Rasta Resin-DMAP and its Use as a Recyclable Catalyst for the Addition of Carbon Dioxide to Epoxides

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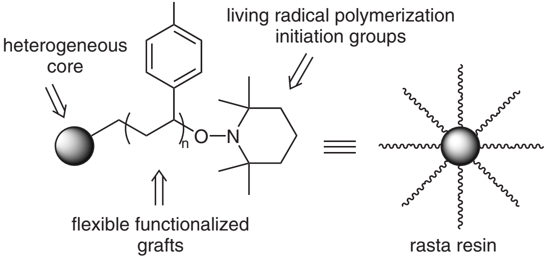
Abstract: Rasta resin-DMAP, a new heterogeneous polystyrene-based amine, has been synthesized and used as a catalyst in addition reactions of carbon dioxide to epoxides to afford cyclic carbonate products. This new material was found to be a more efficient catalyst than divinyl benzene cross-linked polystyrene-supported DMAP, and was readily recovered and reused without significant loss of catalytic activity.

Key words: polymer-supported organocatalyst, polystyrene, DMAP, carbon dioxide, cyclic carbonate

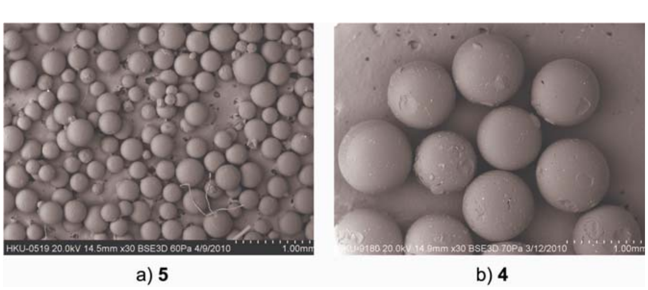
A great number of organic polymers in a wide variety of formats have been used for reagent and catalyst immobilization.[1] For example, the rasta resin architecture, which is characterized by a heterogeneous cross-linked polystyrene core onto which linear polystyrene grafts are attached (Figure 1), was first introduced a decade ago.[2] Since then it has been used as the basis for several polymer-supported reagents and catalysts.[3] Recently, we reported phosphine **1**[4] and bifunctional phosphine/amine analogue **2**[5] as efficient reagents in one-pot Wittig reactions, and phosphonium salt **3**[6] that catalyzed carbonyl cyanosilylation reactions; all of these were based on the rasta resin concept. Importantly, in our studies of **1** and **3** we found that locating the functional groups on the flexible and solvent accessible grafts allowed these materials to be more efficient at mediating the desired reactions than similar polymer-supported phosphines and phosphonium salts based on the Merrifield resin architecture of polystyrene lightly cross-linked with divinyl benzene. In addition to our interest in polymer-supported phosphines,[7,8] we have also studied polymer-supported 2,2′-bipyridine[9] and 4-(dimethyl-amino)pyridine (DMAP),[10] and thus wanted to see if the rasta resin architecture would also serve as an improved heterogeneous platform for DMAP in organocatalytic applications. Thus, herein we report the synthesis of rasta resin-DMAP (**4**), and its use as a catalyst in the addition of carbon dioxide to epoxides to form cyclic carbonates.[11–15]

Polymer **4** was synthesized from JandaJel-based[16] core **5** as shown in Scheme 1. Core **5** was prepared as previously reported[5] and then heated in the presence of DMAP monomer **6**[10] and styrene (for flexibility) in cumene to add the functionalized grafts to afford **4**.[17] Elemental analysis was used to determine the DMAP loading level of **4** to be 1.08 mmol/g, and SEM analysis was conducted to compare the size and morphology of **5** and **4**. As can be seen in Figure 2 (scale: 1 cm = 100 mm) both **5** (Figure 2, a) and **4** (Figure 2, b) are generally spherical in shape, and the latter grew to be much larger in diameter than its precursor.



1 R = H or PPh_2 (6:1 ratio)
2 R = H, PPh_2, or CH_2NEt_2 (5:1:1 ratio)
3 R = H or $^+PPh_2BnCl^-$ (6:1 ratio)

Figure 1 The rasta resin concept



a) **5** b) **4**

Figure 2 SEM images

To assess the utility of **4** in the carbon dioxide addition reactions we chose propylene oxide (**7a**) as the substrate for optimization reactions (Table 1). Using identical reaction conditions, 0.004 equivalents of **4** afforded a slightly lower yield of carbonate **8a** than did DMAP, but a higher yield than did a commercially available 2% divinyl benzene cross-linked polystyrene (entries 1–3). Unfortunately, it was observed that in the absence of a solvent product formation was much less efficient (entry 4) and that THF afforded less satisfactory results (entry 5) than did CH_2Cl_2. The influence of the CO_2 atmosphere pressure on reaction efficiency was also examined. Low conversion of **7a** into **8a** was obtained at 10 bar, and increasing the pressure to 40 bar did not result in a significant increase in

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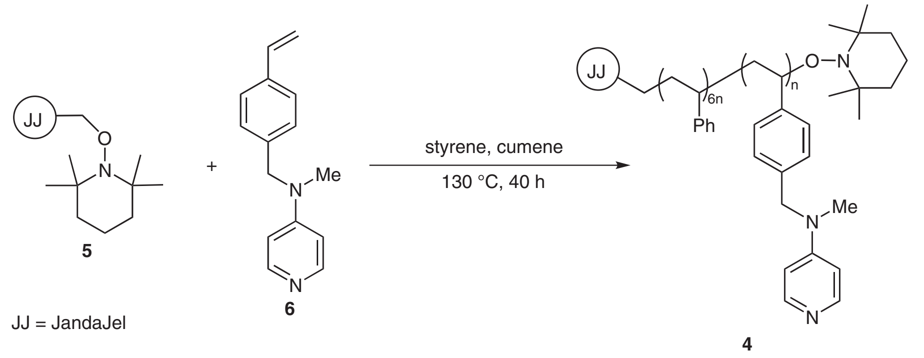
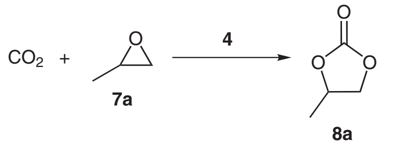


Scheme 1 Synthesis of **4**

product yield (entries 6–9). Thus, it appears that 20–30 bar is the minimum necessary pressure for efficient reactions, and therefore subsequent reactions were performed using a pressure of 30 bar. Furthermore, we noted that the use of 0.01 equivalent of **4** afforded slightly higher yield in less time (entry 8 vs. entry 3), and thus this catalyst loading level was used in subsequent reactions.

Table 1 Optimization of Reactions Catalyzed by **4**

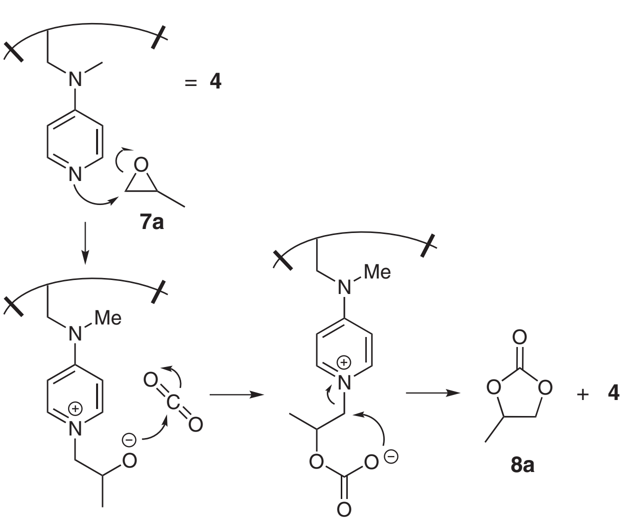


Entry	Catalyst	Solvent	Time (h)	Pressure (bar)	Yield (%)[a]
1	DMAP	CH_2Cl_2	4	30	91
2	PS-DMAP	CH_2Cl_2	4	30	74[b]
3	**4**	CH_2Cl_2	4	30	86
4	**4**	–	6	30	58
5	**4**	THF	1	30	64[c]
6	**4**	CH_2Cl_2	1	10	37[c]
7	**4**	CH_2Cl_2	1	20	84[c]
8	**4**	CH_2Cl_2	1	30	91[c]
9	**4**	CH_2Cl_2	1	40	94[c]

[a] Reaction conditions: **7a** (1.3 g, 22.4 mmol), catalyst (0.4 mol%), and solvent (0.5 mL) heated at 120 °C under an atmosphere of CO_2 at the indicated pressure.
[b] Result using a commercially available PS-DMAP (0.4 mol%) as the catalyst.
[c] Results using 1 mol% of **4**.

With the optimal reaction conditions determined, we next examined the general utility of **4**, and the results of these experiments are summarized in Table 2.[18] Monosubstituted epoxides **7a–f** (entries 1–6) provided satisfying results, and 1,1-disubstituted epoxide **7g** (entry 7) afforded moderate yield of the desired cyclic carbonate **8g** after a prolonged reaction time. However, only low yield of the product **8h** was formed from the reaction of 1,2-disubstituted epoxide **7h**, even after 40 hours (entry 8), and cyclohexene oxide (**7i**) and cyclooctene oxide (**7j**) afforded only trace amounts of the corresponding cyclic carbonates **8i** and **8j** in similar reactions (entries 9 and 10). It should be noted that these reactivity trends mirror what has been reported previously for similar reaction substrates and catalysts.[11,12] For the sake of comparison, commercially available heterogeneous PS-DMAP was used as the catalyst for substrates **7e** and **7d**. However, as with **7a**, it proved to be less efficient than **4** with both of these substrates (entries 4 and 5).

Once the general utility of **4** was demonstrated in the carbonate synthesis reactions, we next examined its recyclability. After each cycle the polymer was filtered, washed with CH_2Cl_2, and dried. As can be seen in Table 3, no significant decrease in the activity of **4** in the conversion of **7a** into **8a** was observed, even in the 8th reaction cycle. The polymer beads became darker in color after reactions, but this visual change did not seem to affect their catalytic efficiency. This strongly indicated that the rasta resin supported DMAP catalyst is highly stable even under high temperature and pressure reaction conditions, allowing for it to be readily recovered and reused.



Scheme 2 Possible mechanism of carbon dioxide addition reactions mediated by **4**

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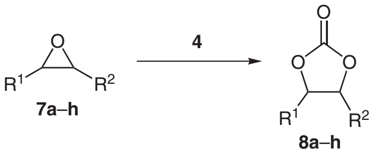
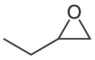
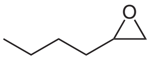
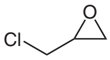
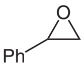
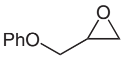
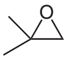
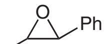
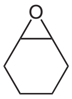
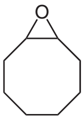
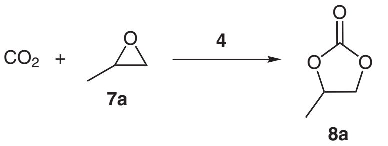
Table 2 Carbon Dioxide Addition Reactions Catalyzed by **4**



Entry	Substrate	Product	Time (h)	Yield (%)[a]
1	 **7a**	**8a**	1	91
2	 **7b**	**8b**	1	90
3	 **7c**	**8c**	0.5	92
4	 **7d**	**8d**	1 (1)[b]	89 (79)[b]
5	 **7e**	**8e**	4 (4)[b]	94 (83)[b]
6	 **7f**	**8f**	3	95
7	 **7g**	**8g**	14	79
8	 **7h**	**8h**	40	31
9	 **7i**	**8i**	40	trace
10	 **7j**	**8j**	40	trace

[a] Reaction conditions: **7a–j** (22.4 mmol), **4** (0.224 mmol), and CH_2Cl_2 (0.5 mL) heated at 120 °C under an atmosphere of CO_2 at 30 bar.
[b] Results using commercially available PS-DMAP as the catalyst.

Table 3 Recycling of **4**



Cycle	1	2	3	4	5	6	7	8
Yield (%)[a]	92	92	91	91	91	90	87	87

[a] Reaction conditions: **7a** (22.4 mmol), **4** (0.224 mmol), and CH_2Cl_2 (0.5 mL) heated at 120 °C under an atmosphere of CO_2 at 30 bar.

A possible mechanism for the addition reactions catalyzed by **4** that is based on what has been reported previously in the literature[11] is outlined in Scheme 2. The low yields observed in Table 2, entries 8–10 can be explained by steric hindrance of the epoxide, which retards nucleophilic attack by the catalyst.

In conclusion, we have synthesized a new heterogeneous polymer-supported DMAP material that is a highly efficient organocatalyst for the addition of carbon dioxide to epoxides to form the corresponding cyclic carbonates. Our studies indicate that the use of the rasta resin architecture in **4** allows it to be a better catalyst in these reactions than does typical commercially available heterogeneous polystyrene-supported DMAP that is based on the Merrifield resin architecture. Furthermore, **4** is robust and amenable for use at high temperature and under high pressure. Thus, it was readily recovered and reused in our reactions. Additional applications of this novel polymer are currently being examined, such as in the DMAP-catalyzed alkyne isomerization reaction,[19] and other recently reported DMAP-mediated processes[20] and results from these studies will be reported shortly.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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References and Notes

(1) Lu, J.; Toy, P. H. *Chem. Rev.* **2009**, *109*, 815.
(2) Hodges, J. C.; Harikrishnan, L. S.; Ault-Justus, S. *J. Comb. Chem.* **2000**, *2*, 80.
(3) (a) Lindsley, C. W.; Hodges, J. C.; Filzen, G. F.; Watson, B. M.; Geyer, A. G. *J. Comb. Chem.* **2000**, *2*, 550.
(b) McAlpine, S. R.; Lindsley, C. W.; Hodges, J. C.; Leonard, D. M.; Filzen, G. F. *J. Comb. Chem.* **2001**, *3*, 1.
(c) Wisnoski, D. D.; Leister, W. H.; Strauss, K. A.; Zhao, Z.; Lindsley, C. W. *Tetrahedron Lett.* **2003**, *44*, 4321.
(d) Fournier, D.; Pascual, S.; Montembault, V.; Haddleton, D. M.; Fontaine, L. *J. Comb. Chem.* **2006**, *8*, 522.
(e) Fournier, D.; Pascual, S.; Montembault, V.; Fontaine, L. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5316.
(f) Pawluczyk, J. M.; McClain, R. T.; Denicola, C.; Mulhearn, J. J.; Rudd, D. J.; Lindsley, C. W. *Tetrahedron Lett.* **2007**, *48*, 1497. (g) Chen, G.; Tao, L.; Mantovani, G.; Geng, J.; Nystroem, D.; Haddleton, D. M. *Macromolecules* **2007**, *40*, 7513.
(4) Leung, P. S.-W.; Teng, Y.; Toy, P. H. *Synlett* **2010**, 1997.
(5) Leung, P. S.-W.; Teng, Y.; Toy, P. H. *Org. Lett.* **2010**, *12*, 4996.
(6) Teng, Y.; Toy, P. H. *Synlett* **2011**, 551.

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(7) For our work regarding cross-linked polymers, see: (a) Kwok, M.; Choi, W.; He, H. S.; Toy, P. H. *J. Org. Chem.* **2003**, *68*, 9831. (b) Zhao, L. J.; He, H. S.; Shi, M.; Toy, P. H. *J. Comb. Chem.* **2004**, *6*, 680. (c) Zhao, L.-J.; Kwong, C. K.-W.; Shi, M.; Toy, P. H. *Tetrahedron* **2005**, *61*, 12026.

(8) For our work regarding noncross-linked polymers, see: (a) Harned, A. M.; He, H. S.; Toy, P. H.; Flynn, D. L.; Hanson, P. R. *J. Am. Chem. Soc.* **2005**, *127*, 52. (b) He, H. S.; Yan, J. J.; Shen, R.; Zhuo, S.; Toy, P. H. *Synlett* **2006**, 563. (c) Kwong, C. K.-W.; Fu, M. Y.; Law, H. C.-H.; Toy, P. H. *Synlett* **2010**, 2617.

(9) Chung, C. W. Y.; Toy, P. H. *J. Comb. Chem.* **2007**, *9*, 155.

(10) Kwong, C. K.-W.; Huang, R.; Zhang, M.; Shi, M.; Toy, P. H. *Chem. Eur. J.* **2007**, *13*, 2369.

(11) For selected reviews regarding the addition of carbon dioxide to epoxides to form cyclic carbonates, see: (a) Dai, W.-L.; Luo, S.-L.; Yin, S.-F.; Au, C.-T. *Appl. Catal., A* **2009**, *366*, 2. (b) Sakakura, T.; Kohno, K. *Chem. Commun.* **2009**, 1312. (c) North, M.; Pasquale, R.; Young, C. *Green Chem.* **2010**, *12*, 1514.

(12) For the organocatalytic addition of carbon dioxide to epoxides, see: (a) Shiels, R. A.; Jones, C. W. *J. Mol. Catal. A: Chem.* **2007**, *261*, 160; and references cited therein. (b) Qi, C.; Jiang, H.; Wang, Z.; Zou, B.; Yang, S. *Synlett* **2007**, 255. (c) Barkakaty, B.; Morino, K.; Sudo, A.; Endo, T. *Green Chem.* **2010**, *12*, 42.

(13) For selected reviews regarding polymer-supported organocatalysts, see: (a) Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.* **2003**, *103*, 3401. (b) Benaglia, M. *New J. Chem.* **2006**, *30*, 1525. (c) Cozzi, F. *Adv. Synth. Catal.* **2006**, *348*, 1367. (d) Gruttadauria, M.; Giacalone, F.; Noto, R. *Chem. Soc. Rev.* **2008**, *37*, 1666. (e) Kristensen, T. E.; Hansen, T. *Eur. J. Org. Chem.* **2010**, 3179.

(14) For the use of polymer-supported organocatalysts in the addition of carbon dioxide to epoxides, see: (a) Xie, H.; Duan, H.; Li, S.; Zhang, S. *New J. Chem.* **2005**, *29*, 1199. (b) Du, Y.; Wang, J.-Q.; Chen, J.-Y.; Cai, F.; Tian, J.-S.; Kong, D.-L.; He, L.-N. *Tetrahedron Lett.* **2006**, *47*, 1271. (c) Jagtap, S. R.; Raje, V. P.; Samant, S. D.; Bhanage, B. M. *J. Mol. Catal. A: Chem.* **2007**, *266*, 69. (d) Qi, C.-R.; Jiang, H.-F.; Wang, Z.-Y.; Zou, B. *Chin. J. Chem.* **2007**, *25*, 1051. (e) Qi, C.; Ye, J.; Zeng, W.; Jiang, H. *Adv. Synth. Catal.* **2010**, *352*, 1925.

(15) For the use of other polymers, such as ion-exchange resins, polyaniline salts, and immobilized ionic liquids, to catalyze the addition of carbon dioxide to epoxides, see: (a) Du, Y.; Cai, F.; Kong, D.-L.; He, L.-N. *Green Chem.* **2005**, *7*, 518. (b) He, J.; Wu, T.; Zhang, Z.; Ding, K.; Han, B.; Xie, Y.; Jiang, T.; Liu, Z. *Chem. Eur. J.* **2007**, *13*, 6992. (c) Xie, Y.; Zhang, Z.; Jiang, T.; He, J.; Han, B.; Wu, T.; Ding, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 7255.

(16) (a) Toy, P. H.; Janda, K. D. *Tetrahedron Lett.* **1999**, *40*, 6329. (b) Toy, P. H.; Reger, T. S.; Janda, K. D. *Aldrichimica Acta* **2000**, *33*, 87. (c) Toy, P. H.; Reger, T. S.; Garibay, P.; Garno, J. C.; Malikayil, J. A.; Liu, G.-Y.; Janda, K. D. *J. Comb. Chem.* **2001**, *3*, 117. (d) Choi, M. K. W.; Toy, P. H. *Tetrahedron* **2004**, *60*, 2903.

(17) See Supporting Information for details.

(18) **General Procedure for CO$_2$ Addition Reactions**
Epoxide **7a–j** (22.4 mmol), CH$_2$Cl$_2$ (0.5 mmol), and **4** (0.224 mmol) were placed in a 25 mL stainless-steel autoclave. Carbon dioxide was then introduced into the reactor at an initial pressure of 20 bar at r.t. The reactor was then heated to 120 °C, and the pressure was adjusted to 30 bar. The reaction mixture was stirred under these conditions for the indicated time, and then the autoclave was cooled using an ice bath. After releasing the pressure, compound **4** was filtered off and washed with CH$_2$Cl$_2$. The filtrate was concentrated in vacuo to afford the product **8a–j**. The identity of the products was confirmed by ^{1}H NMR.

(19) Yue, Y.; Yu, X.-Q.; Pu, L. *Chem. Eur. J.* **2009**, *15*, 5104.

(20) (a) Bollini, M.; González, M.; Bruno, A. M. *Tetrahedron Lett.* **2009**, *50*, 1507. (b) Ko, K.; Nakano, K.; Watanabe, S.; Ichikawa, Y.; Kotsuki, H. *Tetrahedron Lett.* **2009**, *50*, 4025. (c) Deb, I.; Shanbhag, P.; Mobin, S. M.; Namboothiri, I. N. N. *Eur. J. Org. Chem.* **2009**, 4091. (d) Mhasni, O.; Rezgui, F. *Tetrahedron Lett.* **2010**, *51*, 586. (e) Naidu, K. C.; Babu, G. R.; Gangaiah, L.; Mukkanti, K.; Madhusudhan, G. *Tetrahedron Lett.* **2010**, *51*, 1226. (f) Angelini, T.; Fringuelli, F.; Lanari, D.; Pizzo, F.; Vaccaro, L. *Tetrahedron Lett.* **2010**, *51*, 1566. (g) Goncalves, S.; Nicolas, M.; Wagner, A.; Baati, R. *Tetrahedron Lett.* **2010**, *51*, 2348. (h) Aoki, S.; Kotani, S.; Sugiura, M.; Nakajima, M. *Tetrahedron Lett.* **2010**, *51*, 3547. (i) Hudhomme, P. *Synlett* **2010**, 1331. (j) Vuluga, D.; Legros, J.; Crousse, B.; Bonnet-Delpon, D. *Chem. Eur. J.* **2010**, *16*, 1776. (k) Helou, M.; Miserque, O.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *Chem. Eur. J.* **2010**, *16*, 13805.

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