Cross-linking polyethylene through carbenes

de Zwart, F.J.; Bootsma, J.; de Bruin, B.

DOI
10.1126/science.aaz7612

Publication date
2019

Document Version
Final published version

Published in
Science

License
Article 25fa Dutch Copyright Act

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
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 covalent 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 nonfunctionalized polymers, such as polyvinylalcohol (PVA).

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 functionality already present in the polymer (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 carbene can be generated upon photochemical or thermally induced nitrogen (N₃) loss (see the figure). A drawback of molecules containing N₃ 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 carbene that insert into C–H bonds of the polymer.

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 carbene 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 carbene 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 carbene is needed. This could also aid in developing carbene 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

ACKNOWLEDGMENTS
We thank the ARC-CBBC (projects 2016.001.UvA and 2018.O15.C) for financial support.

Van ’t Hoff Institute for Molecular Sciences (HIM), University of Amsterdam (UvA), Science Park 904, 1098 XH Amsterdam, Netherlands. Email: b.debruin@uva.nl

Van ’t Hoff Institute for Molecular Sciences (HIM), University of Amsterdam (UvA), Science Park 904, 1098 XH Amsterdam, Netherlands. Email: b.debruin@uva.nl