Poly(ionic liquid)s Based on Imidazolium Hydrogen Carbonate Monomer Units as Recyclable Polymer-Supported *N*-Heterocyclic Carbenes: Use in Organocatalysis

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ABSTRACT: Synthesis of novel poly(ionic liquid)s, namely, poly(1-vinyl-3-alkylimidazolium hydrogen carbonate)s, denoted as poly([NHC(H)][HCO_3])s or PVRImHCO_3, where R is an alkyl group (R = ethyl, butyl, phenylethyl, dodecyl), is described. Two distinct synthetic routes were explored. The first method is based on the free-radical polymerization (FRP) of 1-vinyl-3-alkylimidazolium monomers featuring a hydrogen carbonate counter anion (HCO_3^-), denoted as VRImHCO_3. The latter monomers were readily synthesized by alkylation of 1-vinylimidazole (VIm), followed by direct anion exchange of 1-vinyl-3-alkylimidazolium bromide monomers (VRImBr), using potassium hydrogen carbonate ($KHCO_3$) in methanol at room temperature. Alternatively, the same anion exchange method could be applied onto FRP-derived poly(1-vinyl-3-alkylimidazolium bromide) precursors (PVRImBr). All PVRImHCO_3 salts proved air stable and could be manipulated without any particular precautions. They could serve as polymer-supported precatalysts to generate polymer-supported *N*-heterocyclic carbenes, referred to as poly(NHC)s, formally by a loss of "H_2CO_3" (H_2O + CO_2) in solution. This was demonstrated through selected organocatalyzed reactions of molecular chemistry, known as being efficiently mediated by molecular NHC catalysts, including benzoin condensation, transesterification and cyanosilylation of aldehyde. Of particular interest, recycling of the polymer-supported precatalysts was possible by re-carboxylation of *in situ* generated poly(NHC)s. Organocatalyzed reactions could be performed with excellent yields, even after five catalytic cycles. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4530–4540

KEYWORDS: *N*-heterocyclic carbenes; organocatalysis; poly(ionic liquid)s; polymer-supported catalysts; radical polymerization; catalysis; synthesis

INTRODUCTION In the last two decades, *N*-heterocyclic carbenes (NHCs) have been employed not only as unique ligands for transition metals,[1–3] but also as true organocatalysts in molecular chemistry for various molecular transformations.[4–6] More recently, NHCs have also served as organocatalysts or building blocks in metal-free polymer synthesis.[7–9] Steric and/or electronic properties of NHCs can be finely tuned through variation of their substituent pattern, which allows modulating their overall reactivity (e.g., nucleophilicity and/or basicity) toward various substrates.[10,11] However, their poor stability when exposed to air makes NHCs difficult to handle.[12–14] To circumvent this limitation, various masked NHCs have proved of practical use, for instance, as precatalysts in molecular and macromolecular reactions.[5,9]

For instance, NHCs can be masked in the form of NHC-Ag(I) complexes[15,16] or 2-alkoxy,[17–20] trichloromethyl,[21] pentafluorophenyl,[21] isothiocyanate,[22] carboxylic acid,[23,24] and NHC-CO_2 adducts.[25,26] The latter zwitterionic azol(in)ium-2-carboxylates usually result from the carboxylation of free carbenes with CO_2. Hence, the intermediacy of air- and moisture-sensitive species is required in most cases.[25,27–30] Therefore, a need still exists to develop air-stable NHC precursors that could be of practical usage for the purpose of organocatalysis or organometallic chemistry.[31–42]

Additional Supporting Information may be found in the online version of this article.

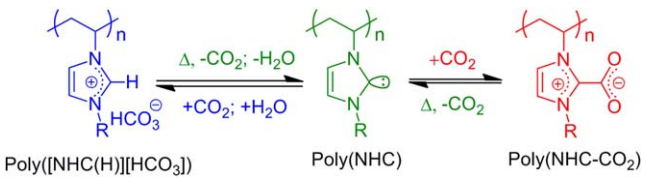
In addition, progressive hydrolysis of NHC-CO_2 adducts, forming imidazol(in)ium hydrogen carbonates, denoted as [NHC(H)][HCO_3], has been reported.[41,43] However, we have shown that these salts can serve as a genuine source of NHCs under very mild conditions, formally by a loss of "H_2CO_3" (H_2O + CO_2).[41,44] Synthesis of [NHC(H)][HCO_3] precursors can be readily achieved in one pot, by anion exchange from commercial imidazol(in)ium halides ([NHC(H)][X]; X = Br or Cl), in the presence of $KHCO_3$ in methanol. Their NHC-like behavior was then experimentally evidenced in model (macro)molecular reactions, and NHC formation was supported by density functional theory (DFT) calculations.[41,45]

We now wish to report polymeric versions of these imidazolium hydrogen carbonates, referred to as poly([NHC(H)][HCO_3])s, and their use in organocatalysis. Catalyst recycling is obviously of prime importance in catalyzed processes,[46–51] including molecular reactions by an organocatalytic pathway.[52] In a previous contribution, we described the synthesis of polymeric analogs of both NHCs and NHC-CO_2 adducts, denoted as poly(NHC)s and poly(NHC-CO_2) adducts.[35] When used as polymer-supported precatalysts for metal-free transesterification and benzoin condensation reactions, poly(NHC-CO_2) adducts proved easier to handle and could be more easily recycled, than their "bare" poly(NHC) counterparts. One limitation of this approach, however, was the need for the prior synthesis of related air sensitive poly(NHC) intermediates.[53] We now provide an easy synthetic access to air-stable and recyclable poly([NHC(H)][HCO_3])s for facile organocatalysis. These salt precursors were thus readily synthesized following two distinct routes that did not require the prior formation of poly(NHC)s. These particular poly(ionic liquid)s (PILs)[54–60] were subsequently used as a source of poly(NHC)s, by analogy with their molecular versions, for selected organocatalyzed molecular reactions. Recarboxylation at the completion of each tested reaction allowed us to recycle the poly([NHC(H)][HCO_3]) precursors (Scheme 1), while maintaining excellent yields, even after five catalytic cycles.

EXPERIMENTAL

Instrumentation

^{1}H NMR and **^{13}C NMR** spectra were recorded on a Bruker AC-400 spectrometer in appropriate deuterated solvents. Molar masses were determined by size exclusion chromatography (**SEC**) in H_2O/formic acid (0.3 M) as the eluent (0.6 mL/min) and with pyridine as a flow marker at 25 °C, using both refractometric (RI) and UV detectors (Varian). Analyses were performed using a PL-GPC50 plus integrated GPC System equipped with PSS SUPREMA Max columns with pore sizes of 30 and 1000 Å, respectively (connected in series), fitted with dual detectors (refractometry and UV). Calibration curve was done using poly(2-vinylpyridine) as polymer standards.



SCHEME 1 Reversible generation of poly(NHC)s **5** from poly([NHC(H)][HCO_3]) salts **4** and poly(NHC-CO_2) adducts **6**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Materials

1-Vinylimidazole (99%), 1-bromobutane (99%), 1-bromoethane (99%), 2-bromoethylbenzene (99%), and 1-bromododecane (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. Dimethylaminopropionitrile (DMAPN, 98%) and potassium persulfate (KPS, 99%) were purchased from Aldrich and used as received. 4,4′-Azobis(4-cyanovaleric acid) (V-501, 99%) and 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, 99%) were purchased from Wako chemicals used as received. Benzyl alcohol (Aldrich, 99%) and benzaldehyde (Aldrich, 99.5%) were distilled before use. Vinyl acetate (Aldrich, 99%) was dried over CaH_2 and distilled before use. Trimethylsilylcyanide (TMSCN, 98%, ABCR) was used as received. Potassium bicarbonate ($KHCO_3$ 99.7%, Aldrich) was dried at 50 °C for 12 h under vacuum before use. Tetrahydrofuran (THF) was distilled over Na/benzophenone. Dimethyl sulfoxide (DMSO 99.5%, Fischer) and ethyl acetate (99.7%, Aldrich) were used without further purification. MeOH was distilled over Na metallic before use. CO_2 (N-45, Air Liquide) was purified by passing through a click-on inline "super clean purifier" (SGT) before use.

Synthesis of 1-Vinyl-3-ethylimidazolium Bromide VEtImBr (1a)

1-Vinyl-3-ethylimidazolium bromide ([NHC(H)][Br]) **1a** was prepared following a procedure already described.[35,61–63] The monomer was recovered as a white solid (100% yield). 1-Vinyl-3-butylimidazolium bromide VBuImBr (**1b**)[61], 1-vinyl-3-(1-phenylethyl)-imidazolium bromide VEtPhImBr (**1c**),[35] and 1-vinyl-3-dodecylimidazolium bromide VDodeImBr (**1d**)[62] were prepared following a similar procedure. NMR data were in accordance with those reported in the literature.[35]

Synthesis of 1-Vinyl-3-ethylimidazolium Hydrogen carbonate VEtImHCO$_3$ (2a)

A mixture of 1-vinyl-3-ethylimidazolium bromide, **1a**, (1 g, 4.92 mmol) and 1.05 equiv of $KHCO_3$ (518 mg, 5.18 mmol) was dried at 60 °C under vacuum for 12 h. Dry methanol (5 mL) was then added, and the resulting suspension was stirred for 24 h at rt. After filtration of the suspension over Celite, methanol was evaporated under vacuum to yield a sticky solid. After trituration of the solid with acetone and filtration, **2a** was obtained as a yellowish powder and dried under dynamic vacuum (yield: 83%). The product was then stored under static vacuum.

^{1}H NMR (CD_3OD): δ 1.56 (d, CH_3—CH_2—, 3H), 4.39 (q, CH_3—CH_2—, 2H), 5.43 (dd, *H*CH=CH—N, 1H), 5.92 (dd, *H*CH=CH—N,

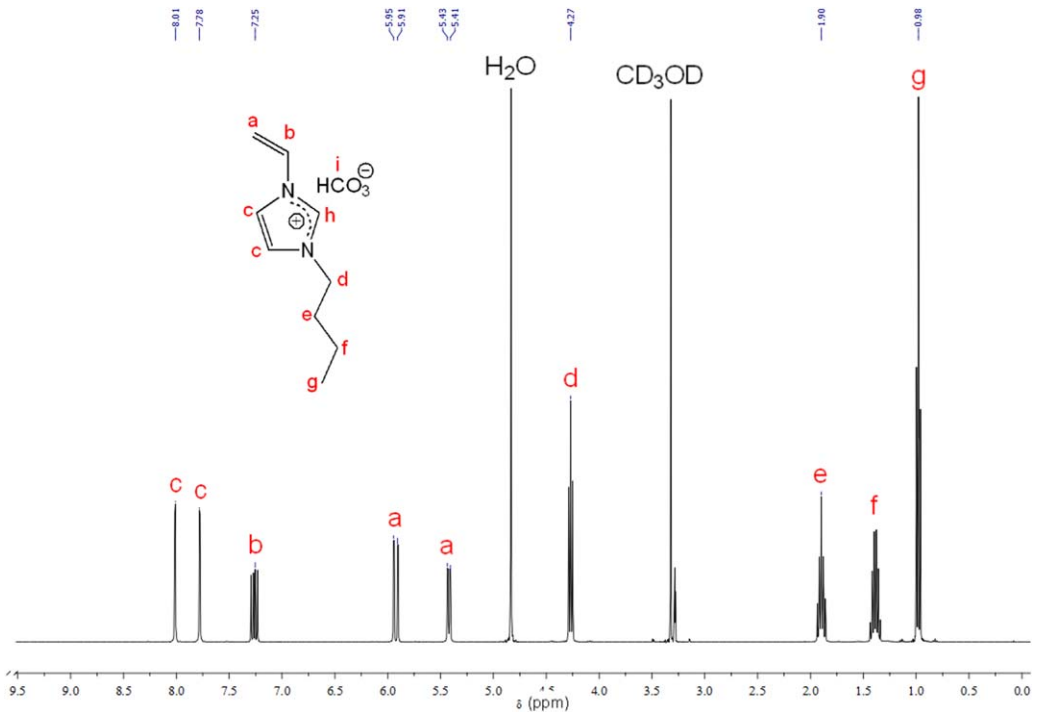


FIGURE 1 ^{1}H NMR spectrum of 1-vinyl-3-butylimidazolium hydrogen carbonate **2b** in CD_3OD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1H), 7.26 (dd, CH_2=C*H*—N, 1H), 7.78 (s, N—CH=C*H*—N, 1H), 8.00 (s, N—C*H*=CH—N, 1H). ^{13}C NMR (CD_3OD): δ 15.41 (*C*H_3—CH_2—), 52.8 (*C*H_2—CH_3), 109.9 (*C*H_2=CH—N), 120.8 (N—*C*H=CH—N), 124.1 (N—CH=*C*H—N), 129.9 (CH_2=*C*H—N), 136.1 (N—*C*H—N), 161.4 (H*C*O_3).

Synthesis of 1-Vinyl-3-butylimidazolium Hydrogen Carbonate VBuImHCO$_3$ (2b)

2b was prepared following a similar procedure to that used for the synthesis of **2a**.

^{1}H NMR (CD_3OD, Fig. 1): δ 0.98 (t, C*H*$_3$—CH_2—CH_2—CH_2—, 3H), 1.32 (s, CH_3—C*H*$_2$—C*H*$_2$—CH_2—, 2H), 1.90 (t, CH_3—CH_2—C*H*$_2$—CH_2—, 2H), 4.27 (t,N—C*H*$_2$—CH_2—CH_2—CH_3, 2H), 5.4 and 4.9 (d, N—CH—C*H*$_2$, 2H), 7.25 (dd, N—C*H*=CH_2, 1H), 7.7 and 8.0 (d, C*H*=C*H*, 2H). ^{13}C NMR (CD_3OD, Fig. 2): δ 13.57 (*C*H_3—CH_2—CH_2—CH_2—), 20.28 (CH_3—*C*H_2—CH_2—CH_2—), 37.72 (CH_3—CH_2—*C*H_2—CH_2—), 50.73 (CH_3—CH_2—CH_2—*C*H_2—), 109.9 (*C*H_2=CH—N), 120.8 (N—*C*H=CH—N), 124.1 (N—CH=*C*H—N), 129.9 (CH_2=*C*H—N), 135.1 (N—*C*H—N), 161.0 (H*C*O_3).

Synthesis of 1-Vinyl-3-(1-phenylethyl)imidazolium Hydrogen Carbonate VEtPhImHCO$_3$ (2c)

2c was prepared following a similar procedure as that used for the synthesis of **2a**.

^{1}H NMR (CD_3OD): δ 1.89 (d, C*H*$_3$—CH—, 3H), 5.42 (dd, *H*CH=CH—N, 1H), 5.83 (m, C*H*—(CH_3)(C_6H_5), 1H), 6.00 (dd, *H*CH=CH—N, 1H), 7.29 (dd, CH_2=C*H*—N, 1H), 7.43 (m, CH—C_6H_5, 5H), 8.00 (s, N—CH=C*H*—N, 1H), 8.25 (s, N—C*H*=CH—N, 1H), 9.84 (s, N—C*H*—N, 1H). ^{13}C NMR (DMSO-d_6): δ 19.36 (*C*H_3—CH—), 58.9 (*C*H—(CH_3)(C_6H_5)), 107.7 (*C*H_2=CH—N), 118.8 (N—*C*H=CH—N), 120.8 (N—CH=*C*H—N), 126.0 and 128.0 (CH—C_6H$_5$), 133.5 (CH_2=*C*H—N), 138.1 (N—*C*H—N), 158.3 (H*C*O_3).

Synthesis of 1-Vinyl-3-dodecylimidazolium Hydrogen Carbonate VDodeImHCO$_3$ (2d)

2d was prepared following a similar procedure to that used for the synthesis of **2a**.

^{1}H NMR (CD_3OD): δ 0.7 (t, C*H*$_3$(—CH_2—)$_{10}$$CH_2$, 3H), 1.2–1.3 (m, CH_3(—C*H*$_2$—)$_9$$CH_2$—$CH_2$, 18H), 1.7 (q, CH_3(—CH_2—)$_9$C*H*$_2$—CH_2, 2H), 4.1 (t, CH_3(—CH_2—)$_9$$CH_2$—C*H*$_2$, 2H), 5.4 (dd, *H*CH=CH—N, 1H), 5.92 (dd, *H*CH=CH—N, 1H), 7.26 (dd, CH_2=C*H*—N, 1H), 7.78 (s, N—CH=C*H*—N, 1H), 8.00 (s, N—C*H*=CH—N, 1H). ^{13}C NMR (CD_3OD): δ 15.1 (*C*H_3—CH_2—CH_2(—CH_2—)$_7$$CH_2$—$CH_2$—), 24.9 ($CH_3$—*C*$H_2$—$CH_2$(—$CH_2$—)$_7$$CH_2$—$CH_2$—), 28.2 ($CH_3$—$CH_2$—*C*$H_2$(—$CH_2$—)$_7$$CH_2$—$CH_2$—), 31.2 ($CH_3$—$CH_2$—$CH_2$(—*C*$H_2$—)$_7$$CH_2$—$CH_2$—), 34.7 ($CH_3$(—$CH_2$—)$_9$C*H*$_2$—$CH_2$—), 54.2 ($CH_3$—$CH_2$—$CH_2$—*C*$H_2$—), 110.5 (*C*$H_2$=CH—N), 122.8 (N—*C*H=CH—N), 124.1 (N—CH=*C*H—N), 130.9 (CH_2=*C*H—N), 137.3 (N—*C*H—N), 161.4 (H*C*O_3).

Synthesis of PVBuImBr (3b) by Polymerization of VBuImBr (1b)

In a typical experiment, a 10-mL Schlenk tube was flame dried and charged with 1 g (4.3 mmol) of **1b**, 12.7 mg (0.08 mmol) of AIBN and 4 mL of methanol. The Schlenk tube was subjected to five freeze-thaw cycles and placed in a thermostated oil bath previously maintained at 80 °C. The reaction was quenched after 3 h by sudden cooling with liquid

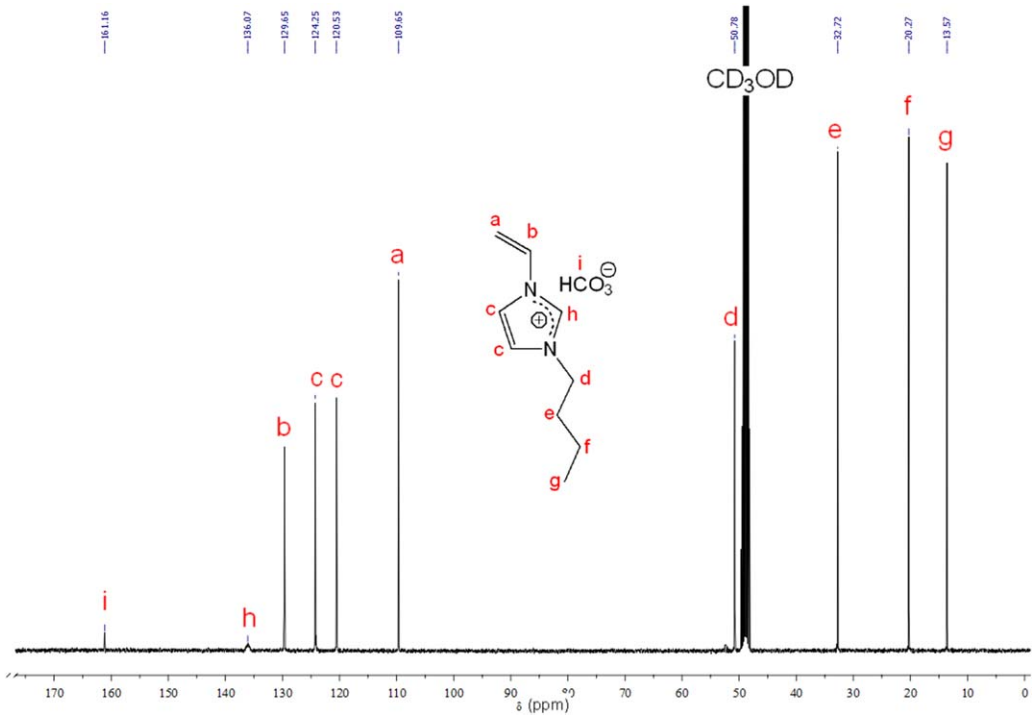


FIGURE 2 ^{13}C NMR spectrum of 1-vinyl-3-butylimidazolium hydrogen carbonate **2b** in CD_3OD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nitrogen. The resulting poly(1-vinyl-3-butylimidazolium) bromide (**3b**) was isolated by precipitation in acetone. After drying under vacuum, **3b** was obtained as a yellowish powder (yield 95%). $M_n = 25{,}000$ g mol^{-1} ($D = 1.45$) by SEC in H_2O/acid formic (0.3 M) (see Fig. 5).

^1H NMR (CD_3OD, see Supporting Information Fig. S7): δ 8.9–9.3 (br, N—C*H*—N, 1H), 7.3–7.8 (br, C*H*=C*H*, 2H), 3.9–4.5 (br, N—CH_2—CH$_2$—CH$_2$—CH$_3$, 2H), 4.4–4.8 (br, N—C*H*—CH$_2$, 1H), 2.4–3.0 (br, N—CH—CH_2, 2H), 1.7–2.1 (br, CH$_3$—CH$_2$—CH$_2$—CH$_2$—, 2H), 1.3–1.6 (br, CH$_3$—CH$_2$—CH_2—CH$_2$—, 2H), 0.9–1.2 (br, CH_3—CH$_2$—CH$_2$—CH$_2$—, 3H). PVEtImBr (**3a**), PVPhEtImBr (**3c**), and PVDodeImBr (**3d**) were obtained following a similar procedure.

Synthesis of PVEtImHCO$_3$ (4a, R = ethyl) by Polymerization of VEtImHCO$_3$

In a typical experiment, a Schlenk tube was flame-dried and charged with 1 g (5.43 mmol) of **2a**, 24.3 mg (0.09 mmol) of KPS and 10 mL of DMSO. The Schlenk tube was subjected to five freeze-thaw cycles before adding 10.1 μL (0.09 mmol) of DMAPN under argon flow. The reaction mixture was stirred for 24 h at room temperature. The obtained polymer was precipitated in acetone to remove residual monomer, filtrated, and dried under vacuum. **4a** was recovered as a yellowish powder (yield: 85%). $M_n = 29{,}000$ g mol^{-1} ($D = 2.3$) by SEC in H_2O/formic acid (0.3 M) (see also Fig. 5).

^1H NMR (CD_3OD, see Supporting Information Fig. S2): 1.4–1.7 (CH_3—CH$_2$, 3H), 2.4–2.7 (H_2C—CH—N, 2H), 4.1–4.4(CH_2—CH$_3$, 2H), 4.4–4.7 (H$_2$C—C*H*—N, 1H), 7.4–8.0 (N—C*H*=C*H*—N, 2H). ^{13}C NMR (CD_3OD, see Supporting Information Fig. S1) : δ 14.7 (CH_3—CH$_2$—), 40.9 (H$_2$C—C*H*—N), 58.3 (CH_2—CH$_3$),120.3 and 122.0 (N—C*H*=C*H*—N), 136.8 (N—C*H*—N), 160.9 (HCO_3).

Synthesis of PVBuImHCO$_3$ (4b, R = butyl) by Polymerization of VBuImHCO$_3$

4b was prepared following a similar procedure to that used for **4a** (yield: 98%). $M_n = 26{,}200$ g mol^{-1} ($D = 1.78$) by SEC in H_2O/formic acid (0.3 M) (see also Fig. 5).

^1H NMR (CD_3OD, see Fig. 3): 0.8–1 (br, CH_3—CH$_2$—CH$_2$—CH$_2$—, 3H), 1.2–1.4 (br, CH$_3$—CH_2—CH_2—CH$_2$—, 2H), 1.6–1.9 (br, CH$_3$—CH$_2$—CH_2—CH$_2$—, 2H), 2.1–2.4 (br, CH_2—CH—N, 1H), 3.7–4.1 (br, CH$_2$—C*H*—N, 1H), 4.2–4.7 (br,N—CH_2—CH$_2$—CH$_2$—CH$_3$, 2H), 7.5–8.0 (br, C*H*=C*H*, 2H), 9.5–10 (br, N—C*H*—N, 1H). ^{13}C NMR (CD_3OD, see Fig. 4): δ 13.5 (CH_3—CH$_2$—CH$_2$—CH$_2$—), 20.28 (CH$_3$—CH_2—CH$_2$—CH$_2$—), 32.0 (CH$_3$—CH$_2$—CH_2—CH$_2$—), 42.2 (CH_2—CH—N), 50.7 (CH$_3$—CH$_2$—CH$_2$—CH_2—), 54.2 (CH$_2$—C*H*—N), 120.8–122.3 (N—C*H*=C*H*—N), 137.1 (N—C*H*—N), 159.0 (HCO_3).

Synthesis of PVPhEtImHCO$_3$ (4c, R= 1-phenylethyl) by Polymerization of VPhEtImHCO$_3$

4c was prepared following a similar procedure to that used for **4a** (yield 95%).

^1H NMR (CD_3OD, see Supporting Information Fig. S4) : 1.7–2.1 (br, CH_3—CH—, D3H), 2.3–3.3 (br, H_2C—CH—N, 2H), 4.6–5.1 (br, CH$_2$—C*H*—N, 1H), 5.3–5.6 (br, C*H*— (CH$_3$)(C$_6$H$_5$), 1H), 7.2–7.7 (br, CH—C$_6H_5$, N—CH=C*H*—N, N—C*H*=CH—N, 7H). ^{13}C NMR (CD_3OD, see Supporting Information Fig. S3): 22.3 (CH_3—CH—), 41.4 (CH$_2$—CH—N), 60.2 (C*H*—(CH$_3$)(C$_6$H$_5$)),

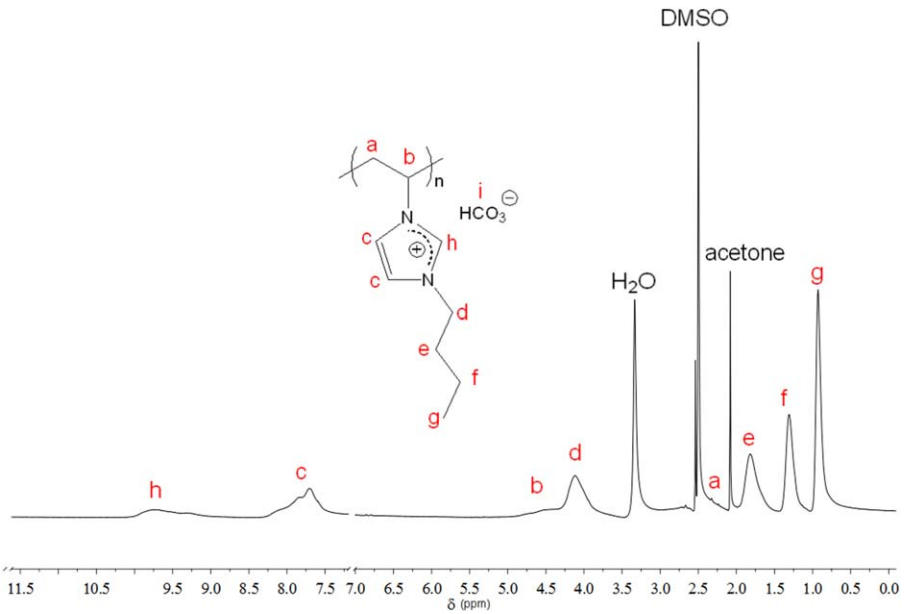


FIGURE 3 ^{1}H NMR spectrum of poly(1-vinyl-3-butylimidazolium hydrogen carbonate) salt **4b** in DMSO-d_6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

61.9 (CH_2—*C*H—N), 121.5 (N—*C*H=*C*H—N), 128.7–136.3 (CH—C_5H_5), 139.8 (N—*C*H—N), 161.4 (HCO_3).

Synthesis of $PVDodeImHCO_3$ (4d, R = dodecyl) by Polymerization of $VDodeImHCO_3$

4d was prepared following a similar procedure to that used for **4a** (yield: 68%).

^{1}H NMR (CD_3OD, see Supporting Information Fig. S6) δ 0.7–0.8 (br, CH_3(—CH_2—)$_{10}CH_2$, 3H), 1.2–1.1–1.4 (br, CH_3(—CH_2—)$_9CH_2$—CH_2, 18H), 1.7–2.0 (br, CH_3(—CH_2—)$_9$ CH_2—CH_2, 2H), 2.−2.5 (br, CH_2—CH—N, 2H), 4.1–4.3 (br, CH_3(—CH_2—)$_9CH_2$—CH_2, 2H), 4.3–4.5 (br, CH_2—CH—N, 1H), 7.5–8.0 (br, CH=CH, 2H). ^{13}C NMR (CD_3OD, see Supporting Information Fig. S5): δ 15.1 (CH_3—CH_2—CH_2(—CH_2—)$_7$ CH_2—CH_2—), 24.9 (CH_3—CH_2—CH_2(—CH_2—)$_7CH_2$—CH_2—), 28.2 (CH_3—CH_2—CH_2(—CH_2—)$_7CH_2$—CH_2—), 31.2 (CH_3—CH_2—CH_2(—CH_2—)$_7CH_2$—CH_2—), 34.7 (CH_3(—CH_2—)$_9CH_2$—CH_2—), 44.2 (CH_2—CH—N), 54.2 (CH_3—CH_2—CH_2—CH_2—), 122.8–124.2 (N—CH=CH—N), 137.3 (N—CH—N), 162.2 (HCO_3).

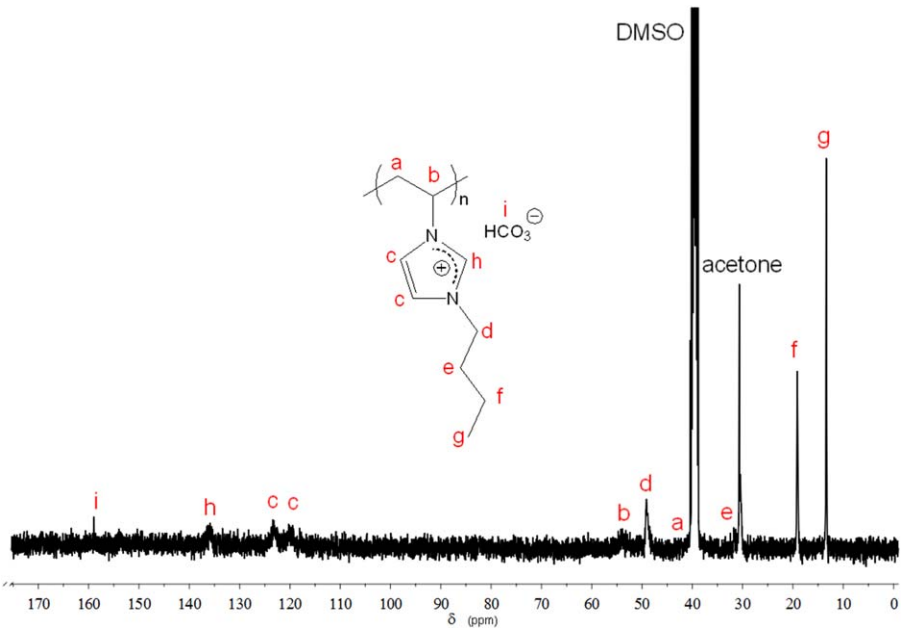


FIGURE 4 ^{13}C NMR spectrum of poly(1-vinyl-3-butylimidazolium hydrogen carbonate) salt **4b** in DMSO-d_6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

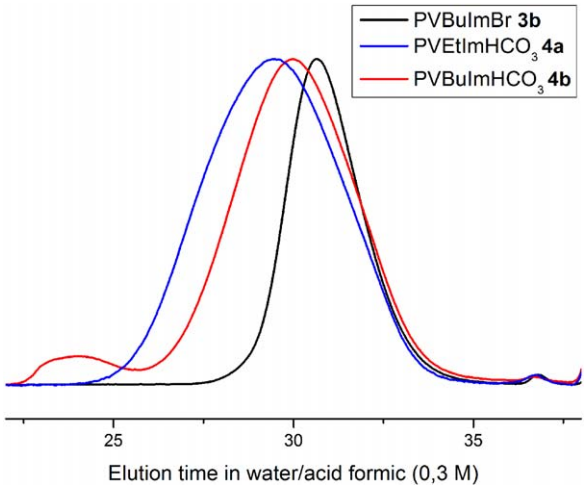


FIGURE 5 Aqueous SEC traces of PVBuImBr **3b**, PVEtImHCO$_3$ **4a** (entry 3, Table 1) and PVBuImHCO$_3$ **4b** (entry 4, Table 1) obtained by free radical polymerization in DMSO at rt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

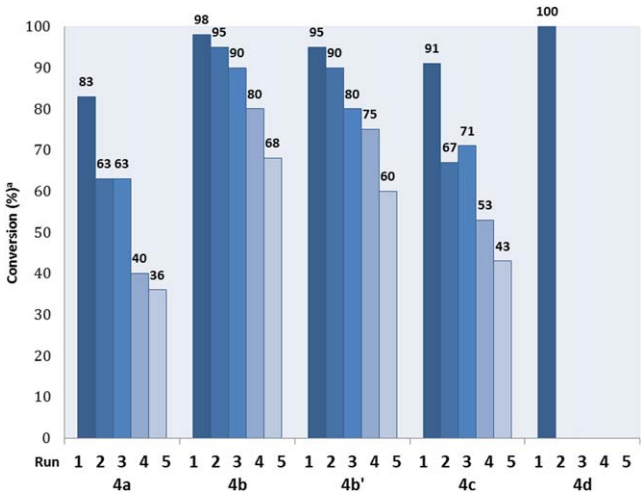


FIGURE 6 Results of the transesterification of benzyl alcohol (1 equiv) and vinyl acetate (1.2 equiv) in THF at 80 °C for 2 h in the presence of poly([NHC(H)][HCO$_3$]) **4** (see also Scheme 2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Synthesis of PVRImHCO$_3$ via Anion Exchange of PVRImBr

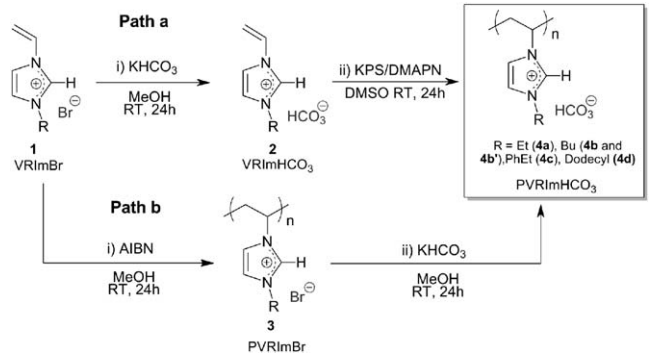
Poly(1-vinyl-3-alkylimidazolium bromide) (4 mmol) **3** were dissolved in dry methanol, and the resulting solution was added to a stirred solution of KHCO$_3$ (1.05 equiv), in methanol. The resulting suspension was stirred for 24 h at rt. After filtration over Celite, methanol was evaporated under vacuum to yield a sticky solid. After trituration of the solid with acetone and filtration, poly(1-vinyl-3-alkylimidazolium hydrogen carbonate) **4** was obtained as a yellowish powder and dried under dynamic vacuum (yield 95%). NMR data were in accordance with **4b** (see Figs. 3 and 4).

Catalytic Tests Using PVRImHCO$_3$ Salt Precursors

All catalytic tests were carried out under a dry and inert atmosphere, at rt and at 80 °C, using Schlenk equipments.

Transesterification

In a typical experiment (see Fig. 6), precursor **4** (0.5 mmol) was introduced in a Schlenk tube. The solid compound was allowed to stir for 1 h under vacuum and the flask was then subjected to three Ar/vacuum cycles. A 5 mL portion of THF, 0.5 mL (5 mmol) of benzyl alcohol, and 0.55 mL (6 mmol) of vinyl acetate were added. The reaction mixture was stirred for 2 h at 80 °C. Note that a suspension was obtained under these conditions owing to the nonsolubility of precursor **4a–c**. After the reaction mixture was allowed cooling to rt, 1 atm of CO_2 was added, to favor the formation of poly(1-vinyl-3-alkylimidazolium carboxylate) **6** from the corresponding poly(NHC) **5** (see Scheme 1). After stirring for 30 min, the mixture was filtered under vacuum, and the filtrate was analyzed by ^{1}H NMR in CDCl$_3$. Conversion in benzyl acetate was calculated by ^{1}H NMR in CDCl$_3$ (Supporting Information Fig. S8) by comparing the integral value of the —CH_2— benzyl alcohol signal (δ 4.5 ppm) to that of the —CH_2— benzyl acetate signal (δ 5 ppm). The recovered polymer was suspended in THF and reused for a next run of catalysis.



SCHEME 2 Synthesis of PVRImHCO$_3$ **4a–d** by anion exchange of VRImBr **1a–d**, followed by FRP of VRImHCO$_3$ **2a–d** (path a) and synthesis of PVRImHCO$_3$ **4b′** by FRP of VRImBr **1b** followed by anion exchange exchange of PVRImBr **3b** (path b).

Cyanosilylation

In a typical experiment (see Fig. 7), a Schlenk tube was charged with **4** (0.25 mmol), and the solid compound was allowed to stir for 1 h under vacuum and the flask was then subjected to three Ar/vacuum cycles. A 5 mL portion of THF followed by 0.5 mL (5 mmol) of benzaldehyde and 0.75 mL of TMSCN (6 mmol) were added. The rest of the procedure was identical to that described above for the transesterification reaction. Conversion in α-trimethylsilyloxy-phenylacetonitrile was determined by ^{1}H NMR in CDCl$_3$ (Supporting Information Fig. S9) by comparing the integral value of the aldehyde signal of benzaldehyde (δ 10 ppm) to that of the —CH— cyanide product (δ 5.5 ppm).

Benzoin Condensation

In a typical experiment (see Fig. 8), **4** (0.5 mmol) and molecular sieves were introduced into a Schlenk tube. The solid

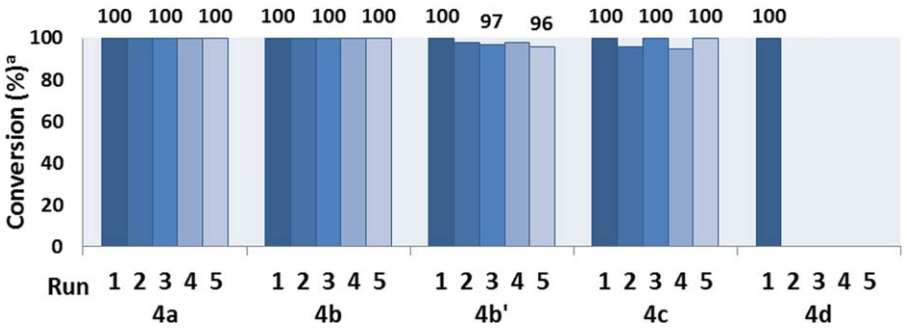


FIGURE 7 Results of the cyanosilylation of benzaldehyde and trimethylsilyl cyanide performed in THF at 80 °C for 1 h in the presence of poly([NHC(H)][HCO_3]) **4** (see also Scheme 2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixture was allowed to stir for 1 h under vacuum and the flask was then subjected to three Ar/vacuum cycles. A 5 mL portion of THF and then 0.5 mL (5 mmol) of benzaldehyde were added. The reaction mixture was stirred for 24 h at 80 °C. The rest of the procedure was identical to that dscribed above for the transesterification reaction. Benzoin conversion was determined by ^{1}H NMR in $CDCl_3$ (Supporting Information Fig. S10) by comparing the integral value of the aldehyde signal of benzaldehyde (δ 10 ppm) with that of the —C*H*— benzoin signal (δ 6 ppm).

RESULTS AND DISCUSSION

Synthesis of Poly(1-vinyl-3-alkylimidazolium hydrogen carbonate)s, 4

Poly(1-vinyl-3-alkyl imidazolium hydrogen carbonate)s **4** synthesized in this work, denoted as poly(VRImHCO_3)s or poly([NHC(H)][HCO_3])s, where R is an alkyl substituent (R = ethyl, butyl, phenylethyl, dodecyl), represent novel poly(ionic liquid)s (PILs).[54–60] As depicted in Scheme 2, synthesis of these specific PILs could be achieved following two distinct routes that did not require the prior formation of poly(NHC) precursors, in contrast to our previous work.[35]

The first synthetic method is based on the free-radical polymerization (FRP) of 1-vinyl-3-alkylimidazolium monomers featuring a hydrogen carbonate (HCO_3^-) counter anion, denoted as VRImHCO_3 (Scheme 2, path a). The latter monomers were readily synthesized by alkylation of 1-vinylimidazole (VIm), followed by direct anion exchange of 1-vinyl-3-alkylimidazolium bromide (VRImBr) monomers, using potassium hydrogen carbonate ($KHCO_3$) in methanol, at room temperature. This method could be generalized to VRImBr monomers carrying various alkyl substituents in 3-position. Four different VRImBr monomers **1a–d** were thus synthesized by quaternization of VIm, using various alkyl (1-phenylethyl, *n*-butyl, ethyl and *n*-dodecyl) bromides, following a well-established procedure.[35,61–63] The four corresponding VRImHCO_3 monomers **2a–d** (R= ethyl, *n*-butyl, 1-phenylethyl and *n*-dodecyl) were next obtained by anion exchange on the basis of our recent reports on molecular imidazolium precursors.[41,44] The novel VRImHCO_3 monomers were characterized by ^{1}H and ^{13}C NMR spectroscopy. Figures 1 and 2 show the NMR spectra of the VBuImHCO_3 **2b** compound. Analysis by ^{1}H NMR in CD_3OD did not allow stating on the quantitative anion exchange, from bromide to hydrogen carbonate (Fig. 1); chemical shifts of protons of the imidazolium backbone were similar to that of the starting material **1b**. In contrast, the characteristic signals of both the N_2CH carbon and the HCO_3^- quaternary carbon atoms were observed by ^{13}C NMR at 136.0 and 161.1 ppm, respectively (Fig. 2). All other signals observed both on the ^{1}H and ^{13}C NMR spectra were consistent with data reported on molecular imidazolium hydrogen carbonate homologs.[41]

Synthesis of PILs by free-radical polymerization (FRP) of 1-vinyl-3-alkylimidazolium is well-documented.[54–60] FRP of VRImHCO_3 monomers **2a–d** was investigated under different conditions, as summarized in Table 1. For instance, attempts to polymerize **2b** using either azobis(2-methylpropionitrile) (AIBN) or 4,4′-azobis(4-cyanovaleric acid) (V-501) as a radical source at 80 °C were not successful, neither in DMSO nor in MeOH as solvent (entry 1). We hypothesized that a too high temperature (80 °C) could lead to the degradation of VRImHCO_3 monomers **2**. 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) was then employed as initiator at 40 °C,

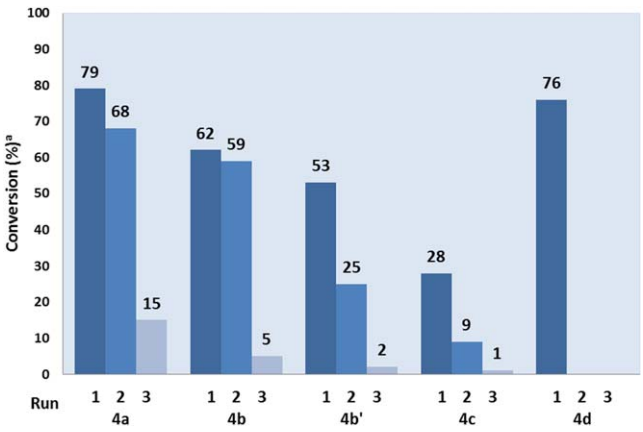


FIGURE 8 Results of the benzoin condensation from benzaldehyde performed in THF at 80 °C for 24 h in the presence of poly([NHC(H)][HCO_3]) **4** (see also Scheme 2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 1 Free-Radical Polymerization of $VRImHCO_3$ Monomers **2**

Entry	Monomer	Initiator[a]	T (°C)	Solvent	Time (h)	Conv. (%)[b]	$\overline{M}_n$ (g mol^{-1})[c]	D[c]
1	**2b**	AIBN or V-501	80	DMSO or MeOH	144	0	–	–
2	**2b**	V-70	40	DMSO	72	30	–	–
3	**2a**	KPS/DMAPN	R.T.	DMSO	18	85	29,000	2.30
4	**2b**	KPS/DMAPN	R.T.	DMSO	18	98	26,200	1.78
5	**2b**	KPS/DMAPN	R.T.	MeOH	18	40	–	–
6	**2c**	KPS/DMAPN	R.T.	DMSO	18	95	–[d]	–[d]
7	**2d**	KPS/DMAPN	R.T.	DMSO	18	68	–[d]	–[d]

[a] A [monomer]/[initiator] ration equal to 60:1 was used.
[b] Conversion was calculated by ^{1}H NMR from the disappearance of the signal at 7.2 ppm and appearance of signal at 0.8 ppm corresponding to the polymer.
[c] Molecular weight and dispersity were determined by SEC in water/formic acid (0.3 M) calibrated with poly(2-vinyl pyridine).
[d] Molecular weight ant dispersity were not determined due to the insolubility of corresponding polymer in aqueous solvent used for SEC.

which allowed the polymerization to proceed, albeit with a low conversion after a reaction time of 72 h (entry 2). In contrast, the redox initiating system utilizing potassium persulfate (KPS) and dimethylaminopropionitrile (DMAPN) at room temperature (rt) enabled quantitative conversion of monomer **2b** in DMSO, after 18 h (entry 4), whereas a low conversion was noted in MeOH, likely owing to the poor solubility of KPS in the latter solvent (entry 5). All monomers **2a–d** were thus efficiently polymerized in DMSO at rt in the presence of KPS/DMAPN, providing polymers, $PVRImHCO_3$ **4a–d**, in near quantitative yields (Table 1). Although the possibility of anion exchange between KPS and $PVRImHCO_3$ cannot be ruled out, this exchange reaction could not be evidenced.

Characterization of these polymers by ^{1}H NMR spectroscopy confirmed the expected structure (Experimental and ESI). In particular, the signal corresponding to the C*H* proton of the imidazolium moiety could be clearly identified at 9–10 ppm. In addition, signals due to the vinylic protons of monomers at 5.4–6 ppm completely vanished, while protons of monomer units C*H*—CH_2 were observed at 4–4.3 ppm (Figs. 3 and 4 and Supporting Information Figs. S1 and S6). While all signals were broadened after polymerization, that corresponding to the H*C*O_3^- carbon atom at 160.0 ppm was found as sharp as in the ^{13}C NMR spectrum of monomer **2** (Fig. 4).

Characterization of PILs by size exclusion chromatography (SEC) is often challenging owing to interactions of these polylectrolytes with SEC columns.[64] Very recently, however, Matyjaszewski et al. reported a "universal" method to analyze well-defined PILs based on imidazolium-based with bis(-trifluoromethanesulfonyl)imide ($^-NTf_2$) counter-anions, by employing THF as eluent in presence of the same $^-NTf_2$ anion. In the present work, analysis of some polymers (PVBuImBr **3b**, $PVEtImHCO_3$ **4a** and $PVBuImHCO_3$ **4b**) by aqueous SEC showed a unimodal molecular weight distribution in each case (Fig. 5), with a dispersity between 1.4 and 2.3. Due to the nonsolubility of **4c** and **4d** in water, analysis of these polymers by aqueous SEC could not be carried out.

An alternative synthetic route to $PVRImHCO_3$ **4** consisted in applying the same anion exchange method described above to FRP-derived poly(1-vinyl-3-alkylimidazolium bromide)s, PVRImBr **3** (Scheme 1, path b). The FRP of VRImBr monomers **1** was already reported.[35,54–56,65,66] For instance, PVBuImBr **3b** was synthesized in methanol using AIBN as a radical source at 80 °C. Characterization of **3b** by ^{1}H NMR spectroscopy confirmed the expected structure (Supporting Information Fig. S7). Corresponding $PVBuImHCO_3$ **4b′** was obtained by anion exchange of **3b** with $KHCO_3$ in methanol at rt for 24 h (see Scheme 2). A similar yellowish powder to **4b** (path a) was obtained, with identical ^{1}H and ^{13}C NMR spectra.

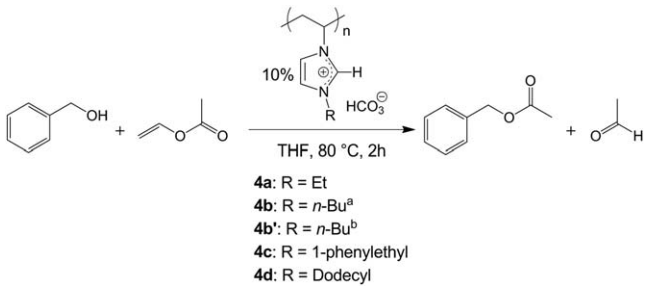
Thus, synthesis of novel 1-vinyl-3-alkyl imidazolium-based PILs with hydrogen carbonate as counter-anion could be readily achieved, following two distinct routes both relying on a simple and direct anion exchange, from Br^- to HCO_3^-.

Use of Poly(1-vinyl-3-alkyl imidazolium hydrogen carbonate)s 4 in Organocatalysis

The potential of poly(vinylimidazolium hydrogen carbonate) salts **4a–d** and **4b′** (see Scheme 2) as polymer-supported precatalysts was then explored. Here we provide our preliminary results regarding their catalytic potential, without a real investigation into the optimization of the catalytic efficiency. It is well established, indeed, that polymer-supported catalysts with optimized catalytic properties requires a specific design and a systematic and logical approach, from the precise understanding of the mechanism of elementary catalytic reactions.[67] Various parameters can be manipulated, including the nature of the polymer support, the nature of the linker, catalyst density along the polymer support, and the nature of the connectivity of the catalyst to the support.

Here, polymers **4a–d** and **4b′** were expected to *in situ* generate poly(NHC)s **5**, as illustrated in Scheme 1, by analogy with their molecular versions.[35] In this regard, **4a–d** and **4b′** are also denoted as poly[NHC(H)][HCO_3]s.

Three different organocatalyzed reactions of molecular chemistry were implemented, namely, transesterification,[35,68–70] benzoin condensation[35,36,70,71] and cyanosilylation of aldehydes,[72,73] known as being efficiently catalyzed by both molecular NHCs and ([NHC(H)][HCO_3]) salt precursors.[44]



SCHEME 3 Use of poly([NHC(H)][HCO_3]) **4** as polymer-supported precatalysts of transesterification between vinyl acetate and benzyl alcohol (see also Scheme 2).

Similar experimental conditions were used for all organocatalytic tests: reagents and polymer salt precursors **4** were mixed in THF and stirred at 80 °C for 1, 2, or 24 h, depending on the implemented reaction. It is worth pointing out, however, that **4** were not soluble under such conditions, organocatalyzed reactions taking place heterogeneously, except in the case of precursor **4d** carrying the dodecyl group on the imidazolium ring. Moreover, access to the NHC catalytic sites—generated from [NHC(H)][HCO_3] units—might be reduced because of the close vicinity of NHCs to the polymer backbone (short linker) and the steric hindrance brought by the alkyl group on the imidazole ring. It is therefore likely that the *in situ* generation poly(NHC)s from poly[-NHC(H)][HCO_3] **4a–d** and **4b′** was not complete. This also explained why a catalytic amount of up to 10%mol. of these polymer-supported precatalysts was employed, while molecular versions, [NHC(H)][HCO_3], required only 0.1–1% mol at room temperature for the same reactions.[44]

Addition of CO_2, at rt, at the completion of each tested reaction, allowed retrieving polymer-supported precatalysts, presumably co-existing in the form of a mixture of poly[NHC(H)][HCO_3] **4** and poly[NHC-CO_2] adducts **6** (see Scheme 1). The as-recovered polymers could thus be filtered off and recycled.

In a typical transesterification reaction, benzyl alcohol (BnOH) and vinyl acetate (VAc) were added to a THF solution containing poly[NHC(H)][HCO_3] salts **4**, and the reaction was stirred for 2 h (Scheme 3). Analysis by ^{1}H NMR spectroscopy of the filtrate confirmed the formation of benzyl acetate and the conversion could thus be determined.

All poly([NHC(H)][HCO_3]) salts exhibited an excellent catalytic activity at the first run, providing excellent conversion of benzyl acetate (83–100%), irrespective of the nature of the alkyl substituent on the imidazolium ring (Fig. 6). This indicated that free poly(NHC)s **5** were efficiently generated at 80 °C, at least partially, from the poly([NHC(H)][HCO_3]) salt precursors, formally by loss of H_2CO_3. In contrast, the same precursors did not show any catalytic activity at rt.

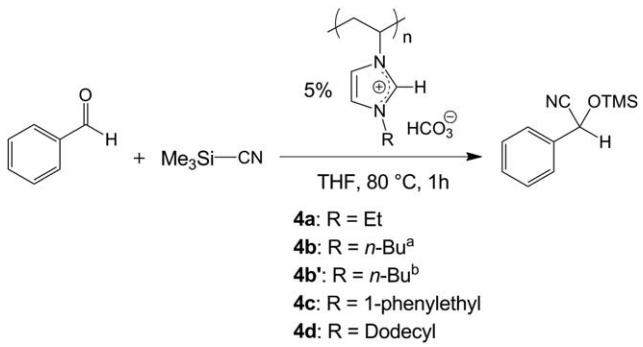
Fairly good conversions (63–98%) were achieved with **4a–c** and **4b′** over 3 runs of organocatalysis, attesting to an efficient recycling with no significant loss of catalytic activity. Precursors **4b** and **4b′**, obtained from path a and path b, respectively (Scheme 2), showed the same catalytic efficiency for this transesterification reaction, indicating that the structure of both polymers was very similar. The poly([NHC(H)][HCO_3]) precursor **4d** allowed reaching a complete conversion in benzyl acetate after the first run (Fig. 6). However, **4d** (or **6d**, Scheme 1) could not be recovered by re-carboxylation due to its solubility in THF, unlike **4a–c** (or **6a–c**). The catalytic efficiency of the latter precursors however decreased progressively with the number of cycles, which might be explained by uncomplete re-incorporation of CO_2 and/or of partial deactivation of *in situ* generated poly(NHC)s **5a–c**.

Precursors **4a–d** were then investigated as polymer-supported precatalysts for the cyanosilylation of benzaldehyde with trimethylsilyl cyanide (TMSCN), another NHC-catalyzed molecular reaction.[72,73] Only one report previously described the use of some polymer-supported version of NHC precursors for this reaction (1 mol % of catalyst, rt, 10 min).[74] Results of the cyanosilylation of benzaldehyde with TMSCN catalyzed by 5%mol. of **4a–d** in THF for 1 h (Scheme 4) are presented in Figure 7.

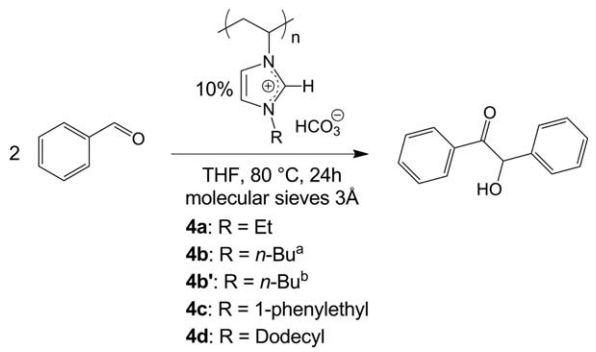
Excellent yields were obtained with **4a–c** and **4b′** up to five catalytic cycles, meaning that all polymer-supported NHC precursors could be readily recycled after carboxylation, without any significant loss of catalytic activity (Fig. 7). For the same reason mentioned above, the THF soluble precursor **4d/6d** could not be recycled, though also providing a quantitative conversion after the first run of organocatalysis.

Then, we examined the catalytic potential of poly([NHC(H)][HCO_3])s **4** for the benzoin condensation, a NHC-catalyzed self-condensation of benzaldehyde forming a β-keto alcohol called benzoin.[35,36,70,71] Reactions were carried out in THF for 24 h at 80 °C, in the presence of 10%mol. of **4** (Scheme 5).

The first catalytic cycle led to benzoin in rather good yield (62–79%) with **4a–b′** and **4d**. In contrast, poor yield (28%) in benzoin was obtained with **4c** after the first run of catalysis. This might be ascribed to the poorer solubility of poly([-NHC(H)][HCO_3]) **4c** in the reaction mixture compared to the other precursors, the corresponding poly(NHC) being more hardly generated or prematurly deactivated. The slow kinetic



SCHEME 4 Use of poly([NHC(H)][HCO_3]) **4** as polymer-supported precatalysts of the cyanosilylation of benzaldehyde with trimethylsilyl cyanide (see also Scheme 2).



SCHEME 5 Use of poly([NHC(H)][HCO_3]) **4** as polymer-supported precatalysts of the benzoin condensation of benzaldehyde (see also Scheme 2).

of the reaction did not allow us to efficiently recycle the polymer precatalyst. A significant decrease of the yield was also noted in the second catalytic cycle both for **4b**′ and **4c** (25 and 9%, respectively), whereas the yield decreased only at the third run both with **4a** and **4b** (5 and 15%, respectively). Increasing the reaction time to 48 h did not allow improving the generation of free poly(NHC)s **5** from **4**, as conversions were close to those obtained after 24 h. Overall, results of the benzoin condensation utilizing polymer precursors **4** are consistent with our previous observations when poly(NHC-CO_2) adduct homologues were employed:[35] the reaction is rather slow, yields drop after a few cycles, and polymer-supported precatalysts can be hardly recycled.

CONCLUSIONS

Novel poly(ionic liquid)s, namely, poly(1-vinyl-3-alkyl imidazolium hydrogen carbonate)s, poly([NHC(H)][HCO_3]), can be readily accessed and serve as air stable polymer-supported precatalysts for organocatalyzed molecular reactions. The *in situ* generation of related polymer-supported NHCs, poly(NHC)s, occurs by a loss of H_2CO_3 (H_2O + CO_2). Recarboxylation of poly(NHC)s allows easily recycling polymer precursors and reusing them for several organocatalytic cycles, especially for transesterification and cyanosilylation reactions. Excellent catalytic activities could be achieved for the latter reactions, whereas benzoin condensation requires longer reaction times, and did not allow efficiently recycling the polymer-supported precatalysts, presumably owing to premature deactivation of poly(NHC)s under forcing conditions. Further optimization of the organocatalytic properties of poly([NHC(H)][HCO_3]) precursors would be needed *via* a systematic approach, including, for instance, the introduction of a spacer group between NHC monomer units and the polymer backbone, and manipulation of the organocatalyst density *via* statistical copolymerization. These experiments are ongoing in our group. We are also currently exploring the potential of these poly(NHC) precursors for further post-polymerization modification, taking benefit of NHC units to selectively react with various substrates at stoichiometry (e.g., transition metals, azides, or thiocyanates).

ACKNOWLEDGMENTS

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