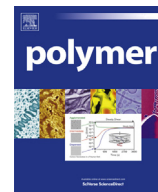




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## Post-polymerization modification and organocatalysis using reactive statistical poly(ionic liquid)-based copolymers

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### ABSTRACT

Copoly(ionic liquid)s (coPILs) based on poly(styrene)-*co*-poly(4-vinylbenzylbutylimidazolium) with different anions ( $\text{Cl}^-$  and  $\text{HCO}_3^-$ ), denoted as PS-*co*-PVBnBulmCl **1** and PS-*co*-PVBnBulmHCO<sub>3</sub> **2**, were used as reactive polymers for the purpose of post-polymerization modification and organic catalysis. While coPIL **1** could be derived into the corresponding poly(*N*-heterocyclic carbene)-silver transition metal complex referred to as poly(NHC–Ag) by a simple deprotonation/metallation sequence utilizing Ag<sub>2</sub>O, coPIL **2** was found to quantitatively react with various electrophiles, including CS<sub>2</sub>, isothiocyanate and transition metals (based on Pd and Au) upon formal loss of “H<sub>2</sub>CO<sub>3</sub>”, affording the post-functionalized poly(NHC–CS<sub>2</sub>), poly(NHC–isothiocyanate) and poly(NHC–Met) (Met = Au, Pd) copolymers. The catalytic activity of both coPILs **1** and **2** was also examined in cyclic carbonate formation by reaction between CO<sub>2</sub> and propylene oxide and in the benzoin condensation, respectively.

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### 1. Introduction

Post-polymerization modification, also referred to as polymer-analogous modification, is part of the common polymer-chemistry toolbox [1–3]. This method consists of synthesizing new polymers by modification of naturally occurring macromolecules or preformed synthetic polymers. These precursors carry handles that can be converted into other functional groups, in a subsequent step of chemical modification. Esterification of cellulose [4,5], crosslinking of polyisoprene by vulcanization [6], or methanolysis of poly(vinyl acetate) [7] are representative examples of post-polymerization modification reactions that are implemented at the industrial level. In recent years, various chemical reactions showing a very high chemoselectivity and/or orthogonality have been adapted to modify “tailor-made” chain-growth polymer precursors carrying handles, enabling the design of functional polymers that would be hardly accessible by a normal direct (co) polymerization technique.

A typical example is the nucleophilic substitution of polymeric activated esters, the synthesis of which can be achieved from

miscellaneous monomers (e.g. *N*-(meth)acryloxysuccinimide [8,9], pentafluorophenyl(meth)acrylate [10], *p*-nitrophenylacrylate [11], etc.), either by (controlled) radical polymerization or by metal-catalysed polymerization.

Many other reactive polymer precursors have served for polymer-analogous modification, for instance, polymers bearing anhydrides, isocyanates, oxazolones, epoxides, aldehydes or ketones that can be engaged in various chemical reactions [12–14]. Modification of preformed polymers by Michael-type addition reaction [15], by thiol exchange, radical thiol reaction [16,17], by the Huisgen 1,3-dipolar cycloaddition reaction [18,19], or by palladium-catalyzed coupling and cross-coupling reactions [20,21] have also been reported.

In this contribution, we wish to explore the reactivity of poly(ionic liquid) (PIL)-based precursors for polymer-analogous modification, and for organocatalysis as well. PILs have emerged as a special class of polyelectrolytes combining the inherent features of ionic liquids (ILs), such as thermal stability, high solid ionic conductivity, or adaptable solubility, with the intrinsic properties of polymers, including mechanical stability and processability [22–27].

Some ILs [28–30] and PILs [31–33] were demonstrated to behave as efficient catalysts (or precatalysts) in selected reactions. In particular, both imidazolium-based ILs and PILs can generate

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*N*-heterocyclic carbenes (NHCs) and poly(NHCs), respectively, for the purpose of organocatalysis [34–39]. A common route to *in situ* generate NHCs or poly(NHCs) is the deprotonation of the acidic proton of imidazol(in)ium IL units by a strong base [40]. However, masked NHCs, e.g. in the form of NHC–Ag(I) complexes [41,42] or NHC–CO<sub>2</sub> adducts [43,44], or 2-alkoxy [45] and trichloromethyl adducts [46], have proved of practical use for organocatalyzed reactions or to transfer the NHC moiety to transition metals. In this context, our group has shown that imidazolium hydrogen carbonate salts, denoted as [NHC(H)][HCO<sub>3</sub>], can also serve as a source of NHCs, formally by a loss of “H<sub>2</sub>CO<sub>3</sub>” (H<sub>2</sub>O + CO<sub>2</sub>) [34–36]. Polymeric versions of these salts, i.e. poly([NHC(H)][HCO<sub>3</sub>])s, were also used as air-stable and recyclable precursors for facile organocatalysis [32]. However, although some molecular NHCs and [NHC(H)][HCO<sub>3</sub>] precursors can quantitatively react with organic and organometallic substrates (e.g. CS<sub>2</sub>, isothiocyanate, or transition metals) [34,35], similar stoichiometric functionalization of homoPILs derived from *N*-vinyl imidazolium hydrogen carbonate met with very limited success [47]. This issue for promoting the quantitative reaction of NHC units from poly(*N*-vinyl imidazolium hydrogen carbonate) was attributed to the poor solubility of the starting materials, and to the high density of the reactive carbenic centres in close vicinity of the polymer backbone.

In this contribution, we demonstrate that statistical poly(ionic liquid)-based copolymers (coPILs) -of poly(*N*-vinylbenzyl imidazolium)-type instead of a poly(*N*-vinyl imidazolium) backbone- can serve as a reactive polymer precursors for various post-chemical modifications, and for organocatalysis as well. As illustrated in Fig. 1, here we wish to highlight the reactivity of simple PIL precursors towards miscellaneous substrates.

Thus, coPIL **2** obtained by anion metathesis from coPIL **1** can react, in a stoichiometric fashion, not only with electrophilic organic substrates, such as CS<sub>2</sub> or isothiocyanate, affording corresponding polybetaines, but also with transition metals, such as Pd, Ag and Au, yielding poly(NHC–Met) complexes (Met = Pd, Ag, Au), upon formal loss of “H<sub>2</sub>CO<sub>3</sub>”. In addition, coPIL **2** can efficiently catalyse the benzoin condensation. Synthesis of a poly(NHC–Ag) complex can also be achieved by direct metallation of coPIL **1** with silver oxide (Ag<sub>2</sub>O), while **1**, as such, is catalytically active in the synthesis of cyclic carbonate from the reaction of CO<sub>2</sub> with propylene oxide.

## 2. Results and discussion

Synthesis of poly(styrene)-*co*-poly(4-vinylbenzylalkyl imidazolium chloride) has been scarcely described in the

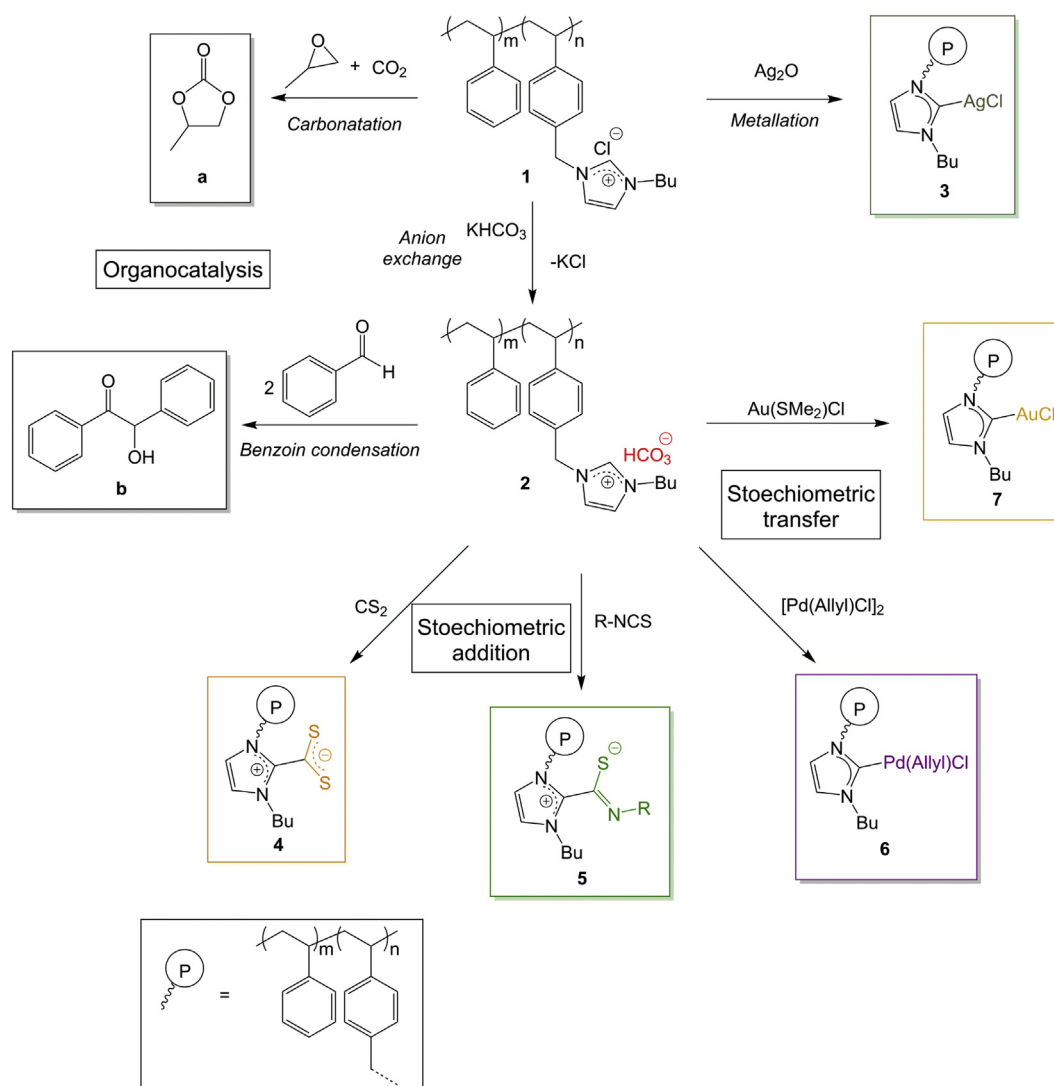


Fig. 1. Copoly(ionic liquid)s, PS-*co*-PVBnBulmCl **1** and PS-*co*-PVBnBulmHCO<sub>3</sub> **2** for various post-polymerization modifications.

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