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Feature Article

Precise synthesis of polymers containing functional end groups by living ring-opening metathesis polymerization (ROMP): Efficient tools for synthesis of block/graft copolymers

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ABSTRACT

This article summarizes recent examples for precise synthesis of (co)polymers containing functional end groups prepared by living ring-opening metathesis polymerization (ROMP) using molybdenum, ruthenium complex catalysts. In particular, this article reviews recent examples for synthesis of amphiphilic block/graft copolymers by adopting transition metal-catalyzed living ROMP technique. Unique characteristics of the living ROMP initiated by the molybdenum alkylidene complexes (so-called Schrock type catalyst), which accomplish precise control of the block segment (hydrophilic and hydrophobic) as well as exclusive introduction of functionalities at the polymer chain end, enable us to provide the synthesis of block copolymers varying different backbones by adopting the "grafting to" or the "grafting from" approach as well as "soluble" star shape polymers with controlled manner. The "grafting through" approach (polymerization of macromonomers) by the repetitive ROMP technique offers precise control of the amphiphilic block segments.

1. Introduction

Precise control over macromolecular structure is a central goal in synthetic polymer chemistry. 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 both controlled molecular weights and narrow molecular weight distributions [1]. Copolymerization is an important method that usually allows the alteration of the (physical, mechanical, and electronic) properties by varying the ratio of individual components.

Amphiphilic block copolymers (ABCs), consisting of both hydrophilic and hydrophobic segments in the polymer molecules, display substantial prominence owing to their ability to exhibit unique structural characteristics such as formation of a diverse range of micellar aggregates (*e.g.* spheres, vesicles, rods, lamellae, etc.) in bulk or solution (in both aqueous and hydrophobic media) [1–5]. As described above, a precise control of the structure and the resulting material properties has been a central goal in the field of synthetic polymer chemistry, and considerable efforts have thus been devoted towards an accomplishment of the new synthetic methodologies for precise placement of the chemical functionality as well as for control over their molecular weight and composition. The unique architectural as well as functional control achieved during their synthesis, by tuning the initial building blocks, *i.e.*, hydrophobic/hydrophilic segments, results in the preparation of various well-defined phase-separated microstructures and nano architectures (spheres, rods, vesicles, lamellae, large compound micelles, nanofibers, nanotubes, etc.), which should offer possibilities of potential applications in pharmaceutical, biotechnological, and polymer sciences. Several variations on copolymer topology have thus been probed including linear [3–12] and double hydrophilic block copolymers [13], miktoarm star copolymers [14], graft copolymers [15–19], dendrons [20], and poly(macromonomer)s [21–25]. The use of polymeric micelle as nano vehicle is effective due to the core-shell morphology leading to the protection of an active agent in the core by the polymer shell, and has recently been exploited for the encapsulation of gold particles [26,27], hydrophilic biofunctional materials [28], hydrophobic anti-inflammatory agents [29], chemotherapeutics [30], and for other pharmaceutical applications [31–40]. The ability of ABCs to serve as delivery agents arises from their unique chemical structures wherein the hydrophobic core segment serves as a reservoir for hydrophobic

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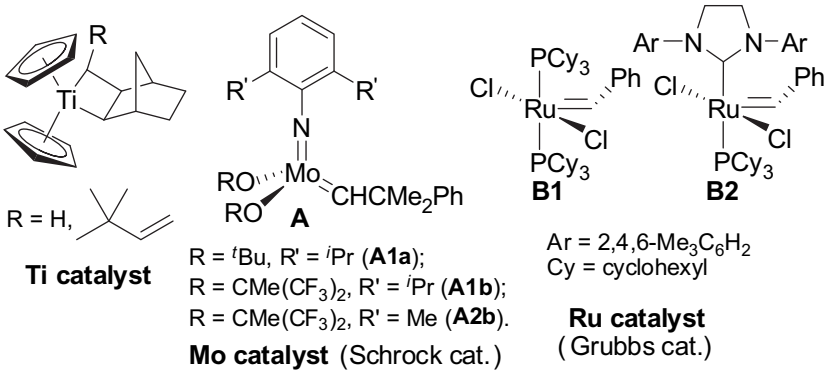


Chart 1. Typical transition metal complex catalysts employed for olefin metathesis.

substances upon micellization, which may be loaded by chemical, physical, or electrostatic means, depending on the specific functionalities of the core-forming block and the solubilizer. Therefore, the current research efforts aim at the preparation of micelles which are capable of responding to the environmental changes, while considerable success has been achieved using external stimuli such as pH [40–44], temperature [45,46], IR [47] and UV light [48] for implementing programmed functions that respond to the signatures *in vivo*.

1.1. Living ring-opening metathesis polymerization (ROMP)

Ring-opening metathesis polymerization (ROMP) has been considered to be a promising polymerization technique, because the resultant polymers possess rather linear structures compared to ordinary vinyl polymers such as poly(acrylamide)s [49]. This thus contributes to better maintain nature of the functionality at the side chain and the polymer chain end, because the functionality should not be (covered and) strongly affected by the polymer main chain. Transition metal carbene (alkylidene) complexes are known to play an essential role as the initiators for this polymerization (Chart 1) [50–54]. It has been well known that the molybdenum alkylidene complexes called Schrock type catalysts are useful initiators for the living ROMP of cyclic olefins, especially substituted norbornenes and norbornadienes (Chart 2) [55–60]. The absence of chain transfer (such as intermolecular/intramolecular metathesis with internal olefins) and termination (including catalyst deactivation) reactions in such polymerization systems allows synthesis of the homopolymers and the block copolymers with narrow molecular weight distributions, and precise control of the functionality in both the initiation and the termination sites can be thus possible (Scheme 1) [55–60]. Being a particularly powerful synthetic tool, the ROMP has found tremendous utility in preparing macromolecular materials displaying promising biological, electronic, and mechanical properties.

Note that the quantitative introduction of a reactive functionality into the polymer chain end can be easily achieved by adopting the living ROMP technique especially using the Schrock type molybdenum alkylidene initiator [7,12,21,61–65]. The exclusive preparation of end-functionalized ring-opened polymers (realized by a living polymerization with quantitative initiation) can be applied not only to prepare block copolymers (ABCs) coupled with another living polymerization techniques [66], but also for preparation of macromonomers, as described below. In contrast, the initiation efficiency is not always perfect as seen in the molybdenum alkylidene initiators, because dissociation of ligand (PR_3 etc.) should be required to generate the catalytically active species in the ROMP with the ruthenium carbene catalysts (Scheme 2) [67–69]. An equilibrium between coordination and dissociation of PR_3 should be present even in the propagation process, and replacement of halogen with the other anionic ligand (and/or replacement of PR_3 with the other neutral donor ligands/substrates) can also be considered as the probable side reactions. Importance of using the molybdenum catalysts should be thus emphasized for their precise preparations, although the initiators are highly sensitive to moisture and both monomers and solvent have to be thus strictly purified to avoid the catalyst decomposition (deactivation).

In this article, we thus introduce recent examples for precise synthesis of amphiphilic block/graft copolymers utilized by the living ROMP technique (via so-called “grafting from” and/or “grafting to” approach), and precise synthesis of graft copolymers, poly(macromonomer)s, by adopting the repetitive living ROMP

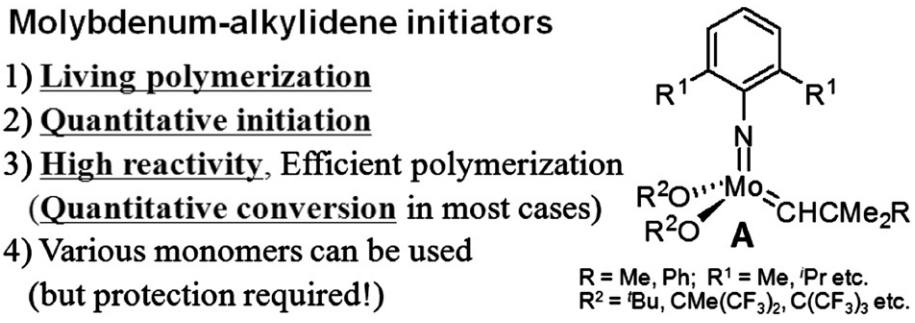
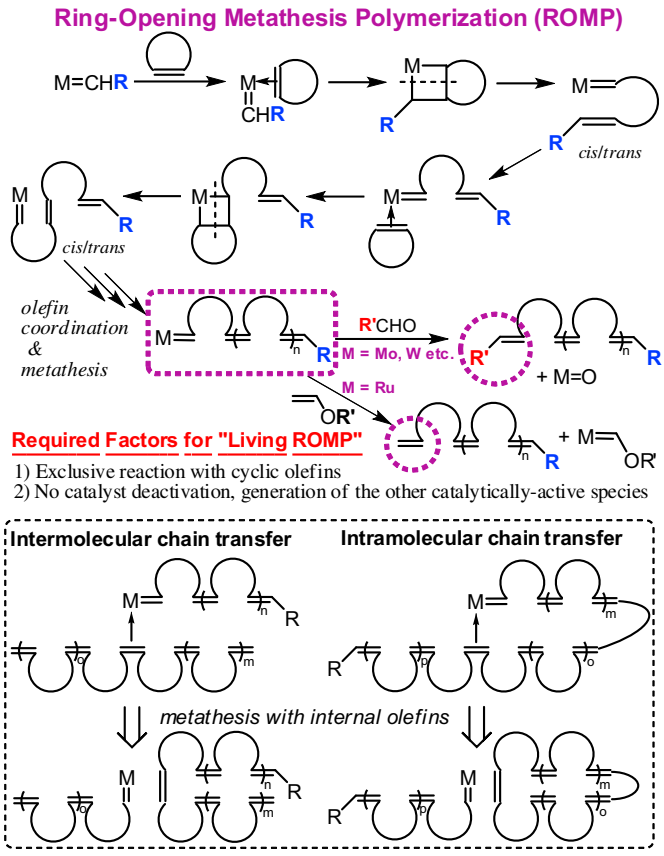


Chart 2. Summary of unique characteristics seen in molybdenum alkylidene complex (so-called Schrock) catalysts for ring-opening metathesis polymerization (ROMP).



Scheme 1. General scheme for ring-opening metathesis polymerization (ROMP).

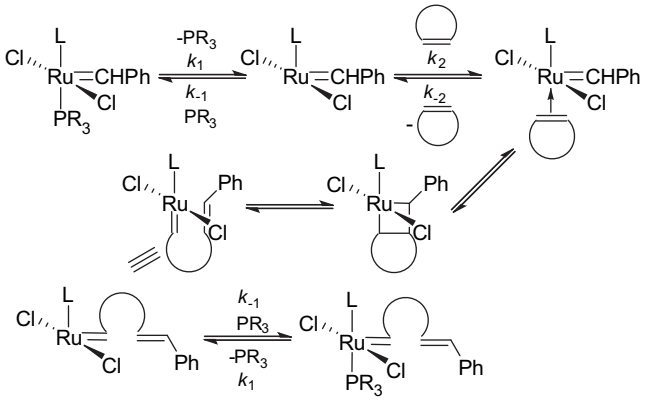
technique ("grafting through" approach) [70]. Moreover, we wish to introduce our recent example for facile synthesis of star shape polymers by adopting the living ROMP technique. Through these examples, we wish to introduce recent trend and update including explanation why the approach using the ROMP seems to be effective for this purpose.

2. Precise synthesis of amphiphilic block/graft copolymers utilized by the living ROMP techniques

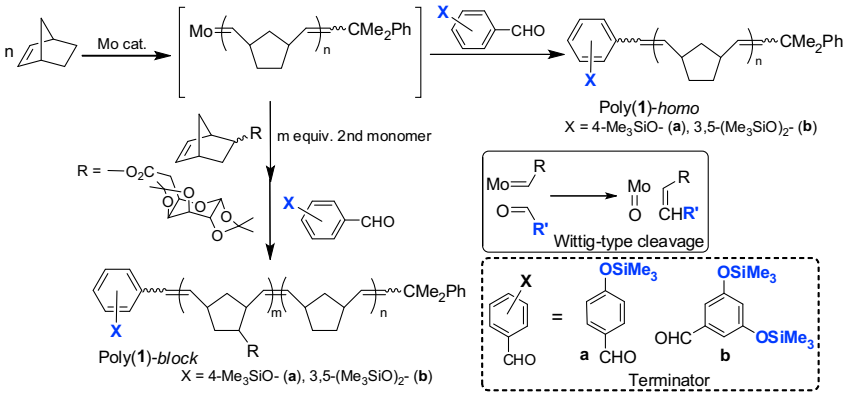
Living polymerizations, such as ring-opening metathesis polymerization (ROMP), group transfer polymerization, controlled radical polymerization, and anionic polymerization, generally provide synthesis of polymers with controlled molecular weights with narrow molecular weight distributions [1]. The unique characteristic features of living polymerization (appropriate initiation, moderate/fast polymerization rates, and the absence of undesirable side reactions such as chain transfer, termination, or cross-linking, branching) can also provide synthesis of well-defined block copolymers by simple sequential addition of monomers. However, due to the (severe) limitation of effective monomers that can be employed in certain living polymerization methods, development of a methodology for preparing two or more independent block by combination of different living polymerization techniques should expand the diversity of accessible block copolymers. Approach for the precise synthesis adopted by the above methodology can greatly expand a potential of the block copolymers, which can be achieved either by the end-functionalization of polymers with complementary groups [71,72] followed by their reaction/condensation ("graft-to approach", Section 2.1) or by accomplishing the transformation of the polymer chain end into an initiator for a different class of polymerization ("graft-from approach", Section 2.3).

2.1. Precise synthesis of amphiphilic block copolymers (ABCs) by grafting poly(ethylene glycol) to end-functionalized block ROMP copolymers

The examples of "grafting to" the ROMP polymer by reaction with another polymer chain end had been limited until recently,



Scheme 2. General scheme for generation of the catalytically active species in ring-opening metathesis polymerization (ROMP) by ruthenium carbene catalysts.



Scheme 3. End-functionalization of ring-opened poly(norbornene)s prepared by ROMP using the molybdenum alkylidene initiator (**A1a**) [7].

due to not only the difficulty in achieving the complete conversion, but also a concern for separation of the unreacted polymers by fractionation etc., as in a previous case, an excess amount of ω-aldehyde-functionalized polystyrene was used to terminate the living ROMP of norbornene [73].

We recently demonstrated a new synthetic methodology to prepare ABCs by adopting the "grafting to" approach [7], whereby poly(ethylene glycol) (PEG) is attached to the ROMP polymers. We herein summarize our results for synthesis of the various ABCs prepared by the living technique using the Schrock type molybdenum initiator [7,21].

A molybdenum alkylidene, [Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (**A1a**)], has been chosen as an initiator due to its ability to prepare multi-block copolymers in a precisely controlled manner [50–66]. Typical procedures for preparation of the end-fuctionalized ring-opened poly(norbornene)s are outlined in Scheme 3. Various block copolymers were prepared by sequential addition of norbornene and its sugar-containing derivative [1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-*O*-yl-5-norbornene-2-carboxylate, *endo*/*exo* = 87/13] (Table 1, run 5–11). The resultant carbohydrate-containing polymers are expected to exhibit strong specific affinity with cell surface proteins, most probably arising from the clustering and binding of the cells by multivalent arrays, thus leading to a greater affinity and specificity than their monovalent counterparts. Norbornene was polymerized in toluene at 25 °C with **A1a** at different monomer/initiator molar ratio and the termination was effected by addition of 4-Me$_3$Si-C$_6$H$_4$CHO and 3,5-(Me$_3$SiO)$_2$-C$_6$H$_3$CHO to afford poly(**1a**) and poly(**1b**), respectively, in high yield (>94%) (Table 1, run 1–4). This is an established procedure to perform the cleavage of the ROMP polymer-metal bonds as reaction of the Mo living ends with aldehyde yielding a carbon–carbon bond in a Wittig-like reaction.

Table 1
Ring-opening metathesis polymerization (ROMP) of norbornene and its carbohydrate derivative with Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (**A1a**) in toluene.[a] Preparation of homo and diblock copolymers, poly(**1**) [7].

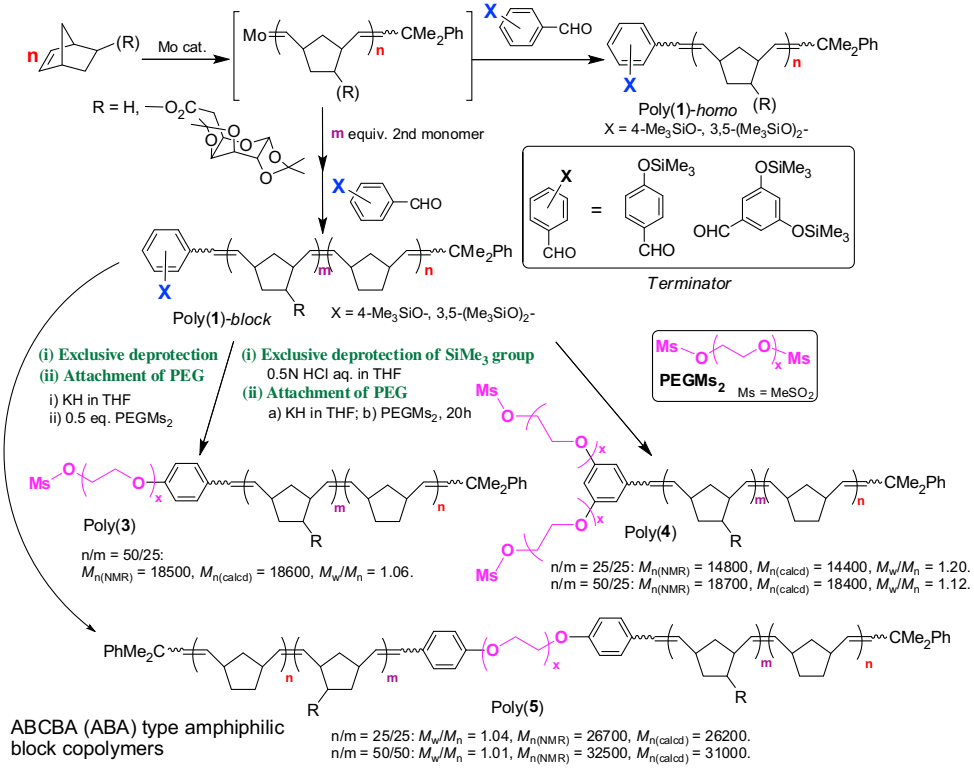
Run	n/m[b] 1st/2nd	time/min 1st/2nd	poly(**1**)	$M_n^c \times 10^{-4}$	M_w/M_n[c]	Yield[d], %
1	50/0	30/–	poly(**1a**)	1.03	1.08	99
2	50/0	30/–	poly(**1b**)	1.03	1.12	96
3	75/0	30/–	poly(**1a**)	1.38	1.1	94
4	100/0	30/–	poly(**1a**)	1.77	1.05	99
5	25/25	20/20	poly(**1a**)	1.53	1.11	99
6	25/25	20/20	poly(**1b**)	1.56	1.11	99
7	50/25	40/20	poly(**1a**)	1.88	1.07	96
8	50/25	40/20	poly(**1b**)	1.85	1.16	99
9	50/35	40/25	poly(**1a**)	2.10	1.09	99
10	50/40	40/30	poly(**1a**)	2.28	1.12	97
11	50/50	40/30	poly(**1a**)	2.37	1.31	96

[a] Polymerization conditions: in toluene, at room temperature (25 °C).
[b] Molar ratio based on Mo (shown in Scheme 3).
[c] GPC data in THF vs polystyrene standards.
[d] Isolated yield.

The M_n value of the ring-opened poly(norbornene)s, determined by GPC, increased linearly upon increasing the monomer/Mo molar ratios while the molecular weight distributions remained narrow (M_w/M_n = 1.05–1.12). The M_n values of the block copolymers also increased linearly upon increasing the added amount of the norbornene containing acetal-protected galactose, indicating livingness of the present polymerization.

The quantitative removal of SiMe$_3$ group of both the homopolymer and the block copolymer, poly(**1**), was achieved by treating the polymers with aqueous HCl solution, yielding the ROMP polymers carrying hydroxy functionality at the chain end, poly(**2**) (yield 91–99%, Scheme 4, and Table 2), whereas the cyclic acetal groups of the carbohydrate residue in the polymer remained intact under these weakly acidic conditions.

The hydroxy group at the polymer chain end in poly(**2a**) was treated with KH in THF, and its subsequent coupling with PEGMs$_2$ [MsO(CH$_2$CH$_2$O)$_n$Ms, Ms = MeSO$_2$] resulted in the diblock linear ABCs consisting of ring-opened poly(norbornene) and PEG, poly(**3**), in high yield (Scheme 4, Table 2). The GPC traces for the resulting poly(**3**) were unimodal and displayed appropriate increment in the M_n values (Fig. 1) with narrow molecular weight distribution in all cases (M_w/M_n = 1.06–1.12). In addition, the M_n values estimated by the ^{1}H NMR spectra (by the integration ratio of olefinic protons to those of PEG) were in good agreement with those calculated on the basis of monomer/initiator ratios. Following the same reaction sequence as described above, the hydroxy functionality at the diblock copolymer chain end in poly(**2a**) was condensed with PEGMs$_2$ to afford linear amphiphilic triblock copolymers, poly(**3**) [M_w/M_n = 1.06–1.22], in relatively high yields. Furthermore, triarm ABCs consisting of ring-opened poly(norbornene) and PEG, poly(**4**) (Scheme 4, Table 2) [M_w/M_n = 1.11–1.12], and those comprising diblock ROMP copolymers and PEG (ABC$_2$ type) poly(**4**) (Scheme 4, Table 2, runs 6 and 8) were synthesized in an analogous manner by the coupling of bi-functionalized ring-opened poly(norbornene)s, poly(**2b**), and diblock copolymers with PEGMs$_2$, respectively. Moreover, the reaction of poly(**2a**) with 0.5 equiv. of PEG in the presence of KH afforded ABA or ABCBA (sandwich) type amphiphilic multi-block copolymers, poly(**5**), in high yields (Scheme 4).



Scheme 4. Precise synthesis of linear, star shape, and ABA or ABCBA type amphiphilic block copolymers by grafting poly(ethylene glycol) (PEG) to end-functionalized block ROMP copolymers [7].

Amphiphilic polymeric architectures containing well-defined hydrophobic and hydrophilic segments form micelles in aqueous conditions, if the water content is equivalent to a given critical mass concentration (CMC). Since linear ABCs were known to be effective for the preparation of micelles, we explored the TEM micrographs of the resultant polymers (Fig. 1). Briefly, a solution of poly(**3**) (0.05 mg per mL THF, $M_n = 1.89 \times 10^4$, $M_w/M_n = 1.13$, prepared independently according to the analogous manner) was added into deionized water. The formed micelles, indicated by an increase in the solution viscosity, were quenched. After removal of THF, the sample was subjected to TEM and from the resulting micrographs (Fig. 1), core-shell structures were clearly visible, with prominent hydrophobic centers evident, due to the more sterically bulky "rod-type" poly(norbornene) based segment, in comparison to the "coil-type" PEG blocks. These micelles have a diameter of $d_{TEM} = 231.3 \pm 17.60$ nm, corresponding to a circumference of 727 nm. The diameters of the core and shell were

Table 2
Synthesis of amphiphilic block copolymers, poly(**3**,**4**) [7].

Run[a]	poly(**1**)	poly(**1**)			poly(**2**)			PEG	poly(**3**) or poly(**4**)				
		n/m[b]	$M_n \times 10^{-4}$ (GPC)[c]	M_w/M_n (GPC)[c]	$M_n \times 10^{-4}$ (GPC)[c]	M_w/M_n (GPC)[c]	Yield, %	M_n	$M_n \times 10^{-4}$ (calcd.)[d]	$M_n \times 10^{-4}$ (NMR)[e]	$M_n \times 10^{-4}$ (GPC)[c]	M_w/M_n (GPC)[c]	Yield[f], %
1	poly(**1a**)	50/0	1.03	1.08	0.99	1.09	98	2200	0.70	0.69	1.41	1.10	86
1	poly(**1a**)	50/0	1.03	1.08	0.99	1.09	98	4600	0.96	0.97	1.61	1.08	86
4	poly(**1a**)	100/0	1.77	1.05	1.82	1.05	98	2200	1.17	1.16	2.15	1.06	82
5	poly(**1a**)	25/25	1.53	1.11	1.47	1.08	95	4600	1.63	1.62	2.30	1.16	68
7	poly(**1a**)	50/25	1.88	1.07	1.92	1.07	98	4600	1.86	1.85	2.38	1.06	72
10	poly(**1a**)	50/40	2.28	1.12	2.25	1.11	99	4600	2.41	2.44	2.69	1.10	82
11	poly(**1a**)	50/50	2.37	1.31	2.42	1.29	98	4600	2.75	2.79	2.83	1.22	88
2	poly(**1b**)	50/0	1.03	1.12	1.02	1.06	96	2200	0.71	1.52	0.72	1.12	50
6	poly(**1b**)	25/25	1.56	1.11	1.42	1.09	91	2200	1.44	1.92	1.48	1.20	93
8	poly(**1b**)	50/25	1.85	1.16	1.91	1.17	97	2200	1.84	2.75	1.87	1.12	83

[a] Run no. in Table 1 (sample of ROMP polymer).
[b] Molar ratio based on Mo (shown in Scheme 3).
[c] GPC data in THF vs polystyrene standards.
[d] Calculated value based on initial feedstock ratio.
[e] Estimated by ^{1}H NMR spectra.
[f] Isolated yield.

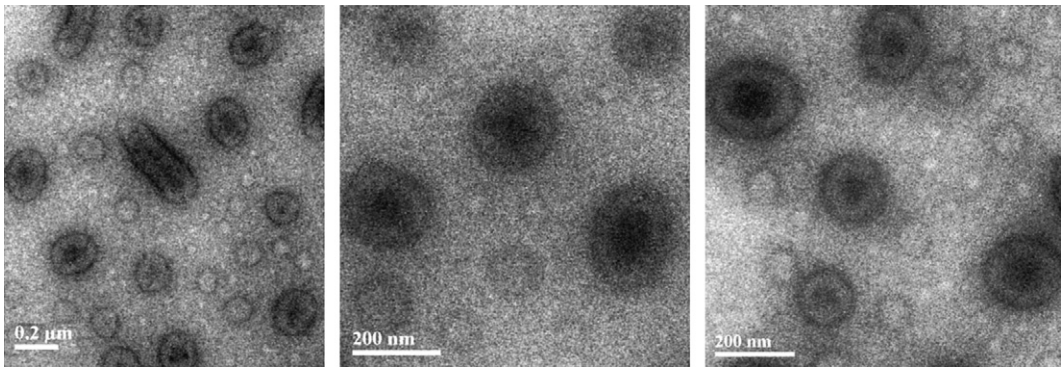
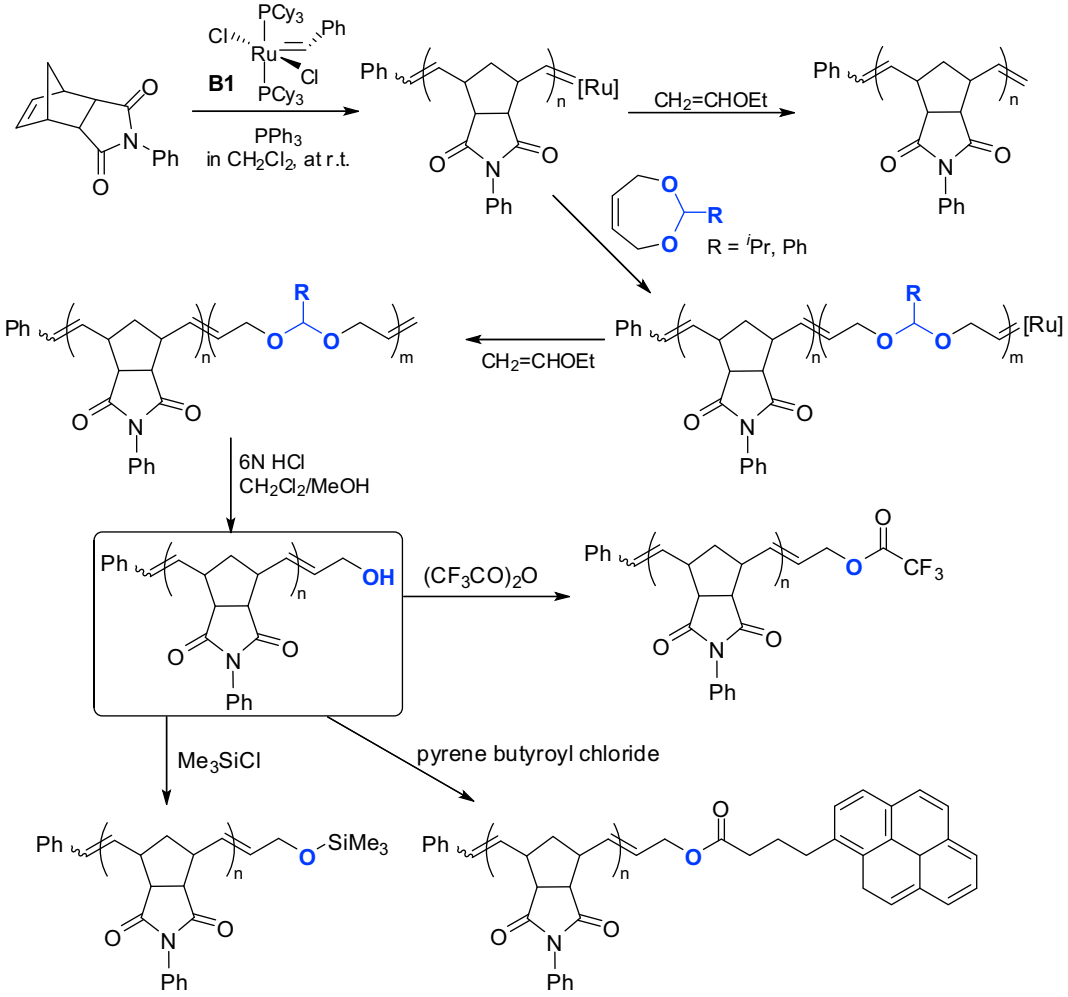


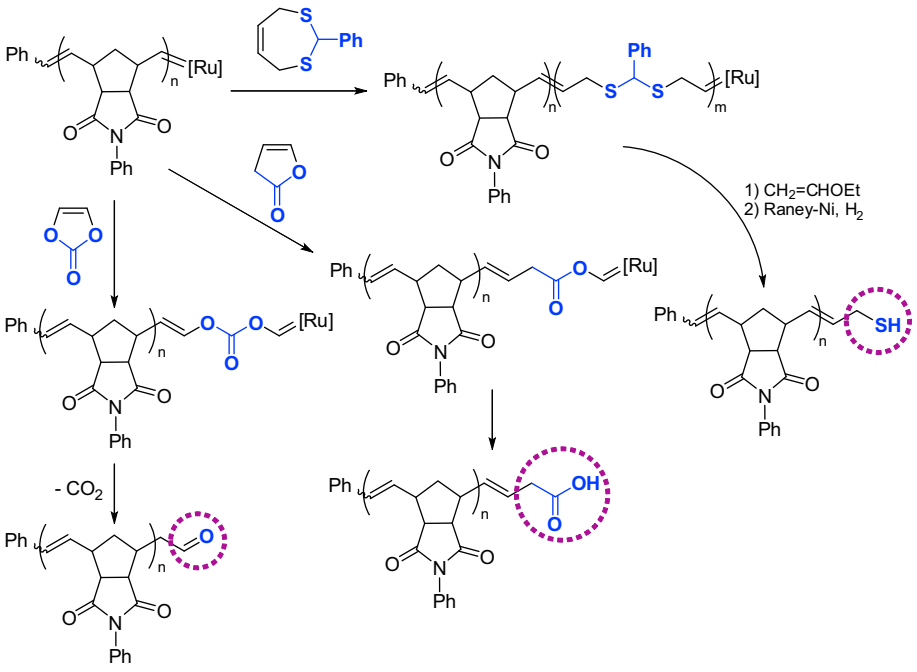
Fig. 1. TEM images of the spherical aggregates derived from the linear ABC (NBE_{20}-*b*-**a**$_{20}$)-*b*-PEG_{110} [poly(**3**), $M_n = 1.89 \times 10^4$, $M_w/M_n = 1.13$, prepared independently according to the analogous manner] at a concentration of 0.05 mg/mL-THF at varying magnification. Bar equivalent to 200 nm. White bright circles would be a TEM artifact formed after rapid evaporation of THF droplet (containing trace amount of 2,6-^{t}Bu$_2$-4-MeC_6H_2OH) *in vacuo* on copper grid covered with a perforated polymer film and coated with carbon [21]. Micrographs shown here are different from those introduced in the reference 21.

107.3 ± 13.8 nm and 123.9 ± 15.1 nm, respectively, the core occupying 44% of the micelle on average, which is excellent compared with the 40% calculated [21].

Cyclic acetals in the ABCs poly(**3**–**5**) could be selectively removed, without accompanying any ester-cleavages, by using a mixture of CF_3CO_2H and water (9/1 v/v) at room temperature (for 15 min), as reported previously [12]. These methods hydrolysis procedures are well established and the isolated yields were high. The deprotected polymers were identified by NMR and FT-IR spectra, and the integration ratios estimated from the ^{1}H NMR spectra for PEG/sugar/ring-opened NBE protons of the resultant polymers were very close to the



Scheme 5. Synthesis of ROMP polymers containing hydroxyl group via "sacrificial synthesis" approach [74,75].



Scheme 6. Syntheses of end-functionalized ROMP polymers via "sacrificial synthesis" approach (2) [78].

calculated values [7]. Since precise control of the repeat units of both norbornene (hydrophobic) and the sugar-substituted norbornene derivatives (rather hydrophilic after deprotection) as well as the attached PEG (hydrophilic) could be possible by using this approach, it can thus be concluded as a promising technique for the preparation of new types of ABCs consisting of ROMP and PEG units in a precise fashion.

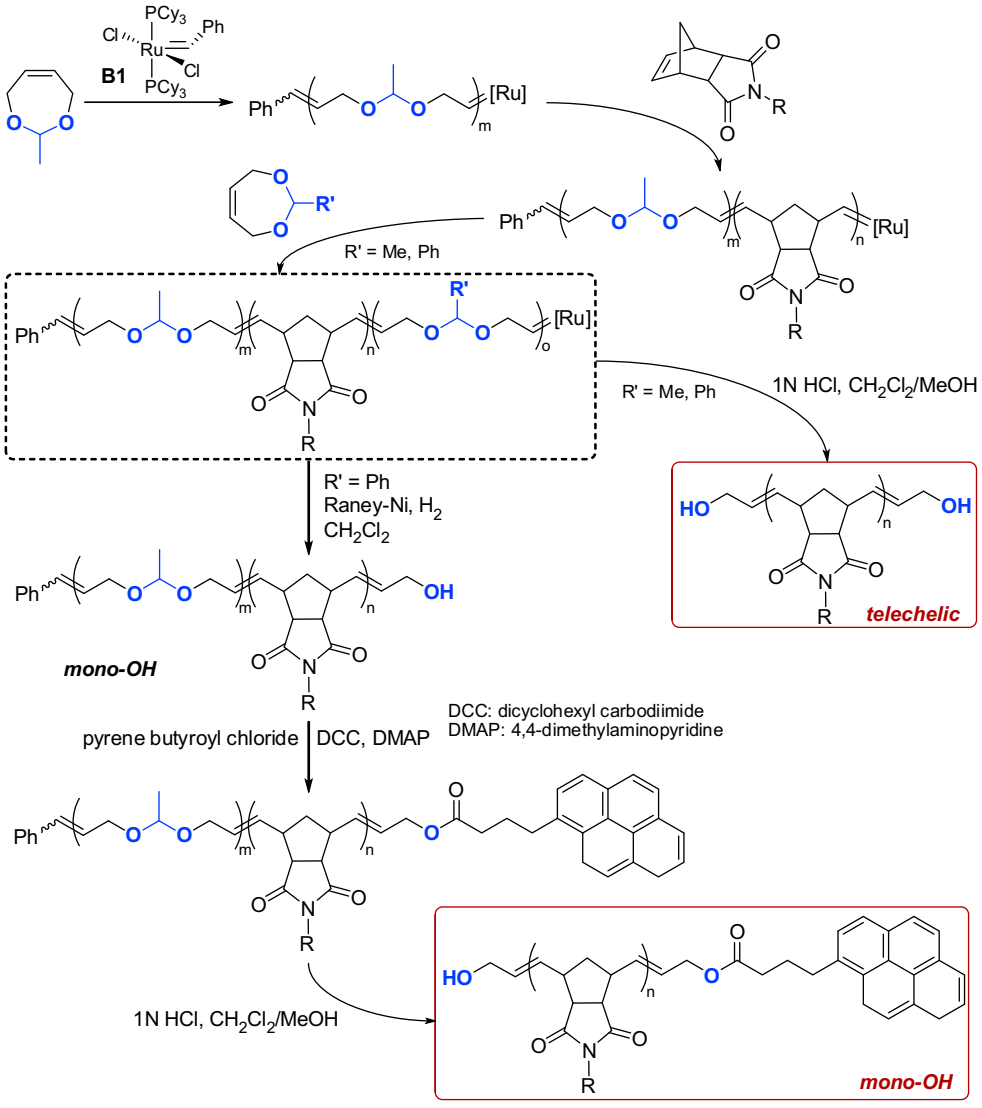
As demonstrated above, a precise control of the amphiphilic block segments in linear (AB or ABC type), triarm (AB_2 or ABC_2 type), and sandwich (ABA or ABCBA) type polymeric architectures can be achieved by grafting PEG to the chain end of the living ROMP polymer. Taking into account these facts, the exhaustive control over functionality placement, molecular weight and polydispersity of the polymers, can be attained through the ROMP technique using the molybdenum alkylidene initiator, followed by the quantitative attachment of PEG, this approach is expected to serve as an efficient synthetic methodology for the precise designing of unique polymeric architectures for desired properties.

2.2. Synthesis of amphiphilic block copolymers (ABCs) by sequential addition of cyclic monomers in the ROMP: an effective methodology for introduction of functional groups in the polymer chain ends via sacrificial approach

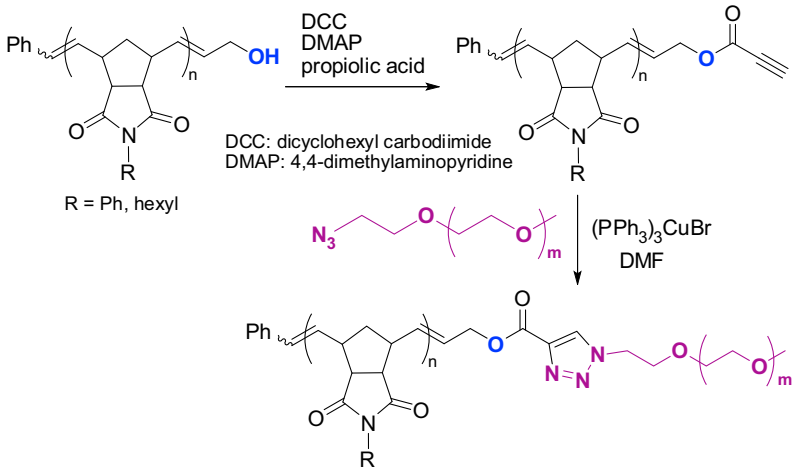
Hydroxy-functionalized ROMP polymers prepared by the ruthenium catalyst was recently demonstrated by Kilbinger et al. so-called "sacrificial synthesis" route [74,75]. The synthetic strategy adopted is shown in Scheme 5, and the route consists of (i) synthesis of diblock copolymers by sequential addition in the living ROMP, and (ii) subsequent treatment of conc. HCl (in $MeOH/CH_2Cl_2$) to cleave the olefinic acetal groups in the second block segment. Due to that the polymerization should proceed in a living manner, both $Ru(CHPh)(Cl)_2(PCy_3)_2$ (**B1**) and *exo-N*-phenylnorbornene-2,3-dicarboximide were chosen according to the previous report [76]. Diblock copolymers were obtained by subsequent addition of dioxepine monomer, and the second polymer block was then decomposed under acidic conditions: PPh_3 was added *in situ* to improve the efficiency and substituent in the dioxepine was important for the efficient synthesis [75]. The presence of the hydroxyl group was confirmed by introduction of $SiMe_3$ group etc. (Scheme 5) [74]. Although the procedure seems apparently tedious compared to the approach by the molybdenum system (simple termination by addition of functionalized aldehyde) and the application may be limited, as shown below, the approach enables us to prepare hydroxyl telechelic polymers in an efficient manner [77] that seems difficult to achieve by adopting the ROMP using the molybdenum system.

The similar approach by adopting for synthesis of thiol-functionalized ROMP polymers by employing thioacetal monomers in place of dioxepine monomer, which can be then cleaved by hydrogenation (by Raney Ni) leaving the desired thiol group behind (Scheme 6) [78]. Moreover, facile end-capping technique for ROMP with living ruthenium carbene chain ends without further chemical transformation steps could be achieved, when vinylene carbonate and 3H-furanone are introduced as the termination agents (Scheme 6). Efficient synthesis of ROMP polymers containing aldehyde or carboxylic acid end groups could be thus achieved by this new method, which involves the decomposition of acyl carbenes to ruthenium carbides. The high degrees of chain end functionality obtained are supported by ^1H NMR spectroscopy, MALDI-TOF mass spectrometry, and end-group derivatization [79].

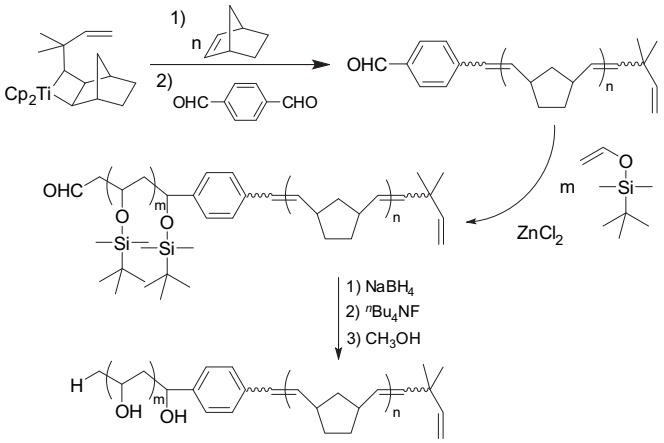
Synthesis of telechelic ROMP polymers containing two hydroxyl groups at the chain ends was achieved by adopting a route shown in Scheme 7 [77]. The route consists of (i) synthesis of triblock copolymers by sequential addition in the living ROMP, and (ii) subsequent treatment of HCl (in $MeOH/CH_2Cl_2$) to cleave the olefinic acetal groups. Introducing cleavable monomers (cyclic acetals, R' = Me, Ph) that can be addressed separately, sequential deprotection was accomplished



Scheme 7. Synthesis of telechelic polymers by '*sacrificial synthesis*' approach [77].



Scheme 8. Synthesis of amphiphilic block copolymers adopted by click chemistry approach [80].



Scheme 9. Pioneering examples for transformation of ROMP propagating titanium species for synthesis of various block copolymers [84,85].

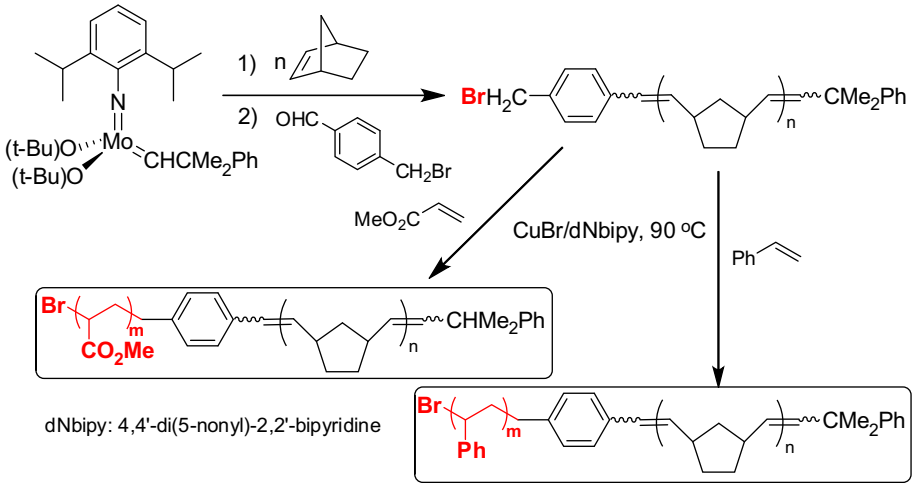
affording polymeric materials bearing different substituents at their respective chain ends. The resultant polymers possessed relatively narrow molecular weight distributions, but the resultant telechelic polymer contained small amount of mono functionalized ROMP polymers probably due to "incomplete initiation" by **B1** under these conditions. The resultant polymers after hydrogenation with Raney Ni and subsequent introduction of pyrene moiety, deprotection under acidic conditions consisted of mono functionalized ROMP polymer (mono hydroxyl group and pyrene moiety) and small amount of the other ROMP polymers (mono hydroxyl group and phenyl group), probably due to incomplete initiation at the first step (Scheme 7) [77]. Although the approach seems highly promising, it seems difficult to prepare the desired ROMP polymers with exclusive selectivity under these conditions (and more precise optimization should be required).

Synthesis of linear amphiphilic block copolymers (ABCs) consisting of ring-opened poly(norbornene) and PEG were also demonstrated by Kilbinger et al. [80], by adopting a route shown in Scheme 8 by treating the hydroxyl group via convergent 'click chemistry' approach. The resultant polymer showed multimodal molecular weight distributions probably due to that yields in each reaction steps were not exclusive: a GPC trace after the separation by preparative GPC contained low molecular weight shoulder peak.

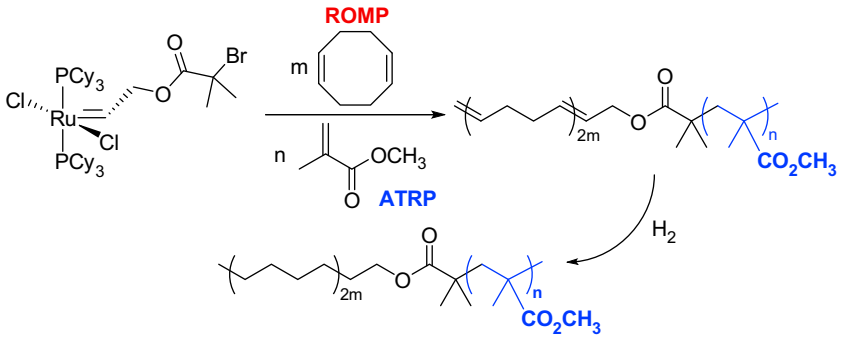
2.3. Precise synthesis of amphiphilic block/graft copolymers by combination of ROMP with other living polymerization techniques

Monomers that can be employed for the living ROMP are limited to highly strained cyclic olefins such as norbornene, norbornadiene, dicyclopentadiene, etc., because the driving force is to release the ring strains [81]. The range of attainable block copolymers would be thus greatly extended, if a methodology for synthesis of block copolymers by coupling with another living polymerization, by which the mechanism of the propagation is changed to the one best suited for the propagation of the second monomer, can be achieved [66,82,83].

As the pioneering efforts to this approach, the methods consisting of the living ROMP coupled with the other living polymerization techniques were explored. Risse and Grubbs demonstrated a route to prepare the well-defined AB diblock copolymers by combining olefin metathesis polymerization and aldol condensation polymerization through a transformation of the metathesis-active end group into an initiator for the aldol-group-transfer polymerization (aldol-GTP). Moreover, the chemical modification of the second block endowed



Scheme 10. Transformation of propagating species: ROMP to ATRP (Atom Transfer Radical Polymerization) [86].



Scheme 11. Synthesis of amphiphilic block copolymers, poly(ethylene-*bl*-MMA), by one pot synthesis by combination of ROMP and ATRP using multifunctional ruthenium catalyst [87].

the block copolymer with the unique feature of amphiphilicity (Scheme 9) [84,85].

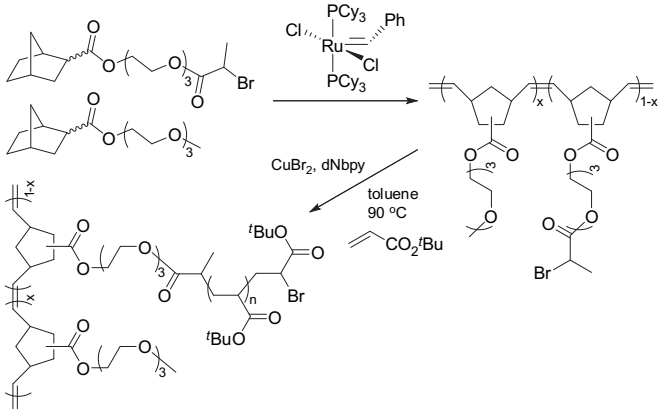
Matyjaszewski et al. reported in the late 90's the first example of transformation involving the living ROMP and the controlled "living" atom transfer radical polymerization (ATRP) for synthesis of the block copolymers of norbornene and dicyclopentadiene with styrene and methyl acrylate (Scheme 10) [86]. A well-defined molybdenum alkylidene initiator, $Mo(CHCMe_2Ph)(NAr)(O^tBu)_2$ (**A1a**, Ar = 2,6-$^iPr_2C_6H_3$), was employed to conduct the living ROMP and subsequent termination with *p*-(bromomethyl) benzaldehyde affording formation of the efficient macro-initiators for homogeneous controlled/living ATRP of styrene and methyl acrylate, catalyzed by CuBr and 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbipy).

Grubbs et al. reported one pot 'tandem' synthesis of amphiphilic block copolymers by combination of living ROMP and ATRP using a multifunctional ruthenium catalyst (Scheme 11) [87]. This is because that $Ru(CHPh)(Cl)_2(PCy_3)_2$ (**B1** in Chart 1) is known to be an effective catalyst not only for the ROMP but also for the ATRP of methyl methacrylate (MMA) [88,89]. Although the molecular weight distributions in the resultant copolymer were rather broad ($M_w/M_n = 1.5–1.6$) due to that the ROMP of 1,5-cylooctadiene afforded poly(butadiene)s with broad molecular weight distributions ($M_w/M_n = 2.0$), they confirmed that the resultant copolymers are real diblock copolymers, poly(butadiene-*bl*-MMA)s. The ruthenium complex can also be used as the hydrogenation catalyst, and poly (ethylene-*bl*-MMA) could be thus prepared in the present tandem system by adopting the multifunctional ruthenium catalyst [87]. Since then the versatile combination of living polymerization techniques of ROMP and ATRP for synthesis of block copolymers has been employed by several other research groups, as described below [15,66,87,89–99].

2.3.1. *Selected examples for synthesis of graft copolymers by combination of ROMP with other living polymerization techniques*

The above methodology (combination of ROMP with the other living polymerization technique like ATRP) was applied to prepare amphiphilic polymer brushes (graft copolymers) [92–99]. For example, Weck et al. reported synthesis of poly(norbornene-*gr*-acrylic acid) by combination of ATRP and ROMP as shown in Scheme 12 [99]. ROMP of norbornene derivatives using $Ru(CHPh)(Cl)_2(PCy_3)_2$ (**B1** in Chart 1) afforded polymers with relatively narrow molecular weight distributions. However, the subsequent ATRP of *tert*-butyl acrylate using CuBr-dNbipy in toluene afforded polymers with broad molecular weight distributions (Table 3) [99], suggesting that certain degree of chain transfer and/or termination reaction accompanied under these conditions [99]. Most probable reason to explain the above fact would be due to coupling of propagating radicals, although the content of radicals should be controlled via equilibrium between active and dormant species. The fact introduced a utility of combination of these two highly controlled polymerization methods which allows for a modular approach toward the synthesis of graft copolymers, since the backbone length, the graft density, and the graft length can be varied in a highly controlled manner.

Since, as demonstrated above [87], $Ru(CHPh)(Cl)_2(PCy_3)_2$ is an effective catalyst not only for the ROMP but also for the ATRP of methyl methacrylate (MMA) [87,88], one pot tandem synthesis of graft copolymers by controlled ROMP and ATRP was reported by Novak et al. (Scheme 13) [98]. The resultant copolymers



Scheme 12. Synthesis of poly(norbornene-*graft*-*tert*-butyl acrylate)s via a combination of ATRP and ROMP [99].

Table 3
Synthesis of graft copolymers of poly(norbornene)s/poly(*tert*-butyl acrylate) (Scheme 12) [99].

poly(norbornene)s			poly(*tert*-butyl acrylate) graft copolymers	
/mol-% init.[a]	M_w[b] $\times 10^{-4}$	M_w/M_n[b]	M_w[b] $\times 10^{-4}$	M_w/M_n[b]
4.9	2.3	1.29	17.0	1.67
9.6	2.5	1.32	18.1	1.72
19.6	2.4	1.31	16.2	1.68

[a] Mole % initiator as determined by ^{1}H NMR spectroscopy.
[b] M_w and PDI values determined by GPC vs. polystyrene standards in CH_2Cl_2.

also possessed broad molecular weight distributions ($M_w/M_n = 1.67–1.89$), and no trace of the homo-ROMP or homo-PMMA polymers was present when the initiator concentration was controlled at least 0.04 M. The conversion of MMA is not complete after 24 h (at 65 °C), and the MMA consumption was found to be a first-order kinetic process, which indicated the absence of chain termination, the major problem often encountered in radical polymerizations [98]. The results thus suggest that the methodology, one pot synthesis approach for the preparation of graft copolymers based on a ROMP skeleton with PMMA grafts using a single catalyst, relies on the controlled activity of $Ru(CHPh)(Cl)_2(PCy_3)_2$ for two distinct polymerization processes with the selected monomer structures.

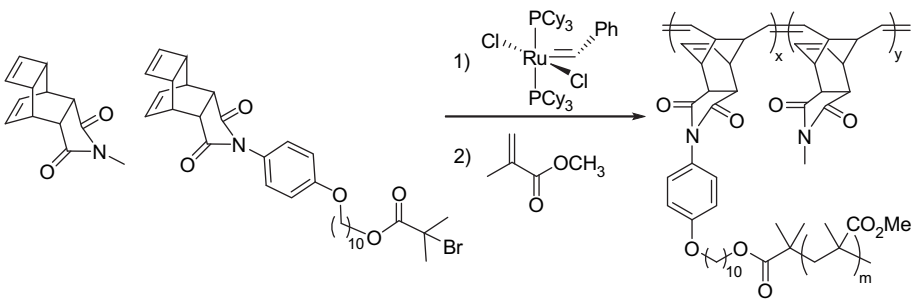
Fontaine et al. reported synthesis of polybutadiene-*gr*-[polystyrene-*bl*-poly(acrylic acid)] copolymers by ROMP of α-cyclobutenyl macromonomers prepared by ATRP using a cyclobutenyl-functionalized initiator [95]. Synthesis of cyclobutenyl macromonomers prepared by ATRP possessed narrow molecular weight distributions, however, the attempted polymerization of macromonomer ($M_n = 4300$, $M_w/M_n = 1.17$) using another (more active) ruthenium catalyst (**B2** in Chart 1, macromonomer/Ru = 10, molar ratio) afforded polymer that possessed rather high molecular weight with rather broad molecular weight distribution ($M_n = 8200$, $M_w/M_n = 1.21$). The result, however, clearly suggests that the ROMP of the macromonomer did not proceed into completion.

Similar to the methodology reported by Novak et al. [98], which $Ru(CHPh)(Cl)_2(PCy_3)$ is an effective catalyst not only for the ROMP but also for the ATRP of methyl methacrylate [87–89], Wooley et al. also demonstrated a facile one pot synthesis of the polymer brushes, by tandem catalysis using a Grubbs' catalyst that is effective for both ROMP and ATRP (Scheme 14) [96]. After separation of low molecular weight polymers (oligomers) using column chromatography (silica, and alumina), the resultant brush polymer macromolecules essentially presented as unimolecular nanoparticles on the surface, measured by tapping-mode atomic force microscopy (AFM). These nanoparticles exhibited ellipsoidal shapes with variable sizes, in agreement with the limited length ratio of the backbone to grafts and somewhat broad molecular weight distributions ($M_n = 5.21 \times 10^5$, $M_w/M_n = 1.45$; $M_n = 9.99 \times 10^5$, $M_w/M_n = 1.67$), and their surface aggregation behaviors are dependent upon the solvent and concentration employed.

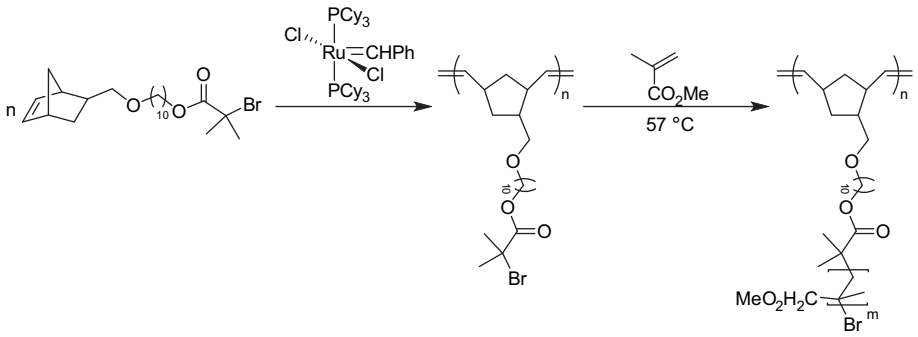
The polymerization methodology was applied to synthesis of core-shell brush copolymers by combination of ROMP and NMP (nitroxide-mediated polymerization), as shown in Scheme 15 [100]. The subsequent NMP using the nitroxide and isoprene (and careful repetitive precipitation using a mixed solution of MeOH–THF for separation) afforded polymer brushes consisting of poly(norbornene)s containing poly(isoprene) side arms with narrow molecular weight distributions [starting macro-initiator: $M_{n(GPC)} = 1.22 \times 10^5$, $M_w/M_{n(GPC)} = 1.13$; polymer brush: $M_{n(GPC)} = 3.66 \times 10^5$, $M_w/M_{n(GPC)} = 1.19$], although degree of grafting (isoprene repeating units) seems low ($DP_n = 18.1$ by GPC, 20.1 by NMR). The subsequent NMP using the nitroxide and *tert*-butyl acrylate followed by flash chromatography (eluting with 10% CH_2Cl_2-hexane) afforded core-shell brush copolymer with narrow molecular weight distribution [$M_{n(GPC)} = 1.41 \times 10^6$, $M_w/M_{n(GPC)} = 1.23$; $DP_n = 41$ by GPC, 39 by NMR]. Although the procedure requires rather tedious separation process in each step and the conversions for grafting were low (conversion of isoprene, *tert*-butyl acrylate for grafting were 1.30, 2.25%, respectively), poly(macromonomer)s with unimodal molecular weight distributions were obtained. The amphiphilic core-shell brush polymer was then obtained by hydrolysis using HCl solution of 10% water-*p*-dioxane (Scheme 15, last step) [100]. These polymer brushes before/after hydrolysis exhibited aggregated structures on mica but presented as collapsed, globular micelles on silicon, as detected by AFM measurement. A peripherally cross-linked brush copolymer was then prepared by treating with 2,2-(ethylenedioxy)bis(ethylamine) and 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide [100].

One pot synthesis of core-shell polymer brushes was also demonstrated by Wooley et al., adopted by combination of ROMP and RAFT (reversible addition-fragmentation chain transfer), as shown in Scheme 16 [101]. After separation of low molecular weight polymer (oligomer) by column chromatography, the resultant polymer possessed rather narrow molecular distribution [$M_{n(GPC)} = 1.20 \times 10^6$, $M_w/M_{n(GPC)} = 1.32$]. Although the method requires a separation procedure, the methodology would be emphasized as a convenient method to prepare various amphiphilic poly(macromonomr)s, polymer brushes in a controlled repeated units.

In contrast to the methodologies by combination of ROMP with ATRP, NMP, RAFT, Feast and Khosravi presented an integration of anionic polymerization (AP) with ROMP leading to the synthesis of quite well-defined, narrow-distribution diblock copolymers,



Scheme 13. One pot tandem synthesis of graft copolymers by controlled ROMP and ATRP reported by Novak et al. [99].

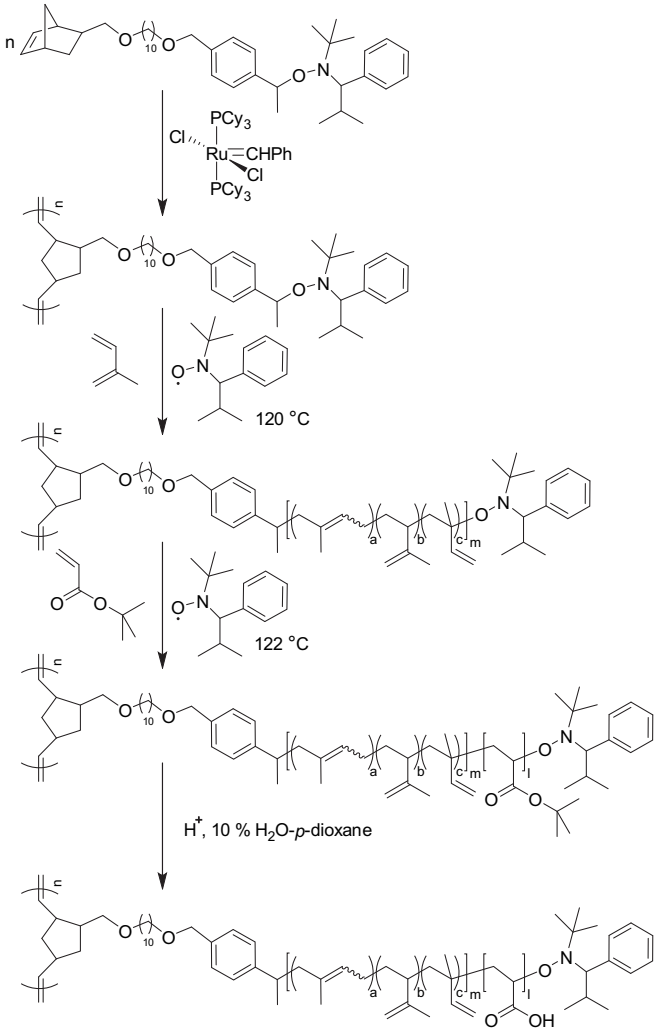


Scheme 14. One pot tandem synthesis of graft copolymers by controlled ROMP and ATRP reported by Wooley et al. [96].

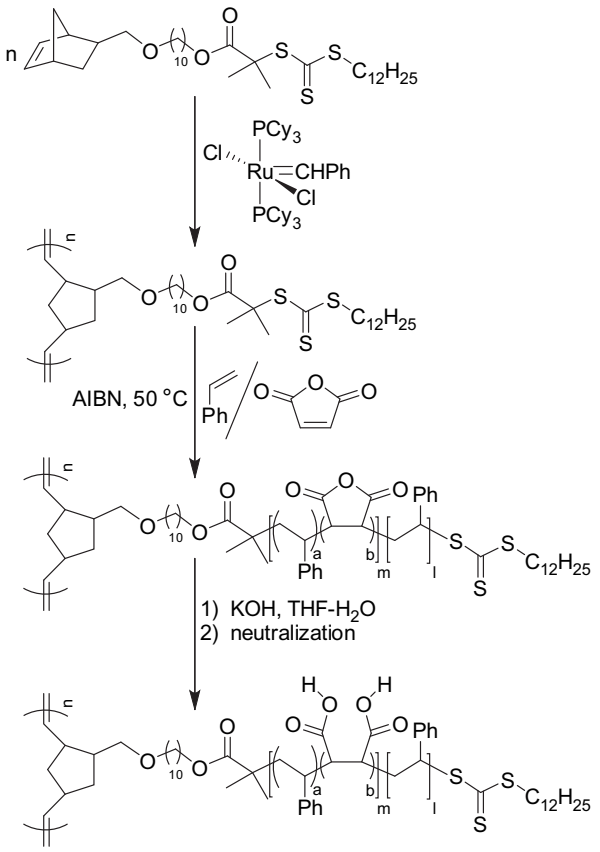
whereas norbornene macromonomer containing polystyrene polymerized by anionic manner were polymerized by ROMP using well-defined molybdenum alkylidene initiators (Scheme 17) [102,103]. The methodology was applied to prepare amphiphilic poly(macromonomer)s (Scheme 18), ring-opened poly(norbornene)s containing poly(styrene-*bl*-ethylene oxide) [104]. Incorporation of styrene repeat units are important to avoid strong interaction between molybdenum and oxygen in PEO [poly (ethylene oxide)] [105].

3. Precise synthesis of block/graft copolymers by the repetitive living ROMP approach: living ROMP of norbornene macromonomers

Poly(macromonomer)s (PMMs) containing ABCs in the side chain are of particular interest not only due to the axisymmetric distribution of the side chains from the central polymeric backbone but also because of their ability to exhibit interesting (spherical, cylindrical, star, and worm-like) morphologies in bulk



Scheme 15. Synthesis of graft copolymers by controlled ROMP and NMP reported by Wooley et al. [100].



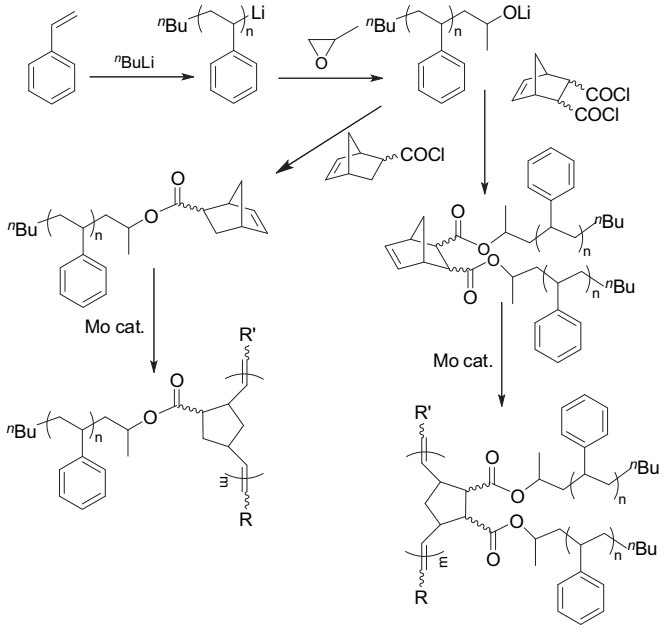
Scheme 16. Synthesis of graft copolymers by controlled ROMP and RAFT reported by Wooley et al. [101].

and solution, which are prone to the variation of the side chain and backbone composition [106–109]. The preparation of amphiphilic PMMs bearing carbohydrates has potential for improved targeting, recognition, and modulation of cell surface processes [110–112]. The increased density of the sugar moieties and the ability to mediate protein–carbohydrate interactions in three dimensions should confer the PMMs with improved properties in comparison with those of the corresponding monovalent or linear polyvalent displays of carbohydrates, as reported previously [113,114]. There have been several reports concerning the synthesis of PMMs by radical [115–119], anionic [120], and metallocene-catalyzed polymerizations [121–124]. We have demonstrated the preparation of amphiphilic PMMs via repetitive ROMP, and this technique allows precise control of the degree of polymerization of the side chain with complete macromonomer conversion [62]. We have recently extended this strategy by incorporating sugar-containing norbornene derivatives, and efficient preparation of PMMs containing acetal/acetyl-protected sugars has been carried out via repetitive living ROMP [21,61].

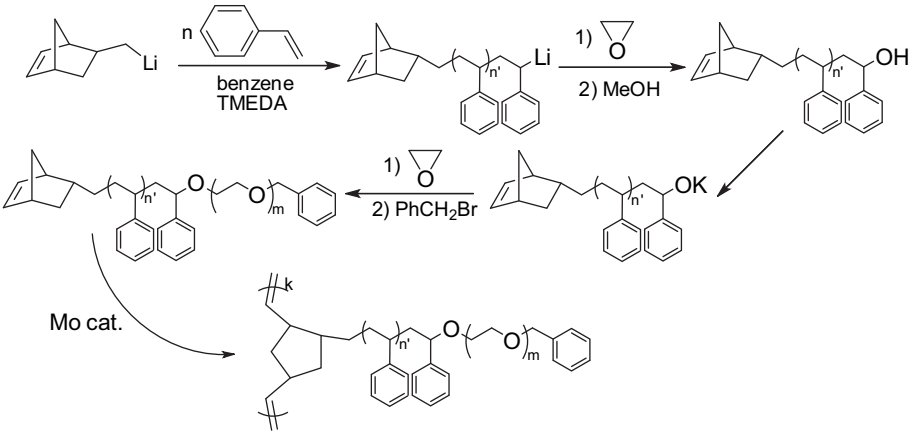
The molybdenum alkylidene catalysts by Schrock [55–60] have proven to be powerful synthetic tools as they facilitate living polymerization affording the precise polyvalent arrangements containing a variety of functionalities [7,12,125–128]. We thus focused on the repetitive ROMP technique using well-defined molybdenum alkylidene initiators of the type, $Mo(CHCMe_2Ph)(NAr)(OR)_2$ (**A**, Chart 1) [55–60]. The macromonomer preparation encompassed the following three key steps: (i) exclusive end-capping of block/homo-ROMP (co)polymer with TMS ($SiMe_3$) protected 4-hydroxybenzaldehyde; (ii) quantitative removal of the TMS moiety to generate OH group on the terminus [7,21,61,62], and (iii) through esterification of the terminal OH group with norbornene carboxylic acid chloride [21,61,62], [ex. poly(**6**) in Scheme 19].

Various poly(macromonomer)s, composed of ring-opened poly(norbornene) backbone and their substituted analogues in the side chain [poly(**A**)–(**D**), Chart 3], have been prepared efficiently by using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)[OCMe(CF_3)_2]_2$ (**A1b**), an effective initiator in order for the polymerization to proceed with complete conversion in a controlled manner [*e.g.*, poly(**7**) in Scheme 19].

Note that synthesis of various amphiphilic poly(macromonomer)s can be achieved via both the homopolymerization of macromonomers containing amphiphilic segments [poly(**A**) &



Scheme 17. Synthesis of comb and graft copolymers containing polystyrene. Combination of ROMP and anionic polymerization [102,103].

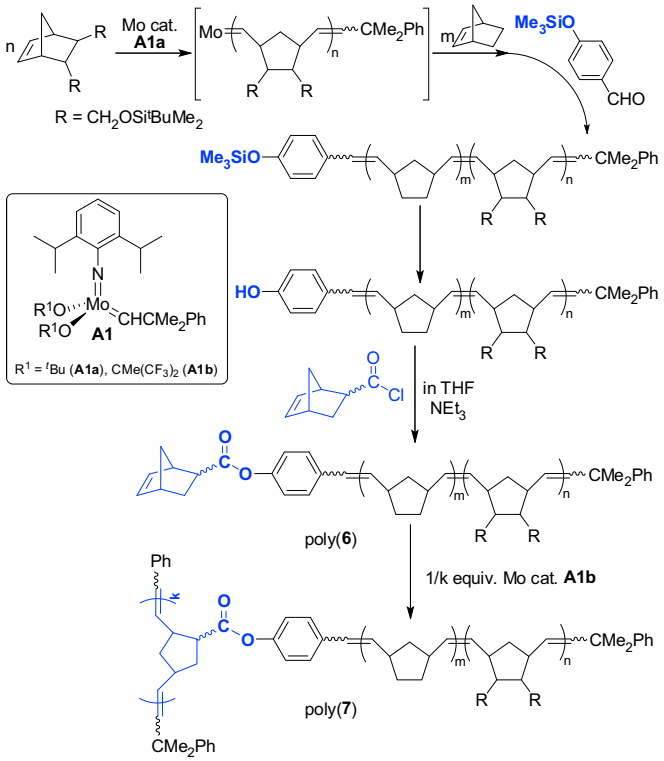


Scheme 18. Synthesis of amphiphilic comb and graft copolymers containing polystyrene and poly(ethylene oxide) segments. Combination of ROMP and anionic polymerization [104,105].

poly(**B**) in Chart 3] and block copolymerization by sequential addition of different macromonomers [poly(**D**)] or substituted norbornene and macromonomers [poly(**C**)] [62]. Since use of the molybdenum alkylidenes allows the precise control of the repeating unit as well as the block segment, the present synthetic approach seems to be of particular significance/quite promising for synthesis of a variety of functional group-containing poly (macromonomer)s, especially for precise synthesis of amphiphilic poly(macromonomer) architectures.

It is generally known that first-order relationships between the propagation rates and the monomer concentrations were observed in all ring-opening metathesis polymerization runs. The estimated rate constants in the ROMP of norbornenes containing acetyl-protected glucose, maltose at 25 °C (Scheme 20) under the same conditions (absolutely water, oxygen free conditions) increased in the order: **A1a** > **B2** ≫ **B1** (Table 4) [127]. Although effect of solvent should play an important role, it is clear that the propagation rates by **B1** are very slow due to less reactivity toward cyclic olefins even in CH_2Cl_2/$CDCl_3$, and the rates were also affected by the steric bulk in the norbornene substituent. These results thus suggest that ROMP of norbornene macromonomers by **B1** may be difficult to reach complete conversion.

In fact, ROMP of norbornene containing ring-opened oligo (*exo*-*N*-phenyl-norbornene-2,3-dicarboximide) by **B1** in CH_2Cl_2 afforded the corresponding ROMP polymers with 5–8 repeating units even after 48 h (Scheme 21) [129]. The GPC trace in the mixture suggest that the resultant polymer still contaminated monomers and were thus required to be purified by preparative GPC procedure: the resultant polymer after purification



Scheme 19. Precise synthesis of amphiphilic poly(macromonomer)s, poly(**7**), by repeating living ring-opening metathesis polymerization by molybdenum catalysts [62].

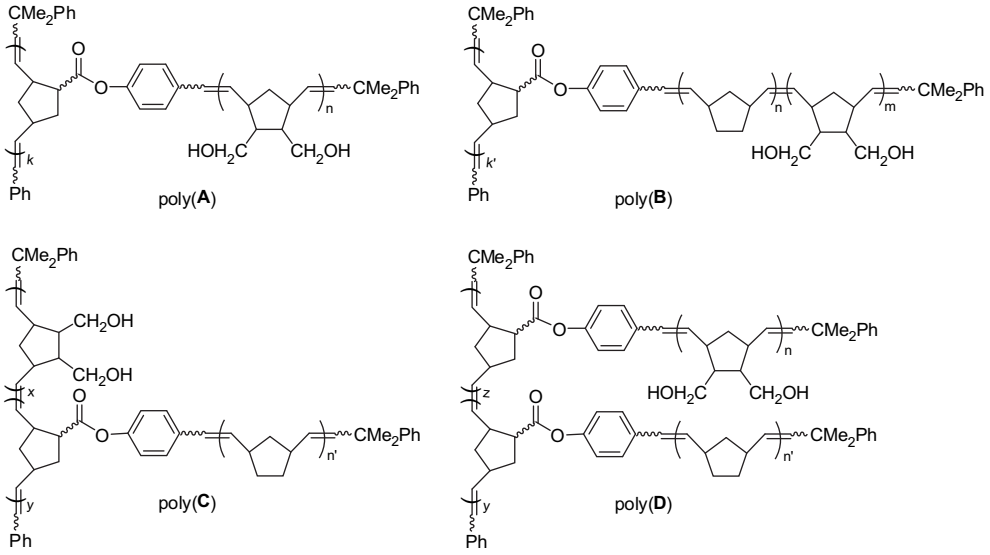
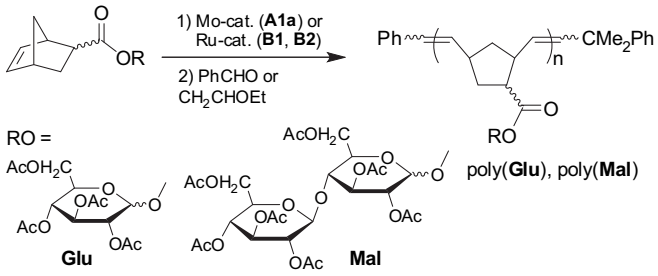


Chart 3. Various amphiphilic block (graft) copolymers prepared by polymerization of macromonomers by repetitive ROMP technique.



Scheme 20. Homopolymerization of norbornenes containing sugar functionality [127].

possessed relatively narrow molecular weight distribution, clearly suggesting that no side reactions such as metathesis with internal olefins (called back-biting) took place under these conditions [129].

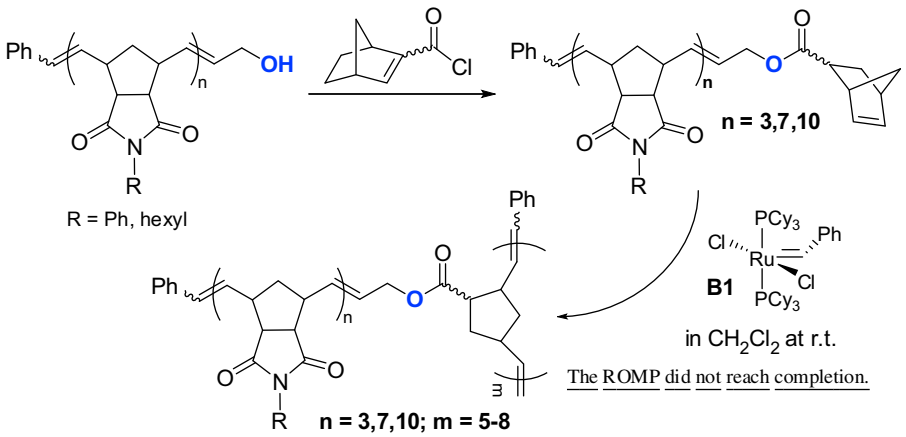
3.1. Precise synthesis of poly(macromonomer)s containing sugars by repetitive ROMP and their attachments to PEG

ROMP of macromonomers bearing galactose [poly(**8a**)] and ribose [poly(**8b**)], effected by the Mo(CHCMe$_2$Ph)(*N*-2,6-Me$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (**A2b**) catalyst, proceeded to completion (Scheme 22) yielding the PMMs, poly(**9a**,**b**), with narrow molecular weight distributions ($M_w/M_n = 1.07–1.22$). By varying the initial feedstock ratio of poly(**8a**)/**A2b**, poly(**9a**)s having different main chain lengths (DP$_n$, estimated based on M_n values by GPC) were obtained in high yields (Table 5, run 16–18) [21,61]. These results demonstrate that the ROMP of the macromonomers by **A2b** in a living-like manner with high initiation efficiency. Furthermore, the complete conversion could also be achieved in the ROMP of the macromonomer containing the triblock copolymer of NBE$_{20}$-*b*-**b**$_{20}$-*b*-**a**$_{20}$, and the GPC traces displayed an increase in the M_n value from 1.82×10^4 for poly(**9b**–**a**) to 17.47×10^4 for the PMM, which corresponds to a main chain of approximately 10 units while maintaining a narrow molecular weight distribution ($M_w/M_n = 1.11$, run 23), illustrating the ability to produce a PMM with three different well-defined blocks in the side chain.

In contrast, Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (**A1b**) and the Grubbs ruthenium carbine, [Ru(CHPh)(Cl)$_2$(I-MesH$_2$)(PCy$_3$)] (**B2** in Chart 1, IMesH$_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene), were not suitable for the complete conversion of the macromonomers, poly(**8a**–**b**) [21,61]. Although the ROMP of poly(NBE)-containing macromonomer by **A2b** proceeded to complete conversion, however, that of poly(**8a**) resulted in a mixture of the trimer, tetramer and poly(**8a**) {conditions: [poly(**8a**)]:[**A1b**] = [10]:[1], Table 5, run 12}, probably due to the insufficient reactivity toward the norbornenyl olefins under these conditions. The same attempt with initiator

Table 4
Summary for kinetic data for the ROMP of norbornenes containing acetyl-protected glucose and maltose residues (at 25 °C) by Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (**A1a**), Ru(CHPh)(Cl)$_2$(PCy$_3$)$_2$ (**B1**), or Ru(CHPh)(Cl)$_2$(IMesH$_2$)(PCy$_3$) (**B2**) [127].

Monomer	Initiator	Solvent	k_{obs}/min^{-1}	Living nature
Glu	**A1a**	toluene	1.5×10^{-1}	Yes
Glu	**B1**	toluene	3.0×10^{-3}	Yes
Glu	**B1**	toluene-d_8	3.0×10^{-3}	Yes
Glu	**B1**	CH_2Cl_2	8.6×10^{-3}	Yes
Glu	**B1**	$CDCl_3$	3.8×10^{-2}	Yes
Glu	**B2**	$CDCl_3$	6.7×10^{-2}	No
Mal	**A1a**	toluene	6.5×10^{-2}	Yes
Mal	**B1**	toluene	1.2×10^{-3}	Yes
Mal	**B1**	CH_2Cl_2	2.5×10^{-3}	Yes
Mal	**B1**	$CDCl_3$	1.3×10^{-2}	Yes
Mal	**B2**	$CDCl_3$	5.9×10^{-2}	No

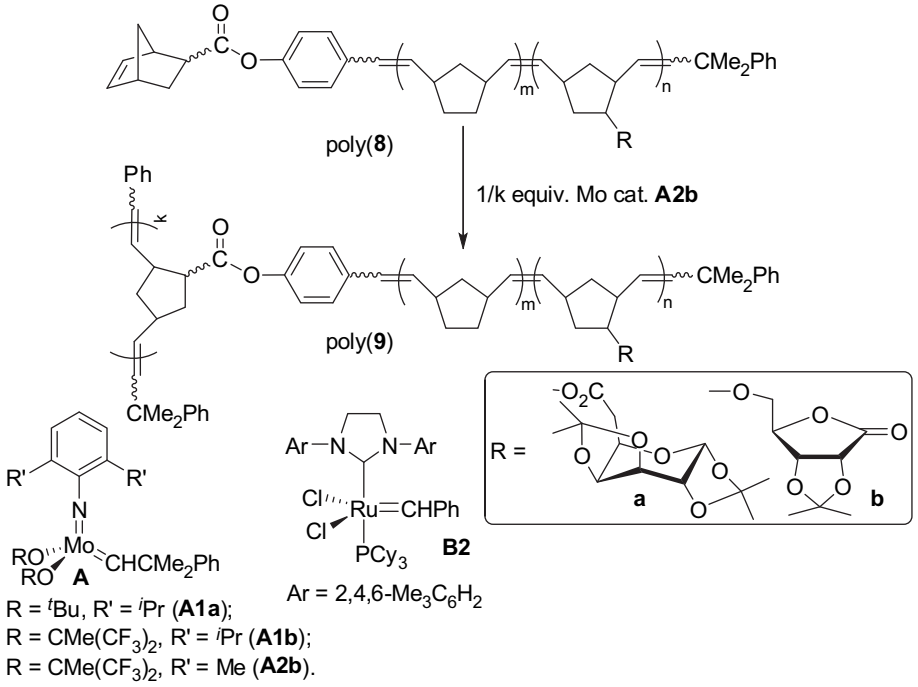


Scheme 21. Ring-opening metathesis polymerization of norbornenes containing ring-opened oligo(*exo*-*N*-phenyl-norbornene-2,3-dicarboximide) in the side chain [129].

B2 gave a polymer with low M_n value and broad distribution (run 13), suggesting occurrence of the metathesis (degradation) with internal olefins rather than the ROMP.

Our extended strategy entails the preparation of a PMM according to the above procedure except that polymerization of the macromonomer was quenched with 4-Me_3SiO-C_6H_4CHO followed by the treatment of PMM with HCl aq. to afford poly (**10**), as shown in Scheme 23. The quantitative removal of TMS protection under mild acidic conditions accompanied no significant decrease in the M_n values with a narrow molecular weight distribution ($M_w/M_n = 1.09$). The phenolic terminus was employed for the KH-mediated grafting of methane sulfonyl protected poly(ethylene glycol) [PEG-Ms_2, $MsO(CH_2CH_2O)_nMs$; $Ms = MeSO_2$] to the PMM, and two PEG samples with different molecular weights [PEG_{47} ($M_n = 2200$) and PEG_{110} ($M_n = 4600$); $M_w/M_n = 1.03$] were pursued as the hydrophilic segment in the preparation of PMM-*block*-PEG amphiphilic architectures (Scheme 23). The attachment of PEG_{47} and PEG_{110} to poly(**10**) afforded poly(**11**) (yield, 82% and 85%), and the M_n values measured by GPC revealed the increment from 5.85×10^4 to 6.11×10^4 (for PEG_{47}) and 6.40×10^4 (for PEG_{110}) with narrow unimodal dispersity of 1.08 and 1.11, respectively (Table 6). These results clearly demonstrate a facile method of preparing amphiphilic architectures by the careful manipulation of the end groups of PMMs.

As shown in Fig. 2, poly(**11**), PMM-*block*-PEG aggregated to form spherical micelles as observed by TEM, revealing spherical aggregates with a diameter, $d_{TEM} = 148.5 \pm 7.2$ nm, corresponding to a circumference of approximately 467 nm [21]. These well-defined micelles are smaller in size to the corresponding PEG-based ABC, poly(**3**), explained by the more facile packing of the linear chains into the hydrophobic centre in comparison to the bulky core-forming PMM of poly(**11**). The ability to uptake the hydrophobic dye (Nile Red) into the micellar cores of a variety of amphiphilic

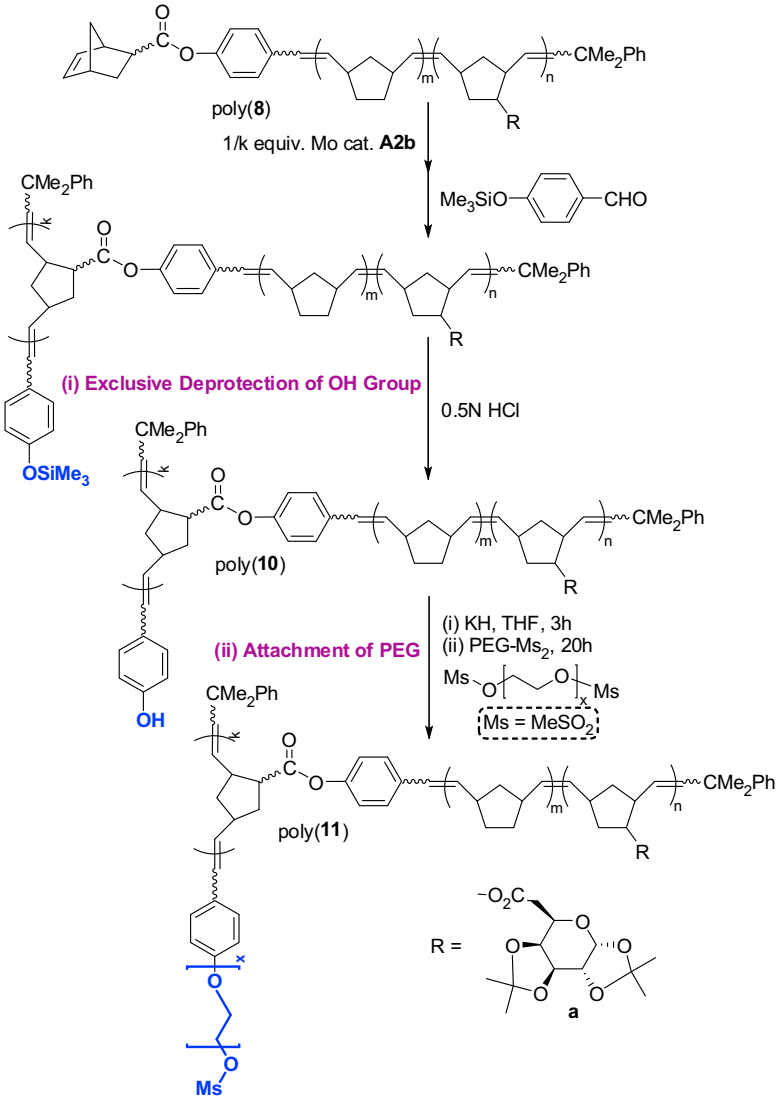


Scheme 22. Precise synthesis of poly(macromonomer)s containing sugars, poly(**9**), by repetitive ROMP using **A2b** [21,61].

Table 5
Preparation of poly(macromonomer)s (PMMs) by repetitive ROMP [21].[a]

Run	poly(**8**)					cat. (equiv.[f]/k)	time, h	poly(**9**), PMMs				
	Monomer feed ratio in poly(**8**)[b]	$M_{n(Calcd)}$[c] $\times 10^{-4}$	$M_{n(GPC)}$[d] $\times 10^{-4}$	$M_{n(NMR)}$[e] $\times 10^{-4}$	M_w/M_n[d]			$M_{n(calcd)}$[c] $\times 10^{-4}$	$M_{n(GPC)}$[d] $\times 10^{-4}$	M_w/M_n[d]	DP_n[g]	Yield[h], %
12	NBE_{25}-*b*-$\mathbf{a}_{25}$	1.18	1.58	1.24	1.1	**A1b** (10)	1.5	11.95	4.50[i]	1.08	–[i]	98
13	NBE_{25}-*b*-$\mathbf{a}_{25}$	1.18	1.58	1.24	1.1	**B2** (10)	1	11.95	1.27	1.7	–	95
14	NBE_{25}-*b*-$\mathbf{a}_{25}$	1.18	1.58	1.24	1.1	**A2b** (5)	2	5.98	8.18	1.15	5.2	98
15	NBE_{25}-*b*-$\mathbf{a}_{25}$	1.18	1.58	1.24	1.1	**A2b** (10)	2.5	11.95	16.45	1.13	10.4	96
16	NBE_{20}-*b*-$\mathbf{a}_{20}$	0.95	1.28	1.02	1.11	**A2b** (10)	2	9.72	11.76	1.07	9.2	96
17	NBE_{20}-*b*-$\mathbf{a}_{20}$	0.95	1.28	1.02	1.11	**A2b** (5)	2	4.83	5.87	1.09	4.6	97
18	NBE_{20}-*b*-$\mathbf{a}_{20}$	0.95	1.28	1.02	1.11	**A2b** (3)	1	2.89	3.99	1.19	3.1	97
19	NBE_{20}-*b*-$\mathbf{b}_{30}$	0.84	1.02	0.92	1.18	**A2b** (10)	2	11.72	14.33	1.22	10.2	97
20	NBE_{10}-*b*-$\mathbf{a}_{20}$	0.85	1.18	0.94	1.12	**A2b** (15)	3	12.77	20.04	1.07	17	>99
21	NBE_{10}-*b*-$\mathbf{a}_{20}$	0.85	1.18	0.94	1.12	**A2b** (5)	2	4.27	5.74	1.17	4.9	98
22	NBE_{20}-*b*-$\mathbf{b}_{20}$	1.15	1.4	1.24	1.16	**A2b** (10)	2	8.42	8.42	1.12	8.3	96
23	NBE_{20}-*b*-$\mathbf{b}_{20}$-*b*-$\mathbf{a}_{20}$	1.56	1.82	1.59	1.08	**A2b** (10)	3	15.62	17.47	1.11	9.6	99

[a] Conditions: toluene (2.0 g), at 25 °C.
[b] Starting feedstock ratio.
[c] Calculated from initial feedstock ratios.
[d] Calculated from GPC data.
[e] Estimated from ^{1}H NMR spectra.
[f] Ratio of macromonomer to initiator (Scheme 22).
[g] Calculated from GPC data.
[h] Isolated yield.
[i] Polymerization did not proceed to completion (mixture of macromoner and oligo(macromonomer)s).



Scheme 23. Preparation of poly(macromonomer)-*graft*-PEG, poly(**11**) [21].

Table 6
Preparation of poly(macromonomer)-*block*-(PEG), poly(**11**) [21].[a]

poly(**8**)/**A2b**, equiv.[b]	poly(**10**)				PEG	poly(**11**)				
	$M_{n(calcd)}$[c] $\times 10^{-4}$	$M_{n(GPC)}$[d] $\times 10^{-4}$	M_w/M_n[d]	Yield, %	M_n	$M_{n(calcd)}$[c] $\times 10^{-4}$	$M_{n(GPC)}$[d] $\times 10^{-4}$	$M_{n(NMR)}$[e] $\times 10^{-4}$	M_w/M_n[d]	Yield[f], %
3	2.88	3.89	1.11	99	4600	3.33	4.77	3.43	1.12	87
5	4.78	5.85	1.09	98	2200	4.99	6.11	5.07	1.08	82
5	4.78	5.85	1.09	99	4600	5.23	6.4	5.29	1.11	85

[a] Based on MM (macromonomer) poly(**8a**$_{20}$); $M_{n(GPC)} = 1.28 \times 10^4$, $M_w/M_n = 1.11$.
[b] **A2b** = $F_6(Me_2)$; ratio of macromonomer to initiator.
[c] Calculated from initial feedstock ratios.
[d] GPC data in THF versus polystyrene standards.
[e] Estimated from ^{1}H NMR spectra.
[f] Isolated yield.

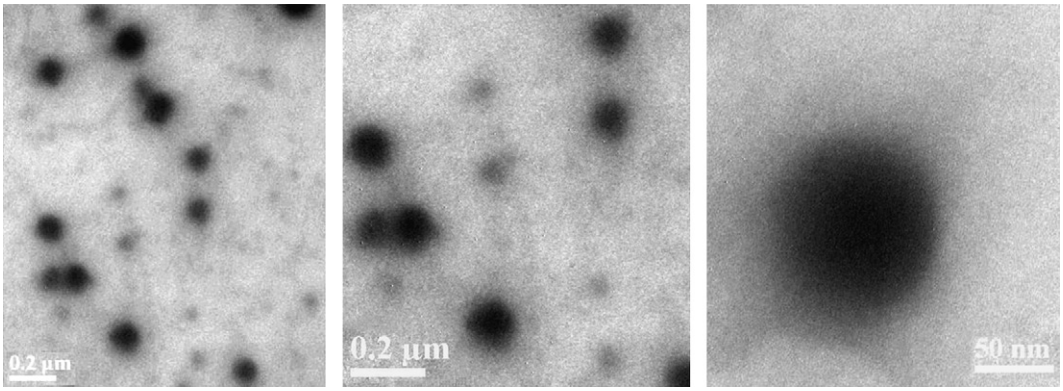


Fig. 2. TEM images of spherical aggregates of poly(NBE$_{20}$-*b*-**a**$_{20}$)$_5$-*b*-PEG$_{110}$ [poly(**11**), $M_n = 6.11 \times 10^4$, $M_w/M_n = 1.08$] at a concentration of 0.05 mg per mL THF at varying magnification.

polymeric fragments is a significant step towards the production of sugar-coated nano-spheres for cell targeting biomimetic applications [21].

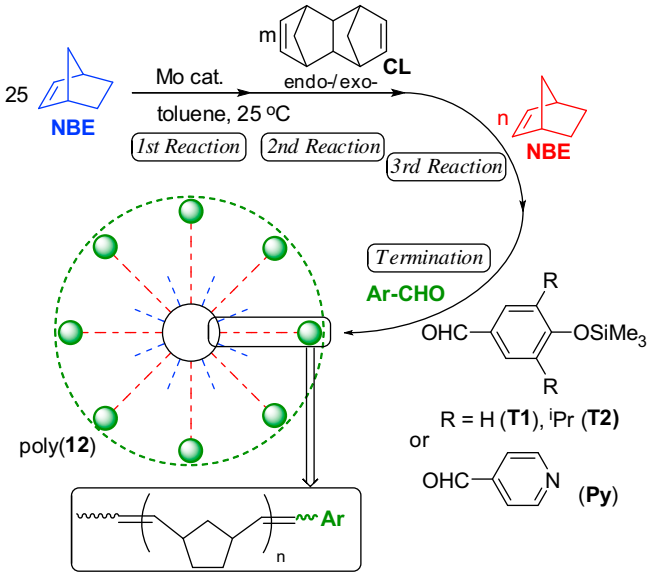
We can demonstrate that precise control of both main and side chain in the new class of amphiphilic poly(macromonomer)s containing sugars can be achieved for the first time by adopting the present repetitive ROMP procedure. Since the present approach should introduce a new possibility to prepare various kinds of amphiphilic nano arrangements containing sugars, unique properties such as both strong and specific affinities based on protein–carbohydrate interactions will be thus expected.

4. Facile controlled synthesis of soluble star shape polymers by ring-opening metathesis polymerization (ROMP)

Unique characteristics of living polymerizations 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 [130,131], and synthetic approaches using the atom transfer radical polymerization (ATRP) have thus been actively investigated recently. The approaches for synthesis of cross-linked polymers by ROMP [50–53] were also known [132–135], especially in terms of application as monolith materials for separation reported by Buchmeiser [133–135], however, reports for precise syntheses of star (ball) shape polymers that are highly soluble in common organic solvents have not so far been reported. We recently demonstrated a synthesis of soluble star (ball) shape ROMP polymers via "core-first" approach in a precise manner, as shown in Scheme 24 [136]. The selected results are summarized in Table 7.

It turned out that syntheses of high molecular weight ring-opened polymers, poly(**12**), with uniform molecular weight distributions ($M_n = 8.97–9.63 \times 10^4$ g/mol, $M_w/M_n = 1.31–1.45$) have been achieved by adopting this approach (sequential addition of NBE and CL) and the results are reproducible under the same conditions.

The M_n values in the resultant ROMP polymers increased upon increasing the amount of NBE in the 3rd polymerization (25 → 50 equiv. to Mo). Since the observed increase in the M_n



Scheme 24. Synthesis of soluble star (ball) shape ROMP polymers [136].

Table 7
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 [136].[a]

Terminator[b]	2nd reaction		3rd reaction		poly(**12**)		
	CL/Mo[c], m	Time, min	NBE/Mo[c], n	Time, min	M_n[d] $\times 10^{-4}$	M_w/M_n[d]	yield[e], %
T1	5	15	25	20	4.71	1.16	98
T1	10	50	25	15	8.97	1.31	95
T1	10	50	25	20	9.53	1.45	94
T1	10	50	50	20	12.7	1.49	96
T2	10	50	25	15	9.15	1.34	98
T2	10	50	50	20	12.1	1.49	93
Py	10	50	25	15	8.47	1.42	95

[a] Conditions (1st 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 of Ref. [136].
[b] Aldehyde for termination shown in Scheme 24.
[c] Starting feedstock ratio (m and n in Scheme 24).
[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.

values were much higher than those in the linear poly(NBE), also since the 1st polymerization of NBE proceeded with high conversion even after 5 min, the results suggest that the resultant ROMP polymers are star shape polymers consisting of a core and NBE branching (1st and 3rd polymerization). It should also be noted that the M_n values in the resultant polymers terminated with 3,5-^{i}Pr$_2$-4-Me$_3$SiO-C$_6$H$_2$CHO (**T2**), 4-pyridinecarboxaldehyde (**Py**) were similar to those terminated with 4-Me$_3$SiO-C$_6$H$_4$CHO (**T1**). 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, although an optimization of the reaction conditions were required for obtainment of the "soluble" ROMP polymers with uniform molecular weight distributions. The resultant polymers are highly soluble in ordinary organic solvent such as toluene, THF, dichloromethane, chloroform, chlorobenzene.

Fig. 3 shows selected TEM micrographs of thin films prepared by casting the resultant ROMP polymers [poly(**12**), $M_n = 1.27 \times 10^5$, $M_w/M_n = 1.49$] on a plastic coated copper grid. The resulting micrographs depict formation of uniform spherical images with average diameters that are somewhat longer than those calculated as the linear ROMP polymer main chains but seemed to correspond with those consisting of the arm and a core. Fig. 4 shows selected (height and phase) AFM images of poly(**12**) ($M_n = 8.97 \times 10^4$, $M_w/M_n = 1.31$) 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). 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 controlled manner by adopting the living ROMP technique using the molybdenum alkylidene initiator via '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. More recently, soluble star polymers containing a sugar residue with uniform molecular weight distributions could be attained by using 1,2:3,4-di-*O*-isopropylidene-α-D-galacto-pyranos-6-*O*-yl 5-norbornene-2-carboxylate [137]. We thus believe that the method would provide a new efficient synthetic methodology in a better controlled manner via 'core-first' approach, and various applications are possible by varying norbornene derivatives (main chain) as well as substituted aldehyde (end group).

5. Summary

In this article, we introduced recent examples for preparation of amphiphilic block/graft copolymers utilized by the living ring-opening metathesis polymerization (ROMP) method. Not only precise control of the block segment (hydrophilic and hydrophobic), but also an exclusive introduction of functionalities at the polymer chain end can be achieved by adopting the living ROMP initiated by molybdenum alkylidene complexes (so-called Schrock type catalyst). The technique enable us to provide the synthesis of block copolymers varying different backbones by adopting the "grafting to" or "grafting from" approach, and of soluble star (ball) shape polymers with controlled length of side arms with well-defined functionality at the surface. Facile one pot synthesis can be used in the combination of ROMP using (so-called Grubbs type) ruthenium carbene catalyst, and the catalyst is also effective for atom transfer radical polymerization (ATRP), affording amphiphilic block copolymers and polymer brushes (graft copolymers) in a controlled manner under appropriate conditions. Moreover, the "grafting through" approach

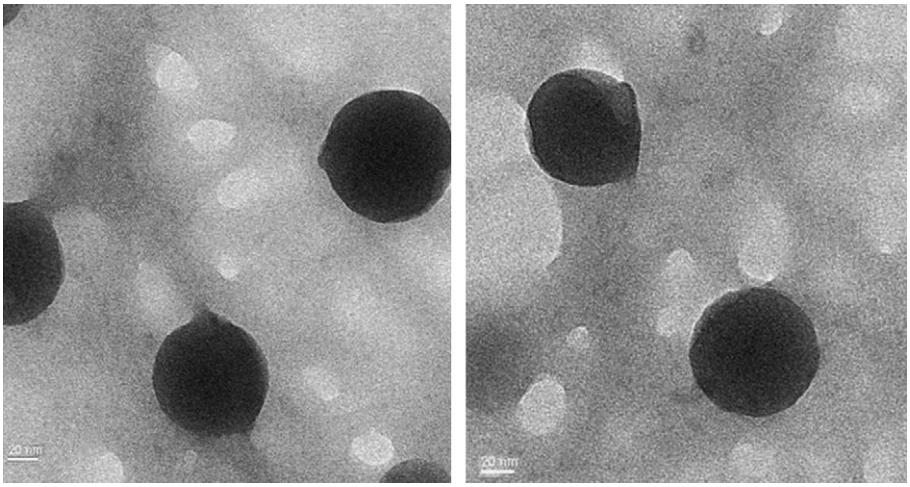


Fig. 3. TEM micrographs of thin film prepared by casting poly(**12**) [$M_n = 1.27 \times 10^5$, $M_w/M_n = 1.49$] on a plastic coated copper grid at a concentration of 10^{-5} mg/mL at varying magnification [136].

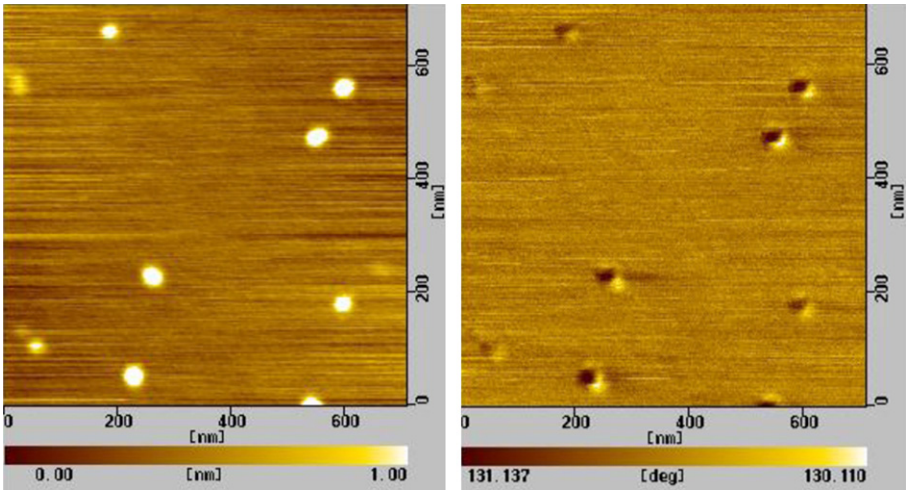


Fig. 4. Selected (height and phase) AFM images of poly(**12**) [$M_n = 8.97 \times 10^4$, $M_w/M_n = 1.31$] on mica substrate cast (spin coated) from THF solution (0.1 mg/mL) [136].

(polymerization of macromonomers) by employing the repetitive ROMP technique, using the molybdenum alkylidene catalysts, offers precise control of the amphiphilic block segments. Although improvement in the reactivity toward cyclic olefin (to afford polymers with longer repeating units) should be required, we believe that these approaches should be promising for precise synthesis of amphiphilic polymers displaying controlled nano architectures as well as unique properties.

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