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A Recyclable, Self-Supported Organocatalyst Based on a Poly(N-Heterocyclic Carbene)

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S Supporting Information

ABSTRACT: We report the synthesis and catalytic activity of a polymeric imidazolium salt. In contrast to the well-known resin-supported N-heterocyclic carbenes (NHCs), the material described herein affords a polymer with NHCs orthogonally positioned along a main chain upon generation in situ. The unique structural characteristics of the corresponding poly(NHC)s enabled the materials to display catalytic activities that were similar or superior to those displayed by monomeric analogues. Moreover, the new catalyst was successfully recovered and reused with minimal loss of performance over several cycles.

Recently, intense interest has emerged in the development of recyclable organocatalysts that may be used to facilitate reactions which typically require transition metals.[1] While resin-supported systems have found success in this regard, the process of attaching the catalyst to the solid support is often low yielding and synthetically challenging.[2] Furthermore, such heterogeneous systems frequently suffer from swelling and mass transport issues and operate via processes that are distinct from those of their homogeneous counterparts.[3] A promising method for overcoming the limitations intrinsic to such approaches is to incorporate an organocatalyst into a soluble, recoverable polymer.[4] Considering that N-heterocyclic carbenes (NHCs) have been proven to be powerful organocatalysts for promoting a broad range of synthetic transformations,[5] efforts were directed toward the development of a recyclable polymeric NHC.[6]

As shown in Figure 1, there are two primary classes of polymers which contain NHCs as integral components of the main chains. The first class comprises diametrically opposed, ditopic NHCs attached to electrophiles or transition metals,[7,8] whereas the second features NHC moieties positioned orthogonally with respect to the polymer backbone, often via metalation.[9] The unique architectures inherent in the latter increase the likelihood of cooperative or synergistic effects between each repeating unit along the polymer chain and could ultimately result in higher efficiencies compared to monomeric analogues. Moreover, modification of such materials may lead to "self-supported" organocatalysts that are conveniently recycled and reused. Herein, we describe a recyclable poly(NHC) polymer that exhibits superior catalytic activity compared to a monomeric analogue and may be recycled repeatedly with only marginal losses in efficacy.

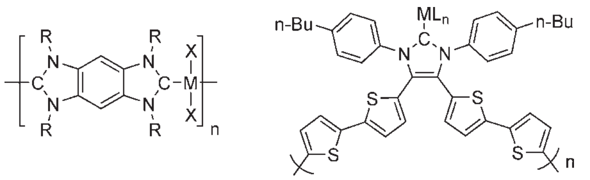
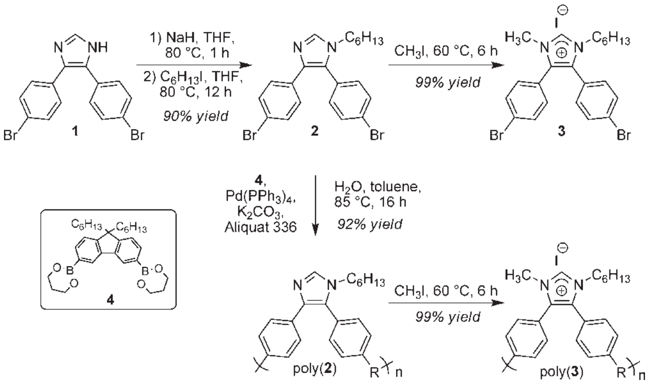


Figure 1. Representative classes of poly(NHC)s.

Scheme 1. Synthesis of Imidazolium Salt 3 and Poly(3) (R = 9,9-Dihexylfluorene)



The synthesis of the aforementioned polymer is outlined in Scheme 1. Alkylation of dibromoimidazole **1**, which was obtained by treating 4,4-dibromobenzil with paraformaldehyde under acidic conditions,[10] afforded **2** in 90% yield. Palladium catalyzed cross-coupling copolymerization of this monomer with a commercially available fluorenyl boronic acid diester (**4**) was used to obtain poly(**2**) in high yield.[11] The polyimidazole exhibited a weight average molecular weight (M_w) of approximately 4500 g/mol, as determined by gel permeation chromatography,[12] and displayed broad ^{1}H NMR signals, as expected for a high molecular weight polymer. Treatment of **2** or poly(**2**) with iodomethane afforded the monomeric catalyst precursor **3** (which served as a control; see below) or poly(**3**), respectively, in high overall yields. In general, the isolated imidazolium salts were found to be hygroscopic[13] but stable in air.

With **3** and poly(**3**) in hand, their abilities to catalyze the benzoin condensation were compared.[14] Initial efforts were

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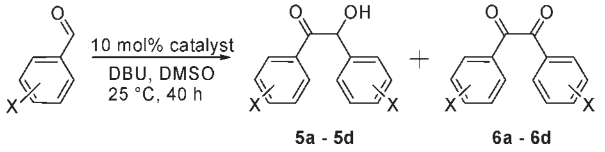
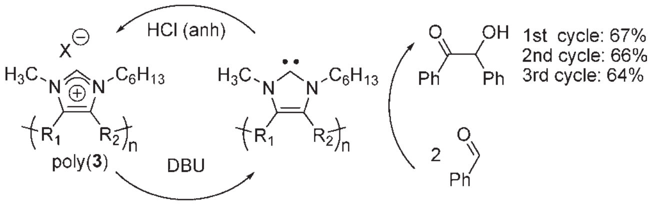
Table 1. Selected Data for the Dimerization of Various Substrates Using Monomeric and Polymeric Imidazolium Salts[a]



substrate	% yield[b] of benzoin product **5** with **3**	% yield[b] of benzoin product **5** with poly(**3**)	% yield[b] of benzil product **6** with **3**	% yield[b] of benzil product **6** with poly(**3**)
X = H	67	67	0	0
X = *m*-Br	15	47	6	10
X = *p*-CF_3	9	43	2	4
X = *p*-OCH_3	29	52	9	9

[a] In a typical experiment, 2.94 mmol of substrate, to mol % of **3** or the repeat unit of poly(**3**), 15 mol % DBU, and 2.0 mL of dry DMSO were stirred for 40 h at 25 °C under argon. [b] Isolated yield.

Scheme 2. Schematic Representation of the Procedure Used to Recycle and Reuse Poly(3)



directed toward optimizing the reaction conditions, which included catalyst loading, temperature, base (to generate the free NHC in situ), solvent, and time (see Supporting Information). Using optimized conditions (DBU as base, minimal DMSO, room temperature, 40 h), the catalytic activities of **3** and poly(**3**) were explored using benzaldehyde and a range of functionalized derivatives. As shown in Table 1, the catalytic activity exhibited by poly(**3**) was similar to that of **3**; however, higher yields of products were obtained with the former when electron-rich or -deficient benzaldehydes were employed. As noted above, the enhanced reactivity may be due to a synergistic effect between the catalytically active sites along the polymer backbone.[15,16] In some cases, the corresponding benzil products were detected in small amounts (≤10%), which may be attributed to the mildly oxidizing properties of DMSO.[17]

The ability of poly(**3**) to be recovered and reused was also explored. After stirring a mixture of benzaldehyde, poly(**3**), DBU, and DMSO under an atmosphere of argon for 40 h, a solution of 4.0 M HCl in dioxane was added. The reaction mixture was stirred for an additional 1 h, after which excess ethyl acetate was added. Subsequent collection of the yellow precipitate via filtration afforded poly(**3**) in an isolated yield of 92%, as verified by ^{1}H NMR spectroscopy (the diagnostic imidazolium proton was observed as a broad singlet at $\delta = 9.50$ ppm; DMSO-d_6). Benzoin was also isolated as a product of this reaction in good yield (Scheme 2) upon aqueous workup of the filtrate and further purification by flash column chromatography. This procedure was repeated twice with only a marginal loss in catalytic efficiency per cycle (see Scheme 2).[18] In contrast, the monomeric analogue **3** could not be recovered following the dimerization reaction using an analogous protocol.

In summary, a catalytically active, "self-supported" poly(NHC) precursor was synthesized via methylation following the cross-coupling copolymerization of **2** with a fluorenyl boronic acid diester. The corresponding catalyst was generated in situ and used to facilitate the dimerization of several benzaldehyde derivatives in good yields. The results presented herein not only demonstrate that NHCs can display enhanced catalytic activities upon incorporation into a polymeric framework but also should enable other NHC-based catalysts to be conveniently regenerated and reused.

ASSOCIATED CONTENT

Supporting Information. Additional experimental details and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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