236i Photopolymerizable Thiol/Vinyl Ether Hybrid Materials

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Hybrid polymerizable systems, systems where one or both of the monomers used in the polymerization contain functional groups which are polymerizable by more than one cure method, have received significant consideration for applications such as coatings and ink technologies in the last few years. Currently, investigations have focused on acrylate/epoxide and acrylate/ vinyl ether hybrid systems, offering synergistic mechanical and kinetic properties. More specifically, reactions involve two different chain growth mechanisms, where one network is polymerized via a radical polymerization, and the other is polymerized via cationic polymerization, with the two polymerizations types occurring either sequentially or simultaneously. While these investigations create resins with combined properties, the chain growth mechanisms make it difficult to achieve resins with low polymerization shrinkage and stress or more flexible resins.

The utilization of hybrid polymerizations incorporating a radical step growth mechanism and cationic chain growth mechanism would offer both tailorable properties, delayed gelation, and reduced shrinkage as a consequence of the step growth polymerization. A thiol/vinyl ether hybrid material offers this unique tailorability, where the vinyl ether monomer participates in both the step growth polymerization with the thiol monomer and homopolymerizes through the chain growth mechanism. Thiol-ene polymerizations are noted for their advantages such as rapid cure time, lack of oxygen inhibition, excellent adhesiveness, and low polymerization shrinkage and shrinkage stress, but the polymers achieve limited mechanical properties. Vinyl ether polymerizations offer low odor, reduced skin irritancy, lack of oxygen inhibition, rapid polymerizations, and hard, high gloss coatings, yet are sensitive to impurities. Hence, the creation of thiol/vinyl ether hybrid resins offers a balance between hardness, flexibility and adhesion, with fast cure speeds, reduced inhibition and toxicity, and low shrinkage and shrinkage stress. In this investigation, the effect of monomer concentration, initiator concentration, light intensity, exposure time, and temperature excursion on the polymer kinetics, mechanical properties and morphology of thiol/vinyl ether hybrid materials will be investigated.