THIOL SUBSTIUTION IN THIOESTER NETWORKS

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Thiol-thioester exchange has received a great deal of attention for generating covalent adaptable networks (CANs) due to efficient exchange at low temperatures, solvent tolerance, orthogonality to a variety of functional groups, and tunable dynamics. Recent work regarding the impact of thiol-substitution on thiol-X reactions indicates that increasing the substitution of the thiol may impact the CANs behavior because of increased steric hinderance that slows the rate of exchange. The work here explores the impact of thiol/thioester substitution in three contexts. The first is a model compound study to determine whether one thiol/thioester pair is favored when a primary thiol is mixed with a secondary thioester, or vice versa, to understand the relative reactivity of secondary thioesters compared to primary analogues. The second consists of a thioester containing thiol-ene networks that are only capable of thiol-thioester exchange. While the third consists of thiol-anhydride-ene networks whose thioester bonds may undergo either thiol-thioester exchange or reversible thiol-anhydride addition. A combination of dielectric spectroscopy, to probe molecular and chain dynamics, and mechanical stress relaxation, to verify observed trends and compare relaxation times and activation energies, were used to evaluate the effect of substitution on the relaxation rates. For the thiol-anhydride networks, the effect of substitution on the prevalence of each dynamic pathway was also evaluated.