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Efficient Synthesis of Long-Chain Highly Branched Polymers via One-Pot Tandem Ring-Opening Metathesis Polymerization and Acyclic Diene Metathesis Polymerization

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ABSTRACT: A facile one-pot synthesis of long-chain highly branched polymers (LCHBPs) was accomplished by a tandem ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization procedure. A telechelic polymer with two terminal allyloxy groups and many pendent acrylates was first prepared through the first generation Grubbs catalyst-mediated chain transfer ROMP of 7-oxanorborn-5-ene-*exo*,*exo*-2,3-dicarboxylic acid bis(2-(acryloyloxy)ethyl) ester in the presence of a symmetrical multifunctional olefin 1,4-diallyloxy-*cis*-2-butene as chain transfer agent (CTA), and then utilized as an A_2B_{2n}-type macromonomer in subsequent ADMET polymerization between allyloxy and acrylate triggered by the most activated second generation Grubbs catalyst, yielding LCHBPs as the reacton time prolonged. The CTA, monomer, macromonomer, and the resulting LCHBPs were characterized by mass spectroscopy, elemental analysis, gel permeation chromatography with multiangle laser light scattering, NMR and matrix-assisted laser desorption ionization time-of-flight mass measurements. The LCHBPs have comparatively high molecular weights and relatively moderate polydispersity indices.

Introduction

Long-chain branched polymers (LCBPs), as one type of hyperbranched polymers,[1] have attracted increasing attention due to their unique architectures and properties including higher solubility, lower solution or melt viscosity, stronger melt elasticity and storage modulus, and special strain hardening in elongational flow relative to their linear analogues.[2−5] Generally, LCBPs can be obtained from the polymerization of AB_2-type macromonomers in either chain-growth fashion or step-growth fashion. The former strategy has been extensively utilized in the synthesis of graft-copolymers[6] and the LCBPs with different branch densities by the chain-extending reaction of linear multifunctional prepolymers.[7] The latter strategy, founded on the conversion of α,ω-functional AB_2 macromonomers into LCBPs, is primarily actualized through Williamson coupling reaction,[8−14] esterification,[15−17] and hydrosilylation reaction.[18,19] Using the same concept, the LCBPs based on AB_n-type macromonomers are constructed by the esterification reaction.[20] The common drawbacks for these conventional polycondensation processes, however, are that the resulting polymers have broad molecular weight distribution and low branched degree of polymerization, and only a few systems allow the control over molecular weight and molecular weight distribution of the LCBPs. For instance, the well-defined long-chain hyperbranched polystyrenes with high degree of polymerization and narrow molecular weight distribution[21] have recently been prepared by click reaction of AB_2 macromonomer.

Olefin metathesis polymerization, as one of the most convenient synthetic tool for the synthesis of polyolefins, had an enormous impact on polymer chemistry,[22] especially on the field of the living polymerization[23] to prepare highly functional polymers.[24] A well-known method for controlling molecular weight, tailoring polymeric architecture, and enduing the polymer with functionality is the ruthenium-catalyzed chain transfer ring-opening metathesis polymerization (ROMP or ROMP-CT) of cyclic monomers in the presence of functional chain transfer agents (CTAs).[25] When the symmetrical CTAs of α,ω-allylic ether or ester deduced from *cis*-1,4-butenediol are employed, the telechelic polymers can be obtained and the number-average degree of chain-end group functionality (F_n) values approaching two are typically achieved. Usually, ROMP-CT of high or even low ring strained cycloolefins is readily accomplished by adopting the first generation Grubbs catalyst (**Ru−I**),[26] while it is necessary for using the highly active and more functional group tolerance of the second generation Grubbs catalyst (**Ru−II**) to initiate the lower ring strained cyclooctene with large pendant substituents[27] and/or CTAs capped with either bulky dendrons or Lewis basic functionalities.[25,28] However, as far as we are concerned there are few literature examples to date describing the synthesis of long-chain highly branched polymers (LCHBPs) and not so many examples regarding the synthesis of LCBPs via olefin metathesis techniques including ROMP and acyclic diene metathesis (ADMET) polymerization. Grubbs et al.[29] synthesized a series of hyperbranched polymers by means of ADMET polymerization of AB_n monomers with one terminal olefin and two or more acrylates using the metathesis catalyst **Ru−II**. Subsequently, Meier and co-workers[30] investigated acyclic triene metathesis of a triglyceride using different amounts of methyl acrylate as a chain stopper to prevent full cross-linking and obtain branched polymers in a straightforward one step one-pot polymerization. Mathers et al.[31] provided a different ROMP-based approach for the preparation of functional hyperbranched polymers using the one-pot polymerization of dicyclopentadiene. Moreover, a simple route through ADMET polymerization of AB_2 monomer containing an azo-moiety to generate a functional hyperbranched polymer has been exhibited in our previous work.[32]

Despite having developed some strategies for the preparation of branched polymers, constant efforts are needed to devote to

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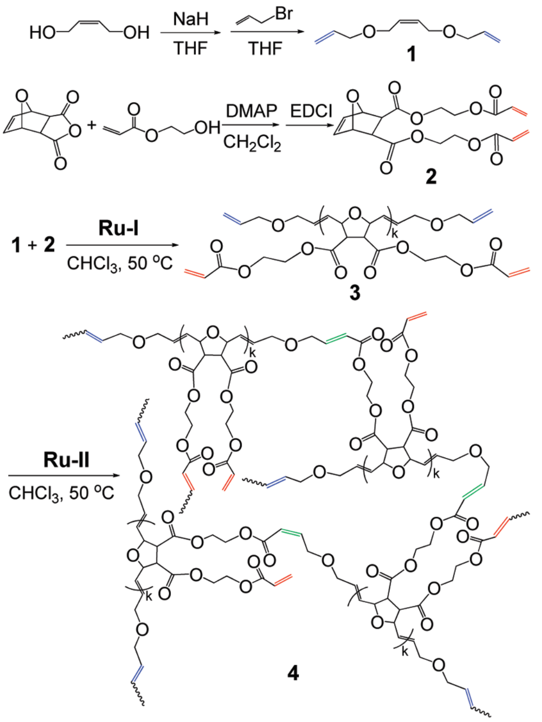
Scheme 1. One-Pot Synthesis of Long-Chain Highly Branched Polymers via the Combination of ROMP and ADMET Polymerization



seek more efficient and versatile methods for the synthesis of LCBPs through olefin metathesis polymerization. It is known that ROMP of norbornene and its derivatives is extremely fast because of the release of large amounts of ring strain, with rate constants several orders of magnitude faster than cross metathesis reactions. Similarly, cross metathesis is several orders of magnitude faster than secondary metathesis (back-biting) of substituted polynorbornenes. On the basis of the great differences in reactivity between ROMP, cross metathesis, and secondary metathesis,[33,34] we expected that a combination of various metathesis polymerizations would be possible to synthesize functional polymers in one-pot. To achieve the attractive goal, herein, we originate a tandem ROMP and ADMET polymerization method to prepare LCHBPs using different ruthenium metathesis catalysts in one-pot procedure under certain conditions (Scheme 1). First, a deliberately designed telechelic polymer bearing electron-rich olefins—two terminal allyloxy groups at the polymer chain ends—and electron-poor olefins—many pendent acrylates along the polymer chain—was synthesized by ROMP-CT[25] of oxanorbornenyl derivative in the presence of a CTA using **Ru−I** as the initiator; and then cross metathesis could be utterly transformed into ADMET polymerization between allyloxy and acrylate of the functional telechelic polymer (acted as an A_2B_{2n}-type macromonomer, and the A and B functionalities readily react with each other, but neither one reacts with itself or do so very slowly[29,34−36]) when treating it with catalyst **Ru−II**, yielding finally the LCHBPs.

Results and Discussion

Monomer and CTA. Novel versatile CTA and monomer were designed tactfully and prepared readily by the conventional methods (Scheme 1). Multiallylic CTA, 1,4-diallyloxy-*cis*-2-butene (**1**), was obtained by the Williamson coupling reaction of *cis*-2-butene-1,4-diol with an inexpensive allyl bromide in a high yield. The structure and purity of CTA were fully tested by GC-MS, elemental analysis, and ^{1}H NMR and ^{13}C NMR spectroscopy (Figure S1, Supporting information). The functional monomer, 7-oxanorborn-5-ene-*exo*,*exo*-2,3-dicarboxylic acid bis(2-(acryloyloxy)ethyl) ester (**2**) bearing a cyclic norbornenyl group and two acyclic acrylates, was synthesized through a similar procedure as the previous reports.[37] Elemental analysis, and ^{1}H NMR and ^{13}C NMR spectroscopy (Figure S2, Supporting Information) affirmed the successful preparation of monomer **2** with the expected chemical structure.

Functional Telechelic Polymer by ROMP-CT. It has been shown that in a ruthenium-catalized metathesis/chain transfer system, ROMP is favorably realized in a chain growth fashion and subsequently chain transfer events.[25] That is to say a chain transfer cross metathesis reaction happened between the ruthenium alkylidene species at the end of a living ROMP polymer chain and CTA, which shorten the polymer chains, and over time the amount of CTA on polymer chain end steadily increased.[28,38] In this case, taking advantage of ROMP-CT for synthesis of the functional telechelic polymer **3** with the terminal allyloxy and the pendent acrylate, three crucial aspects are the most concerned with monomer, CTA, and catalyst: (i) monomer **2** provides an apparently reactive norbornenyl functionality for ROMP-CT and two essentially latent acrylate functionalities, which is a potentially useful precursor and will become the reactive functionality for subsequent ADMET polymerization; (ii) differing from the commonly CTA of α,ω-allylic *cis*-olefin, CTA **1** is such a symmetrical multiallylic ether of *cis*-1,4-butenediol containing one internal *cis*-olefin and two α,ω-diallyl end olefins, although it is of seldom use as CTA in ROMP, that guarantees the telechelic polymer chain end-capped with two allyloxy groups by means of this special CTA being whether cleaved the internal *cis*-olefin into two symmetrical fragments or metathesized any one of the two end allylic olefins via ruthenium carbene since it exhibits the high rate of reactivity toward terminal olefins;[38,39] (iii) catalyst **Ru−I** is of an optimal candidate for ROMP-CT, based on the comprehensive considerations of its moderate functional group tolerance, proper metathesis activity, and good control over the polymer structure and molecular weight in the metathesis-mediated polymerizations, to precisely tailor the telechelic polymer architecture and depress possibly secondry metathesis reactions (such as back-biting) or even ADMET polymerization of allyloxy groups.

The great advantage of ROMP-CT for the preparation of telechelic polymers is the ability to conveniently control the molecular weight through regulating the molar ratio of monomer to CTA.[26] In order to get the telechelic polymer **3** with relatively low molecular weight, the polymerization of monomer **2** in the presence of CTA **1** is initiated by catalyst **Ru−I** using the monomer to CTA and catalyst ratios of 1000/200/1, i.e., a low monomer to CTA ratio of 5/1 and a high CTA to catalyst ratio of 200/1 are employed according to that of previous studies where a CTA/catalyst ratio of 200 or more is necessary to ensure the prepared telechelic polymers with difunctionality.[25,40] After the metathesis polymerization/chain transfer reaction being conducted for 24 h, the end-capping of a ROMP polymer chain with a CTA has reached completion. In other words, at thermodynamic equilibrium, every CTA molecule has been incorporated into the polymer chain,[33,41] affording a functionalized telechelic polymer with high F_n and in a high yield. A monomodal peak in the GPC chromatogram (Figure 1) is observed for this as-obtained telechelic polymer **3** with a relatively low polydispersed index (PDI) of 1.45, and the molecular weight ($M_{n,GPC}$) is found to be 3.8 kDa as envisioned low (Table 1).

To make more accurate exploration, the absolute molecular weight characterization method of gel permeation chromatography (GPC) with multiangle laser light scattering (MALLS) is employed, and the MALLS chromatogram of telechelic polymer is shown in Figure 2. The MALLS-derived molecular weight ($M_{n,MALLS}$) of telechelic polymer **3** is 3.1 kDa, which is slightly lower than that of $M_{n,GPC}$.

The ^{1}H NMR spectrum and the corresponding peak assignments of telechelic polymer **3** are shown in Figure 3a. Compared to that of monomer **2**, it is clearly detected that a clean chemical shift of alkene protons *g* on oxanorbornene ring initially at 6.41 ppm in Figure S2 (Supporting Information) to higher field approximately at 5.88−5.59 ppm in Figure 3a for the protons of alkene on polymer chain after ring-opened. Moreover, the resonance signals of protons *a* (5.86 ppm), *c* (5.27 ppm), and *d* and *e* (3.99−3.96 ppm), corresponding to the chemical structure of CTA **1**, are also observed. These characteristic proton resonances indicate that ROMP is performed under good control and the CTA has been successfully incorporated into the polymer chain. Furthermore, other types of end-groups, specifically terminal phenyl and ruthenium carbene species, are not observed in their expected regions of the ^{1}H NMR spectrum (7.2−7.4 ppm for phenyl and 19.5−20 ppm for ruthenium carbenes). Hence, the result of terminal-group analysis by ^{1}H NMR spectroscopy has demonstrated that the polymer obtained under the situations of **Ru−I** as catalyst and CTA/catalyst ratio of 200 is really a functionalized telechelic polymer with a high degree of allyloxy end group functionality ($F_n \approx 2$). Additionally, the average degree of polymerization (DP) and the molecular weight are calculated from the end-group analysis of the ^{1}H NMR spectrum. DP is estimated by the integral intensity ratio of olefinic protons on each monomer unit at 6.17−6.11 ppm (H_p, 2 protons for each unit) [$I_p = S_p/2$] to that of methylene protons on polymer chain at 3.99−3.96 ppm (H_{d+e}, 8 protons for end groups) [$I_{d+e} = S_{d+e}/8$] as follows: $DP = k = I_p/I_{d+e} = (S_p/2)/(S_{d+e}/8) = 4S_p/S_{d+e}$. The value of *k* is found to be eight and then used to determine the number-average molecular weight of telechelic polymer **3**, $M_{n,NMR} = k \times M_{(\text{monomer } \mathbf{2})} + M_{(\text{CTA } \mathbf{1})} = 3.2$ kDa. It is delighted to note that such a good agreement between the absolute molecular weight ($M_{n,MALLS}$) obtained from GPC utilizing a light scattering detector and the molecular weight ($M_{n,NMR}$) determined by ^{1}H NMR end group analysis indicates that the polymer is telechelic,[27] and also can serve as an additional evidence for the end group difunctionality[42] of telechelic polymer **3**.

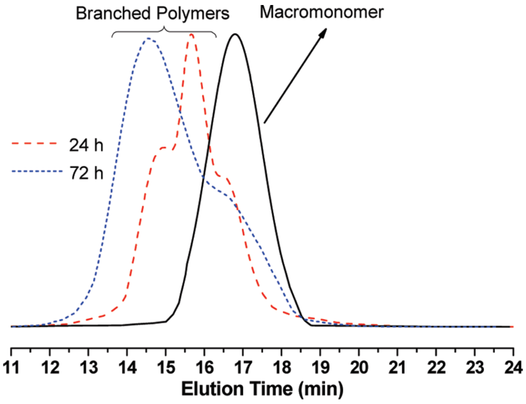


Figure 1. Gel permeation chromatography (GPC) traces of telechelic polymer (A_2B_{2n}-type macromonomer) **3** and highly branched polymers **4**.

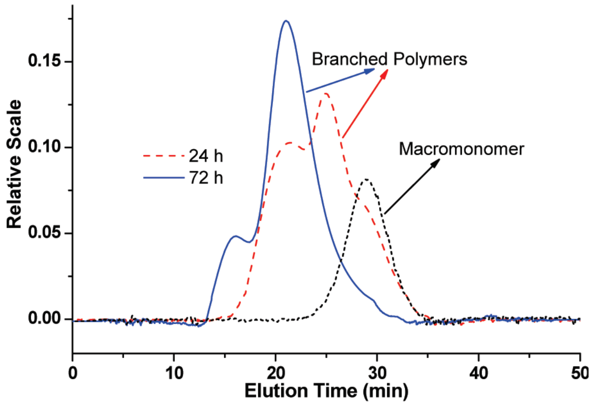


Figure 2. Representative multiangle laser light scattering-gel permeation chromatography chromatograms for A_2B_{2n}-type macromonomer **3** and long-chain highly branched polymers **4**.

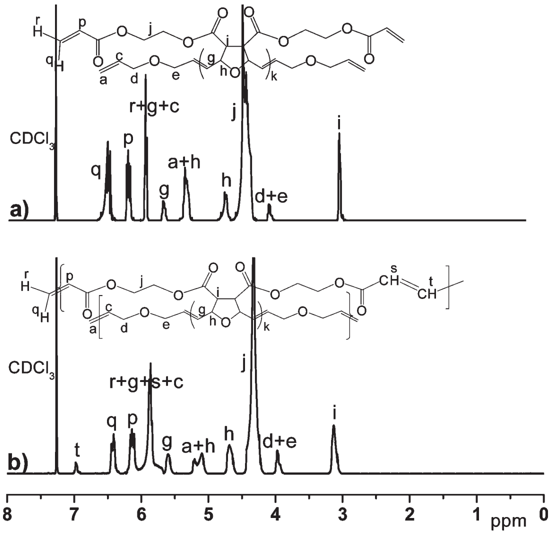


Figure 3. ^{1}H NMR spectra for (a) A_2B_{2n}-type macromonomer **3**, and (b) highly branched polymer **4b**.

Table 1. Characteristics of Telechelic Polymer by ROMP[a] and Long-Chain Highly Branched Polymers via ADMET Polymerization[b]

	t (h)			GPC analysis[d]		MALLS analysis[e]				
polymer	ROMP	ADMET	conversion[c] (%)	M_n (kDa)	PDI	M_n (kDa)	M_w (kDa)	PDI	$M_{n,NMR}$ (kDa)	DP
3	24		91	3.8	1.45	3.1	4.3	1.42	3.2[f]	nd[g]
4a		24	87	13.9	1.98	36.7	79.3	2.16	nd	18[h]
4b		72	89	49.6	1.89	89.3	180.4	2.02	92.8[i]	42[h]

[a] Reaction conditions for preparation of **3**: polymerization temperature = 50 °C, polymerization time = 24 h, $[M]_0 = 0.4$ mol/L, [**Ru−I**] = 4×10^{-4} mol/L, [M]/[CTA] = 5/1. [b] Reaction conditions: polymerization temperature = 50 °C, [**Ru−II**] = 1.6×10^{-3} mol/L for preparation of **4**. [c] Obtained gravimetrically from the dried polymer. [d] Number-average molecular weight (M_n) and polydispersed index (PDI) were determined by gel permeation chromatography in THF relative to monodispersed polystyrene standards. [e] Obtained from MALLS analysis. [f] $M_{n,NMR} = (4S_p/S_{d+e}) \times M_{(\text{monomer } \mathbf{2})} + M_{(\text{CTA } \mathbf{1})}$ was calculated by ^{1}H NMR spectroscopy assuming $F_n = 2.0$, where $M_{(\text{monomer})} = 380.3$ and $M_{(\text{CTA})} = 168.2$ are the molar masses of monomer **2** and CTA **1**, respectively. [g] Not determined. [h] $DP_{w,MALLS} = M_{w(\mathbf{4})}/M_{w(\mathbf{3})}$, where $M_{w(\mathbf{4})}$ and $M_{w(\mathbf{3})}$ were determined by MALLS. [i] $M_{n,NMR} = m \times M_{n(\mathbf{3})}$, where *m* is calculated from the formula: $8(m + 1)/m = S_{d+e}/S_t$, and $M_{n(\mathbf{3})}$ is the molar mass of macromonomer obtained by ^{1}H NMR spectroscopy.

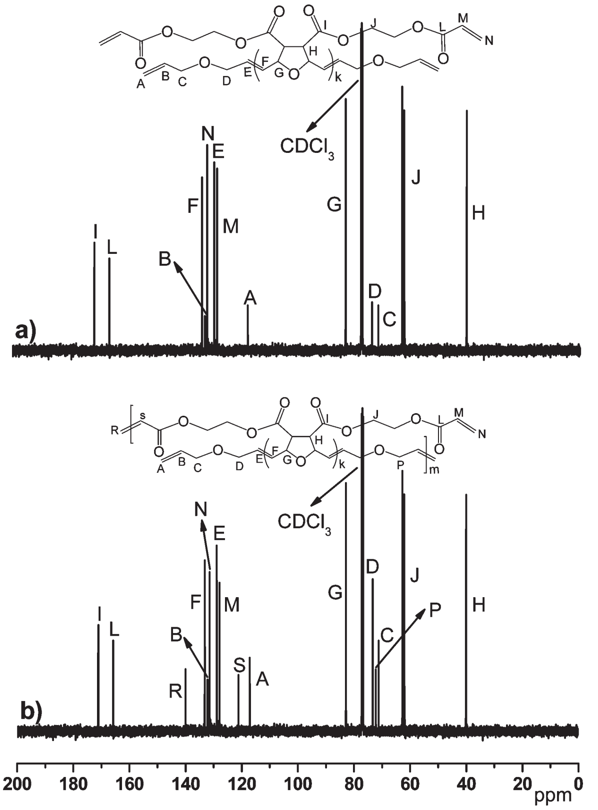


Figure 4. ^{13}C NMR spectra for (a) A_2B_{2n}-type macromonomer **3**, and (b) highly branched polymer **4b**.

Beyond our expectations, however, the ^{1}H NMR spectrum of telechelic polymer **3** shows no (or as low as undetectable) resonances at around 6.99 ppm in Figure 3a, which is deemed as the evidence for none of the newly formed internal acrylates and the branched structures. The macromonomer **3** is also characterized using ^{13}C NMR spectroscopy as shown in Figure 4a. The strong resonances of methylene, methine, and acrylate carbons from monomer **2** are observed at about 172.5, 166.3, 131.3, 127.9, 82.6, 62.4, and 39.9 ppm. Simultaneously, the resonance signals of carbons A (117.8 ppm), B (132.4 ppm), C (71.8 ppm), and D (74.3 ppm), corresponding to the chemical structure of CTA **1**, are still presented. Additionally, the ^{13}C NMR spectrum of **3** shows none of the newly formed internal acrylate peaks in Figure 4a, indicating the absence of cross-linked or branched structures. These observations confirmed that the telechelic polymer has a linear architecture, and also excluded the possible occurrence of cross-metathesis between pendent acrylate and terminal allyloxy or chain backbone olefin under given conditions, making ADMET polymerization be temporarily "frozen" on the early stage of reaction because of the stability of the ruthenium carbene species toward the acrylate groups[42,43] despite the absence of a free-radical inhibitor.

Figure 5 shows the MALDI−TOF spectrum for macromonomer **3**. The peaks are separated by 380 mass units, which corresponds to the molecular weight of each monomer unit (380.34). M_n of **3** calculated from the MALDI−TOF spectrum is 3196, which is in good agreement with the value determined by MALLS−GPC (3100) and calculated by ^{1}H NMR (3200). Furthermore, the enlarged region of MALDI−TOF MS spectrum of macromonomer **3** in Figure 5 reveals a difference of 71 mass units corresponding to a terminal group ($CH_2OCH_2CH{=}CH_2$) between two adjacent peaks among the group, suggesting that all of the polymer chains are capped at both ends.[26a,44] These data provide evidence for the formation of a telechelic polymer with the CTA functionality successfully being placed onto both ends of each polymer chain.

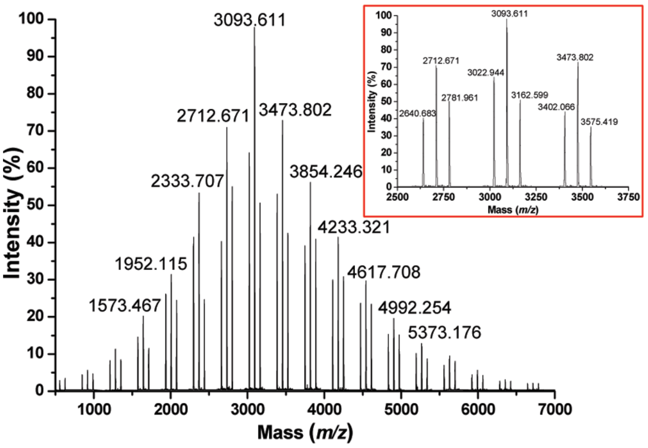


Figure 5. MALDI−TOF MS spectrum of A_2B_{2n}-type macromonomer **3**.

Long-Chain Highly Branched Polymers by ADMET Polymerization. The allyloxy functionality on the telechelic polymer chain ends has been proved to be "unreactive" to both ADMET polymerization with itself (maybe stemming from the lack of strong enough metathesis reactivity or very low concentration of allyloxy in the closed reaction system) and cross metathesis with acrylate within a limited time scale, allowing for ROMP-CT developed adequately. On the other hand, as the time prolonged, allyloxy will take eventually part in ADMET polymerization with acrylate in an equilibrium step propagation condensation fashion,[45] either on the basis of some extent electron-rich feature of the allyloxy functionality itself, which matched the requirement of the cross metathesis after all, or stimulated by a more active ruthenium catalyst than **Ru−I**. Therefore, the telechelic polymer **3** bearing allyloxy and potential activated acrylate can be used as an A_2B_{2n}-type macromonomer for ADMET polymerization, where electron-poor acrylate olefins do not homopolymerize or even homodimerize but do participate in a cross metathesis reaction with more reactive electron-rich allyloxy olefins.

Followed by addition of highly active catalyst **Ru−II** to the rest of above-mentioned ROMP mixture in an opened reaction system, as expected, ADMET polymerization of macromonomer **3** is actually promoted and gradually formed the LCHBPs **4**. To provide a better understanding of the polymerization systems described above, the GPC method is used to trace the polymerization of macromonomer **3**, and the results are listed in Table 1. GPC curves of the LCHBPs displayed multiple peaks including unreacted macromonomer. For the LCHBP **4a** formed at the early polymerization stage for 24 h after adding **Ru−II**, it had a remarkably increase in molecular weight ($M_{n,GPC}$ = 13.9 kDa) and a broad molecular weight distribution (PDI = 1.98) as shown in Figure 1 compared to its macromonomer. Considering the length of the catalyst's lifetime in the reaction solution,[29] a fresh batch of 0.5 mol equivalent of **Ru−II** was then added to the reaction vessel at about 36 to 48 h intervals to ensure the effectiveness of prolonging the polymerization time past 36 h. With evolution of ADMET polymerization, the peaks at low molecular weight positions decreased, and after polymerization for 72 h, the LCHBP **4b** showed almost unimodal GPC trace with little unreacted macromonomer, and the elution curve of branched polymer was gradually shifted to much higher molecular weight region ($M_{\mathrm{n,GPC}}$ = 49.6 kDa) and molecular weight distribution also became narrow (PDI = 1.89), indicating longer polymerization time resulted in higher molecular weight and lower molecular weight distribution. Although GPC is well-known to determine the molecular weight and molecular weight distribution for linear polymers by using calibration with linear polystyrene, for branched polymer, its size is smaller than that of linear ones with same molecular weight because of the difference in hydrodynamic volume.[46] Therefore, an absolute molecular weight characterization method of MALLS was employed to further characterize the branched polymers. The typical MALLS chromatograms of the LCHBPs obtained from different polymerization time are shown in Figure 2. Indeed, the molecular weights $M_{\mathrm{n,MALLS}}$ of LCHBPs are significantly higher than their GPC values based on polystyrene calibration, which is consistent with the general trends for branched polymers. The LCHBPs **4a** and **4b** have the moderate to high molecular weights ranging from 36.7 kDa to 89.3 kDa with PDIs within 2.16 to 2.02.

Figure 3b shows the ^{1}H NMR spectrum of polymer **4b** with extending the polymerization time to 72 h. Notably, the curve of branched polymer is similar to its macromonomer as their structures mostly alike. Inspiringly, a new peak appeared obviously at 6.99 ppm (*t*) due to the formation of internal acrylates (cross-metathesized AB olefins). Figure 4b shows the typical ^{13}C NMR spectrum of LCHBP **4b**, as excepted, two new peaks appeared at about 139.7 (*R*) and 121.6 ppm (*S*). Moreover, there is another observation of a chemical shift from 71.2 ppm (*C*) to the lower field at 73.8 ppm (*P*) for part of the methylene carbons in allyloxy groups after forming internal acrylates. All these points are the strongly evidence for the branched structure of the resulting polymer, indicating ADMET polymerization has occurred overwhelmingly in the manner of the cross metathesis reaction between pendent acrylate and terminal allyloxy, and the branched structure of the resulting polymer has formed. Although an example has been reported to describe ADMET-triggered formation of cross-linked nanotubes between allylic ether groups on the assembled amphiphile surface by catalyst **Ru−I** under certain conditions,[47] no sufficient data (such as DP) were given to support the polymerization taken place effectively, because the oligomerization of these assembled allyloxy groups may also result in the same cross-linked nanostructures. Generally, in ADMET polymerization the polymerizability of a monomer is limited by the number of methylene spacers between the olefin and the ether oxygen or the ester from the oxygen side. To avoid suffering a negative neighboring group effect, the number of methylene spacers between these functionalities is at least two for successful metathesis to occur,[48] despite in some classical catalyst systems, reactivity has been observed in systems with only one methylene spacer present.[49] Consequently, the acrylate functionality and diallylic ether as well as some symmetrical diallylic esters are always failed to (homo)polymerize but the later two do oligomerize or isomerize sometimes.[29,34,36,50]

The specific resonances of the internal acrylate protons can be used to calculate the molecular weight of LCHBPs. Interestingly, a regular change is discovered from the intimately insight into the concept structure of LCHBP in Figure 6, and various characteristics are displayed in Table 2. For once cross metathesis reaction between pendent acrylate (red spherule) and terminal allyloxy (blue spherule), it forms a new internal acrylate (green spherule), meanwhile, gives three terminal allyloxy groups and eight methylene groups adjacent to the allylic ether oxygen (not including any methylene between two carbonyloxy groups from acrylate) on both polymer chain and allyloxy end. For one more reaction, there are an extra increase of one internal acrylate, one allyloxy end, and four methylene groups beside the allylic ether oxygen. That is, each cross metathesis would form a new internal acrylate and simultaneously promote the addition of one allyloxy end or four methylene groups beside the allylic ether oxygen. If the number of newly formed internal acrylate is *m*, the number of terminal allyloxy groups is equal to ($m + 2$), and the number of methylene groups beside the allylic ether oxygen will reach to ($4m + 4$) = $4(m + 1)$. Correspondingly, the number of protons on each type of group is twice as the group(s) number, means that there are 2*m* of olefin protons on newly formed internal acrylate, $2(m + 2)$ of olefin protons on allyloxy end, and $2 \times 4(m + 1)$ of methylene protons beside the allylic ether oxygen on each polymer chain, respectively. It should be pointed out that the newly formed internal acrylate protons are in two categories (H_s, H_t) with equal number according to different chemical environments, thus there are *m* of olefin protons (H_t) and *m* of olefin protons (H_s) on this internal acrylate. Because the terminal alkene (allyloxy) protons (H_a, H_c) and the olefin protons (H_s) on newly formed internal acrylate overlapped with other olefin protons, we finally chose the integration area ratio of methylene protons beside the allylic ether oxygen at 3.99−3.96 ppm (H_{d+e}) to that of olefin protons on newly formed internal acrylate at 6.99−6.90 ppm (H_t) to calculate the value of *m*, namely the DP for the branching reaction. It can be derived from the following formula: $2 \times 4(m + 1)/m = S_{d+e}/S_t$, and thus $m = 8S_t/(S_{d+e} - 8S_t)$. For the branched polymer **4b**, *m* is found to be as high as 29, and the value of $m = 29$ is used to determine the number-average molecular weight: $M_{\mathrm{n,NMR}} = m \times M_{\mathrm{n}(\mathbf{3})}$ = 92.8 kDa, which is in excellent accord with the value of $M_{\mathrm{n,MALLS}}$. In conclusion, all these results have demonstrated that upon completion of ROMP-CT of a strained cyclic olefin with a CTA, addition of solely a more active catalyst can successfully trigger ADMET polymerization and facilitate the formation of LCHBPs in practically one-pot successive procedure.

The degree of branching (DB) is one of the important molecular parameters to verify that the polymer does in fact

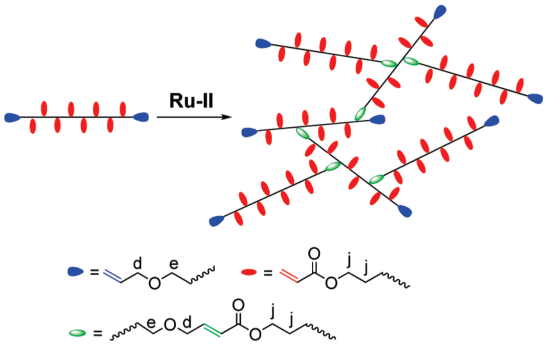


Figure 6. Schematic illustration of the structural transformation from A_2B_{2n}-macromonomer to long-chain highly branched polymer by cross metathesis reaction.

Table 2. Various Characteristics of Branched Polymer Structure

number of cross metathesis reaction	number of newly formed internal acrylate	number of terminal allyloxy	number of methylene beside the allylic ether oxygen
1	1	3	8 (=4 × 1 + 4)
2	2	4	12 (=4 × 2 + 4)
3	3	5	16 (=4 × 3 + 4)
m	*m*	$m + 2$	$4m + 4$

Table 3. Solubility and Intrinsic Viscosity Data for LCHBPs Synthesized from Macromonomer 3

polymers	$[\eta]_B$[a] (dL/g)	$[\eta]_L$[a] (dL/g)	g'[b]	solubility[c] THF	CH_2Cl_2	$CHCl_3$	acetone	DMF	DMSO	toluene	dioxane
4a	0.202	0.399	0.55	++	++	++	−	++	++	−	+−
4b	0.279	0.716	0.39	++	++	++	−	++	++	−	+−

[a] Measured by Ubbelohde viscometer. The B refers branched polymers, and the L refers linear polymers with the same molecular weights of branched polymers. [b] $g' = [\eta]_B/[\eta]_L$. [c] Key: ++, soluble; +−, partially soluble; −, insoluble.

have a branched architecture. However, DB of the LCHBPs **4** cannot obtain from the common technique using ^{1}H NMR spectra of polymer because *of* the characteristic protons overlapped. Therefore, we got some idea of DB from the branching factor g', which was calculated by the ratio of the intrinsic viscosity of the branched polymer $[\eta]_B$ to the intrinsic viscosity of a linear polymer $[\eta]_L$ with the same molecular weight,[11,21,51] and the results are listed in Table 3. The $[\eta]_B$s and the $[\eta]_L$s were measured by Ubbelohde viscometer. Since the branched polymers have smaller hydrodynamic volumes and more compact structures than linear polymers of identical molecular weight, the $[\eta]_B$s therefore are much lower than the $[\eta]_L$s (Table 3). The g' values of the LCHBPs decreased with the increase of DP_w (Table 1). In a word, the lower the g' value is, the higher DP and DB values are.

Besides, the solubility of LCHBPs **4** were also investigated simply. Despite their high molecular weight, they showed excellent solubility in various organic solvents such as THF, CH_2Cl_2, $CHCl_3$, DMF, and DMSO (Table 3). Thus, we can predict that the LCHBPs **4** are organosoluble polymers, and do not form cross-linked structure.

Effect of Different Monomer or CTA on ROMP and ADMET Polymerization. For comparison, we first designed a comparative experiment to investigate the effect of different monomer on polymerization. All polymerization conditions are the same as those for macromonomer **3** and LCHBPs **4**, except for the monomer **2** with two acrylates being replaced by ONBDM without acrylate (Scheme S1, Supporting Information).

The polymers **5** and **6** obtained from ROMP-CT and ADMET reaction are characterized by GPC and NMR measurements, and the results are listed in Table S1 (Supporting Information). The monomodal GPC trace (Figure S3, Supporting Information) reveals that $M_{n,GPC}$ of polymer **5** is 2.4 kDa with a low PDI of 1.30, suggesting ROMP-CT is carried out under good control, and further reaction between the growing polymer chains and the CTA is severely suppressed. The unimodal GPC curves of polymers **6** are also detected even extending the reaction time to 72 h, which is different distinctly from that of the LCHBPs **4**. As compared to polymer **5**, it is clearly observed that a clean shifts of the elution peaks of polymers **6** to the slightly higher molecular weight positions, but no significant changes are seen in the values of $M_{n,GPC}$ (5.1−5.5 kDa) and PDI (1.31−1.33) for polymers **6** no matter the reaction time shorter or longer. Viewing these points, we can deduce that after adding a solution of **Ru−II** to the rest of ROMP system, only a simple intermolecular metathesis coupling reaction (not a really ADMET polymerization but an oligomerization) of the chain end diene occurred to yield polymers with low DP of 2−3, without other secondary metathesis reaction between the terminal alkenes and the backbone olefins (less reactive in ROMP and ADMET polymerization) happened due to the steric hindrance of the adjacent centers on substituted polyoxynorbornenes.[38]

Furthermore, the obtained polymer chain structures are confirmed by ^{1}H NMR spectroscopy (Figure S4, Supporting Information), and $M_{n,NMR}$ of polymers is also estimated. The ^{1}H NMR spectrum of polymer **6b** is the same as that of polymer **5**, and no resonances for unwanted branching structure are detected, indicating polymers **5** and **6b** have the same linear structures. The $M_{n,NMR}$ values of polymers **5**, **6a** and **6b** calculated from ^{1}H NMR spectra in Figure S4 (Supporting Information) are 1.8, 3.8, and 4.1 kDa (Table S1, Supporting Information), respectively, which are relatively low and in reasonable agreement with those of $M_{n,GPC}$. The results of polymers **6** are much contrary to those of LCHBPs **4**, suggesting that the pendent acrylates in macromonomer **3** play a role of key component to form the branched polymer with high molecular weight.

We then adopted another comparative experiment to explore the effect of different CTA on polymerization. CTA **7** with saturated diester structure was given by esterification of *cis*-2-butene-1,4-diol with butyric acid (Scheme S2, Supporting Information). The structure and purity of **7** were tested by GC-MS, and ^{1}H NMR (Figure S5a, Supporting Information) spectroscopy.

The characteristic results of polymers **8** and **9** obtained from ROMP-CT and ADMET reaction are listed in Table S2 (Supporting Information). The monomodal GPC trace (Figure S6, Supporting Information) reveals that polymer **8** has a $M_{n,GPC}$ of 4.4 kDa and a PDI of 1.42. For polymers **9a** and **9b**, there were no significant changes in the values of $M_{n,GPC}$ (4.7−4.9 kDa) and PDI (1.47−1.49) when compared with polymer **8**. In the light of these results, we can deduce that after adding a solution of **Ru−II** to the rest of ROMP system, no other metathesis reactions happened.

The ^{1}H NMR spectrum of polymer **9b** (Figure S5c, Supporting Information) is wholly similar to that of polymer **8** (Figure S5b, Supporting Information), indicating polymers **8** and **9b** have the same linear structures. The molecular weight results (Table S2, Supporting Information) of polymers **9a** ($M_{n,NMR} = 3.3$ kDa) and **9b** ($M_{n,NMR} = 3.4$ kDa) are close to that of polymer **8** ($M_{n,NMR} = 2.9$ kDa) calculated from ^{1}H NMR spectra in Figure S5 suggesting that the pendent acrylates could not actualize cross-metathesis with themselves or chain backbone olefins.

From the two comparative experiments, we concluded that the terminal allyloxy groups could not form high molecular weight polymers via ADMET, and the pendent acrylates are also impossible to result in cross-linked or branched structures. These conclusions further illuminated that LCHBPs **4** were given just through cross metathesis between acrylate and terminal alkene, rather than other secondary metathesis reaction.

Conclusions

In this work, a new strategy for the synthesis of polymers with a long-chain highly branched architecture and many reactive groups was developed through a simply tandem ROMP and ADMET polymerization method under mild conditions. ROMP of a functional oxanorbornene with two acrylates in the presence of an extremely effective multiallylic *cis*-olefin CTA was performed using catalyst **Ru−I** in the predetermined reaction time, producing a linear functional telechelic polymer bearing two terminal allyloxy groups and many pendent acrylates, which can be used as an A_2B_{2n}-type macromonomer in subsequent

ADMET polymerization between allyloxy and acrylate triggered substantially by adding a highly active metathesis catalyst **Ru−II**, yielding the LCHBPs as the reacton time prolonged. The MALLS analysis showed that the telechelic polymer has low molecular weight of 3.1 kDa with a narrow PDI of 1.42, and the LCHBPs have reasonably high molecular weights of 36.7−89.3 kDa with high branched DP of more than 20 and PDIs of 2.16−2.02. These results clearly demonstrated that it is possible to prepare highly branched materials in a straightforward approach via merely olefin metathesis chemistry resorting to an ingenious combination of monomer, CTA, and catalysts. This would lead to the possibility of including new functionalities in polymers directly in order to make the polyolefin materials sensitive to other type of stimulus with a view to a future modification to their properties and architectures. For instance, the highly branched polymer structure inherently bearing a great number of the peripheral reactive acrylates would be changed into the permanent nanostructure through the intramolecular cross-linking reaction induced by UV-irradiation.[52] The extension of this work is further exploited.

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Supporting Information Available: Experimental procedures, scheme, table, and figures showing GPC chromatograms and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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