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Pulsed-Addition Ring-Opening Metathesis Polymerization: Catalyst-Economical Syntheses of Homopolymers and Block Copolymers

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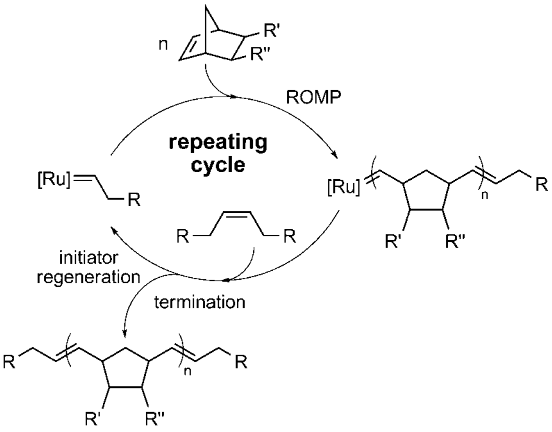
Abstract: Poly(*tert*-butyl ester norbornene imide) homopolymers and poly(*tert*-butyl ester norbornene imide-*b*-*N*-methyloxanorbornene imide) copolymers were prepared by pulsed-addition ring-opening metathesis polymerization (PA-ROMP). PA-ROMP is a unique polymerization method that employs a symmetrical *cis*-olefin chain transfer agent (CTA) to simultaneously cap a living polymer chain and regenerate the ROMP initiator with high fidelity. Unlike traditional ROMP with chain transfer, the CTA reacts only with the living chain end, resulting in narrowly dispersed products. The regenerated initiator can then initiate polymerization of a subsequent batch of monomer, allowing for multiple polymer chains with controlled molecular weight and low polydispersity to be generated from one metal initiator. Using the fast-initiating ruthenium metathesis catalyst $(H_2IMes)(Cl)_2(pyr)_2RuCHPh$ and *cis*-4-octene as a CTA, the capabilities of PA-ROMP were investigated with a Symyx robotic system, which allowed for increased control and precision of injection volumes. The results from a detailed study of the time required to carry out the end-capping/initiator-regeneration step were used to design several experiments in which PA-ROMP was performed from one to ten cycles. After determination of the rate of catalyst death, a single, low polydispersity polymer was prepared by adjusting the amount of monomer injected in each cycle, maintaining a constant monomer/catalyst ratio. Additionally, PA-ROMP was used to prepare nearly perfect block copolymers by quickly injecting a second monomer at a specific time interval after the first monomer injection, such that chain transfer had not yet occurred. Polymers were characterized by gel permeation chromatography with multiangle laser light scattering.

Introduction

Ring-opening metathesis polymerization (ROMP) has emerged as a powerful technique for creating a wide variety of polymer architectures from strained cyclic olefins.[1] Dominated by early transition metal molybdenum catalysts and late transition metal ruthenium catalysts, multiblock,[2] star,[3] graft,[4] dendronized,[5] and other types of polymer architectures can be produced by ROMP, often with precise control over molecular weight, molecular weight distribution, and composition. ROMP has been used industrially in various applications,[6] but the preparation of ROMP polymers with controlled structures often requires high catalyst loadings.

Scheme 1. Mechanism of PA-ROMP



Highly efficient, expensive metal catalysts are used in the synthesis of several types of polymers, most notably polyolefins.[7] An important quality of polyolefin catalysts is their ability to produce hundreds to thousands of polymer chains from an individual metal center. ROMP catalysts also extremely efficient,

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with turnover numbers as high as 4000 in solution[8] and over 60 000 in bulk in the case of dicyclopentadiene.[9] However, in the production of living ROMP polymers where the metal complex acts as an initiator, this does not translate into low product cost because each catalyst molecule is capable of producing only one living polymer chain.

Our strategy to regenerate a ROMP initiator is to cleave the metathesis catalyst from the living polymer chain end with a *cis*-olefin chain transfer agent (CTA), simultaneously reform the active initiator species, and subject the regenerated initiator to an additional portion of monomer (Scheme 1). If the reactivity of the monomer is much greater than that of the CTA, then polymerization and initiator regeneration can be performed in one pot, making this technique a potentially attractive polymerization method. In this situation, the ROMP reaction occurs selectively in the presence of CTA until monomer consumption is complete, at which point the end-capping and catalyst regeneration reaction takes place. Attempts to effect this type of repeating cycle have only been described twice.[10] In one report using a molybdenum catalyst, Crowe and co-workers were able to polymerize ten batches of norbornene using styrene as a CTA.[10a] The product showed a significant high molecular weight shoulder, likely due to a small amount of incomplete chain transfer. Additionally, because of the air, moisture, and functional group sensitivity of this catalyst, the practical applications of this system are limited. In another example by Gibson, the ruthenium olefin metathesis catalyst $(PCy_3)_2(Cl)_2RuCHPh$ was recycled eight times in the polymerization of a *tert*-butyl ester-functionalized norbornene using *cis*-1,4-diacetoxy-2-butene as the CTA.[10b] The polymer product in this case showed a low molecular weight tail due to a considerable amount of chain transfer during the polymerization. The occurrence of chain transfer in the presence of a reactive norbornene is likely a result of poor matching of the reactivities of the monomer and the CTA with the catalyst. Although the topic has been only very briefly explored, this polymerization technique, called pulsed-addition ROMP (PA-ROMP), has the potential to improve the efficiency of ROMP and increase the number of applications of ROMP polymers.

In addition to its economic benefits, PA-ROMP would also reduce the ruthenium contamination in the product. The amount of metal needed in metal-catalyzed living polymerization has been reduced to 10 ppm or lower in many examples in the case of copper-mediated atom transfer radical polymerization (ATRP) by the development of ARGET (activators regenerated by electron transfer) ATRP.[11] However, reduction of the metal contamination in ROMP polymers remains an unsolved problem. Cleavage of the catalyst from the polymer chain end with ethyl vinyl ether followed by precipitation of the product is typically used remove the catalyst. However, this method often does not completely remove the catalyst, leaving the resulting polymers contaminated with ruthenium. While low metal contamination is acceptable in polymers in many cases, removal of potentially toxic metals is absolutely crucial in pharmaceutical products. Considering recent studies using ROMP polymers in biological applications, metal contamination in the products is expected to be a problem as these developments move toward in vivo applications.[12] The need for developing new methods to remove metal contaminants in ROMP polymers could be circumvented by simply using less metal to carry out ROMP.

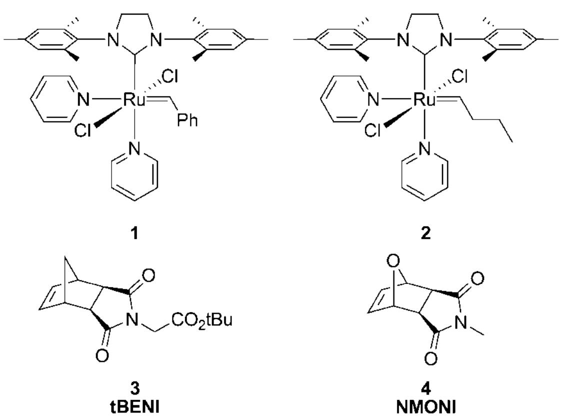

Figure 1. Ruthenium olefin metathesis catalysts and monomers used in PA-ROMP reactions.

To make PA-ROMP feasible, a highly active and functional group tolerant metathesis catalyst needs to be used. Recently, pyridine-containing, fast-initiating ruthenium catalysts have shown remarkable reactivity as initiators for living ROMP.[1b,2c,13,14] We investigated PA-ROMP with one such catalyst, $(H_2IMes)(Cl)_2(pyr)_2RuCHPh$ (**1**). Additionally, we extended its application to block copolymers, further illustrating the power of this approach.

Results and Discussion

We recently reported on the synthesis of low polydispersity ROMP-ATRP diblock copolymers using catalyst **1**.[14] The ROMP polymers were end-capped by adding the symmetrical *cis*-olefin (*Z*)-but-2-ene-1,4-diyl bis(2-bromopropanoate) to the reaction mixture after ROMP was complete. Because no secondary metathesis reactions (backbiting) occur with substituted norbornenes, the α-bromoester ATRP initiating group was added only to the active chain end. We expected that during this process the ruthenium catalyst was also functionalized with an α-bromoester, and we elected to investigate the possibility of using this regenerated initiator for subsequent polymerization by ROMP. However, the end-capping of the polymer chain with this CTA took 3 h to reach completion. A faster end-capping reaction would be required to make PA-ROMP practically useful.

The end-capping of a ROMP polymer chain with an internal olefin CTA is simply a cross metathesis reaction between the ruthenium alkylidene species at the end of a living polymer chain and the internal olefin CTA. Previous studies from our group have demonstrated that sterically unhindered and electron-rich

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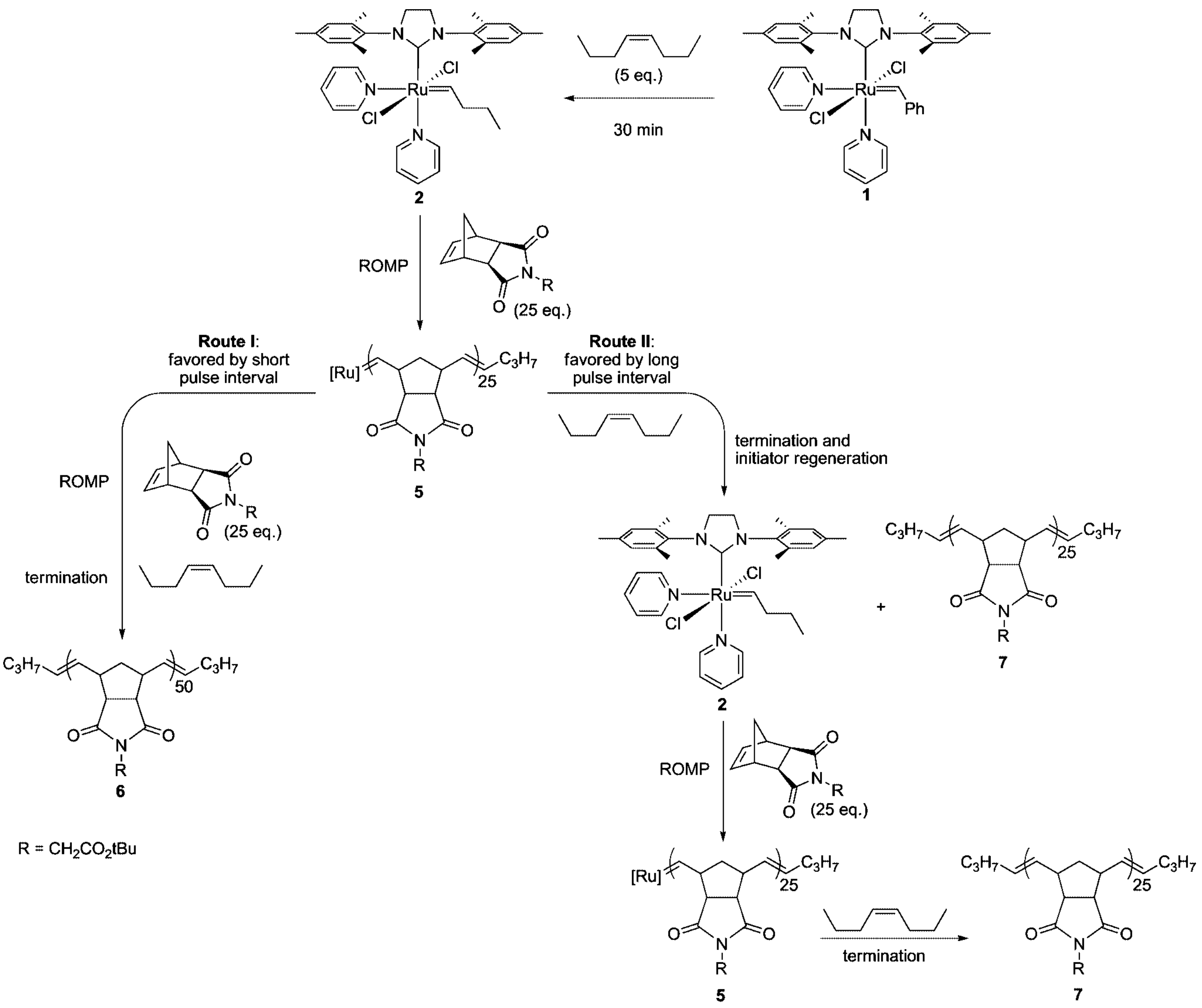
Scheme 2. Experiment Designed To Determine the Optimal Pulse Interval Required for PA-ROMP



olefins have the highest reaction rates for cross metathesis.[15] In this study, *cis*-4-octene was chosen as the CTA because of its favorable cross metathesis activity, commercial availability, and relatively high boiling point. ROMP of norbornenes is extremely fast because of the release of large amounts of ring strain, with rate constants several orders of magnitude faster than even the best cross metathesis reactions. Similarly, cross metathesis is several orders of magnitude faster than secondary metathesis of substituted polynorbornenes. Based on the great differences in reactivity between ROMP, cross metathesis, and secondary metathesis, we expected that PA-ROMP would be possible in one pot, even with a very reactive CTA.

A Symyx robot system was used for all experiments to provide an extremely high degree of precision and consistency in addition volumes. Our group[16] and others[17] have used robotic systems to assay catalytic activity and optimize reaction conditions, but to our knowledge this is the first report of a systematic study of polymer synthesis done using a robotic system. All stock solutions were prepared in a nitrogen-filled glovebox and capped with screw-cap, septum-topped vials with vent needles. Reactions were run in open vials in a nitrogen-filled glovebox to eliminate potential coupling from oxygen.[18] *tert*-Butyl ester norbornene imide (tBENI) (**3**) was chosen for all homopolymer experiments because of the ease of synthesizing the material in high purity.

Pulse Interval Optimization. An initial experiment designed both to examine whether PA-ROMP was possible over two cycles with catalyst **1** and to optimize the pulse interval (elapsed time between additions) was setup as shown in Scheme 2. Equal amounts of a solution containing catalyst **1** and *cis*-4-octene were added into 10 vials. All reaction vials and stock solutions were kept at 25 °C. This solution was allowed to stand for 30 min as catalyst **2** formed. A stock solution containing monomer **3** was also prepared. Vial A was used as a control and received only one addition of the monomer solution. Vials B through J

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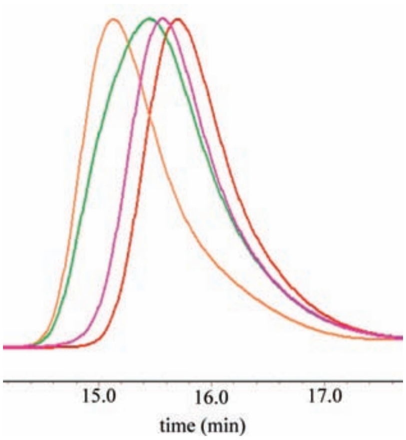

Figure 2. GPC traces of products **A** (red; 100% polymer **7**), **B** (orange; 100% polymer **6**), **F** (green; 47% polymer **7**, 53% polymer **6**), and **J** (purple; 100% polymer **7**) from pulse interval optimization experiment.

Table 1. Characterization of the Products Formed in the Pulse Interval Optimization Experiment

product mixture	pulse interval (min)	M_n (Da)	PDI	% polymer 7[a]
A	N/A	8100	1.04	100
B	0.5	16200	1.04	0
C	1.3	15600	1.05	7
D	2.1	14900	1.06	16
E	2.9	14200	1.06	24
F	4.9	12400	1.08	47
G	8.3	10800	1.08	66
H	14.0	9920	1.06	77
I	23.7	9380	1.04	84
J	40	9120	1.04	100[b]

[a] All values except for product **J** are assigned assuming no catalyst death occurred between pulses, meaning that only products **6** and **7** are present in the mixture. [b] This value is assumed to be 100% based on no observation of uncapped polymer in subsequent experiments. The discrepancy in M_n between product **A** and product **J** is assumed to be a result of catalyst death.

each received two additions of monomer, and the pulse interval was varied between 0.5 min (vial B) and 40 min (vial J). Forty minutes after the second addition was complete for all vials, the polymer products were recovered by precipitation and filtration. For product mixtures **B** through **J**, a combination of polymer products **6** (DP = 50) and **7** (DP = 25) was expected, depending on the amount of end-capping that occurred during the time between the two pulses. Shorter pulse intervals were expected to favor route I because the second addition of monomer occurs before ruthenium-bound polymer **5** has reacted with *cis*-4-octene. This route produces 1 equiv of polymer **6**. Longer pulse intervals were expected to favor route II; a longer interval allows for the reaction of *cis*-4-octene with ruthenium-bound polymer **5** to regenerate initiator **2** and form polymer product **7**. A second addition of monomer then produces another equivalent of polymer **7**.

Gel permeation chromatography (GPC) with multiangle laser light scattering was used to determine the absolute molecular weight and molecular weight distribution of the polymer products. Figure 2 shows the GPC traces of product mixtures **A**, **B**, **F**, and **J**, and Table 1 compares the molecular weight and polydispersity index (PDI) of each of the polymer samples. Product mixture **A** (control sample) contains only polymer **7** and shows a molecular weight of 8100 Da, which is in reasonable agreement with the theoretical molecular weight of 7100 Da. Product mixture **B** shows a monomodal GPC peak with a molecular weight of 16 200 Da, indicating that only product **6** was formed. This shows that with a pulse time of 30 s, only route I is followed, meaning that no end-capping occurs within 0.5 min of the first monomer addition. The remaining molecular weight data demonstrate that as the pulse interval increases, route II becomes favored, and the molecular weight decreases, approaching that of pure polymer **7**. Product mixture **J** nearly reaches the original molecular weight of polymer **7**, but catalyst death occurring during the time between the pulses prevents a complete return to the original molecular weight of 8100 Da. Another feature of the polymerization is revealed by examining the molecular weight distribution. The PDI increases up to product mixture **F**, which is a mixture of approximately 53% **6** and, 47% **7**.[19] At this point the PDI begins to drop again as an increasing amount of product **7** is formed from the second monomer addition. On the basis of these results, we chose a pulse interval of 30 min for the subsequent experiments.

It should be noted that this method provides a synthetic route for the production of living, telechelic polynorbornenes with narrow polydispersities. CTAs are typically used to synthesize telechelic ROMP polymers,[20] but these polymers all have PDIs near 2.0. While high PDIs are acceptable for some purposes, low PDIs are required for many applications, such as when specific morphologies of block copolymers are desired. Broad polydispersities are observed when ROMP with extensive chain transfer reaches thermodynamic equilibrium. In our route, the bulky backbone of the P(tBENI) prevents chain transfer except at the chain end. Low polydispersity, telechelic polynorbornenes can thus be obtained by the method described above, even without the use of a robot.

Homopolymers by PA-ROMP. On the basis of the data from the pulse interval optimization trials, a set of experiments investigating the feasibility of PA-ROMP over 10 cycles was devised. In these experiments, equal amounts of a stock solution containing catalyst **1** and 5 equiv of *cis*-4-octene were added by the robot to each of 10 vials (designated K through T), each maintained at 25 °C. After 30 min was allowed for catalyst **2** to form, 120 μL from a stock solution containing 25 equiv of monomer **3** and 1.1 equiv of *cis*-4-octene (both relative to catalyst) were added to each vial, ultimately forming polymer **8** (Scheme 3). The additional *cis*-4-octene was added to keep the concentration of CTA constant over the entire reaction. After another 30 min, 120 μL from this stock solution was added only to vials L through T. This process was continued, eliminating one vial during each 30 min pulse interval, such that vial K received one addition of monomer solution, vial L received two additions, up to vial T, which received ten additions. This allowed us to examine the product mixtures formed in each cycle, shown in Table 2.

A trend of slowly decreasing peak retention time and slowly increasing peak width is observed in the GPC traces (Figure 3). It is important to note that no high molecular weight shoulders or secondary peaks are present. The lack of high molecular weight species indicates that the chain termination and catalyst regeneration portions of the cycle were complete each time before additional monomer was added. The molecular weight data are shown in Table 2. The theoretical molecular weight of the polymer based on the initial monomer/catalyst

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(19) These percentages are calculated by assuming that the M_n of 12 400 Da is a combination of pure products **6** and **7**.

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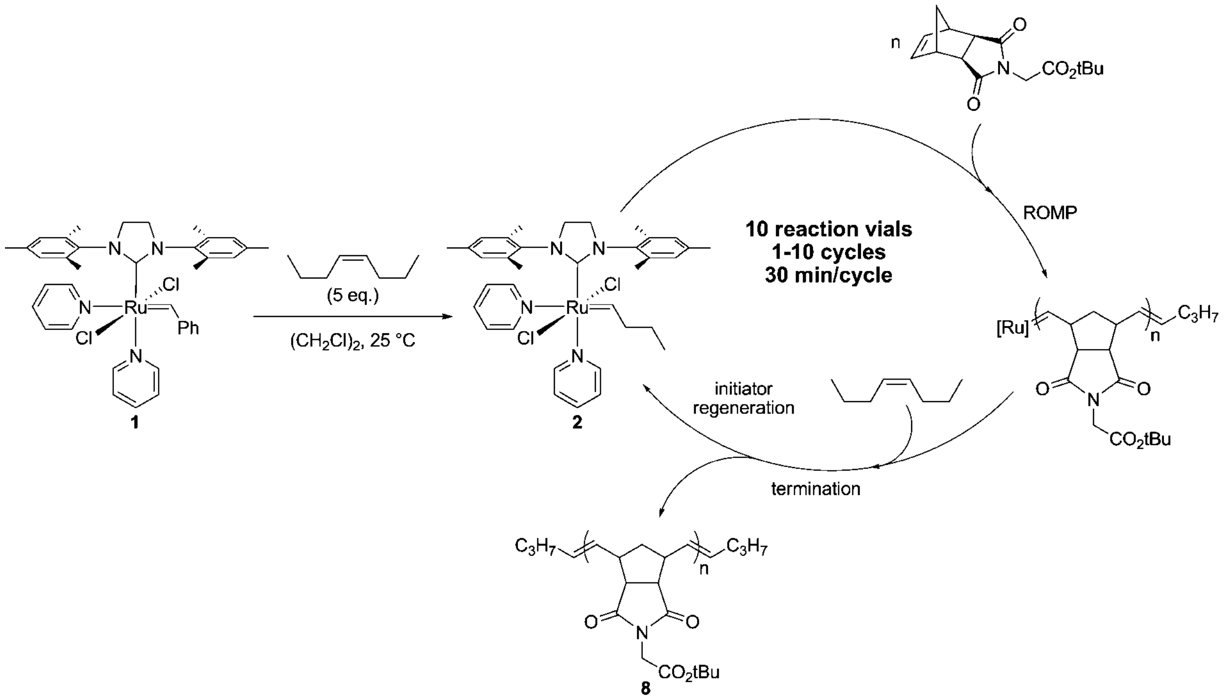
Scheme 3. Synthesis of Polynorbornenes by PA-ROMP



(M/C) ratio of 25 was 7100 Da, and the molecular weight of the product mixture **K** was 7430 Da, indicating that a small amount of catalyst death occurred during the formation of catalyst **2**. The subsequent products all show slowly increasing molecular weights. We attribute this slow increase to catalyst death during both the polymerization and the end-capping reactions. Because 100% initiator efficiency is observed for pyridine-containing metathesis catalysts such as **1**, the degree of polymerization of a given polymer is determined by the M/C ratio. Even after ten cycles, product mixture **T** had a molecular weight of 11000 Da and a relatively low PDI of 1.12. Figure 4 shows the molecular weight and polydispersity data graphed with a well-fitting exponential curve[21] fitted to the molecular weight data, indicating a nearly constant level of catalyst death. Analysis of the data (Supporting Information) shows that approximately 8.5% of the catalyst available at the beginning of a cycle dies during the polymerization and end-capping reactions.

To demonstrate the usefulness of PA-ROMP for synthesizing a single polymer product with low polydispersity using a low catalyst loading, we constructed a one-vial experiment in which the amount of monomer solution added in each cycle was varied

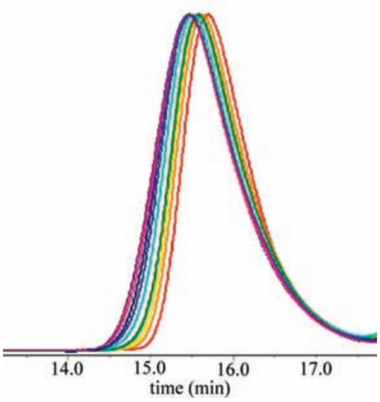


Figure 3. GPC traces of product mixtures **K** (red), **L** (orange), **M** (yellow), **N** (light green), **O** (green), **P** (light blue), **Q** (royal blue), **R** (dark blue), **S** (light purple), and **T** (dark purple) from one (product mixture **K**) to ten (product mixture **T**) cycles of PA-ROMP.

Table 2. Characterization of P(tBENI) Homopolymer Products by GPC from 10 Cycles of PA-ROMP at 25 °C with M/C = 25 and a Pulse Interval of 30 min

product mixture	additions received	M_n (Da)	PDI
K	1	7430	1.05
L	2	7660	1.09
M	3	7990	1.06
N	4	8180	1.09
O	5	8360	1.09
P	6	9250	1.11
Q	7	9960	1.11
R	8	10800	1.09
S	9	10800	1.16
T	10	11000	1.12

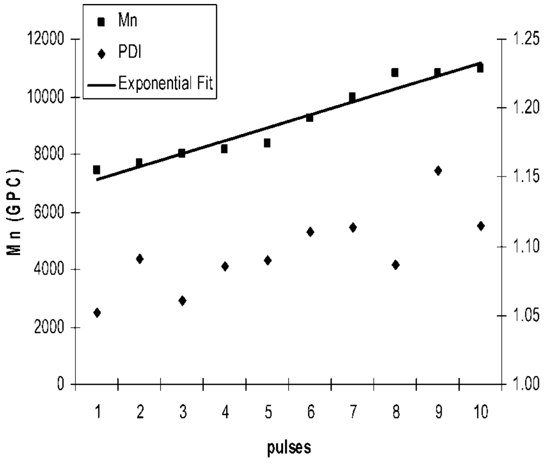


Figure 4. Dependence of M_n and PDI on number of cycles of PA-ROMP.

Scheme 4. Synthesis of a Single Batch of Low Polydispersity Hompolymer by PA-ROMP

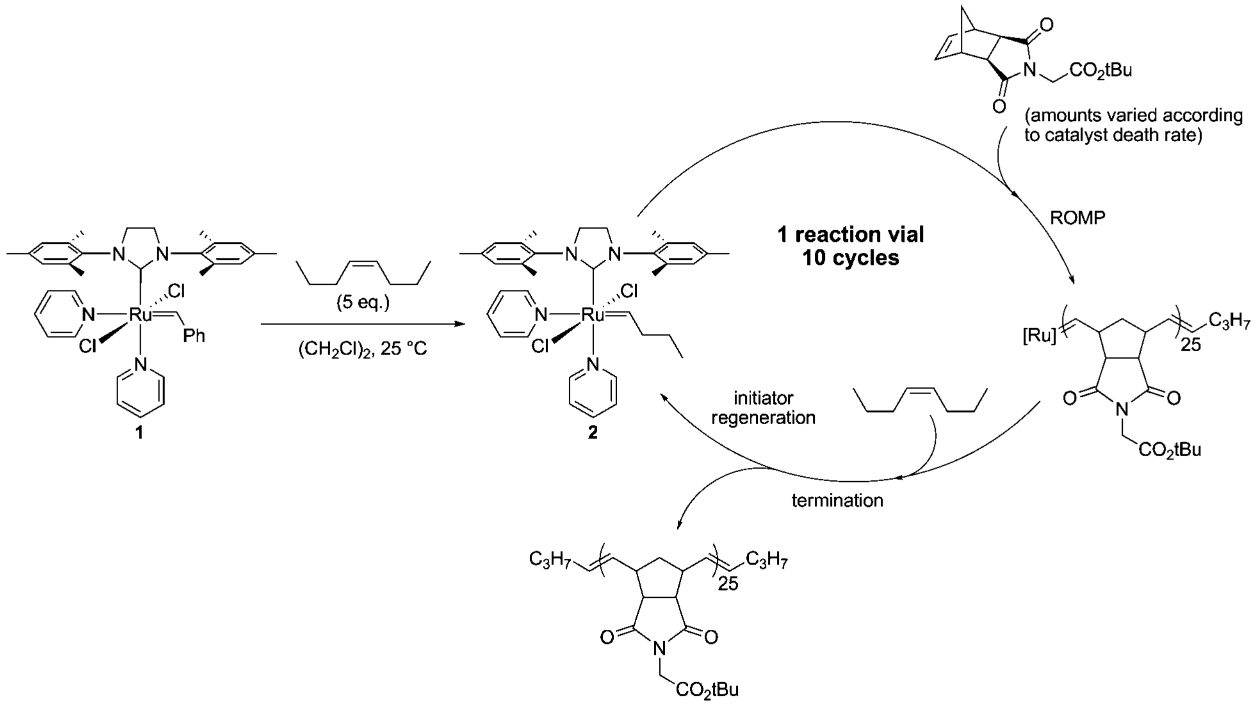


Table 3. Addition Volumes of Monomer Solution Assuming 8.5% Catalyst Death Rate for Each of Ten Cycles of PA-ROMP

pulse	% catalyst still alive	volume added (μL)
1	100	120.0
2	91.5	109.8
3	83.7	100.4
4	76.6	91.9
5	70.1	84.1
6	64.1	76.9
7	58.7	70.4
8	53.7	64.4
9	49.1	58.9
10	44.9	53.9

Table 4. Characterization of P(tBENI) Homopolymer Products by GPC from 10 Cycles of PA-ROMP at 25 °C with M/C = 100 and a Pulse Interval of 30 min

product mixture	additions received	M_n (Da)	PDI
U	1	28600	1.07
V	2	47100	1.08
W	3	58000	1.14
X	4	64500	1.20
Y	5	68700	1.20
Z	6	75700	1.22
AA	7	80700	1.22
BB	8	84600	1.24
CC	9	89400	1.23
DD	10	93600	1.24

in accordance with the observed rate of catalyst death (Scheme 4). By decreasing the amount of monomer added in each pulse to keep a constant M/C ratio, we hoped to observe a single final polymer product with low polydispersity and a controllable molecular weight. Conditions of 25 °C with a pulse interval of 30 min, an initial M/C ratio of 25, and an assumed 8.5% catalyst death rate were used. The robot was programmed to add monomer solution in volumes outlined in Table 3, all into a single reaction vial. Ten pulses of 30 min each were performed at 25 °C. The product showed an M_n = 9640 Da and PDI = 1.08, which is in reasonable agreement with the theoretical molecular weight of 7100 Da. This experiment demonstrates that PA-ROMP is capable of producing a single, low polydispersity product with a controllable molecular weight. Notably, 132 mg of polymer was produced from 2 mg of catalyst in this synthesis. A traditional ROMP synthesis of 132 mg of a polymer with this molecular weight would require 14 mg of catalyst. This 7-fold decrease in catalyst consumption illustrates the power of PA-ROMP to maximize the efficiency of ROMP catalysts.

In order to probe the limits of PA-ROMP, a second set of ten reactions were performed under identical conditions to the first ten-vial experiment, except an initial M/C ratio of 100 was used (polymer theoretical molecular weight of 27 200 Da). The resulting polymer characterization data of product mixtures **U** through **DD** are shown in Table 4. Product **U** matches the theoretical molecular weight, but the subsequent products have much higher molecular weights and broader polydispersities compared with the same experiment using a M/C ratio of 25. Analysis of the molecular weights (Supporting Information) showed that approximately 16.5% of the available catalyst died during each cycle. This is nearly twice the rate at which catalyst died when polymers with an initial M/C ratio of 25 were synthesized. Clearly this increase in the catalyst death rate can be attributed to decomposition during the ROMP reaction. Because the decomposition pathways of olefin metathesis catalysts active during ROMP have not been studied, it is difficult to predict what modifications could be made to improve PA-ROMP of larger polymers with catalyst **2**. These results demonstrate the need for more stable olefin metathesis catalysts.

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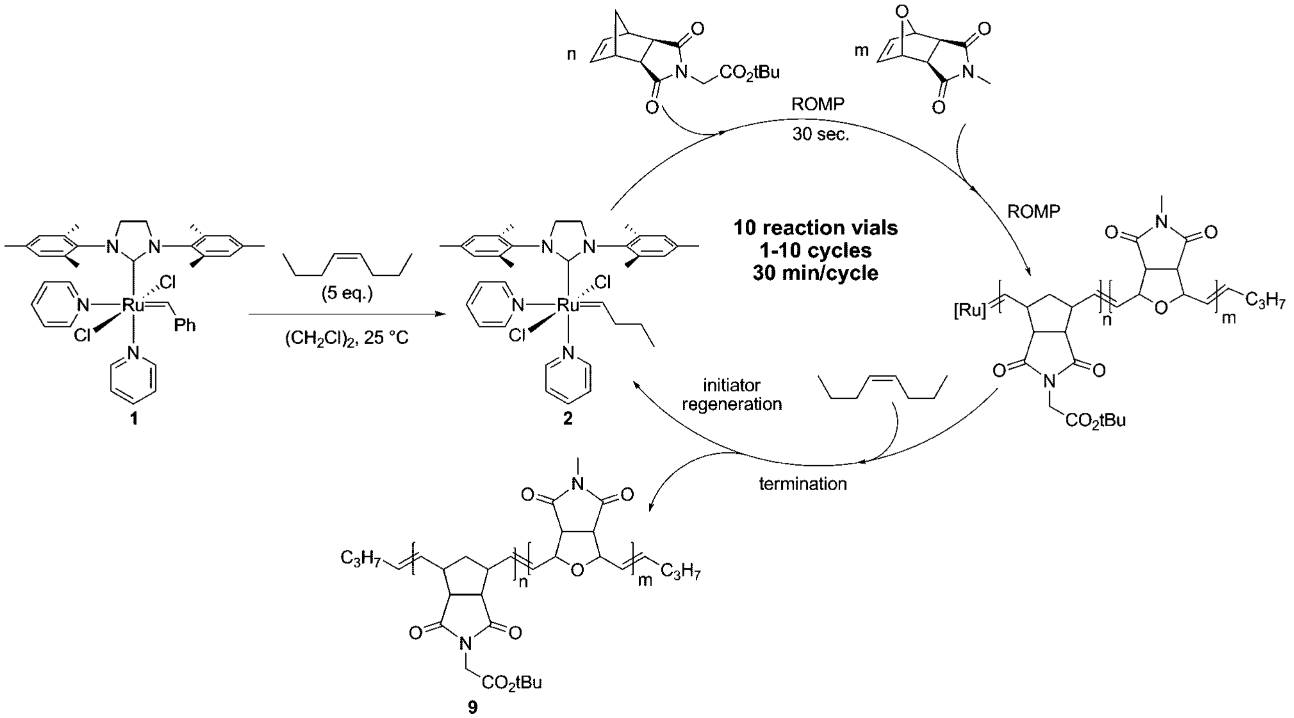
(21) While a linear fit to the data presented here is also reasonable, molecular weight is expected to depend on the number of cycles in PA-ROMP in an exponential fashion. When a constant catalyst death rate is assumed, plotting pulses vs molecular weight out to 40 cycles clearly shows that an exponential fit is the better choice for the data. A theoretical demonstration of this relationship is shown in the Supporting Information.

Scheme 5. Synthesis of P(tBENI-*b*-NMONI) Block Copolymers by PA-ROMP



Block Copolymers by PA-ROMP. The ability to synthesize block copolymers with control over block lengths, ratios, and composition has led to a dramatic increase in the number and variety of polymeric materials available to the synthetic chemist. Block copolymers are unique structures that are especially suited to meet specific needs because the desirable properties of two different polymers can be combined into one product.[22] The synthesis of block copolymers on a large scale, however, is seldom feasible because nearly all techniques yield only one polymer chain per initiator molecule. Unless this barrier can be overcome, expensive metal catalysts, such as those used for ethylene and propylene polymerization and for ROMP, render block copolymerization uneconomical.

Recently, Arriola et al. developed a method termed chain shuttling polymerization that facilitates the economical synthesis of polyolefin block copolymers by producing many polymer chains from each metal initiator.[23] Inspired by this report, we examined whether catalyst **1** could be used to synthesize block copolymers by the PA-ROMP technique. Because this strategy allows for multiple polymer chains to be produced from one metal center, PA-ROMP may also enable the large scale synthesis of block copolymers by reducing catalyst loading.

In order to synthesize block copolymers, a solution of a second monomer needs to be added to the reaction mixture after ROMP of the first block is complete but before any end-capping has occurred. ROMP is known to be extremely fast,[20] but it is vital to the synthesis of block copolymers that no end-capping occurs before the second monomer is added. Results obtained from the pulse interval optimization experiments (Table 1) indicate that no observable amount of end-capping occurs in the first 0.5 min after addition of monomer, but end-capping does begin within 1.2 min after monomer addition. With these values in mind, we designed a set of 10 experiments similar to those performed in the homopolymer syntheses. In these experiments, the robot made additions in pairs, adding monomer **3** first, followed 0.5 min later by *N*-methyloxanorbornene imide (NMONI) (**4**) to ultimately form polymer **9** (Scheme 5). Ten reaction vials, designated **EE** through **NN**, were set up at 25 °C with 30 min pulse intervals and a total monomer to catalyst ratio of 25 (12.5 for each monomer), adding monomer solutions to one less vial in each pulse, as was done with the homopolymer experiments. A 5-fold excess of *cis*-4-octene was included in the catalyst solution, and additional *cis*-4-octene was added with the second monomer to maintain a constant concentration of CTA in the reaction mixture. GPC traces of the isolated polymer product mixtures **EE** through **NN** are shown in Figure 5.

Table 5. Characterization of P(tBENI-*b*-NMONI) Block Copolymer Products by GPC from Ten Cycles of PA-ROMP at 25 °C with M/C = 25 and a Pulse Interval of 30 min

product mixture	additions received	M_n (Da)	PDI
EE	1	6320	1.10
FF	2	6430	1.14
GG	3	6920	1.14
HH	4	7670	1.14
II	5	8480	1.16
JJ	6	9510	1.18
KK	7	10200	1.23
LL	8	12100	1.22
MM	9	12700	1.26
NN	10	13300	1.30

The polymer characterization data from the block copolymer experiments are shown in Table 5. As was observed in the homopolymer experiments, the vial that received only one pair of additions (product mixture **EE**) had a molecular weight of 6320 Da, which is in good agreement with the theoretical

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[22] Hamley I. W. *The Physics of Block Copolymers*; Oxford Univ. Press: Oxford, 1998).

[23] Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714–719.

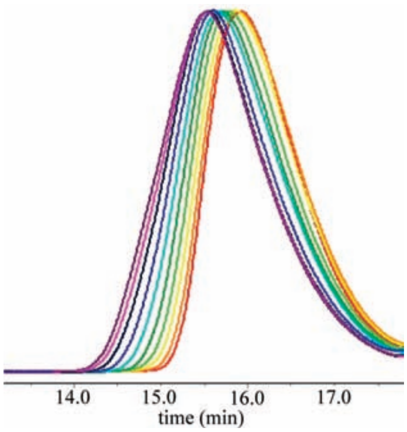

Figure 5. GPC traces of block copolymer product mixtures **EE** (red), **FF** (orange), **GG** (yellow), **HH** (light green), **II** (green), **JJ** (light blue), **KK** (royal blue), **LL** (dark blue), **MM** (light purple), and **NN** (dark purple) from one (product mixture **EE**) to ten (product mixture **NN**) cycles of PA-ROMP.

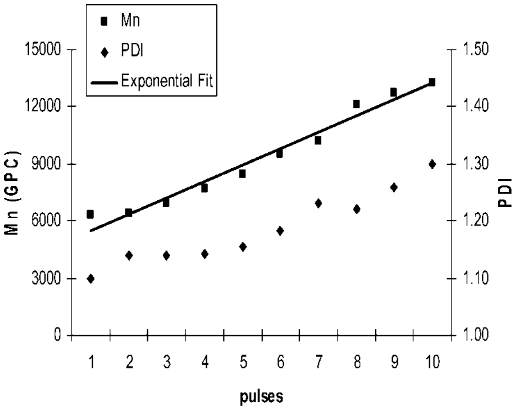

Figure 6. Dependence of M_n and PDI on Number of Cycles of PA-ROMP for P(tBENI-*b*-NMONI) Block Copolymers.

molecular weight of 5820 Da, assuming a small amount of catalyst death. The molecular weight of the products slowly increased as catalyst death occurred at a rate of 14.5% per cycle. Figure 6 shows the data plotted with a well-fitting exponential trendline.

A single vial experiment was run to determine whether complete consumption of monomer **3** was complete before monomer **4** was added 0.5 min later. This experiment was set up in the same way as the block copolymer experiments, except that the reaction was quenched after 0.5 min with ethyl vinyl ether (100 equiv) instead of adding monomer **4**. Evaluation of the products by ^{1}H NMR spectroscopy showed that typically 75% of monomer **3** was consumed at this point. This indicates that a small amount of monomer **3** may be present in the second block, but thermal analysis (described below) shows that phase separation of the blocks still occurs. We chose not to increase the interval between the addition of monomer **3** and monomer **4** in order to avoid premature end-capping, which would result in a small amount of dead P(tBENI) homopolymer. A less reactive CTA would likely allow for a longer interval between the two monomer additions, yielding perfect block copolymers.

Differential scanning calorimetry (DSC) was used to evaluate whether the products were indeed block copolymers capable of phase separation. Very broad T_g's were observed for the unsaturated polymers, which we attribute to the mixture of cis and trans olefinic stereochemistry in the polymer backbones. Sharper T_g's were observed when the polymers were hydrogenated using tosyl hydrazide or Wilkinson's catalyst under 600 psi H_2 (Supporting Information). A T_g of 111 °C was observed for the hydrogenated P(tBENI) homopolymer, and a T_g of 159 °C was observed for the hydrogenated P(NMONI) homopolymer. For the hydrogenated P(tBENI-*b*-NMONI) block copolymer, T_g's of 117 and 159 °C were observed. These values are in good agreement with the T_g's of the constituent homopolymers. A P(tBENI-*ran*-NMONI) random copolymer was also prepared and hydrogenated. This polymer showed a single T_g of 136 °C, which lies in between those of the constituent blocks, as is expected for random copolymers. To our knowledge, this is the first example of low polydispersity block copolymers prepared by a regenerated-initiator method. We expect that synthesis of tri- and higher multiblock ROMP polymers could also be prepared by PA-ROMP by simple extension of the current procedure.

Conclusions

PA-ROMP is a useful strategy for synthesizing homopolymers and block copolymers with much lower catalyst loadings than traditional ROMP. A Symyx robotic system was used to investigate the ability of ruthenium metathesis catalyst **1** to mediate PA-ROMP in several ten-reaction experiments. Using *cis*-4-octene as a CTA to end-cap growing polymer chains and regenerate the ruthenium initiator, up to ten pulses of monomer were successfully polymerized. Under our best conditions, catalyst death was observed to occur at a rate of approximately 8.5% per cycle. This was overcome in a one reaction experiment by varying the amount of monomer injected during each cycle in accordance with the catalyst death rate. This experiment produced a low polydispersity P(tBENI) homopolymer using seven times less catalyst than traditional ROMP. Furthermore, block copolymers were prepared by PA-ROMP. By waiting 0.5 min between injections of tBENI and NMONI into the reaction vials, nearly perfect P(tBENI-*b*-NMONI) block copolymers were prepared in up to ten cycles of PA-ROMP. This represents the first synthesis of low polydispersity block copolymers that is not limited by the one-chain-per-initiator convention. The technique of PA-ROMP is expected to facilitate the emergence of ROMP polymers on the market by reducing cost because of decreased catalyst loading. Additionally, considering the decreased metal contamination in PA-ROMP polymers compared with traditional ROMP polymers, we anticipate that this technique will be valuable for biological applications of ROMP polymers.

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Supporting Information Available: Experimental procedures, GPC traces, and derivation of catalyst death rates. This material is available free of charge via the Internet at http://pubs.acs.org.

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