

MECHANISMS FOR LOW STRAIN FORCE-INDUCED CHEMICAL REACTIONS

Brett A. Beiermann^{1,*}, Sharlotte L.B. Kramer¹, Jeffrey S. Moore², Scott R. White³, Nancy R. Sottos¹

¹University of Illinois, Department of Materials Science and Engineering

²University of Illinois, Department of Chemistry

³University of Illinois, Department of Aerospace Engineering

*Email: bbeierm2@illinois.edu

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ABSTRACT

Damage in polymeric materials is preceded by complex spatial and temporal changes in stress state. Mechanical force can activate covalent bonds in the polymer, but the typical result is chain scission and ultimately failure. The goal of current research is to utilize changes in stress state to mechanically activate chemical changes that favorably alter the material properties of the polymer, prior to failure. Mechanoresponsive polymeric materials are created by directly linking force-activated mechanophores into the polymer chains or by using the mechanophores as crosslinkers between polymer chains. The mechanophore motif requires efficient transfer of force to a relatively small number of specific bonds in the polymer. Here we explore physical mechanisms for effective force transfer and mechanophore activation. The mechanophore under investigation is spiropyran (SP), which reacts via an electrocyclic ring-opening reaction to a colored, fluorescent merocyanine (MC) form under mechanical force or UV-light. SP-linked poly(methyl acrylate) (PMA), an elastomeric polymer, and poly(methyl methacrylate) (PMMA), a glassy polymer, were studied.

SP was incorporated into linear PMMA backbones, in an attempt to impart high force to the mechanophore at low strain. At room temperature, under tension, this system exhibited brittle failure with no apparent activation of the SP mechanophore. For increased temperatures (90-105 °C), the polymer exhibited drawing behaviour, accompanied by substantial activation of the mechanophore, signified by a strong purple color (Figure 1). At yet higher temperatures, ≥ 120 °C, the polymer drew to strains of over 100% without activation. The authors attribute this to insufficient stress in the polymer.

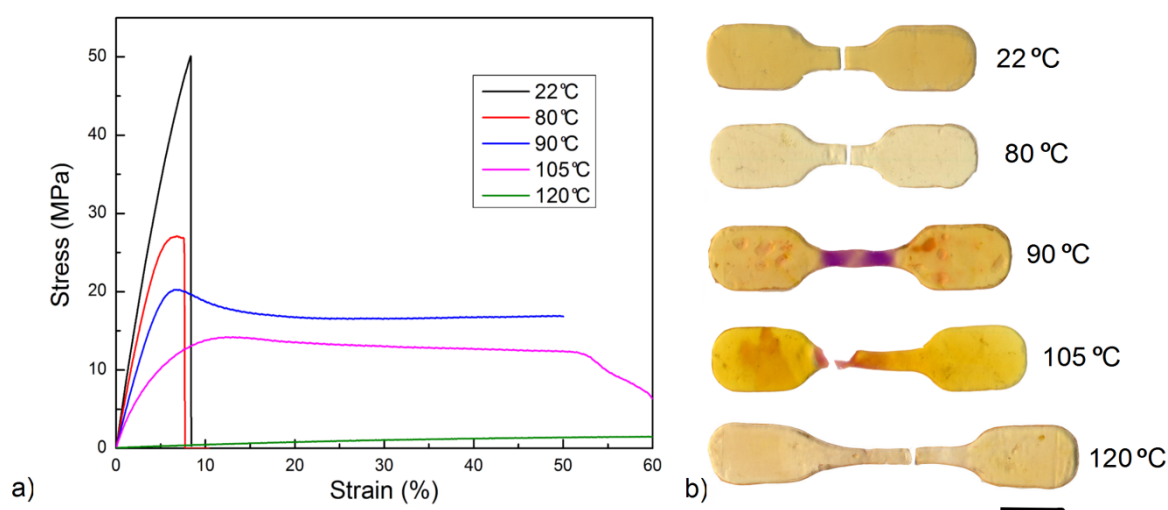


Figure 1. Tensile testing of linear SP-linked PMMA. a) Mechanical properties at varied testing temperatures, and b) corresponding optical images for samples after testing. Scale bar = 6 mm.

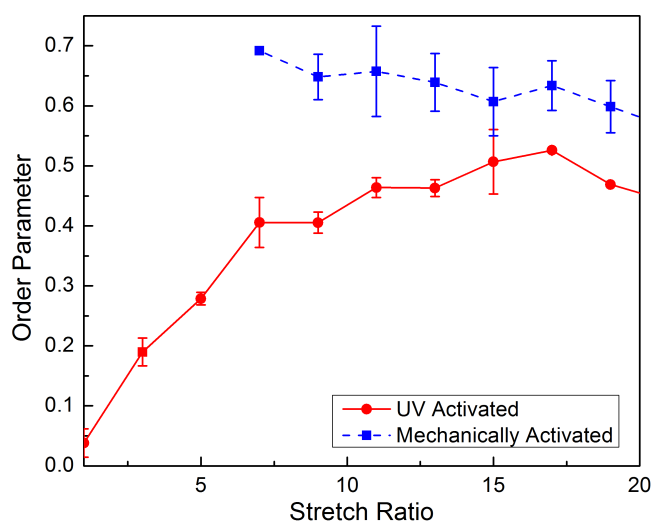
Mechanical properties of linear SP-linked PMMA were varied at room temperature by introducing a plasticizing solvent. At a mass uptake of 15-25% methanol, the samples could be drawn and exhibited activation. The onset of activation occurred at strains below 10% - significantly lower than in previous mechanochemical systems. Additionally, some polymer mobility was necessary for mechanochemical activation in SP-linked PMMA.

The average orientation of mechanophores was measured via the fluorescence polarization of the reacted MC form molecule. Fluorescence emitted from the MC form has polarization roughly in the direction of the long molecular axis [1]. The unreacted, SP form, exhibits virtually no fluorescence, and thus did not affect the order parameter. The average MC orientation was analysed by placing a polarizer between the sample and detector. An order parameter, S , can be defined with this analysing polarizer oriented parallel and perpendicular to the direction of tensile force[2]:

$$S = \frac{(I_{\parallel} - I_{\perp})}{(I_{\parallel} + 2I_{\perp})} \quad (1)$$

I_{\parallel} and I_{\perp} denote the fluorescence intensity with the polarizer parallel and perpendicular, respectively, to the direction of force. S varies from 0, for a randomly oriented sample, to 1 for perfect alignment of mechanophores in the draw direction.

The order parameter was characterized in elastomeric SP-linked poly(methyl acrylate) (PMA) because in this polymer system SP could be reacted to MC using UV light, allowing comparison of UV- and mechanically-activated MC. As shown in Fig. 2, the order parameter was measured as a function of stretch ratio (ratio of length to initial length) for mechanically-activated and UV-activated specimens. For UV-activated specimens, virtually all SP species were driven to the MC form, allowing observation of all mechanophores within the polymer. Prior to testing, the orientation parameter in the specimens was nearly zero, implying little or no chain alignment. The order parameter increased with stretch ratio until reaching plateau value, indicating that the mechanophores align in the loading direction. In mechanically activated PMA specimens, the incorporated mechanophores were driven to the non-fluorescent (closed) SP form by exposure to green light ($\lambda=532$ nm) prior to testing, and thus had an undefined order parameter until mechanical activation occurred at a stretch ratio ≈ 6 .



tension activated preferentially. Experiments are in progress to align polymer and mechanophores in the tensile direction prior to mechanical testing, in order to further minimize strain to activation.

Figure 2. Order parameters as a function of stretch ratio in linear SP-linked PMA.

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