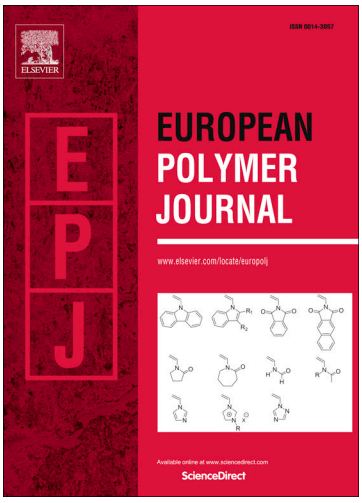

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Facile Synthesis of Reversibly Crosslinked Poly(ionic liquid)-type Gels: Recyclable Supports for Organocatalysis by *N*-Heterocyclic Carbenes

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ABSTRACT:

Owing to their broad modularity, polymeric versions of ionic liquids, referred to as poly(ionic liquids) (PILs), have attracted increasing attention as recyclable polymer-supported (pre)catalysts for various chemical transformations. Herein, an imidazolium-based statistical copolymer based on PIL (= coPIL) is specifically designed by free-radical copolymerization of styrene and 4-vinylbenzylethyl(benz)imidazolium chloride. A selective ion-exchange reaction can be subsequently achieved to incorporate bio-sourced difunctional sebacate-type counter-anions, causing the physical crosslinking of the coPIL precursor via electrostatic interactions between pendant imidazolium moieties and sebacate dianions. The as-obtained gel-type precursor exhibits a thermally latent behavior in THF, proving advantageous for a facile manipulation and practical use for organocatalysis. Upon heating, typically at 80 ºC, interaction between the sebacate dianion and the proton in C2-position of the imidazolium moieties generates polymer-supported *N*-heterocyclic carbene units that act as catalytic active species towards NHC-organocatalyzed reactions, namely, benzoin condensation, transesterification and cyanosilylation. The PIL-based gel precursors can be restored, recycled and reused by simply cooling down, *i.e.* with no need of an external chemical reagent, due to the shift of the intramolecular equilibrium towards the formation of imidazolium sebacate-type units. Overall, this novel gel-type copolymeric platform shows a thermo-responsive behaviour, and proves particularly versatile for heterogeneous organocatalysis.

KEYWORDS: *N*-Heterocyclic carbene, organocatalysis, poly(ionic liquid), masked-carbene