Facile Controlled Synthesis of Soluble Star Shape Polymers by Ring-Opening Metathesis Polymerization (ROMP)

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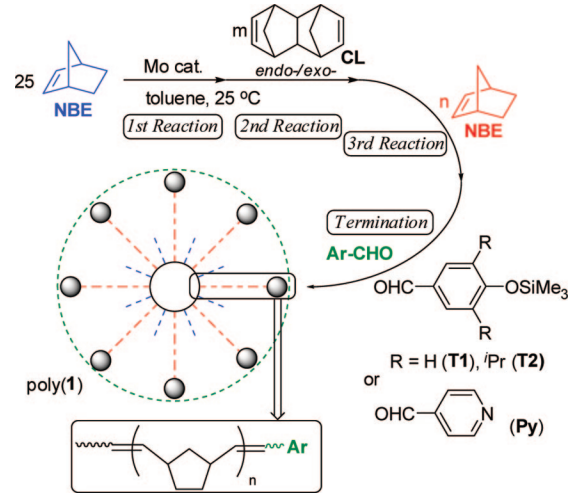
Introduction. Unique characteristics of living polymerizations (absence of undesirable side reactions such as chain transfer and termination) are accomplished through techniques such as ring-opening metathesis polymerization (ROMP), group transfer polymerization, controlled radical polymerization, and anionic polymerization. These methods generally provide synthesis of polymers with controlled molecular weights and narrow molecular weight distributions.[1] Star polymers containing multiple linear arms connected at a central branched core represent one of the simplest nonlinear polymers,[1,2] and synthetic approaches the using atom transfer radical polymerization[3] via the "core-first",[4] "coupling-onto",[5] or "arm-first"[6] approach has thus been actively investigated recently. The approaches for synthesis of cross-linked polymers by ROMP[7] were also known,[8−10] especially in terms of application as monolith materials for separation reported by Buchmeiser;[9,10] however, reports for precise syntheses of star (ball) shape polymers that are highly soluble in common organic solvents have not so far been reported. Since exclusive preparation of the end-functionalized ring-opened polymers can be easily achieved by a living ROMP of norbornene derivatives especially using the Schrock type molybdenum alkylidene initiator,[11,12] we thus explored a possibility to prepare soluble star (ball) shape ROMP polymers via the "core-first" approach in a precise manner. We herein present a facile controlled synthesis of the star shape ROMP polymers by the sequential living ROMP using the molybdenum−alkylidene initiator.[13]

Results and Discussion. The method consists of three key steps outlined in Scheme 1, and Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ has been chosen as the initiator due to its ability to prepare the multiblock ring-opened copolymers in a precise manner with moderate propagation as well as with complete conversion of monomers.[11,12] This is also due to that the initiator shows markedly higher reactivity toward *strained* cyclic olefins (norbornene derivatives) than the internal olefins (in the ring-opened polymers).[12d,f] 1,4,4a,5,8,8a-Hexahydro-1,4,5,8-*exo*-*endo*-dimethanonaphthalene (**CL**, *exo*:*endo* = 0.17:1.00)[14] has also been chosen as a cross-linking reagent, and the polymerization was terminated with 4-Me$_3$SiO−C$_6$H$_4$CHO (**T1**), 3,5-^{i}Pr$_2$-4-Me$_3$SiO−C$_6$H$_2$CHO (**T2**), or 4-pyridinecarboxaldehyde (**Py**). The results are summarized in Table 1.[15]

It turned out that syntheses of high molecular weight ring-opened polymers, poly(**1**), with uniform molecular weight distributions (M_n = (8.97−9.63) × 10^4 g/mol, M_w/M_n = 1.31−1.45, runs 4−7) have been achieved by adopting this approach (sequential addition of NBE and CL), and the results

Scheme 1. Present Method for Synthesis of Soluble Star (Ball) Shape ROMP Polymers



are reproducible under the same conditions.[15] The resultant polymers are highly soluble in ordinary organic solvent such as toluene, THF, dichloromethane, chloroform, chlorobenzene, etc. Optimization of the reaction conditions was required for obtainment of the "soluble" ROMP polymers with uniform molecular weight distributions. Use of CL as the first monomer resulted in the formation of insoluble gel polymers, and the polymerization under rather diluted conditions was necessary for improvement of the viscosity in the reaction solution.[15,16] Moreover, the reaction time after addition of CL (second reaction, 50 min in the present ROMP) seemed important to obtain the high molecular weight ROMP polymers with uniform molecular weight distributions as well as with better reproducibility.[15]

Note that the M_n values in the resultant ROMP polymers increased upon increasing the amount of NBE in the third polymerization (25 → 50 equiv to Mo, runs 4−7 vs runs 8 and 9). Since the observed increases in the M_n values [ca. 34 000 (by GPC vs polystyrene standards) from runs 4−9] were much higher than those in the linear poly(NBE) [increased 25 NBE repeating units, 2354 by molecular weight], also since the first polymerization of NBE proceeded with high conversion even after 5 min,[16] the results suggest that the resultant ROMP polymers are star shape polymers consisting of a core and NBE branching (first and third polymerization).[17] It should also be noted that the M_n values in the resultant polymers terminated with **T2** and **Py** (runs 10−12) were similar to those terminated with **T1** (runs 4−9).[15] The facts thus suggest that preparation of end-functionalized polymers (introduction of functionalities into surface of the star shape polymers) can be achieved by adopting this approach. As reported previously,[12a,d,f] the SiMe$_3$ group in the polymer termini could be cleanly hydrolyzed using 0.5 M HCl(aq) solution in THF (yield >95%) without any notable changes in the M_n values by GPC.[15]

Figure 1 shows selected TEM micrographs of thin films prepared by casting the resultant ROMP polymers [poly(**1**), run 6 (top) and run 8 (bottom)] on a plastic-coated copper grid. The resulting micrographs depict formation of uniform spherical images with average diameters of 52 nm (run 6) or 74 nm (run 8).[18] These diameters are somewhat longer than those calculated as the linear ROMP polymer main chains (25 and 50 repeating

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Table 1. Selected Results for Syntheses of Star (Ball) Shape Polymers by Sequential Additions of Norbornene (NBE) and Cross-Linker (CL) in the Ring-Opening Metathesis Polymerization (ROMP) Using Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ in Toluene[a]

		second reaction		third reaction		poly(**1**)		
run	terminator[b]	CL/Mo[c]/m	time/min	NBE/Mo[c]/n	time/min	M_n[d] × 10^{-4}	M_w/M_n[d]	yield[e]/%
1	**T1**	5	15	25	20	4.71	1.16	98
2	**T1**	10	30	25	20	8.35	1.45	89
3	**T1**	10	40	25	20	8.70	1.44	88
4	**T1**	10	50	25	20	9.53	1.45	94
5	**T1**	10	60	25	20	9.67	1.44	93
6	**T1**	10	50	25	15	8.97	1.31	95
7	**T1**	10	50	25	30	9.23	1.48	96
8	**T1**	10	50	50	20	12.7	1.49	96
9	**T1**	10	50	50	20	12.8	1.48	97
10	**T2**	10	50	25	15	9.15	1.34	98
11	**T2**	10	50	50	20	12.1	1.49	93
12	**Py**	10	50	25	15	8.47	1.42	95

[a] Conditions (first reaction): Mo cat. 1.82 × 10^{-5} mol, NBE (norbornene) 25 equiv to Mo, toluene (10.0 g), 25 °C, 5 min, and detailed procedures are described in the Supporting Information. [b] Aldehyde for termination shown in Scheme 1. [c] Starting feedstock ratio (m and n in Scheme 1). [d] GPC data in THF vs polystyrene standards. [e] Isolated yields. **T1**: 4-Me$_3$SiO-C$_6$H$_4$CHO; **T2**: 3,5-^{i}Pr$_2$-4-Me$_3$SiO-C$_6$H$_2$CHO; **Py**: 4-pyridinecarboxaldehyde.

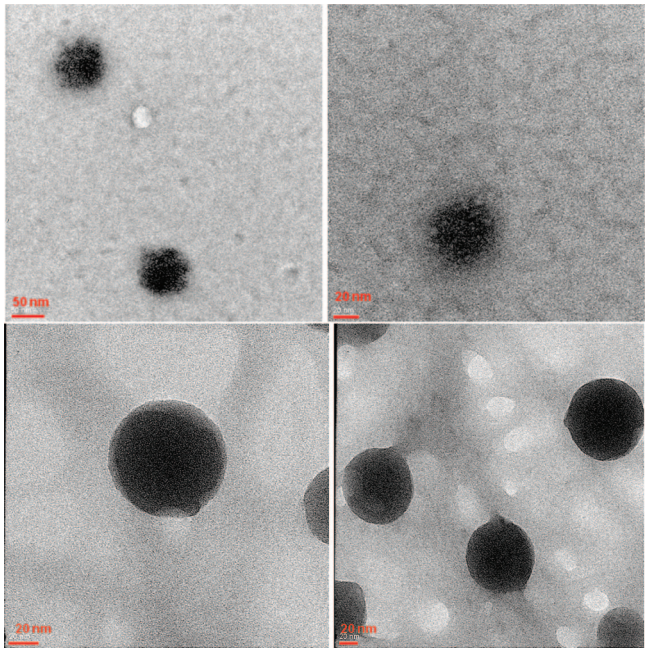

Figure 1. TEM micrographs of thin film prepared by casting poly(**1**) [run 6 (top) and run 8 (bottom)] on a plastic-coated copper grid at a concentration of 10^{-5} mg/mL at varying magnification.[18]

units, 27.8 and 55.6 nm,[12f] respectively) but seemed to correspond with those consisting of the arm and a core.[18] Similar spherical images were observed in the STEM measurements (shown in the Supporting Information), and the average diameters were very close to those observed in the TEM micrographs [average diameters of 54 nm (run 6) and 71 nm (run 9)].[18] These clearly suggest that the observed spherical micrographs should be ascribed to a single star (ball) shape polymers prepared by adopting the present ROMP methodology.

Figure 2 shows selected (height and phase) AFM images of poly(**1**) (Table 1, run 6) on a mica substrate cast (spin-coated) from diluted THF solution. The observed spherical AFM images were good agreement with those observed in both TEM and STEM micrographs (even with diameters) and possessed controlled height (1.5−1.7 nm).[18] Taking into account the above results not only in the TEM and STEM micrographs but also in the AFM micrographs, it is thus clear that the resultant ROMP polymers possess spherical morphologies with controlled diameter and height under these diluted conditions.

We have demonstrated that a facile synthesis of "soluble" star shape polymers has been accomplished in a precisely

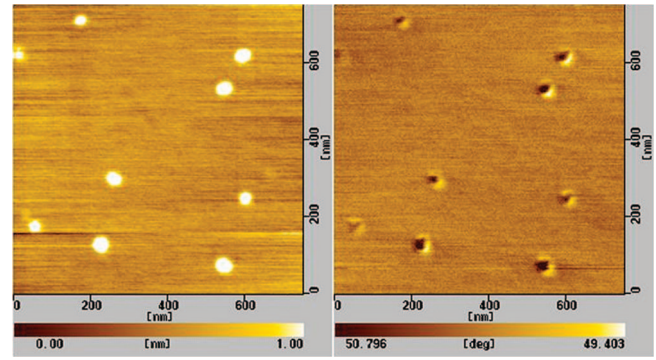

Figure 2. Selected (height and phase) AFM images of poly(**1**) (Table 1, run 6) on mica substrate cast (spin-coated) from THF solution (0.1 mg/mL).[18]

controlled manner by adopting the living ROMP technique using the molybdenum−alkylidene initiator via the "core-first" approach by simple sequential additions of norbornene and the cross-linker. The present approach also enables us to introduce functionalities at the polymer chain end (into the star polymer surface) exclusively. We thus believe that the method would provide a new efficient synthetic methodology in a better controlled manner via the "core-first" approach, and various applications are possible by varying norbornene derivatives (main chain) as well as substituted aldehyde (end group). We are now exploring more details including synthesis of "sugar-coated" star (ball) shape polymers as one of the promising application[12b,d,f] as well as recyclable spherical supported catalysts for efficient organic transformations.[12c,e]

A facile, precise synthesis of "soluble" star (ball) shape polymers has been accomplished by adopting sequential living ring-opening metathesis polymerizations (ROMP) of norbornene and cross-linking reagent using the molybdenum−alkylidene initiator via the "core-first" approach. The resultant ROMP polymers possessed uniform molecular weight distributions, and their spherical images with controlled diameters/height were confirmed in their TEM, STEM, and AFM micrographs.

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Supporting Information Available: Text giving (1) general experimental procedures, (2) additional polymerization results, (3)

additional data (selected GPC charts, ^{1}H NMR spectra), and (4) additional explanation including additional micrographs for the resultant polymers by TEM, STEM, AFM, and their data analyses. This material is available free of charge via Internet at http://pubs.acs.org.

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(15) Detailed experimental procedures, additional polymerizations results, and selected GPC charts are shown in the Supporting Information.

(16) Although we did not see any significant differences in both the M_n and M_w/M_n values by GPC (vs polystyrene standards) in the resultant polymers prepared for 5−20 min (5 min: $M_n = 3900$, $M_w/M_n = 1.14$; 10 min: $M_n = 4000$, $M_w/M_n = 1.14$; 20 min: $M_n = 3900$, $M_w/M_n = 1.16$), the ROMP of norbornene (NBE) with imperfect conversion (at the first stage) seems to be important for obtainment of soluble polymer with uniform distribution, This would be probably because that the subsequent (co)polymerization of (residual, small amount of) NBE and CL (affording relatively a large core) seems to be effective to improve the solubility and would lead uniform reactivity (of the propagating alkylidenes) in the subsequent ROMP (third polymerization forming NBE branching).

(17) As described in the text, the number of polymer chains (arms after third polymerization) may be simply assumed on the basis of observed increase in the M_n values [34 000 (by GPC vs polystyrene standards) from runs 4−9 (estimated from average M_n values)] and the M_n value of linear poly(NBE) [increasing 25 NBE repeating units, 2354 by molecular weight, and ca. 4000 (by GPC vs polystyrene standards) from ref 16]. The value (34 000/4000 = 8.5, total number of arms from first and third polymerization was assumed as 16−18) suggests that the resultant polymers are star polymers consisting of a core and NBE branching.

(18) Additional explanation including additional micrographs for the resultant polymers by TEM, STEM AFM, and data analyses are shown in the Supporting Information.

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