

Polymer Mechanochemistry

International Edition: DOI: 10.1002/anie.201510171
German Edition: DOI: 10.1002/ange.201510171 **Mechanochromism and Mechanical-Force-Triggered Cross-Linking from a Single Reactive Moiety Incorporated into Polymer Chains**Huan Zhang⁺, Fei Gao⁺, Xiaodong Cao, Yanqun Li, Yuanze Xu, Wengui Weng,^{*} and Roman Boulatov

Abstract: Incorporation of small reactive moieties, the reactivity of which depends on externally imposed load (so-called mechanophores) into polymer chains offers access to a broad range of stress-responsive materials. Here, we report that polymers incorporating spirothiopyran (STP) manifest both green mechanochromism and load-induced addition reactions in solution and solid. Stretching a macromolecule containing colorless STP converts it into green thiomerocyanine (TMC), the mechanically activated thiolate moiety of which undergoes rapid thiol–ene click reactions with certain reactive C=C bonds to form a graft or a cross-link. The unique dual mechanochemical response of STP makes it of potentially great utility both for the design of new stress-responsive materials and for fundamental studies in polymer physics, for example, the dynamics of physical and mechanochemical remodeling of loaded materials.

Polymer mechanochemistry is a field of modern chemistry that studies how exogenous forces drive chemical changes.^[1] Suitably designed reactive sites (so-called mechanophores) offer the potential to harness otherwise destructive mechanical loads into productive functionality.^[2] Examples of mechanochemical responses demonstrated to date include mechanochromism (change in the optical properties of material under load)^[3] and mechanoluminescence,^[4] load-induced cross-linking,^[5] altered product distribution,^[6] stabilization of transient states,^[7] mechanocatalysis,^[8] and release of small molecules.^[9] Of particular interest are mechanophores that combine two or more responses, for example, mechanochromism with load-induced cross-linking, as such composite mechanochemistry would enable the design of materials with a greater range of useful macroscopic responses to loads that is currently possible.

The combination of mechanochromism and load-induced cross-linking is particularly attractive because it would simultaneously reveal the regions of high stress and autono-

mously reinforce them to reduce the chance of catastrophic failure. Load-induced cross-linking was pioneered by the research group of Craig using, e.g., *gem*-dibromocyclopropane, bicyclo[4.2.0]octane (BCO) and benzocyclobutene that generate reactive products capable of addition to complementary reactive sites within the polymer matrix.^[5] Examples of mechanochromic (albeit not cross-linking or self-strengthening) polymers are more numerous. Relevant to this report are materials, introduced by Davis and co-workers, containing colorless spiropyran (SP) in macromolecular backbones.^[3a] Upon loading, the equilibrium between SP and its red-purple merocyanine (MC) isomer in chains that experience force on the order of 200 pN or more^[10] is shifted almost exclusively to the MC side (<0.1% of SP). Our group recently developed several SP-containing thermoplastic elastomers^[3b–e] and employed SP to study the force distribution around a running crack-tip.^[3f]

Herein, we demonstrate that spirothiopyran (STP, Figure 1) is the first example of a composite mechanophore that manifests both mechanochromism and load-triggered addition reactions. STP was previously shown to undergo thermo- and photoactivated isomerization^[11] and photoactivated thiol Michael addition.^[12] When STP is a part of a polymer backbone, mechanical load triggers both responses in solution and solid state without any additional stimulus or catalyst. These properties could make STP of considerable utility both for the creation of practically useful stress-responsive polymers and for studies of fundamental questions in polymer dynamics.

We studied mechanochemistry of STP using polyester and polyurethane containing multiple STP moieties distributed throughout the backbone (see Supporting Information for details). STP mechanochromism in solution was established by sonicating polyester **PES1** ($M_n = 59$ kDa; polydispersity index, PDI = 1.3; 1.95 mmol g^{−1} STP; Table S1) in DMF (4 mg mL^{−1}).^[3d] The starting solution was light yellow (Figure 2a) with no absorption band at wavelengths above 550 nm, indicating the absence of the thiomerocyanine (TMC) form. After 3 minutes sonication, the solution turned green (Figure 2b and Movie M1) accompanied by the growth of a broad absorption band centered at 635 nm (Figure 2b). The same transformation was induced without sonication by irradiating the solution at 365 nm, which is known to isomerize STP into TMC^[11b] (Figures S13,14). In both cases, the green color faded away within two minutes (in dimethylformamide, DMF) or less than 30 s (in tetrahydrofuran, THF) after sonication or irradiation was stopped, consistent with metastability of TMC in solution. Similar

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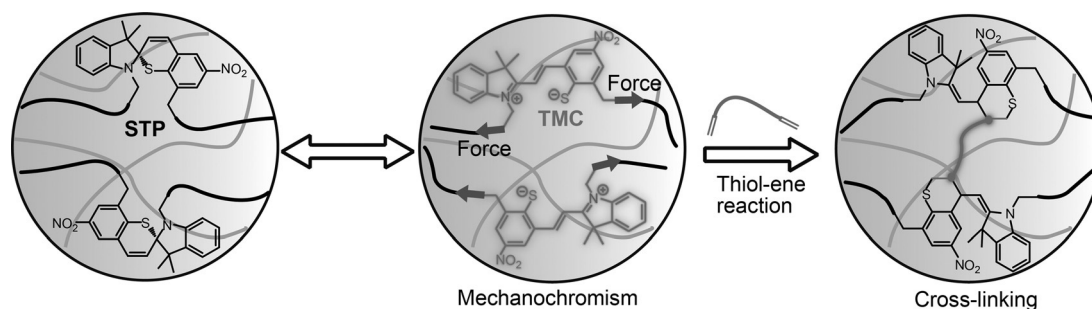


Figure 1. Dual mechanochemistry of spirothiopyran. In loaded materials colorless spirothiopyran rapidly isomerizes into green thiomercyanine, resulting in mechanochromism. The thiolate of thiomercyanine makes it reactive toward C=C bonds, endowing the material with the capacity to undergo load-triggered cross-linking.

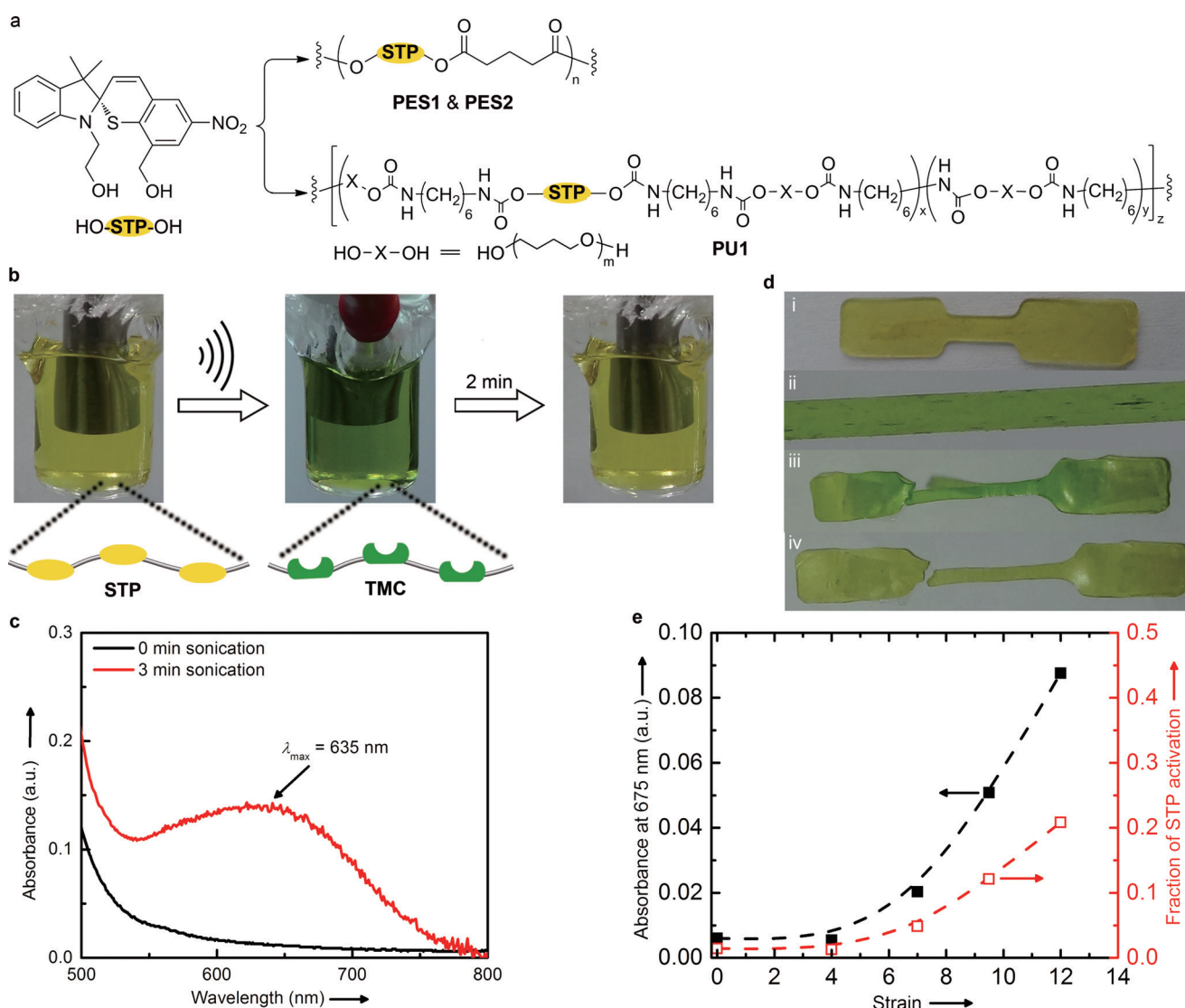


Figure 2. a) Schematics of polymers used in this study. Mechanochromism of STP-containing polymers in solution and bulk material: b) Images and c) the corresponding absorption spectra of polyester **PES1** in the range of 500 to 800 nm. The numbers indicate the sonication times and the black arrow denotes the characteristic absorption band of thiomercyanine. d) Mechanochromism of bulk spirothiopyran-modified polyurethane: i) unstrained, ii) at nominal strain of 12, iii) failed, iv) after 5 h resting. e) Normalized absorbance at 675 nm and fraction of STP moieties that isomerized to TMC as a function of nominal strain. The dashed line is a guide for the eyes.

results were also seen in polyurethane **PU1** solution upon sonication (Figure S17).

We studied solid-state mechanochromism of STP-containing polymers by uniaxially stretching films of polyurethane **PU1** (0.03 mmol g^{-1} STP). Loading (at an initial rate of 0.03 s^{-1}) caused the color of the gauge section of the specimen to change gradually from pale yellow to green (Figure 2c), with the absorbance at 675 nm increasing approximately proportionally to strain above 6 (Figure 2d and Figure S19). About 20% STP in **PU1** were activated to TMC at a strain of 12, as quantified by a previously described method.^[3b] Unlike in solution, the green color of the solid samples persisted for at least 2 h (Figure S20). In contrast, control polyurethane samples containing STP physically blended in the polymer matrix (as opposed being a part of the backbone) did not change color when stretched up to failure strain (Figure S21). Collectively, these results demonstrate that mechanical loading can isomerize colorless STP to green TMC in both solution and bulk material, that is, STP is mechanochromic.

We studied the capacity of STP to effect load-induced grafting by sonicating polyester **PES1** (4 mg mL^{-1} , THF) in the presence of *N*-ethylmaleimide (NEM, 19.5 mg mL^{-1} , the molar ratio of STP:NEM = 1:20). We periodically withdrew aliquots of the sonicated solution and analyzed them by UV/Vis spectroscopy, gel permeation chromatography (GPC), FTIR and ^1H NMR spectroscopy. The following evidence supports our view that sonication induced thiol–ene click addition between TMC and NEM (Figure 3a). First, the

green color appeared after the start of the sonication but quickly disappeared upon further sonication. This cannot be attributed to the reversion of TMC to STP, because sonication was also accompanied by a decrease in the intensity of the characteristic band of STP at 365 nm (Figure 3b), which did not recover when sonication was ceased (Figure S25). The same behavior was observed upon irradiation of a mixed solution of STP and NEM at 365 nm. Second, FTIR of the sonicated polymer (after precipitation and intense washing to remove unreacted NEM) revealed a new peak at 1655 cm^{-1} in addition to the 1700 cm^{-1} C=O stretch of NEM (Figure S28): this shift in the frequency of the C=O stretch is consistent with the loss of conjugation after thiol addition to C=C of NEM.^[13] Third, sonication produced a new set of ^1H NMR resonances which is characteristic of the STP-NEM adduct (Figure 3c; detailed spectroscopic characterization of the STP-NEM adduct is described in Figures S22–S24). The mechanochemical nature of the described reactivity is confirmed by the observation that sonicating an STP-modified polyester **PES2** ($M_n = 14 \text{ kDa}$, PDI = 1.2, 1.95 mmol g^{-1} STP, Table S1), that is too short to be hydrodynamically stretched,^[6b] for 5 h in the presence of NEM did not modify the STP moieties (Figure S32). In stark contrast to STP, SP-containing polymers of any length did not react with NEM under sonication or UV irradiation (Figure S33).

Despite a large excess of NEM, only about 60% of STP converted to the STP-NEM adduct upon prolonged sonication, as judged by both the change in absorbance at 365 nm and the integrations of ^1H NMR signals (Figure 3d and

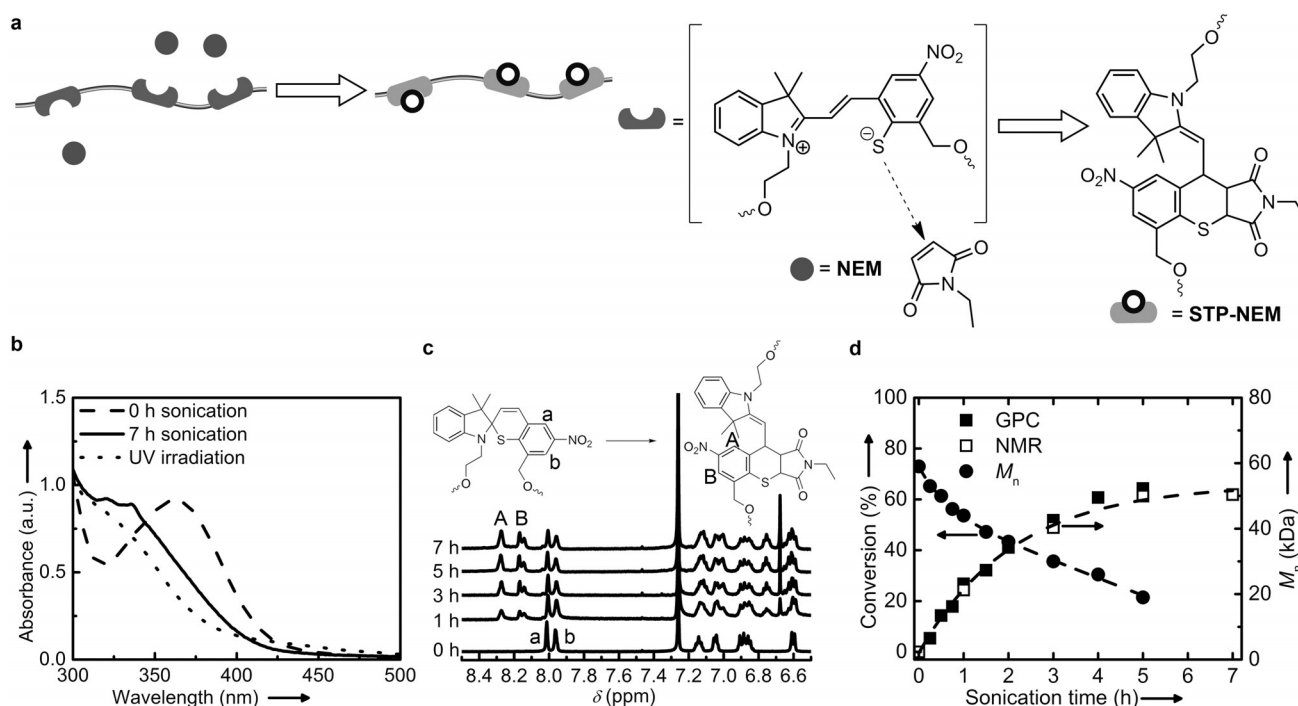


Figure 3. Force-induced thiol–ene click addition between spirothiopyran (STP) and *N*-ethylmaleimide (NEM). a) Schematics of the reaction. b) UV/Vis spectra of spirothiopyran-modified polyester before and after sonication and after irradiation (at 365 nm) without sonication, all in the presence of NEM (156 mM, 20 equiv). c) ^1H NMR spectra of polymers obtained by sonicating spirothiopyran-modified polyester in the presence of NEM. Note the upfield shifts of the spirothiopyran signals, H_a at 8.01 ppm and H_b at 7.96 ppm, to 8.28 ppm (H_a) and 8.16 ppm (H_b), respectively, upon the formation of the STP-NEM adduct. d) The degree of conversion of spirothiopyran determined from ^1H NMR spectroscopy and from GPC as well as the number average molecular weight, M_n , as a function of sonication time. The dashed lines are guides for the eyes.

Figure S29). The non-quantitative conversion can be attributed to the mechanochemical activation of only a fraction of STP moieties close to the center of mass of the chains.^[3a,6b] As is often observed with other polymers (e.g., refs. [5b] and [15], and citations therein), sonication also induced non-selective fragmentation of the polymer, with an average of 50 % of STP sites adding NEM molecules per each chain scission (Figure 3d, Figures S30 and S31).

As we expected, we observed the formation of insoluble material when we repeated the above sonication experiments with cross-linker 1,6-bismaleimido-hexane (BMH) (Figure 4a) and polyester **PES1** at 25 mg mL⁻¹ (which exceeds its critical overlap concentration of 13.8 mg mL⁻¹ and the molar ratio of STP:BMH = 1:0.15, Figure 4c). Prolonged sonication resulted in the conversion of about 35 wt % of **PES1** into the material that was insoluble in CH₂Cl₂, THF or DMF even upon heating (**PES1** is soluble in all these solvents). The FTIR spectra of the material contain the intense peak at 1655 cm⁻¹ characteristic of the STP-BMH adduct. The formation of the insoluble material suggests the rate of the bond-forming reactions (cross-linking) exceeded the rate of chain scission.

Although we at present lack the direct evidence that load-induced cross-linking occurs in solid state, Figure 5 indicates

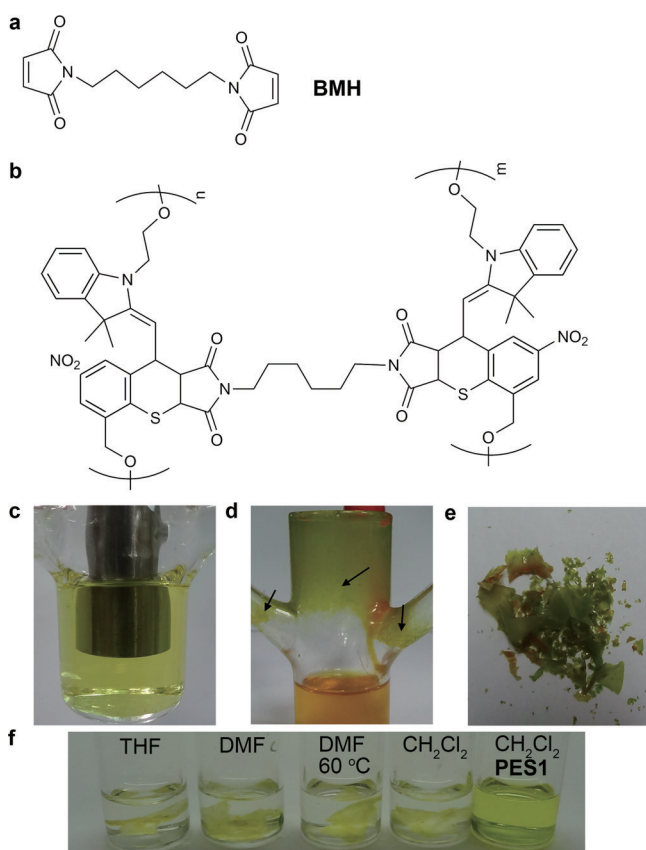


Figure 4. Mechanochemical cross-linking of polyester **PES1** in solution. a) The chemical structure of cross-linker 1,6-bismaleimido-hexane (BMH) and b) a plausible network resulting from sonication. c,d) The sonication apparatus before and after 20 min of sonication. e,f) The material peeled from the walls of the sonication cell, was insoluble in THF, DMF, and CH₂Cl₂, whereas the starting material **PES1** was soluble in CH₂Cl₂.

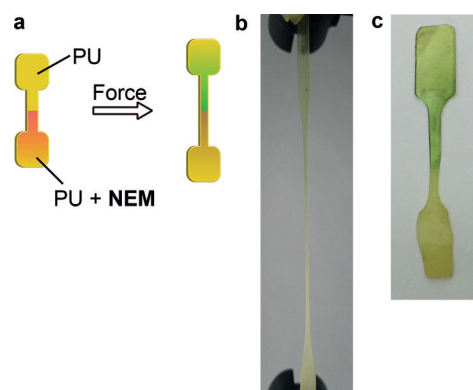


Figure 5. Load-triggered thiol-ene reaction in solid state. a) Schematic drawing of the testing sample. Half of the polyurethane **PU1** film was doped with NEM to demonstrate the elimination of the green color after reaction with TMC. b,c) Optical images of the doped film during tensile stretching and at rest.

that TMC and NEM react in bulk material as well. Figure 5a illustrates what happened when a “hybrid” specimen of STP-modified polyurethane **PU1**, one half of which was doped with NEM, was stretched. The undoped section acquired the expected green color (Figure 5b and c, compare to Figure 2d), whereas the color of the doped half did not change, suggesting a reaction between NEM and TMC.

Spirothiopyran (STP) described above integrates in a single moiety two distinct mechanochemical responses that hitherto required two separate reactive sites, such as red-mechanochromic spiropyran (SP) (which produces inert merocyanine, Figure S33)^[3a] or colorless bicyclocyclohexene (BCO) dicarboxylates (which allow load-triggered cross-linking in the presence of free thiols and a catalyst).^[5b] We suggest that STP could be particularly useful for the design of stress-responsive materials in combination with such single-mode mechanophores. For example, material containing both SP and STP may allow one to understand the dynamic interplay between physical and mechanochemical remodeling of material in loaded polymers, a problem of great interest in polymer mechanochemistry.^[14] The red mechanochromism of SP-containing polymers fades fairly quickly under static load, which is generally attributed to relaxation of individual polymer chains (physical remodeling) that reduces the strain exerted on merocyanine thus shifting the equilibrium back to the colorless SP isomer. Under comparable conditions, the green thiomercyanine appears to be far slower to revert to colorless STP but this process is accelerated greatly by the presence of certain C=C bonds, to which merocyanine is inert. Monitoring the absorbance of a material containing SP, STP and certain C=C bonds at 450 nm and 675 nm simultaneously could reveal the real-time dynamics of both physical and mechanochemical remodeling of a loaded material.

Based on preliminary DFT calculations, any force above 400 pN shifts the STP/TMC equilibrium to TMC (< 0.1 % of STP), whereas practically useful rates of C=C bond generating isomerization of the known mechanophores require higher forces (e.g., 1.5 nN to lower the half-life of Craig’s BCO^[5b] mechanophore to the millisecond timescale). There-

fore, combining caged enes, such as various cyclobutane derivatives^[5b,15] with STP may yield the first practical material capable of sequential damage sensing and load-triggered self-strengthening, that is, mechanochromism for stress sensing at initial loading stages followed by cross-linking for material strengthening upon further loading. The use of STP also eliminates the two major drawbacks of the reported mechanically facilitated thiol-ene reactions: the need for catalyst and for free thiols,^[5b] which are prone to oxidation by air. Because the reactive TMC readily reverts to inert STP, any thiolate generated by the load that does not react with uncaged C=C bonds before the load dissipated would revert back to oxidatively stable STP, and thus will be available for cross-linking once the local load exceeds the STP-to-TMC isomerization threshold again. Equivalently, the use of caged C=C bonds would insure that cross-linking occurs only in areas where local forces exceed the forces required for generation of C=C bonds, that is, where the probability of materials failure is fairly high.

We are currently conducting experiments to test these hypotheses using polymers bearing both STP and either SP or caged ene units in individual polymer chains.

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