RSC Advances

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2014, **4**, 32371

Received 29th May 2014
Accepted 16th July 2014

DOI: 10.1039/c4ra05073h

www.rsc.org/advances

Poly(4-vinylimidazolium) iodides: a highly recyclable organocatalyst precursor for benzoin condensation reaction†

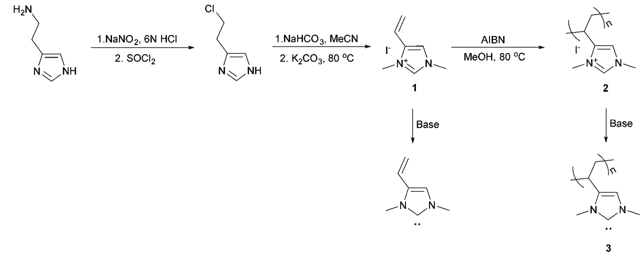
Ue Ryung Seo and Young Keun Chung*

The development of highly efficient, recyclable poly(4-vinylimidazolium) iodides (**2**) for the benzoin condensation reaction under mild reaction conditions is discussed: poly(4-vinyl *N*-heterocyclic carbene)s (**3**) obtained from **2** showed higher catalytic activity than monomeric 4-vinyl *N*-heterocyclic carbene and could be successfully recovered and reused over seven times without loss of performance.

Organocatalysis related to green chemistry has attracted much attention and has significantly progressed in recent years.[1] Imidazoles obtained from heterocycles are widely used as Lewis basic organocatalysts.[2] One of the most studied reactions by organocatalysis is the benzoin condensation reaction which affords α-hydroxyketones (acyloins) *via* the self-condensation of two aromatic aldehydes.[3] α-Hydroxyketones are important building blocks in organic synthesis and found in many biologically active compounds.[4]

Organocatalytic reactions are usually carried out under homogeneous conditions. However, due to the economic and environmental issues, many studies have been focused on reducing waste and reusing materials. In this regard, several studies on the heterogenization of organocatalysts using organic polymers[5] or mesoporous materials[6] have been reported. However, some of them suffered from relatively low yields and poor recyclability, probably because of poor stability or degradation of the catalysts under the basic conditions. Recently, a self-supported poly(NHC) (NHC = *N*-heterocyclic carbene), with *in situ* generated NHCs orthogonally positioned along a main chain was reported.[7] However, the catalytic activity of this catalyst for benzoin condensation was not satisfactory. The recyclability of the catalyst (10 mol%) was investigated only in three successive benzoin condensation reactions (67%, 66%, and 64% yields, respectively).

Recently, poly(NHC)s iodides, being polymeric ionic liquids (PILs) or poly(ionic liquid)s, obtained from 4-vinylimidazolium iodide have attracted our interest. Because PILs can combine the unique properties of ionic liquids and mechanical stability of polymers, they would offer a great versatility in the catalyst design.[8] we envisioned that poly(4-vinylimidazolium) iodides would be a very useful polymeric support material and function as a polymerized catalyst (Scheme 1).[9,10] In our previous study, we reported[10] the preparation of poly(4-vinylimidazolium)s and its application in the cycloaddition of CO_2 to epoxides using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and $ZnBr_2$. Herein we communicate the use of poly(4-vinylimidazolium)s as an organic precatalyst for *N*-heterocyclic carbene-catalyzed benzoin condensation reaction and the tandem reaction of benzaldehyde and methyl acrylate to afford γ-butyrolactone. The *in situ* generated poly(NHC)s exhibits higher catalytic activity than the corresponding monomeric analog and can be recycled repeatedly without loss in performance in the benzoin condensation reaction. Recently, Taton *et al.* reported the use of poly(1-vinyl-3-alkylimidazolium)s as a precatalyst in benzoin condensation reactions.[11] However, poor recyclability with a lower yield was observed. As far as we are aware, our study shows the first successfully recyclable catalytic system for benzoin condensation reaction.

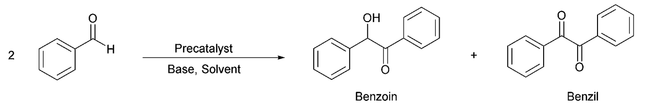


Scheme 1 Synthesis of **1** and **2** from histamine.

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea. E-mail: ykchung@snu.ac.kr

† Electronic supplementary information (ESI) available: All experimental procedures, characterization data, and the copies of the ^1H NMR and ^{13}C NMR spectra are provided. See DOI: 10.1039/c4ra05073h

Starting from histamine, 4-vinylimidazolium (**1**) and poly(4-vinylimidazolium)s (**2**) were prepared.[10] With **1** and **2** in hand, their abilities to catalyze the benzoin condensation were investigated (eqn (1)).

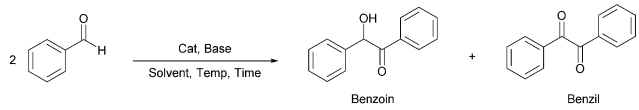


(1)

First, the reaction conditions were investigated, including the reaction temperature, solvent and base to optimize the yield of benzoin (Table 1).[12]

The yield of the reaction in the presence of **2** was highly sensitive to the base, reaction solvent, and reaction temperature. In the absence of a base or in the presence of triethylamine (TEA) as the base, no reaction was observed (entries 1 and 3). A particular range of reaction temperature (40–50 °C) in dimethyl formamide (DMF) maximized the yield of the reaction (entries 5–9). The amount of DBU could be reduced to 0.3 equiv. without decreasing the yield (entries 10–11). As shown in Table 1, benzoin was obtained as the major product with benzil in various yields as the byproduct. The yields and product distributions were also highly dependent on the trituration method (entry 11 *vs.* 12) because the remaining DBU functioned as a catalyst in the conversion of benzoin to benzil.[13] The acidification of reaction mixture before exposing to air protects the transformation of benzoin to benzil in air. Thus, when the reaction mixture was treated with 4 M HCl in dioxane after the reaction, the best result was achieved (entry 12).[14] The optimum reaction conditions were as follows: 7 mol% **2**, 0.3 equiv. DBU, 1 mL DMF, 40 °C, and 24 h. Moreover, the catalytic activity of **2** was higher than that of **1** (entry 12 *vs.* 13).

Table 1 Optimization of reaction conditions[a]



				Isolated yield (%)		
Entry	Base	Solvent	Temp (°C)	Benzoin	Benzil	Total
1	None	DMF	40	0	0	0
2	*t*-BuOK	DMF	60	11	9	20
3	TEA	DMF	60	0	0	0
4	DBU (1 eq.)	H_2O	60	0	1	1
5	DBU (1 eq.)	DMF	60	60	21	81
6	DBU (1 eq.)	DMF	80	31	20	51
7	DBU (1 eq.)	DMF	50	69	22	91
8	DBU (1 eq.)	DMF	40	62	33	95
9	DBU (1 eq.)	DMF	r.t	21	21	42
10	DBU (0.5 eq.)	DMF	40	74	22	96
11	DBU (0.3 eq.)	DMF	40	82	15	97
12[b]	DBU (0.3 eq.)	DMF	40	96	1	97
13[c]	DBU (0.3 eq.)	DMF	40	62	10	72

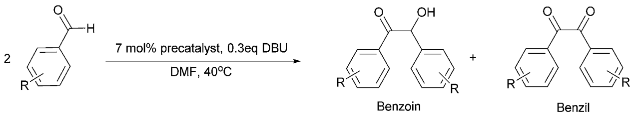
[a] Reaction conditions: 1.8 mmol benzaldehyde, 7 mol% catalyst, appropriate equiv. of base were reacted in 1 mL solvent were reacted under nitrogen atmosphere. [b] Acidification after reaction. [c] **1** as a catalyst precursor.

Using the optimized reaction conditions, the catalytic activity of **1** and **2** were investigated for diverse functionalized derivatives (Table 2). Benzoins were obtained as the major products with benzil as the byproduct in various yields (less than 7%). Interestingly, the yields and distributions of the products were highly dependent on the substituent on the benzaldehydes. The yields of benzoin products in the presence of **2** were moderate to excellent (48–96%). The electronic and steric nature of the substituents did not affect the yield of the benzoins. The total yields of the benzoin and benzil in the presence of **2** were moderate to excellent (52–97%). As expected, higher yields were observed in the presence of **2** in all the cases than **1**. Strangely, when 4-methoxybenzaldehyde was used as the substrate, a poor yield (<10%) was obtained. However, when the reaction temperature was raised to 80 °C, the expected reaction product was obtained in 77% yield and with 21% recovery of the reactant (entry 5). Notably, pyridine-3-carboxaldehyde in the presence of **2** afforded a benzil derivative, 1,2-di(pyridine-3-yl) ethane-1,2-dione, as the only product in 93% yield (by^{1}H NMR) (data not shown in Table 2). It has been reported that 2-pyridinecarboxaldehyde is easily oxidized to α-pyridil in methanol at room temperature in air.[15]

The reusability of **2** was also examined (Fig. 1). The polymer catalyst was recovered by the addition of excess acetone into the reaction mixture. The precipitate was filtered and washed with acetone and dried. Because a small amount of **2** was used as the catalyst, the effect of loss during the separation seemed to be very significant. After seven reaction cycles, 15% of **2** was lost.

As shown in Fig. 1, the catalyst was successfully reused without loss of performance over seven cycles. Our excellent result is in contrast to that obtained for poly(1-vinylimidazolium)s.[11] In that study, poor recyclability with lower yields was observed even after the first and subsequent recycling

Table 2 Benzoin reactions with various benzaldehydes



		Yield[a] by **1**			Yield[a] by **2**		
Entry	R	Benzoin	Benzil	Total	Benzoin	Benzil	Total
1	H	69	3	72	96	1	97
2	*m*-Br	69	11	80	81	7	88
3	*p*-Br	40	9	49	48	4	52
4	*p*-Me	68	5	73	72	3	75
5	*p*-MeO	75	0	75	77[b]	0	77
6	*p*-CF_3	40	5	45	71	4	75
7	*p*-Cl	68	8	76	80	4	84

[a] Isolated yields. [b] Reaction temp. 80 °C.

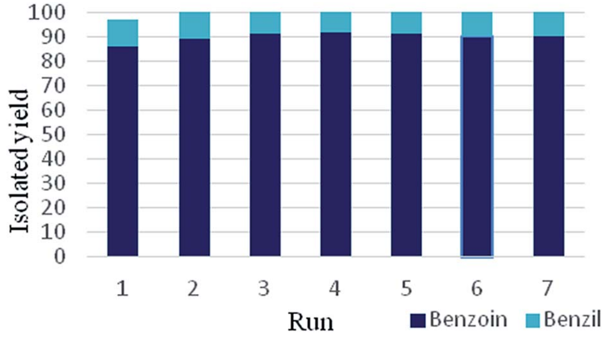
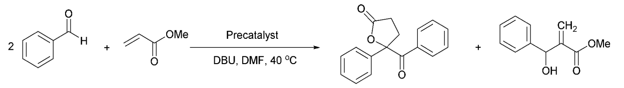


Fig. 1 Recycling of polymer catalyst in benzoin condensation reaction.

catalytic reactions and a partial deactivation of poly(1-vinylNHC)s due to the trace impurities was proposed. The deactivation of *in situ* generated poly(1-vinylNHC)s is more likely to occur because of relatively high temperature (80 °C). However, we expected that the significant difference in the reusability between poly(1-vinylNHC)s and poly(4-vinylNHC)s might arise from the stability of poly(NHC)s under the reaction and workup conditions.

Zhai *et al.* reported[16] the one-step synthesis of γ-butyrolactones from benzoins/benzaldehydes and methyl acrylate in the presence of a catalyst generated from the reaction of 1,3-dimethylimidazolium with a base. We also investigated the tandem reaction of benzaldehyde and methyl acrylate catalyzed by **2** in the presence of DBU. After the reaction, γ-butyrolactone was isolated in 78% yield and with a concomitant formation of an allylic alcohol in 6% yield (eqn (2)).

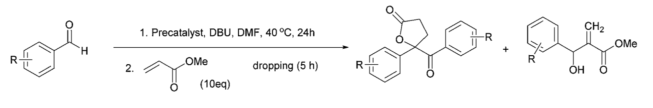


(2)

DBU-catalyzed Baylis–Hillman reaction afforded allylic alcohol.[17] However, allylic alcohol was not obtained in the presence of 1,3-dimethylimidazolium and a base (KO^{t}Bu).[16] We investigated the substrate scope of this tandem reaction in the presence of **1** or **2** as the catalyst precursor (Table 3). In the presence of **2** and DBU, the yields of lactones were reasonable to high (44–78%). However, the yields in the presence of **1** and DBU were poor to moderate (26–60%). Thus, precatalyst **2** afforded lactones in higher yields than **1**. Allylic alcohols were obtained in better yields for benzaldehyde and *m*-bromobenzaldehyde than for other aldehydes (trace amounts). When *p*-methoxybenzaldehyde was used, a considerable amount of the reactant was recovered.

Recently, Cowley *et al.* synthesized[7] poly(NHC)s, with a different backbone from our poly(NHC)s, and used in benzoin condensation reaction. They also observed higher catalytic activity of poly(NHC)s than the corresponding monomeric analog. Xie *et al.* investigated[18] di- and triimidazolium salts as the catalysts for benzoin condensation reaction. In contrast to our results, the catalytic activity of di- and triimidazolium salts was inferior to that of the catalyst with only one imidazolium moiety, probably because of the increase in the steric hindrance by adding of an imidazolium ring. The highly enhanced reactivity of **2** may be attributed to the synergistic effect between the catalytically active sites along the polymer backbone[7,19] or a higher density of active sites. In addition, the active sites linked to the polymer backbone in a pendant fashion may help to increase the reactivity.

Table 3 Reaction of aromatic aldehydes with methyl acrylate[a,b]



		Yield (%) by **1**		Yield (%) by **2**	
Entry	R	Lactone	Ally alcohol	Lactone	Ally alcohol
1	H	60	8	78	6
2	*m*-Br	26	6	44	2
3	*p*-Me	60	Trace	72	Trace
4	*p*-Cl	34	Trace	42	Trace
5	*p*-MeO	50[c]	Trace	52[d]	Trace

[a] Reaction conditions: 1.8 mmol benzaldehyde, 7 mol% catalyst, 0.3 equiv. DBU, 1 mL of DMF at 40 °C for 24 h under N_2/18 mmol methyl acrylate for 5 h. [b] Isolated yield. [c] 23% of reactant was recovered. [d] Reaction temp. 80 °C and 36% of reactant was recovered.

Conclusions

In conclusion, we developed a polymer-based organocatalytic system (**2**) that shows high catalytic activity in benzoin condensation reaction and the tandem formation of γ-butyrolactone from benzaldehyde and methyl acrylate. Precatalyst **2** showed higher catalytic activity than monomeric analog (**1**). Moreover, **2** showed higher catalytic activity and reusability in the benzoin condensation reaction compared to the polymerized precatalysts obtained from 1-vinylimidazolium. Organocatalytic system **2** synthesized in three steps from commercially available materials, has great potential for practical use and recovery of the polymerized catalysts in benzoin condensation reaction. Further investigations of the polymer based organocatalytic system to other reactions are ongoing in our laboratory.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea Government (2007-0093864 and 2014-011165). URS thanks the Brain Korea 21 Plus Fellowships.

Notes and references

1 (*a*) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606–5655; (*b*) P. H.-Y. Cheong, C. Y. Legault, J. M. Um, N. Çelebi-Ölçüm and K. N. Houk, *Chem. Rev.*, 2011, **111**,

5042–5137; (*c*) C. M. R. Volla, I. Atodiresei and M. Rueping, *Chem. Rev.*, 2014, **114**, 2390–2431; (*d*) N. Mase and C. F. Barbas, III, *Org. Biomol. Chem.*, 2010, **8**, 4043–4050; (*e*) R. C. Wende and P. R. Schreiner, *Green Chem.*, 2012, **14**, 1821–1849; (*f*) J.-F. Brière, S. Oudeyer, V. Dalla and V. Levacher, *Chem. Soc. Rev.*, 2012, **41**, 1696–1707; (*g*) D. J. Liu and E. Y.-X. Chen, *Green Chem.*, 2014, **16**, 964–981; (*h*) J. Alemán and S. Cabrera, *Chem. Soc. Rev.*, 2013, **42**, 774–793; (*i*) X. Bugaut and F. Glorius, *Chem. Soc. Rev.*, 2012, **41**, 3511–3522.

2 (*a*) A. Grossmann and D. Enders, *Angew. Chem., Int. Ed.*, 2012, **51**, 314–325; (*b*) K. Hirano, I. Piel and F. Glorius, *Chem. Lett.*, 2011, **40**, 786–791; (*c*) T. Dröge and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 6940–6952; (*d*) H. Zhao, F. W. Foss, Jr and R. Breslow, *J. Am. Chem. Soc.*, 2008, **130**, 12590–12591; (*e*) S. E. Denmark and L. B. Gregory, *Angew. Chem., Int. Ed.*, 2008, **47**, 1560–1638; (*f*) N. Marion, S. Díez-González and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2007, **46**, 2988–3000; (*g*) B. Bantu, G. M. Pawar, K. Wurst, U. Decker, A. M. Schmidt and M. R. Buchmeiser, *Eur. J. Inorg. Chem.*, 2009, 1970–1976; (*h*) B. Bantu, G. M. Pawar, U. Decker, K. Wurst, A. M. Schmidt and M. R. Buchmeiser, *Chem.–Eur. J.*, 2009, **15**, 3103–3109; (*i*) K. Thiel, R. Zehbe, J. Roeser, P. Strauch, S. Enthalerd and A. Thomas, *Polym. Chem.*, 2013, **4**, 1848–1856; (*j*) K. Zeitlera and I. Magera, *Adv. Synth. Catal.*, 2007, **349**, 1851–1857; (*k*) A. B. Powell, C. W. Bielawski and A. H. Cowley, *Comments Inorg. Chem.*, 2010, **31**, 75–82.

3 (*a*) Z.-J. Jia, K. Jiang, Q.-Q. Zhou, L. Dong and Y.-C. Chen, *Chem. Commun.*, 2013, **49**, 5892–5894; (*b*) P. Dominguez de Maria and S. Shanmuganathan, *Curr. Org. Chem.*, 2011, **15**, 2083–2097; (*c*) K. Thai, S. M. Langdon, F. Bilodeau and M. Gravel, *Org. Lett.*, 2013, **15**, 2214–2217; (*d*) T. Ema, K. Akihara, R. Obayashi and T. Sakai, *Adv. Synth. Catal.*, 2012, **354**, 3283–3290.

4 C. Palomo, M. Oiarbide and J. M. García, *Chem. Soc. Rev.*, 2012, **41**, 4150–4164 and references therein.

5 (*a*) J. D. Storey and C. Williamson, *Tetrahedron Lett.*, 2005, **46**, 7337–7339; (*b*) K. Thiel, R. Zehbe, J. Roeser, P. Strauch, S. Enthaler and A. Thomas, *Polym. Chem.*, 2013, **4**, 1848–1856; (*c*) K. Zeitler and I. Mager, *Adv. Synth. Catal.*, 2007, **349**, 1851–1857; (*d*) M. Tan, Y. Zhang and J. Y. Ying, *Adv. Synth. Catal.*, 2009, **351**, 1390–1394; (*e*) G. M. Pawar and M. R. Buchmeiser, *Adv. Synth. Catal.*, 2010, **352**, 917–928; (*f*) O. Bortolini, A. Cavazzini, P. Dambruoso, P. P. Giovannini, L. Caciolli, A. Massi, S. Pacifico and D. Ragno, *Green Chem.*, 2013, **15**, 2981–2992.

6 (*a*) S. Shylesh, Z. Zhou, Q. Meng, A. Wagener, A. Seifert, S. Ernst and W. R. Thiel, *J. Mol. Catal. A: Chem.*, 2010, **332**, 65–69; (*b*) Z. Zhou, Q. Meng, A. Seifert, A. Wagner, Y. Sun, S. Emst and W. R. Thiel, *Microporous Mesoporous Mater.*, 2009, **121**, 145–151.

7 A. B. Powell, Y. Suzuki, M. Ueda, C. W. Bielawski and A. H. Cowley, *J. Am. Chem. Soc.*, 2011, **133**, 5218–5220.

8 (*a*) J. Texter, *Macromol. Rapid Commun.*, 2012, **33**, 1996–2014; (*b*) J. Yuan, D. Mecerreyes and M. Antonietti, *Prog. Polym. Sci.*, 2013, **38**, 1009–1036; (*c*) D. Mecerreyes, *Prog. Polym. Sci.*, 2011, **36**, 1629–1648.

9 (*a*) H. G. Alt, *J. Chem. Soc., Dalton Trans.*, 1999, 1703–1710; (*b*) J. Zhang, X. Wang and G.-X. Jin, *Coord. Chem. Rev.*, 2006, **250**, 95–109 and references therein; (*c*) A. Zulauf, M. Mellah and E. Schulz, *J. Org. Chem.*, 2009, **74**, 2242–2245.

10 U. R. Seo and Y. K. Chung, *Adv. Synth. Catal.*, 2014, **356**, 1955–1961.

11 (*a*) J. Pinaud, J. Vignolle, Y. Gananou and D. Taton, *Macromolecules*, 2011, **44**, 1900–1908; (*b*) P. Coupillaud, J. Pinaud, N. Guidolin, J. Vignolle, M. Fèvre, E. Veaudecrenne, D. Mecerreyes and D. Taton, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 4530–4540.

12 After the reaction was carried out, excess acetone was poured into the reaction flask to precipitate **2**. The precipitates were filtered off and the filtrate was added to a solution of 4 M HCl in dioxane. After the solution was filtered off, the filtrate was concentrated and chromatographed on a silica gel column.

13 Y. Shimakawa, T. Morikawa and S. Sakaguchi, *Tetrahedron Lett.*, 2010, **51**, 1786–1789.

14 After the reaction was carried out, a solution of 4 M HCl in dioxane was added to the reaction mixture. The resulting solution was stirred for 1 h. Excess acetone was poured into the reaction flask. After precipitates were filtered off, the filtrate was concentrated and chromatographed on a silica gel column.

15 V. Hada, A. Tungler and L. Szepesy, *J. Catal.*, 2002, **209**, 472–479.

16 W. Ye, G. Cai, Z. Zhuang, X. Jia and H. Zhai, *Org. Lett.*, 2005, **7**, 3769–3771.

17 V. K. Aggarwal and A. Mereu, *Chem. Commun.*, 1999, 2311–2312.

18 G. Gao, R. Xiao, Y. Yuan, C.-H. Zhou, J. You and R.-G. Xie, *J. Chem. Res., Synop.*, 2002, 262–263.

19 P. K. Dahl, B. B. De and S. Sivaram, *J. Mol. Catal. A: Chem.*, 2001, **177**, 71–87.