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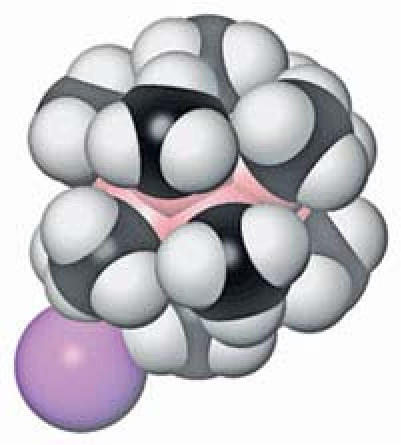
**Macromolecular Chemistry**

# New Radical Route To Polyolefins

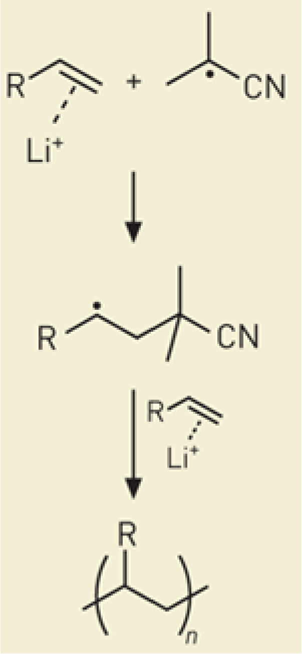
## Weakly solvated 'naked' $Li^+$ promotes novel radical polymerization of alkenes

**Steve Ritter**

An accidental observation followed by a little detective work has led to the discovery that weakly solvated lithium ions can catalyze the radical polymerization of terminal alkenes, dienes, and acetylenes under mild conditions (*J. Am. Chem. Soc.* **2006,** *128*, 5610 and 5680). The finding, reported by Josef Michl and coworkers at the University of Colorado, offers a potentially less expensive route to some polyolefins, such as polyisobutylene, that normally can't be made by the radical route.



**Radical Step** "Naked" $Li^+$ coordinates to an alkene to catalyze radical polymerization initiated by the cyanoisopropyl (from AIBN) radical. In the carborane catalyst (top), $LiCB_{11}(CH_3)_{12}$, Li is purple; B, pink; $CH_3$, black and gray.



Uncatalyzed radical polymerization of ethylene typically requires high temperature and pressure, and the method isn't efficient for longer simple terminal alkenes, Michl explains. Thus, transition-metal coordination catalysts or Lewis acid catalysts (such as $BF_3$) for cationic polymerization are required, he notes.

Postdoc Stefanie Körbe in Michl's group observed by chance that lithium salts of alkene-substituted and permethylated carborane anion cage compounds formed oligomers when stored in air. The researchers were investigating these compounds as precursors for making polymers with pendant carborane anion groups, and the spontaneous oligomerization left them perplexed.

Michl happened to hear a lecture by Timothy Clark of the University of Erlangen-Nuremberg, in Germany, in which he mentioned in passing a prediction he had made in a computational paper in 1986 that $Li^+$ should catalyze methyl radical addition to ethylene.

"A bulb lit in my brain," Michl tells C&EN. "It's not much of an extrapolation to expect the propagation step in the radical polymerization of ethylene and other simple alkenes to be catalyzec by $Li^+$ as well."

But no one seems to have pursued Clark's idea, Michl says. He believes this is because lithium salts, such as LiCl, which have been used to catalyze other radical polymerizations, aren't soluble in nonligating solvents.

Michl's group, including postdoc Kamesh Vyakaranam and graduate student Josiah B. Barbour, proceeded to test the idea by polymerizing alkenes in a solution of $LiCB_{11}(CH_3)_{12}$ in dichloroethane in which the $Li^+$ ions are only weakly coordinated by the dichloroethane. This "naked" $Li^+$ is thought to coordinate to the alkene double bond, and a radical is formed with the aid of an initiator, which can be azobisisobutyronitrile (AIBN), di-*tert*-butyl peroxide, or oxygen in the air. Both the radical formation and polymerization steps are catalyzed by $Li^+$, Michl says.

The need for a radical initiator and the polymer properties are indicative of a radical polymerization mechanism, the researchers note. In addition, polymerization doesn't occur when $Li^+$ is trapped by crown ethers, when $Li^+$ is replaced with larger alkali-metal cations, or when a ligating solvent such as tetrahydrofuran is used.

The chemistry may be "the first really new development in radical polymerization of alkenes in a number of years," Michl says. There are some potential commercial applications, Michl adds, and he is discussing development opportunities with several companies.

The $Li^+$-catalyzed polymerization is "a great piece of work" and a "landmark" in the radical polymerization of unactivated terminal alkenes and acetylenes, comments chemistry professor Virgil Percec of the University of Pennsylvania. "I expect this elegant discovery will change the way we are going to look at radical polymerizations" and will affect many synthetic organic methods.

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