The Mechanochemistry of the Cross-linked Polymer Containing Cyclic Mechanophores

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Keywords: *Mechanochemistry, Mechanophore, Macrocycles, Mechanical property, Network polymer*

Force-responsive molecules, called mechanophores, enable the functionalization of the polymeric materials induced by mechanical stimulus. In this work, we developed a novel cyclic mechanophore which can be cleaved homolytically without chain scission and generate the corresponding stable sulfur radicals, upon the mechanical stimuli. We chose bis(2,2,6,6-tetramethylpiperidin-1-yl)disulfide (BiTEMPS) (**Figure 1a**), which is known as dynamic covalent disulfide bond having low bond dissociation energy (26.2 kcal/mol),[1] as a mechanophore. A macrocyclic mechanophore containing BiTEMPS unit (BCM) was newly designed and synthesized (**Figure 1b**). Cross-linked poly(hexyl methacrylate)s (CPHMA) possessing BCM at the cross-linking points (BCM-CPHMA) were synthesized by free radical polymerization. The stress relaxation test and the tensile test revealed the unique mechanical properties of BCM-CPHMA based on the cleavage reaction of BCM at the cross-linked points upon mechanical stimulus (**Figure 1c**). Moreover, we found out the mechanical self-strengthening of BCM-CPHMA. The tensile tests and swelling tests showed the successful strengthening of BCM-CPHMA after compression without any additives such as monomer and modifier, and any other stimulus (**Figure 1d**).

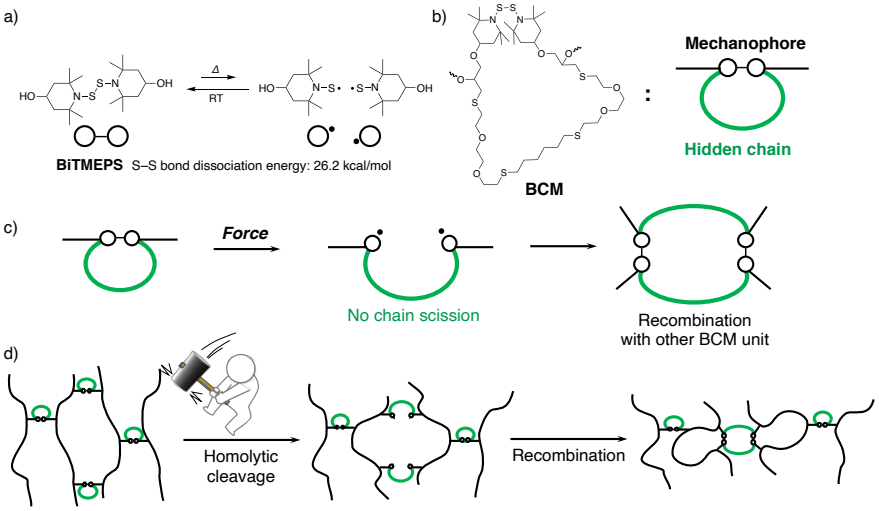

Figure 1. a) Dynamic behavior of BiTEMPS. b) Chemical structure of BCM. c) Cleavage and recombination of BCM. d) Mechanism of mechanical self-strengthening of cross-linked polymer possessing BCM (BCM-CPHMA).

1) H. Otsuka et al., *Angew. Chem. Int. Ed.* **2017**, *56*, 2016.