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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)-3H-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 cross-linking of polymeric materials is highly desirable. Mechanical properties of surface modification and cross-linking are thus important material properties such as microstructure and molecular weight can become difficult to control (3). 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 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 (4). 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 pathways 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.

REFERENCES AND NOTES

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Polyethylene chain
N=N
F3C
N=N
Light or heat releases N2
A strong adhesive
Carbene-glued polyethylene (PE) sheets are difficult to rip apart.
Polyethylene chain
N=N
F3C
N=N
Unlocked carbenes
Release of N2 creates carbene (C) that bond to polyethylene chains.

Getting a grip on polyethylene

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

\[ N=N \quad (\text{bis-diazirine}) \]

Tri- and tetravalent photodeactivatable 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 (N2) loss (see the figure). A drawback of molecules containing N2 expelling motifs (such as diazirines) is explosion risk, and the authors assumed 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 pathways 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).

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