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Exploiting the Reversible Dimerization of *N*-Heterocyclic Carbenes to Access Dynamic Polymer Networks with an Organocatalytic Activity

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ABSTRACT: The capability of some *N*-heterocyclic carbenes (NHCs) to reversibly dimerize is exploited to access dynamic polymer networks. Benzimidazolium motifs serving as NHC precursors have thus been supported onto copolymer chains by reversible addition fragmentation chain transfer (RAFT) copolymerization of styrene and up to 20% mol. of 4-vinylbenzyl-ethyl-benzimidazolium chloride. Molecular versions of 1,3-dialkyl benzimidazolium salts have first been synthesized as models, the deprotonation of which with a strong base yields the NHC dimers in the form of tetraamino-alkenes. The crossover reaction between two distinct NHC homodimers, forming heterodimers, is then evidenced. Applying this deprotonation method to the RAFT-derived copolymers leads to polymer networks, with cross-links consisting of labile dimerized NHC motifs. These networks can be subsequently de-cross-linked using two distinct triggers, namely, a monofunctional NHC precursor as competitor, and carbon dioxide (CO₂). In the latter case, regeneration of the network occurs by chemically fueling the linear copolymer bearing benzimidazolium motifs with *t*BuOK in the presence traces of H₂O. The same networks can also be used as latent precursors of transient polyNHCs to catalyze the benzoin condensation upon heating. The polymer-supported organocatalysts can thus be used in successive catalytic cycles.

Since pioneering works by Bertrand *et al.*¹ and Arduengo *et al.*,² a variety of stable singlet carbenes have been isolated. In particular, cyclic diaminocarbenes, referred to as *N*-heterocyclic carbenes (NHCs), are among the most studied reactive species in chemistry.³ Owing to their strong σ -donor properties, NHCs are widely employed as Lewis bases, not only as ligands for transition metals, but also as organic catalysts for (macro)molecular synthesis.^{4,5} On the other hand, the use of carbenes as building blocks for polymer chains is relatively well documented.⁶⁻⁹ One strategy involves the chain-growth polymerization of carbene precursors, in the form of diazoacetates, referred to as C1-polymerization, affording poly(alkoxycarbonylmethylene)s bearing an alkoxycarbonyl group on every carbon atom (Figure 1a).¹⁰⁻¹⁴ C1-polymerization typically uses palladium or rhodium catalysts under homogeneous conditions, which in some cases, show a “controlled/living” character, enabling the synthesis of well-defined polymers and block-copolymers.¹⁵⁻¹⁸ Another strategy is to engage carbenes in step-growth polymerizations (Figure 1b). This approach takes advantage of the ability of some carbenes - in this case bis-carbenes- i) to selectively dimerize^{19,20} or ii) to react with antagonistic difunctional monomers, *e.g.* divalent metal precursors^{21,22} or bifunctional carbodiimides (CDI's).²³ Carbene dimerization provides a useful way to construct C=C double bonds and is well documented in molecular chemistry.²⁴⁻²⁶ In polymer science, bis-benzimidazol-2-ylidenes were reported to undergo such a dimerizing step-growth polymerization to produce thermally reversible dynamic conjugated linear polymers.^{19,20} Poly(phenylene vinylene)-type polymers could also be achieved from bis-diazo- or bis-iminium-type precursors generating bis-carbenes *in situ*, in this case of non-NHC-types.²⁶⁻²⁸ Following a step-growth polymerization principle forming NHC-CDI monomer units, main-chain zwitterionic poly(azolium amidinate)s were also designed.²⁹

Examples where carbenes have been used as cross-linking agents to access polymer networks are scarcer. Trifluoromethyl aryl diazirines were designed for polymer cross-linking (Figure 1c).^{30,31} Upon activation with light or heat, the diazirine group loses nitrogen (N₂), releasing a reactive bis-carbene able to insert into C-H bonds of a range of polymers.³² Carbene-mediated polymer cross-linking employing rationally designed diazo-type carbene cross-linker precursors has also been reported recently.^{33,34} Thermal decomposition generates the corresponding multifunctional carbenes to cross-link linear polymer chains by C-H insertion. Very recently, a platform based on diazirine polymers was developed for efficient cross-linking of C-H-containing polymers, such as poly(meth)acrylates.³⁵ These examples, however, refer to permanently cross-linked polymers with a fixed topology. While this allows improving the mechanical performances of thermoplastics, the presence of non-dynamic cross-links impedes these materials to be recycled, which raises the general concern of their end-of-life. To tackle this challenge,³⁶⁻³⁸ degradable or dynamic cross-links featuring carbonate, oxalate or silyl ether cleavable bonds based on carbenic species deriving from bis-diazirine cross-linkers have been reported.³⁹

In the present work, we leverage the ability of benzimidazolylidene-type NHCs to dimerize into their enamine-type homodimers as a means to design dynamic polystyrene (PS) networks (Figure 1d). As cross-linking points consist of reversible covalent bonds, we show that it is possible to de-cross-link these PS networks by simple addition of CO₂ as chemical fuel, so as to reform soluble copolymers, and then to re-cross-link the latter, with this time *t*BuOK as fuel. Moreover, these copolymer networks exhibit catalytic activity upon heating, as the NHC dimers constitute masked forms of NHCs. As a proof of concept of their robustness for organocatalysis, we have successfully conducted benzoin condensation reactions and show that these networks can be readily recycled and reused.

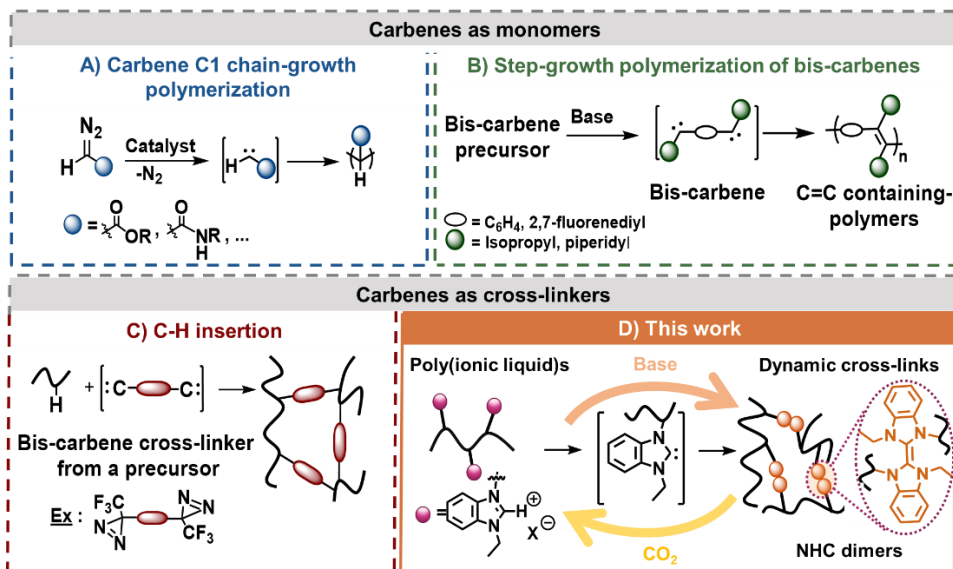


Figure 1. Synthetic strategies employing carbenes as building blocks for polymer synthesis: A) C1-chain polymerization of carbene precursors; B) step-growth polymerization involving bis-carbenes; C) C-H insertion-mediated polymer crosslinking using bis-carbene precursors as crosslinkers; D) NHC dimerization-mediated polymer crosslinking and CO_2 -fueled decrosslinking of polymer network.

Dimerization of NHCs can be made reversible depending on the nature of the carbenes.^{40,41,42} Although the principle of dynamic exchange between distinct NHC homodimers was established,^{43,44} we wanted to first synthesize NHC dimers from 1,3-dialkyl benzimidazolium salts, to ensure about the efficiency and dynamics of this exchange. The synthesis of these homodimers and the principle of the exchange reaction are illustrated in Figure 2A (see also ESI). 1,3-Diethylbenzimidazolium bis(trifluoromethanesulfonyl)imide (**3a**) and 1,3-dimethylbenzimidazolium bis(trifluoromethanesulfonyl)imide (**3b**) were synthesized following a three-step procedure, involving alkylation of benzimidazole, leading to **1a** and **1b**, followed by a quaternization reaction, yielding **2a** and **2b**. An anion exchange metathesis reaction, from the halide to the bis(trifluoromethanesulfonyl)imide, generated **3a** and **3b**.⁴⁵ Addition of *t*BuOK then enables the C2-position of benzimidazolium rings of **3a** and **3b** to be deprotonated, yielding the homodimers **4a-DiEt** and **4b-DiMe**. Not only was the chemical structure of the as-obtained homodimers authenticated by mass spectrometry and by ^1H and ^{13}C NMR (Figure S5-S12), but it was also found consistent with reported data for dimerized NHCs.^{22,46-48} For instance, the diagnostic signal of the quaternary carbon atom of the C=C bond was observed at 118.28 ppm. Synthesis of **4a-DiEt** and **4b-DiMe** was also successful by deprotonating **2a** and

2b under the same conditions. We then examined the dynamic character of NHC homodimers **4a-DiEt** and **4b-DiMe** by subjecting them to a crossover reaction. This was achieved by reacting stoichiometric amounts of **4a-DiEt** and **4b-DiMe** in THF at 100 °C for 24 h. Analysis by mass spectrometry (FD-MS) revealed the formation of the heterodimer, **5-DiMeEt** ($m/z = 320.14$; Figure S13), in equilibrium with both homodimers (**4a-DiEt**: $m/z = 348.245$ and **4b-DiMe**: $m/z = 292.187$). The chemical structure of **5-DiMeEt** was confirmed by NMR spectroscopy, with 2D HSQC and HMBC NMR analyses (Figure 2B-C). In particular, signals at 117.71 and 124.16 ppm could be ascribed to the resonance of quaternary carbon atoms 3^{\wedge} and 3^{*} of **5-DiMeEt**, respectively. A close inspection of the resonance zone of the *N*-substituents revealed the presence of peaks due to both the methyl (5^{*}) and the ethyl groups (2^{*} and 4^{*}), at 36.34, 9.57 and 40.67 ppm, respectively. The presence of the free NHC **6** arising from precursor **3a** was also established through signals appearing at 16.13 (2°) and 121.65 ppm (1°). The relative molar ratios were calculated as being equal to: **6/4a-DiEt/4b-DiMe/5-DiMeEt** = 0.15/0.16/0.26/0.43 (Figure S14). These results therefore attest to the cross-exchange in solution between the NHC homodimers forming the corresponding heterodimer, by simple heating.

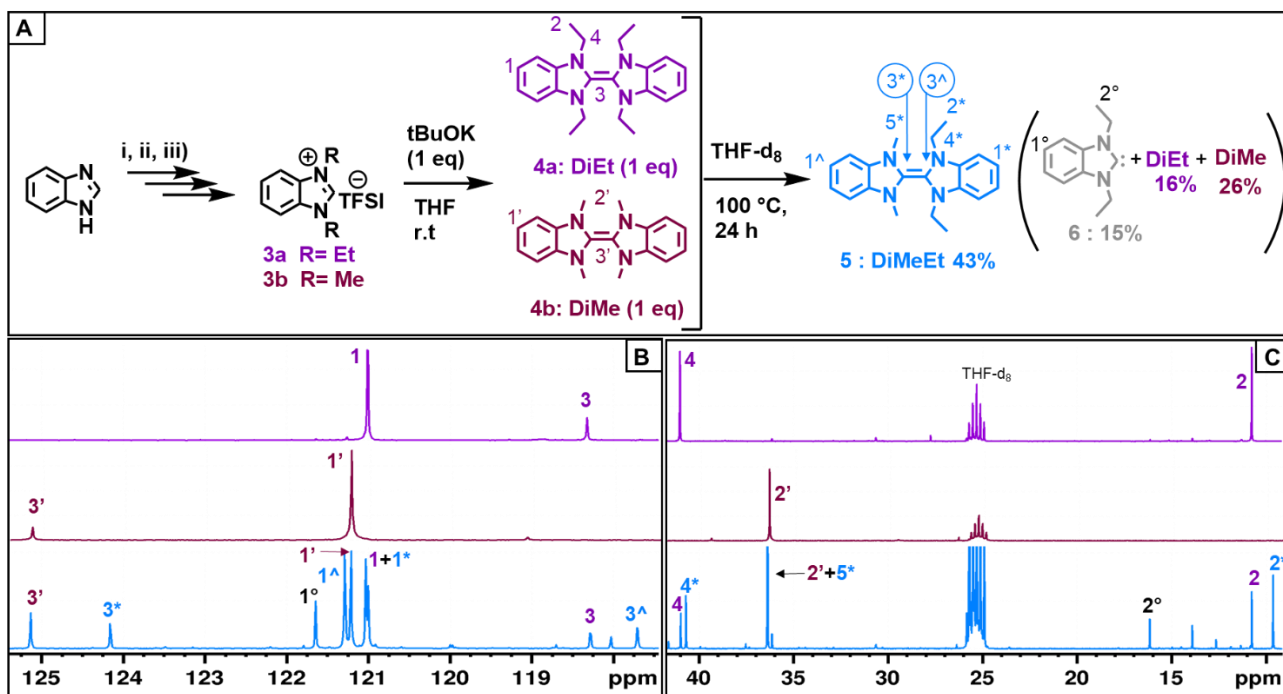


Figure 2. A) Sequential synthesis of benzimidazolium salts **3a** and **3b**: i) EtBr or MeI (1 eq.), KOH (2 eq.) in DMF or THF at r.t. for 24 h, ii) EtBr or MeI (1 eq.) in toluene at 110 °C for 24 h, iii) LiTFSI (1.2 eq.) in MeOH at r.t. for 3 h, dimerization through deprotonation using tBuOK (1 eq.) in THF at r.t. for 24 h yielding **4a-DiEt** and **4b-DiMe** and cross-over reaction of **4a-DiEt** and **4b-DiMe** in THF-d₈ at 100 °C for 24 h yielding **5-DiMeEt**; B) and C) Zoom on ¹³C NMR spectra of **4a-DiEt** (purple), **4b-DiMe** (pink) and product of the cross-over reaction **5-DiMeEt** (blue)

In order to exploit the reversibility of the NHC dimerization reaction to create copolymer networks featuring dynamic covalent bonds, we had to synthesize the parent linear copolymers. The NHC units were thus incorporated in the form of their benzimidazolium precursors into polystyrene-type copolymer chains. These were synthesized by reversible addition fragmentation chain transfer (RAFT) copolymerization of styrene and 4-vinylbenzyl-ethyl-benzimidazolium chloride (**7**), in view of controlling the copolymers molecular weight (Scheme 1). The comonomer feed ratio was adjusted using 5%, 10% or 20% of comonomer **7**, as a means to vary the cross-linking density of the copolymer networks upon deprotonation (see further; see also Table 1). With an incorporation of 5, 8 and 22% of benzimidazolium units, as determined by ¹H NMR spectroscopy (Figure S17), the copolymer compositions were in good agreement with the initial comonomer feed ratio. Analyses by size

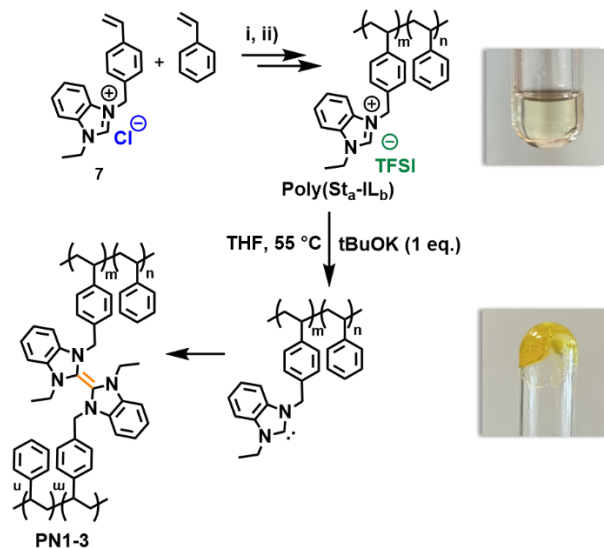
exclusion chromatography (SEC) revealed the formation of copolymers with relatively narrowly distributed molar masses (dispersity, $D < 1.4$; Figure S18). Characterization by DSC showed that the copolymers were all amorphous with a glass transition temperature (T_g) ranging from 96 to 149 °C. These values were strongly affected by the content in benzimidazolium units (Figure S19). The copolymers proved to be thermally stable up to 244 °C (TGA; Figure S20). In order to ensure good solubility of the copolymers in THF and enable their further cross-linking by dimerization, ion exchange from Cl⁻ to TFSI⁻ was carried out. This step caused the T_g value of all resulting copolymers to decrease down to around 96 ± 3 °C, while their thermal stability increased up to 320 °C (Figure S19-S20). TFSI anions thus provide much less robust ionic interactions compared to chloride anions. Likewise, decreasing the nucleophilicity of the counter-anion leads to an increase of thermal stability, which is well-documented.⁴⁹⁻⁵⁴

Table 1. Properties of copoly(ionic liquids) with different compositions and counter ions.

Polymer	Designation	\overline{M}_n (g/mol) ^a	\overline{M}_w (g/mol) ^a	D^a	Cl ⁻		TFSI ⁻	
					T_g (°C) ^b	$T_{d5\%}$ (°C) ^c	T_g (°C) ^b	$T_{d5\%}$ (°C) ^c
Poly(St ₉₅ -IL ₅)	P1	17 500	24 400	1.4	96	244	99	328
Poly(St ₉₂ -IL ₈)	P2	18 300	25 400	1.4	116	217	99	316
Poly(St ₇₈ -IL ₂₂)	P3	17 400	23 700	1.3	149	218	93	317

^aDetermined by SEC in THF+LiTFSI using a PS calibration; ^bDetermined by DSC, ^cDetermined by TGA.

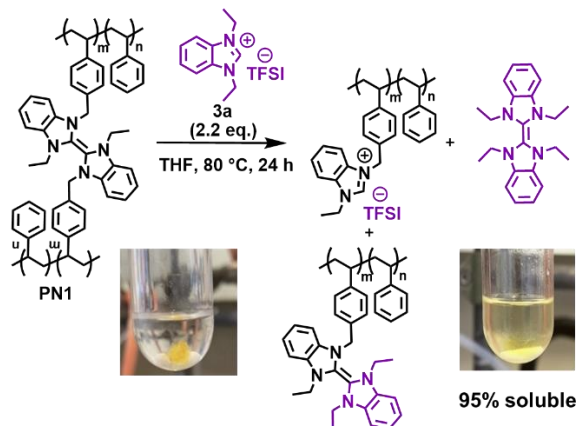
We then tested the deprotonation method we established above with molecular models. Thus, upon heating at 55 °C for 16 h with 1 eq. of *t*BuOK, the initial THF solutions of the linear copolymers turned immediately viscous to rapidly yield insoluble solid compounds. These observations strongly suggested the occurrence of crosslinking through dimerization of *in situ* generated transient NHC units (**Scheme 1**). The solid compounds recovered after filtration were then subjected to solubility and swelling tests by immersing them in THF for 24 h (see Table S1). The insoluble fraction of the collected product was relatively high and increased from 86 to 99% with increasing the benzimidazolium content. Moreover; the swelling ratios of the copolymer networks decreased from 6.8 to 2.4 as the level of benzimidazolium units -*i.e.*, the cross-linking density resulting from dimerization- increased.



Scheme 1. Synthesis of copolymer networks and visual aspect of the starting solution and product.: i) AIBN, RAFT agent in MeOH for 48 h ii) LiTFSI (1.5 eq.) in MeOH.

We next investigated whether the presence of dimerized NHC units could confer reprocessability and recyclability to these copolymer networks, in the same way as for adaptive covalent networks (CANs).^{36,55–58} Attempts to process our copolymer networks after drying by subjecting them to hot pressing were made. However, the obtained film-like materials showed a highly heterogeneous surface, irrespective of the working temperature and composition of the parent copolymers (Figure S21). We hypothesized that the complications in making our materials behave like CANs might be due to oxidation and/or hydrolysis of the C=C double bonds hanging in the tetraamino-alkene cross-links. The sensitivity to air or moisture of amino-alkene bonds has indeed been reported.^{59–61} We then sought for another way to leverage the dynamic units within these networks and turned towards chemical recycling. First, the possibility of breaking the tetraamino-alkene cross-links was demonstrated by adding a monofunctional benzimidazolium salt competitor, onto a swollen copolymer network. In practice, the **PN1** network with a 95/5 composition was heated at 80 °C in THF,

in the presence of diethylbenzimidazolium bis(trifluoromethanesulfonyl)imide **3a** (**Scheme 2**). After 24 h, the mixture evolved from an insoluble gel to a yellow transparent solution, though with some remaining (5%) of an insoluble fraction. SEC analysis of the soluble part showed the presence of the starting linear copolymer, along with populations of higher molar masses. These could be attributed either to chains resulting from some branching or to incomplete de-cross-linking (Figure S22).



Scheme 2. De-cross-linking reaction of **PN1** copolymer network in presence of **3a** as competitor.

The ¹H NMR spectrum of the soluble copolymer showed the same peaks to those of the starting linear copolymer, including the signal of the benzimidazolium proton at the C2-position at 9.95 ppm (Figure S23). These results prompted us to investigate another chemical means for manipulating the tetraamino-alkene cross-links of our networks and eventually to trigger successive cycles of re-solubilization (de-cross-linking) and dimerization-induced re-crosslinking. NHCs are known to selectively react with CO₂, forming stable zwitterionic NHC-CO₂ adducts.^{62–67} These can serve as air-stable precursors of NHCs for synthesis purposes.^{68–71} Interestingly, NHC-CO₂ adducts of benzimidazolium have been shown to undergo either thermal activation or water-assisted decarboxylation to generate the corresponding NHC homodimers for further use as organic electron donors.^{47,72} On this basis, we hypothesized that dimer dissociation could be induced by feeding with CO₂ to form an NHC-CO₂ adduct. The reaction was first studied with the molecular NHC dimer **4b-DiMe**, a THF solution of which was bubbled with CO₂. After a few seconds, a white solid compound precipitated out from the solution, which was authenticated as the NHC-CO₂ adduct **8** by ¹H NMR (Figure 3). It was then tempting to try to reform the parent dimer **4b-DiMe** from **8** in non-dry THF. This reaction was carried out successfully, since after treatment of **8** with *t*BuOK, we observed a homogeneous reaction medium and were able to recover the homodimer **4b-DiMe**. This reaction cycle can be rationalized by the mechanisms shown in Figure 3. Regeneration of homodimer **4b** is explained by the reaction of **8** with traces of water (non-dry solvent), forming the benzimidazolium hydrogen carbonate salt. Such salts can serve as a genuine source of NHCs, by formal loss of “H₂CO₃” (H₂O + CO₂).⁷³ Addition of *t*BuOK as fuel then enabled that salt to be deprotonated, generating NHC *in situ* and triggering its dimerization.

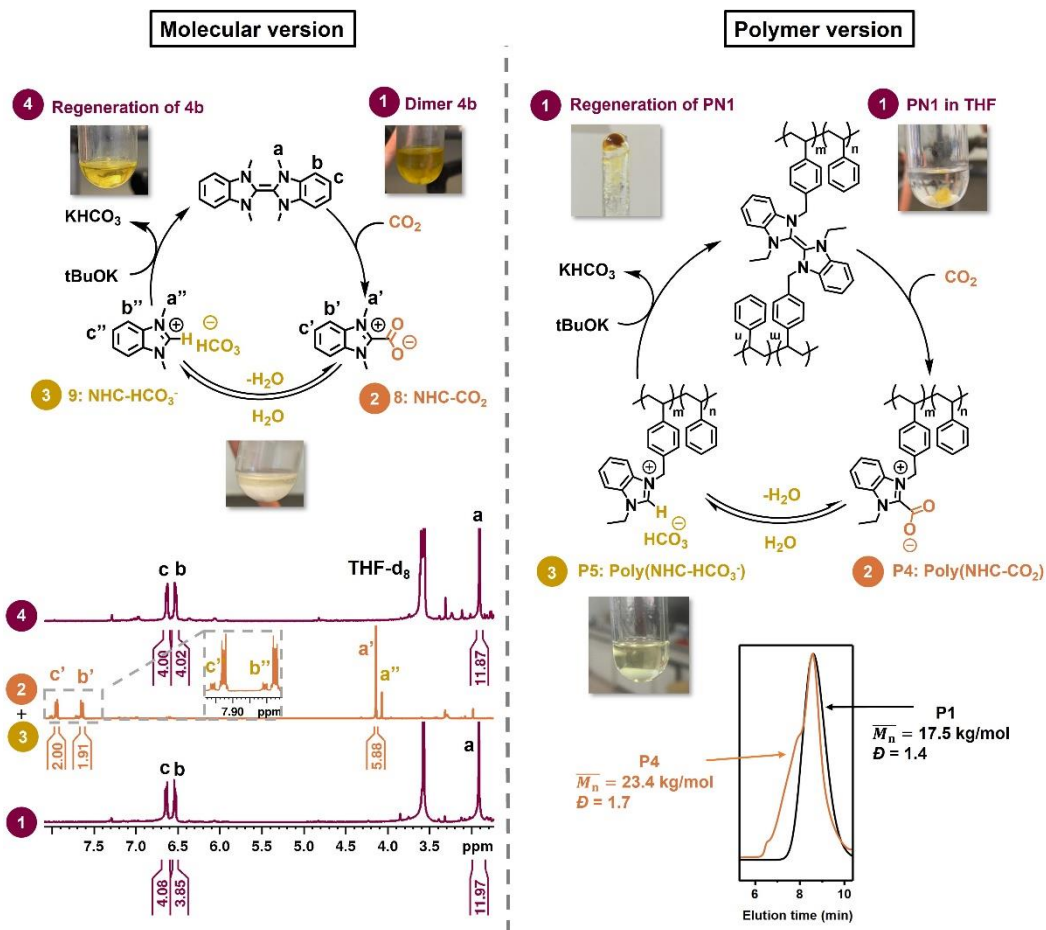


Figure 3. (left) Reaction cycle including: formation of NHC-CO₂ adduct **8** upon CO₂ bubbling, followed by regeneration of **4b-DiMe** by fueling with tBuOK₂ and ¹H NMR of the starting **4b-DiMe** (bottom), the NHC-CO₂ **8** and NHC-HCO₃⁻ **9** (middle) and the regenerated **4b-DiMe** after 1 cycle (top). (right) Scheme of the de-cross-linking/re-cross-linking of the polymer network **PN1** (including the formation of the intermediate linear polymer **P4**) via successive fueling with CO₂ and tBuOK and overlay of the SEC chromatograms of the starting polymer **P1** and the de-cross-linked polymer **P4**.

The same concept was then applied to our copolymer networks. Sample **PN1** was thus redispersed in THF before bubbling with CO₂ (Figure 3 right). After 2 h of reaction, complete re-solubilization of the resulting copolymer was noted, a signature of disrupted linkages between the copolymer chains and concomitant formation of the poly(NHC-CO₂) adduct **P4**. Analysis by SEC of the as-recovered copolymer showed the presence of a main population of molar masses at the same elution time as that of the starting linear copolymer. However, this SEC trace proved slightly broader ($\bar{D} = 1.7$ after de-cross-linking vs. $\bar{D} = 1.4$ before cross-linking) showing shouldering in the high molar mass region, probably due to some branching reactions (Figure 3). After adding tBuOK onto a THF solution of this poly(NHC-CO₂) adduct **P4**, gelation was again observed, suggesting restoration of the network. A new cycle of this reaction sequence involving CO₂ and tBuOK to de-cross-link the network and re-cross-link the linear chains, respectively, could be successfully performed to demonstrate the repeatability of the whole process.

Another advantage of the equilibrium between free NHCs and their homodimers is that the latter may be used as reservoirs

of NHCs for organocatalyzed reactions. These have been extensively studied as organic catalysts, not only in molecular chemistry but also in macromolecular synthesis.^{3,74–78} We thus hypothesized that the dynamic covalent copolymer networks incorporating NHC dimers as cross-links could dissociate upon heating and generate free polymer-supported NHCs *in situ* for organocatalysis purposes. The copolymer network incorporating 22% molar of NHC dimers (**PN3**) was tested for the benzoin condensation (Scheme S2).⁷⁸ After 24 h of reaction, a conversion of 97% of benzaldehyde into 2-hydroxy-1,2-diphenylethan-1-one (benzoin, Figure S25) was determined. The copolymer network **PN3** could be readily recovered by simple filtration and reused for a new catalytic run. Conversions slightly decreased, from 97% to 70%, after five consecutive catalytic cycles (Figure S26). This loss in catalytic activity might be ascribed to some hydrolysis and/or loss of the copolymer during workup. In any case, these results attested to the potential of copolymer networks incorporating dimerized NHCs as cross-links as heterogeneous and recyclable organic catalysts.

In summary, we have introduced dimerized NHC motifs in the form of tetraamino-alkene as dynamic cross-links in copolymer networks. For this purpose, styrenic-type copolymers

have been designed by RAFT copolymerization to immobilize pendant benzimidazolium-type units, serving as resting forms of NHC motifs. In presence of a strong base, the C2-position of these motifs is deprotonated, which triggers chemical cross-linking of the parent copolymer chains *via* the *in situ* generation of transient NHCs able to intermolecularly dimerize. These cross-links can be subsequently chemically cleaved off in presence of a benzimidazolium salt as competitor, or by simply bubbling the network with CO₂, thus restoring the linear copolymer chains. The copolymer networks could then be reformed by addition of *t*BuOK in the presence traces of H₂O. More generally, we have developed a dynamic polymeric platform based on benzimidazolium units able to undergo repeated cycles of reaction sequence, involving dimerization of NHCs to cross-link the starting copolymers, followed by carboxylation of tetraaminoalkenes, to de-crosslink the corresponding networks. The chemically-triggered reaction sequence proceeds in a closed loop and can be programmed in time by fueling the cycles with simple reagents. In addition, the same copolymer networks can operate as reservoirs of NHCs for organocatalysis purposes. They indeed prove efficient heterogeneous and recyclable polymer-supported NHC precursors. This versatile and convenient way of cross-linking and de-cross-linking polymers with catalytic activity provides new opportunities for designing dynamic and functional polymeric materials.

ASSOCIATED CONTENT

The Supporting Information is available free of charge *via* the Internet at <http://pubs.acs.org>.

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