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COMMUNICATION

Flow-Facilitated Ring Opening Metathesis Polymerization (ROMP) and Post-Polymerization Modification Reactions

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This communication describes the use of flow to facilitate ring opening metathesis polymerization (ROMP) reactions of norbornene-derivatives. Homo-and block copolymers can be prepared with moderate control over molecular weight. These reactions are operationally simple and complete in seconds. Additionally, thio-bromo "click" post-polymerization modifications can be carried out inline.

Although the concept of "living" polymerizations was introduced in the mid-20th century, the last few decades have been witness to an explosion of reports detailing the development and use of a variety of controlled/living polymerizations.[1-7] Most of these examples rely on typical batch reactors and meticulously air-free conditions using relatively sophisticated apparatus (glove boxes or Schlenk lines) so, one might think that their scale-up and use in high-throughput processes would be hampered. However, the use of continuous flow to facilitate high-throughput macromolecular synthesis[8-26] has experienced a renaissance since its initial inception more than 50 years ago.[27,28]

The allure of continuous flow lies within its widely accepted attributes of superior heat transfer, more efficient mixing, accelerated reaction rates, etc.[29,30] Although many of these characteristics have been disputed[31], it does appear that continuous flow can simplify scale-up[32] and can allow for greater control over reaction time. So, *even if* the former attributes are exaggerated, the latter two alone warrant the implementation of continuous flow into existing processes.

Considering the popularity that ring opening metathesis polymerization (ROMP) has acquired, it is surprising that no reports describe its facilitation under flow. Buchmeiser's laboratory has used ROMP to prepare monolithic supports for flow reactors, and his group (and others) has used continuous flow to facilitate ring closing- and cross-metathesis reactions.[33-39] Guironnet's laboratory[26] has recently utilized continuous flow to prepare norbornene-terminated poly(lactide) macromonomers, while Lin and Chen[40] used continuous flow to synthesize unsymmetrical cyclooctenes. However, in both cases ROMP reactions were carried out under standard batch conditions. Inspired by these reports, we reasoned that the relatively rapid rates (as well as the benchtop-stability of Grubbs-type initiators) would allow for ROMP reactions to be carried out in flow using operationally simple apparatus. We are pleased to report our results herein.

No matter their complexity, most continuous flow systems have at least a few things in common: solvent/reagent delivery system, mixer, and reactor components.[29,30,41-44] We opted to utilize a simple and cost-effective system based on a standard dual syringe pump (solvent/reagent delivery), T-mixer (mixing), and PTFE tubing (reactor). Schematic cartoon depictions of the flow systems used are shown in Figure 1 and a photograph of the actual system can be found in the supporting information (ESI, Figure S1). Upon the construction of the rudimentary flow system shown in Figure 1a, we attempted to carry out the ROMP of norbornene **2** using Grubbs 2nd generation initiator. This involved loading CH_2Cl_2 solutions of **2** (0.48 M) and initiator (0.0021 M) to separate 6 mL plastic syringes that were connected to a T-mixer through PTFE tubing (length = 10 cm, i.d. = 1.016 mm). These syringes were then loaded into a dual syringe pump and the reaction was carried out using a flow rate of 1 mL/min (45 s residence time (t_R)) with a reactor tube length of 92 cm and volume of 0.75 mL. Unfortunately, this initial experiment resulted in an extremely viscous polymer solution that clogged the reactor tubing and rendered characterization difficult.

This viscosity issue was prevented by decreasing the initial monomer and initiator concentrations ($[M]_o$ and $[I]_o$) to 0.38 and 0.0017 M, respectively, and switching to the faster-initiating Grubbs 3rd generation initiator **1**. Using a flow rate of 2 mL/min (t_R of 22.5 s), we were able to obtain polynorbornene in > 95 % conversion, as observed by ^{1}H NMR (Table 1, entry 1).

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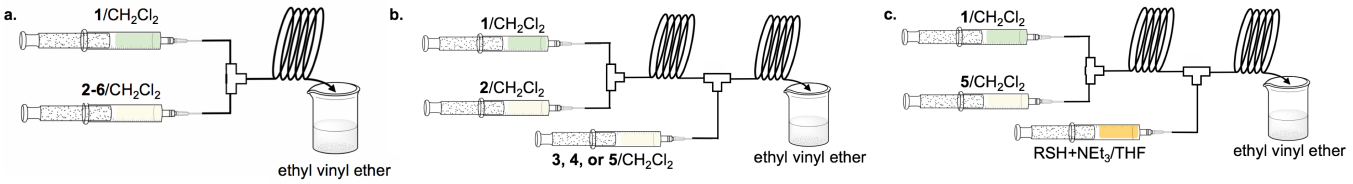


Fig. 1 Cartoon depictions of continuous flow systems used in this study for (a.) homopolymerizations, (b.) block copolymerizations, and (c.) homopolymerizations followed by post-polymerization modification.

We next carried out GPC analysis and found that the dispersity (*Đ*) and M_n values were higher than anticipated (Table 1, entry 1). Similar to an earlier report[45], we found that cooling the reaction led to a slight improvement (Table 1, entry 2). This was accomplished by submerging the tubular reactor and T-mixer in an ice-water bath.

Table 1 Homopolymerizations under flow conditions

Entry[a]	Mon.	Conv. (%)[b]	$M_{n(theor.)}$ (Da)	M_n (Da)[d]	*Đ*[d]
1	**2**	> 95	21,372	44,200	1.18
2[c]	**2**	> 95	21,372	32,000	1.14
3	**3**	94	34,547	43,400	1.30
4	**4**	93	63,678	54,000	1.16
5	**5**	90	58,825	44,000	1.33
6[e]	**6**	76	48,169	52,000	1.24

[a]Conditions: M:**1** = 227:1, $[M]_o$ = 0.38 M, $[\mathbf{1}]_o$ = 0.0017 M, t_R = 22.5 s, tubular path length = 92 cm, room temperature. [b]Determined by ^{1}H NMR. [c]Conducted at 0 °C. [d]Determined by GPC. [e] t_R = 450 s.

This process was next expanded toward other monomers (Figure 2). We were discouraged to find that the polymerization of commercially-available $\mathbf{3}_{endo/exo}$ led to considerably lower conversions and provided much less control over M_n and *Đ* values (ESI). We hypothesized that this was a consequence of the presence of significant amounts of the slower-reacting *endo* isomer. Interestingly though, it was found that this reaction led to a slight selectivity for polymerizing the *exo* isomer (Figure S2, ESI). We are currently investigating methods to increase this selectivity, as the exclusive polymerization of *exo* norbornenes directly from *endo*/*exo* mixtures would result in a greener process than what is currently used for *endo*/*exo* separations.[45]

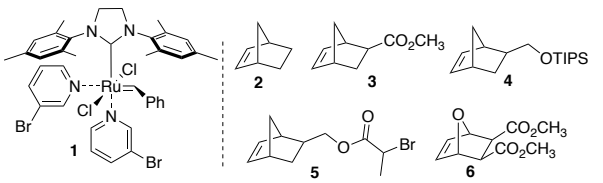


Fig. 2 Initiator (**1**) and monomers (**2**-**6**) used in this study. All monomers are *exo*, unless otherwise stated.

Subjecting pure *exo* **3**[46,47] to the same flow conditions provided product in much higher conversions, albeit with modest control over M_n and *Đ* (Table 1, entry 3). We next carried out the polymerizations of protected alcohol **4**[48,49] and α-bromo ester **5**[50-52] (Table 1, entries 4 and 5). This led to products with M_n and *Đ* of 54,000 Da and 1.16 and 44,000 Da and 1.33, respectively. Unfortunately, we found that this system is not without limitations. Case-in-point, polymerization of oxanorbornene **6**[47] led to very low conversions, possibly due to coordination of the oxanorbornene oxygen to the Ru centre.[53] To remedy the low conversions, the t_R could be increased from 22.5 to 450 s (Table 1, entry 6). Still, the conversion of this monomer was lower than norbornene-derivatives **2**-**5**. Similarly, it was observed that less strained monomers like cyclooctene and cyclooctadiene provided low conversions (ca. 20 %) and inconsistent results.

Table 2 Homopolymerizations under flow conditions

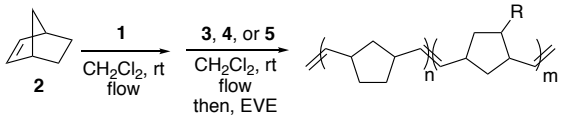
Entry[a]	Mon.	Conv. (%)[b]	$M_{n(theor.)}$ (Da)	M_n (Da)[c]	*Đ*[c]
1	**2**	> 95	21,372	36,500	1.07
3	**3**	86	34,547	34,900	1.11
4	**4**	>95	63,678	68,300	1.18
5[d]	**5**	83	58,825	45,200	1.12

[a]Conditions: M:**1** = 227:1, $[M]_o$ = 0.38 M, $[\mathbf{1}]_o$ = 0.0017 M, t_R = 7.5 s, tubular path length = 92 cm, room temperature. [b]Determined by ^{1}H NMR. [c]Determined by GPC. [d]$[M]_o$ = 0.50 M, $[\mathbf{1}]_o$ = 0.0022 M.

Further, even though GPC traces for entries 1-5 were monomodal, *Đ* values were higher than expected and M_n values were not in great agreement with theoretical values. We found that this could be improved by reducing the t_R (from 22.5 to 7.5 s), instead of lowering the temperature, which resulted in lower conversions and much less control over M_n and *Đ* (Table S1, ESI). This was accomplished by increasing the flow rate to 6 mL/min (the upper limit of this syringe pump). This offered an improvement over reaction time as well as better control over M_n and *Đ* in some cases (Table 2, entries 1, 3, and 5). However, *Đ* values were still higher than what is typically observed in batch reactions[45,54-56], suggesting other factors are at play.[57] Furthermore, no clear universal trends were evident on the effect that flow rate had on either M_n, *Đ*, or even conversion. For example, monomer **5** had to be polymerized under higher concentrations (Table 2, entry 5), as the standard conditions provided low conversions (ca. 33 %) and much less control.

One of the main advantages of ROMP is that its living nature allows for the preparation of block copolymers, materials that have found wide applicability for a number of applications.[58] There exist many examples in the literature exploiting continuous flow for the preparation of block copolymers using a variety of polymerization methods.[9,11,15,20,23,59-62] Because of this, we were curious if the same flow concept outlined above

could be adapted for the preparation of block copolymers using ROMP. In order to accomplish this, it was necessary to install a second T-mixer junction, syringe and syringe pump for sequential monomer addition (Figure 1b).



Scheme 1. Formation of block copolymers in flow.

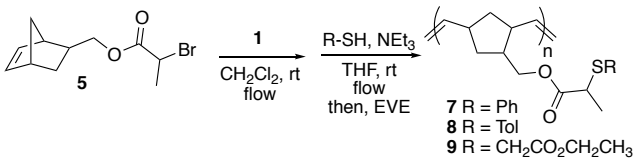
As proof-of-concept, we used this flow apparatus to prepare three block copolymers. Preparation of the first block (monomer **2**) was carried out at a flow rate of 2 mL/min into a second junction in which a CH_2Cl_2 solution (0.33 M) of M2 (**3**, **4**, or **5**) was introduced at a flow rate of 2 mL/min (Scheme 1 and Table 3). We were restricted to a t_R of 22.5 s for each reactor because of limitations of the second syringe pump. The reaction was quenched by addition into ethyl vinyl ether. Subsequent analysis by ^{1}H NMR revealed > 95 % conversion with respect to each monomer. GPC analysis shows a clear shift from lower to higher molecular weights, indicating successful chain extension (Table 3 and ESI).

Table 3 Block copolymerizations under flow conditions

Entry[a]	M2	Conv. (%)[b]	$M_{n(theor.)}$ (Da)	M_n (Da)[c]	$Đ$[c]
1	**3**	> 95	24,634	35,600	1.21
2	**4**	> 95	37,467	44,500	1.25
3	**5**	> 95	35,329	43,600	1.27

[a]Conditions: **2**:M2:**1** = 100:100:1, $[M1]_o = [M2]_0$ = 0.33 M, $[I]_o$ = 0.0033 M, reactor 1 t_R= 22.5 s, reactor 2 t_R = 22.5 s, total t_R = 45 s, tubular path length = 92 cm for each reactor. [b]With respect to both monomers, determined by ^{1}H NMR. [c]Determined by GPC.

For all polymerizations described in Tables 1-3, GPC analysis showed monomodal molecular weight distributions. Though, it should be noted that once the reaction and syringe pump have ceased, there exist a small amount of reaction solution left in the system. Collection of this material along with the rest of the product can lead a small higher-molecular weight trailing peak in the GPC. This can be avoided by not collecting this material.



Scheme 2. Polymerization and click modification of **5**.

For the last few years, our laboratory has been interested in the utilization of thio-bromo "click" reactions (first described by Percec's laboratory[63,64]) as tools for post-polymerization modifications (Scheme 2).[51-53] As is the case with most other post-polymerization functionalizations, these processes relied on the preparation, isolation, and purification of the unmodified polymer. Subsequent modification was carried out in another batch reaction. These processes can be time-intensive and require multiple reaction flasks, solvent precipitations, and purifications, resulting in the generation relatively large amounts of waste. Because of these reasons, interest in the use of continuous flow to accomplish post-polymerization modifications has grown.[19,65,66]

Table 4 Homopolymerization of **5** and click modification under flow conditions

Entry[a]	Prd	Conv. (%)[b]	$M_{n(theor.)}$ (Da)	M_n (Da)[c]	$Đ$[c]
1	**7**	> 95	65,403	43,200	1.21
2	**8**	> 95	68,583	48,100	1.22
3	**9**	> 95	67,738	40,000	1.21

[a]Conditions: **5**:thiol:NEt_3:**1** = 227:681:681:1, $[5]_o$ = 0.38 M, $[thiol]_0$ = 2.25 M, $[I]_o$ = 0.0017 M, reactor 1 t_R = 22.5 s, reactor 2 t_R = 22.5 s, total t_R = 45 s, tubular path length = 92 cm for each reactor. [b]With respect to both ROMP and click reactions, determined by ^{1}H NMR. [c]Determined by GPC.

Likewise, we were interested in determining if flow could be used to carry out thio-bromo click modifications in line without the need to isolate the unmodified parent polymer. Gratifyingly, we found that this was possible. This was achieved by polymerizing a CH_2Cl_2 solution **5** at a flow rate of 2 mL/min, followed by introduction of a THF solution of thiol and triethylamine to a second T-junction at a flow rate of 2mL/min (Figure 1c). THF had to be used instead of CH_2Cl_2 because of the insolubility of the triethylammonium salt formed with the thiol. Nonetheless, these reactions provided modified polymers **7**-**9** in high conversions, as ascertained from the disappearance of the olefinic signals associated with **5** as well as the broad signal between 4.94-4.43 ppm (-C*H*BrCH_3) in the ^{1}H NMR spectrum (Table 4 and Figure S3). However, the resulting polymers exhibited lower M_n values than expected, an explanation of which can be found the ESI.

Conclusions

We have successfully demonstrated that continuous flow techniques can be used to prepare polymers using ROMP. These experiments are operationally simple and can be performed on the benchtop under air. Norbornene derivatives are able to be polymerized to provide both homo-and block-copolymers in a matter of seconds. Furthermore, we show that *in situ* generated polymers carrying electrophilic α-bromo ester groups can be transformed via a post-polymerization, thio-bromo "click" reaction in flow without the need to isolate the parent polymer. However, the limitations of the system described above warrant further exploration. Studies investigating the effects that flow rate, concentration, temperature, feed ratio, and atmosphere have on M_n and $Đ$ values (as well as expanding this system to other monomers) are underway and will be published at a later date.

Conflicts of interest

There are no conflicts to declare.

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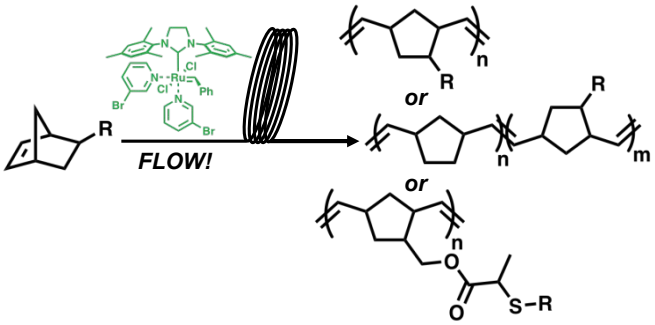

Continuous flow facilitates ROMP reactions to prepare homopolymers and block copolymers and allows for in-line post-polymerization click modifications.