Site-Specific Mechanochemical Activation of Link-Functionalized Polymers

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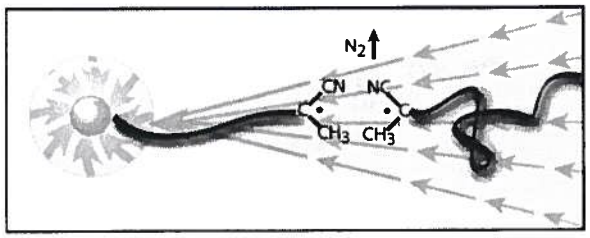
The relationship between mechanical energy and chemical reactivity is not well understood, yet the activation of chemical bonds by mechanical forces is a common occurrence that contributes to the degradation of polymeric materials. To investigate this relationship, the mechanochemical effects on azo link-functionalized poly(ethylene glycol) polymers were studied. Upon exposure to ultrasound, link-functionalized poly(ethylene glycol) polymers containing a centered azo moiety were found to cleave site-specifically; the rate of chain scission increased with increasing molecular weight. An off-center, link-functionalized polymer was found to cleave at the off-center azo linkage, despite mechanical forces being strongest at the center of the polymer chain. The site-specific activation of link-functionalized polymers can further be applied to the study of mechanochemically-initiated reactions.



Diastereoselective [4+2] Annulation of Vinyl Carbodiimides with *N*-alkyl Imines. Asymmetric Synthetic Access to the Batzelladine Alkaloids

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The batzelladine family of polycyclic guanidine alkaloids is among the most noteworthy of marine natural product classes isolated in recent decades. As a result of their interesting biological activity, as well as their complex molecular architecture, this family of alkaloids has been the focus of extensive synthetic studies. Our synthetic strategy focused on a diastereoselective [4+2] annulation of vinyl carbodiimide **2** with chiral *N*-alkyl imine **3** as a means to access the stereochemically rich tricyclic core of the batzelladine alkaloids. This strategy culminated in the shortest asymmetric synthesis of batzelladine D (**1**) reported to date. Current efforts are focused on applying this methodology to the synthesis of other members of the batzelladine alkaloids.