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Sequestering CO_2 for Short-Term Storage in MOFs: Copolymer Synthesis with Oxiranes

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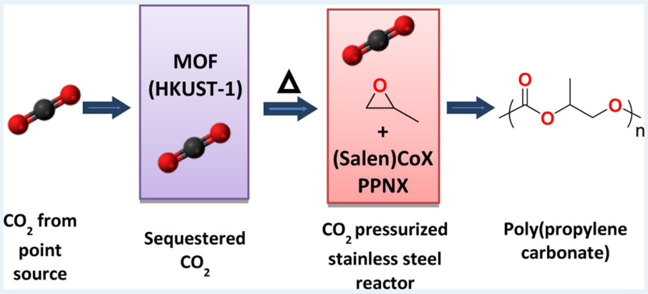
Supporting Information

ABSTRACT: It is presently well-established that the synthesis of polycarbonates or cyclic carbonates from metal-catalyzed reactions of CO_2 and oxiranes provides a viable industrial process for the production of these important chemicals. In this study, we have demonstrated that CO_2 collected under aerobic conditions at atmospheric pressure over $[Cu_3(btc)_2(H_2O)_3]$ (btc = benzene-1,3,5-tricarboxylate) or HKUST-1, a commercially available metal−organic framework material (MOF), can be utilized to synthesize poly(propylene carbonate) from propylene oxide and CO_2 catalyzed by Co(III) salen catalysts at optimal pressure. That is, CO_2 thermally released from the MOF material selectively affords copolymer in the pressure range that is not rate-limiting. Similar results were noted for the copolymerization of the much less reactive *cis*-2-butylene oxide monomer with CO_2. Comparative studies using CO_2 provided directly from a compressed gas source gave similar results. This investigation provides a baseline study for the practical use of atmospheric pressure or below CO_2 captured from point sources for the synthesis of useful chemicals without requiring mechanical compression.

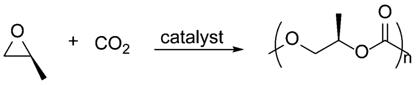


KEYWORDS: *carbon dioxide, polycarbonates, epoxides, metal−organic framework, copolymerization*

INTRODUCTION

One of the major challenges of the next few decades will be redesigning our present chemical industry to accommodate the widespread use of renewable resources. A viable contribution to this matter will be to convert some of the carbon dioxide emissions into important chemicals and materials needed by the chemical industry. Indeed, carbon capture and utilization used in conjunction with carbon storage not only can provide an alternative and renewable feedstock for the chemical industry but also can generate revenue to offset the cost of carbon capture and storage.

Much current research is being directed worldwide toward the development of processes that use carbon dioxide as a feedstock for producing useful chemicals.[1] One of the processes that has proven to be viable, having been commercialized, is the production of polymers derived from CO_2 and propylene oxide.[2] Indeed, presently there are several oxiranes that undergo copolymerization with CO_2 to afford completely alternating copolymers (eq 1).[3] In addition, this coupling reaction can as well be made selective for producing cyclic carbonates from the cycloaddition of CO_2 and oxiranes (eq 2).[4] Although for both of these processes there are several catalytic systems which operate at 1 atm of CO_2 pressure, in general, these processes are enhanced in rate in the presence of higher pressures of CO_2.[5]



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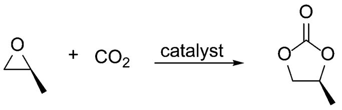

(2)

Hence, for processes utilizing CO_2 from stationary point sources at or below atmospheric pressure, such as coal-based power generating plants or natural gas production facilities, it would be necessary to first mechanically compress the carbon dioxide to enhance the rates of these chemical reactions. Since much progress has been made in the synthesis of metal−organic framework materials (MOFs) for the selective adsorption of CO_2, an alternative approach would be to first sequester the CO_2 employing a solid porous adsorbent material or a metal−organic framework material.[6] This captured CO_2 could subsequently be released at higher pressures from such origins using heat generated elsewhere in the plant or from solar heat sources.[7]

Herein, we describe the use of a commercially available metal−organic framework (MOF) material, $[Cu_3(btc)_2(H_2O)_3]$ (btc = benzene-1,3,5-tricarboxylate), otherwise referred to as HKUST-1, for the short-term capture and

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storage of CO_2 and its utilization in the copolymerization with propylene oxide to afford poly(propylene carbonate).[8] The aim of this study is to examine whether CO_2 collected continuously over a MOF material at atmospheric pressure under aerobic conditions can be effectively copolymerized with epoxides to provide polycarbonates. Comparative studies employing CO_2 from compression storage under anaerobic conditions are also reported. These findings are ultimately necessary as baseline studies for comparable reactions carried out using CO_2 from point source of emission.[7]

■ RESULTS AND DISCUSSION

The MOF material chosen for these studies is the commercially available, highly porous $[Cu_3(btc)_2(H_2O)_3]$ (btc = benzene-1,3,5-tricarboxylate) referred to as HKUST-1.[8,9] The material used herein was synthesized following a slightly modified procedure similar to that reported by Rowsell and Yaghi.[10] The adsorption properties we determined for this metal organic framework are shown in Figure 1 and Table 1.

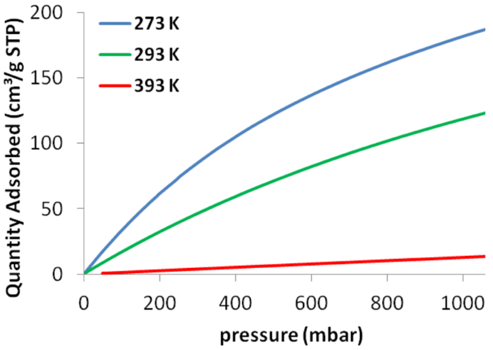


Figure 1. Adsorption properties of our sample of HKUST-1 determined as a function of temperature and pressure.

Table 1. Quantities of CO_2 Adsorbed on Our Sample of HKUST-1 at Atmospheric Pressure

	273 K	293 K	393 K
cm^3 CO_2 (STP)/g MOF	182	118	14
mole CO_2/g MOF	0.008 109	0.005 292	0.000 639
total g CO_2 adsorbed (8 g MOF)	2.85	1.86	0.22

The reaction initially examined was the copolymerization of propylene oxide and carbon dioxide (eq 1), a process well-studied and known to selectively afford completely alternating copolymers of narrow polydispersity. Two types of experiments were performed. The first was designed to test the reproducibility of the process. This was done by carrying out a series of reactions in which the MOF vessel was refilled with CO_2 before each run and the copolymerization process was repeated in a similar manner. The MOF-captured CO_2 was thermally released into a reaction vessel that contained propylene oxide in the presence of a binary catalyst system, (salen)CoDNP/PPNDNP, where DNP = deprotonated 2,4-dinitrophenol. The schematic of the process is depicted in Scheme 1 and Figure 2. Pretreatment of the MOF material was accomplished by drying under vacuum at 130 °C. Subsequently, no care was taken to exclude moist air during refilling cycles of the MOF vessel with CO_2.

Scheme 1. Schematic of the Process[a]

[a](a) 10 mL stainless steel vessel filled with 6.1 g of HKUST-1 and 1.2 g of CO_2. (b) 10 mL stainless steel reactor containing 1.0 mL (14.3 mmol) of propylene oxide and 5.6 mg (7.1 μmoles) of catalyst with 1 equiv of PPNDNP.

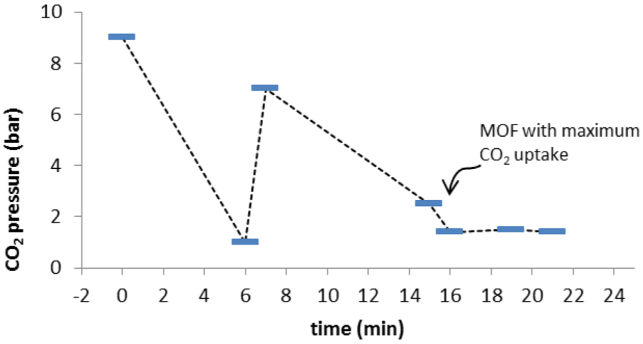


Figure 2. Illustration of CO_2 adsorption process at ambient temperature by HKUST-1, where vessel **a** was pressurized at 9 and 7 bar to reach maximum CO_2 uptake.

Figure 2 indicates the pressure swings in the MOF vessel during each refilling cycle, where after maximum CO_2 uptake, excess pressure is released leading to vessel **a** being at atmospheric pressure at ambient temperature. *A note of importance*: the process described in Figure 2 could as well be achieved adsorbing CO_2 at atmospheric pressure. The employment of higher pressure CO_2 uptake with subsequent release to atmospheric pressure is utilized as a matter of convenience for saving time. The graph in Figure 3 represents the time-dependent CO_2 pressure increases upon heating MOF vessel **a** at 120 °C, that is, prior to injecting CO_2 into reactor **b**.

The copolymerization results obtained for 10 reaction cycles of propylene/CO_2 employing the same MOF sample are illustrated in Figure 4 and listed in Table 2. All reactions were carried out under the same conditions as indicated in Scheme 1, and the conversions to copolymer are based on spectroscopic (^{1}H NMR) yields. Since these processes are carried out in the absence of added solvent, the copolymerization reactions were terminated at <60% conversion; otherwise, the reaction mixture becomes too viscous. The CO_2 pressure in the reaction vessel **b** upon opening vessel **a** at 120 °C was consistently around 11.0 bar. As indicated in Figure 5 and Table 3, in the CO_2 pressure range between 9 and 15 bar, the rate of the copolymerization reaction is independent of the pressure of CO_2.

Despite some random variations in the quantity of copolymer produced, the MOF material held up well to

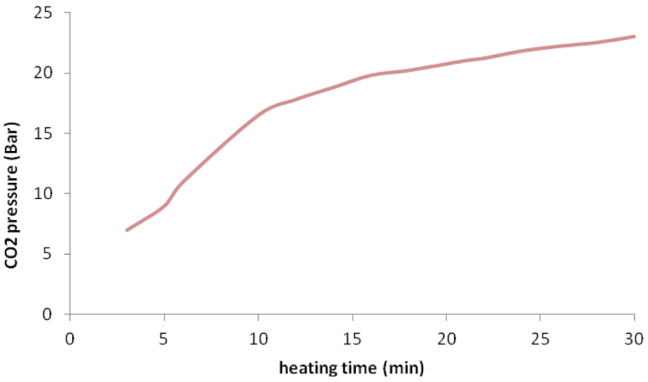


Figure 3. CO_2 released by MOF in vessel **a** upon heating at 120 °C.

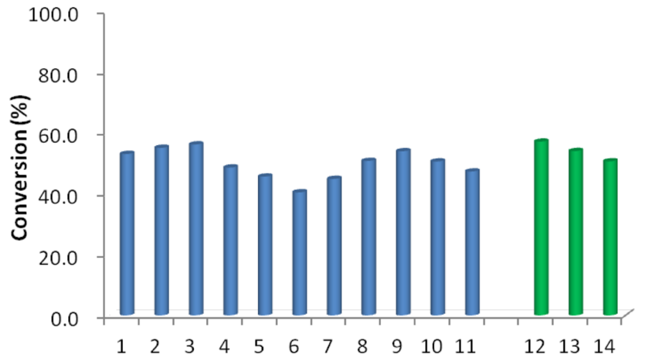


Figure 4. Conversion of propylene oxide/CO_2 to copolymer for reactions carried out for 5 h at ambient temperature.

Table 2. Copolymerization Reactions of Propylene Oxide/CO_2

run	conv (%)	TOF (h^{-1})	M_n (kDa)	PDI
1	53.0	212.0	8.87	1.06
2	55.0	220.1	8.90	1.05
3	56.1	224.5	9.14	1.05
4	48.6	194.2	7.93	1.05
5	45.6	182.3	7.01	1.06
6	40.4	161.6	7.40	1.05
7	44.8	179.2	6.76	1.06
8	50.7	202.9	8.60	1.06
9	53.9	215.6	9.81	1.07
10	50.5	202.1	8.65	1.06
11[a]	47.3	189.0	9.79	1.12
12[b]	57.1	228.2	12.73	1.06
13[b]	54.0	215.9	13.04	1.08
14[b]	50.6	202.3	12.72	1.08

[a] MOF was exposed to 1 atm CO_2 for 18 h instead of pressurizing to 9 bar in CO_2 adsorption process. [b] Reactions carried out with CO_2 obtained directly from high pressure tank.

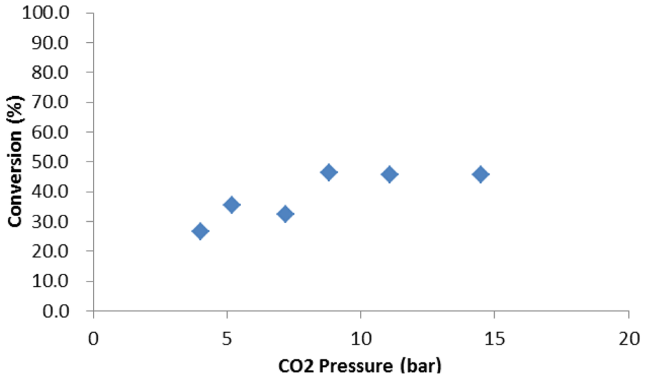


Figure 5. Copolymerization runs as a function of CO_2 pressure. Reaction conditions as in Figure 4

Table 3. Copolymerization Data As a Function of CO_2 Pressure

entry	CO_2 pressure (bar)	conv (%)	TOF (h^{-1})	M_n (kDa)	PDI
1	14.5	45.5	182.0	8.62	1.06
2	11.1	45.8	183.2	9.32	1.06
3	8.8	46.4	185.7	8.44	1.05
4	7.2	32.4	129.5	5.96	1.07
5	5.2	35.5	142.1	6.58	1.06
6	4.0	26.5	106.0	4.99	1.06

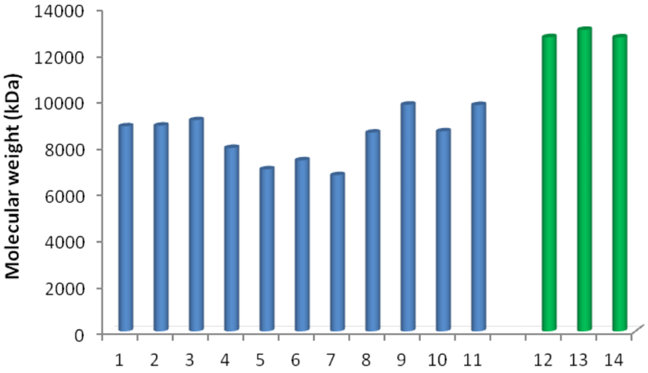


Figure 6. Molecular weight results from 10 consecutive runs and the three runs without HKUST-1 (entries 12–14). The T_g's of entries 4 and 13 were 34.2 and 38.6 °C, respectively.

continued filling under aerobic conditions and thermally releasing of CO_2. The average propylene oxide/CO_2 conversion to poly(propylene carbonate) over the 10 runs was 49.9%. This was only slightly lower than that observed for three identical processes (entries 12–14) carried out under anaerobic conditions with CO_2 taken directly from a pressurized cylinder of 53.9%. Furthermore, the polymeric material afforded from the two different pathways possessed similar T_g's, molecular weights, and polydispersities (see Figure 6). The slight increase in molecular weights of the copolymers produced using CO_2 directly from the CO_2 cylinder are likely due to an increased trace of water in the MOF-captured CO_2 reactions. This is seen in the bimodal molecular weight distributions in the GPC traces in Figure 7 for the two different processes. Numerous references to this prevalent phenomenon observed during these polymerization processes can be found in the published literature.[5,11]

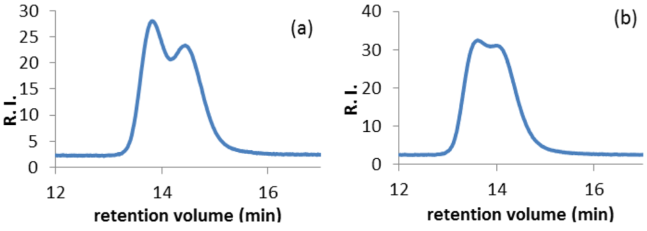


Figure 7. GPC traces for polymer from Table 2 entries 1 (a) and 12 (b).

The second set of experiments performed involved the use of a MOF filled vessel which was loaded with CO_2 at 0 °C, as described previously (Figure 2). This vessel then served as a gas storage unit for carrying out a series of propylene oxide/CO_2 copolymerization reactions. These data are represented in Table 3, where over the series of copolymerization reactions, the pressure decreased from 14.5 to 4.0 bar with a concomitant decrease in reactivity occurring below a CO_2 pressure of ∼9 bar. Over the course of the six polymerization cycles, 72% of the CO_2 adsorbed on the MOF was converted to poly(propylene carbonate). Also apparent from the data in Table 3, there is a linear relationship between M_n and percent conversion (Figure 8). This, coupled with the narrow molecular weight distribution clearly illustrates these processes to be well-controlled.

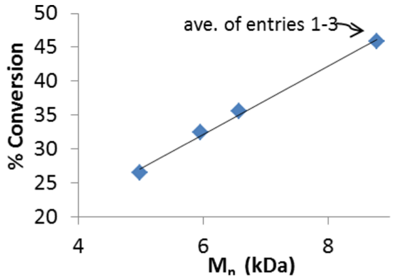
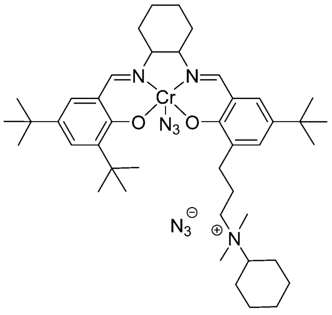


Figure 8. Linear relationship between M_n and percent conversion for the copolymerization of propylene oxide and CO_2. Data are found in Table 3. % conversion = 5.03 M_n + 2.01. R^2 = 0.996.

A much less reactive epoxide, *cis*-2-butylene oxide, was examined for its copolymerization characteristics employing CO_2 from the two sources. To our knowledge, there is only a brief mention of the copolymerization of *cis*-2-butylene oxide and CO_2 in the open literature.[12] Employing the bifunctional catalyst (**1**) at 70 °C, *cis*-2-butylene oxide and CO_2 produced copolymers with a selectivity of 79% when using pressurized CO_2 directly or CO_2 released following storage over HKUST-1. Poly(butylene carbonate) with a narrow PDI was isolated in both instances with a T_g of 65.3 °C. We will report a complete study of the copolymerization of CO_2 with the isomers of butylene oxide at a later date. Nevertheless, it suffices to state that the copolymer obtained from *cis*-2-butylene oxide and CO_2 is the same as that reported on Empower Materials Web site based on the similarities of their T_g values.[2b]



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In conclusion, a process for the synthesis of polycarbonates from the metal-catalyzed copolymerization of propylene oxide and CO_2 has been reported, in which the CO_2 utilized was collected over the MOF material, HKUST-1 under aerobic conditions and thermally released at the optimal pressure for efficient synthesis. These studies have focused on the *practical*, incorporating our fundamental understanding of CO_2/epoxide coupling reactions, in an effort to begin the long term challenge of utilizing the abundant and renewable CO_2 source for the production of chemicals and fuels.[13] It should be noted that there are reports that active (salen)cobalt or (porphyrin)cobalt catalysts are parts of the coordinated conjugated microporous polymer or metal−organic framework structures that have been employed as catalysts for CO_2/epoxide coupling to produce cyclic carbonates.[14,15] However, synthesizing the alternative copolymer products utilizing these catalysts is not possible.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, including HKUST-1 synthesis and characterization, and polymer preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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