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Poly(*N*-heterocyclic-carbene)s and their CO_2 Adducts as Recyclable Polymer-Supported Organocatalysts for Benzoin Condensation and Transesterification Reactions

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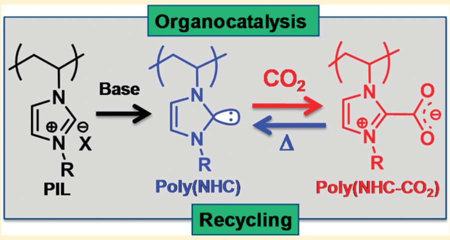
S *Supporting Information*



ABSTRACT: The synthesis of poly(*N*-heterocyclic carbene)s, denoted poly(NHC)s, and of their poly(NHC−CO_2) adducts for a use in organocatalysis is described. Poly(NHC)s were readily obtained in a three-step sequence of reactions, involving i) the free-radical polymerization of ionic liquid monomers, that is, 1-vinyl-3-alkylimidazolium-type monomers with bromide (Br^-) as counteranion, followed by ii) anion exchange of Br^- for bis(trifluoromethanesulfonyl)imide ($^-NTf_2$), of the poly(1-vinyl-3-alkylimidazolium bromide) precursors, affording poly(1-vinyl-3-alkylimidazolium bis(trifluoromethanesulfonyl)imide) derivatives, and iii) deprotonation of the latter polymeric ionic liquids with a strong base. Carbon dioxide (CO_2) was found to reversibly react with poly(NHC)s forming relatively air-stable and thermolabile poly(NHC−CO_2) adducts. Both poly(NHC)s and their poly(NHC−CO_2) adducts were used as polymer-supported organic catalysts and precatalysts, respectively, in transesterification and benzoin condensation reactions under homogeneous conditions. Both types of polymer-supported NHCs were recycled and used several times, but the manipulation of poly(NHC)s −like their molecular NHC analogues- was more complicated owing to their air and moisture sensitivity. In this regard, zwitterionic poly(NHC−CO_2) adducts like their molecular NHC−CO_2 analogues could be easier manipulated than their bare poly(NHC) counterparts, providing good to excellent yields even after several organocatalytic cycles, in particular toward the transesterification reaction.

■ INTRODUCTION

Since the isolation of the first carbenes in the 1990s,[1,2] these species have received a considerable attention in molecular chemistry.[3−5] Stable singlet carbenes, in particular *N*-heterocyclic carbenes (NHCs), have not only become versatile ligands for transition metals in coordination chemistry,[5] but are also used as true organocatalysts for various organic transformations, such as benzoin condensation, transesterification, cyanosilylation, Stetter reactions, etc.[4] This is due to their unique electronic and steric properties that can be finely tuned through variation of their substituent pattern, offering many possibilities to modulate their reactivity. Organic catalysts in general also appear as viable alternatives to metal-based catalysts for precision polymer synthesis, providing high rates and selectivities, and tolerance to functional groups.[6] A few research teams have resorted to NHCs to trigger metal-free polymerization reactions, including chain growth processes such as ring-opening[7] and group transfer polymerizations,[8] as well as step-growth polymerization reactions.[9]

NHCs are generally prepared by deprotonation of air-stable imidazol(in)ium salts with a strong base. Although this method allows one to generate NHCs in situ, it is restricted to base tolerant substrates. In most applications, it is required to isolate the NHCs, which is not often trivial given their air and moisture sensitivity. A few strategies have thus been developed to facilitate their handling and to in situ generate NHCs without the need for a strong base.[10−12] For instance, the thermal activation of 2-alkoxy,[10] trichloromethyl[11] or pentafluorophenyl[12] adducts of NHCs generates free carbenes. However, these methodologies cannot be applied to generate imidazol-2-ylidenes (unsaturated NHCs). Another route to thermal-induced formation of NHCs employs so-called NHC-betaine adducts.[13] Of particular interest are air-stable imidazol(in)ium-2-carboxylates (NHC−CO_2 adducts) whose reversible decarboxylation leads to the formation of free imidazol(in)-2-ylidenes.[14] In contrast to the aforementioned 2-adducts of NHCs, NHC−CO_2 adducts are readily formed by reaction of virtually all types of NHCs with CO_2. These zwitterionic adducts have been extensively used as NHC transfer agents in organometallic chemistry for the synthesis of NHC metal complexes[15] and, more seldom, as latent organic (pre)catalysts in organic[16] and polymer chemistry.[17]

Whereas significant efforts have been directed toward an easier handling of NHCs, their recycling has been little explored. Recent works by Ying et al. have shown that cross-linked polymer-supported NHCs (poly(NHC)s) can be used as

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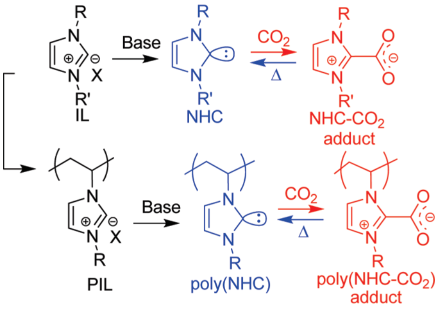
Scheme 1. Formation of *N*-Heterocyclic Carbenes (NHCs) and NHC$-$CO$_2$ Adducts from 1,3-Dialkylimidazolium-Based Ionic Liquids, And Polymeric Analogues Proposed in This Work



recyclable active organocatalysts for a variety of reactions, such as the hydrosilylation of ketones and imines, the cyanosilylation of aldehydes and ketones and the benzoin condensation. These poly(NHC)s were obtained via quaternization of bisimidazole with 2,4,6-tris(bromomethyl)mesitylene forming cross-linked poly(imidazolium) salts, followed by deprotonation with a strong base.[18] Poly(NHC$-$CO$_2$) adducts have been even more scarcely investigated and two synthetic routes involving either the carboxylation of poly(NHCs) or the polymerization of NHC$-$CO$_2$-containing monomers have been reported. Lu et al. have thus derived linear poly(NHC)s by post modification of presynthesized poly(*p*-chloromethylstyrene) with a 1-alkylimidazole moiety, followed by deprotonation of the ensuing poly(imidazolium) salts.[19] Corresponding poly(NHC)s were evaluated to reversibly capture and release CO$_2$ at various temperatures, but no mention of their use in organocatalysis has been reported. Buchmeiser et al. have developed cross-linked poly(NHCs-CO$_2$)-based materials by ring-opening metathesis polymerization of norbornenyl monomers containing the NHC$-$CO$_2$ moiety.[20] These cross-linked polymers were shown to exhibit excellent catalytic activity in the organocatalyzed cyanosilylation of various carbonyl compounds upon in situ thermal generation of poly(NHCs). The ability of these poly(NHC$-$CO$_2$) adducts to react as masked poly(NHCs) was also demonstrated with the preparation of polymer-supported NHC-based metal complexes.

In this contribution, we describe the synthesis of linear and soluble polymeric analogues of both NHCs and NHC$-$CO$_2$ adducts, namely poly(NHCs) and poly(NHC$-$CO$_2$), and their use as recyclable polymer-supported organic (pre)catalysts.[21] For this purpose, we first prepared poly(1-vinyl-3-alkylimidazolium halide)s as precursors, by analogy with the generation of NHCs by deprotonation of 1,3-dialkylimidazolium salts with a strong base (Scheme 1). Poly(1-vinyl-3-alkylimidazolium) derivatives are part of an emerging class of polymeric materials referred to as polymeric ionic liquids (PILs).[22] PILs combine the physicochemical qualities of ionic liquids, such as ionic conductivity, and tunable solubility and viscosity through variation of the cation and anion pairing, with the specific properties of polymers. PILs find potential applications as supports of catalysts, polymeric surfactants, CO$_2$ absorbing resins, polymer electrolytes, etc.[22]

Both poly(NHC)s and poly(NHC$-$CO$_2$) adducts described here have been used as (pre)catalysts under homogeneous conditions, for metal-free transesterification and benzoin condensation reactions. It is shown that poly(NHC$-$CO$_2$) adducts are easier to handle and can be readily recycled compared with their bare poly(NHC) counterparts.

■ EXPERIMENTAL SECTION

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 spectrometer in appropriate deuterated solvents. A Bruker Tensor 27 spectrometer was used for ATR-FTIR analysis. TGA analyses were performed on a TA Instruments, TGA-Q500, under an inert atmosphere of argon at a heating rate of 5 °C/min. Molar masses were determined by size exclusion chromatography (SEC) using a PL-GPC50 plus Integrated SEC system, equipped with PSS SUPREMA Max columns connected in series with pore sizes of 30 and 1000 Å respectively, fitted with dual detectors (refractometry and UV) and a water/formic acid (0.3 M) as the mobile phase at a flow rate of 0.6 mL/min. Pyridine was used as a flow-marker and the calibration was done using poly(2-vinylpyridine) standards.

Materials. 1-Vinylimidazole (99%), 1-bromobutane (99%), 2-bromopropane, and 2-bromoethylbenzene (99%) were obtained from Alfa Aesar and used as received. Azobis(2-methylpropionitrile) (AIBN, 99%) was received from Aldrich and was purified by recrystallization from methanol. NaH (Aldrich, 60% in mineral oil), *t*-BuOK (Aldrich), potassium bis(trimethylsilyl)amide (KHMDS, Aldrich), lithium bis(trifluoromethanesulfonyl)imide (LiNTf$_2$, 98%, TCI) were used as received. Benzyl alcohol (Aldrich, 99%) and benzaldehyde (Aldrich, 99,5%) were distilled prior to use. Vinyl acetate (Aldrich, 99%) was dried over CaH$_2$ and distilled prior to use. THF was distilled over Na/benzophenone. Diethyl ether was distilled over polystyryllithium (PS-Li). CO$_2$ (N-45, Air Liquide) was purified by passing through a click-on inline "super clean purifier" (SGT) prior to use.

Synthesis of 1-Vinyl-3-isopropylimidazolium Bromide (ViPrIm$^+$Br$^-$). 1-Vinyl-3-isopropylimidazolium bromide was prepared following the procedure described in the literature.[23] Under vigorous stirring, 9.3 g (0.075 mol; 7.1 mL) of 2-bromopropane were added dropwise onto 5 g (0.053 mol, 4.8 mL) of 1-vinylimidazole in a 100 mL, round-bottomed flask. The reaction mixture was then refluxed for 16 h. Upon cooling to room temperature, a white-yellow powder was formed, which was extracted with ethyl acetate. Removing of the solvent yielded **ViPrIm$^+$Br$^-$** as a white solid, which was further dried under vacuum until constant weight (11.5 g, 100% yield). ^{1}H NMR (CD$_3$OD): δ 9.6 (s, N$-$C*H*$-$N, 1H), 8.2 (s, N$-$C*H*═CH$-$N, 1H), 8.1 (s, $-$CH═C*H*$-$N, 1H), 7.5 (dd, *J* = 8.7 and 15.7 Hz, CH$_2$═C*H*$-$N, 1H), 6.1 (d, *J* = 15.7 Hz, HCH═C*H*$-$N, 1H), 4.9 (d, *J* = 8.7 Hz, HC*H*=CH$-$N, 1H), 4.9 (sept, *J* = 6.7 Hz, (CH$_3$)$_2$C*H*$-$, 1H), 1.8 (d, *J* = 6.7 Hz, (C*H*$_3$)$_2$CH$-$, 6H). ^{13}C NMR (CD$_3$OD): δ 136.1 (N$-$CH$-$N), 130.1 (CHN), 123.5 (CHN), 121.7 (CHN), 110.7 (CH2), 55.9 (CH$_3$)$_2$CH$-$), 23.7 (CH$_3$)$_2$CH$-$). IR (ATR): 3059, 3022, 2976, 1648, 1551, 1286, 1266, 1165, 1153, 959, 919, 850, 755.

Synthesis of 1-Vinyl-3-butylimidazolium bromide (VBuIm$^+$Br$^-$). 1-Vinyl-3-butylimidazolium bromide was prepared following the procedures described in the literature.[23] Under vigorous stirring, 13.7 g (0.1 mol, 9.5 mL) of bromobutane were added dropwise to 5 g (0.053 mol, 4.8 mL) of 1-vinylimidazole in a 100-mL, one-necked, round-bottom flask. The reaction mixture was then refluxed for 24 h and the resulting brown viscous liquid was allowed to cool down to room temperature. After washing several times with ethyl acetate, **VBuIm$^+$Br$^-$** was obtained as a viscous yellowish oil and dried under dynamic vacuum (10.6 g, 87% yield). The product was then stored under static vacuum. NMR data were found in accordance with those reported in the literature.[23]

Synthesis of 1-Vinyl-3-(1-phenylethyl)imidazolium bromide (VPhEtIm$^+$Br$^-$). 1-Vinyl-3-(1-phenylethyl)imidazolium bromide was prepared following the procedures described in the literature.[23] Under vigorous stirring, 2.8 g (0.015 mol, 2 mL) of 1-phenylethylbromide were added dropwise to 1.04 g (0.011 mol, 1 mL) of 1-vinylimidazole in a 100-mL, one-necked round-bottom flask. The mixture was refluxed for 20 h and the resulting brown viscous liquid was allowed to cool down to room temperature. After washing several times with ethyl acetate and THF, **VPhEtIm$^+$Br$^-$** was obtained as a viscous brownish oil and dried under dynamic vacuum (2.6 g, 85% yield). The product was then stored under static vacuum. ^{1}H NMR (MeOD): δ 9.6 (s, N−C*H*−N, 1H), 8.0 (s, N−C*H*═CH−N, 1H), 7.8 (s, N−CH═C*H*−N, 1H), 7.3−7.5 (m, Ph, 5H), 7.2 (dd, J = 8.7 and 15.6 Hz, $\mathrm{CH_2}$═C*H*−N, 1H), 5.8 (dd, J = 2.8 and 15.6 Hz, *H*CH═C*H*−N, 1H), 5.8 (q, J = 7.0 Hz,−C*H*−(CH3)Ph, 1H), 5.5 (dd, J = 8.7 and 2.8 Hz, HC*H*═C*H*−N, 1H), 2.0 (d, J = 7.0 Hz, −CH−(CH_3)−Ph, 3H). ^{13}C NMR (MeOD): δ 140.7 (C_{arom}), 136.6 (N−CH−N), 131.3 ($\mathrm{CH_{arom}}$), 131.2 ($\mathrm{CH_{arom}}$), 130.7 (CHN), 128.8 ($\mathrm{CH_{arom}}$), 124.2 (CHN), 121.9 (CHN), 111.0 ($\mathrm{CH_2}$), 62.5 (Ph($\mathrm{CH_3}$)CH−), 22.1 (Ph($C\mathrm{H_3}$)CH−). IR (ATR): 3060, 2985, 1651, 1545, 1455, 1159, 1025, 958, 918, 761, 707.

Polymerization of 1-Vinyl-3-alkylimidazolium-Type Monomers. In a typical experiment, a 10 mL Schlenk tube was flame-dried and charged with 4 mmol of monomer, 0.13 mmol of AIBN and 2 mL of methanol. The Schlenk tube was subjected to five freeze−thaw cycles and placed in a thermostatted oil bath previously maintained at 80 °C. The polymerization reaction was quenched after 3 h by sudden cooling with liquid nitrogen. The resulting poly(1-vinyl-3-alkylimidazolium) salts **1** were isolated by precipitation in chloroform or acetone. After drying under vacuum, **1** were obtained as a yellowish powder.

Synthesis of Poly(ViPrIm$^+$Br$^-$) ***1a***. ViPrIm$^+$Br$^-$ (1 g; 4.7 mmol); AIBN (25 mg; 0.15 mmol). Precipitated in $\mathrm{CHCl_3}$. (1 g, Yield 99%); M_n = 4600 g·mol^{-1} by SEC. PDI = 2.48. ^{1}H NMR (MeOD, see Figure S01 of the Supporting Information): δ 9.3−10.0 (br, N−C*H*−N, 1H), 7.5−8.3 (br, C*H*═CH, 2H), 4.5−5.2 (br, N−C*H*−$\mathrm{CH_2}$ and N−C*H*−$\mathrm{(CH_3)_2}$,2H), 2.5−3.3 (br, N−CH−CH_2, 2H), 1.4−1.9 (br, N−CH−(CH_3)$_2$, 6H). ^{13}C NMR ($\mathrm{CD_3OD}$): δ 136.1 (br, N−CH−N), 124.3 (br, CHN), 121.9 (br, CHN), 56.2 (br, CHN), 55.3 $\mathrm{(CH_3)_2CH}$−), 41.9 (br, $\mathrm{CH_2}$), 23.2 $\mathrm{(CH_3)_2CH}$−). IR (ATR): 3056, 3024, 2991, 1649, 1556, 1400, 1288, 1190, 1167, 1154, 1142, 916, 753.

Synthesis of Poly(VPhEtIm$^+$Br$^-$) ***1b***. ViEtBIm$^+$Br$^-$ (1 g; 3.6 mmol); AIBN (19 mg; 0.12 mmol). Precipitated in acetone. Not soluble in water. (1 g, 99% yield). ^{1}H NMR (DMSO-d_6, see Figure S03 of the Supporting Information): 8.9−9.8 (br, N−C*H*−N, 1H), 6.8−8.0 (br, C*H*═C*H* and aromatic protons, 7H), 5.1−5.9 (br, N−C*H*−$\mathrm{CH_2}$ and N−C*H*−($\mathrm{CH_3}$)−ph, 2H), 3.6−4.0 (br, N−CH−CH_2, 2H), 1.6−2.0 (br, N−CH−(CH_3)−Benzyl, 3H). ^{13}C NMR (DMSO-d_6): δ 139.1 (br, C_{arom}), 135.3 (br, N−CH−N), 129.3 (br, $\mathrm{CH_{arom}}$), 127.5 (br, $\mathrm{CH_{arom}}$), 123.0 (br, CHN), 120.7 (br, CHN), 59.7 (br, Ph($\mathrm{CH_3}$)CH−), 54.1 (br, CHN), 20.7 (br, Ph($\mathrm{CH_3}$)CH−). IR (ATR): 3030, 2978, 2935, 1544, 1495, 1455, 1151, 758, 703.

Synthesis of Poly(VBuIm$^+$Br$^-$) ***1c***. ViBuIm$^+$Br$^-$ (1 g; 4.3 mmol); AIBN(24 mg; 0.14 mmol). Precipitated in acetone. (1 g, Yield 99%); M_n = 8722 g·mol^{-1} by SEC, PDI = 2.9. ^{1}H NMR ($\mathrm{D_2O}$, see Figure S02 of the Supporting Information): δ 8.9−9.3 (br, N−C*H*−N,1H), 7.3−7.8 (br, C*H*═CH, 2H), 3.9−4.5 (br, N−CH_2−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_3}$, 2H), 4.4−4.8 (br, N−C*H*−$\mathrm{CH_2}$, 1H), 2.4−3.0 (br, N−CH−CH_2, 2H), 1.7−2.1 (br, $\mathrm{CH_3}$−$\mathrm{CH_2}$−CH_2−$\mathrm{CH_2}$−, 2H), 1.3−1.6 (br, $\mathrm{CH_3}$−CH_2−$\mathrm{CH_2}$−$\mathrm{CH_2}$−, 2H), 0.9−1.2 (br, CH_3−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_2}$−, 3H); ^{13}C NMR ($\mathrm{D_2O}$): δ 134.7 (br, N−CH−N), 124.2 (br, CHN), 120.3 (br, CHN), 55.6 (br, CHN), 50.3 ($\mathrm{CH_2N}$), 40.1 (br, $\mathrm{CH_2CH}$), 30.9 ($\mathrm{CH_2}$), 19.2 ($\mathrm{CH_2}$), 12.9 ($\mathrm{CH_3}$); IR (ATR): 3055, 2959, 2933, 2871, 1568, 1549, 1461, 1435, 1161, 1115, 829, 751.

Anion Exchange. We dissolved 4 mmol of poly(1-vinyl-3-alkylimidazolium bromide) **1** in water or methanol, and the resulting solution was added to a stirred solution of $\mathrm{(CF_3SO_2)_2NLi}$ (8 mmol), previously dissolved in water or methanol. After mixing, the corresponding poly(vinylimidazolium *N*-triflate) **2** immediately precipitated out of the solution as a white powder. After filtration, the polymers were dried under vacuum overnight.

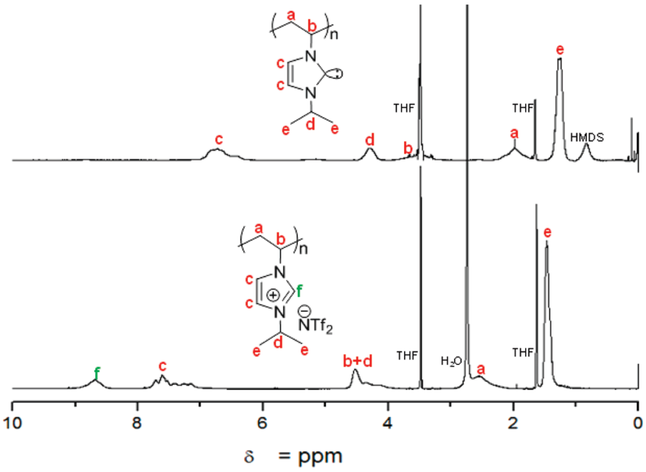


Figure 1. ^{1}H NMR spectrum (THF-d_8) of the poly(1-vinyl-3-isopropyl imidazolium bis(trifluoromethanesulfonyl)imide) **2a** and its poly (*N*-heterocyclic carbene) derivative **3a**.

Synthesis of Poly(ViPrIm$^+$NTf$_2^-$) ***2a***. The anion exchange was carried out in water (92% yield). ^{1}H NMR (THF-d_8, see Figure 1): δ 1.3−1.6 (br, N−CH−(CH_3)$_2$, 6H), 2.2−2.9 (br, N−CH−CH_2,2H), 4.0−4.6 (br, N−C*H*−$\mathrm{CH_2}$ and N−C*H*−$\mathrm{(CH_3)_2}$, 2H), 7.0−8.0 (br, C*H*═C*H*, 2H), 8.5−9.0 (br, N−C*H*−N, 1H). ^{13}C NMR (THF-d_8, see Figure S04 of the Supporting Information): δ 21.2 (br, N−CH−$\mathrm{(CH_3)_2}$), 41.1 (br, N−CH−$\mathrm{CH_2}$), 55.4 (br, N−CH−$\mathrm{CH_2}$ and N−CH−$\mathrm{(CH_3)_2}$), 112.6 (br, *C*H═CH), 119.3 (q, J_{CF} = 333.0 Hz, NTf$_2^-$), 134.7 (br, N−CH−N); IR (ATR): 3139, 2967, 1548, 1343, 1172, 1128, 1051, 791, 740.

Synthesis of Poly(VPhEtIm$^+$NTf$_2^-$) ***2b***. The anion exchange was carried out in methanol. After 2 h of stirring, water was added to the reaction mixture to precipitate **2b** (70% yield). ^{1}H NMR (THF-d_8, see Figure S05 of the Supporting Information): δ 8.8−9.7 (br, N−C*H*−N, 1H), 7.0−8.0 (br, C*H*═C*H* and aromatics, 7H), 5.3−6.0 (br, N−C*H*−$\mathrm{CH_2}$, 1H), 4.2−5.1 (br, N−C*H*−($\mathrm{CH_3}$)−Ph, 1H), 2.3−3.3 (N−CH−CH_2, 2H), 1.8−2.1 (br, N−CH−(CH_3)−Ph, 3H). ^{13}C NMR (THF-d_8, see Figure S06 of the Supporting Information): δ 137.8 (br, N−CH−N), 128.2 (br, Ph), 119.9 (q, J_{CF} = 333.0 Hz, NTf$_2^-$), 122.6 (br, *C*H═CH), 61.4 (br, N−CH−$\mathrm{CH_2}$), 56.1 (br, N−CH−($\mathrm{CH_3}$)−Ph), 40.5 (br, N−CH−$\mathrm{CH_2}$, 2H), 20.1 (br, N−CH−(CH_3)−Ph, 3H); IR (ATR): 3144, 2970, 1550, 1343, 1179, 1127, 1049, 790, 740, 706.

Synthesis of Poly(VBuIm$^+$NTf$^-$) ***2c***. The anion exchange was carried out in water (86% yield). ^{1}H NMR (THF-d_8): δ 8.6−8.9 (br., N−C*H*−N, 1H), 7.2−8.0 (br, C*H*═CH, 2H), 4.0−4.5 (br, N−CH_2−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_3}$, and N−C*H*−$\mathrm{CH_2}$, 3H), 2.4−3.0 (br, N−CH−CH_2, 2H), 1.8−2.1 (br, N−$\mathrm{CH_2}$−CH_2−$\mathrm{CH_2}$−$\mathrm{CH_3}$, 2H), 1.4−1.6 (br, N−$\mathrm{CH_2}$−$\mathrm{CH_2}$−CH_2−$\mathrm{CH_3}$, 2H), 1.0−1.2 (br, N−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_2}$−CH_3, 3H). ^{13}C NMR (THF-d_8): δ 135.4 (br, N−CH−N), 119.8 (br, *C*H═CH), 119.4 (q, J_{CF} = 333.0 Hz, NTf$_2^-$), 48.3 (br, N−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_3}$, and N−CH−$\mathrm{CH_2}$), 32.3 (br, N−CH−$\mathrm{CH_2}$), 29.1 (br, N−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_3}$), 19.8 (br, N−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_3}$, 2H), 16.9 (br, N−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_2}$−$\mathrm{CH_3}$, 3H). IR (ATR): 3139, 2966, 1545, 1343, 1179, 1127, 1050, 791, 740, 706.

Synthesis of Poly(NHC)s ***3***. All deprotonations were carried out under an inert atmosphere, using Schlenk techniques.

3a: A Schlenk tube was charged with 417 mg (1.00 mmol) of poly(ViIPrIm$^+$NTf$_2^-$) **2a**. After being dried azeotropically with dioxane, **2a** was suspended in 10 mL of dry THF, and the reaction mixture was cooled to −80 °C. To this solution was added KHMDS (2.00 mmol) in 10 mL of THF. The reaction mixture was then allowed

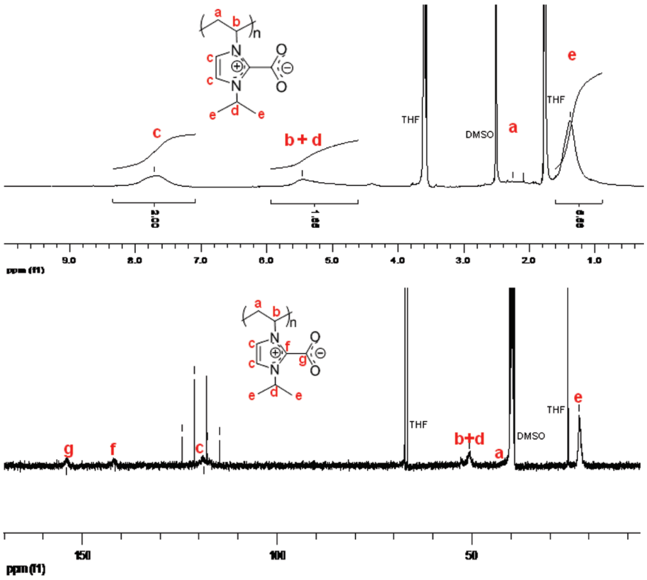


Figure 2. ^{1}H NMR and ^{13}C NMR spectrum of poly(NHC−CO_2) adduct **4a** in DMSO-d_6.

to warm slowly to room temperature and was stirred for 45 min. The resulting clear orange solution was directly used for catalysis experiments. ^{1}H NMR (THF-d_8, see Figure 2): δ 1.2−1.5 (br, N−CH−(CH_3)$_2$, 6H), 1.9−2.4 (br, N−CH−CH_2,2H), 3.4−3.8 (br, N−*CH*−CH_2, 1H), 4.3−4.6 (br, N−*CH*−$(CH_3)_2$, 1H), 6.2−6.9 (br, *CH*═*CH*, 2H).

3b,c: A Schlenk tube was charged with 1 mmol (431 mg) of poly(ViBuIm$^+$$NTf_2^-$) **2c** or 479 mg of poly(ViEtBIm$^+$$NTf_2^-$) **2b**. After being dried azotropically with dioxane, **2b,c** was dissolved in 10 mL of THF, and this solution was added at −80 °C to a suspension of NaH (2 mmol, 80 mg) and *t*-BuOK (0.2 mmol, 22 mg) in 10 mL of THF. The reaction mixture was allowed to warm slowly to room temperature and was filtered to remove the excess of NaH. The resulting orange solution was directly used for catalysis experiments. ^{1}H NMR of **3b** (THF-d_8, see Figure S07 of the Supporting Information): δ 7.2−8.0 (br, aromatics, 7H), 6.5−7.1 (br, *CH*═*CH*, 2H) 5.2−5.7 (br, N−*CH*−CH_2 and N−*CH*−(CH_3)−Ph, 2H), 1.4−1.9 (br, N−CH−CH_2, 2H), 1.0−1.3 (br, N−CH−(CH_3)−Ph, 3H).

Transesterification Using Poly(NHC)s 3 As Polymer-Supported Catalysts.

In these organocatalyzed reactions, the ratio between the benzyl alcohol substrate and the free poly(NHC) was equal to 10 mol % relatively to the repeating monomer unit.

*Transesterification with **3a**.* A Schlenk tube was charged with a solution of **3a** (1 mmol in 10 mL of THF), benzyl alcohol (9.7 mmol, 1.0 mL), and vinyl acetate (13 mmol, 1.2 mL). The reaction mixture was stirred for 30 min at room temperature, and 50 mL of dried diethyl ether was added to precipitate **3a**. The reaction mixture was then filtered under vacuum. The solvents and the excess of vinyl acetate were evaporated from the filtrate, and the resulting yellowish liquid was analyzed by ^{1}H NMR in $CDCl_3$. The conversion of the reaction was determined by measuring the relative intensities of the CH_2 signals at 5.0 and 4.5 ppm corresponding to benzyl acetate and benzyl alcohol, respectively. The identity of the product was confirmed by comparing their ^{1}H NMR spectrum with those of standard (commercial) samples. The recovered poly(NHC) **3a** was then reused for the next run of transesterification.

*Transesterification with **3b,c**.* A Schlenk tube was charged with a solution of **3b** or **3c** (1 mmol in 10 mL of THF), benzyl alcohol (9.7 mmol, 1.0 mL), and vinyl acetate (13 mmol, 1.2 mL). The reaction mixture was stirred for 30 min at room temperature and **3b,c** were precipitated by the addition of dry diethyl ether. After filtration under vacuum, the solvents and the excess of vinyl acetate were evaporated from the solution, yielding a yellowish liquid, which was analyzed by ^{1}H NMR in $CDCl_3$. The recovered poly(NHCs) **3b,c** were then dissolved in 10 mL of THF and reused for the next run of transesterification.

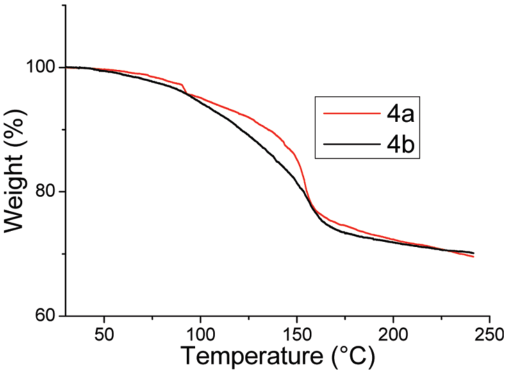


Figure 3. TGA of polyNHC−CO_2 adducts **4a** and **4b** from 25 to 250 °C.

Benzoin Condensation Using Poly(NHC)s 3 As Polymer-Supported Catalysts.

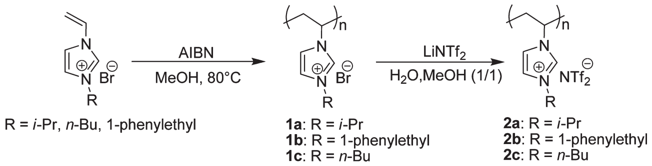
The ratio between the benzaldehyde substrate and the free poly(NHC) was equal to 10 mol % relatively to the repeating monomer unit. A Schlenk tube was charged with a solution of **3** (1 mmol in 10 mL of THF) and benzaldehyde (9.9 mmol, 1 mL). After stirring for 24 h at room temperature, poly(NHCs) **3** were precipitated by the addition of dry diethyl ether and recovered by filtration under vacuum. The solvents were evaporated from the filtrate, and the residue was analyzed by ^{1}H NMR in DMSO-d_6. The identity of the product was confirmed by comparing its ^{1}H NMR spectrum with those of standard (commercial) samples. The recovered poly(NHCs) **3** were then dissolved in 10 mL of THF and reused for the next run of benzoin condensation.

*Synthesis of Poly(NHC−CO_2) Adducts **4a,b**.* A Schlenk tube was charged with 1 mmol of poly(ViPrIm$^+$$NTf_2^-$) **2a** (417 mg) or poly(VPhEtIm$^+$$NTf_2^-$) **2b** (479 mg). After being azeotropically dried with dioxane, **2a,b** were dissolved in 10 mL of THF, and the reaction mixture was cooled to −80 °C. To this solution was added KHMDS (1.5 mmol). After 15 min of stirring at −80 °C, the reaction mixture was allowed to warm to room temperature and was further stirred for 45 min to generate **3a,b**. We then introduced 1 atm of CO_2 to the Schlenk tube, causing the immediate precipitation of **4a,b**. The resulting suspension was stirred for 1 h under 1 atm of CO_2. After filtration under vacuum, **4a, b** were recovered as an orange powder. (70−90% yield) These polymers were directly used for catalysis experiments or kept in a glovebox to avoid hydration ($t_{1/2} \approx 3$ h).

4a. ^{1}H (DMSO-d_6, see Figure 2): δ 1.0−1.6 (br., N−CH−(CH_3)$_2$, 6H), 2.0−2.8 (br., N−CH−CH_2, 2H), 4.6−5.9 (br., N−*CH*−CH_2 and N−*CH*−$(CH_3)_2$, 2H), 7.2−8.3 (br., *CH*═*CH*, 2H). ^{13}C NMR (DMSO-d_6, see Figure 3): δ 21−24 (br., N−CH−$(CH_3)_2$), 50−54 (br., N−CH−CH_2, N−CH−CH_2 and N−CH−$(CH_3)_2$), 116−121 (br., *CH*═CH), 114, 118, 121, and 124 (s, NTf_2^-), 140−143 (br., (N)$_2$−*C*−C), 153−156 (br., C−CO_2). IR (ATR): νCO 1670 cm^{-1}. TGA (see Figure S09 of the Supporting Information): A weight loss of 25% corresponding to the loss of CO_2 was observed, in agreement with the theoretical value of 25% calculated for the full conversion of **3a** to **4a**. **4a** was soluble in polar solvents (DMSO, acetone) and protic solvents (MeOH, EtOH) but insoluble in THF and CH_2Cl_2.

4b. ^{13}C NMR (DMSO-d_6, see Figure S08 of the Supporting Information): δ 161−163 (br., C−CO_2), 136−141 (br., (N)2−*C*−C), 128−132 (br., aromatics), 114, 118, 121, and 124 (s, NTf_2^-), 120−128 (br., *CH*═CH), 61−63 (br., N−CH−CH_2), 53−55 (br.,

Scheme 2. Synthesis of Poly(1-vinyl-3-alkylimidazolium chloride)s and Anion Exchange



N−CH−(CH$_3$)−Ph), 40−47 (br., N−CH−CH$_2$), 21−24 (br., N−CH−(CH$_3$)−Benzyl). IR (ATR): νCO 1670 cm^{-1}. TGA (see Figure S09 of the Supporting Information): a weight loss of 25% corresponding to the loss of CO$_2$ was observed, in agreement with the theoretical value of 25% calculated for the full conversion of **3b** to **4b**. **4b** was soluble in polar solvents (DMSO, acetone) and protic solvents (MeOH, EtOH) but insoluble in THF and CH$_2$Cl$_2$.

Transesterification and Benzoin Condensation Using Poly(NHC−CO$_2$) Adducts 4a,b as Polymer-Supported Precatalysts. In a typical experiment, a Schlenk tube was charged with 1 mmol of **4a** or **4b** and 10 mmol of reactants, suspended in 5 mL of THF. The flask was then placed in an oil bath at 80 °C for 2 (transesterification) or 24 h (benzoin condensation) under vigorous stirring. After this period, the reaction mixture was allowed to cool to room temperature, and 1 atm of CO$_2$ was added, leading to the precipitation of **4a,b**. After stirring for 15 min, the mixture was filtered under vacuum, and the filtrate was analyzed by ^{1}H NMR, as described above. The identity of the products was confirmed by comparing their ^{1}H NMR spectrum with those of standard (commercial) samples. The recovered polymer **4a,b** was then suspended in THF and reused for the next run of catalysis.

RESULTS AND DISCUSSION

Synthesis of Poly(NHC)s and Their Evaluation in Organocatalysis. Among PILs, those based on imidazolium moieties have been the most investigated.[22] The solubility of these PILs, like their molecular IL analogues (Scheme 1), is mainly influenced by the anion, ranging from a high solubility (e.g., with Br$^-$ as anion) to immiscibility in water (with Tf$_2$N$^-$). We have recently reported the synthesis and self-assembling properties of IL-based block copolymers.[24] The self-assembly was triggered by a simple anion exchange, giving rise to either polymeric micelles or polymeric vesicles in aqueous solutions, depending on the overall hydrophilic mass fraction of the block copolymers.

To generate poly(NHC)s that could be used as polymer-supported organocatalysts, we turned to poly(1-vinyl-3-alkylimidazolium) (PVRIm$^+$) precursors whose synthesis by free-radical polymerization of 1-vinyl-3-alkylimidazolium-type monomers (VRIm+) is well-documented.[22,24] A series of PVRIm$^+$ with bromide as counteranion, denoted PVRIm$^+$Br$^-$, and different substituents (R = *i*-Pr, *n*-Bu, 1-phenylethyl, Scheme 2) was thus synthesized in methanol using AIBN as radical source at 80 °C. PVRIm$^+$Br$^-$ with R = *i*-Pr, R = *n*-Bu, and R = 1-phenylethyl has already been reported.[23] Their characterization by ^{1}H NMR spectroscopy confirmed the expected structure.(See the Experimental Section and ESI.) In particular, the signal corresponding to the C*H* proton of the imidazolium moiety could be clearly identified at 9 to 10 ppm.

Characterization of PILs by SEC is always complicated owing to possible interactions between these peculiar polylectrolytes and the columns or the solvent, making difficult an accurate molecular weight measurement.[22] Two PVRIm$^+$Br$^-$ samples (**1a** and **1c**) were thus analyzed by aqueous SEC, affording information about their dispersity and their apparent values of molecular weight (Table 1), although these numbers must be taken with caution for the reasons mentioned above. Unimodal molar masses distribution were observed with a dispersity ($D = M_w/M_n$) between 2 and 3. Because of the insolubility of **1b** in water, analysis of this polymer by aqueous SEC could not be carried out.

These PVRIm+Br- materials were soluble in polar protic solvents and insoluble in apolar organic solvents (Table 1). As mentioned above, this solubility could nonetheless be tuned by changing the counteranion from Br$^-$ to Tf$_2$N$^-$ (Scheme 2). Accordingly, the resulting PILs, denoted PVRIm$^+$Tf$_2$N$^-$, were soluble in aprotic solvents such as acetone, DMSO, and THF, in contrast with their counterparts carrying the bromide counter-anion. For the latter reason, we used PVRIm$^+$Tf$_2$N$^-$ as precursors to get access to poly(NHC)s, as discussed further.

Following the common synthetic route to NHCs, that is, by deprotonation of the acidic proton of 1,3-dialkylimidazolium salts by a strong base,[2,3] PVRIm$^+$Tf$_2$N$^-$ was treated by an excess of NaH (or KHMDS) in THF at −80 °C to generate the desired poly(NHC)s (Scheme 3). For polymers that were soluble in THF, NaH was preferred over KHMDS as deprotonating agent of PVRIm$^+$Tf$_2$N$^-$ precursors, the excess of this base being easily removed by filtration. For precursors that could be not solubilized in THF (i.e., **2a**), KHMDS was used instead.

This chemical modification could be monitored by ^{1}H NMR spectroscopy through the complete disappearance of the signal corresponding to proton f of PVRIm$^+$Tf$_2$N$^-$, after treatment with NaH or KHMDS. A representative example of this deprotonation is illustrated in Figure 1, showing the ^{1}H NMR spectrum of PV*i*PrIm$^+$Tf$_2$N$^-$ **2a**. Nevertheless, the ^{13}C NMR spectra of these poly(NHC)s could not be analyzed with accuracy because of the extreme broadening of the signals. Because of their air and moisture sensitivity, the as-prepared poly(NHC)s **3** were further handled in a dry THF solution, in particular, for the purpose of organocatalysis.

The three poly(NHC)s **3a,b,c** were then investigated as polymer-supported organocatalysts in both transesterification and benzoin condensation. These reactions are known to be efficiently catalyzed by molecular NHCs.[4,9b] In a typical transesterification reaction, benzyl alcohol (BnOH) and vinyl acetate (VAc) were added to a THF solution containing the poly(NHC) **3**, and the reaction was stirred for 30 min at room temperature (Scheme 4). Adding dry diethyl ether onto the latter solution led to the precipitation of the poly(NHC), allowing its easy recovery by filtration, whereas the transesterified benzyl acetate remained soluble. Analysis by ^{1}H NMR spectroscopy of the filtrate confirmed the formation of the reaction product and allowed the conversion to be determined (ESI).

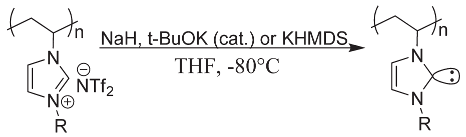
As can be seen in Table 2, the three poly(NHC)s tested all exhibit excellent catalytic activity in the first run, providing excellent yield of benzyl acetate (85−100%), irrespective of the nature of the substituent on the imidazol-2-ylidene. After the first recycling, however, a significant decrease in the yield of the transesterified product was noted with poly(NHC)s **3a** and **3c** (R = *i*-Pr and *n*-Bu; yield = 14 and 27%, respectively), whereas a moderate yield (57%) could be achieved with poly(NHC) **3b** (R = PhEt) under the same conditions. This loss in catalytic activity of the poly(NHC)s after recycling might be ascribed to their partial deactivation, likely because of their sensitivity to

Table 1. Molecular Characteristics and Solubility Properties of PVRIm+ with Br^- or Tf_2N^- as Counter Anion in Different Solvents[a]

	PViPrIm$^+$X$^-$ (M_n = 4600 g·mol^{-1}; PDI = 2.48)		PVPhEtIm$^+$X$^-$		PVBuIm$^+$X$^-$ (M_n = 8700 g·mol^{-1}; PDI = 2.90)	
	X: Br **1a**	X: NTf$_2$ **2a**	X: Br **1b**	X: NTf$_2$ **2b**	X: Br **1c**	X: NTf$_2$ **1c**
H_2O	+	−	−	−	+	−
MeOH	+	−	+	+	+	+−
EtOH	+	−	+	+−	+	−
acetone	−	+	−	+	−	+
THF	−	+−	−	+	−	+

[a] +: soluble; −: insoluble; +−: swollen but not soluble.

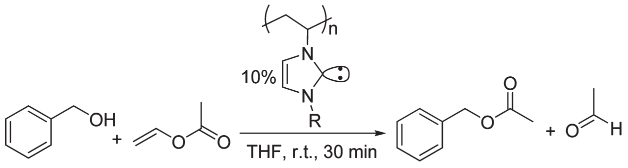
Scheme 3. Synthesis of Poly(NHC)s from PVRIm+Tf_2N^-



2a: R = *i*-Pr
2b: R = 1-phenylethyl
2c: R = *n*-Bu

3a: R = *i*-Pr
3b: R = 1-phenylethyl
3c: R = *n*-Bu

Scheme 4. Poly(NHC)-Catalyzed Transesterification Reaction



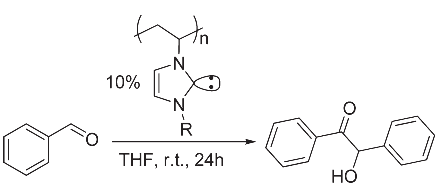
3a: R = *i*-Pr
3b: R = 1-phenylethyl
3c: R = *n*-Bu

Table 2. Yield of Benzyl Acetate Obtained in the Poly(NHC)-Catalyzed Transesterification of Benzyl Alcohol and Vinyl Acetate[a]

polyNHC catalyst	**3a** R=*i*-Pr	**3b** R=PhEt	**3c** R=Bu
run	yield (%)	yield (%)	yield (%)
1	100	100	85
2	14	57	27
3	13	10	
4		12	

[a] Benzyl alcohol (1 equiv), vinyl acetate (1,2 equiv), and polyNHC (cat.: 10% mol of active species) in THF at r.t. and for 30 min. Yield in benzyl acetate was determined by ^{1}H NMR (ESI).

Scheme 5. Poly(NHC)-Catalyzed Benzoin Condensation Reaction



3a: R = *i*-Pr
3b: R = 1-phenylethyl
3c: R = *n*-Bu

Table 3. Poly(NHC)-Catalyzed Benzoin Condensation in THF at Room Temperature for 24 h NMR[a]

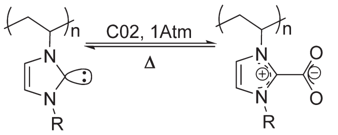
catalyst	**3a**	**3b**	**3c**
run	yield (%)	yield (%)	yield (%)
1	92	85	28
2	20	72	23
3	13	46	
4		35	

[a] All reactions were carried out with benzaldehyde (1 equiv) and desired polyNHC (cat.: 10% mol of active species) in THF at room temperature for 24 h. Yield in benzoin was determined by ^{1}H.

trace impurities and/or by a dimerization reaction pathway,[25] as discussed further. After the second recycling, no transesterified product was formed at all with poly(NHC) **3c**, suggesting a complete degradation of the catalyst, whereas the conversion reached only 10% with poly(NHC)s **3a** and **3b**. Poly(NHC) **3b** was found to retain a catalytic activity in the fourth run (giving 12% conversion). The catalytic efficiency of poly(NHC)s **3** can be correlated with the steric hindrance around the carbene center, which allows us and to rank them as follows according to the size of the substituents on the imidazole framework: **3b** (*R* = 1-phenylethyl) > **3a** (*R* = *i*-Pr) > **3c** (*R* = *n*-Bu).

Next, we examined the catalytic potential of these poly(NHC)s for the so-called benzoin condensation, that is, the self-condensation of benzaldehyde leading to the formation of aromatic *β*-keto alcohol, also called benzoin (Scheme 5). This C−C bond formation reaction is also known to be selectively catalyzed by carbenes.[4,26] The poly(NHC)-catalyzed benzoin condensation was carried out in THF for 24 h at room temperature, and results are shown in Table 3. As in the case of transesterification reactions, the polymer-supported organocatalyst could be recovered by simple filtration upon the addition of diethyl ether. The first run led to benzoin in excellent yield (85−92%) with poly(NHC)s **3a** and **3b** as polymeric catalysts, whereas poly(NHC) **3c** afforded much lower yield (28%). After the first recycling, only poly(NHC) **3b** retained a fairly good catalytic activity (72% yield). In contrast, the yield of benzoin significantly decreased for both poly(NHC)s **3a** and **3c**, in line with the observation previously made about the transesterification carried out in the presence of these polymer-supported catalysts.

Scheme 6. Reversible Formation of Poly(NHC−CO_2) Adducts by Carboxylation of Poly(NHC)s



3a: R = *i*-Pr
3b: R = 1-phenylethyl
4a: R = *i*-Pr
4b: R = 1-phenylethyl

We could thus demonstrate that these poly(NHC)s efficiently catalyze both transesterification and benzoin condensation, although their manipulation was complicated because of their air and moisture sensitivity, similarly to that of their molecular NHC counterparts.[1−4] This directly impacted the recycling process as lower yields were obtained upon the first and subsequent recycling for both catalytic reactions tested. Partial deactivation of poly(NHC)s might result from the presence of trace impurities and occurred more readily with a decrease in the steric hindrance around the carbene center. However, deactivation might also be due to a dimerization reaction of the poly(NHC)s. Such dimerization reactions are likely to occur with molecular free NHCs, in particular, with NHC compounds possessing poorly hindered substituents around the carbene center.[25] As mentioned above, the ^{13}C NMR spectra of poly(NHC)s described did not provide any clear information about their structure owing to the broadening of the signals. Therefore, an experimental proof for the dimerization reaction from our poly(NHC)s could not be established, with the characteristic signal, if present, being overlapped with the CH of the imidazole backbone.

Synthesis of Poly(NHC−CO_2) Adducts and Their Evaluation in Organocatalysis. To improve the stability and facilitate the recycling of poly(NHC)s, we looked into the possibility of forming air-stable poly(NHC−CO_2) adducts and use them as latent polymer-supported catalysts. Release of the free poly(NHC)s was expected to occur in situ by thermal activation of such poly(NHC−CO_2) adducts, by analogy to the generation of NHC from molecular NHC−CO_2 adducts. (See Scheme 1.)[13−15] As already mentioned, there are only a few reports on the synthesis of poly(NHC−CO_2) adducts[19,20] and, to the best of our knowledge, their use as polymer-supported precatalysts in organic reactions has been described only once.[20] In the latter case, the organocatalysis occurred under heterogeneous conditions due to the cross-linked nature of the polymeric support.[20]

Here poly(NHCs-CO_2) adducts **4** were easily generated by carboxylation of freshly prepared poly(NHC)s **3** by flushing the reaction vessel with 1 atm of CO_2, in THF, at room temperature (Scheme 6).

Immediate precipitation of an orange solid was observed upon addition of CO_2. Analysis by IR spectroscopy of the solid compound recovered at room temperature showed the presence of a band at 1670 cm^{-1}, characteristic of the carboxylate group.[14] The formation of the poly(imidazolium-2-carboxylate betaine) adducts **4** was further confirmed by NMR spectroscopy, and a representative example of ^{1}H and ^{13}C NMR spectra of such adducts is provided in Figure 2 for compound **4a**. In the ^{1}H NMR spectrum of **4a**, the signal corresponding to protons *c* of the imidazole backbone (δ = 7.2−8.3 ppm) was shifted downfield compared with that of the poly(NHC) precursor **3a** (δ = 6.2−6.9 ppm), in agreement with the formation of such an imidazolium-type structure. The presence of diagnostic signals at 140 and 160 ppm in the ^{13}C NMR spectrum of **4a**, attributable, respectively, to the quaternary carbon atom of the imidazolium moiety C_f and to that of the carboxylate group C_g, unambiguously established the imidazolium-2-carboxylate betaine structure (Figure 2).

Table 4. Poly(NHC−CO_2)-Catalyzed Transesterification of Benzyl Alcohol and Vinyl Acetate Carried out in THF at 80 °C for 2 h[a]

cycle	1	2	3	4	5	6	7	8
yield (%) with **4a**	94	51	23					
yield (%) with **4b**	83	77	74	70	77	76	77	70

[a] Benzyl alcohol (1 equiv); vinyl acetate (1,2 equiv), and poly(NHC−CO_2)adduct (10% mol of active species) were added to THF at 80 °C for 2 h. Yield in benzyl acetate was determined by ^{1}H NMR.

Characterization by TGA of the polymeric materials obtained after carboxylation showed a weight loss of ∼5% due to CO_2 release at ∼150 °C (Scheme 4), in agreement with temperatures reported for the loss of CO_2 in molecular imidazolium carboxylates adducts.[14] The TGA results were also consistent with the expected composition of the two poly(NHC−CO_2) adducts **4a, b**. This allowed us to conclude that poly(NHC)s were quantitatively transformed into their poly(NHC−CO_2) derivatives by simple carboxylation with 1 atm of CO_2. Interestingly, poly(NHC−CO_2) **4a** and **4b** decomposed at much higher temperature (T > 250 °C) compared with molecular NHC−CO_2 adducts featuring alkyl substituents on the nitrogen atom.[14b] This can be attributed to the higher thermal stability brought by the polymeric backbone of the poly(NHC−CO_2) adducts. It is also worth mentioning that, unlike their poly(NHC) precursors **3**, polymeric adducts **4** are air stable and can be manipulated much more easily. It must be noted, however, that prolonged exposure to air leads to their progressive hydration (complete hydration in about 6 h) as deduced from the change of the chemical shift of the CO_2 moiety in the ^{13}C NMR spectrum of **4a,b**.

The potential of such poly(NHC−CO_2) adducts as polymer-supported precatalysts for the transesterification reaction was next investigated. Similar experimental conditions to those mentioned for poly(NHC) catalysts were used (Scheme 4), except that the temperature was raised to 80 °C to in situ generate free poly(NHC)s under homogeneous conditions.[27] Good to excellent yields of benzyl acetate were thus obtained using **4a** (94%) and **4b** (83%) for the first run (Table 4). This indicated that free poly(NHC)s were efficiently generated by decarboxylation upon heating the poly(NHC−CO_2) adducts at 80 °C. The reaction medium was cooled to room temperature and CO_2 was added, which resulted in the immediate precipitation of the thus regenerated poly(NHC−CO_2) adducts; the latter could be filtered off and reused. The as-recovered polymer-supported precatalysts were indeed subjected to new runs of organocatalysis. Fairly good conversions (70−77%) were achieved with **4b** over a total of eight runs, attesting to their efficient recycling with virtually no loss of catalytic activity. In contrast, yields of transesterificaion with **4a** significantly dropped from the first to the second and third runs (from 94 to 51 to 23%).

Characterization by TGA of **4a** recovered after the first and the second run revealed a weight loss of CO_2 of 23% for the first run,

Table 5. Poly(NHC$-$CO$_2$)-Catalyzed Benzoin Condensation in THF at 80 °C for 24 h[a]

cycle	1	2	3
yield (%) with **4a**	71	27	8
yield (%) with **4b**	65	35	21

[a] All reactions were carried out with benzaldehyde (1 equiv) and desired polyNHC (cat.: 10% mol of active species) in THF at 80°C for 24 h. Yield in benzoin was determined by ^{1}H NMR.

instead of the expected 25%, and of 15% for the second run, instead of the 23% observed after the first run (ESI). This means that CO$_2$ was only partially reincorporated, most likely because of a partial deactivation of the in situ generated poly(NHC).

Poly(NHC$-$CO$_2$) adducts **4a,b** were then investigated as precatalysts for the benzoin condensation at 80 °C in THF for 24 h (Table 5). Surprisingly, moderate yields of benzoin were obtained with both **4a** and **4b** (71 and 65% respectively) during the first run of catalysis, which contrasted with the excellent yields reached for the same reaction with poly(NHC)s **3a,b** as polymer-supported catalysts. Interestingly, the removal of KNTf$_2$ from the catalysts by washing several times **4a,b** with THF allowed us to increase the yield of benzoin to 93% under otherwise identical conditions. We postulate that KNTf$_2$ might be able to deactivate indirectly the polymer catalyst by forming stable poly(NHC$-$PhCHO$-$COO$-$KNTf$_2$) adducts, by analogy to the reaction of molecular NHC$-$CO$_2$ adduct with benzaldehyde in the presence of NaBPh$_4$, as described by Tommasi et al.[28] Note that these adducts formally result from irreversible trapping of the so-called Breslow intermediate by CO$_2$.

Upon the first recycling, a marked decrease in yield was observed for both **4a** and **4b** (27 and 35% respectively), whereas the conversion reached only 8 and 21% with **4a** and **4b**, respectively, in the third run. In the case of **4a,b** free of KNTf$_2$, only 5$-$10% of benzoin was obtained during the second run, suggesting that KNTf$_2$ might be involved in the stabilization of the generated poly(NHC)s, probably by coordination of the potassium cation to the carbene center. These results suggest that deactivation of in situ generated poly(NHC)s **3a,b** is more likely to occur because of the long reaction time (24 h) and the relatively high temperature (80 °C). Decreasing the reaction time from 24 to 12 h in the presence of 20% mol of KNTf$_2$ free catalyst still provided a good yield (75%) of benzoin at 80 °C, but recycling was not possible. The temperature could be lowered to 60 °C, but 24 h of reaction was necessary to obtain 80% yield of benzoin. Here again the recycling was precluded because of excessive catalyst deactivation. Attempts to generate poly(NHC)s **3a,b** by heating **4a,b** to 80 °C under vacuum for 2 h in the absence of substrate, followed by the addition of benzaldehyde, resulted in no conversion after 24 h at room temperature. Optimization of the experimental conditions of the benzoin condensation reaction catalyzed by poly(NHC$-$CO$_2$) adducts **4a,b** is currently underway.

■ CONCLUSIONS

Poly(*N*-heterocyclic carbenes)s, referred to as poly(NHC)s, and their poly(NHC$-$CO$_2$) adducts can be viewed as polymer-supported versions of the well-established molecular NHCs and NHC$-$CO$_2$ adducts, respectively. Both poly(NHC)s and their poly(NHC$-$CO$_2$) adducts have been synthesized and used as organocatalysts and yet soluble polymers, which could be easily separated from the reaction mixture. The synthesis of poly(NHC)s could be achieved from ionic liquid monomers in a three-step sequence, involving the free-radical polymerization of 1-vinyl-3-alkylimidazolium bromide monomers, followed by an exchange of bromide for bis(trifluoromethanesulfonyl)imide anion, and a last step of deprotonation with a strong base. As for poly(NHC$-$CO$_2$) adducts, they could be readily prepared by carboxylation of the parent poly(NHC)s with 1 atm of CO$_2$. This carboxylation step is reversible and provides a convenient method to mask and unmask poly(NHC)s, paving the way toward a practical use and recovery of these polymer-supported catalysts. As their molecular analogues, poly(NHC)s are less air-stable than their zwitterionic poly(NHC$-$CO$_2$) counterparts, a premature deactivation being observed in the former case. In the latter case, excellent yields of organocatalysis could be achieved for the transesterification reaction, although the proper choice of the alkyl substituent on the imidazol-2-ylidene appears to be crucial. Indeed, the poly(NHC$-$CO$_2$) adduct derived from poly(1-vinyl-3-phenylethylimidazolium) has proven to be more efficient than its poly(1-vinyl-3-isopropylimidazolium) homologue. In the case of benzoin condensation catalyzed by poly(NHC$-$CO$_2$) adducts, the slow kinetic of the reaction and the relatively high temperature required have not allowed us to recycle efficiently the polymer catalyst, likely because of its premature deactivation. Optimization of the reaction conditions to generate smoothly poly(NHC)s from poly(NHC$-$CO$_2$) adducts is underway. We are also currently investigating the behavior of poly(NHC$-$CO$_2$) adducts when exposed to air for prolonged time as well as the catalytic efficiency of corresponding poly(NHC)s generated by thermolysis as a function of the substituents of the carbene. Application of such recoverable polymer-supported NHCs to other organocatalyzed reactions, including cyanosilylation, Stetter reactions, or even organocatalyzed polymerization reactions, for example, group transfer or ring-opening polymerizations, among others, is also in progress.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** ^{1}H and ^{13}C NMR spectra of compounds **2a**, **2b**, **3b**, **4b** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Igau, A.; Grutzmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463.

(2) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(3) For an Editorial on Carbenes, Guest Eds.: Arduengo, A. J. and Bertrand, G., see:(a) *Chem. Rev.* **2009**, *109*, 3209. See also: (b) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

(4) For reviews on the use of NHCs as organocatalysts, see(: a) Nair, V.; Bindu, S.; Sreekumar, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5130. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (c) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988.

(5) For reviews on the use of carbenes as ligands in coordination chemistry, see: (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Hahn, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1348.(c) *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Topics in Organometallic Chemistry Series 21; Springer-Verlag: Berlin, 2007. (d) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (e) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (f) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677. (g) Arnold, P. L.; Casely, I. J. *Chem. Rev.* **2009**, *109*, 3599.

(6) For recent reviews about organocatalyzed polymerization reactions, see:(a) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813. (b) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093.

(7) For recent articles on ring-opening polymerizations catalyzed by NHCs, see:(a) Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G. G.; Culkin, D. A.; Hagberg, E. C.; Nyce, G. W.; Waymouth, R. M.; Hedrick, J. L. *Polymer* **2006**, *47*, 4018. (b) Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2009**, *131*, 4884. (c) Kamber, N. E.; Jeong, W.; Gonzalez, S.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2009**, *42*, 1634. (d) Raynaud, J.; Absalon, C.; Gnanou, Y.; Taton, D. *J. Am. Chem. Soc.* **2009**, *131*, 3201. (e) Raynaud, J.; Absalon, C.; Gnanou, Y.; Taton, D. *Macromolecules* **2010**, *43*, 2814. (f) Raynaud, J.; Nzahou Ottou, W.; Gnanou, Y.; Taton, D. *Chem. Commun.* **2010**, *46*, 3203. (g) Guo, L.; Zhang, D. *J. Am. Chem. Soc.* **2009**, *131*, 18072. (h) Rodriguez, M.; Marrot, S.; Kato, T.; Stérin, S.; Fleury, E.; Baceiredo, A. *J. Organomet. Chem.* **2007**, *692*, 705. (i) Guo, L.; Zhang, D. *J. Am. Chem. Soc.* **2009**, *131*, 18072.

(8) (a) Raynaud, J.; Ciolino, A.; Baceirdo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. *Ang. Chem., Int. Ed.* **2008**, *47*, 5390. (b) Raynaud, J.; Gnanou, Y.; Taton, D. *Macromolecules* **2009**, *42*, 5996. (c) Scholten, M. D.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2008**, *41*, 7399.

(9) (a) Jones, R. A.; Karatza, M.; Voro, T. N.; Civcir, P. U.; Franck, A.; Ozturk, O.; Seaman, J. P.; Whitmore, A. P.; Williamson, D. J. *Tetrahedron* **1996**, *52*, 8707. (b) Jones, R. A.; Civcir, P. U. *Tetrahedron* **1997**, *53*, 11529. (c) Nyce, G. W.; Lamboy, J. A.; Connor, E. F.; Waymouth, R. M.; Hedrick, J. L. *Org. Lett.* **2002**, *4*, 3587. (d) Pinaud, J.; Vijayakrishna, K.; Taton, D.; Gnanou, Y. *Macromolecules* **2009**, *42*, 4932.

(10) (a) Wanzlick, H.-W.; Esser, F.; Kleiner, H.-J. *Chem. Ber.* **1963**, *96*, 1208. (b) Cetinkaya, B.; Cetinkaya, E.; Chamizo, J. A.; Hitchcock, P. B.; Jasim, H. A.; Kücükbay, H.; Lappert, M. F. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2047. (c) Arduengo, A. J.; Calabrese, J. C.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta* **1999**, *82*, 2348. (d) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546.

(11) (a) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J. P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021. (b) Teles, J. H.; Melder, J. P.; Ebel, K.; Schneider, R.; Gehrer, E.; Harder, W.; Brode, S.; Enders, D.; Breuer, K.; Raabe, G. *Helv. Chim. Acta* **1996**, *79*, 61. (c) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (d) Csihony, S.; Culkin, D. A.; Sentman, A. C.; Dove, A. P.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 9079. (e) Coulembier, O.; Dove, A. P.; Pratt, R. C.; Sentman, A. C.; Culkin, D. A.; Mespouille, L.; Dubois, P.; Waymouth, R. M.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4964.

(12) Nyce, G. W.; Csihony, S.; Waymouth, R. M.; Hedrick, J. L. *Chem.—Eur. J.* **2004**, *10*, 4073.

(13) Delaude, L *Eur. J. Inorg. Chem.* **2009**, 1681.

(14) (a) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. *Chem. Commun.* **2004**, 112. (b) Van Ausdall, B. R.; Glass, J. L.; Wiggins, K. M.; Aarif, A. M.; Louie, J. *J. Org. Chem.* **2009**, *74*, 7935.

(15) (a) Voutchkova, A. M.; Appelhans, L. N.; Chianese, A. R.; Crabtree, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 17624. (b) Tudose, A.; Demonceau, A.; Delaude, L. *J. Organomet. Chem.* **2006**, *691*, 5356.

(16) (a) Zhou, H.; Zhang, W.-Z.; Liu, C.-H.; Qu, J.-P.; Lu, X.-B. *J. Org. Chem.* **2008**, *73*, 8039. (b) Naik, P. U.; Petitjean, L.; Refes, K.; Picquet, M.; Plasseraud, L. *Adv. Synth. Catal.* **2009**, *351*, 1753. (c) Kayaki, Y.; Yamamoto, M.; Ikariya, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 4194.

(17) (a) Bantu, B.; Pawar, G. M.; Wurst, K.; Decker, U.; Schmidt, A. M.; Buchmeiser, M. R. *Eur. J. Inorg. Chem.* **2009**, 1970. (b) Bantu, B.; Pawar, G. M.; Decker, U.; Wurst, K.; Schmidt, A. M.; Buchmeiser, M. R. *Chem.—Eur. J.* **2009**, *15*, 3103.

(18) Tan, M.; Zhang, Y.; Ying, J. Y. *Adv. Synth. Catal.* **2009**, *351*, 1390.

(19) Zhou, H.; Zhang, W.-Z.; Wang, Y.-M.; Qu, J.-P.; Lu, X.-B. *Macromolecules* **2009**, *42*, 5419.

(20) Pawar, G. M.; Buchmeiser, M. R. *Adv. Synth. Catal.* **2010**, *352*, 917.

(21) For recent reviews on polymer-supported catalysts, see: (a) Akiyama, R.; Kobayashi, S. *Chem. Rev.* **2009**, *109*, 594. (b) Barbaro, P.; Liguori, F. *Chem. Rev.* **2009**, *109*, 515. (c) Ikegami, S.; Hamamoto, H. *Chem. Rev.* **2009**, *109*, 583. (d) Lu, J.; Toy, P. H. *Chem. Rev.* **2009**, *109*, 815. (e) Buchmeiser, M. R. *Chem. Rev.* **2009**, *109*, 303. (f) Bergbreiter, D. E.; Tian, J.; Hongfa, C. *Chem. Rev.* **2009**, *109*, 530.

(22) (a) Green, M. D.; Long, T. E. *J. Macromol. Sci., Part C: Polym. Rev.* **2009**, *49*, 291. (b) Green, O.; Grubjesic, S.; Lee, S.; Firestone, M. A. *J. Macromol. Sci., Part C: Polym. Rev.* **2009**, *49*, 339. (c) Lu, J.; Yan, F.; Texter, J. *Prog. Polym. Sci.* **2009**, *34*, 431. (d) Anderson, E. B.; Long, T. E. *Polymer* **2010**, *51*, 2447. (e) Jaeger, W.; Bohrisch, J.; Laschewsky, A. *Prog. Polym. Sci.* **2010**, *35*, 511.

(23) (a) Marcilla, R.; Blazquez, J. A.; Rodriguez, J.; Pomposo, J. A.; Mecerreyes, D. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 208. (b) Zhao, F.; Meng, Y.; Anderson, J. L. *J. Chromatogr., A* **2008**, *1208*, 1. (c) TaeYoung, K.; Minwon, S.; Soon Jae, K.; Tae Hee, L.; Jong Eun, K.; You Jong, L.; Joo Hyung, K.; MunPyo, H.; Kwang, S. S. *Macromol. Rapid Commun.* **2009**, *30*, 1477. (d) Marcus, D.; Helmut, R. *Macromol. Chem. Phys.* **2009**, *210*, 776.

(24) (a) Vijayakrishna, K.; Jewrajka, S. K.; Ruiz, A.; Marcilla, R.; Pomposo, J. A.; Mecerreyes, D.; Taton, D.; Gnanou, Y. *Macromolecules* **2008**, *41*, 6299. (b) Vijayakrishna, K.; Mecerreyes, D.; Gnanou, Y.; Taton, D. *Macromolecules* **2009**, *42*, 5167.

(25) Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schütz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896.

(26) (a) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719–3726. (b) Zhao, H.; Foss, F., W., Jr.; Breslow, R. *J. Am. Chem. Soc.* **2008**, *130*, 12590.

(27) The temperature for the release of CO_2 was determined by variable temperature NMR experiments in DMSO-d_6.

(28) Tommasi, I.; Sorrentino, F. *Tetrahedron Lett.* **2005**, *46*, 2141.