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POLYMER CHEMISTRY

Cross-linking polyethylene through carbenes

A carbene-forming molecule can glue various polymers, even ones lacking functional groups

By **Felix J. de Zwart, Johan Bootsma, Bas de Bruin**

The development of universal methods for surface modification and cross-linking of polymeric materials is highly desirable. Mechanical properties of natural and synthetic materials rely on the ability of the polymeric chains to form a three-dimensional (3D) network, for example, through cross-linking (1, 2). On page 875 of this issue, Lepage *et al.* (3) show that a rationally designed *bis*-diazirine inspired by the well-known 3-aryl-3-(trifluoromethyl)-3*H*-diazirine motif can be used for the cross-linking of nonfunctionalized saturated hydrocarbon polymers.

In natural macromolecules such as chitin and synthetic materials such as Kevlar, hydrogen-bond formation between amide groups form noncovalent cross-links. Many oil-based polymer coatings used in paintings and to protect wooden structures derive their 3D structure and strength from covalent cross-links formed in radical-based processes. Other examples of covalent cross-linking, such as vulcanization of rubber and the drying of glues, rely on reactive functional groups already present in the polymer.

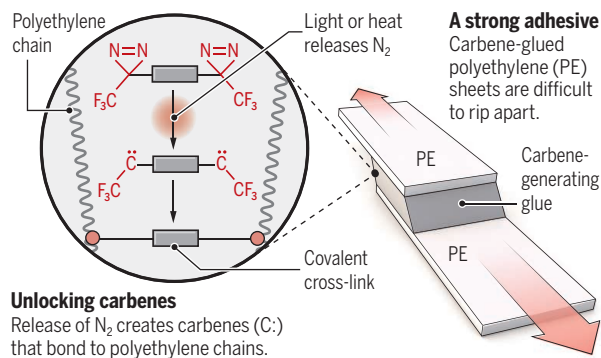
Polymers such as polyethylene (PE) and polypropylene (PP) lack reactive cross-linkable groups, but cross-linking can be essential to tune mechanical properties. Copolymerization of ethylene or propylene with functionalized olefins can introduce reactive groups, but the scope of suitable comonomers is limited, and important material properties such as microstructure and molecular weight can become difficult to control (4, 5). It is especially challenging to synthesize high-molecular weight copolymers with tunable amounts of functional groups (5). Mildly efficient cross-linking strategies that break carbon-hydrogen (C–H) bonds by using high-energy radiation or peroxides exist for PE, but these

methods degrade PP (6). High-energy reactants tend to react through hydrogen-atom abstraction (HAA) and related radical-type pathways that damage the polymer.

Free (singlet) carbenes and transition-metal carbene complexes can undergo direct C–H insertion instead of HAA to form covalent carbon-carbon bonds even from unactivated C–H bonds. Carbenes are used for polymer postfunctionalization, as polymerization catalysts and as polymer backbone

Getting a grip on polyethylene

Lepage *et al.* designed a molecule that generates highly reactive carbenes that can cross-link unreactive alkyl polymers.



(4, 5, 7). Tri- and tetravalent photoactivatable azides and diazirines can cross-link polyethylene glycol, but efficient generic cross-linkers for the strengthening of unfunctionalized polyolefins have not been developed (8).

Lepage *et al.* now report a carbene cross-linker containing two diazirine motifs. Free carbenes can be generated upon photochemically or thermally induced nitrogen (N_2) loss (see the figure). A drawback of molecules containing N_2 expelling motifs (such as diazirines) is explosion risk, and the authors abandoned known *bis*-diazirine compounds because of their volatile and explosive nature. They rationally designed a *bis*-diazirine cross-linker that finely balances risk and reactivity and generates two free carbenes that insert into C–H bonds of the polymer. The tethered structure forms cross-links between different polymer chains, even those of PE and PP. The molecular weight of PP increased with the

amount of cross-linker added, corroborating successful cross-linking of the substrate. The *bis*-diazirine also cross-linked several other polymers, such as polyvinylalcohol (PVA). For PVA, whether carbene insertion occurred through C–H or O–H bonds was not investigated, but the latter seems most likely (9). This cross-linking methodology could find applications in upgrading biopolymers in which O–H bonds are ubiquitous.

The authors also explored application of the cross-linker as an adhesive for high-density PE (HDPE). Adhesion to this low-surface-energy material is difficult—it failed for a control sample with a commercial adhesive (Super Glue). However, the *bis*-diazirine cross-linker showed high performance in adhesion tests, and analysis of ripped samples revealed a cohesive failure mechanism indicative of cross-linking to the HDPE surface. The cross-linker was also an effective synthetic fabric strengthener.

Lepage *et al.* assume that in their reactions, singlet carbenes are generated that insert in a concerted manner into C–H bonds, which makes sense given the relatively controlled reactivity toward cyclohexane. But formation of triplet carbenes that react through radical processes cannot be fully excluded (10). Radical-type pathways could damage polymer integrity, so examining the electronic structure of the formed carbenes is needed. This could also aid in developing carbenes that can be generated at lower temperatures, possibly through transition-metal catalysis (4).

The cross-linker developed by Lepage *et al.* not only has potential applications as an adhesive, but similar reagents could be used in paints and coatings. Prospective bio-based binders such as cellulose and lignin lack readily cross-linkable groups such as isocyanates, ketones, or alkenes. The cross-linking method of Lepage *et al.* may help turn biomass-based macromolecules into functional materials. ■

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