

# Deformation Signaling in Polymeric Materials *via* Non-Sacrificial Interactions

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Damage in polymeric materials is typically accompanied by the uncontrolled, irreversible breakage of chemical bonds. Mechanophores, *i.e.*, chemical entities that feature force-responsive chemical bonds, have been incorporated into a range of polymers and enable the study of the mechanisms through which materials resist damage and ultimately fail. Selected mechanophores equipped with chromogenic moieties (*e.g.*, dyes or fluorophores) indicate bond breakage events through an optical signal and thus permit the spatiotemporal tracking of molecular-level stresses in a wide range of materials. However, a disadvantage of many mechanophores is that the breakage of the covalent bonds is irreversible and typically requires a high threshold stress for activation, effectively limiting their output to a one-time "on/off" signal after significant damage has already occurred.

In the present thesis, supramolecular (*i.e.*, non-covalent) interactions are explored as alternative force-sensitive motifs in polymeric materials that may offer significant advantages over conventional "covalent" mechanophores. The investigations center on two non-sacrificial mechanoresponsive entities that change their fluorescence color in response to externally applied forces, and in doing so provide a ratiometric optical response that allows for the highly sensitive and reversible detection of bulk strains and stresses in real time. The first motif, a telechelic macromolecule terminated with excimer-forming oligo(*p*-phenylene vinylene) fluorophores (tOPV), is used as an additive to endow a variety of different polymers with mechanochromic properties *via* a simple blending approach. *In-situ* confocal microscopy imaging is used to show that the additive forms micrometer-sized inclusions that deform in line with the host matrix. This phase-separated morphology gives rise to a highly sensitive and reversible response to mechanical strain that mirrors the properties of the matrix polymer. In a second approach, a new non-sacrificial mechanophore (UPy-bispyrene or UPB) was developed by modifying the hydrogen-bonding 2-ureido-4-pyrimidinone (UPy) motif with excimer-forming pyrene fluorophores, and the mechanophore is exploited for the quantitative, real-time monitoring of bulk stresses in supramolecularly cross-linked polyacrylate films. The fluorescence signal is found to be directly correlated to the number of UPy motifs that form supramolecular dimers, thus enabling the tracking of the formation and disruption of hydrogen-bonding interactions in the polymer films at different stages of processing, after subjection to heat, or in response to mechanical force. Moreover, the mechanofluorescent response of UPB cross-links correlates with the applied *stress* – in contrast to more weakly associated motifs that display a *strain*-correlated mechanochromic response. Taken together, the investigations of the mechanochromic behavior of self-reporting additives and hydrogen-bonding dimers detailed in this thesis showcase the versatility of non-sacrificial interactions for translating bulk mechanical forces into easily detectable optical signals.

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