Chapter 4:

Multiple Olefin Metathesis Polymerizations (MOMP)

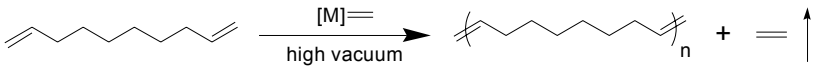
Abstract

Olefin metathesis polymerization, in particularly ring-opening metathesis polymerization (ROMP), has been a popular topic of modern research. Two other types are acyclic diene metathesis polymerization (ADMET) and cyclopolymerization of diynes. To date, there has been no report on a metathesis polymerization utilizing more than one metathesis process. Herein, the concept of multiple olefin metathesis polymerizations (MOMP) is introduced where two or three types of olefin metathesis reactions are used to generate well-defined polymer architectures. In the first half of this chapter, ROMP and ADMET processes are combined to produce highly A,B-alternating copolymers. In the second half, a polymerization where ROMP and cyclopolymerization are performed in a domino fashion is disclosed. Finally, a transformation involving all three types of olefin metathesis reaction, ring-opening, ring-closing, and cross metathesis cooperatively and orderly generate only one uniform polymer microstructure.

Background

Among the various olefin metathesis processes, ring-opening metathesis polymerization (ROMP) is the oldest reaction. ROMP has attracted the attention of polymer chemists for its many advantages over other polymerization methods.[1] With the right choice of catalyst and monomer, living polymerization to produce well-defined polymers with good molecular weight control and a narrow polydispersity index (PDI) is possible by ROMP.[2] With functional group tolerant catalysts, polymerization operates under mild conditions, such as room temperature, bench-top chemistry and short reaction times.[3] Furthermore, these catalysts allow the production of highly functionalized polymers and biologically relevant polymers.[4] Lastly, end-functionalized telechelic polymers are efficiently prepared by ROMP with the use of chain transfer agents.[5]

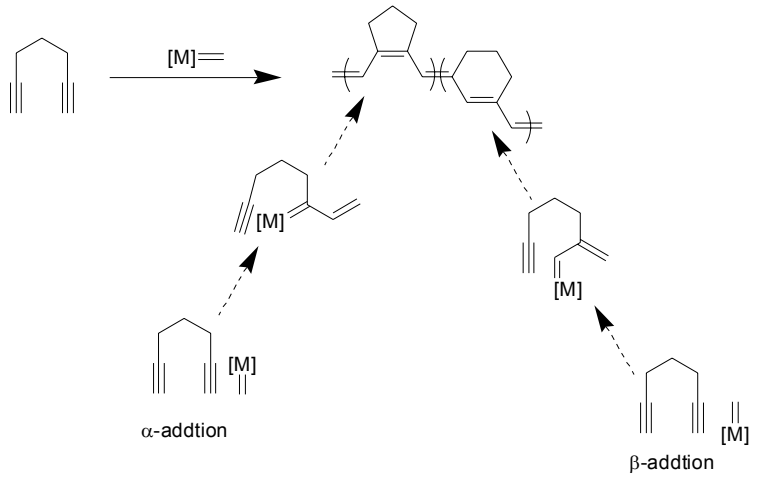
In addition to ROMP, there are two other metathesis polymerization methods, acyclic diene metathesis polymerization (ADMET) and cyclopolymerization. ADMET is a step-growth polymerization where dienes are polymerized by continuous cross metathesis (Scheme 1).[6] Therefore, by nature, ADMET produces polymers with broad PDIs and poor molecular weight control. It is hard to prepare high molecular weight polymers by ADMET since the thermodynamic control of olefin metathesis process does not facilitate conversions necessary to reach high molecular weight. The main shortcoming is that the enthalpically neutral bond formation in ADMET process does not provide a strong thermodynamic driving force for polymerization. In order to overcome the equilibrium issue, high vacuum system is used to entropically force the polymerization by removing ethylene gas.



Scheme 1. An example of ADMET

Cyclopolymerization occurs when diynes are treated with the right choice of catalyst (Scheme 2).[7] With the well-defined molybdenum catalyst, living polymerization is also possible to produce polymers with a narrow PDI and good molecular weight control.[8] The polymerization

goes to high conversion because the alkynes transform into conjugated dienes with a substantial gain in enthalpy. However, the generation of two possible polymer microstructures by α, and β-addition complicates the study of the resulting polymers.[7, 9] In addition, only early transition metal-based catalysts which are very sensitive to many functional groups, can promote the efficient polymerization. Unfortunately, attempts to promote cyclopolymerization by various functional group tolerant catalysts such as $Cl_2(PCy_3)_2Ru=CHPh$ (**1**)[3], $Cl_2(PCy_3)(IMesH_2)Ru=CHPh$ (**2**)[10], Hoveyda-Grubbs catalyst,[11] and Cl_2(3-BrPyr)$_2(IMesH_2)Ru=CHPh$ (**3**)[12] were unsuccessful, only yielding low molecular weight oligomers. This drawback has inhibited the general use of cyclopolymerization.



Scheme 2. An example of cyclopolymerization and two microstructures

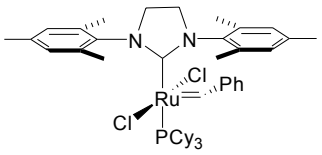
Although ADMET and cyclopolymerization have been far less investigated for the reasons stated before, these two polymerizations have their certain advantages over ROMP. ADMET sometimes provides an easier access to monomers when attaching a desired monomer precursor to a strained cycloalkene is problematic. Cyclopolymerization provides an efficient route to conjugated polymers which exhibit interesting physical properties such as conductivity and luminescence.[13] Therefore, developing new olefin metathesis polymerization and new monomers to produce new microstructures will further expand the utility of the metathesis reaction. For example, no general metathesis methods exist to produce A,B-alternating

copolymers or hyperbranched polymers. In this chapter a new concept of multiple olefin metathesis polymerizations (MOMP) is introduced.[14]

Part I. Synthesis of A,B-Alternating Copolymers by Ring-Opening Insertion Metathesis Polymerization (ROIMP)

Introduction

Alternating copolymers are normally formed by step-growth polymerization of AA and BB or AB type monomers[15] and in some special chain growth reactions, for example, copolymerization of ethylene and CO by Pd catalyst.[16] Although recent developments in ring opening metathesis polymerization (ROMP)[1] and acyclic diene metathesis polymerization (ADMET)[6] have extended the versatility of both chain-growth and step-growth reactions, these metathesis polymerizations have not provided a general solution to alternating copolymers. Examples of alternating copolymers by ROMP are rare due to the difficulty of finding systems in which there is an alternation in the affinity of the propagating metal carbene for the monomers.[17] Although ADMET is a step growth polymerization, examples of alternating copolymerization with two monomers by this mechanism have not been reported since most olefins studied have similar reactivity and would produce only random copolymers.[18] Therefore, a general metathesis route toward A,B-alternating copolymers would allow for the synthesis of new functional polymers.



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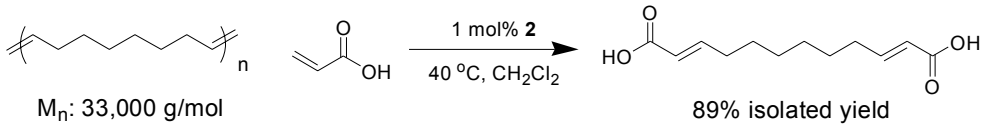
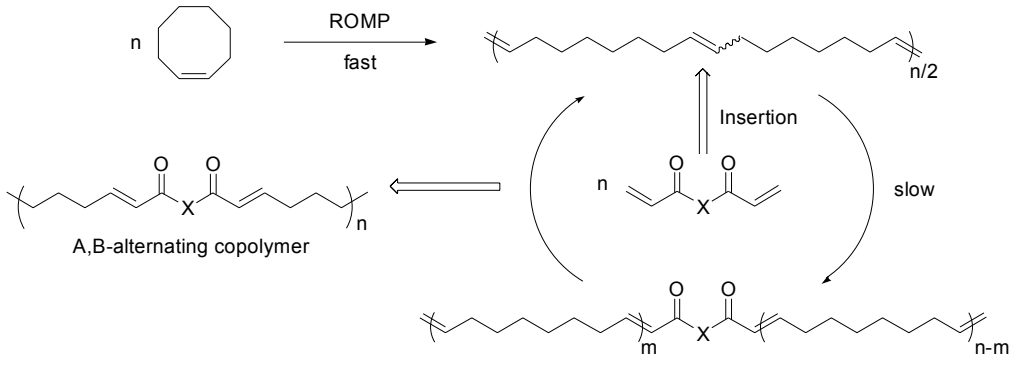
Although well-defined olefin metathesis catalysts such as $((CF_3)_2MeCO)_2(ArN)$-Mo=CH(*t*-Bu) and $Cl_2(PCy_3)_2Ru$=CHPh (**1**) have proven useful for polymer synthesis, the highly active molybdenum catalyst suffers from sensitivity to some polar functional groups[2] while the

functional group tolerant catalyst **1** shows decreased reactivity.[3] These disadvantages were recently addressed with the development of catalyst **2**, which exhibits high activity and remains tolerant of many functional groups.[10] Furthermore, catalyst **2** promotes ring-closing metathesis and selective cross metathesis (CM) of α,β-unsaturated carbonyl olefins with high conversions,[19] thereby expanding the scope of olefin metathesis in organic synthesis. In addition, a polyoctenomer synthesized by ROMP of cyclooctene was efficiently depolymerized using acrylic acid and catalyst **2** (Scheme 3).[20] This suggests that catalyst **2** should be able to produce polymers



Scheme 3. Depolymerization of polyoctenomer

from α,β-unsaturated carbonyl olefins. Also, if the coupling between internal olefins and α,β-unsaturated carbonyl olefins is selective, as is the case in cross metathesis, diacrylate monomers should be selectively inserted into ROMP polyolefins to yield alternating copolymers (Scheme 4). Herein, we report the development of a general method for synthesizing A,B-alternating copolymers by ring opening insertion metathesis polymerization (ROIMP).



Scheme 4. Proposed Mechanism for ROIMP

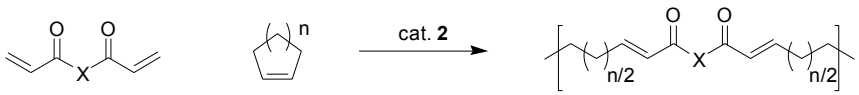
Results and Discussion

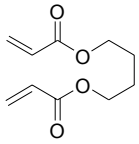
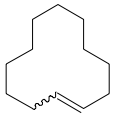
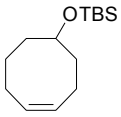
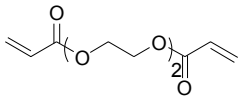
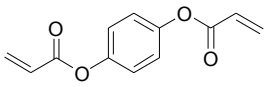
Treatment of a 1:1 mixture of monomers A (diacrylate) and B (cycloalkene) with catalyst **2**, indeed, yielded highly A,B-alternating copolymers in high yields. Examples of alternating

copolymers generated from a variety of diacrylates and cycloalkenes are shown in Table 1. For example, using a total monomer to catalyst ratio of just 290:1, a 1:1 mixture of 1,4-butanediol diacrylate and cyclooctene gave a copolymer with up to 99% A,B-alternation and a molecular weight of 90,100 g mol^{-1} with expected broad PDI (entry 1). It is important to match the stoichiometry of cyclooctene and diacrylates because any excess of cyclooctene results in oligocyclooctene blocks, lowering alternation, and a shortage limits the molecular weight of the polymer.

The extent of alternation could be easily determined by ^{1}H NMR, since olefinic protons for alternating units have a distinct chemical shift well resolved from the starting materials and homo-coupled units. *E*-Acrylate dimers produce a sharp singlet at 6.9 ppm (Figure 1a), while polycycloalkenes display a multiplet at 5.4 ppm (Figure 1c). On the other hand, A,B-alternating units produce a doublet of triplets at 7.0 ppm and a doublet at 5.8 ppm (Figure 1b). Therefore, the extent of A,B-alternation can be easily calculated by integrating these peaks. The sharp coupling patterns demonstrate a highly uniform polymer structure with *E* olefin isomer (J =15.9 Hz). ^{13}C NMR also shows high alternation, displaying only two olefinic carbon peaks for carbons α and β to the carbonyl group (Figure 1d). Such observation of the sharp peaks by ^{1}H, and ^{13}C NMR is very rare for polymers which tend to give broad signals.

Table 1 Examples of ROIMP products.



entry	acylic diene	cycloalkene[a]	[M] /[C][b]	conc.[c] [M]	yield[d] [%]	A,B-alt.[e] [%]	Mn / PDI[f] [10^{-3}g mol^{-1}]
1			290	0.2	84	99	90.0 / 1.73
2			125	0.4	75	96	20.3 / 1.58
3			125	0.4	93	97	14.0 / 1.80
4			200	0.5	91	94	26.1 / 1.71
5			250	0.4	69	94.5	21.4 / 1.43
6			200	0.2	99	98.5	26.5 / 1.80
7			100	0.1	98	97	25.2 / 2.06

[a] 1.0 eq of cycloalkene was used except cyclopentene (1.3 eq) [b] Ratio of total monomer to catalyst
[c] Concentration with respect to acyclic diene [d] Isolated yields after precipitation into hexane or methanol
[e] Determined by ^{1}H NMR [f] Determined by CH_2Cl_2 GPC relative to polystyrene standards

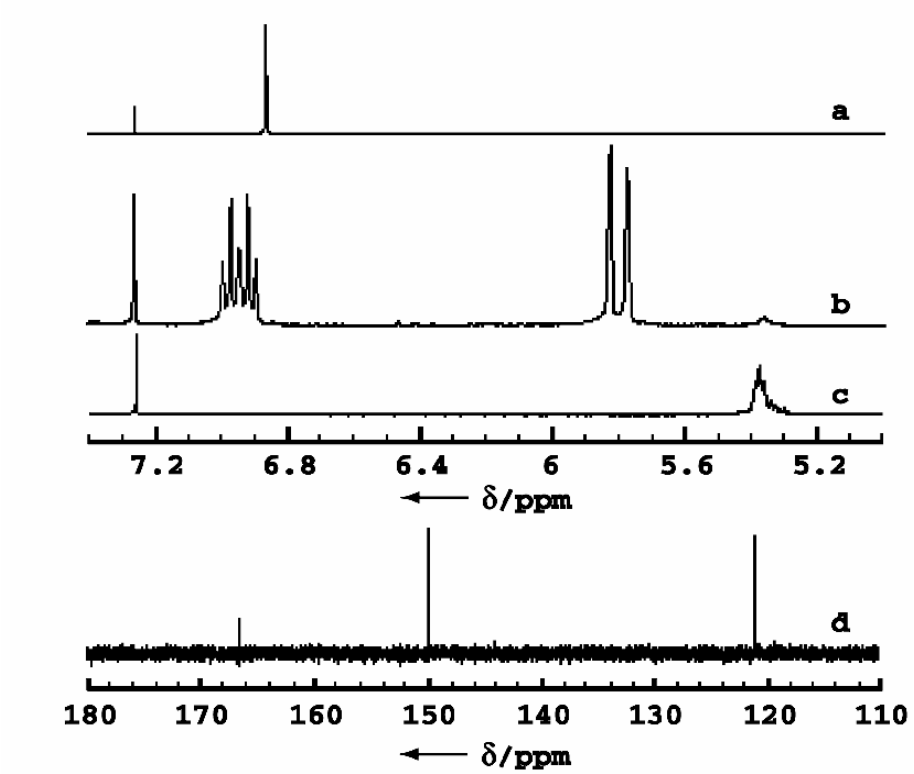


Figure 1. NMR spectra for a ROIMP product

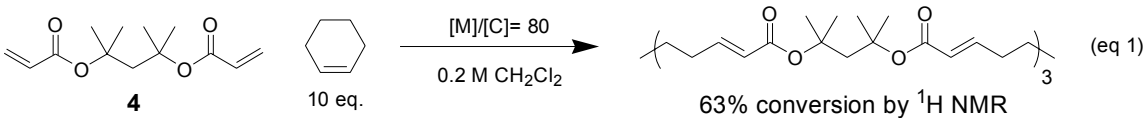
In support of the mechanism shown in Scheme 4, an independently prepared polyoctenamer was treated with 1,4-butanediol diacrylate and catalyst **2**, and the reaction also yielded an copolymer similar to the product of entry 1 in Table 1. In addition, monitoring a ROIMP reaction by ^{1}H NMR showed the rapid and complete ROMP of cyclooctene followed by gradual appearance of peaks corresponding to A,B-alternating units. Furthermore, when a ROIMP reaction was terminated after 20 minutes, a polymer enriched in homo-polycycloalkene olefin units was obtained. These results strongly suggest a mechanism whereby ROMP of the cycloalkene initially produces an unsaturated polymer scaffold to which subsequent insertion of the diacrylate forms the final A,B-alternating structure.

Other cycloalkenes were also viable ROIMP monomers and yielded highly alternating polymers (Table, entries 2 – 4). However, monomers with particularly low ring strains, such as cyclopentene and cycloheptene, required a lower monomer to catalyst ratio of 125:1 due to the slow rate of ROMP.[5a] In order to obtain a high A,B-alternation with volatile cyclopentene (bp 44

^{o}C), a slight excess of 1.3 equiv. of the cycloalkene relative to the diacrylate was used to produce a copolymer with 96% alternation. Even with 2.0 equiv. of cyclopentene, a polymer with higher than 85% A,B-alternation was obtained. Also, treating an isolated polymer of lower A, B-alternation with fresh catalyst **2** yielded a final polymer with higher A,B-alternation. These results suggest that the equilibrium for cyclopentene lies toward the cyclic form at 40 ^{o}C. Therefore, excess homo-polycyclopentene units depolymerize back to cyclopentene and leave the system by evaporation.[21]

Synthesis of A,B-alternating copolymers with cyclohexene was also attempted. Due to very low ring strain, it can not typically be polymerized by olefin metathesis process. Only one report is known for ring opening of cyclohexene where oligomers are formed in low yield by ill-defined classical metathesis catalyst WCl_6 with a turnover number less than 1 at -80 ^{o}C.[22] Recently, after the discovery of the ring-opening of cyclohexene by enoic carbene catalyst,[23] the first catalytic ring-opening of cyclohexene by catalyst **2** and acrylates was reported to produce bis-capped ring-opening-cross products (Chapter 2).[24] This methodology was applied to synthesize A,B-alternating copolymers from cyclohexene.

From the enoic carbene studies, it was known that bulky acrylates generated more stable enoic carbenes. Therefore substrate **4** and cyclohexene were used for ring-opening-cross metathesis polymerization (eq 1). Not surprisingly, low activity and poor stability of enoic carbenes only yield perfectly A,B-alternating oligomers (average of 3 alternating repeat units corresponding to M_n of 900 g/mol) with 63% conversion.



4 10 eq. 63% conversion by ^{1}H NMR (eq 1)

Notably, various functional groups can be incorporated into ROIMP copolymers. 5-*t*-Butyldimethylsilyloxycyclooctene proved to be a viable monomer, comparable to the parent cyclooctene (Table 1, entry 5). In this way, free alcohol groups could be installed into alternating

monomer units upon simple deprotection. 5-Acetoxycycloctene is also a viable monomer for ROIMP reaction, but requires higher catalyst loading presumably due to carbonyl group of the monomer slowing down the insertion by the chelation effect.[19c] Further variations such as ethylene glycol and phenyl groups can be substituted into diacrylate units as shown in entries 6 and 7. These results demonstrate that the regioselective incorporation of functional groups is possible by the appropriate choice of monomers A and B, thus opening up a new class of polymers that can be synthesized by ROIMP.

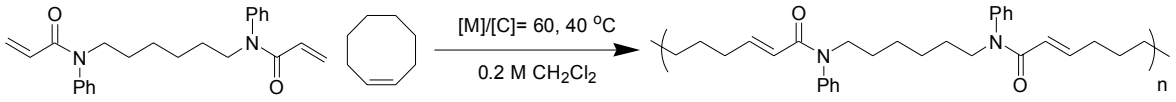
ROIMP exhibits remarkable conversion and selectivity. Compared to ADMET, where high vacuum and elevated temperature are required to drive the polymerization to high conversion by removal of ethylene gas,[6] ROIMP can give high conversion under gentle reflux conditions for two reasons. First, ROMP of cycloalkenes is efficient in making the initial polyalkenomers chains. Second, the formation of 1,2-disubstituted α,β-unsaturated carbonyl cross product is enthalpically favored by more than 3 kcal mol^{-1}.[25] These enthalpic factors, combined with the loss of ethylene, drive the reaction to high conversion. Additionally, the unfavorable oligomerization of diacrylates, where the intermediate is an unstable enoic carbene, leads to high A, B-alternation.[25] Therefore, ROIMP combines benefits of both chain-growth and step-growth polymerization, leading to high molecular weight and high selectivity.

To optimize conversion, other polymerization conditions were investigated. It was found that 0.1-0.5 M solutions in CH_2Cl_2 at 40 ^oC yield the best results. In contrast to ROMP, increasing the concentration beyond 0.5 M resulted in lower conversions. Switching to toluene or 1,2-dichloroethane as solvent also gave lower conversions, at either 40 ^oC or 60 ^oC. While there is precedence for CH_2Cl_2 being the best solvent for cross metathesis of functionalized olefins,[24] the concentration dependence for ROIMP is somewhat surprising, since concentrations of 0.1–0.5 M are considered dilute conditions for conventional step growth polymerization reactions.

Controlling the molecular weight of polymers is a very important issue since polymers with different molecular weights exhibit different properties. For alternating copolymers

produced by ROIMP, the molecular weight can be roughly controlled by changing the relative stoichiometry of the two monomers. For example, using 0.96 equiv. of cyclooctene to 1.0 equiv. of hydroquinone diacrylate gave 17,800 g mol^{-1} with 98% A,B-alternation (PDI = 1.64). In contrast, a copolymer of 45,200 g mol^{-1} and 95.5% alternation (PDI = 1.69) was obtained by increasing to 1.06 equiv. of cyclooctene. These results show that, compared with the 1:1 case (entry 7, Table 1), using a slight excess of hydroquinone diacrylate shortens the polymer chain, but a slight excess of cyclooctene gives higher molecular weight at the cost of alternation due to the oligomeric blocks of polycyclooctene.

This polymerization was further expanded to the synthesis of polyamides by incorporating diacrylic amides into the ROMP polymers. However, as seen in Chapter 2, CM efficiency of acrylic amides by catalyst **2** is heavily dependent on the substituents on the nitrogen.[19c] Similar trends appear to hold true for ROIMP. Insertion of *N*,*N*-dialkyl acrylic amides was very poor, yielding a copolymer with low A,B-alternation. Insertion of *N*-alkyl acrylic amides was more successful, but premature precipitation of polymers occurred since the resulting polyamides are highly insoluble due to their hydrogen bonding ability with other polymer chains. These polyamides were only soluble in strong acids, such as TFA, formic acid and sulfuric acids, similar to commercial Nylons. A ROIMP polymer was successfully prepared from *N*,*N*-diphenyl 1,6-hexyl diacrylic amide and cyclooctene, yielding polyamides with excellent yield and alternation and with moderate molecular weight (Scheme 5). Higher catalyst loading (M/C= 60) was required to improve the insertion of the diacrylic amide.



99% isolated yield, 95% alternation
Mn: 9,700 g/mol, PDI: 1.5

Scheme 5. Synthesis of polyamide by ROIMP

Conclusion

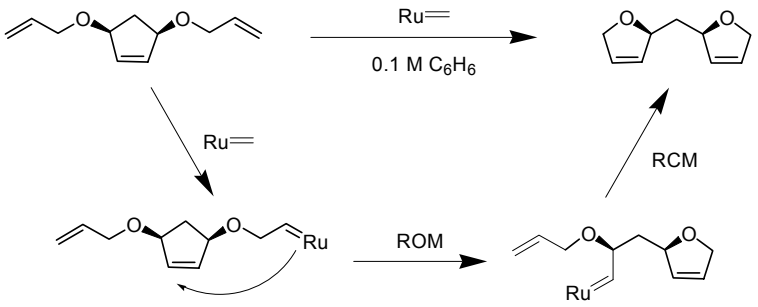
In this section, we have demonstrated a new, general method for synthesizing highly alternating copolymers by olefin metathesis. The high conversion and degree of alternation arise from the thermodynamically driven selective bond formation between diacrylates and cycloalkenes.

Part II. Ring-Opening-Closing-Addition Metathesis Polymerization

Introduction

There are three main transformations in olefin metathesis, ring-opening, ring-closing and cross metathesis reactions. These transformations are well applied to polymerization, ring-opening olefin metathesis polymerization (ROMP),[1] cyclopolymerization[16] and acyclic diene metathesis polymerization (ADMET),[17] respectively. All the polymerizations so far reported use only one of the three types of polymerizations because combining more than one polymerization produces ill-defined random polymers due to lack of control of polymer microstructures. Ring-opening insertion metathesis polymerization (ROIMP),[14] described in part I of this chapter, presents the first example of multiple olefin metathesis polymerization (MOMP) where ring-opening and cross metathesis reactions are combined in one pot to produces A,B-alternating copolymers.

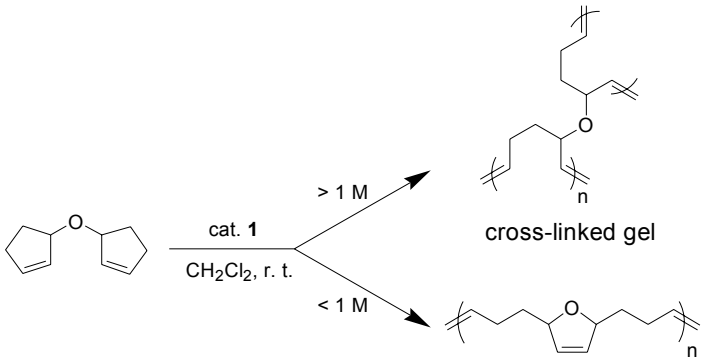
In search for a new olefin polymerization method, applying tandem ring-opening/ ring-closing metathesis presented in Chapter 3[26] to polymerization was envisioned (Scheme 6). In theory this polymerization will combine ROMP and RCM in one pot. Furthermore, incorporating CM into this process will provide a polymerization where three metathesis transformations are combined to produce one uniform polymer microstructure. This section describes efforts to achieve MOMP with 2-cyclopenten-1-yl ether and diacrylates.



Scheme 6. Tandem ring-opening/ring-closing metathesis reaction

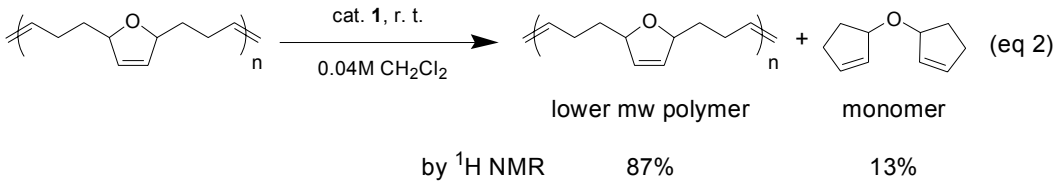
Results and Discussion

2-Cyclopenten-1-yl ether (**5**) has two cyclopentene moieties which can be polymerized by ROMP. Indeed, under typical conditions for the ROMP of cyclopentene (2 M, 23 ^{o}C), a solution of **5** became viscous upon the addition of catalyst **1** implying polymer formation. After 10 minutes, the solution turned into a gel. It is no surprise that **5** having two polymerizable functional groups, cyclopentene moiety, can cross-link to produce insoluble gel. However, in dilute conditions (< 1.0 M) totally different polymers were obtained (Scheme 7). At 0.1 M, ^{1}H NMR showed that **5** was polymerized into poly(2,5-disubstituted-2,5-dihydrofuran) with 87% conversion and E : Z = 3: 1 for acyclic olefins after 24 hours. Increasing the concentration also increased the conversion of the monomers, for example, at 0.5 M and M/C= 100 a conversion of 97% was observed by ^{1}H NMR. Precipitation into methanol gave a rubbery polymer in moderate yield with M_n of 59,000 g/mol. Broad PDI of 1.67 obtained by CH_2Cl_2 GPC relative to polystyrene standards is expected since the reaction appears to be reversible and extensive chain transfer occurs at the acyclic internal olefins.



Scheme 7. Concentration-dependent polymerization

The polymerization appears to be in thermodynamic equilibrium, thus reversible. The isolated polymers were re-dissolved to make 0.04 M CH_2Cl_2 solution and fresh catalyst was added. After 12 hours, 13 mol% of monomers was observed by ^{1}H NMR implying depolymerization in dilute conditions (eq 2). Furthermore, the cross-linked gel obtained at a 2.0 M concentration of **5** was diluted to 0.5 M and the gel disappeared completely after 6 hours yielding mainly a soluble polymer with microstructure of dihydrofuran moiety. It is believed that in dilute concentrations, the degree of cross-linking is reduced due to depolymerization or back-biting to produce cyclized poly(2,5-dihydrofuran).



Poor molecular weight control is observed for this polymerization. Increasing the monomer to catalyst ratio does not linearly increase the molecular weight of the polymers (Table 2). Other catalysts also promote this polymerization, but catalyst **1** outperforms other more reactive catalysts. Catalyst **2**[10] reaches the equilibrium much slowly due to its slower initiation,[27] and ultra-fast initiating catalyst **3** gives polymer with low conversion (25% by ^{1}H NMR) due to the instability of the resulting terminal alkylidene.[12] Unfortunately, monomer to catalyst ratio higher than 300 completely shut down the polymerization. At [M]/[C] = 500, only monomer remained with none of the peaks corresponding to polymer observed by ^{1}H NMR. The catalyst

appeared to be totally decomposed or at least became metathesis inactive catalyst because even the addition of reactive monomers such as norbornene into the solution did not yield polynorbornene. Other more reactive catalysts were used to polymerize with [M]/[C] = 500 and the conversions lower than 25% were observed by ^{1}H NMR. It is speculated that a small amount of 2-cyclopenten-1-yl ether isomerized to enol ethers which react with the catalysts to form catalytically inactive Fischer carbenes.

Table 2. Domino polymerization of **5**[a]

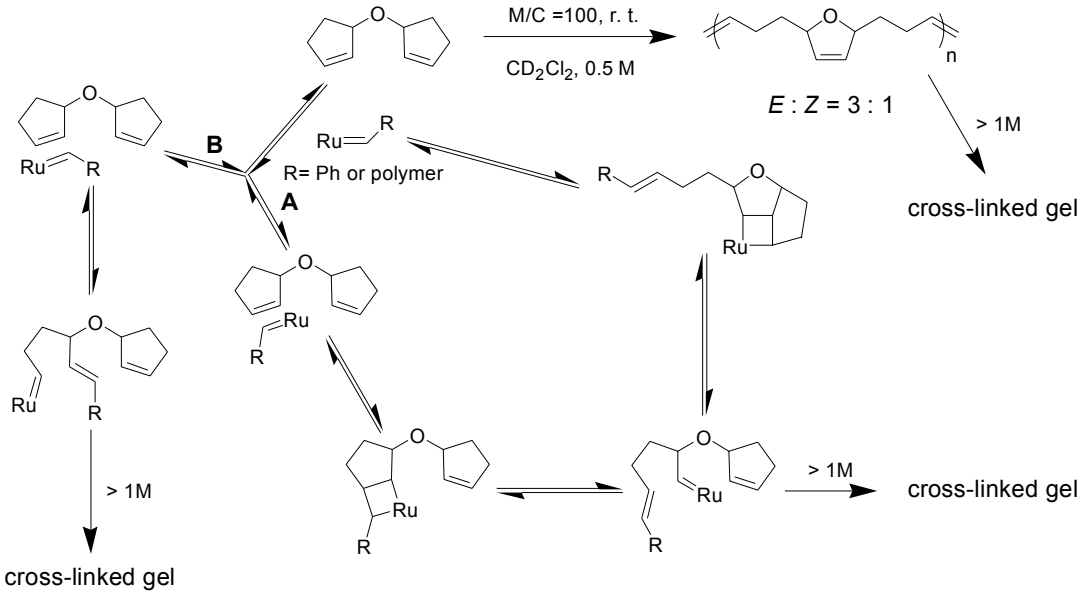
[M]/[C]	M_n[b] [x10^3 g/mol]	PDI[b]
50	52	1.7
100	59	1.7
200	72	2.9
250	128	2.5

[a] Cat. **1** in 0.06 M CH_2Cl_2 at 23 ^oC.[b] Determined by CH_2Cl_2 GPC relative to polystyrene standards

It is likely that the polymerization occurs by a systematic domino metathesis reaction of ring-opening/ring-closing polymerization (Scheme 8). To investigate the mechanism of the polymerization, the reaction was monitored ^{1}H and ^{13}C NMR. Firstly, monitoring the reaction at high concentration (2 M) revealed the peak corresponding to the desired cyclized polydihydrofuran as well as several other peaks corresponding to randomly cross-linked polymers. However, at 0.5 M, ^{1}H and ^{13}C NMR only shows the peak corresponding to the desired polymer throughout the polymerization. This implies that at 0.5 M, only domino metathesis reactions of ring-opening-closing polymerization is operative, and the reversible formation to the desired polymer microstructure from the cross-linked random polymerization is less likely to occur.

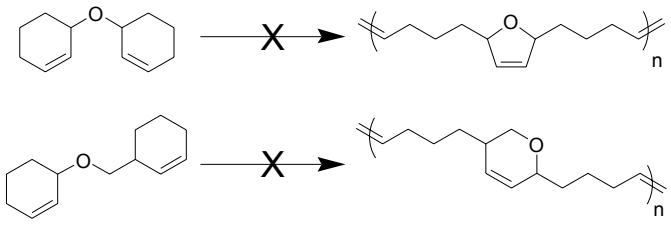
Although there are two possible binding modes for the catalyst, only the path **A** results in the desired domino ring-opening/ring-closing polymerization (Scheme 8). At low concentration, the path **B** do not intervene the polymerization since the ring-opened alkylidene should reversibly go back to the monomer by the non-productive intramolecular RCM. However, at high

concentration, intermediates of both path **A** and **B** as well as the final product can form the cross-linked gel. Notably, this polymerization is the first example to produce polymers by using both ring-opening and ring-closing metathesis reactions.



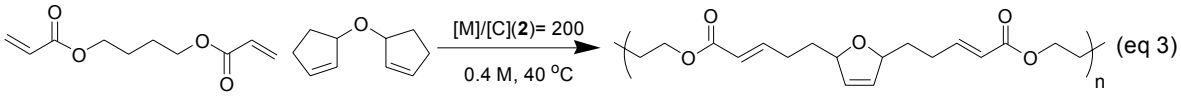
Scheme 8. Proposed mechanism of ring-opening/ring-closing metathesis polymerization

Interestingly, 2-cyclopenten-1-yl ether can be polymerized at even below 0.1 M despite possessing the low-strained olefin. In contrast, cyclopentene does not undergo ROMP at dilute concentration (< 1 M) because the concentration is below the critical concentration for cyclopentene meaning that ring-closing rate is much faster than the rate of ROMP rate at concentrations below 1 M. This difference can be explained by the fact that the facile domino ring-opening/ring-closing metathesis produces lower ring-strained 2,5-dihydrofuran. Also, due to the substitutions at the 2 and 5-positions of the dihydrofuran, the backward domino reaction to depolymerize the chains is slowed down relative to chain propagation. Encouraged by this result, attempts to polymerize challenging monomers containing a cyclohexene moiety were made (Scheme 9). Cyclohexene and its derivatives have been impossible to polymerize by olefin metathesis.[1] Unfortunately, monomers of similar structures to 2-cyclopenten-1-yl ether but with cyclohexenyl rings did not polymerize, and only the starting materials remained.



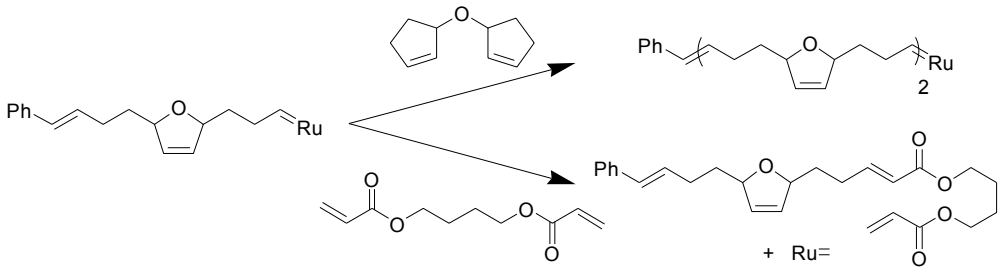
Scheme 9. Attempts to polymerize monomers with cyclohexene moieties

This multiple olefin metathesis polymerization (MOMP) can be further extended by combination with ROIMP.[14] Treating 2-cyclopenten-1-yl ether and 1,4-butanediol-diacrylate with catalyst **2** produced polymer with high A,B-alternation in high yield (eq 3). Here the concentration of the reaction is also crucial as a cross-linked gel is formed at high concentrations. This is the first polymerization where all three types of olefin metathesis transformation (ring-opening, ring-closing and cross metathesis reactions) are combined in orderly manners to produce a uniform polymer microstructure.



99% isolated yield, 97% A,B-alternation
Mn= 13,800 g/mol, Mw= 27,000 g/mol, PDI= 1.95

To understand the detailed mechanism of ring-opening-closing-addition metathesis polymerization, the reaction was monitored by ^{1}H NMR. Unlike the ROIMP case, the chain propagation of 2-cyclopenten-1-yl ether is not as fast as ROMP of cyclooctene. ^{1}H NMR spectra reveal that the chain propagation of 2-cyclopenten-1-yl ether to another monomer unit is about as fast as the cross coupling with the diacrylates (Scheme 10). Therefore, a mixture of the polymer chains with different microstructures grows at the beginning of the reaction, which gradually converge into one uniform microstructure at the end of the polymerization. It is notable that three different metathesis reactions are independently and simultaneously occurring in one-pot, but cooperatively produce the final polymer with one well-defined polymer microstructure.



Scheme 10. Similar rates for the both reactions

Conclusion

To summarize 2-cyclopenten-1-yl ether undergoes domino ring-opening/ring-closing metathesis polymerization at dilute concentration. When combined with ROIMP, a polymerization where all three types of olefin metathesis, ring-opening, ring-closing, and cross metathesis are utilized, is possible. This chapter demonstrates that mechanistically interesting multiple olefin metathesis polymerizations can produce well-defined polymer microstructures.

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Experimental Section

General Experimental Section. NMR spectra were recorded on Varian Mercury-300 NMR (300 MHz for ^{1}H and 74.5 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), and multiplet (m). The reported ^{1}H NMR data refer to the major olefin isomer unless stated otherwise. The reported ^{13}C NMR data include all peaks observed and no peak assignments were made. Gel

permeation chromatography (GPC) analysis in CH_2Cl_2 was obtained on a HPLC system using a Shimadzu LC-10AP_{vp} pump, Shimadzu DGU-14A degasser, a Rheodyne model 7125 injector with a 100 *u*l injection loop through Polymer Standard 10 micron mixed bed columns, and a Knauer differential refractometer. Molecular weights and molecular weight distributions, M_w/M_n, are reported relative to narrow disperse polystyrene standards (Showa Denko).

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. All other chemicals were purchased from the Aldrich, Strem, or Nova Biochem Chemical Companies, and used as delivered unless noted otherwise. CH_2Cl_2 was purified by passage through a solvent column prior to use.

Procedure for Scheme 3: To a flask charged with polyoctenomer (56.0 mg, 0.51 mmol) in 0.5 ml of CH_2Cl_2, catalyst **2** (4.3 mg) and acrylic acid (87 *u*l, 1.27 mmol) were added. Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product (102 mg, 89%) was precipitated from the solution. The solid was filtered and washed with CH_2Cl_2. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 10.66 (2H, br), 6.87 (2H, dt, J= 15.6, 6.9 Hz), 5.78 (2H, dd, J= 15.6, 1.5 Hz), 2.20 (4H, m), 1.47 (4H, m), 1.35 (4H, m). HRMS (EI) calcd. for $C_{12}H_{18}O_4$: 227.1283, found 227.1292.

Procedure for Table 1, entry 1: To a flask charged with 1,4-butanediol diacrylate (90 mg, 0.45 mmol) in 2 ml of CH_2Cl_2, catalyst **2** (2.7 mg) and cyclooctene (65 *u*l, 0.45 mmol) were added. Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product (108 mg, 84%) was precipitated into methanol. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.93 (1H, dt, *J*= 7.2, 15.9 Hz), 5.77 (1H, d, *J*= 15.9 Hz), 4.13 (2H, br), 2.12 (2H, m), 1.73 (2H, m), 1.43 (2H, m), 1.30 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.8, 149.6, 121.3, 64.0, 32.5, 29.3, 28.2, 25.8.

Procedure for Table 1, entry 2: To a flask charged with 1,4-butanediol diacrylate (34 mg, 0.15 mmol) in 0.4 ml of CH_2Cl_2, catalyst **2** (2.3 mg) and cyclopentene (20 *u*l, 0.15 mmol) were added. Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product (37 mg, 75%) was precipitated into hexane. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.85 (1H, dt, *J*= 7.2, 15.9 Hz), 5.82 (1H, d, *J*= 15.9 Hz), 4.10 (2H, br), 2.22 (2H, m), 1.60-1.75 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.5, 148.4, 121.9, 64.0, 31.7, 30.7, 26.6, 25.6.

Procedure for Table 1, entry 3: To a flask charged with 1,4-butanediol diacrylate (60 mg, 0.30 mmol) in 0.8 ml of CH_2Cl_2, catalyst **2** (4.1 mg) and cycloheptene (35.5 *u*l, 0.30 mmol) were added. Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product (74 mg, 93%) was precipitated into hexane. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.93 (1H, dt, *J*= 6.9, 15.3 Hz), 5.78 (1H, dt, *J*= 1.5, 17.0 Hz), 4.13 (2H, br), 2.17 (2H, m), 1.72 (2H, m), 1.30- 1.42 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.8, 149.5, 121.4, 64.0, 32.4, 29.0, 28.1, 25.8.

Procedure for Table 1, entry 4: To a flask charged with 1,4-butanediol diacrylate (60 mg, 0.30 mmol) in 0.6 ml of CH_2Cl_2, catalyst **2** (2.6 mg) and cyclododecene (58 *u*l, 0.30 mmol) were added. Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product (92 mg, 91%) was precipitated into methanol. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.94 (1H, dt, *J*= 7.2, 15.3 Hz), 5.80 (1H, dt, *J*= 1.5, 15.9 Hz), 4.13 (2H, t, *J*= 5.1 Hz), 2.16 (2H, dt, *J*= 6.9, 6.6 Hz), 1.73 (2H, t, *J*= 3.0 Hz), 1.42 (2H, m), 1.24 (7H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.9, 149.9, 121.2, 64.0, 32.6, 29.9, 29.8, 29.5, 28.4, 25.8.

Procedure for Table 1, entry 5: To a flask charged with 1,4-butanediol diacrylate (40 mg, 0.20 mmol) in 0.5 ml of CH_2Cl_2, catalyst **2** (1.4 mg) and cyclododecene (54 mg, 0.20 mmol) were added. Quick degassing by dynamic vacuum was conducted and the flask was fitted with a

condenser and refluxed under argon for 6 hours. The product (60 mg, 69%) was precipitated into methanol. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.96 (1H, dt, *J*= 6.6, 16.2 Hz), 5.80 (1H, d, *J*= 15.9 Hz), 4.16 (2H, br), 3.69 (1H, m), 2.20 (2H, m), 1.75 (2H, br), 1.58 (1H, m) 1.46 (2H, m), 0.90 (9H, s), 0.03 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.7, 149.6, 149.3, 121.5, 121.2, 71.4, 64.0, 36.7, 35.5, 21.7, 28.3, 26.2, 25.8, 24.0, 18.4, -3.9, -4.0.

Procedure for Table 1, entry 6: To a flask charged with tri(ethylene glycol) diacrylate (53 mg, 0.21 mmol) in 1 ml of CH_2Cl_2, catalyst **2** (1.8 mg) and cyclooctene (28 *u*l, 0.21 mmol) were added. Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product (68 mg, 99%) was precipitated into hexane. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.95 (1H, dt, *J*= 6.9, 15.9 Hz), 5.82 (1H, d, *J*= 15.9 Hz), 4.26 (2H, t, *J*= 4.8 Hz), 3.70 (2H, t, *J*= 5.1 Hz), 3.64 (2H, s), 2.16 (2H, dt, *J*= 6.6, 6.6 Hz), 1.42 (2H, m) 1.29 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.7, 150.0, 121.2, 70.8, 69.6, 63.6, 32.5, 29.3, 28.2.

Procedure for Table 1, entry 7: To a flask charged with hydroquinone diacrylate (44 mg, 0.21 mmol) in 1 ml of CH_2Cl_2, catalyst **2** (3.5 mg) and cyclooctene (27.5 *u*l, 0.21 mmol) were added. Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product (60 mg, 98%) was precipitated by hexane. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 7.11- 7.20 (3H, m), 6.00 (1H, d, *J*= 15.3 Hz), 2.27 (2H, dt, *J*= 6.9, 6.3 Hz), 1.52 (2H, broad), 1.37 (2H, broad). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 165.0, 152.0, 148.2, 122.6, 120.7, 32.7, 29.3, 28.2.

Procedure for Scheme 5: To a flask charged with diamides (58 mg, 0.16 mmol) in 1 ml of CH_2Cl_2, catalyst **2** (4.4 mg) and cyclooctene (21 *u*l, 0.16 mmol) were added. Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product (76 mg, 100%) was precipitated by hexane. ^{1}H NMR (300MHz,

$CDCl_3$, ppm): δ 7.2- 7.4 (6H, m), 7.1 (4H, d, *J*= 6.9 Hz), 6.81 (2H, dt, *J*= 15.6, 6.6 Hz), 5.57 (2H, d, *J*= 15.0 Hz), 3.69 (4H, t, *J*= 6.9 Hz), 1.94 (4H, m), 1.47 (4H, br), 1.25 (8H, br) 1.11 (4H, br).

Procedure for 5: To a vial charged with **5** (64 *u*l, 0.41 mmol) in 0.7 ml of CH_2Cl_2, catalyst **1** (1.2 mg) was added. Quick degassing by dynamic vacuum was conducted and stirred for 12 hours. The product (42 mg, 68%) was precipitated by methanol. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 5.76 (2H, m), 5.43 (2H, m), 4.80 (2H, br), 2.06 (4H, br), 1.58 (4H, br). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 130.3, 130.2, 130.1, 130.0, 129.8, 85.5, 85.4, 37.1, 36.2, 23.7.

Procedure for eq 3: To a flask charged with 5 (50 *u*l, 0.32 mmol) and 1,4-butanediol diacrylate (62.5 mg, 0.32 mmol) in 1 ml of CH_2Cl_2, catalyst **2** (3.5 mg). Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product (60 mg, 98%) was precipitated by hexane. ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 7.11- 7.20 (3H, m), 6.00 (1H, d, *J*= 15.3 Hz), 2.27 (2H, dt, *J*=6.9, 6.3 Hz), 1.52 (2H, broad), 1.37 (2H, broad). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.7, 149.2, 149.0, 130.3, 130.1, 121.6, 121.4, 85.2, 85.1, 64.0, 35.2, 34.4, 28.6, 28.2, 25.7.

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