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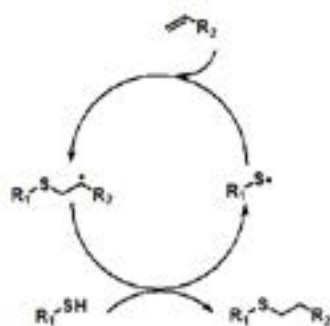
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Furious and tranquil radicals: A computational study of sulfur-centered radical chemistry

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Recently, there has been growing interest in both the thiol-ene (Scheme 1) and thiol-yne sister reactions in various application areas from polymer field to bioconjugative materials due to the extraordinary advantages of these reaction techniques in, for example, forming uniform polymer networks with narrow T_g values and low shrinkage stress. The most outstanding feature of these reactions is combination of the advantages of both step growth and chain growth polymerization reactions. Another attractive subject is self-healing polymeric materials that have been brand-new of interest in polymer science. Some of these materials utilize trithiocarbonate or thiuram disulfide units in the polymer structure which allows healable backbone of polymer chain. It is well known that the sulfur-centered radicals play a vital role in these thiol reactions or self-healing processes. To better understand the structure-reactivity trends of these extraordinary radicals, we have used computational chemistry (at the G3(MP2)-RAD//MP2/6-31G(d) level of theory) to study the highly reactive alkyl thiyl radical addition reaction to the C=C and S=C double bonds of various compounds. In addition to this, the high stability of the sulfur-centered radicals has been extensively studied to elaborate controversial behavior of these radical species. We find that the high SOMO energy of the radicals has the ability to undergo resonance interactions with π^* of the substrate and this allows formation of stabilized transition state structure in radical addition reactions. The same effect is account for enormous stability of sulfur-centered radicals which are more effectively conjugated with heavier lone-pair donor and π -acceptor substituents than carbon-centered radical analogues.



Scheme 1: Representation of the most significant steps of thiol-ene reaction mechanism.

Biography

Isa Degirmenci completed his under-graduated from Marmara University in 1998-2002 and graduated from Boğaziçi University in 2002-2005 respectively. He was awarded PhD from Gent University, Belgium and completed Post-doctoral studies from Australian National University. He has his expertise in "Structure-reactivity relationships in the free radical polymerization reactions". His investigations combine the structure properties of radical species and monomers with application of quantum chemical tools. His recent studies have simply explained the extraordinary reactivity and stability behavior of sulfur-centered radicals. These findings can be considered as paving the way for further utilizing recently emerged thiol-ene and thiol-yne polymerization reactions.

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