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Quantum chemical study on tuning thiol-ene polymerization

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Recently, there has been a growing interest in the thiol-ene polymerization in many application areas from material science to bioorganic chemistry due to the production of uniform polymer network, reduction of polymer shrinkage stress and obtaining narrow the T_g range. The most prominent feature of this polymerization is combination of the advantages of both step growth and chain growth polymerizations. The thiol-ene polymerization is involved in the initiation, propagation and chain transfer steps. This procedure is mostly governed by ratio of the propagation (k_p) and chain transfer (k_{CT}) reaction rates (k_p/k_{CT}). Recent experimental and theoretical studies have focused on ene functionality to evaluate the reaction procedure while the thiol functionality has been ruled out. However, this study has suggested that the thiol functionality also have to be taken into account to adjusting properties of a polymer. For this aspect, phenyl thiol derivatives have been considered for the thiol-ene polymerization of various monomers from electron deficient to electron rich alkenes. To evaluate kinetic and energetic features of the thiol-ene procedure, M06-2X/6-31++G(d,p) level of theory was used for all geometry optimizations and frequency calculations. It was revealed that electrophilic nature of the phenylthio radicals and the stability of the RS-ene⁺ configuration predominates effect of the S-T gap of the ene functionality during addition reactions. Moreover, intermolecular interactions, such as π - π , have crucial role on the transition state of the chain transfer step. These interactions can diminish the strong influence of stability of intermediate carbon-centred radical on the chain transfer activation barrier. As a consequence, it was proved that the k_p/k_{CT} ratio is affected not only by ene functionality but also by the thiol functionality. This information can be taken into consideration for tailoring mechanical and physical properties of a polymer without changing the alkene structure to obtain industrially desirable polymer.

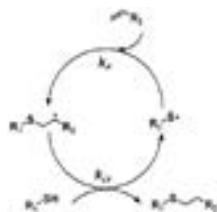


Figure 1: Representation of the most significant steps of the thiol-ene reaction mechanism.

Recent Publications

1. Degirmenci I and Coote M L (2016) comparison of thiyl, alkoxyl, and alkyl radical addition to double bonds: the unusual contrasting behavior of sulfur and oxygen radical chemistry. *J. Phys. Chem. A*. 120(10):1750-1755.
2. Degirmenci I and Coote M L (2016) Effect of substituents on the stability of sulfur-centered radicals *J. Phys. Chem. A*. 120(37):7398-7403.
3. Degirmenci I and Coote M L (2016) Understanding the behaviour of sulphur-centred radicals during polymer self-healing *J. Turk. Chem. Soc. Sect. A: Chem.* 3(3):707-720.
4. Degirmenci I et al. (2013) Origins of the solvent effect on the propagation kinetics of acrylic acid and methacrylic acid *J. Polym. Sci. Part A: Polym. Chem.* 51(9):2024-2034.

Biography

Isa Degirmenci completed his under-graduation from Marmara University in 1998-2002 and graduation 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 understanding 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-centred radicals. These findings can be considered as paving the way for further utilizing recently emerged thiol-ene and thiol-yne polymerization reactions and also for further benefitting from self-healing reaction mechanisms of polymeric materials.

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