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Self-Healing Polymer Via Olefin Metathesis

Tech ID: 23528 / UC Case 2013-103-0

BRIEF DESCRIPTION

Introducing self-healing capability into materials would greatly improve their safety feature, lifetime, and energy efficiency. A significant amount of effort has been devoted to this field in recent years, and several groups have reported different selfhealing polymer designs through the incorporation of encapsulated monomers, dynamic non-covalent bonding, and reversible or irreversible covalent bonds into polymers. Recently, dynamic covalent chemistry techniques such as thermal and light-catalyzed cycloaddition, transesterification, radical reactions, thiol-disulfide exchange, hydrazone formation, and siloxane equilibration have attracted much attention for their applications in self-healing or malleable polymer designs. Most dynamic covalent bonds used for self-healing applications involve heteroatoms in dynamic exchange reactions. In principle, reversible carbon-carbon bond formation should be particularly attractive for such applications because the high stability of C-C bonds may offer the possibility of designing stronger self-healing materials. Among the few examples of dynamic C-C bond-based selfhealing polymers, those involving strong C-C bonds, such as reversible Diels-Alder reactions and photochemical cycloaddition reactions, require substantial inputs of external energy in the form of heat or light to trigger the reversible C-C bond formation. On the other hand, the one using weak dynamic C-C bonds, which can self-heal without providing external energy, only results in relatively weak self-healing polymer gels. In addition, most of those self-healing systems require specially designed monomers or polymers to serve the purpose. It would be highly desirable to develop a simple strategy for effective polymer healing through dynamic exchange of strong C-C bonds under ambient conditions. Toward this goal, herein we report a simple, efficient selfhealing polymer design employing transition-metal-catalyzed olefin metathesis for reversible C-C double bond exchange . Olefin metathesis reaction is attractive for this purpose because it is highly efficient for shuffling strong C-C double bonds under ambient conditions. In the current study, we have shown that by introducing a very low level of the Grubb's second-generation Ru metathesis catalyst into a readily available polybutadiene (PBD) network, the material can heal efficiently under mild conditions. With moderate pressure, this material can effectively heal in the air, at ambient or even subambient temperature. Given the efficiency and versatility of olefin metathesis as well as the abundance of olefin-containing polymers, we envision that this could be a powerful approach for self-healing material design.

ADVANTAGES

It is demonstrated for the first time that a bulk polymer could effectively heal via dynamic covalent bond formation at sub-ambient temperature. The Ru-loaded PBD samples not only heal well with themselves but also with control samples without any catalyst. Furthermore, a completely Ru-free PBD network can heal effectively upon simply applying a very small amount of Ru catalyst only at the fracture surface. The simplicity and effectiveness of this self-healing approach make it potentially applicable to a wide range of olefin-containing polymers.

PATENT STATUS

Country	Type	Number	Dated	Case
United States Of America	Issued Patent	9,133,313	09/15/2015	2013-103

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