

## ATRP Quats and Polyquats

By: Robert B. Login [rloginconsulting.com](http://rloginconsulting.com)

The ATRP literature is extensive with many reviews. A selection of several follows:

Matyjaszewski, K. (1998). Radical nature of Cu-catalyzed controlled radical polymerizations (atom transfer radical polymerization). *Macromolecules*, 31(15), 4710-4717.

Matyjaszewski, K., & Xia, J. (2001). Atom transfer radical polymerization. *Chemical reviews*, 101(9), 2921-2990.

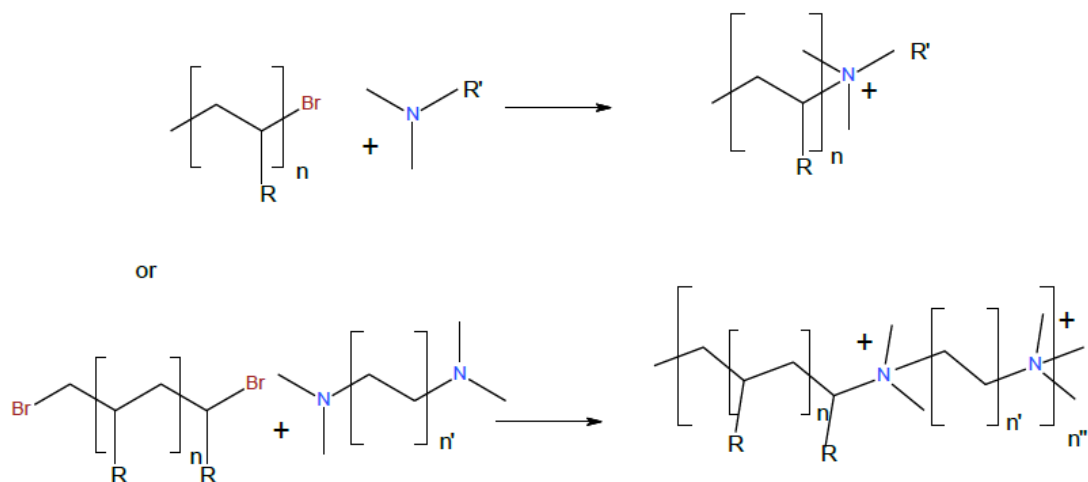
Braunecker, W. A., & Matyjaszewski, K. (2007). Controlled/living radical polymerization: Features, developments, and perspectives. *Progress in Polymer Science*, 32(1), 93-146.

Matyjaszewski, K. (2012). Atom transfer radical polymerization (ATRP): current status and future perspectives. *Macromolecules*, 45(10), 4015-4039.

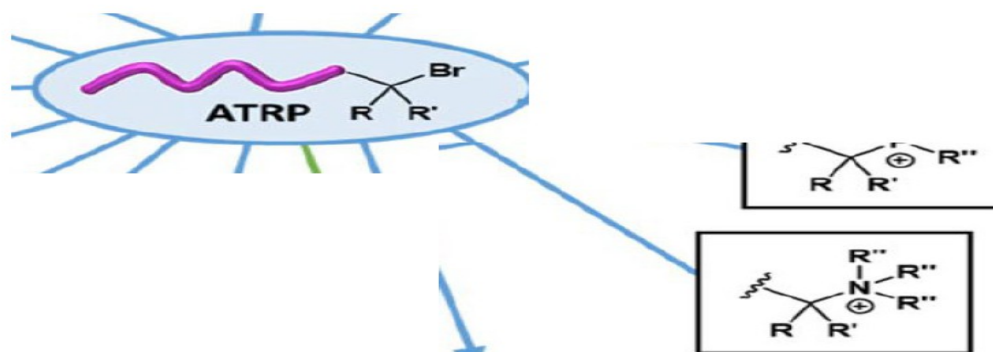
Boyer, C., Corrigan, N. A., Jung, K., Nguyen, D., Nguyen, T. K., Adnan, N. N. M., ... & Yeow, J. (2016). Copper-mediated living radical polymerization (atom transfer radical polymerization and copper (0) mediated polymerization): from fundamentals to bioapplications. *Chemical reviews*, 116(4), 1803-1949.

Ribelli, T. G., Lorandi, F., Fantin, M., & Matyjaszewski, K. (2019). Atom transfer radical polymerization: Billion times more active catalysts and new initiation systems. *Macromolecular rapid communications*, 40(1), 1800616.

Disclaimer: After looking at these ATRP reviews and numerous journal articles, I must admit that the references I may have needed were possibly in journals I don't subscribe to. Also I found only one example(?) but no reference to my proposals that is illustrated in scheme 1.



Scheme 1: The idea to use ATRP Br chain ends to prepare quats. I have had a hard time finding references to this reaction except for the following:



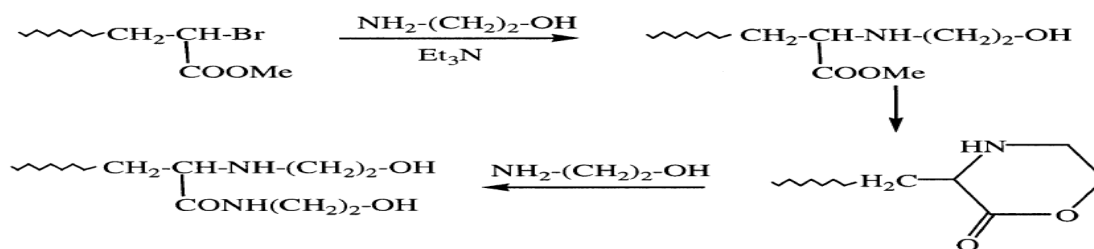
Lunn, D. J., Discekici, E. H., Read de Alaniz, J., Gutekunst, W. R., & Hawker, C. J. (2017). Established and emerging strategies for polymer chain-end modification. *Journal of Polymer Science Part A: Polymer Chemistry*, 55(18), 2903-2914.

Searching through this paper, I have not found the reference for the illustrated quat ? I also thought that the authors might mean the R'' are actually protons because the reaction with amines would first produce a cationic group but not a quat?

“The ligands, used to complex the metal are mostly tertiary amino compounds. However, amines can interact with the halogen end groups of the initiator molecules or of the growing chains. Our investigations concerning this issue indicate that under the experimental conditions used during the polymerization process, interactions of end groups with tertiary amines are negligible. Ammonia and primary amines, e.g., n-butylamine, however can react with the halogen end groups. Moreover, after the polymerization reaction they can be used as nucleophilic agents to replace the halogens by other functional end groups. The use of difunctional molecules such as ethanolamine leads to the incorporation of alcohol end groups at the chain ends.”

COESSENS, V., & MATYJASZEWSKI, K. (1999). Synthesis of polymers with amino end groups by atom transfer radical polymerization. *Journal of Macromolecular Science, Part A*, 36(5-6), 811-826.

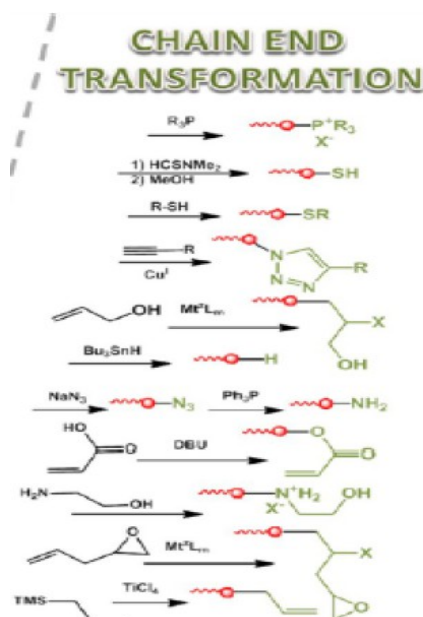
I don't have this reference just the above abstract which indicates that tertiary amines are not good nucleophiles as far as bromine end groups are concerned. That is why acrylic monomers like DMAEMA can be used in ATRP without crosslinking with the halogen end groups(?). Alternatively primary amines will react with the bromine end groups.



Scheme 7.

Coessens, V., Pintauer, T., & Matyjaszewski, K. (2001). Functional polymers by atom transfer radical polymerization. *Progress in polymer science*, 26(3), 337-377.

Matyjaszewski, K. (2012). Atom transfer radical polymerization (ATRP): current status and future perspectives. *Macromolecules*, 45(10), 4015-4039.

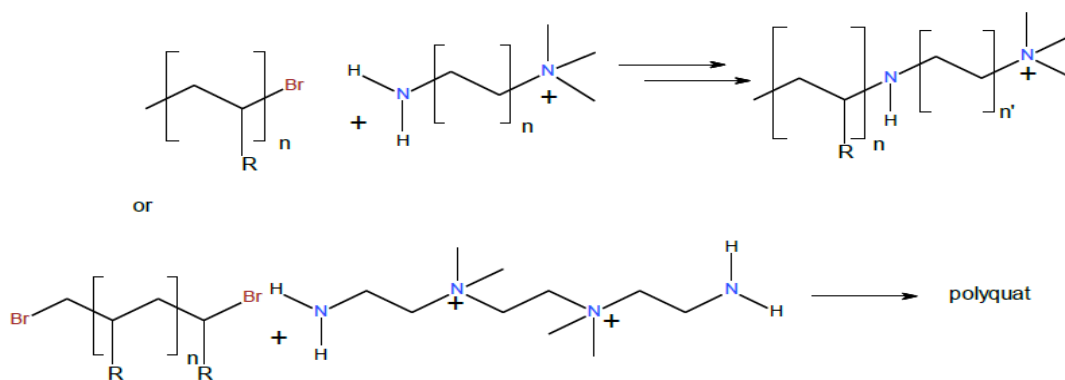


Matyjaszewski, K. (2018). Advanced materials by atom transfer radical polymerization. *Advanced Materials*, 30(23), 1706441.

I really don't understand why tertiary unhindered amines will not react with unhindered bromine end groups. I could see where if the polymer bromine end group had a methyl group instead of a hydrogen there might be steric hindrance? So since primary amines are known to react then I am thinking of using them if it's necessary to get around this problem? I do believe however that said bromine end groups will react to form quats!

### Derivatised primary amines:

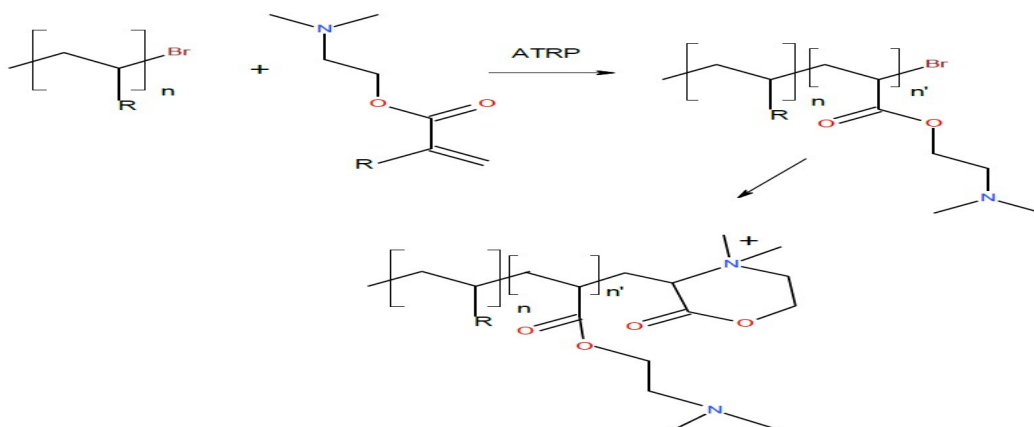
N,N Dialkyl diamines are well known and several are commercially available. Whether or not the tertiary amine group will compete to cause some elimination will require experimentation. I would also consider first protecting the primary amine and then quaternizing the tertiary amine and then freeing the primary amine and condensing it with the bromine ATRP polymer terminal in a polar solvent like water. For example:



Scheme 2: Use of primary amines. Many additional structural variations of the above idea can be conceived of.

### DMAEA:

After thinking about synthesizing polymeric quat chain ends by ATRP, I decided that the most straight forward way would be to add the absolute minimum amount of DMAEA as the final monomer in a block copolymer which should cyclized to a cyclohexyl quat. For example:



Scheme 3: Note the DMAEA R group is hydrogen. With ATRP its possible to have a difunctional initiators so the quats can be put at both ends of the polymer. Here I'm betting that a minimum of the DMAEA tertiary amine monomer can be used to terminate the block copolymer. The neat thing here is the quat should be favored by the formation of a six-membered ring. I have to also mention that should a multiplicity of DMAEA type monomers be employed the others that are not terminal could also be post quaternized or even transformed into amine oxides.

With a difunctional bromine initiator, quats could form on both ends. I show an extra DMAEA in scheme 3 because I would think putting just one at terminus seems unlikely?

Obviously ATRP allows a wide variety of copolymer architectures.

Depending on the comonomer a plethora of free radical polymerizable monomers can be

copolymerized as “blocks” with quat terminals with DMAEA by ATRP or its variants.

Quats are very useful compounds!

Jiao, Y., Niu, L. N., Ma, S., Li, J., Tay, F. R., & Chen, J. H. (2017). Quaternary ammonium-based biomedical materials: State-of-the-art, toxicological aspects and antimicrobial resistance. *Progress in Polymer Science*, 71, 53-90.

Thank you for reading these proposals. I would be delighted if I received any feedback either positive or negative concerning any of my ideas!

Dr. Robert B. Login [rloginconsulting.com](http://rloginconsulting.com)