Summer Scholar Report

Living Polymerization Mediated by Metal-Organic Framework-Encapsulated Catalysts

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Abstract:

Living polymerization is a chain-growth polymerization in which the propagating chain remains unterminated. We encapsulated catalysts in metal-organic framework (MOF) by aperture opening method and postsynthetic linker exchange method to mediate living polymerization.

Introduction:

The emergence of living polymerization techniques in the past decade have enabled the synthesis of a plethora of functional synthetic polymers with ever-increasing complex structures. Living polymerization requires rapid initiation and a high polymerization rate and low dispersity ($Đ$) (defined as the ratio of weight average molecular weight M_w to number average molecular weight Mn). It is therefore imperative to develop new strategies that can prolong catalyst activity and reduce the chain termination in polymerization.

Recently, MOF has been employed to host molecular catalysts, either through catalytically active constituents of the framework or by catalyst encapsulation. The advantages of catalytically active MOF system include its high level of activity, selectivity, and recyclability (Li et al. 2018). Inspired by the recent work of Li et al., which demonstrated the successful encapsulation of (tBuPNP)Ru(CO)HCl for CO_2 hydrogenation into a MOF host UiO-66 by opening an aperture on the framework, we propose to encapsulate ring-opening metathesis polymerization (ROMP) catalysts Grubbs catalyst 2nd and 3rd-generation (G2 and G3) in MOF to improve the livingness of the polymerization.

Further, we propose to install N-heterocyclic carbene (NHC) moieties on MOF by postsynthetic linker exchange (PSE) method. The absence of metal center that avoids the interference with transition metal clusters of MOF would improve the possibility of successful installation. Further, easy deprotonation of carbene enables installation of carbene moiety in its more stable salt form. The recent work of Zhang et al. showed that NHC functionalized MOF maintains catalytic activity to catalyze hydrosilylation of CO_2. Inspired by the promising result reported, we propose to install ring-opening polymerization (ROP) catalyst NHC moiety on MOF by linker exchange to achieve living polymerization of lactides.

Experiments:

ROMP of norbornene with free G3. Control experiment for ROMP of norbornene (**Nb**) (**Scheme 1**) was carried out using standard Schlenk flask under an argon atmosphere. In a Schlenk flask, **Nb** was dissolved in vigorously degassed dichloromethane. In a separate vial, catalyst was dissolved in degassed dichloromethane. The catalyst solution was rapidly added to the Schlenk flask containing monomer using syringe. After 30 minutes of stirring at -20 °C, excess ethyl vinyl ether was added to quench the reaction. The polymer was precipitated in methanol and was collected by centrifugation. The NMR and SEC data for purified polymer is shown below (**Figure 1**). The molecular weight remained high and dispersity wide as expected.
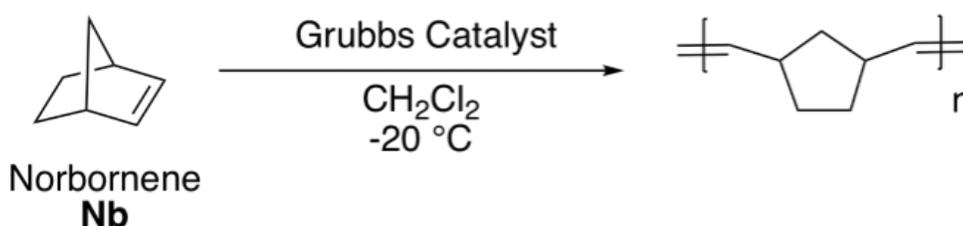
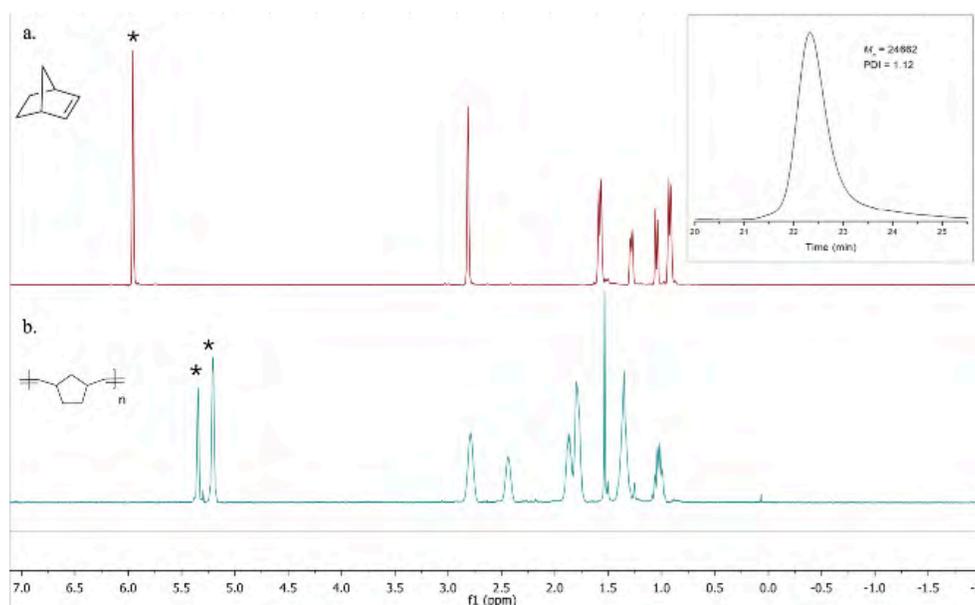*Scheme 1. Ring-opening metathesis polymerization of norbornene by Grubbs catalysts.*

Figure 1. a. ^1H NMR spectrum for norbornene substrate. b. ^1H NMR spectrum for crude polymer product catalyzed by G3. Figure 2 inset. SEC spectrum of polymer synthesized.

Encapsulation of G3 in UiO-66. UiO-66 was selected as an optimal candidate for encapsulation according to the analysis of aperture size (15.75 Å) and pore size (11.14 Å), which is compatible with the catalyst size (14.19 Å) (**Scheme 2.**). Solvent test

showed that the catalyst exhibited best stability in acetonitrile, thus acetonitrile was selected as the optimal protic solvent for aperture-opening encapsulation solvent.
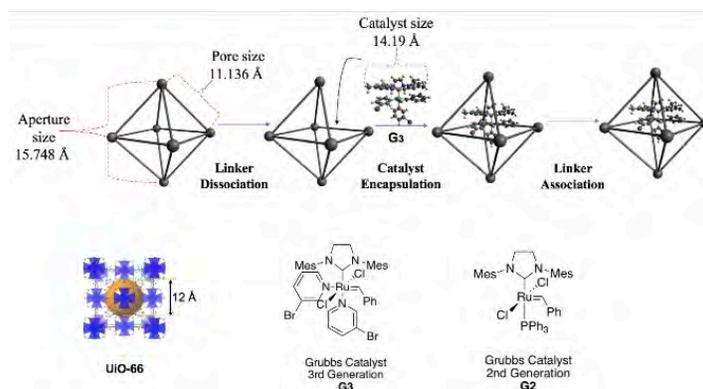
Scheme 2. Aperture-opening encapsulation of catalysts.

The encapsulation was carried out in the glove box under nitrogen atmosphere. In a Schlenk flask, G3 (3mg) was mixed with UiO-66 (30mg), then acetonitrile (5ml) was added. The reaction was heated to 55 °C for 24 hours. The solution was then centrifuged without additional wash to obtain [G3]@UiO-66. The catalyst loading was measured by ICP-OES, which showed 0.139 ppm by weight for Ru. 1H NMR analysis of supernatant did not show characteristic signals corresponding to the catalyst.

ROMP of norbornene with [G3]@UiO-66. In the glove box, monomer (35mg) and [G3]@UiO-66 (10mg) was added to a flask, and dichloromethane was added. The reaction was carried out for 30 minutes at -20 °C, followed by standard workup described above. Molecular weight and dispersity was measured by size-exclusion chromatography (SEC). However, no signal corresponding to the polymer was observed from NMR and SEC (**Figure 2**).
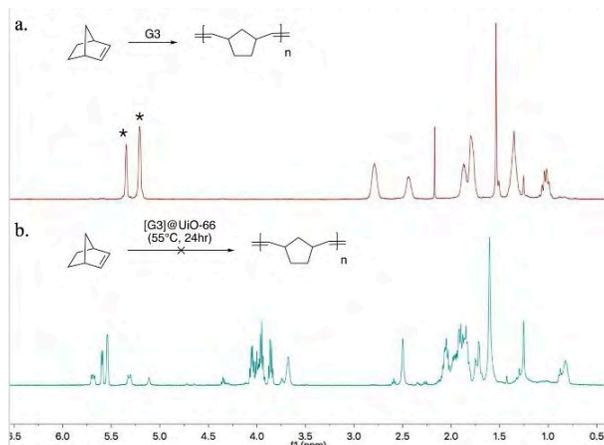

*Figure 2. a. 1H NMR spectrum for control ROMP with * for polymer signals;
b. crude 1H NMR spectrum for ROMP with [G3]@UiO-66.*

Encapsulation of G2 and G3 in UiO-66. Speculating the high temperature of the encapsulation condition might have led to the dissociation of catalyst, we proposed to modify the reported encapsulation condition to mitigate deactivation of catalysts. The encapsulation was conducted at room temperature for prolonged time (2~5 days). Grubbs second-generation catalyst (G2) was also chosen as a candidate catalyst.

ROMP of norbornene with [G3]@UiO-66 (2-day). When the ROMP was carried out with [G3]@UiO-66 that has been collected by centrifugation without additional wash, and polymer with high molecular weight was obtained. The polymer signal obtained by SEC is shown below (**Figure 3**). When the encapsulated catalyst was washed with acetonitrile 3 times and ROMP was performed again, no polymer was obtained.
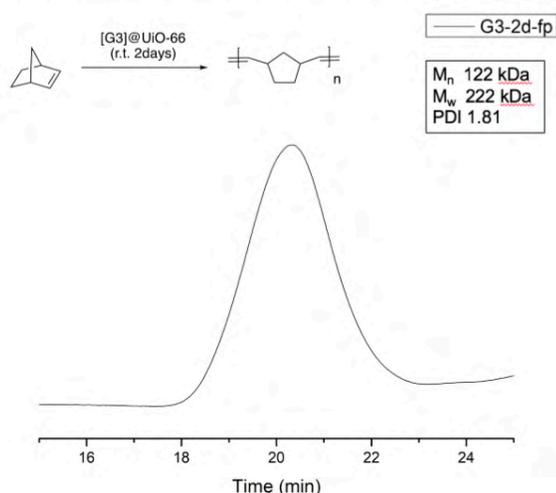

Figure 3. SEC of polymer obtained by ROMP using [G3]@UiO-66 (2- day).

ROMP of norbornene with [G3]@UiO-66 (5-day). ROMP was carried out using [G3]@UiO-66 (5-day) after wash by acetonitrile. The crude NMR showed polymer peaks (**Figure 4**), which was further confirmed by SEC (Figure 4).
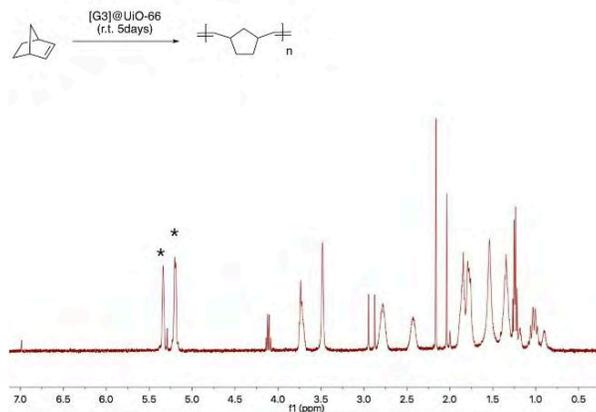

Figure 4. ^{1}H NMR spectrum for ROMP with [G3]@UiO-66 (5day)

ROMP of norbornene with [G2]@UiO-66 (5-day). [G2]@UiO-66 collected as described above led to successful polymerization of norbornene. The polymer obtained is analyzed by SEC.

Synthesis of UiO-68. We moved on to test our second approach – ROP of L-lactide (**Scheme 3**) by NHC installed on UiO-68 through postsynthetic linker exchange method (**Scheme 4**). The procedure for the synthesis of UiO-68 was slightly modified from *Chem. Eur. J., 20: 14965-14970* (**Scheme 5**). UiO-68 synthesis was carried out in open air. 2,5-dibromoaniline (1.13g), (methoxycarbonyl)phenylboronic acid (2.49g), CsF (4.52g), Pd(OAc)2 (339mg) and triphenylphosphine (904mg) was added to a vial and was dissolved in THF (30ml). The reaction was stirred at 60°C for 48 hours. Then deionized water (50ml) was added and the aqueous phase was extracted with dichloromethane. The organic phase was dried in vacuo. The resulting product **1** was purified by silica gel chromatography to yield yellow solid (277mg, 17% yield). Then **1** (0.72g) was suspended in THF (60ml). KOH (5.59g) was dissolved in methanol (5.5M) and was added to the solution. The reaction was stirred at 40°C overnight. Then the reaction was cooled to room temperature and the precipitate was collected by centrifuge. The precipitate was washed with THF (20ml) and was centrifuged again to obtain light yellow solid. Then the solid was suspended in THF (30ml). Trifluoroacetic acid (3.84ml) was added to the solution. The reaction was stirred at room temperature for 2 hours. Then deionized water (65ml) was added to the solution, and the product **2** was collected by vacuum filtration. The solid was washed rigorously by diethyl ether and was dried in vacuo. ^{1}H NMR (500MHz, (CD3)2SO): δ 12.94 (br, 2H, OH), 8.02 (d, 4H), 7.74 (d, 2H), 7.60 (d, 2H), 7.15 (d, 2H), 7.02 (d, 2H), 5.10 (br, 2H, NH2). Then the linker was assembled to obtain UiO-68 by mixing 2 with ZrCl4, benzoic acid in DMF and water at 70°C for 3 days. Then UiO-68 was obtained after extensive washing by DMF and EtOH followed by drying in vacuo.

**Scheme 3.** *Ring-opening polymerization (ROP) of l-lactide.*
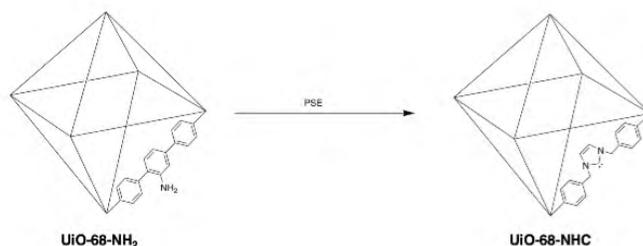
Scheme 4. *Post-synthetic linker exchange of UiO-68 with NHC linker.*
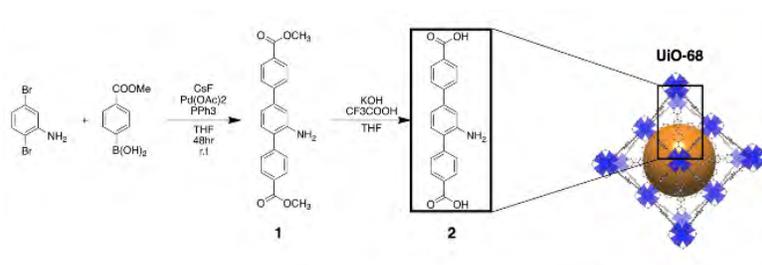
Scheme 5. *Synthetic route of UiO-68*

Synthesis of NHC-linker. The NHC-linker was synthesized with slight modification from X. Zhang Angew. Chem. Int. Ed. 2019, 58, 2844 (**Scheme 6**). Imidazole was dissolved in dichloromethane in 0°C. Then sodium hydride was added and the solution was stirred for 1 hour. Then methyl 4-(bromomethyl) benzoate was added, and the solution was stirred at room temperature overnight. The product **3** was collected by vacuum filtration, washed extensively with dichloromethane, and was dried in vacuo. Then the **3** and methyl 4-(bromomethyl)benzoate was dissolved in N,N-dimethylformamide and the reaction was stirred at 120°C overnight. The N,N-dimethylformamide was evaporated by a rotary vacuum evaporator and the product **4** was collected. Then 3M NaOH aqueous solution was added to **4** and the solution was stirred for 3 hours at room temperature. Then HCl was added until pH=1. The product **5** was collected by vacuum filtration, washed extensively with water and was dried under vacuum. ^{1}H NMR (500MHz, (CD$_3$)$_2$SO): δ 13.12 (br, 2H), 9.57 (s, 1H), 7.98 (d, 4H), 7.91 (d, 2H), 7.54 (d, 4H), 5.57 (s, 4H). ^{13}C NMR (150MHz, (CD$_3$)$_2$SO): δ 167.21 (s, 1H), 139.82 (s, 1H), 137.36 (s, 1H), 131.51 (s, 1H), 130.32 (s, 5H), 128.86 (s, 5H), 123.55 (s, 2H), 52.04 (s, 2H). ESIMS(+): m/z 337.1 [M]$^+$.
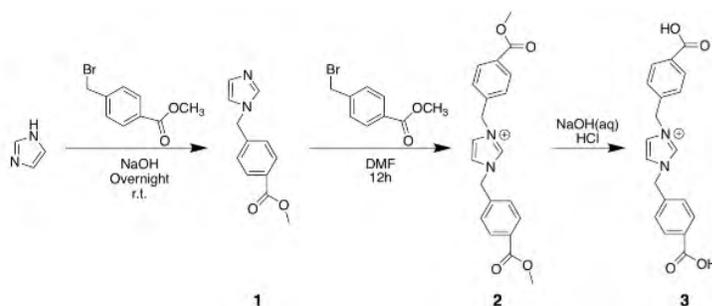
Scheme 6. *Synthetic route of NHC-linker.*

Installation of NHC-linker on UiO-68 via PSE. UiO-68- NHC was assembled by first dissolving 5 in 4% KOH solution for activation of catalyst. Then the solution was neutralized to pH=6 with HCl. Then UiO-68 and DMF was added and the reaction was stirred at room temperature for 12 hours. Then the solid was collected by centrifugation and was washed extensively with methanol. The solid was soaked in methanol for 3 days

with fresh methanol replaced everyday. After three days of PSE, the UiO-68-NHC was collected by centrifugation and was dried in vacuo.

ROP of L-Lactide by UiO-68-NHC. To the solution of UiO- 68-NHC dispensed in DCM, L-lactide was added and the solution was stirred. Then the crude NMR was obtained to check for the presence of polymer. However, no polymer peak was observed.

Results and Discussions:
Although the prolonged encapsulation time improved the loading rate of the catalyst as determined by ICP-OED, the loading rate remained very low (**Table 1.**), close to the lowest detection limit of the measurement. Therefore, it is hard to conclude that the catalysts had ben actually encapsulated in the cavity of MOF. The inefficient encapsulation can be attributed to the relatively large size of the Grubbs catalyst compared to the previously reported catalysts for encapsulation. Therefore, the catalyst might not have been able to enter the cavity of UiO-66. In the future, more experiments can be conducted to test encapsulation in MOF structures with larger cavity size such as UiO-67 and UiO-68.

Catalyst	Temperature	Encapsulation time	Loading Rate (Ru wt%)
G3	55°C	24 hr	0.000014
G3	r.t.	2 days	0.000052
G3	r.t.	5 days	0.000055
G2	r.t.	5 days	0.000038

Table 1. Encapsulation conditions and loading rates by aperture-opening encapsulation.

The initial ROMP of norbornene using [G3]@UiO-66 (2-day) that has not been washed with acetonitrile is considered false positive result. There might be free catalysts that have not been encapsulated in UiO-66 without the additional washing procedure. However, the false positive result indicates that the encapsulation condition modified to room temperature does not affect catalytic activity. The absence of polymer product using the encapsulated catalysts after three extensive wash by acetonitrile also indicates that the washing is necessary and highly efficient in removing free catalysts.

Further, although ROMP using [G2]@UiO-66 (5-day) and [G3]@UiO-66 (5-day) after extensive washing still produced polymers intended, the polymers obtained are likely catalyzed by the catalysts adsorbed to the MOF. More control experiments need to be conducted to determine the precise location of the catalysts on MOF. This can be done by

treating the encapsulated catalysts with toxins that deactivated the catalysts adsorbed on the surface but not the encapsulated ones inside MOF cavity. Further, it is necessary to study whether the adsorbed catalysts would have any effect on polymerization, with MOF functioning as solid state support instead of encapsulating cage.

ROP using UiO-68-NHC did not produce polymer. Although the UiO-68-NHC has been activated according to literature (Zhang, 2019), we suspect that additional activation steps need to be carried out for activation of carbene moiety necessary for ROP catalysis. Standard NHC activation requires potassium tert-butoxide for deprotonation and generation of carbene. Since the deprotonation on MOF has not examined by any previous work, it is worth testing whether the traditional deprotonation agents such as potassium tertbutoxide is compatible with the MOF and whether the NHC can be properly activated.

Conclusion:
We have tested several catalysts, encapsulation conditions and methods to achieve controlled polymerization. While further improvements are necessary, our work demonstrated the viability of the catalysts in typical encapsulation condition. Next, we will further explore the location of catalysts, improve the loading rate and achieve polymerization using encapsulated catalysts.

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