Green Chemistry

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Cite this: *Green Chem.*, 2013, **15**, 110

Catalytic fixation of CO_2 to cyclic carbonates by phosphonium chlorides immobilized on fluorous polymer†

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Received 1st August 2012,
Accepted 24th September 2012

DOI: 10.1039/c2gc36210d

www.rsc.org/greenchem

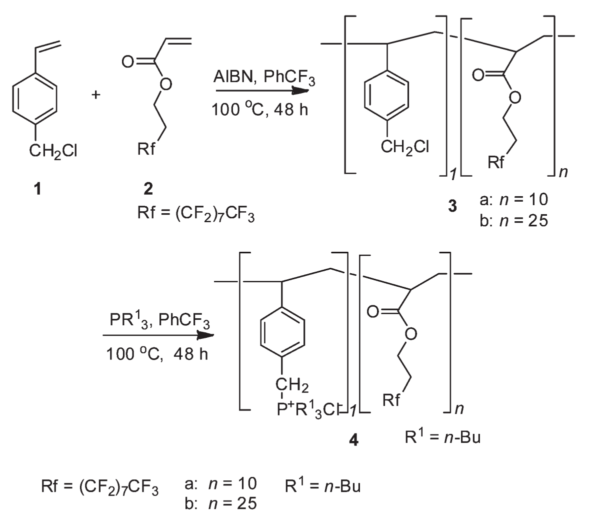
Phosphonium chloride covalently bound to the fluorous polymer is proved to be an efficient and recyclable homogeneous CO_2-soluble catalyst for organic solvent-free synthesis of cyclic carbonates from epoxides and CO_2 under supercritical CO_2 conditions. The catalyst can be easily recovered by simple filtration after reaction and reused with retention of high activity and selectivity. In addition, the effects of various reaction variables on the catalytic performance are also discussed in detail. The process represents a simpler access to preparing cyclic carbonates with the ease of homogeneous catalyst recycling.

Introduction

Recently, CO_2 fixation has received much attention because CO_2 is the most inexpensive and renewable carbon resource from the viewpoint of green chemistry and atom economy.[1] Development of a truly environmentally friendly process utilizing CO_2, which is the largest single source of greenhouse gas and can also be regarded as a typical renewable natural resource, has drawn current interest in synthetic chemistry from the viewpoint of environmental protection and resource utilization. In this regard, chemical fixation of CO_2 onto industrial useful materials is one of the most promising methods because there are many possibilities for CO_2 to be used as a safe and cheap C_1 building block in organic synthesis.[2] On the other hand, supercritical CO_2 ($scCO_2$) is considered to be a green solvent, and thus substantial effort has been devoted to developing chemical processes in which $scCO_2$ is used to replace hazardous organic solvent.[3]

Organic cyclic carbonates such as ethylene carbonate and propylene carbonate (PC) have been widely used for various purposes, for instance, electrolytic elements of lithium secondary batteries, polar aprotic solvents, monomers for synthesizing polycarbonates, and chemical ingredients for preparing medicines or agricultural chemicals.[4]

For the cyclic carbonate synthesis from CO_2 and epoxides, numerous effective catalytic systems have been developed including homogeneous[5] and heterogeneous catalysis.[6] We have reported that a fluorous phosphonium catalyst[5k] can be used in $scCO_2$ as a homogeneous catalyst, and this process offers the advantage of allowing the synthesis of *e.g.* PC to take place under supercritical conditions with the direct and spontaneous separation of the carbonate. Recently, attachment of fluorinated chains to chelating agents, surfactants, and catalyst ligands could generally enhance the solubility of such compounds in $scCO_2$, and thus can be used to design CO_2-soluble catalysts.[7] In this context, a phosphonium chloride covalently bound to the fluorous polymer (Scheme 1) was



Scheme 1 Synthesis of fluorous polymers supported phosphonium chloride.

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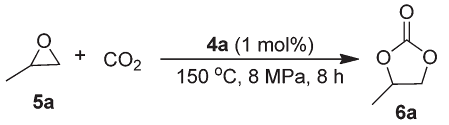
† Safety warning: Experiments using compressed CO_2 gas are potentially hazardous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.



Scheme 2 Synthesis of propylene carbonate from propylene oxide and CO_2.

employed to design such a supported catalyst that can homogeneously dissolve during the reaction and precipitate quantitatively in the separation stage.

The fluorous polymers **4a** and **4b** were identified by ^1H NMR, ^{13}C NMR, ^{19}F NMR, FT-IR elementary analysis[7d] and GPC measurement. The reaction of propylene oxide (PO) and CO_2 performed well with 98% of PC yield and excellent selectivity, as shown in Scheme 2. Notably, incorporation of the fluorinated chain in the polymer effectively enhance the solubility of phosphonium salts which are usually insoluble in $scCO_2$, thus providing a simple way for performing homogeneous catalysis under $scCO_2$ conditions.

Results and discussion

The coupling of PO and CO_2 was conducted in a batch-wise operation in the presence of 1 mol% of the catalyst with respect to the initial amount of PO under identical conditions (150 °C, 8 MPa, 8 h). The results are summarized in Table 1. It is worthwhile mentioning that the fluorous polymer (**3a**) itself can hardly catalyze the cycloaddition reaction under the reaction conditions (entry 3, Table 1). Interestingly, phosphonium chloride covalently bound to fluorous polymers (**4a** and **4b**) exhibited high activity, higher than Bu_4PCl (entries 1, 2 *vs.* 4), the corresponding lower molecular weight catalyst; even higher than KI and Bu_4NBr (entries 1, 2 *vs.* 5, 6), traditional homogeneous catalysts for PC synthesis in industrial application. It is most possible that the incorporation of the fluorinated side chain in the polymer effectively enhances the solubility of phosphonium salts that are usually insoluble in $scCO_2$. Therefore, the catalyst (**4a**) was selected as the model catalyst for further investigation.

The influence of reaction temperature on PC yield was further studied. It was found that the yield of PC was strongly affected by the reaction temperature. The yield and selectivity of PC increased with the reaction temperature up to 150 °C (entries 1 and 7–9, Table 1), whereas further increase in the temperature caused a decrease in the selectivity, possibly due to facile formation of side-products at the higher temperature, *i.e.* the isomerisation of PO to acetone and the ring opening by water to propylene glycol. From a practical viewpoint, apparently, 150 °C could be the optimal and desirable temperature.[2f] Moreover, 1 mol% of the catalyst is a proper amount for the reaction (entries 1, 10, 11).

Fig. 1 shows the influence of reaction time on PC yield. The supported phosphonium chloride-catalyzed PC synthesis from PO and CO_2 proceeded rapidly, and more than 80% PC yield was obtained within the first 2 h at 150 °C. The PC yield experienced a continuing growth within 6 h, while the selectivity of PC remained almost constant during the whole course of the reaction. Consequently, a reaction time of 6 h was required for almost complete PO conversion.

It is well-known that the properties of supercritical fluids are sensitive to pressure, and thus pressure may drastically influence the reaction outcome when a reaction takes place in supercritical conditions. The effect of CO_2 pressure on the yield and selectivity of PC is depicted in Fig. 2. The selectivity

Table 1 Synthesis of propylene carbonate from propylene oxide and CO_2 using various catalysts[a]

Entry	Cat.	Temperature (°C)	Yield[b] (%)	Selectivity[b] (%)
1	**4a**	150	98	99
2	**4b**	150	97	97
3	**3a**	150	5	–
4	Bu_4PCl	150	90	99
5	Bu_4NBr	150	95	98
6	KI	150	89	96
7	**4a**	90	21	99
8	**4a**	120	58	>99
9	**4a**	180	81	90
10[c]	**4a**	150	82	99
11[d]	**4a**	150	98	99

[a] Reaction conditions: propylene oxide (28.6 mmol); 1 mol% of the catalyst based on propylene oxide; CO_2 8 MPa; 8 h. [b] Determined by GC using biphenyl as an internal standard. [c] 0.5 mol% of the catalyst. [d] 2 mol% of the catalyst.

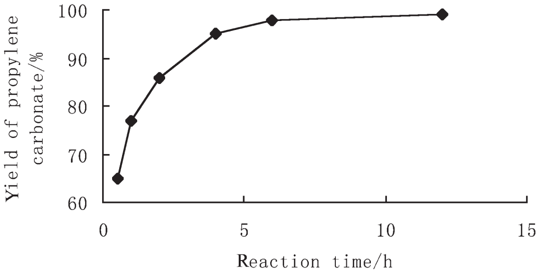


Fig. 1 Reaction time – the PC yield profile. Reaction conditions: propylene oxide (28.6 mmol); catalyst **4a** (1 mol%); 150 °C; 8 MPa.

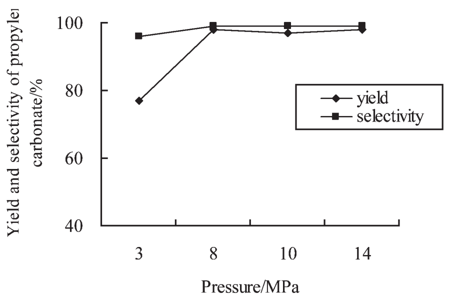
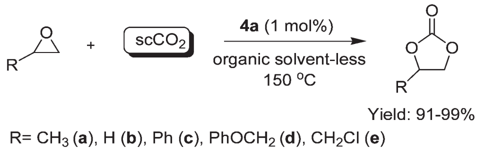


Fig. 2 Reaction pressure – the PC yield profile. Reaction conditions: propylene oxide (28.6 mmol); catalyst **4a** (1 mol%); 150 °C; 8 h.



Scheme 3 Synthesis of various carbonates catalyzed by fluorous polymers-$R_3P^+X^-$.

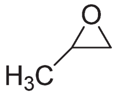
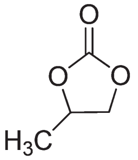
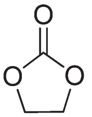
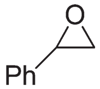
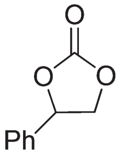
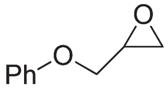
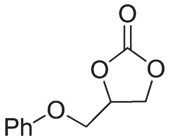
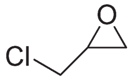
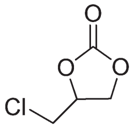
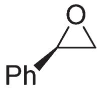
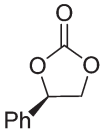
slightly changed in the range of 3–14 MPa. As easily seen, the best PC yield could be achieved under $scCO_2$ conditions, demonstrating the preferential effect of the supercritical conditions, while the yield was remarkably influenced by the pressure below 8 MPa. Possibly, the isomerisation to acetone increased or the CO_2 insertion step was limited at low CO_2 pressure.

The scope of the substrates was further explored as shown in Scheme 3 and Table 2. Several terminal epoxides were chosen to be tested under the optimized reaction conditions. The catalyst (**4a**) was found to be applicable to a variety of terminal epoxides, yielding the corresponding cyclic carbonates in excellent yields with more than 99% selectivity (entries 1–5, Table 2). This catalyst can also be utilized in the coupling reaction of CO_2 and optical pure epoxide, (*R*)-styrene oxide to conveniently obtain (*R*)-1-phenyl-1,2-ethanediol carbonate (***R*-6c**) in 99% ee with retention of stereochemistry (entry 6).[8]

The facility of recycling the catalysts is one of the key advantages in this catalytic system. As shown in Fig. 3, a single homogeneous phase was formed under reaction conditions (100 °C, 14 MPa[5k] or 150 °C, 8 MPa). Indeed, the phase behaviour of the reaction visually inspected through a sapphire window attached to the autoclave[6q] revealed that the reaction mixture initially formed a uniform phase, while propylene carbonate formed a new phase upon the reaction. After the reaction, the catalyst was precipitated as a solid upon venting CO_2. As a result, the catalyst was easily recovered by simple filtration. A series of repeated reactions run continuously to investigate the constancy of the catalyst activity. In each cycle, the catalyst was separated by filtration and then used for the next run directly. The results show that the catalyst can be reused at least 7 times without significant loss of catalytic activity, while the excellent selectivity of propylene carbonate is nearly unchanged. Furthermore, the purity of the product separated directly by filtration from the reaction mixture, reached 99% without further purification process.

A possible mechanism for the fluorous polymer supported phosphonium chloride-catalyzed coupling of epoxides with CO_2 in this study would be similar to that of ammonium/phosphonium salt catalysis.[5d,s] The proposed mechanism involves the activation of propylene oxide by the phosphonium cation, the ring-opening of the epoxide *via* nucleophilic attack of chloride at the least-hindered carbon, and the insertion of CO_2 into the N–O bond. Subsequent cyclization *via* an intramolecular nucleophilic attack leads to the cyclic carbonate and the regeneration of the catalyst.

Table 2 Cycloaddition of CO_2 with various epoxides catalyzed by **4a**[a]

Entry	Substrate	Product	Yield[b] (%)	Selectivity (%)
1	 **5a**	 **6a**	98 (93)	99
2	 **5b**	 **6b**	97 (95)	>99
3	 **5c**	 **6c**	95 (91)	99
4	 **5d**	 **6d**	99 (94)	99
5	 **5e**	 **6e**	91 (88)	98
6	 **R-5c**	 **R-6c**	97	99

[a] Reaction conditions: epoxide (28.6 mmol); catalyst **4a** (1 mol%); temperature 150 °C; CO_2 8 MPa; 8 h. [b] Determined by GC using biphenyl as an internal standard; value in parentheses refers to isolated yield column chromatography with ethyl acetate–petroleum as the eluent.

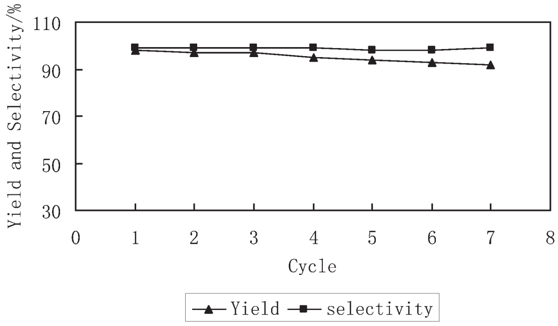


Fig. 3 Catalytic activity of the reused CO_2-soluble catalyst (**4a**). Reaction conditions: propylene oxide (28.6 mmol); catalyst **4a** (1 mol%); 150 °C; 8 MPa; 8 h.

Experimental

Chemical reagents

All chemicals, except CO_2, were handled under a nitrogen atmosphere. The catalysts were synthesized by a modified method described in the literature.[7d–l]

Preparation of fluoroacrylate copolymer (3a). 1*H*,1*H*,2*H*,2*H*-Heptadecafluorodecyl acrylate (**1**) (6.64 g, 12.8 mmol) and *p*-chloromethylstyrene (**2**) (0.118 g, 0.77 mmol) were dissolved in 50 mL of benzotrifluoride. The flask was evacuated and flushed with argon three times and then fitted with a reflux condenser. After heating to 80 °C, azobisisobutyronitrile (AIBN, 0.025 g, 0.15 mmol) in 5 mL of benzotrifluoride was added. The reaction was stirred for 2 d at 100 °C and was then cooled to room temperature. The copolymer **3** was precipitated into 75 mL of methanol. ^1H NMR analysis indicated the presence of monomer, so the dissolution and precipitation were repeated again. The copolymer was isolated by filtration and dried under vacuum overnight to give a white solid.

*Compound **3a***: ^1H NMR (perfluoro-compound FC 77 with drops $CDCl_3$) δ 7.01–7.35 (br m, 1H), 4.27 (s, 5H), 2.46 (s, 5H), 1.40–1.90 (br m, 15H); ^{13}C NMR (100.6 MHz, FC 77 with an external chloroform-d lock) δ 175.52 (s, C=O), 105.73–126.03 (m, Rf), 58.01 (s, OCH_2), 31.78 (s, CH_2Rf).

Preparation of fluoroacrylate copolymer (3b). 6.64 g of 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate (**1**, 12.8 mmol) and 4-chloro-α-methylstyrene (**2**) (0.118 g, 0.77 mmol) were dissolved in 50 mL of benzotrifluoride. The Schlenk flask used was evacuated and flushed with argon three times and then fitted with a reflux condenser. AIBN (0.025 g, 0.15 mmol) was added after heating to 80 °C. The reaction was allowed to proceed for 2 d at 100 °C under argon and was then cooled to room temperature. The volume of the solution was reduced to 50 mL by vacuum and the copolymer (**3b**) was precipitated by adding the solution into 75 mL of freshly-distilled methanol. The copolymer was isolated by filtration and dried under vacuum to give 4.98 g of a white solid (yield 75%).

*Compound **3b***: ^1H NMR (FC 77) 7.14–7.70 (br m, 1H), 4.52 (s, 12H), 1.41–2.63 (br s, 30H).

Synthesis of tributylbenzylphosphonium chloride ligated fluoroacrylate polymer (4a, 4b). In a typical procedure, copolymer **3b** (4.98 g) was dissolved in 5 mL of trifluorotoluene under argon in an oven-dried flask. After the flask was flushed with argon, a solution of 202 mg of tributylphosphine in trifluorotoluene (10 mL) was then added. The reaction was stirred at 100 °C for 1 d under an argon atmosphere. The product was precipitated into 30 mL of freshly-distilled MeOH and isolated by filtration and dried for 6 h under vacuum to give slightly yellow solid. Gel permeation chromatography (GPC) measurements were carried out on PL-GPC-220 in hexafluoroisopropanol.

*Compound **4a***: colorless solid. ^1H NMR (FC 77) 7.10–7.90 (br m, 2H), 4.46 (s, 25H), 1.40–2.57 (br s, 75H); ^{13}C NMR (FC 77) 175.22 (s, C=O), 102.98–125.57 (m, Rf), 57.73 (s, OCH_2), 42.14 (s, CH_2Ph), 31.39 (t, CH_2CF_2, J_{FC} = 21.49 Hz), 25.00 (s); ^{31}P NMR (FC 77) 32.97. IR (ν, cm^{-1}), 2973 (C–H), 1737 (C=O), 1249 (C–F), 1103, and 1012, and 711 (phosphonium salt), 653; Anal. Calcd for (**4a**): C, 32.76; H, 1.93; F, 58.3; P, 0.56. Found: C, 32.43; H, 1.90; F, 57.4; P, 0.44. Mw: 5536.

*Compound **4b***: ^1H NMR (FC 77 with an external chloroform-d lock) 7.08–7.64 (br m, 1H), 4.28 (br m, 5H), 3.49 (s, 5H), 2.50 (m, 5H), 1.57–1.89 (br m, 20H); ^{13}C NMR (100.6 MHz, FC 77 with an external chloroform-d lock) 175.50 (s, C=O), 106.61–125.67 (m, Rf), 57.76 (s, OCH_2), 42.40 (s, CH_2Ph), 31.48 (t, CH_2Rf, J_{FC} = 20.63 Hz), 25.33 (s), 14.47 (s); ^{31}P NMR (161.9 MHz, FC 77 with an external chloroform-d lock) 34.64. IR (ν, cm^{-1}) 2965 (C–H), 1740 (C=O), 1255 (C–F); Anal. Calcd for (**4b**): C, 31.49; H, 1.66; F, 60.3; P, 0.29. Found: C, 31.14; H, 1.57; F, 60.2; P, 0.24. Mw: 10 718.

Representative procedure for the cycloaddition reaction

In a typical reaction, the cycloaddition reaction of CO_2 to propylene oxide was carried out in a stainless steel autoclave (25 cm^3 inner volumes). Prior to the reaction, the catalyst was evacuated at 150 °C for 3 h. CO_2 (gas, 4.0 MPa) was introduced to a mixture of propylene oxide (28.6 mmol), catalyst (**4a**, 1 mol%), and biphenyl (80 mg, an internal standard for GC analysis) at room temperature. The gauge was used to monitor the pressure of the system. The initial pressure was adjusted to 8 MPa at 150 °C and the autoclave was heated at that temperature for 8 h. After cooling, the products were analyzed on a gas chromatograph (Agilent 6890) equipped with a capillary column (HP-5 30 m × 0.25 μm) using a flame ionization detector. The structure and the purity of the products were further identified using GC-MS (HP G1800A) by comparing retention times and fragmentation patterns with those of authentic samples. The solvent was removed, and the residue was subjected to column chromatography with ethyl acetate–petroleum as the eluent to obtain the desired product.

The products were also characterized by NMR. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-plus 400 spectrometer. Chemical shifts were given as δ values referenced in parts per million (ppm) from tetramethylsilane (TMS) as an internal standard. Spectral characteristics of the products (cyclic carbonates **2a–e**) in Table 2 were provided as follows:

4-Methyl-1,3-dioxolan-2-one (6a). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.43 (d, ^3J = 6.0 Hz, 1H, CH_3), 3.98 (t, ^3J = 8.4 Hz, 1H, OCH_2), 4.51 (t, ^3J = 8.4 Hz, 1H, OCH_2), 4.82 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.14, 70.52, 73.47, 154.95.

1,3-Dioxolan-2-one (6b). ^1H NMR ($CDCl_3$, 400 MHz) δ 4.52 (s, 4H, OCH_2); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 64.55, 155.36.

4-Phenyl-1,3-dioxolan-2-one (6c). ^1H NMR ($CDCl_3$, 400 MHz) δ 4.35 (t, ^3J = 8.4 Hz, 1H, OCH_2), 4.80 (t, ^3J = 8.4 Hz, 1H, OCH_2), 5.70 (t, ^3J = 8.0 Hz, 1H, OCH), 7.36 (d, ^3J = 7.6 Hz, 2H, C_6H_5), 7.44 (d, ^3J = 6.4 Hz, 3H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 66.17, 68.84, 74.11, 114.57, 121.92, 129.62, 154.65, 157.71.

4-Phenoxymethyl-1,3-dioxolan-2-one (6d). ^1H NMR ($CDCl_3$, 400 MHz) δ 4.15 (dd, ^3J = 4.4 Hz, ^2J = 10.8 Hz, 1H, OCH_2), 4.24 (dd, ^3J = 3.6 Hz, ^2J = 10.8 Hz, 1H, OCH_2), 4.55 (dd, ^3J = 8.4 Hz, ^2J = 6 Hz, 1H, $PhOCH_2$), 4.62 (t, ^3J = 8.4 Hz, 1H, $PhOCH_2$), 5.03

(m, 1H, OCH), 6.91 (d, ^3J = 8.0 Hz, 2H, C_6H_5), 7.02 (t, ^3J = 7.4 Hz, 2H, C_6H_5), 7.31 (t, ^3J = 8.0 Hz, 2H, C_6H_5); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 66.17, 68.84, 74.11, 114.57, 121.92, 129.62, 154.65, 157.71.

4-Chloromethyl-1,3-dioxolan-2-one (6e). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.71 (dd, ^3J = 3.2 Hz, ^2J = 12.0 Hz, 1H, $ClCH_2$), 3.80 (dd, ^3J = 5.2 Hz, ^2J = 12.0 Hz, 1H, $ClCH_2$), 4.39 (dd, ^3J = 6.0 Hz, ^2J = 8.4 Hz, 1H, OCH_2), 4.58 (t, ^3J = 8.4 Hz, 1H, OCH_2), 4.98 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 43.83, 66.84, 74.29, 154.28.

4-Isopropoxy-1,3-dioxolan-2-one (6e). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08 (t, ^3J = 6.4 Hz, 6H, 2 × CH_3), 3.62–3.51 (m, 3H, $(CH_3)_2CHO$, $(CH_3)_2CHOCH_2$), 4.30 (dd, ^3J = 8.0 Hz, ^2J = 15.6 Hz, 1H, OCH_2), 4.42 (dd, ^3J = 8.0 Hz, ^2J = 15.6 Hz, 1H, OCH_2), 4.74 (m, 1H, CHO); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.52, 21.64, 66.15, 66.88, 72.58, 75.18, 155.02.

Conclusions

In summary, phosphonium chloride covalently bound to fluorous polymers is proved to be an efficient and recyclable homogeneous CO_2-soluble catalyst for solvent-free synthesis of cyclic carbonate from propylene oxide and carbon dioxide under supercritical conditions. Incorporation of the fluorinated chain in the polymer effectively enhance the solubility of phosphonium salts which are usually insoluble in $scCO_2$, thus providing a simple way for performing homogeneous catalysis under $scCO_2$ conditions. Furthermore, the catalyst can be easily recovered upon releasing CO_2 and is reusable for up to 7 cycles without significant loss of activity, while the selectivity of propylene carbonate remained >99%.

Acknowledgements

This work was partially supported by the National Science Foundation of China (Grant 21172125).

Notes and references

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