

Metal-Free Ring-Opening Metathesis Polymerization with Hydrazonium Initiators

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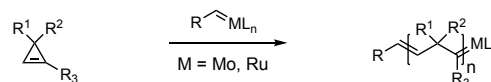
Abstract: A new strategy for the ring-opening metathesis polymerization (ROMP) of cycloalkenes using hydrazonium initiators is described. The initiators, which are formed by the condensation of 2,3-diazabicyclo[2.2.2]octane and an aldehyde, polymerize cyclopropene monomers by a sequence of [3+2] cycloaddition and cycloreversion reactions. This process generates short chain polyolefins ($M_n \leq 9.4$ kg/mol) with relatively low dispersities ($D \leq 1.4$). The optimized conditions showed efficiency comparable to that achieved with Grubbs' catalyst. A positive correlation between monomer to initiator ratio and degree of polymerization was revealed through NMR spectroscopy.

Ring-opening metathesis polymerization (ROMP) is used extensively in both industrial and fine-chemical synthesis to convert feedstock cyclic olefins into high-value polymers.^[1–3] These unique polymerizations have been enabled by a variety of heterogeneous and homogeneous transition metal catalysts, including those based on tungsten,^[4–6] titanium,^[7–9] tantalum,^[10,11] niobium,^[11] rhenium,^[12] iron,^[13] and especially ruthenium^[14–16] and molybdenum^[5,6,17] complexes (Figure 1A). While the impact of these reactions on the field of chemistry, and indeed human society, has been profound, there are some well-recognized drawbacks to the use of transition metal reagents. In particular, issues of toxicity,^[18] expense, scarcity, and complex purification^[19,20] can complicate the utilization of ROMP polymers. In addition, certain applications such as those involving biomedical devices or electronics are incompatible with polymeric materials that contain metal impurities. Thus, there has been an interest in the discovery of non-metal alternatives for ROMP.^[21] Most notable in this regard, Boydston developed an elegant photoredox-mediated ROMP that utilized vinyl ethers as the propagating functionality.^[22,23] Despite the highly creative and useful nature of this chemistry, issues of generality and scalability present challenges for its wider adoption. Thus, the development of alternatives to metal-based ROMP chemistries remains a goal of high interest.

Conceptually related to olefin metathesis, carbonyl-olefin metathesis has emerged as a prominent area of research over the past decade.^[24–36] In 2012, our group reported the first catalytic strategy for carbonyl-olefin metathesis using hydrazine catalysts.^[37] In this chemistry, hydrazonium intermediates and [3+2]-cycloadditions / cycloreversions play an analogous role to the metal alkylidenes and [2+2] processes found in traditional olefin metathesis. While closure of the catalytic cycle for this carbonyl-olefin metathesis reaction requires hydrolysis of the metathesized hydrazonium intermediate **1** (Figure 1B), we recognized that preventing this step could allow for the engagement of an additional olefin substrate in the cycloaddition / cycloreversion sequence. In this case, the transformation would be an *olefin metathesis*, and iteration would result in a ROMP

reaction. Such a process would be closely analogous to the metal alkylidene based approach but would utilize only a simple organic initiator. In this Communication, we demonstrate the feasibility of this proposal with the hydrazonium-initiated ring-opening metathesis polymerization of cyclopropenes.

A. Metal-alkylidene mediated ROMP of cyclopropenes



B. Hydrazonium mediated ROMP platform

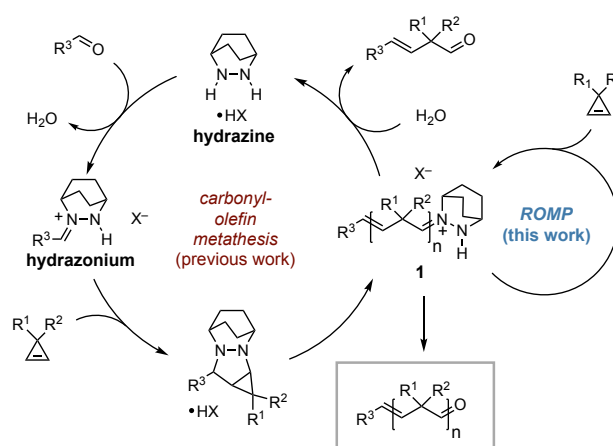


Figure 1. A. Metal alkylidene-mediated ROMP. B. Catalytic cycle for hydrazone-catalyzed carbonyl-olefin metathesis and the alternative hydrazonium-mediated ROMP of cyclopropenes.

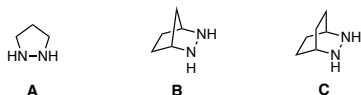
Despite an interesting polymeric thermal profile and a large amount of ring-strain, cyclopropene monomers have been underutilized for ROMP. Schrock, Binder, Buchmeiser and Xia demonstrated the formation of homopolymers with unique elastomeric properties from 1,1- and 1,2-disubstituted cyclopropenes, but only a few examples were shown.^[38–43] In a more recent case, Xia engaged 1-aryl-1-(benzoyloxymethyl)- and 1-methyl-1-carboxylate-cyclopropenes in an alternating ROMP reaction with cyclohexene and norbornene; however, this process was predicated on the cyclopropene undergoing only single monomer addition and not homopolymerization.^[44–46] Thus, the intriguing physical properties of polycyclopropenes and the relative paucity of methods to access them warrant further investigations into cyclopropene ROMP.

As a first indication that the hydrazonium-mediated ROMP described above might be viable, we observed that reaction of benzaldehyde (**2**) and cyclopropene **3** with 10 mol% of various hydrazine salts at 90 °C in dichloroethane (DCE) led to the

production of the ring-opening carbonyl-olefin metathesis (ROCOM) product **4** contaminated by various amounts of oligomeric products **5** (Table 1). A brief survey of conditions revealed that both the structure of the hydrazine and the co-acid salt impacted the ratio of these two products. Pyrazolidine **A** was the least efficient and generated only the ROCOM adduct **4** in low yield (entry 1), while [2.2.1]-bicyclic hydrazine **B** led to an 8:1 mixture in favor of **4**, regardless of the co-acid (entries 2 and 3). On the other hand, the [2.2.2]-bicyclic hydrazine **C** resulted in the largest proportions of the oligomeric product **5** (entries 4-6). The co-acid impacted this ratio, with the largest proportion of oligomer (~33%) formed with the bis-HBF₄ salt of **C**. We presume that the amount of oligomer formation was inversely proportional to the propensity of the ring-opened hydrazonium intermediates (**1** in Figure 1B) to undergo hydrolysis.

Table 1. Observation of ROMP products in the catalytic ROCOM of cyclopropene **3**.^[a]

$\text{PhCHO} + \text{Ph-Me-Cyclopropene} \xrightarrow[\text{DCE (0.6 M), 90 }^\circ\text{C, 18 hr}]{\text{10 mol \% R-HN-NH-R} \cdot 2\text{HX}} \text{Ph-CH=CH-C(=O)Me} + \text{Ph-CH}_2\text{-CH(C(=O)Me)-CH}_2\text{O}$				
entry	hydrazine	HX	yield (%)	4:5
1	A	HCl	5	100:0
2	B	HCl	75	8:1
3	B	TFA	69	8:1
4	C	HCl	80	5:1
5	C	TFA	79	6:1
6	C	HBF ₄	78	2:1



^[a] See ESI for experimental details. Yields reflect isolated and purified ROCOM product.

To parlay the findings shown in Table 1 into a cyclopropene ROMP reaction (Table 2), we sought to suppress chain-end hydrolysis by using preformed hydrazonium **6** as the initiator. Thus **6** was prepared by the condensation of the bistetrafluoroborate salt of hydrazine **C** with benzaldehyde (**2**). Tetrafluoroborate was chosen as the counterion based on the results described above and because of the high crystallinity and relative non-hygroscopicity it imparted to the hydrazonium **6**. After the reaction of cyclopropene monomer **3** with this initiator **6** (40:1) at 60 °C for 60 h, the polymerization was terminated by hydrolysis at 90 °C for two hours with water (20 equiv) and TFA (2 equiv). The polymeric product **5** was then recovered via centrifugal precipitation from CH₂Cl₂/MeCN. GPC analysis referenced to polystyrene standards revealed the number average molar mass (*M_n*) to be 6.1 kDa with a dispersity (*Đ*) of 1.5. Despite the relatively good agreement between the theoretical and experimental *M_n*, repeated trials resulted in variable results (*M_n* as low as 3.6 kDa or as high as 9.2 kDa, Table S1).

Table 2. Optimization of ROMP of cyclopropene **3** with hydrazonium **6**.^[a]

$\text{Ph-Me-Cyclopropene} \xrightarrow[\text{M/I = 40}]{\text{heat, 18 hr}} \text{Ph-CH}_2\text{-CH(C(=O)Me)-CH}_2\text{O}_n$						
entry	temp (°C)	DP	<i>M_n</i> theo (kDa)	<i>M_n</i> exp (kDa)	<i>Đ</i>	yield (%)
1 ^[b]	60	46	5.2	6.1	1.5	25
2	70	50	5.2	6.6	1.3	23
3	80	35	5.2	4.6	1.3	27
4	90	25	5.2	3.4	1.3	29
5	100	29	5.2	3.9	1.3	18
6 ^[c]	90	0	5.2	0	0	0
7 ^[d]	90	0	5.2	0	0	0

^[a] See ESI for experimental details. The degree of polymerization (DP), was calculated from *M_n* exp. Yields reflect isolated and purified polymer. ^[b] Reaction time 60 h. ^[c] No initiator was used. ^[d] NEt₃·HBF₄ used instead of **6**.

In order to ensure the validity and reproducibility of the results, the temperature optimization for the ROMP reaction was performed in triplicate (Table 2, entry 1-3, Table S1, entry 1-6), or quadruplicate (Table 2, entry 1-3, Table S1, entry 7-12). Assessment of the optimized conditions was done on the basis of reproducibility of the obtained polymer chain length and *Đ*. Among the temperatures screened between 60-100 °C, 90 °C provided the most consistent experimental *M_n* between quadruplicate runs and resulted in the highest average yield while maintaining a relatively low *Đ*. Therefore, the optimal temperature for ROMP of cyclopropene **3** was determined to be 90 °C.

Control experiments with no initiator (entry 6), or using an ammonium salt NEt₃·HBF₄ (entry 7) did not result in polymerization products. In the absence of initiator, 3,3-methylphenylcyclopropene largely underwent thermal decomposition after being heated at 90 °C for 18 hours. In the presence of NEt₃·HBF₄, however, the starting material decomposed completely and gave rise to a complex mixture. While this complex mixture of side products was observed in all crude reactions, attempts to isolate and identify such products were unsuccessful. These control experiments demonstrated that the [2.2.2]-hydrazonium **6** was an active ROMP initiator for cyclopropene **3** and that the thermal degradation of cyclopropene under acidic condition likely inhibits high yielding polymerization.

Consistent with our previous report with Houk,^[47] density functional theory (DFT) calculations using the M06-2X functional revealed that cycloaddition ($\Delta G^\ddagger_{\text{CA}} = 18.2$ kcal/mol) was the rate-determining step during initiation rather than the more facile cycloreversion ($\Delta G^\ddagger_{\text{CR}} = 12.1$ kcal/mol). More importantly the subsequent, propagating cycloadditions were predicted to be slower than that of the initiation ($\Delta G^\ddagger_{\text{propagate}} = 19.6$ kcal/mol). These calculations support our observation of relatively narrow molar mass distributions (*Đ* ≤ 1.4), which are typically associated with well-controlled polymerizations.

To investigate if the polymer chain length could be further extended, the monomer to initiator ratio (M/I) was increased to 80 °C or 160 °C (Table 3, entries 1 and 2). At a cyclopropene loading of 160 the average molecular weight increased to 6.9 KDa while the *Đ* was 1.4. However, the relatively low yield, along with the

discrepancy between the targeted and experimental M_n values, underscored the fact that acid-catalyzed thermal decomposition reactions still posed a challenge.

Table 3. Effect of higher cyclopropene loading table and scope table in [2.2.2]-hydrazonium initiated ROMP.^[a]

entry	Initiator	Cyclopropene	M/I	M_n theo (kDa)	M_n exp (kDa)	\bar{D}	% yield
1	6	3	80	10.4	5.1	1.3	25
2	6	3	160	20.8	6.9	1.4	20
3 ^[b]	11	3	100	13.1	5.9	1.6	30
4	12	3	80	10.5	3.4	1.3	22
5	6	8	80	11.9	9.4	1.2	6

11

12

8

^[a] See ESI for experimental details. Yields reflect isolated and purified polymer.

^[b] Stirred at room temperature for 24 h in DCM (0.2 M), then terminated with ethyl vinyl ether (0.1 eq) and polymer was precipitated by addition to methanol.

We note that Grubbs' 2nd generation catalyst **11**, while able to effect ROMP with cyclopropene, did not result in a substantially larger polymer or a better yield compared to the hydrazonium initiator (entry 3). Additionally, the larger dispersity (\bar{D} = 1.6) was likely the result of a slower initiation rate of the Ru–benzylidene species at room temperature (prior literature reported 54% consumption after 1 h and 95% consumption after 15 h).^[42] The issue of slow initiation was known and had been addressed by increasing the reaction temperature to 50 °C, leading to complete consumption of the initiator within 46 minutes.^[41] Nevertheless, most reported Ru–benzylidene initiated polymerization trials to produce large polymers have been conducted at room temperature, under the conjecture that higher temperatures could cause decomposition of the monomer and/or result in large \bar{D} values. It is noteworthy that while it had been reported that alkylidene **11**-initiated ROMP had low dispersity (\bar{D} ≤ 1.4)^[41], at various M/I loadings the targeted and experimental M_n values for those reactions disagreed by at least 3.2 kDa (up to 82 kDa)^[41], with the exception of two entries. This discrepancy, as observed with both hydrazonium **6**- and ruthenium alkylidene **11**-initiated polymerizations, speaks to the inherent instability of the highly strained cyclopropene **3** under the reaction conditions.

To demonstrate the utilization of an alternative initiator, hydrazonium **12** gave rise to the terminal fluorine-tagged polymer **9** (entry 4, M_n = 3.6 kDa, \bar{D} = 1.4). In addition, the utilization of a different cyclopropene monomer **8** led to the production of the corresponding polymer **10** (entry 5, M_n = 9.4 kDa, \bar{D} = 1.2).

Differential scanning calorimetry (DSC) of polymer **5** revealed a glass transition temperature of (T_g) of 48.1 °C and no observable melting transition (T_m). The lower T_g than reported^[41] is likely due to the shorter chain length of the polymer and its atactic nature, which was confirmed by ¹³C NMR analysis.

Thermogravimetric analysis (TGA) of the polymer showed a relatively high decomposition temperature of 300 °C, which was lower than the reported 395–396 °C of polymer initiated by **11**.^[41]

Mechanistic investigation of hydrazonium-initiated polymerization was attempted through *in situ* NMR reaction monitoring. Diffusion filtered NMR ascertained that the aldehyde signal, and more importantly, the styrenyl chain-end used to estimate degree of polymerization, belonged to the polymer. Chain length measurement obtained by ¹H NMR analysis was comparable to the values obtained from differential refractive index GPC (GPC-DRI) referenced to polystyrene standard and light scattering GPC (GPC-LS) (d_n/d_c measured in THF = 0.2149, $DP_{GPC-DRI}$ = 49, DP_{GPC-LS} = 50, DP_{NMR} = 65).

Our attempt to correlate monomer conversion with chain length extension over time was complicated by the rapid decomposition of the monomer (42% conversion after 27 minutes and 69% conversion after 87 minutes), in contrast to the slower rate of initiation (9% hydrazonium initiated after 27 minutes and 27% hydrazonium initiated after 87 minutes) (Fig. S10). As postulated (*vide supra*), this observation offers a viable explanation for the lower than expected M_n experimental at elevated temperatures. Furthermore, the propagating chain was highly sensitive to hydrolysis, as brief exposure to air (<2 s) prompted termination of the growing polymer.

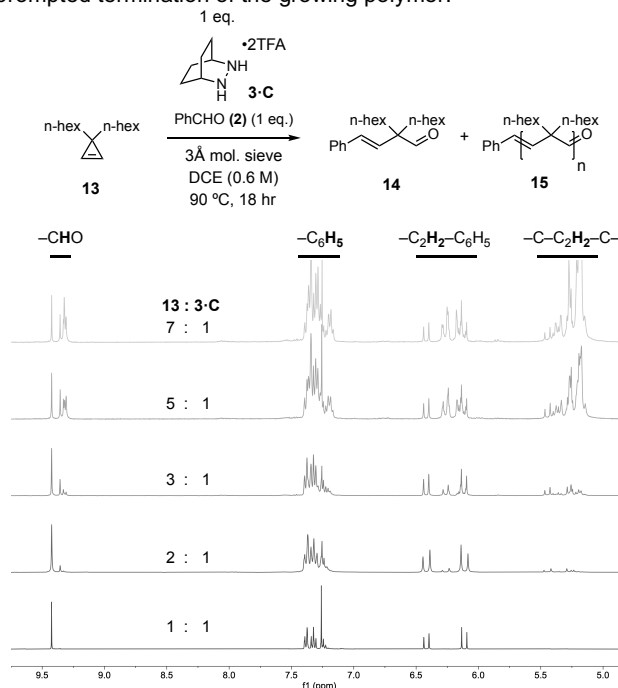


Figure 2. Stacked NMRs of cyclopropene **13** oligomerization via *in situ* initiator generation via [2.2.2]-hydrazonium **3-C** and benzaldehyde, **2**, with increasing monomer : initiator loading from 1:1 to 7:1. Stacked NMRs are scaled by the aldehyde signal of ROCOM product, alkenal **14**.

Cyclopropene **13** demonstrated higher-order oligomerization with increasing M:I loading (Figure 2). With the aldehyde signal (δ 9.71 ppm) of the ROCOM alkenal **14** as reference, the abundance of oligomers **15** incrementally increased from <5% under stoichiometric conditions to 80% when the M:I was 7:1. The distribution of lower ordered oligomers (up to the tetramer), could be clearly determined by their aldehydic proton resonances. While this study did not provide a definitive linear relationship of monomer consumption versus chain length propagation, chiefly due to thermal decomposition of the

cyclopropene monomers, it demonstrated evidence of a positive correlation between M/I ratio and the degree of polymerization.

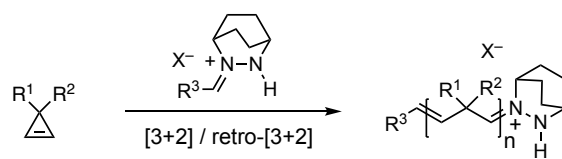
The current work demonstrates that polycyclopropenes can also be accessed with simple hydrazonium initiators, thus demonstrating the ability to access ROMP polymers without metals or irradiation. For cyclopropene monomers, the efficiency of the hydrazonium initiator was comparable to that of traditional ruthenium alkylidenes. We anticipate that the development of more reactive initiators will enable a broader range of monomers and expand the application of this non-metal ROMP platform.

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**hydrazonium-mediated
ROMP**

The metal-free ring-opening metathesis polymerization (ROMP) of 3,3-disubstituted cyclopropenes with hydrazonium initiators utilizing the principle of carbonyl-olefin metathesis is demonstrated.