

THE MECHANISM OF THE SELF-INITIATED THERMAL THIOL-ENE POLYMERIZATION: SOLUTION OF A CLASSIC PROBLEM

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Radical-mediated thiol–ene chemistry refers to the addition of thiyl radicals to C=C double bonds. Thiol–ene reactions are most commonly photoinitiated, and generally employed for the synthesis of cross-linked poly(thioether) materials via photopolymerization. While the acrylic family of polymer is presently the overwhelming choice in the field of photopolymerization, thiol-ene systems have gained acceptance in overcoming the problems associated with the monomer toxicity or the volume shrinkage. However, many examples in the literature show the challenge of achieving shelf-life stability of thiol-ene monomer mixtures in bulk under conditions that avoid the formation of free radicals. Several mechanisms for the spontaneous thermal polymerization of thiol-ene monomers have been proposed since 40 years, but there is currently no consensus as to the correct mechanism. Today, the polymer community has focused on finding suitable inhibitors to prevent premature reaction, but has demonstrated less interest in the fundamental understanding of thiol-ene self-initiation mechanism. Using a range of spectroscopic techniques (real-time FTIR, electron spin resonance and ^1H NMR), we provide experimental evidence that self-initiation proceeds via two concurrent pathways: firstly, the one-electron transfer reaction from thiol to molecular oxygen, secondly, the hydrogen atom abstraction from the thiol to form C-H bond at the olefin.