

Self-Initiated Thermal Thiol-ene Polymerization : Elucidation of the Mechanism

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Résumé

The radical-initiated addition of thiols to alkenes to yield thioether products has been known for more than a century.¹ However, it is only since the 2000s that this reaction has been the subject of a renewed interest as part of efforts to find chemical reactions meeting the “click” chemistry criteria.² The major use for thiol-ene reaction is in polymerization.³ Generally, a thiol-ene step polymerization involves a radical photoinitiator and neat monomers with two or more SH/C=C groups per molecule in order to generate a crosslinked structure. The most significant and unresolved problem of thiol-ene systems remains spontaneous polymerization.⁴ Lack of chemical stability has been reported in the literature for a broad range of thiol-ene monomers, generally without solvent, at ambient temperature and under conditions avoiding the formation of radicals. The mechanism of spontaneous thiol-ene polymerization is not well established.⁵ It is considered to involve a self-initiated polymerization process since the thermal homolysis of impurities present in the monomers (e.g., peroxides or hydroperoxides) is assumed to be negligible. A major development in the thiol-ene polymer field would be the elucidation of the self-initiation mechanism. By this way only, efficient mitigation strategies could be found to prevent early thermal polymerization. It is the goal of this research to elucidate the main mechanism(s) of self-initiation of thiol-ene monomers, and to determine the factors that underlie the reactivity of a self-initiated thiol-ene polymerization, in particular as regards to experimental conditions (solvent, atmosphere) and the structure of ene and thiol compounds.

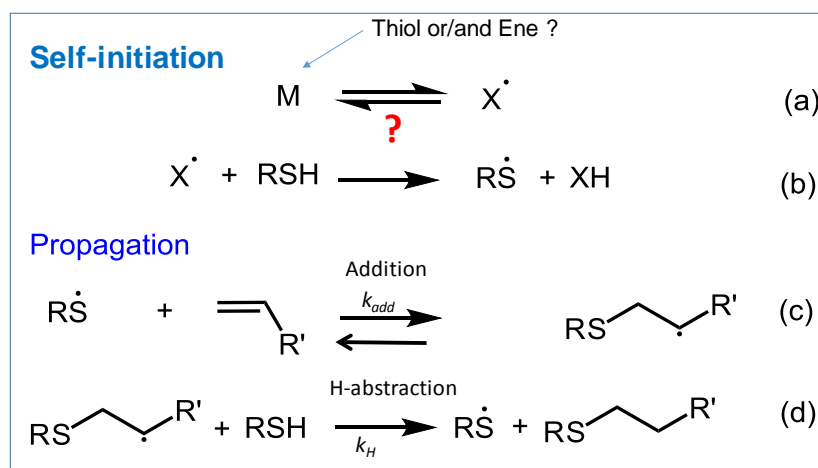


Figure 1. Mechanism of self-initiated thiol-ene polymerization

Références

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