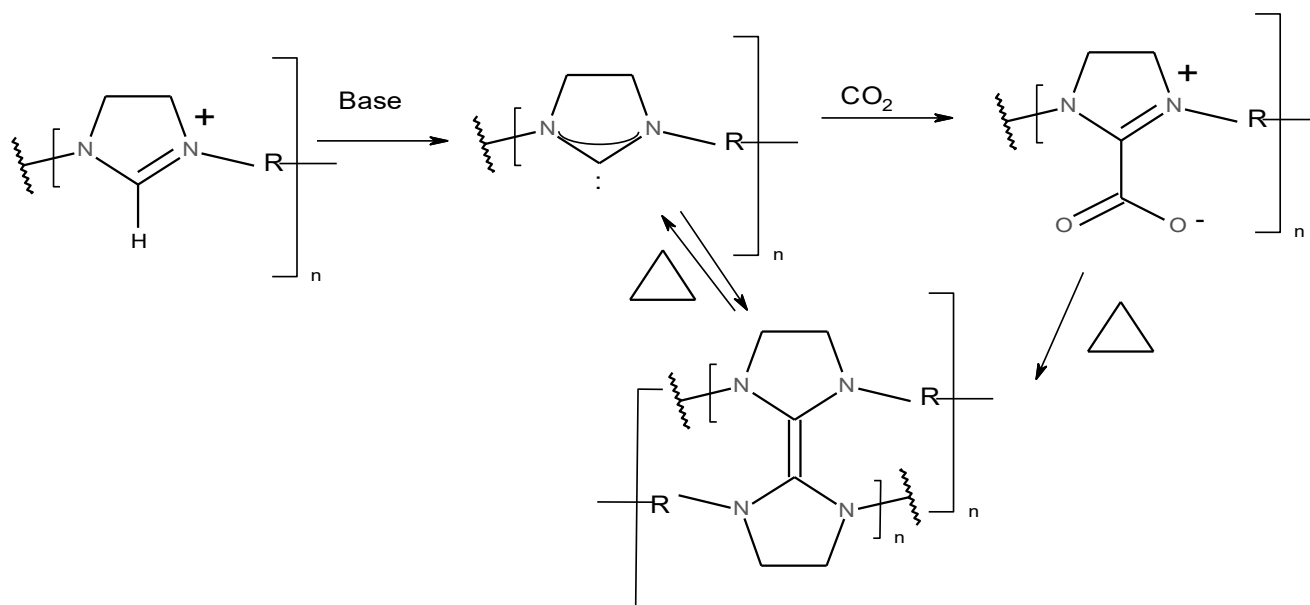


Reversibly Cross-Linkable Polymers based on NHC Dimers

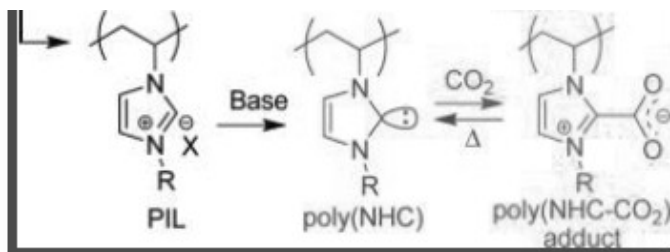
By: Robert B Login

N-Heterocyclic Carbenes have become very important to Organic synthesis; not only as critical transition metal ligands but also for several reactions where they are employed by themselves as catalysts. Interest in NHC's really got started when it was discovered that stable carbenes could be obtained if the R groups on nitrogen were bulky enough to prevent dimerization(Wanzlick equilibrium). If they are not sufficient to prevent dimerization then that is the reaction that occurs if the resulting imidazolium salt is saturated at the 4,5 position (See Tetrahedron Letters 40(1999) 2057-2060). However, this dimerization can be reversed (there are examples of this from Prof Bielawski's group, but there is much controversy whether or not this dimerization is reversible) with moderate heat. NHC's that readily dimerize can be protected by reacting with CO₂ resulting in a stable betaine in water. When the betaine is dried down and heated it will lose CO₂ generating the corresponding NHC which could then dimerize. Subsequently, the dimer could be reheated to once again reveal the NHC(?) an so forth..

If the NHC-CO₂, in the betaine form, is part of the repeating monomer units in a cationic polymer, then it would exhaust onto hair or cotton for example where it would form a film on dry down. This film would not be cross-linked and would allow hair to be styled; however, using a curling iron said polymer would loose CO₂ and would cross-link affording a more permanent styling result. Since the cross-link is reversible, further manipulations with the curling iron could be performed but with subsequent cross-linking upon cooling. This then is a method of safely performing a unique “permanent wave” treatment. For example:

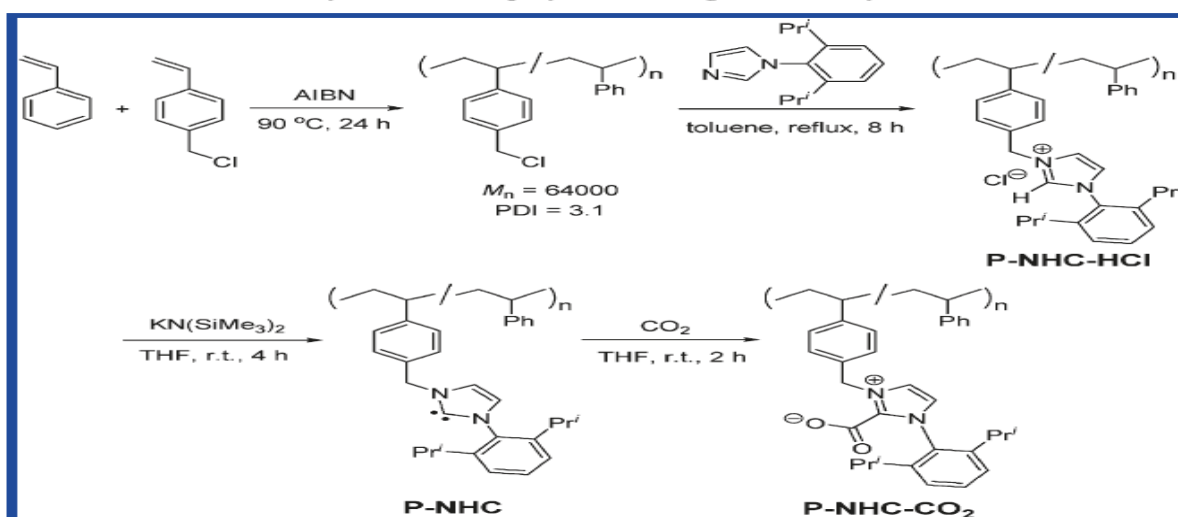


The above reactions are known and have a significant literature. For example:



Macromolecules 2011, 44, 1900–1908

Scheme 1. Synthesis of Copolymer Bearing *N*-Heterocyclic Carbene



Macromolecules 2009, 42, 5419–5421

DOI: 10.1021/ma901109j

In the above example, the authors did not want dimerization, hence the bulky group on the NHC.

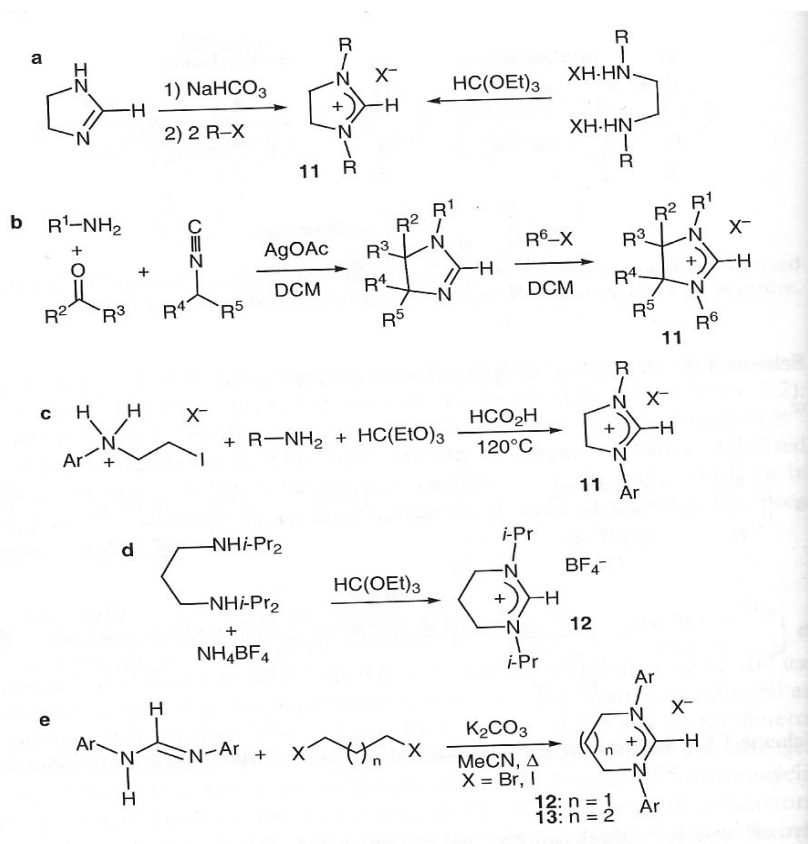
Polymerization:

A suitable polymer for this styling application would be cationic, water soluble and stable and could then be cross-linked reversibly with heat at a temperature that is available with a typical curling iron (or wrinkle removing iron in the case of textiles).

These requirements, I visualize can be accomplished with a variety of ionene/NHC-CO₂ betaine polymers.

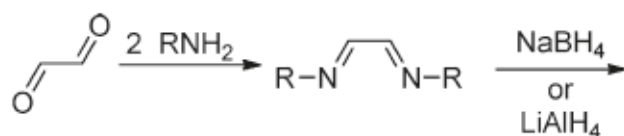
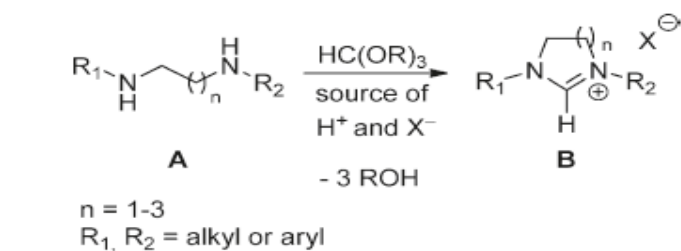
NHC Synthesis:

There are several known routes to the synthesis of saturated NHC's:

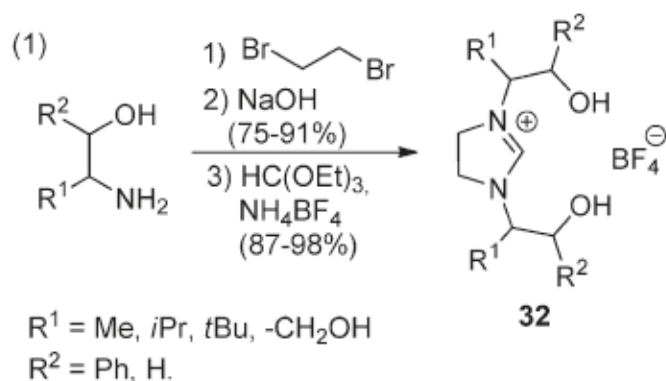


From "N-Heterocyclic Carbenes", S. Diez-Gonzalez, RSC pub. 2011.

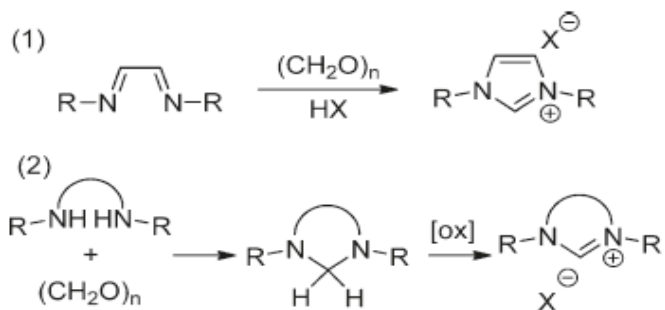
Scheme 1. General Route to the Cyclic Formamimidium Salt B by Condensation of a Diamine with Trialkyl Orthoformate



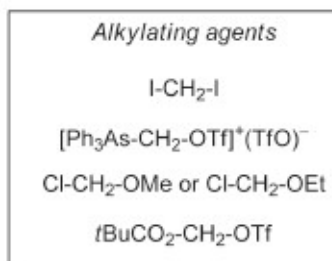
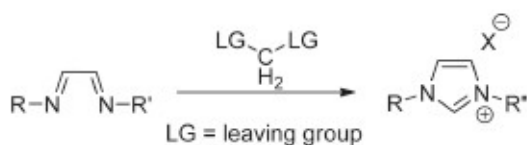
Starting from 1,2-Dibromoethane



Scheme 28. Synthesis of Unsaturated or Saturated NHC Precursors Using Paraformaldehyde as C₁ Building Block



Scheme 22. Formation of Imidazolium Salts by Means of 1,1-Bis(electrophile) Compounds

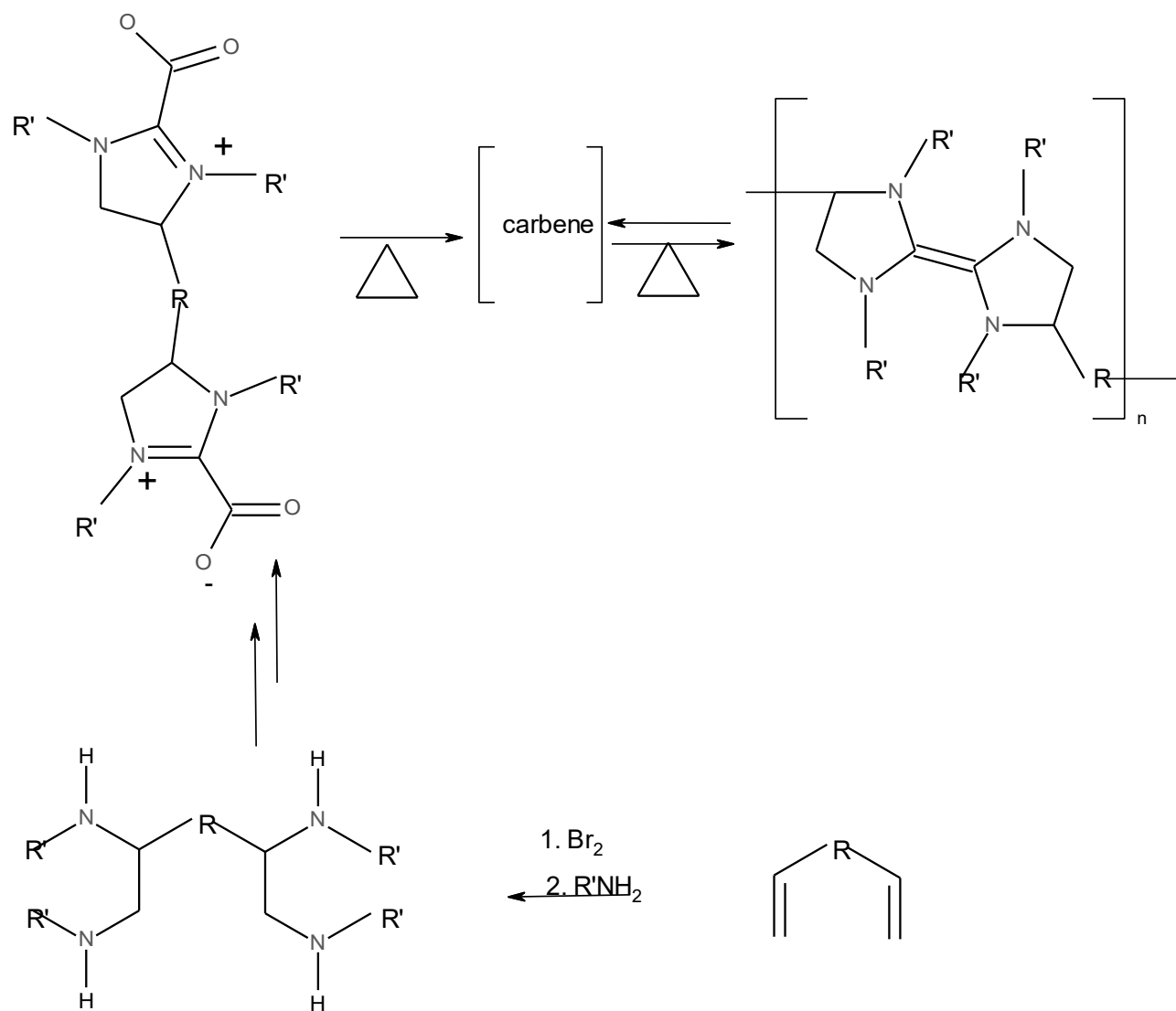


[dx.doi.org/10.1021/cr100328e](https://doi.org/10.1021/cr100328e) | *Chem. Rev.* 2011, 111, 2705–2733

As can be seen, there are several ways to synthesize suitable NHC's that will form dimers. Please look at *Chem. Rev.* 2011, 111, 2705-2733 for a complete review of NHC synthesis.

Dimerization:

The Wanzlick dimerization is more facile with saturated NHC's. So the following is another approach to said invention. The intermediate betaine is stable as long as moisture is avoided.



In the above scheme, reversal of the dimer to the corresponding NHC with heat is implied as is reversal back to the dimer depending on conditions.

Not shown in the above NHC synthesis examples are NHC precursors prepared from imidazole itself. For a review of this subject see: *Macromol. Rapid Commun.* **2012**, *33*, 1996–2014 and *Polym. Bull.* (2011) 67:623–629 and *Nano Today* (2009) **4**, 13–20 for examples:

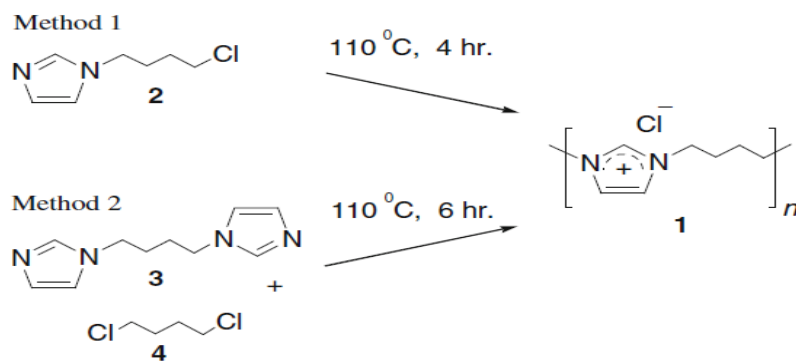
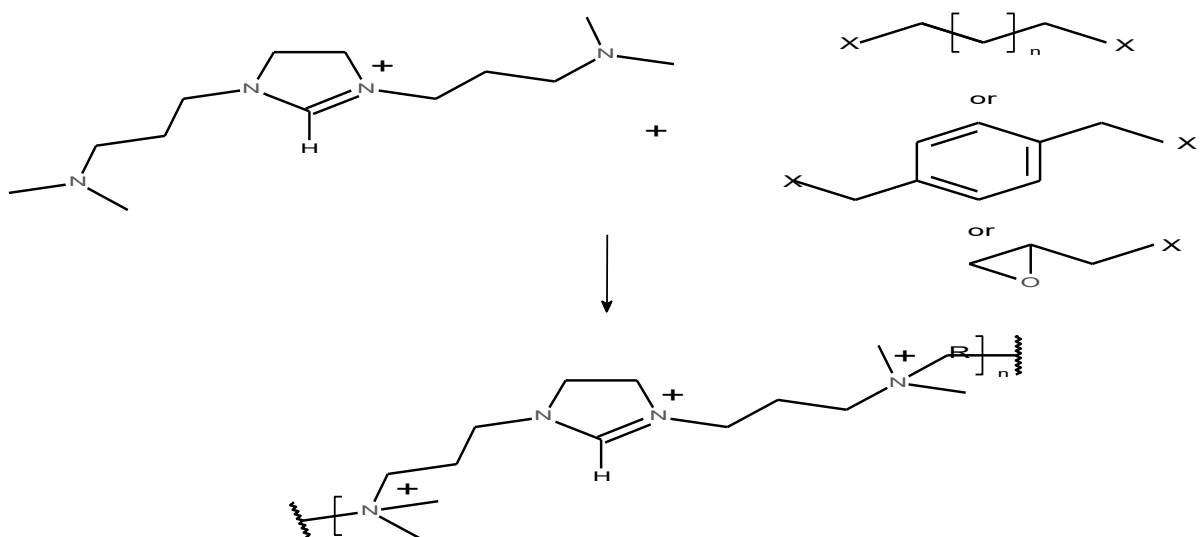


Fig. 1 Preparation of polymeric ionic liquid poly(imidazolium chloride-1,3-diybutane-1,4-diyli) (1) using two different methods

By employing N,N-Dimethylpropylamine several ionene/NHC polymers can be synthesized. The R group can also be a repeating ionene segment not including the NHC moiety.



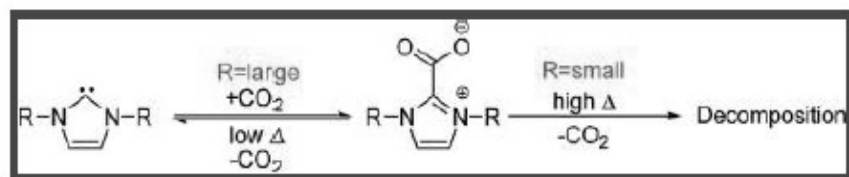
Obviously, many variations of the above ionene/NHC can be visualized. It may be a copolymer with non-quat units, derived from the plethora of reported ionene repeat units. See: *Macromolecules Vol. 5, No. 3, May-June 1972* *Polymer Preprints 2008*, 49(1),875 *USP 3,856,714; 4,075,136; 4,157,388; 4,395,5414,506,081; 5,575,993; 7,122,618 and many more.*

The ionene/NHC structures I revealed are not meant to be limiting as other repeat units not containing NHC's in said copolymers can be visualized especially after reading the above references.

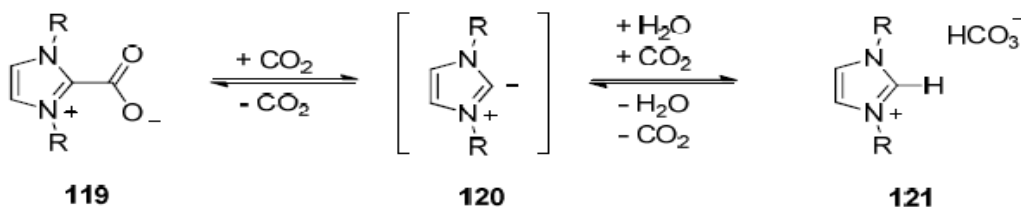
Why then have a Quat repeat unit? The reason is that the Imidazolium is converted with base to the NHC in the presence of CO₂ to form the stable betaine which is not substantive to hair or textiles. The quat guarantees that the polymer is attached to the target substrate before heat is applied to then generate the NHC which can dimerize or revert back to the imidazolium structure.

Stability of CO₂ adduct:

The stability of said betaines has been studied and can be visualized as follows:



I think that in a polymer backbone R would be similar to these large R groups and the decarboxylation temperature could easily be achieved.



Scheme 31. Carbon dioxide trapping and extrusion.

In the presence of water, as can be seen, it reverts back to the Imidazolium salt. This subject has been reviewed extensively. See:

J. Org. Chem. Vol. 74, No. 20, 2009

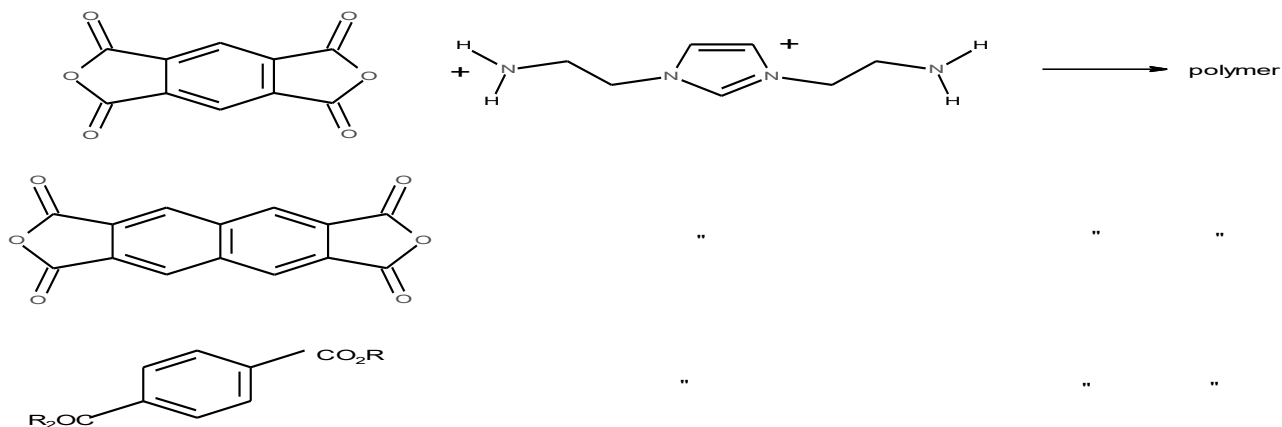
J. Org. Chem. Vol. 73, No. 20, 2008

ARKIVOC 2013 (i) 424-469

Antimicrobial activity:

The search for biologically benign imidazolium salts that can form NHC complexes to silver is actively being pursued. This is because presently used silver salts don't last very long in chloride containing saline body fluids and in many cases the residual monomeric imidazolium salts are toxic. Silver bioicides are very important for preventing infection for burn victims. Silver complexes of the above said polymers would slowly release silver ions but the residual polymer would have a good chance of being non-toxic. Silver ions kill practically all bacteria and does not harm cells. Finding a magic silver bullet to kill all bacteria is currently an important subject (Chem. Rev. **2005**, 105, 3978-4008) . There are however downsides to silver especially argyria or skin and eye pigmentation after heavy repeated contact. Well for those interested the whole picture has been reviewed in-depth in *Chem Rev.* 2009 109(8): 3859–3884.

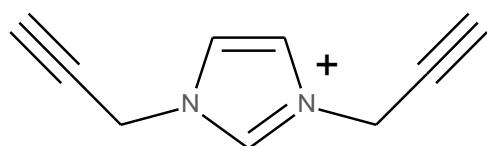
Another possibility comes to mind, namely that NHC's are powerful ligands for metals; therefore, can polymers containing NHC's or NHC precursors adhere to metal surfaces as protective coatings or as adhesives. The structures of such polymers could be based on condensation polymers known for their toughness or vinyl polymers with pendant azolium moieties which are known polymers. The design of such polymers would be conceivable; for example:



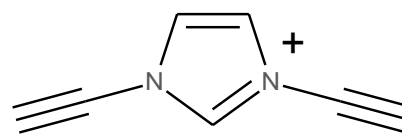
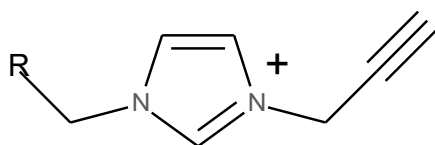
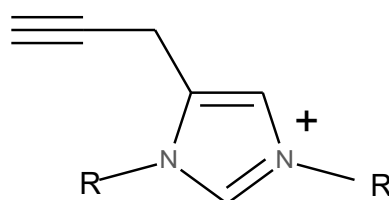
Also urethanes and epoxies etc.

Obviously there are many more structures that can be visualized and the above also would include the typical other difunctional compounds with the imidazolium diamine being a co-reactant.

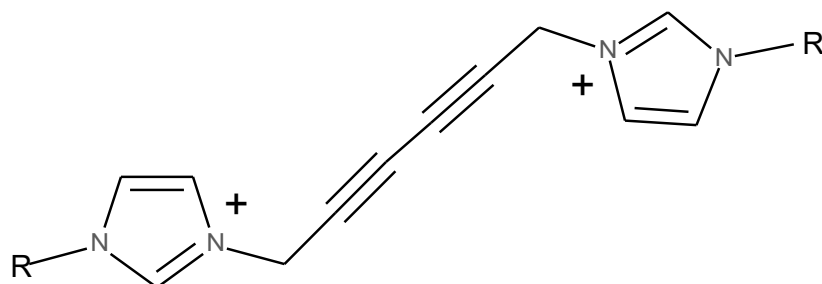
Acetylenic imidazoliums are also conceivable; however, a search on Google revealed one reference to related compounds suggesting these alkyne substituted imidazoliums have not been studied? For example:



1,3-bis(prop-2-ynyl)imidazole



1,3-diethynylimidazole



Polymerization of acetylenics is reviewed in a pdf on my web page entitled “The Chemistry of Acetylenic Derivatives of Pyrrolidone “ (rloginconsulting.com) and the above monomers would be expected to polymerize by those reactions. Other alkyne

monomers can be visualized and the above chart is not meant to be exhaustive. After polymerization the corresponding NHC can be generated by known reactions.

I Claim:

1. (Reversibly) cross-linkable cationic ionene polymers comprising those containing from 1-50% NHC carbon dioxide backbone betaine complexes that can generate said NHC by being heated to modest temperatures of 50-150 C.
2. The cationic polymers of claim 1 wherein the cationic charge results when said polymers contain 1-50% ionenes moieties.
3. The cationic polymers of claim 1 wherein the NHC-CO₂ betaine complex and the ionene moieties are prepared from N,Ndimethylpropylenediamine(DMAPA) chain extended with dialkylating agents such as alkyldi(terminal)halogens of 2-20 carbon atoms optionally substituted...
or di(halogen methylene) aromatic derivatives, or epichlorohydrin and so forth.
4. The cationic polymers of claim 3 wherein in addition to DMAPA, other primary diamines can be partially substituted for said DMAPA so that they are 1-50% of said cationic polymers.
5. Polymers comprising silver NHC complexes wherein the NHC is an integral part of said polymer backbone.
6. The polymers of claim 5 wherein said polymers function as antibiotics.
7. Cross-linkable polymers or oligomers containing NHC-CO₂ betaine end groups that generate said NHC when heated that then form Wanzlick dimers (reversibly).
8. Condensation polymers containing said NHC-CO₂ betaines that form adhesive free NHC's that enhance adhesion to metal surfaces.
9. Alkyne derivatives of said precursor NHC's that are polymerizable.