was used in the dry-box as received (Aldrich Chemical Co., St. Louis, MO, USA) without further purification.

Molecular weights and the molecular weight distributions of the resultant polymers were measured by gel–permeation chromatography (GPC). HPLC-grade THF (Wako Pure Chemical Ind., Inc., Tokyo, Japan) was used for GPC and was degassed prior to use. GPC were performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd., Kyoto, Japan) in THF (containing 0.03 wt % 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mmφ) were calibrated versus polystyrene standard samples. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV500 spectrometer (^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz), and all chemical shifts are quoted in ppm and are referenced to SiMe$_4$. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C.

4.2. General Polymerization Procedure

A typical polymerization procedure (run 35, Method 2, Table 2) is as follows. A toluene solution (1.0 g) containing Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (2.00 × 10^{-5} mol) was added in one portion to a rapidly stirred toluene solution (10.0 g) containing the norbornene (25 equiv. to Mo) at room temperature (25 °C), and the solution was stirred for 4 min. A toluene solution (4.0 g) containing 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphtalene (CL, 20 equivalent to Mo) and norbornene (NBE, 5 equivalent to Mo) was then added into the solution, and the mixture was stirred for the prescribed time (50 min). Then, a toluene solution (5.0 g) containing NBE (25 equivalent to Mo) was added in one portion to the mixture, and the reaction solution was further stirred for 15 min. The polymerization was quenched by adding 4-pyridine carboxaldehyde (ca. >10 mg, excess), and the solution was stirred for 1 h for completion. The mixture was then removed in vacuo until it was dissolved in the minimum amount of toluene. The solution was poured dropwise into methanol to afford pale white precipitates. The polymer was then collected by filtration and dried in vacuo. In Method 1, the basic procedure was the same except that a toluene solution containing only CL (15.0/20.0 equivalent to Mo) was added in the second step.

In Method 3, the basic procedure was the same except for the amount of toluene at each step; the polymerization procedure of Method 3 (run 45, Method 3, Table 3) is as follows. A toluene solution (1.0 g) containing Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (2.00 × 10^{-5} mol) was added in one portion to a rapidly stirred toluene solution (4.0 g) containing the norbornene (25 equiv. to Mo) at room temperature (25 °C), and the solution was stirred for 4 min. A toluene solution (3.0 g) containing 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphtalene (CL, 10 equivalent to Mo) and norbornene (NBE, 5 equivalent to Mo) was then added into the solution, and the mixture was stirred for 10 min; afterwards, a toluene solution (3.0 g) containing 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphtalene (CL, 10 equivalent to Mo) was further added, and the mixture was stirred for the prescribed time (50 min). Then, a toluene solution (4.0 g) containing NBE (25 equivalent to Mo) was added in one portion to the mixture, and the reaction solution was further stirred for 15 min. The polymerization was also quenched by adding 4-pyridine carboxaldehyde (ca. >10 mg, excess), and the solution was stirred for 1 h for completion.

Selected NMR spectra of star-shaped polymer were confirmed in the previously report [21]. ^{1}H NMR (in CDCl$_3$ at 25 °C) (Table 1, run 9): δ 5.35 and 5.21 (br.s, 2H olefinic), 2.79 and 2.43 (br.s, 2H), 1.85 and 1.03 (m, 2H), 1.78, and 1.36 (m, 4H) ppm. Moreover, resonance ascribed to the pyridine end group (8.54 and 8.50 (d) ppm) was also observed. ^{13}C NMR (in CDCl$_3$ at 25 °C) (Table 1, run 4): δ 133.9, 133.0, 128.2, 43.1, 38.6, 33.2, 32.2 ppm.

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