LIGANDS FOR ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

Me_6TREN and TPMA

BUILDING POLYMERS FOR TOMORROW'S PRODUCTS
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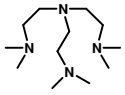
Product Description

The ATRP process provides a simple route to many well-defined (co)polymers with precisely controlled functionalities, topologies, and compositions. It has been very successfully applied to the preparation of many nanocomposites, hybrids, and bioconjugates. One drawback of classical ATRP is the use of high amounts of CuX / *ligand* catalyst complex.

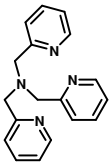
ATRP Solutions, Inc. is happy to announce the release of two new *ligands*, tris[2-(dimethylamino)ethyl]amine (Me_6TREN) and tris(2-pyridylmethyl)amine (TPMA) which alleviate this problem. Only these *ligands* can be used in new techniques called Activators ReGenerated by Electron Transfer (ARGET) and Initiators for Continuous Activator Regeneration (ICAR) which allow to decrease amount of catalyst to only few ppm (1000 to 10,000 ppm are used in traditional ATRP). For many of applications, in these new systems the residual copper can be left in the final colorless products.

LIGANDS:

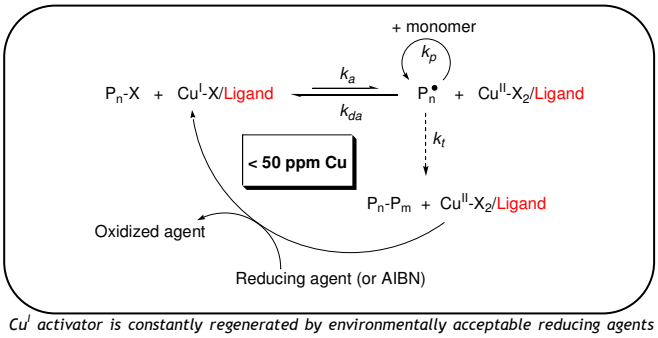
Me_6TREN



TPMA



Mechanism for ARGET (and ICAR) ATRP with ppm amounts of catalyst

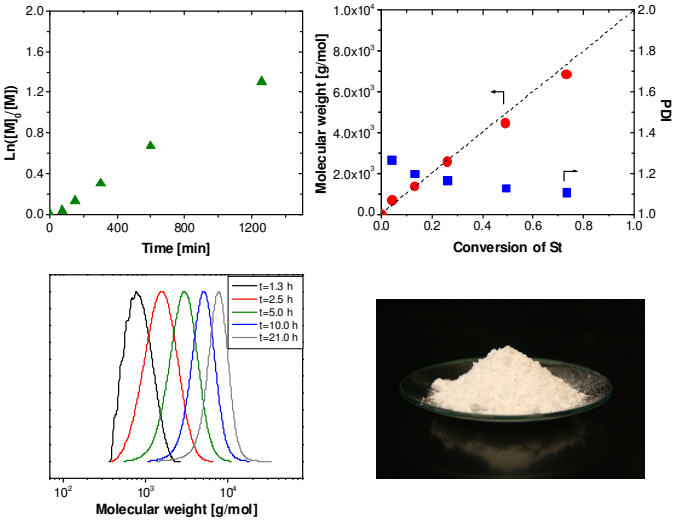


Cu^I activator is constantly regenerated by environmentally acceptable reducing agents (e.g. FDA approved compounds, sugars etc.) or organic radicals

Example of Use: Polymerization of styrene via ICAR ATRP

The ARGET and ICAR ATRP process makes it possible to reduce the amount of catalyst one thousand times. Only very active catalyst derived from Me_6TREN and TPMA can be used in these new techniques. The figure below presents the kinetic plot, evolution of molecular weights and polydispersities with conversion and GPC traces for polymerization of styrene (St) with 50 ppm of $CuBr_2$/TPMA catalyst in the presence of AIBN as reducing agent. Molecular weight control was excellent and followed theoretical values based on quantitative initiation. Polymer, after precipitation in hexane, appeared as a white solid powder with only 5 ppm of the residual catalyst. If more Cu removal is needed, we recommend to use the *ATRP pure®* resin.

Polymerization conditions for ICAR ATRP of styrene:
$[St]_0$ / $[EtBiB]_0$ / $[CuBr_2]_0$ / $[TPMA]_0$ / $[AIBN]_0$ = 100 / 1 / 0.005 / 0.005 / 0.2
T = 70 °C; DMF as internal standard (5 vol% versus St)



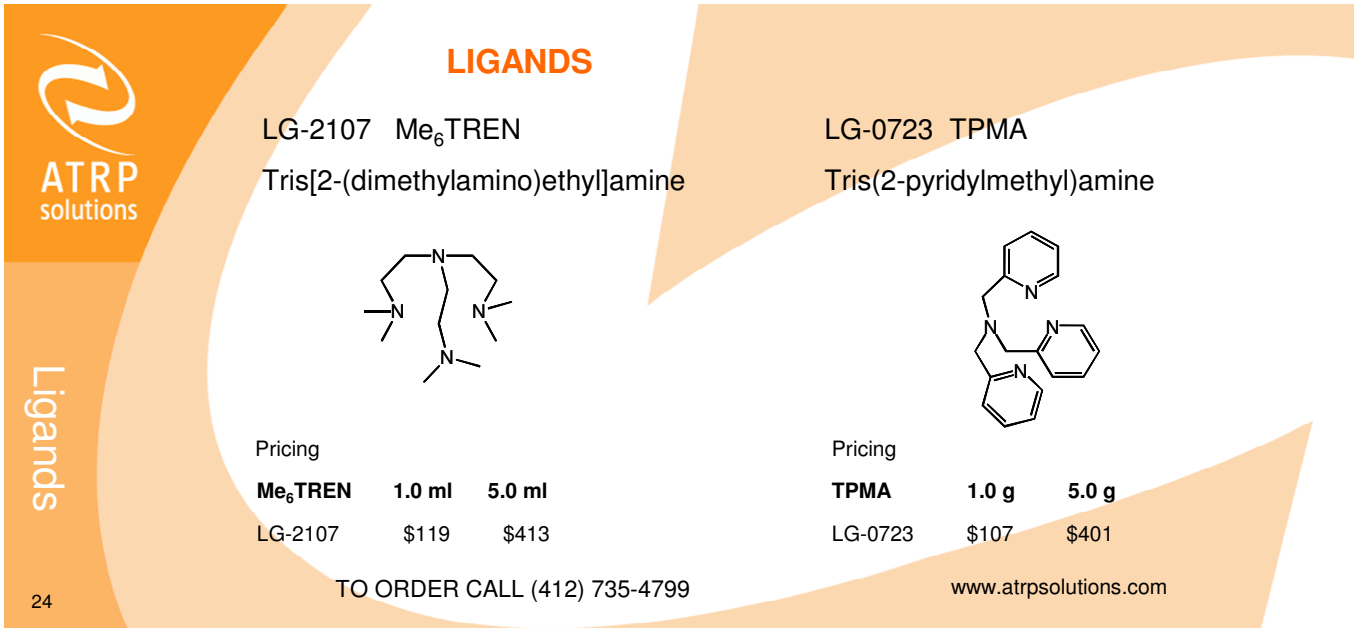
Kinetic plot (upper left)
Molecular weight and polydispersity as a function of conversion (upper right)
Evolution of GPC traces (bottom left)
Photograph of polymer after precipitation in hexane (bottom right)

Suggestion for Other Applications

Me_6TREN and TPMA were successfully used in ICAR and ARGET ATRP of various monomers such as: styrene, methyl acrylate, butyl acrylate, methyl methacrylate, butyl methacrylate, acrylonitrile. They can also be used in classical ATRP of coordinating monomers (e.g. 4-vinylpyridine). However milder conditions (e.g. low temperature, high dilution) have to be applied in order to achieve good control over the polymerization process.

For Technical and Ordering Information

ATRP Solutions, Inc.
166 N. Dithridge St. Suite G4
Pittsburgh, PA 15213
Phone: (412) 735-4799
Email: information@atrpsolutions.com



Sample Page from 2009 Spring Catalog

Helpful references

ARGET and ICAR ATRP: a) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. A.; Tsarevsky, N. V., *Proc. Nat. Acad. Sci. U.S.A.* **2006**, *103*, 15309, **b)** Jakubowski, W.; Matyjaszewski, K., *Angew. Chem. Intl. Ed.* **2006**, *45*, 4482, **c)** Jakubowski, W.; Min, K.; Matyjaszewski, K., *Macromolecules* **2006**, *39*, 39.

Me_6TREN and TPMA: a) Tsarevsky, N. V.; Matyjaszewski, K., *Chem. Rev.* **2007**, *107*, 2270, **b)** Tsarevsky, N. V.; Braunecker, W. A.; Brooks, S. J.; Matyjaszewski, K. *Macromolecules* **2006,** *39*, 6817, **c)** Xia, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5958, **d)** Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000,** *33*, 8629.

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Catalog and Brochure for 2009 Spring are available online.

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