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Polymers With Safe Amounts Of Copper

New polymerization techniques that reduce catalyst contamination of products could find broad industrial use

Stu Borman

Thanks to reduced requirements for metal catalysts, two new polymerization techniques—one that modifies and improves an important polymerization process and another that converts that process into a completely different procedure—could see broad industrial use for synthesis of a wide range of commercial polymers.

Atom transfer radical polymerization (ATRP), a type of controlled or living radical polymerization (LRP), is of central importance in polymer chemistry. This is because it is easy to carry out and can be used to make polymers with predictable structures and highly targeted molecular weight ranges.

But a major disadvantage of ATRP is that it requires high concentrations of transition-metal catalysts, primarily copper halides, which end up in the products. These copper contaminants have to be removed for the polymer products to be useful commercially, and separation is difficult and expensive.



Carnegie Mellon University

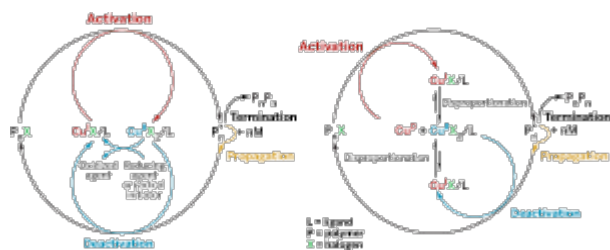
ATRP Group Jakubowski (from left), Matyjaszewski, Min, Tsarevsky, Huang, Braunecker, and Tang developed the ARGET and ICAR variations of ATRP.

ATRP has been used commercially in the U.S., Europe, and Japan, according to ATRP pioneer Krzysztof Matyjaszewski, professor of chemistry at Carnegie Mellon University. But the need to remove copper from ATRP polymers has limited wider commercial adoption of the technique.

Both new polymerization techniques greatly reduce the amount of copper halide catalyst required in ATRP. Polymers made with the new techniques end up containing only small amounts of copper that are considered safe and do not need to be removed, thereby making industrial applications much more feasible.

In ATRP, a Cu(I)-based catalyst is continually oxidized to a Cu(II) compound during polymerization. The Cu(I) catalyst is replenished by recycling, but unavoidable radical termination reactions cause the replenishment to be incomplete. Hence, a substantial amount of Cu(I) catalyst must be used to prevent its depletion during the reaction.

Earlier this year, Matyjaszewski and coworkers Wojciech Jakubowski, Ke Min, Nicolay V. Tsarevsky, Jinyu Huang, Wade A. Braunecker, and Wei Tang reported an ATRP variation called ARGET (activators regenerated by electron transfer), in which the catalyst is continuously replenished by environmentally safe reducing agents (*Angew. Chem. Int. Ed.* **2006**, *45*, 4482; *C&EN*, Oct. 16, page 44). They now report another variation called ICAR (initiators for continuous activator regeneration), in which radical initiators are used for the same purpose (*Proc. Natl. Acad. Sci. USA*, DOI: 10.1073/pnas.0602675103). Both variations reduce the concentration of copper catalyst needed to 10-50 ppm, from a typical 0.1 M in conventional ATRP.



Courtesy of Virgil Percec

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Cyclic In ATRP polymerization (left), a Cu(I) catalyst is reversibly oxidized when it converts halogenated monomer or polymer (P_nX) to a radical ($P_n\bullet$). One or several monomer units (M) add to the radical, increasing the size of the polymer. Cu(II) deactivates the radical product to a halide, completing the cycle. $P_n\bullet$ can also participate in undesirable early termination reactions. In ARGET and ICAR versions of ATRP, reducing agents or radical initiators reduce the required amount of Cu(I) catalyst to tens-of-ppm levels. In SET-LRP (right), Cu(0) is the catalyst, and disproportionation reactions provide Cu(II) needed in the polymerization cycle. Only tens-of-ppm levels of Cu(0) are required.

The studies by Matyjaszewski and coworkers demonstrate "that polymers with narrow molecular weight distributions and targeted molecular weights are obtainable with ATRP even when low amounts of copper catalyst are utilized," comments assistant professor of chemistry and biochemistry [Heather D. Maynard](#) of the University of California, Los Angeles. "This is beneficial, especially for producing polymers for biomedical applications."

Meanwhile, a new copper-based complex that also can be used at tens-of-ppm levels to catalyze ATRP polymerizations has been developed by assistant professor of chemical and petroleum engineering [Youqing Shen](#) and coworkers at the University of Wyoming, Laramie, in collaboration with Matyjaszewski's group. The work is soon to be published in the *Journal of the American Chemical Society*.

Taking a different approach, chemistry professor [Virgil Percec](#) and coworkers at the University of Pennsylvania have converted ATRP into a more industrially friendly process by redesigning it completely (*J. Am. Chem. Soc.* **2006**, *128*, 14156). In their new technique, called SET-LRP (single-electron transfer LRP), elemental copper, Cu(0), activates polymerization and is converted to a Cu(I) intermediate in the process. A spontaneous disproportionation of the intermediate, mediated by environmentally friendly solvents such as water or alcohols, then generates Cu(II), which is also needed to drive the polymerization cycle.



Paul R. Marchesano

SET-LRP Team Guliashvili (from left), Ladislav, Sienkowska, and Percec developed the SET-LRP technique, along with (not shown) Wistrand, Stjerndahl, Monteiro, and Sahoo.

Percec redesigned the polymerization with coworkers Tamaz Guliashvili, Janine S. Ladislav, Monika J. Sienkowska, Anna Wistrand, Anna Stjerndahl, Michael J. Monteiro, and Sangrama Sahoo.

The Cu(0) catalyst in SET-LRP is so much more reactive than the Cu(I) species used in ATRP that only a small amount needs to be used-tens-of-ppm levels, about the same range as in ARGET and ICAR. So here, too, there is no need to remove copper from the polymers produced.

According to Percec, advantages of SET-LRP are that it takes place at room temperature and below; undesirable side reactions such as early chain termination are undetectable; reaction times are fast; polymers with molecular weights in the multiple millions are accessible; and both nonactivated halogenated monomers such as vinyl chloride and activated monomers such as acrylates and methacrylates can be used with parts-per-million amounts of catalyst.

"The dramatic drop in the amount of catalyst, accompanied by the almost unbelievably high molecular weights, makes this work stand out," says chemistry professor David M. Haddleton of the University of Warwick, in England, of the SET-LRP study. Percec and coworkers "have taken the chemistry apart and put it back together again in a refreshing way that will make it possible to synthesize polymers not available before," he says.

Both Matyjaszewski's group and Percec's are currently pursuing industrial adoption of the new techniques.

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