

MECHANOCHEMISTRY

Feel the force

“ We are working to ... expand this chemistry to new photoswitches with unique properties ”

Engineers have long studied the forces acting on macroscopic objects, but only in recent years have chemists begun to apply these principles on a molecular level. These are perhaps best observed in polymers, including archetypal materials in which colourless spiropyran units, when under tension, undergo ring-opening to afford red–purple merocyanines. Such materials enable force to be transduced into an optical readout — but take away the force and each merocyanine relaxes back to its more compact spiropyran form.

Writing in *Journal of the American Chemical Society*, Maxwell Robb and co-workers sought to “make the mechanochemical transformation more permanent, so that the mechanical history of a polymeric material could be preserved and later visualized.” Their new work demonstrates mechanochemically gated photoswitching, whereby stress breaks bonds in a polymer to reveal a group that subsequently undergoes a photochemical reaction.

If a material is subjected to one stimulus, it might convert into a new material that is

only then susceptible to a second stimulus. This principle is known for mechanical gating of mechanochemistry, and reactivity gating of diarylethene photoswitching. Robb’s team combined these two concepts to design a new approach in which a force-sensitive group — known as a mechanophore — is converted into a light-sensitive group. The latter took the form of a functionalized 1,2-bis(3-thiophenyl)cyclopentadiene that can undergo UV-light-triggered electrocyclicization, a reaction signalled by the formation of a red cyclohexadiene product. However, this reaction cannot occur if the cyclopentadiene is trapped with an alkene as part of a Diels–Alder adduct. Such a norbornene is photochemically inert but mechanically sensitive because it can dissociate under stress through a retro-Diels–Alder reaction. The most promising design was an adduct between a 1,2-bis(3-thiophenyl)cyclopentadiene and a maleimide. Indeed, density functional theory calculations indicate that if the molecule pictured is stretched from its equilibrium geometry by just over 3 Å, it experiences enough force to break into its two constituents. Comparing the rupture force to calculations of other known mechanophores, it seemed reasonable that the reaction could be reproduced in a laboratory.

Robb’s team took their Diels–Alder adduct and decorated the maleimide and one thiophene each with a bromoisobutryl ester — a radical polymerization initiator from which poly(methyl acrylate) chains were grown. The norbornene

was now in the middle of ~90 kDa of poly(methyl acrylate) and susceptible to forces transmitted through its two long arms. These forces were applied using solution-phase ultrasonication, whereby cavitation leads to stresses that are greatest near the centre of a polymer chain. Thus, the norbornene groups ruptured to afford maleimide and 1,2-bis(3-thiophenyl)cyclopentadiene units, both of which featured similar poly(methyl acrylate) arms. The mixture remained colourless after ultrasonication, and it was only upon subsequent UV irradiation that electrocyclicization of the 1,2-bis(3-thiophenyl)cyclopentadiene gave the corresponding red cyclohexadiene — an encouraging proof-of-concept of the new stress sensor.

The gating observed by Robb and his colleagues opens many possibilities, including single-molecule force measurements. Moreover, one could envisage a polymer in which loops are each cinched with a mechanophore, the cleavage of which still leaves the polymer intact. “We are working to streamline the synthesis, expand this chemistry to new photoswitches with unique properties and also modulate the mechanochemical activity,” shared Robb. Once these aspects are addressed, the responsive materials may well find new applications in patterning, data storage and stress sensing.

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