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Polystyrene-Supported Amino Acids as Efficient Catalyst for Chemical Fixation of Carbon Dioxide

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Abstract: Four new polystyrene-supported amino acids have been synthesized and applied to the chemical fixation of carbon dioxide for the first time. Two series of experiments with polystyrene-supported threonine (PS-Thr) and polystyrene-supported tyrosine (PS-Tyr) as catalyst, respectively, were conducted to study the effect of the reaction conditions on the carboxylation of propylene oxide/carbon dioxide. There was no considerable decrease in the yield of propylene carbonate after the polystyrene-supported amino acids were used five times, indicating that these catalysts are very stable. It was demonstrated that these catalysts were very efficient in the carboxylation of various epoxides and aziridines with carbon dioxide under mild conditions without any solvents. The mechanism for this carboxylation is also discussed.

Keywords: amino acids; aziridines; carbon dioxide; cycloaddition reation; epoxides; polystyrene

Introduction

Due to human industrial activities, the fossil fuel source is limited and the production of carbon dioxide is increasing which causes a variety of environmental problems such as global warming and acid rain. Therefore, there is an urgent need to develop new chemical processes using renewable resources and to reduce carbon dioxide emissions. The transformation of carbon dioxide into industrially valuable chemicals is generally regarded as an excellent route in this respect because of its significant values in both environmental preservation and resource utilization.[1] In this respect, a great deal of work, in many different fields, has been undertaken to produce organic carbonates using CO_2 as the feedstock.[1a,2] In particular, one promising methodology in the chemical fixation of CO_2 is to efficiently convert CO_2 to five-membered heterocycles such as oxazolidinones or cyclic carbonates. The resulting cyclic carbonates are excellent aprotic solvents, pharmaceutical and fine chemical intermediates, precursors for polycarbonate materials, intermediates in organic synthesis,[3] and oxazolidinones are also important heterocyclic compounds showing a large scope of application as intermediates and chiral auxiliaries in organic synthesis.[4]

The cycloaddition of CO_2 with epoxides or aziridines is known to be catalyzed by alkali metal salts,[5] organic bases,[6] metal oxides,[7] transition metal complexes,[8] quaternary ammonium and phosphonium salts,[9] ionic liquids,[10] and dual catalysts.[11] Recently, many functional polymers[10d,12] have been used as catalysts or catalyst supports for this transformation due to their attractiveness for technological applications and manufacturing processes with simplified product recovery. The use of polymers instead of homogeneous catalysts in the insertion of CO_2 will lead to environmentally more benign processes for the manufacture of chemicals using CO_2 as a raw material. Divinylbenzene (DVB) cross-linked polystyrene is one of the most useful polymers owing to its compatibility with a wide range of reaction conditions.[13] Furthermore, because of its easy preparation, recyclability, environmental stability, low cost, and non-solubility in any commonly used organic solvent and water, DVB cross-linked polystyrene has attracted much attention as an efficient heterogeneous catalysts support.[12a,14]

Although the addition of CO_2 with epoxides or aziridines to produce five-membered heterocycles has been studied extensively, there is continuing motivation for developing efficient catalysts for chemical fixation of CO_2 which would ideally carboxylate both

epoxides and aziridines. Our studies showed that α-amino acids, which are commonly found in nature and hence relatively inexpensive, are highly efficient catalysts for the coupling of epoxides and carbon dioxide under mild conditions.[11a] However, there are two existing problems that need to be solved. One is how to avoid the use of solvents under mild conditions, and the other is how to separate the catalyst from the product without decomposition of the catalyst or formation of by-products. Considering the advantages of using DVB cross-linked polystyrene as catalyst support, we envisioned that functionalized polystyrene, with α-amino acid as a catalytically active species being covalently grafted onto polystyrene, could be utilized as an active and recyclable heterogeneous catalyst for the chemical fixation of CO_2. Herein, we have developed four new polystyrene-supported amino acids catalysts: polystyrene-supported threonine (PS-Thr), polystyrene-supported tyrosine (PS-Tyr), polystyrene-supported hydroproline (PS-HPro), and polystyrene-supported serine (PS-Ser) (Figure 1). During the course of this work, we discovered that these catalysts have high chemical and thermal stability leading to high catalytic activity for the carboxylation of both epoxide and aziridine substrates, and also could be easily separated from the product and reused. To the best of our knowledge, this is the first work to combine these two kinds of compounds for the chemical fixation of CO_2. We believe that these catalysts could have great potential in industrial application, because they have some unusual advantages, such as their easy preparation, low cost, high activity and selectivity, stability, recyclability.

Results and Discussion

Divinylbenzene cross-linked polystyrene was functionalized with four different α-amino acids using a modification of a procedure in the literature.[15] The preparation of PS-Tyr is shown in Scheme 1. The polymer obtained was characterized by using IR, SEM, TGA/DSC and elemental analysis.

The organic composition of the four polymers (C, H, N and Cl) was determined by elemental analysis (EA) (see Table S1 in the Supporting Information). The effect of immobilization was explicitly evident from the elemental analysis. The increase of the amount of nitrogen, which may correspond to the amino group of the amino acids, indicated that the amino acid is present in the polystyrene resin. Moreover, the amount of chlorine changed noticeably after the polymer had been functionalized. This is probably due to the fact that the OH group of α-amino acids reacts with the Cl of the DVB cross-linked chloromethylated polystyrene, forming C–O bonds and eliminating HCl during covalent anchoring to the polystyrene resin. The loading of the catalysts on each support (2.39–2.62 mmol/g) was estimated by the nitrogen content of each polymer.

FT-IR spectroscopy provided clear evidence for amino acid incorporation and organo-functionalization (Figure S1 in the Supporting Information). The IR peaks at 3400 cm^{-1} are probably due to the N–H stretching mode of the functionalized amino acids.

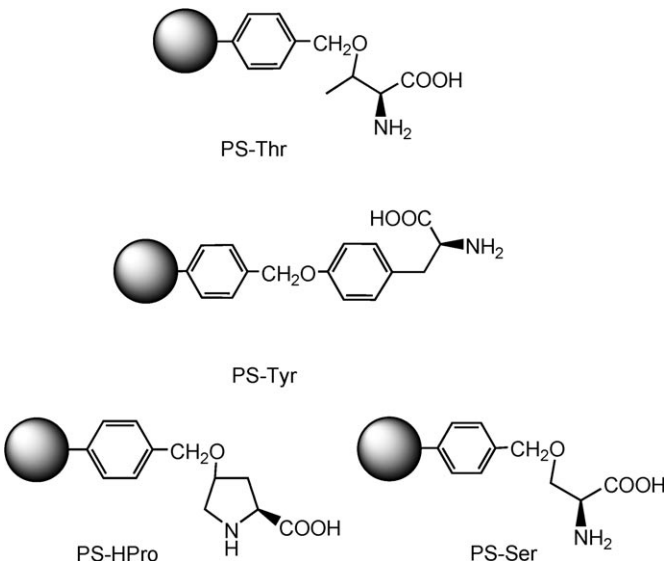
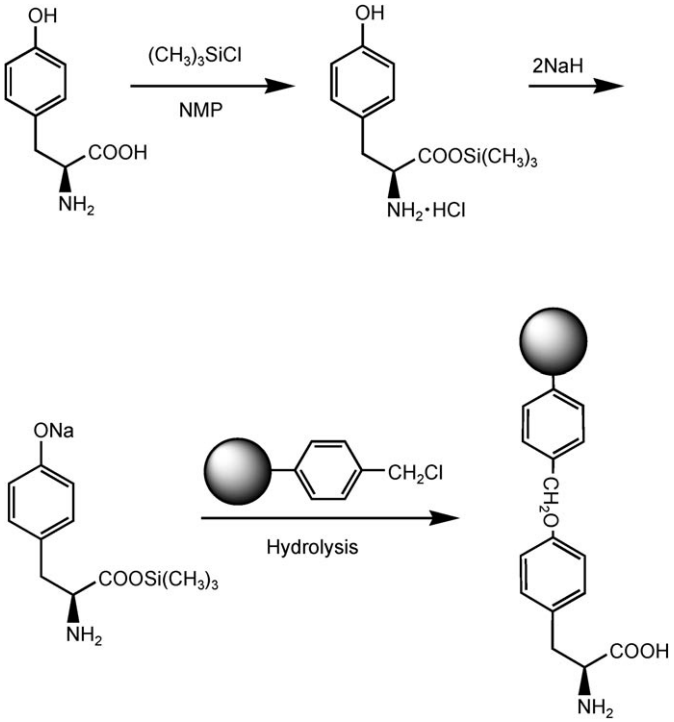


Figure 1. Structures of the four cross-linked-polystyrene-supported amino aicds.



Scheme 1. Synthetic route to cross-linked-polystyrene-supported L-tyrosine.

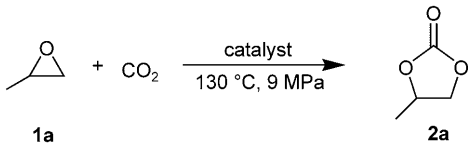
And, in principle, they can also correspond to the overtones of the bands in the range 1560–1640 cm^{-1}. Furthermore, evidence for the presence of amino acids was obtained from the sharp, characteristic peaks at 1600 cm^{-1} which corresponds to the C=O group of amino acids. It should be noted that these peaks are absent in non-functionalized polystyrene resin. In addition, the bands at 1262 cm^{-1} and 671 cm^{-1} which correspond to C–Cl group become weak in the polystyrene-supported amino acids owing to the elimination of HCl in the process.

The morphology of PS-amino acids was observed using scanning electron microscopy (SEM: see Figure S2 and Figure S3 in the Supporting Information). The figure shows that the microscopic appearance of the polymer changed obviously after it had been fixed with amino acids. The surface of the functionalized polymer became rough compared with the chloromethylated polystyrene (PS-CH_2Cl). Although the agglomeration of the particles is irregular, the size of the particles was on the nanometer scale both on the surface and inside of the polystyrene-supported amino acids.

For a polymer support, a certain thermal stability is required because the polymer has to be subjected to vigorous shaking, filtration, and drastic acid-base treatment during the reaction. The thermal stability of our catalyst system was estimated using TAG and DSC (Table S2, Figure S4 and Figure S5 in the Supporting Information). It is observed that the weight loss of the catalysts occurred at slightly under 200 °C, which may correspond to the loss of physisorbed water molecules in the polymer matrix.[16] The significant weight loss that occurred in the region 370–450 °C is attributed to the decomposition of the polymer.

Structural characterization results show that amino acids are firmly held inside the polystyrene resin. Hence, the present polymers were applied to the chemical fixation of carbon dioxide. At first, studies were performed to investigate the effect of different amino acids on the coupling of CO_2 and propylene oxide (PO) under the standard conditions. The results are summarized in Table 1. Without any catalyst, the coupling reaction of PO/CO_2 did not occur at all (Table 1, entry 1), and PS-CH_2Cl alone was found to be inactive for the reaction (Table 1, entry 2). Although an α-amino acid itself can catalyze the coupling of CO_2 and PO under supercritical conditions, their activities remain low even under conditions of 0.8 mol% catalyst over 48 h (Table 1, entries 3–6). In contrast, polystyrene-supported amino acids showed superior activity without the need of any additives (Table 1, entries 7–10). It is evident that all of the four supported amino acids have a marked influence on the reaction rate. The enhancement of catalytic performance for the PS-supported amino acids is presumably attributed to the benefits from changes in the physical properties[17] of the reaction mixture, such as low viscosity and increased solubility for reactants. Besides, the special structure of the PS-amino acids (analyzed by SEM in the Supporting Information) would have a great influence on the catalysts activity. Consequently, the α-amino acids anchored on the 2% DVB-cross-linked polystyrene can be considered as the active species for the reaction and the CO_2-expandable polymer improves the catalytic activity. For all the experiments with different catalysts, no by-product was detected.

Table 1. Comparison of catalytic activities of polymer-supported amino acids with those of small molecular amino acids.[a]



1a 2a

Entry	Catalyst	Yield[b] [%]
1	0	0
2	PS-CH_2Cl	trace
3[c]	L-tryrosine	36
4[c]	L-threonine	34
5[c]	L-serine	14
6[c]	L-hydroproline	31
7	PS-Tyr	93
8	PS-Thr	96
9	PS-Ser	91
10	PS-HPro	95

[a] *Reaction conditions:* propylene oxide 20 mmol, CO_2 pressure 9 MPa, catalyst 0.6 mol%, time 24 h, temperature 130 °C.
[b] Determined by GC using tridecane as internal standard.
[c] The catalyst was 0.8 mol% of PO, reaction time: 48 h.

Two series of experiments with PS-Thr and PS-Tyr as catalyst, respectively, were conducted to study the carboxylation of PO under a variety of reaction conditions, which included changes in catalyst loading (0.1–0.8 mol%), temperature (90–140 °C), CO_2 pressure (2–11 MPa) and reaction time (6–48 h).

The catalytic activities of PS-Thr and PS-Tyr for the reaction of PO/CO_2 were first studied as shown in Figure 2. It is obvious that both the two catalysts were active for the carboxylation of PO with CO_2. Even when the amount of PS-Thr was as low as 0.2 mol%, the coupling reaction proceeded smoothly to give an 80% yield of propylene carbonate (PC). It is noteworthy that decrease in catalyst amount reduced the reaction rate, but the reaction selectivity was not changed. Shown in Figure 3 are the activities of PS-Thr and PS-Tyr as a function of reaction time in the reaction of CO_2 and PO. This illustrates that the yield of PC increased smoothly with the reaction time, and nearly

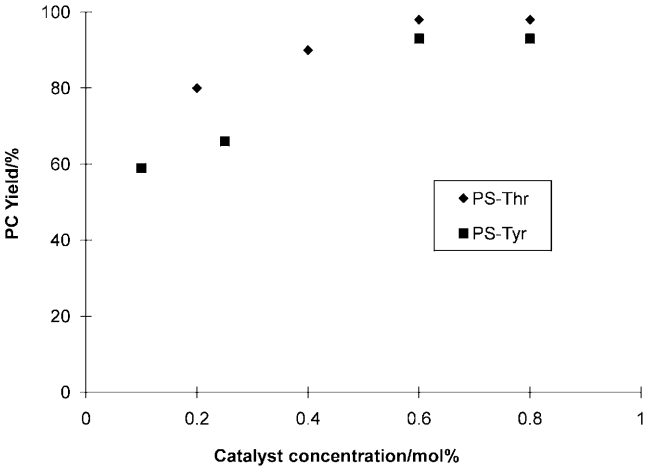


Figure 2. Dependence of yield of PC on the amount of PS-Thr and PS-Tyr. *Reaction conditions:* 20 mmol PO, 9 MPa CO_2, 130 °C, 24 h.

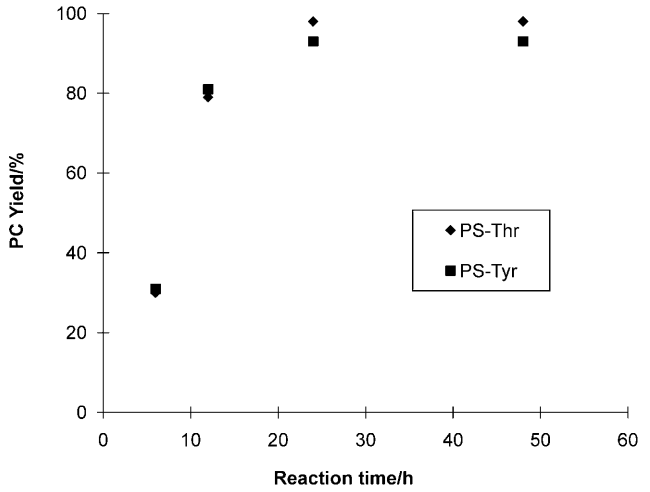


Figure 3. Dependence of yield of PC on the reaction time. *Reaction conditions:* 20 mmol PO, 0.6 mol% PS-Thr/PS-Tyr, 9 MPa CO_2, 130 °C.

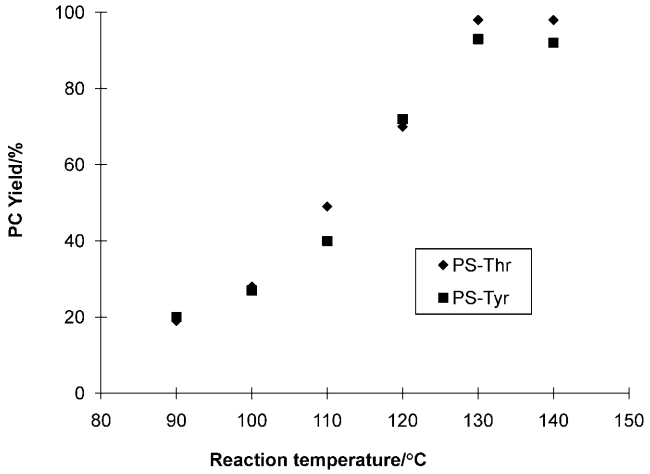


Figure 4. Dependence of yield of PC on the reaction temperature. *Reaction conditions:* 20 mmol PO, 0.6 mol% PS-Thr/PS-Tyr, 9 MPa CO_2, 24 h.

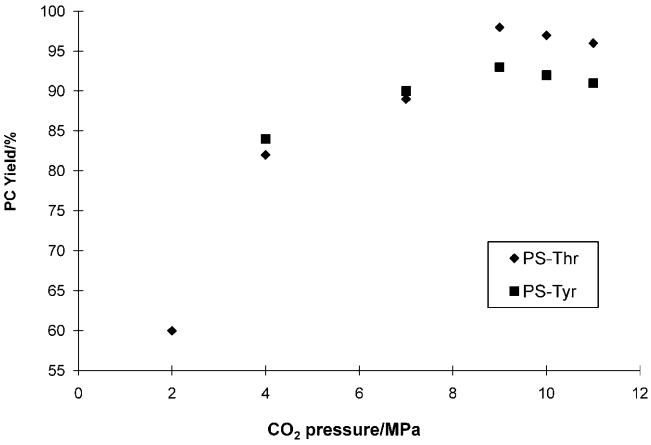


Figure 5. Dependence of yield of PC on CO_2 pressure. *Reaction conditions:* 20 mmol PO, 0.6 mol% PS-Thr/PS-Tyr, 130 °C, 24 h.

all the PO could be converted within 24 h in the two series of experiments.

The influence of temperature on the yield of PC was investigated using PS-Thr and PS-Tyr as catalysts at 9 MPa CO_2 with a reaction time of 24 h. As is easily seen from Figure 4, the activity of our catalyst system is strongly dependent on reaction temperature. In the lower temperature region (90 to 130 °C), the total yield of PC increases sharply with increasing temperature, while no significant change is observed from 130 to 140 °C.

On the basis of the above results, we continued to examine the dependence of PC yield on pressure at 130 °C with a reaction time of 24 h. As is easily seen from Figure 5, pressure has a great influence on the reaction rate with variations of the CO_2 pressure from 2 to 11 MPa in the two series of experiments. The yield reached a maximum at about 9 MPa near the critical pressure of CO_2 and a further increase in pressure to 11 MPa led to a depression in the yield. This interesting phenomenon is almost certainly due to the phase behaviour in this set of experiments and is in general agreement with a previous report.[18]

Furthermore, the more important investigations about the recyclability of PS-Thr and PS-Tyr were also performed using PO as the substrate at the optimized reaction conditions. In each cycle, PS-Thr/PS-Tyr could be readily recovered by filtration and rinsed with acetone, respectively. After drying, the catalyst was reused for the next run. The yields of PC for the five repeated runs are shown in Figure 6. There was no considerable decrease in the yield of PC, indicating that the catalyst was very stable. The excellent stability was also supported by the results of

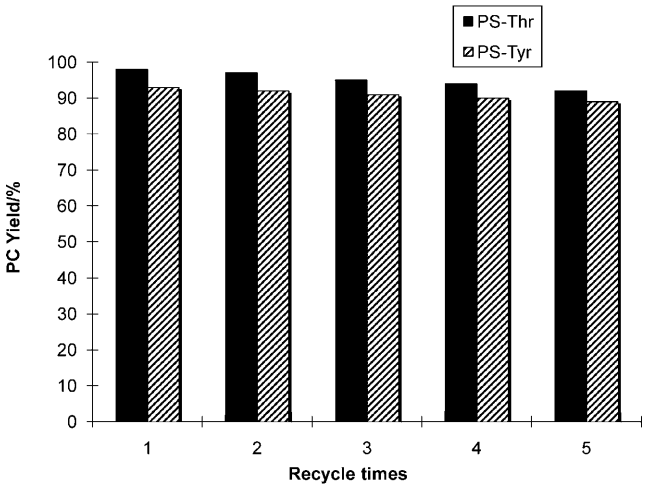


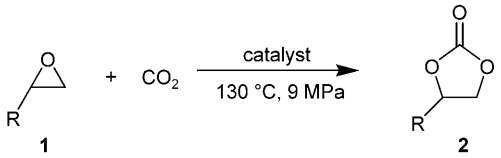
Figure 6. Reuse of PS-Thr. *Reaction conditions:* 20 mmol PO, 0.6 mol% PS-Thr, 9 MPa CO_2, 130 °C, 24 h.

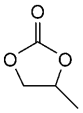
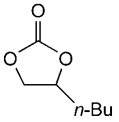
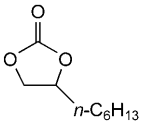
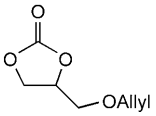
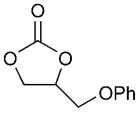
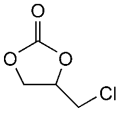
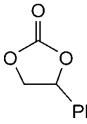
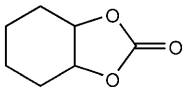
TGA/DSC analyzed before. The decomposition of the polymer occurred in the region 370–450 °C, which is much higher than the reaction temperature (130 °C) in our catalytic experiments.

Once having established that the polystyrene-supported amino acid was an excellent catalyst for the coupling reaction of CO_2 and PO, the capabilities of PS-Thr and PS-Tyr as catalysts were further investigated using a variety of challenging epoxide substrates to synthesize the corresponding cyclic carbonates. The results are summarized in Table 2. Both PS-Thr and PS-Tyr were found to be applicable to a variety of terminal epoxides with different substituted groups, providing the corresponding cyclic carbonates as the sole product in good to high yields. With PS-Thr as a catalyst, epoxides **1a–1f** gave the corresponding cyclic carbonates in over 85% yields (Table 2, entries 1–6). When styrene oxide (**1g**) was used as substrate, the yield was reduced to 78%, which is probably due to the low reactivity of its β-carbon centre (Table 2, entry 7). Besides the terminal epoxides, cyclohexene oxide (**1h**) was also used as substrate with PS-Thr as catalyst under the same reaction conditions (Table 2, entry 8). Although the selectivity was nearly 100%, the yield of the product was only 70%, which may result from the high steric hindrance of cyclohexene oxide.

Encouraged by the successful results of CO_2-fixation using epoxides as substrate, we next targeted the aziridine substrates, which are the nitrogen analogues of epoxides. In contrast with the analogous epoxide/CO_2 coupling, the carboxylation of aziridines with CO_2 could proceed under milder conditions with PS-Thr as catalyst. As shown in Table 3, the use of PS-Thr gave rise to a high yield and regioselectivity for oxazolidinones synthesis under organic solvent-free conditions. It is worth mentioning that 5-aryl-2-oxazo-

Table 2. Synthesis of various cyclic carbonates under the optimized conditions.[a]

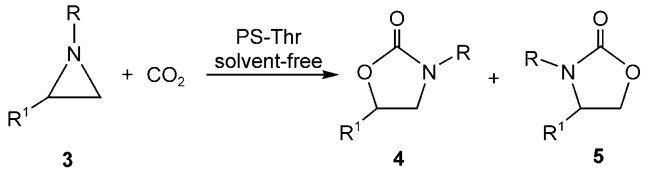


Entry	Product	Catalyst	Yield [%][b]
1	 **2a**	PS-Thr	98
		PS-Tyr	93
2	 **2b**	PS-Thr	90
		PS-Tyr	89
3	 **2c**	PS-Thr	87
		PS-Tyr	88
4	 **2d**	PS-Thr	92
		PS-Tyr	90
5	 **2e**	PS-Thr	99
		PS-Tyr	99
6	 **2f**	PS-Thr	87
		PS-Tyr	94
7	 **2g**	PS-Thr	78
		PS-Tyr	91
8	 **2h**	PS-Thr	70

[a] *Reaction conditions:* epoxide (20 mmol), catalyst (0.6 mol%), CO_2 pressure (9 MPa), 130 °C, 24 h.

[b] Yields were determined by GC using tridecane as internal standard.

Table 3. Oxazolidinones synthesis under solvent-free conditions.[a]



3 4 5

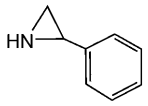
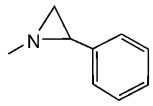
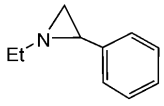
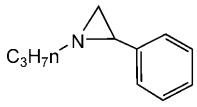
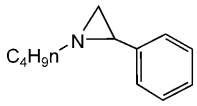
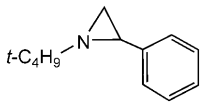
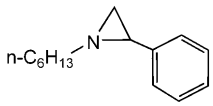
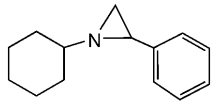
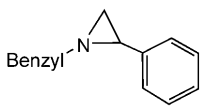
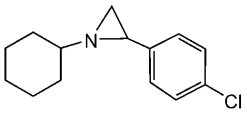
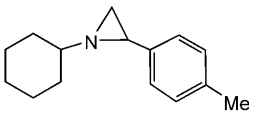
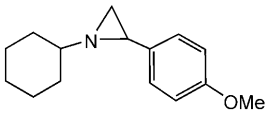
Entry	Substrate	Conversion[b]/ yield[c] [%]	Molar ratio of **4**:**5**[d]
1	 **3a**	>99/61	85:15
2	 **3b**	>99/80	95:5
3	 **3c**	>99/98	98:2
4	 **3d**	>99/93	90:10
5	 **3e**	>99/96	95:5
6[e]	 **3f**	53/50	100:0
7	 **3g**	>99/96	97:3
8	 **3h**	>99/94	99:1
9	 **3i**	>99/97	100:0

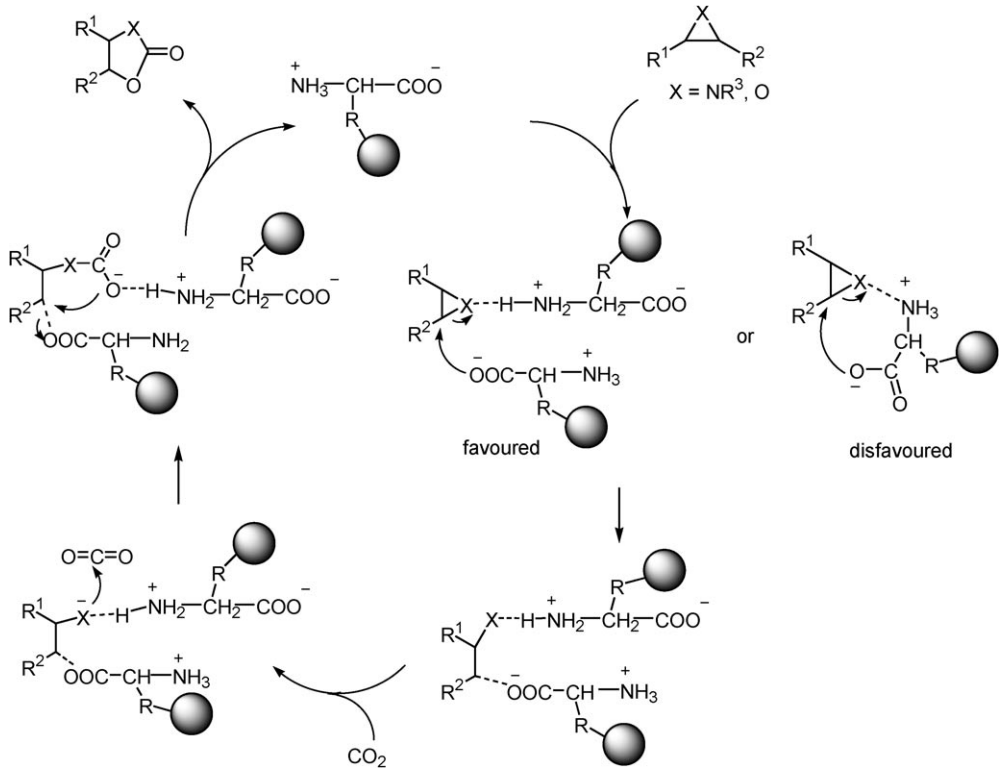
Table 3. (Continued)

Entry	Substrate	Conversion[b]/ yield[c] [%]	Molar ratio of **4**:**5**[d]
10	 **3j**	>99/95	99:1
11	 **3k**	>99/96	99:1
12	 **3l**	>99/90	100:0

[a] *Reaction conditions:* substrates (2 mmol), PS-Thr (5.0 mg, 0.012 mmol), 24 h, CO_2 8 MPa, 100 °C.
[b] Determined by GC.
[c] The total yield of **4** and **5**.
[d] Determined by ^{1}H NMR.
[e] The reaction time is 48 h.

lidinones were preferentially formed with high regioselectivity with a variety of aziridines under identical reaction conditions. Especially, 2-phenylaziridine (**3a**) and 1-methyl-2-phenylaziridine (**3b**) afforded relatively low yields of the desired products because self-oligomers were formed during the reaction (Table 3, entries 1 and 2). Aziridines (**3c–3e** and **3g–3i**) bearing alkyl groups or cyclohexyl at the nitrogen atom afforded the corresponding oxazolidinones in good to high yields (Table 3, entries 3–5 and 7–9), and 5-substituted oxazolidinones were the major isomer. Unfortunately, substrate **3f** showed low activity which may result from the high steric hindrance of the nitrogen atom, however, it gave 3-*tert*-butyl-5-phenyloxazolidin-2-one (**4f**) as the sole product (Table 3, entry 6). It can be suggested from the above results that the product regioselectivity mainly depends on the substituent group at the nitrogen atom; increasing steric hindrance of N-substituted group R leads to an enhancement of the regioselectivity of the product. In this study, the regioselectivity can be also enhanced from 85:15 to 100:0 with variation of the alkyl substituent at the nitrogen atom. Table 3 also shows that aziridines with either an electron-donating group or an electron-withdrawing group on the C-1-aryl group could react with CO_2 and give oxazolidinones in high yield and regioselectivity (Table 3, entries 10–12).

As for the catalytic mechanism of the carboxylation of both epoxides and aziridines, we speculated a unifying mechanism containing hydrogen binding based



Scheme 2. Plausible reaction mechanism.

on the special structure of polystyrene-supported amino acids and the experimental results. The mechanism shown in Scheme 2 involves the activation of the ring of the epoxide or aziridine by an amino acid through hydrogen bonding, followed by the nucleophilic ring-opening of the substrate by another amino acid, and subsequent insertion of CO_2 to form the final product *via* an intramolecular cyclization and regenerate the catalyst. Likewise, the nucleophilic attack would not occur by the carboxylate ion of the same amino acid which activated the substrate ring through hydrogen bonding according to the Baldwin's rule for cyclization.[19]

Conclusions

In summary, we have developed an efficient, simpler and environmentally friendly process for the carboxylation of various epoxides and aziridines with high conversion and selectivity by using polystyrene-supported amino acids as solid catalyst without any solvents or additives. This catalyst system is easy to prepare and can be easily separated from the products and reused. We believe that this route to synthesize the five-membered heterocycles will have great potential in industrial applications, because the polystyrene-supported amino acids have some unusual advantages, such as their easy preparation, high activity, selectivity, stability, low cost and simple work-up procedure.

Experimental Section

Carbon dioxide with a purity of 99.99% was commercially available. Dichloromethane, triethylamine and *N*-methylprrolidone (NMP) were distilled from calcium hydride. Compounds **3a**–**3k** were produced according to the reported literatures.[20] All the other chemicals were purchased from Aldrich Chemicals and used as received. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer (100 MHz for carbon) and respectively referenced to 7.27 and 77.0 ppm for chloroform-*d* solvent with TMS as internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050 A at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. Elemental analysis was performed on a Vario EL elemental analyzer. Analytical thin-layer chromatography (TLC) was performed using commercially prepared 100–400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. GC analyses were performed on a Shimadzu GC-2014, equipped with a capillary column (RTX-5, 30 m × 0.25 μm) using a flame ionization detector. TGA-DSC was performed on a TAINC-Q600SDT system at a heating rate of 10 °C min^{-1}. SEM was performed on QUANTA400F.

General Procedure for the Synthesis of Polystyrene-Supported Amino Acids (PS-Tyr)

To a suspension of L-Tyr (5 g, 27.6 mmol) in 100 mL NMP, chlorotrimethylsilane (2.98 g, 27.6 mmol) was added at room temperature. A clear solution was obtained after 2 h of stirring at room temperature. To this homogeneous solution 2 equiv. of NaH (1.325 g, 55.2 mmol) were added portionwise at 0 °C for 15 min. 2% DVB cross-linked chloromethylated polystyrene (*ca.* 5 mmol Cl/g) (2.5 g) was added at once and whole mixture was stirred for 3 days at room temperature. Then the mixture was heated to 120 °C with stirring for 1 day. After cooling, the polymer was treated with 1 N HCl aqueous solution to complete removal of trimethylsilyl groups, followed by neutralization with aqueous ammonia. The polymer obtained on a glass filter was washed with MeOH (100 mL), THF (100 mL), THF-H_2O (100 mL) and $CHCl_3$ (100 mL), respectively. After drying under vacuum at 50 °C for 24 h, white beads of polystyrene-supported tyrosine were obtained; yield: 4.2 g.

General Procedure for the Synthesis of Aziridines

(1) Bromodimethylsulfonium bromide SA: Dimethyl sulfide (6.2 g, 0.1 mol) and bromine (16.0 g, 0.1 mol) were separately dissolved in dry dichloromethane (20 mL and 20 mL, respectively). The bromine solution was then added dropwise over 30 min to the ice-cooled solution of dimethyl sulfide. During the addition, light orange crystals of bromodimethylsulfonium bromide began to separate. After the addition of bromide was completed, the crystals of **SA** were collected by filtration and then washed with dry ether and dried under vacuum; yield: 70%.

(2) Styrenesulphonium bromide SB: The olefin (70 mmol) was added dropwise to 70 mL CH_3CN solution of compound **SA** (31.2 g, 70 mmol) in an ice-water bath. During the addition, a white solid began to separate. The solution was stirred for 10 min after the addition of olefin was completed. The crystals of **SB** were collected by filtration and dried under vacuum; yield: 28%.

(3) Synthesis of aziridines: To a stirred solution of styrenesulphonium bromide **SB** (10 mmol) in 20 mL of water at room temperature, a solution of amine (20–50 mmol) in water was added dropwise and the resulting mixture was stirred overnight. The mixture was poured into 20 mL of saturated brine, extracted with diethyl ether (3 × 20 mL), dried with $MgSO_4$ and the solvent evaporated under reduced pressure. The pure product was obtained by distillation under reduced pressure; yield: 80–100%.

General Procedure for the Carboxylation of Epoxides with CO_2

Epoxide (20 mmol) and PS-Thr (50 mg, 0.12 mmol) were added to a 15-mL stainless autoclave reactor with a magnetic stirrer. CO_2 was introduced into the autoclave and then the pressure was generally adjusted to 9 MPa at 130 °C. The mixture was stirred continuously at 130 °C for 24 h, and the pressure was kept constant during the reaction. After the reaction, the reactor was cooled in ice-water and extra CO_2 was vented slowly. An aliquot of sample was taken from the resultant mixture and dissolved in CH_2Cl_2 for GC analysis. The yields were determined by GC using tridecane as internal standard. The crude product was purified by distillation and cyclic carbonates were obtained and identified by IR, GC-MS and ^{1}H NMR.

General Procedure for the Carboxylation of Aziridines with CO_2

Aziridine (2 mmol) and PS-Thr (5 mg, 0.012 mmol) were added to a 15-mL stainless autoclave reactor with a magnetic stirrer. CO_2 was introduced into the autoclave and then the pressure was generally adjusted to 8 MPa at 110 °C. The mixture was stirred continuously at 110 °C for 24 h, and the pressure was kept constant during the reaction. After the reaction, the reactor was cooled in ice-water and extra CO_2 was vented slowly. An aliquot of sample was taken from the resultant mixture and dissolved in CH_2Cl_2 for GC analysis. The residue was purified by flash silica gel chromatography using petroleum ether:ethyl acetate = 10:1 to 1:1 as eluant to afford the product. The products were further identified by ^{1}H NMR, ^{13}C NMR and MS.

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