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The ring-opening metathesis polymerization (ROMP) of 1,2-disubstituted cyclopropenes (CPs) has been explored for the first time using Grubbs 3^rd^ generation catalyst. A range of 1,2-CPs yielded polymers with controllable MWs and low dispersitities, and allowed the synthesis of block copolymers, absent from secondary metathesis. However, there existed a competing intramolecular termination pathway for these monomers, limiting the timescale for their ROMP to stay living.

Ring-opening metathesis polymerization (ROMP) has emerged as a powerful technique for synthesizing functionalized polymers thanks to the development of efficient and functional group tolerant catalysts.[1-5] ROMP is typically driven by the release of monomer ring strain. Strained norbornene (NBE) or oxanorbornene (oNBE) derivatives have been predominantly used as monomers for controlled ROMP with all common metathesis catalysts, since the first report on ROMP of NBE in 1960.[6] Using appropriate catalysts, NBE or oNBE derivatives can undergo rapid ROMP to yield functional polymers with controllable molecular weight (MW) and low dispersity ($Đ_M$).[7-9] Additionally, various cyclobutenes have also been investigated for ROMP.[10-12]

Cyclopropenes (CPs) are the smallest and most strained cyclic olefins with strain energy nearly twice that of NBE (depending on the substitution).[13] A wide range of disubstituted 1,2- and 3,3-CPs have been synthesized, and are stable at ambient conditions.[14] These CPs have been used for further organic transformations[14] and bioconjugation[15-17]. Surprisingly, however, CPs have been largely overlooked as monomers for ROMP. The only examples on ROMP of CPs come from the Schrock group[18-20] and the Binder and Buchmeiser groups[21-22], and only relatively simple unfunctionalized 3,3-disubstituted CPs have been investigated in these reports. Our research group has become interested in CPs as novel ROMP monomers, not only because of their high ring strain, but also because various substitutions on CP can tune the steric and electronic environment proximal to the olefin of the monomer and resulting polymer, as well as the propagating metal carbene, thus creating diverse reactivities for olefin metathesis. We have recently reported a family of 1,1-CPs that undergo selective ring-opening without homopropagation, but perform living ROMP with low-strain cyclic olefins to yield precisely alternating polymers.[23] To the best of our knowledge, 1,2-disubstituted CPs have never been investigated for ROMP. We suspect that the tertiary allylic positions on the formed ROMP polymers from 1,2-CPs will prevent chain transfer and give rise to a living polymerization. Furthermore, the resulting polymers will have much more flexible backbones compared to polyNBEs, therefore expanding the repertoire of living ROMP monomers. Herein, we report the synthesis of a series of 1,2-disubstituted CPs and the first study on their ROMP, which exhibited both expected and unexpected reactivities.

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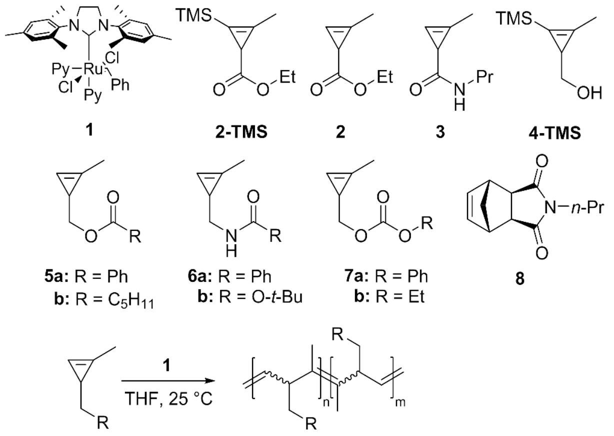
Disubstitution on CPs is usually required for stability. We have synthesized large quantities (>10 g) of 1-carboxylate-2-methyl-3-(trimethylsilyl) CP (**2-TMS**) by slow addition of commercially available diazoacetate to a solution of 1-TMS-propyne in the presence of 0.25 mol% $Rh_2(OAc)_4$ catalyst. **2-TMS** was used as the principal starting material to derivatize all other CPs used in this study (CPs **2-7** were obtained from **2-7-TMS** after removal of the TMS group on olefin). **2-TMS** can be converted to amide **3** or reduced to alcohol **4-TMS**. **4-TMS** can then be converted to esters **5a,b-TMS**, amide **6a-TMS**, protected amine **6b-TMS**, and carbonates **7a,b-TMS**. These derivatives allowed us to explore the effect of substituents on the 1-position and to expand the functionalities on CP. We observed that reserving the TMS group on the CP olefin during derivatization greatly enhanced the stability of CPs under various reaction and workup conditions, and therefore the TMS group was only removed in the final step in the syntheses of CP **2-7** by TBAF treatment. The final products were isolated cleanly after being passed through a plug of neutral alumina, although this deprotection step often resulted in moderate yields. While the TMS protected CPs were bench stable under ambient conditions for months, gradual decomposition of the deprotected CPs was observed over a week of benchtop storage. However, the deprotected CPs were stable at -15 °C for months. Therefore, we generally keep these CPs in the TMS protected form for long-term storage. Additionally, it should be noted that using silica gel for the purification of TMS-deprotected CPs led to product decomposition within hours of isolation.

To probe ROMP reactivity, these CPs were subjected to 2 mol% Grubbs catalyst **1**, which is well-known to mediate living ROMP of oNBE derivatives. Surprisingly, **2** and **3** caused immediate decomposition of the catalyst with no polymer or oligomer formed. The catalyst decomposition was evident from monitoring the equimolar reaction between **2** and **1** by ^1H NMR spectroscopy (Figure S1). The nature of catalyst decomposition is unclear, but we suspect that it may be related to the generation of the labile/acidic doubly allylic 1-proton upon ring-opening of 1-carboxylate CPs since no catalyst decomposition has been observed for various 1,1-disubstituted CPs.



Scheme 1. Structures of catalyst and monomers used in ROMP study.

Table 1. ROMP of 1,2-Disubstituted CPs.[a]

Entry	CP	$[CP]_0$	$[CP/\mathbf{1}]_0$	$M_{n,\,MALLS}$[b] (kDa)	$Đ_M$[b,c]
1	**5a**	0.01	50	9.2	1.23
2	**5a**	0.1	50	7.5	1.06
3	**5a**	0.5	50	7.4	1.02
4	**5a**	0.5	100	13.4	1.03
5	**5a**	0.5	200	26.0	1.07
6	**5b**	0.5	50	8.9	1.09
7	**5b**	0.5	100	14.4	1.14
8	**5b**	0.5	200	22.6	1.20
9	**6a**	0.5	50	11.1	1.19
10	**6b**	0.5	50	8.5	1.31
11	**7a**	0.5	50	7.5	1.07
12	**7b**	0.5	50	10.7	1.04

[a] ROMP was run in THF at 25 °C under N_2 atmosphere. [b] Determined by GPC MALLS analysis in THF. [c] M_n/M_w

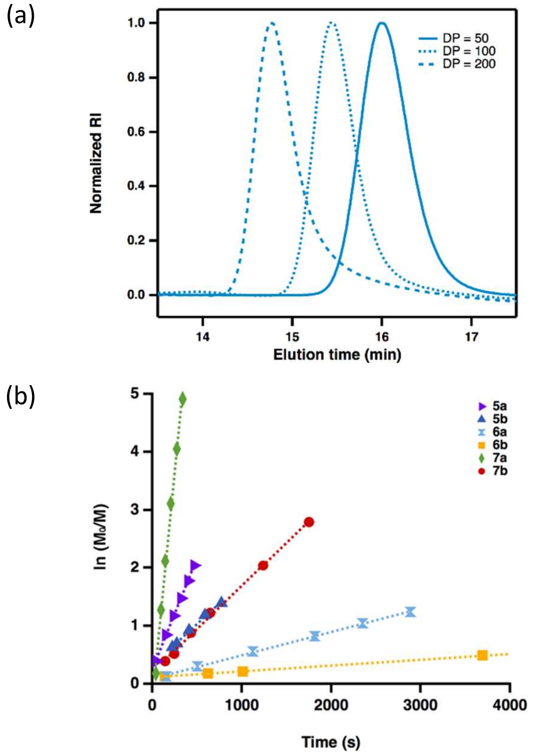


Figure 1. (a) GPC traces of poly(**5a**) varying $[\mathbf{5a}]_0$:$[\mathbf{1}]_0$ from 50 to 200 (entries 3, 4, and 5, Table 1); (b) first order kinetics for ROMP of 1,2-CPs in $CDCl_3$ at 25 °C.

Table 2. Polymerization Rate Constants.[a]

CP	k_p (M^{-1} s^{-1})
5a	1.92
5b	0.71
6a	0.20
6b	0.05
7a	7.80
7b	0.74

[a] ROMP was run in THF at 25 °C under N_2 atmosphere.

In contrast, other CPs **5**-**7** without the 1-carbonyl group all polymerized rapidly to yield polyCPs with controlled MW and low $Đ_M$ (Table 1). The ratio of monomer to initiator **1** could be used to control the degree of polymerization (DP) while maintaining low $Đ_M$. MALDI-TOF MS of poly(**5a**), as an example, also revealed the expected end groups (Figure S2), demonstrating the controlled nature of the polymerization.

The electronic nature of the substituents for CPs **5-7** had a noticeable effect on their polymerization rate constants (k_p) (Figure 1b, Table 2). CPs with benzoic ester or phenyl carbonate substituents (**5a**, **7a**) showed faster polymerization than their aliphatic analogues (**5b**, **7b**). A similar trend was also observed in our recent study of 1,1-CP living alternating ROMP.[10] The slower propagation for **6a** and **6b** likely contributed to the higher $Đ_M$s of their resulting polymers (*vide infra*).

^{1}H NMR and ^{13}C NMR signals of the polymer backbone olefins were broad, suggesting mixed *E*,*Z*- and/or regioisomeric structures (see SI). To probe the regiochemistry of ring-opening, we performed an equimolar reaction of **5a** and **1** and analysed the organic products isolated after quenching with vinyl ether. Two regioisomers at a ratio of ~1:5 were identified originating from mono- and disubstituted ruthenium alkylidenes, respectively (Figure S8), with the major product coming from the intermediate with the olefinic methyl group positioned α to ruthenium. The high, instead of exclusive, regioselectivity in ring-opening of these CPs is surprising. If non-exclusive regioselectivity exists in ROMP of 1,2-CPs, some tetrasubstituted polymer backbone olefins would have been formed, which are usually hindered products in cross metathesis that require Grubbs catalysts with less hindered ligands.[24-25] Furthermore, Hillmyer and coworkers have reported highly regioselective ROMP of 3-methyl cyclooctenes from Grubbs 2nd generation catalyst, resulting in polymers with predominantly head-to-tail regioregularity.[26-27] Despite the non-exclusive regioselectivity in ROMP of 1,2-CPs, the two possible alkylidenes at the active chain end clearly still led to polymers with controlled MW and low $Đ_M$.

When ROMP of 1,2-CPs was performed at low monomer concentrations (0.01M), low MW tailing and a shift of peak to higher MW were observed in the GPC trace (Table 1, entry 1 and Figure S5), but the tailing disappeared at higher monomer concentrations (≥ 0.1 M). This tailing cannot be attributed to chain transfer via secondary metathesis, because upon complete conversion of CP at 0.01M, no noticeable peak broadening was observed after 2 days. Additionally, when ~100 equiv of *cis*-3-hexene was added to poly(**5b**) at the end of ROMP, no decrease in MW was observed after 12 h (Figure S6), suggesting that the backbone olefins were inert to secondary metathesis as we expected. We suspect that an intramolecular side reaction may slowly occur at the propagating metal centre to terminate the active chain end. This terminating reaction essentially competes with propagation depending on their relative rates. Because the rate of intramolecular reaction is not concentration dependent while that of propagation is, higher monomer concentrations or faster-propagating monomers significantly reduce the effect of this side reaction. The nature of this termination remains unknown in olefin metathesis and may be due to the presence of the labile doubly allylic protons on these poly(1,2-CP) backbones. We believe this termination reaction is similar in nature to the observed catalyst decomposition caused by ring-opening of 1-carbonyl CP **2** and **3** (which give rise to an even more labile doubly allylic proton upon ring-opening), but occurs at a much slower rate.

We also attempted the synthesis of block copolymers (BCPs) from CP and NBE, as well as from different CPs. Addition of CP to a living polyNBE chain resulted in a narrowly dispersed NBE-CP diblock copolymer (poly(**8**-*b*-**5a**), Figure 2a). However, due to the slow competing termination, when poly(1,2-CP) was used as the first block, timely addition of the second monomer after the completion of the first block was important for the successful synthesis of BCPs with low $Đ_M$s

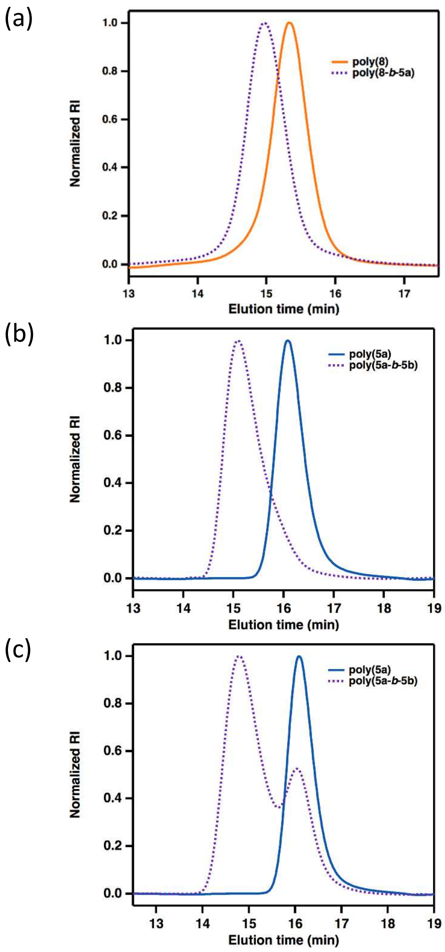


Figure 2. GPC traces of (a) poly(**8**) and poly(**8**-*b*-**5a**) (entry 1, Table 3); (b) poly(**5a**) and poly(**5a**-*b*-**5b**) with addition of **5b** after 20 min (entry 2, Table 3) and (c) after 240 min (entry 3, Table 3).

Table 3 GPC Data for Block Copolymers.

Entry	Copolymer	$[CP]_0^a$ (M)	Time at 2nd monomer addition^b (min)	$M_{n\ MALLS}{}^c$ (kDa)	$Đ_M{}^{c,d}$
1	$\mathbf{8}_{50}\mathbf{5a}_{50}$	0.5	20	13.3	1.08
2	$\mathbf{5a}_{50}\mathbf{5b}_{50}$	0.5	20	15.9	1.05
3	$\mathbf{5a}_{50}\mathbf{5b}_{50}$	0.5	240	13.8	1.17
4	$\mathbf{5b}_{50}\mathbf{5a}_{50}$	0.5	20	11.2	1.09

^{a}Initial CP concentration. ^{b}Elapsed time between initiation and addition of 2nd monomer. ^{c}Determined by GPC MALLS analysis in THF. $^dM_n/M_w$

(Figure 2b). Prolonged waiting after full monomer conversion resulted in a bimodal MW distribution (Figure 2c) due to the partial termination of the first block.

Poly(1,2-CP)s have considerably more flexible and less hydrophobic backbones than polyNBEs. For example, DSC measurements of poly(**5b**) showed a glass transition temperature (T_g) of around -45 °C, similar to that of poly(*n*-butyl acrylate) (T_g of -52 °C)[28], a common low T_g polymer synthesized by radical polymerizations. The reduced T_g of poly(1,2-CP) backbone compared to polyNBEs may be advantageous for applications where relatively low annealing temperatures or more elastomeric materials are required.

In summary, we report the first study on the ROMP reactivity of 1,2-disubstituted CPs, which are among the family of rarely explored but most-strained cyclic olefins. ROMP of these CP-methanol/methylamino derivatives resulted in polymers of controlled MW and low $Đ_M$, expanding the current repertoire of ROMP polymers. However, a slow competing termination was observed for these CP monomers, which required careful timing and conditions for the optimal synthesis of their homopolymers and BCPs.

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