doi.org/10.1002/cplu.201900737

Chemistry Europe
European Chemical Societies Publishing

Methods for Exerting and Sensing Force in Polymer Materials Using Mechanophores

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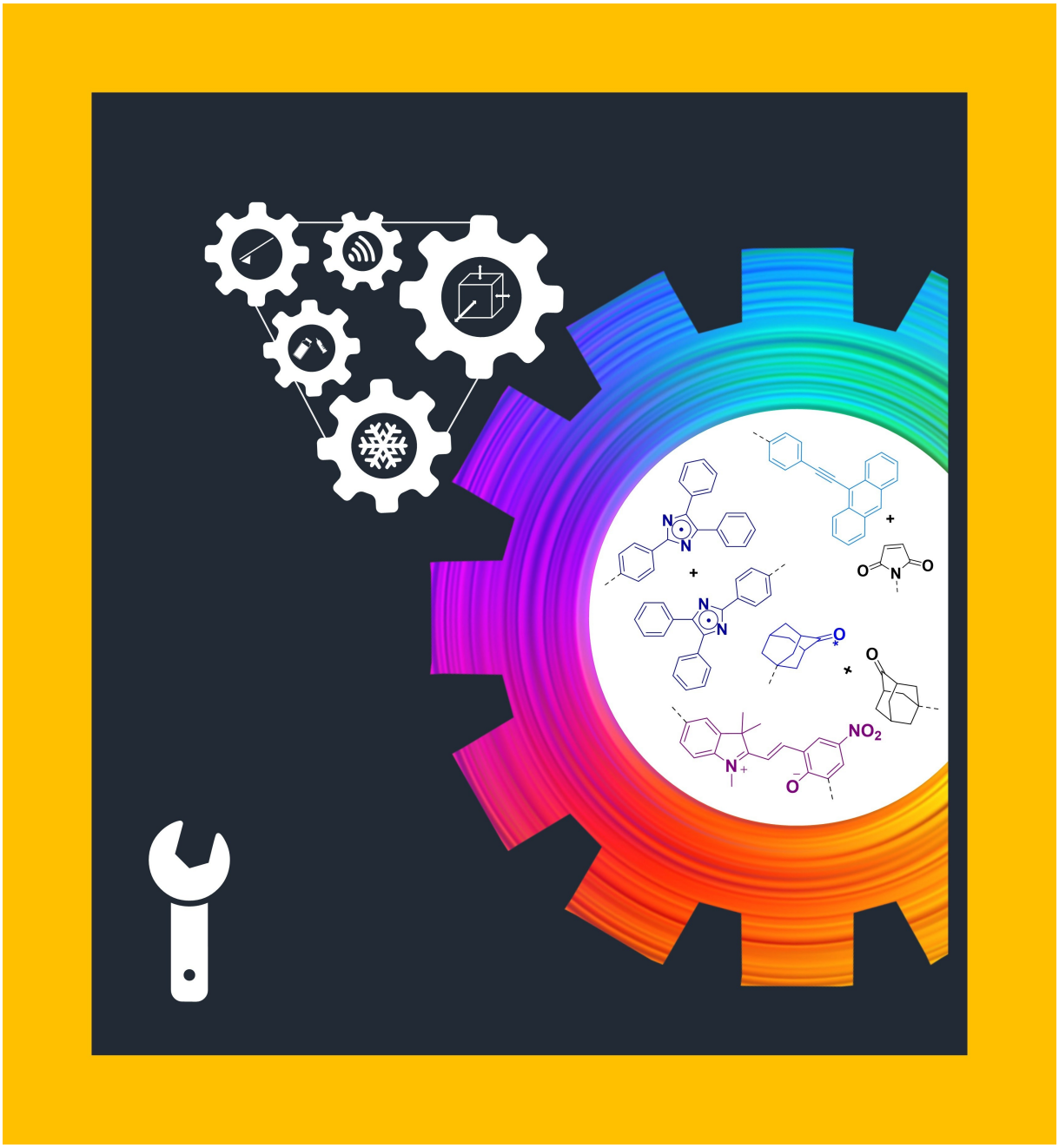

In recent years, polymer mechanochemistry has evolved as a methodology to provide insights into the action-reaction relationships of polymers and polymer-based materials and composites in terms of macroscopic force application (stress) and subsequent deformation (strain) through a mechanophore-assisted coupling of mechanical and chemical phenomena. The perplexity of the process, however, from the viewpoint of mechanophore activation *via* a molecular-scaled disruption of the structure that yields a macroscopically detectable optical signal, renders this otherwise rapidly evolving field challenging. Motivated by this, we highlight here recent advancements of polymer mechanochemistry with particular focus on the establishment of methodologies for the efficient activation and quantification of mechanophores and anticipate to aptly pinpoint unresolved matters and limitations of the respective approaches, thus highlighting possible developments.

Introduction

Polymeric materials are versatile and broadly applicable due to their unique and advantageous properties. Yet, as all materials are predetermined to ultimately fail, polymers are also confronted with fracture and possible subsequent catastrophic failure scenarios. Take for example the initiation and propagation of cracks that emanate in the structure of bulk polymer materials and diminish their macroscopic mechanical response.[1] On a molecular level, crack initiation and propagation may be expressed *via* polymer chain extension, scission, and pull-out events (Figure 1) within the structure ahead of the evolving crack plane.[2,3] In view, however, of the complexity of these individual but interrelated processes, a fusion of disciplines is necessary to address the arising scientific challenges from a fracture mechanics perspective. On account of that, polymer mechanochemistry engages in the coupling of molecular level disruption and macroscopic mechanical response.

The concept of mechanophores[4] has been widely introduced into the field of polymer mechanochemistry.[5–8] More specifically, a plethora of force-sensitive functional units that change their optical properties (*i.a.* mechanochromophores and mechanofluorophores) were designed and incorporated into the structure of polymers to visualize force-induced events.[9] Along the backbone or within crosslinks, they selectively undergo mechanochemical activation upon the application of force expressed in different manifestations, such as bond-cleavage that ultimately leads to the localized fracture of the polymer, non-scissile transformations that release small molecules and leave the parent structure intact, or elongation of the polymeric chain in which they are situated. Among those, the motifs most relevant to the development of current stress exerting and sensing methodologies reviewed here are spiropyran (SP)[4,10,11] (Figure 2a), Diels-Alder (DA) adducts of anthracene[12–16] (Figure 2b), dioxetane[17–20] (Figure 2c), and latent persistent radicals,[21,22] such as hexaarylbiimidazole (HABI) (Figure 2d).[23]

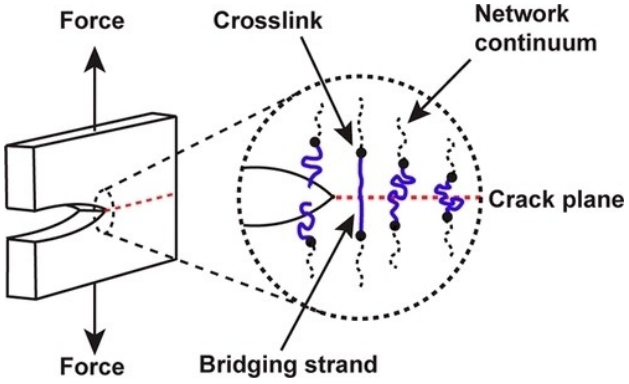

Figure 1. Schematic illustration showing polymer chain strands at the crack front of a specimen with an edge crack under tensile force. Reprinted with permission from reference [2]. Copyright 2019 American Chemical Society.

Setting aside the synthetic and functional perspectives of the actual force probes, for which the reader is referred to excellent existing reviews within the literature,[8,24,25] or other aspects of mechanochemistry, such as autonomous materials reinforcement,[26] mechanocatalytic[27] and photogating[28] activity, or externally imposed factors having an effect on mechanophore activation,[29] we here discuss current developments with regard to methodologies for stress exerting and sensing in polymer materials. Through the deconvolution of critically selected works, we explore the experimental advancements towards an assembly of quantifiable methods and data aiming to obtain a more elaborate view on the kinetics and dynamics of the mechanophore activation mechanisms in relation to the materials they are embedded in.

Methods to Exert Force

The means of mechanochemical activation of mechanophores are, as anticipated, largely dependent on the state of the matter in which they are anchored. For glassy polymers[30,31] and complex interfaces,[12,32–34] as representative paradigms of solid-state polymeric systems, typical activation methods include conventional mechanical testing such as compression and tension[35] or shear loading,[36] other means of mechanical disruption,[37] laser-induced stress waves,[34] or solvent ingress.[19] Cavitation induced by subjecting a solution to ultrasound waves is a widely adopted activation mechanism for materials in the liquid state,[38] while for surface-bound polymers, single-molecule force spectroscopy (SMFS) methods, such as atomic force microscopy (AFM),[12,39,40] are favorable approaches.

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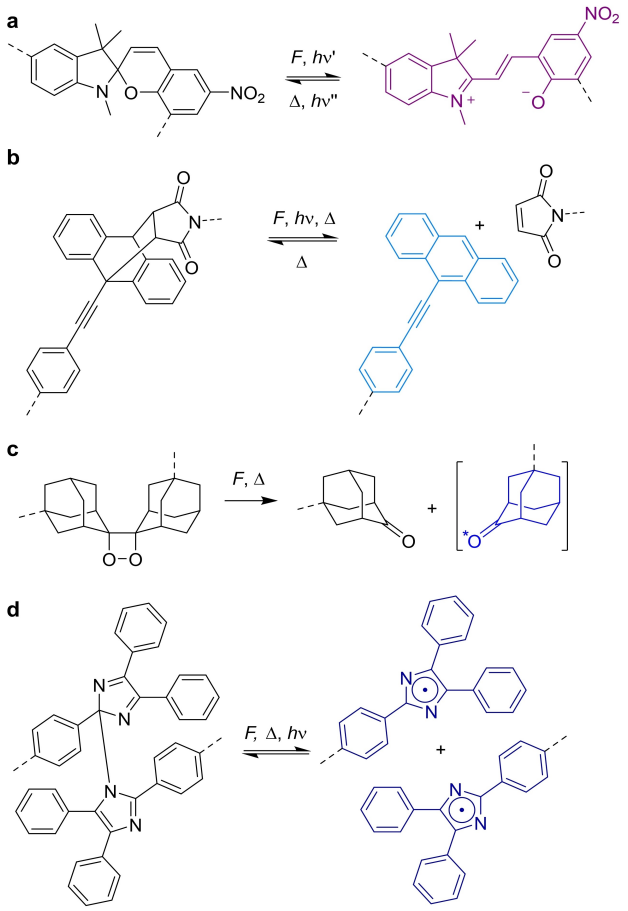

Figure 2. Overview of mechanochromophores and mechanofluorophores illustrating their chemical transformations upon force-activation: (a) Non-scissile, reversible ring-opening of colorless spiropyran (SP) to purple merocyanine (MC). (b) Scissile cycloelimination of a Diels-Alder (DA) adduct liberating cyan fluorescent 9-π-extended anthracene and maleimide. (c) Cycloelimination of 1,2-dioxetane generating a chemiluminescent adamantone. (d) Dissociation of hexaarylbiimidazole (HABI) into blue triphenylimidazolyl (TPI) radicals.

Repeatable and Reversible Mechanical Deformation

Generally, materials are subjected to a variety of external loads and stresses throughout their lifetime; compression and tension being two fundamental ones. The deformation they induce on the material can be irreversible, in that it remains even after stress application has ceased. Typical examples that suffer such irreversible strain are glassy polymers with limited chain mobility, which due to their common use have attracted immense attention. Recently, however, focus has also been placed on elastomeric materials that undergo reversible deformation, particularly polydimethylsiloxane (PDMS), a highly stretchable viscoelastic polymer with complex rheological behavior and interesting applications.[41] To thoroughly investigate and harness this reversibility, however, incorporating a mechanophore that can also reversibly sustain the macroscopic load is necessary. Here, polymer mechanochemistry benefits from the integration of non-scissile mechanophores into polymer structures.

Non-scissile and reversible SP, for example, can be repeatedly activated over multiple mechanical testing cycles of tensile elongation when integrated into a PDMS elastomeric network.[42] Due to irreversible stress-softening induced during the first cycle (the Mullins effect),[43] hysteresis was observed, followed by elongation to failure after 10 consecutive cycles. A blue-to-purple coloration shift (blue under strain but purple when relaxed) confirmed the activation of SP and its transition to MC under film extension (note here that a deep purple color is observed upon the photochemically induced conversion of SP to MC as well)[44] while thermal back isomerization to colorless SP was achieved after 1 h. A differentiation in SP-MC isomerization behavior was discerned for sphere compression with only a blue coloration being displayed that faded rapidly as MC to SP conversion was achieved in less than 2 min (Figure 3a).

The authors attributed this discrepancy to both some residual xylene and an isomerization about the methine bridge of the activated MC. It is possible, however, that the macroscopic recovery of the bulk material under uniaxial extension was not accompanied by simultaneous transition of the mechanophore given the activated colored mode that remained for longer times than that under compression. Certainly, the magnitude of force as well as the sample size and shape must have varied to accommodate each mechanical testing technique possibly affecting the response of the material. Barreling, for instance, of a spherical sample during compression might induce an uneven distribution of stresses through-

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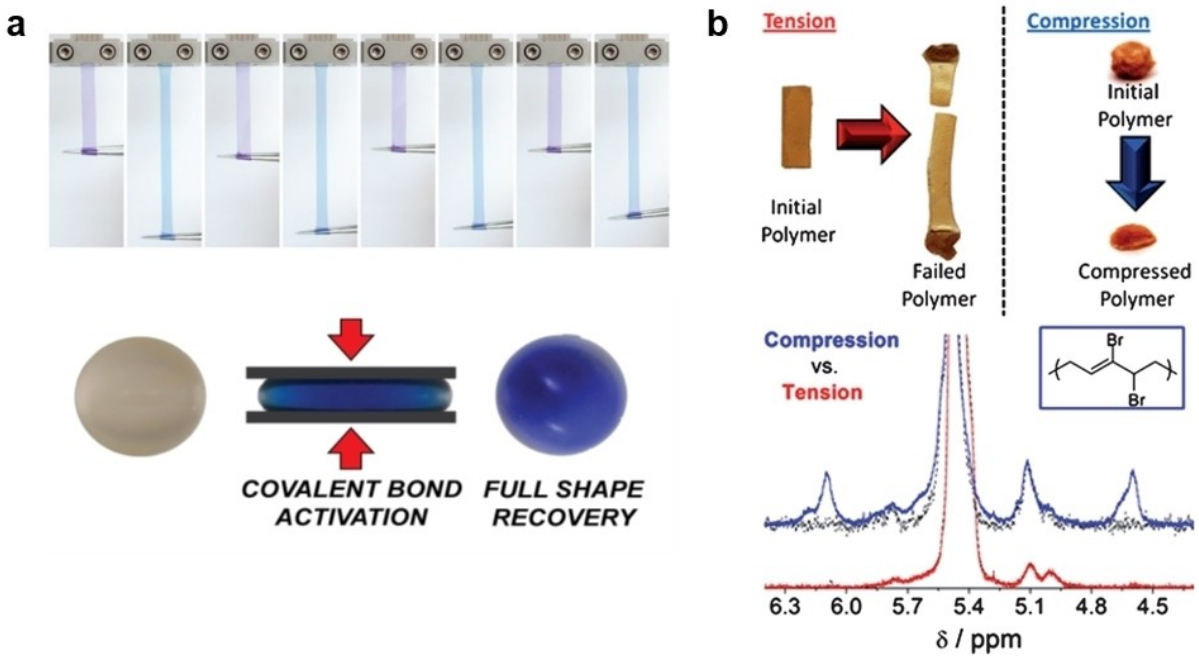

Figure 3. (a) Covalent bond activation with full shape recovery over multiple cycles for tensile elongation that leads to blue-to-purple coloration (top) and sphere compression that leads to blue coloration (bottom) in SP-embedded PDMS elastomeric networks. Adapted with permission from reference [42]. Copyright 2014 American Chemical Society. (b) *gem*-dibromocyclopropane (*g*DBC) polymer samples under compression resulting in ring opening of small blocks, and under tension not leading to activation (top) as shown in the respective ^{1}H-NMR spectra (bottom). Reproduced from reference [35] with permission from The Royal Society of Chemistry.

out the structure, while differences in elastic and compressive moduli values of PDMS might also contribute to this divergence.[45] On the other hand, as the long chains of PDMS give rise to a time-dependent elastic deformation, remaining stresses in the system might be sufficient to advance the mechanochemical activation of the mechanophore although macroscopic deformation of the bulk material fades away.[46]

Differences in mechanophore activation upon different mechanical testing methods were also reported for *gem*-dibromocyclopropane (*g*DBC) functionalized individual polybutadiene (PB) chains.[35] In contrast to tensile load application, compression of the samples resulted in measurable mechanophore activation which was further enhanced with subsequent compression cycles and refolding the samples in half. To trigger the electrocyclic ring-opening of the mechanophore under tensile load, the authors proceeded with pre-stretching of the samples, as chain alignment in the direction of force has been reported to favor, for instance, the activation of the SP mechanophore in various polymers.[47–49] The application of substantially higher stresses, however, even up to material failure, did not promote the mechanochemical reaction (Figure 3b). To interpret the results, the authors discussed the one order of magnitude deviation in stresses between the two force application methods, as well as the possibility of tensile and shear forces being exerted on the mechanophores during compression amplifying the effect and successfully causing ring-opening. On account of the individual PB chains, though, it is likely that under tension the chains extend and then slide past each other since these are not bonded with each other, in contrast to compression during which the chains are more crowded, raising the issue of deformation asymmetries exhibited by polymers when loaded under different mechanical modes.

Low-Level Mechanical Disruption and Crack Propagation

Surpassing conventional force application methods and motivated by the biological and biomedical applications of hydrogels, a methodology for the visualization of stresses in soft materials was recently introduced.[37] A minute amount of a 9-π-extended anthracene and maleimide DA with enhanced sensing capability[14,15] was integrated as a covalent crosslinker into poly (*N*-isopropylacrylamide) (PNIPAAm) hydrogel networks with different hydration ratios. The authors report proceeding with a low level mechanical disruption of the network structures by puncturing them with a needle. With the aid of confocal laser scanning microscopy (CLSM), a precise detection of mechanophore fluorescence and localization of stress accumulation around a defined region of interest were achieved. By that means, the fluorescence intensity over a range of swelling degrees was quantified and further correlated to the macroscopic mechanical response of the hydrogels. Although the unknown level of applied force during the needle-puncturing of the hydrogels could be considered restraining given that a dry sample is in a glassy state while a swollen sample is in a

rubbery state, it has to be noted that the needle was inserted through each sample which is translated into the scission of a finite number of polymer chains. In a further step, and by simply compressing the punctured samples with laboratory tweezers, crack propagation paths were formed and clearly discerned under CLSM (Figure 4a).

Owing to the high-resolution, minimum requirements for sample preparation, and efficacy to pinpoint the exact location site of mechanical disruption, this fractographic approach, with the aid of fluorescence microscopy, was proposed for the study of soft matter and the visualization of crack patterns, akin to the examination of the fractured surfaces of glasses and ceramics *via* conventional optical microscopy techniques. Important information regarding mechanophore activation ahead of a crack tip during mechanical testing and subsequent fracture have also been revealed upon exploitation of fluorescence imaging for glassy polymers[49] (Figure 4b) and multinetworks.[20]

Solvent Ingress, Swelling, and Crack Propagation with Time

In respect to the subjection of polymers to traditional forces, a swelling process is yet another loading scenario capable of inducing their deformation or even failure. To better understand and decipher the physical processes accompanied by solvent sorption of polymers, in view of their frequent exposure to a number of them, a scissile bis(adamantyl-1,2-dioxetane) mechanophore was incorporated into glassy PMMA as a covalent crosslinker.[19] The samples were swollen with chloroform *via* a syringe-injection process, and bursts of light could be discerned by naked eye in a darkened room due to the mechanoluminescent character of the mechanophore. A mapping of events resulting from covalent bond scission upon sorption was captured with a photodetector with visualization of the fracture progress and crack propagation through the material in space and time (Figure 4c). In spite of the spatiotemporal sensitivity of the method, however, it is possible that this response is induced upon sorption of the particular solvent as it favored a fast and large swelling of samples, in contrast to other solvents, such as acetonitrile, acetone, and tetrahydrofuran as reported by the authors. Further it appears that the stresses exerted on the sample during sorption and subsequent swelling cannot be directly controlled but rather indirectly *via* the proper solvent selection.

The mechanical activation of SP to MC has also been associated to PMMA swelling upon sorption of a solvent due to forces that are exerted on the weak C–O bond.[50] The crosslinked networks were swollen with different solvents and images were captured with the use of an inverted fluorescence microscope. The study suggested that acetone, acetonitrile, tetrahydrofuran, and dimethylformamide induced the activation of the mechanophore. Toluene, on the other hand, was very slow in swelling the specimens and induced no color change,

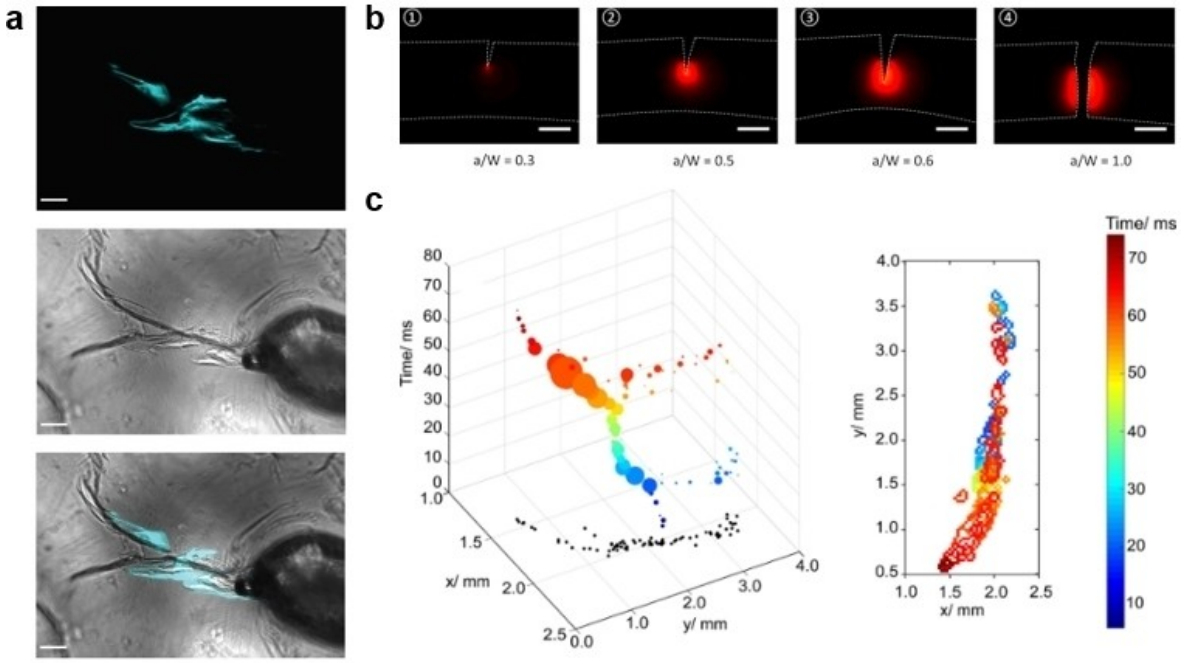

Figure 4. A selection of visualized crack propagation manifestations in different activated mechanophore-crosslinked polymeric systems: (a) Confocal laser scanning microscopy images of swollen PNIPAAm hydrogel networks crosslinked with anthracene-based Diels-Alder adduct mechanophore showing crack propagation after puncturing with a needle and subsequent compression with tweezers. Scale bar: 100 μm. Reproduced from reference [37] with permission from The Royal Society of Chemistry. (b) Sequence of fluorescence images of a rubber toughened poly(methyl methacrylate) (PMMA) specimen crosslinked with SP mechanophore during single edge notch tension (SENT) test showing evolution of fluorescence with crack propagation. Scale bar: 2 mm. Reprinted from reference [49]. Copyright 2014, with permission from Elsevier. (c) Plots of dioxetane-PMMA networks showing crack propagation in time and space due to sorption and swelling with chloroform. Reproduced from reference [19] under CC-BY-NC-ND 4.0 license.

while chloroform was very fast and, although it induced color change, it resulted in fragmentation of the sample in a few minutes.

Given that these studies on solvent swelling-induced mechanophore activation incorporate a PMMA matrix but display diverse responses upon swelling with the same solvents,[19,50] signifies not only the impact of solvent selection and its physicochemical properties thereafter, but also highlights the possible influence of sample surface, shape, and size.[51]

Freeze-Induced Mechanochromism (FIM)

Mechanical forces may also be generated and exerted along polymer chains in solution upon solvent freezing and subsequent crystallization, as the chains adhere to the newly formed crystallites. This approach harnesses the insight that has been attained on the degradation of polymers in solution induced by consecutive freezing cycles of the solvent in liquid nitrogen,[52] and enables freezing-induced polymer mechanochemistry; a tailored method for thermally labile mechanophores for which differentiation between mechanochemical and thermal activation is not facile.

Linear polymers and crosslinked polymer networks with integrated diarylbibenzofuranone (DABBF) mechanochromophore, that produces blue-colored persistent radicals upon activation, were accordingly frozen to liquid nitrogen temperature.[21] The swollen crosslinked polymer networks turned blue upon freezing, signifying mechanical stress accumulation along the polymer chains. This contrasts with solutions of linear polymers for which the forces were not sufficiently high to cleave the covalent C–C bonds. Further, and unlike anticipated, bond scission was not successfully triggered under tension, compression, and shear-loading, *i.e.* conventional forms of force application, which was attributed to improper design of the polymer structure to transfer macroscopic forces to the labile linkages.

In a later study,[22] solutions of linear polymers and crosslinked dioxane-swollen gels with integrated tetraarylsuccinonitrile (TASN) derivative that produces pink-colored radicals and emits yellow light under UV were frozen with liquid N_2. A reversible dissociation, even after ten cycles, of the C–C bond was achieved for gel cubes (Figure 5a), in contrast to linear polymers as previously reported.[21] The authors concluded that color change was observed for gels with high swelling degrees and ones that were swollen with solvents of relatively high melting points. They also noted the importance of affinity between the polymer chain and each solvent used to facilitate the method, which possibly applies to other methods as well as previously discussed for solvent swelling-induced mechanochemical reactions. Apparently, freezing of swollen crosslinked polymer networks and linear polymer solutions yields different responses in terms of mechanophore activation and reveals the variation in the dynamics of the polymer chains between solutions and gels stemming possibly from the absence of crosslink points in the case of solutions,[53] or the highly likely phenomenon of a swollen gel already experiencing a pre-stretched state.[37]

Freezing-induced mechanochemical activation has also been reported in solid, physically crosslinked polyurethane (PU) networks with a colorless HABI motif within the PU main chain, which reversibly dissociates into highly colored persistent TPI radicals.[23] Upon immersion into liquid N_2, the DMF-swollen PU networks exhibited color change from yellow to green (Figure 5b), confirming the activation of the mechanophore. Most notably, however, and in contrast to other results,[21] here the solid-state PU networks also revealed a coloration upon compression with a pellet press.

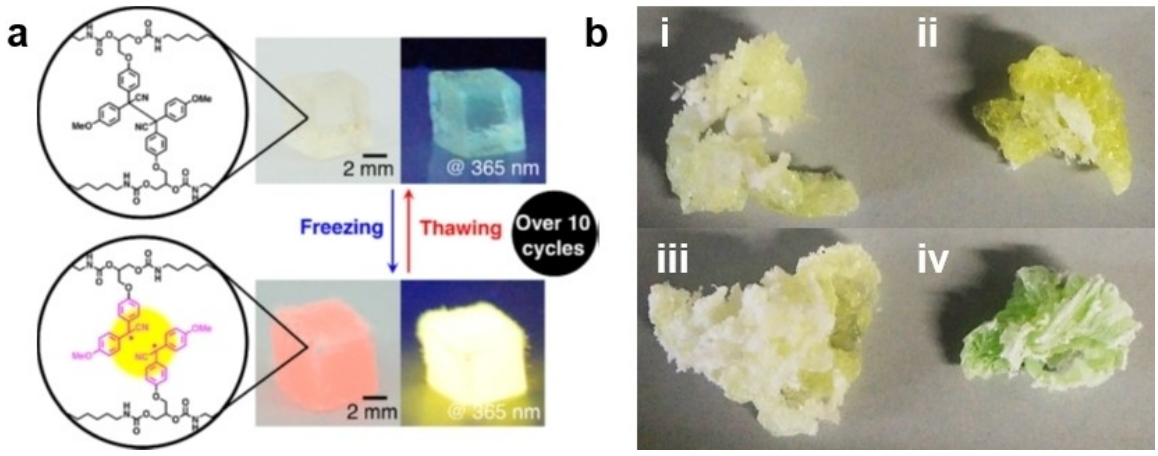

Figure 5. (a) Dioxane-swollen gels with TASN derivative exhibiting reversible freezing-induced mechanochromism and mechanoluminescence under ambient conditions and under UV irradiation. Reprinted with permission from reference [22]. Copyright 2018 American Chemical Society. (b) DMF-swollen samples before (i, iii) and after freezing in liquid N_2 (ii, iv), where i and ii bear blended HABI and iii and iv bear covalently anchored HABI. Note the green coloration resulting from superposition of blue TPI radicals and yellow material. Reproduced from reference [23] with permission from The Royal Society of Chemistry.

Ultrasonication and Cavitation in Solution

In view of the bio-centered and medical applications stemming from its non-invasive character, a number of studies have applied ultrasonication in solution as a mechanism to induce mechanophore activation.[17,54,55] During ultrasonication, nucleation of microbubbles in the solution is initiated, which then grow and collapse due to pressure waves that are formed and transmitted through the liquid material.[38] Upon this complex phenomenon, which encloses challenges, such as the generation of radicals in the cavitation bubbles,[56] the long polymeric chains undergo coil-to-stretch transition due to elongational flow and subsequently mechanochemical chain scission. Despite the ambiguous effects, either solely or in conjunction, of the several sonication parameters,[57,58] solution volume, polymer concentration, amplitude, frequency, time, temperature, solvent viscosity, to mention a few, it is widely established that polymer chain scission under ultrasonication is preferential at the center of the chain due to stress accumulation. Based on this, pulsed ultrasonication has been methodically exploited to investigate the competition between non-scissile *gem*-dichlorocyclopropane (*g*DCC) ring-opening mechanophores and scissile weak bonds (C–N, C–S, C–O) within a single polymer chain.[54]

Recently, a more advanced method with applications in synthetic and medicinal chemistry systems due to its biocompatible character,[59] high-intensity focused ultrasound (HIFU), has been reported as a promising external trigger with deep penetration for the activation of integrated mechanophores into aqueous systems.[60] Surpassing regular ultrasonication, HIFU allows the local and targeted application of ultrasound with high intensity leaving non-irradiated (biological) sample area mostly untouched. Its applications, however, are not limited exclusively to materials in the liquid state, but rather expand to solids as reported for HIFU-activated naphthopyran and dioxetane mechanophores incorporated into bulk elastomeric PDMS networks.[61]

Atomic Force Microscopy for Individual Force-Induced Events

Single molecule force spectroscopy (SMFS) is a well-established tool comprising of various techniques,[62] that applies to the study of a plethora of systems ranging from polymers to cells.[63] Despite that single-chain mechanochemistry is a field that confronts a limited number of recorded events and a resultant statistical uncertainty,[8] valuable information about the mechanical behavior of individual proteins[64] or the rupture events of single bonds[65] can be extracted *via* atomic force microscopy (AFM), for instance, owing to the precise control of bond orientation and recording of pulling speed with respect to the (rather low) applied force to unfold a domain. The contribution of AFM to the field of polymer mechanochemistry lies on the ability to study the behavior of one individual and isolated polymeric chain under mechanical stress. This is accomplished by tracking changes in the end-to-end length of a chain as it is initially stretched with its covalent bonds being further extended upon higher forces. Examples of the productive exploitation of AFM enhancing polymer mechanochemistry are the quantification and differentiation of the required force threshold to activate two mechanochemically active forms of spiropyran,[66,67] benzocyclobutene,[40] and the determination of the activation threshold of a maleimide-anthracene mechanophore immobilized between interfaces of poly(glycidyl methacrylate) (PGMA) polymer brushes and Si wafer surfaces (Figure 6).[12]

However, although the behavior of isolated single chains or strands may well be studied with this technique, it must be acknowledged that their response might differentiate in the actual polymer material due to interactions with other chains or strands. The anchoring of the molecule between the probe and the surface is also controversial in that it introduces uncertainties in the measurement, while ambiguous conclusions have also been drawn for the origin of the reactions and the statistical analysis in the case of a mechanically-induced ring-opening mechanophore with a triazole moiety[68] which is, apparently, open to question.[69–71] On the other hand, employing AFM in particular systems might resolve limitations introduced in other methods of force application, such as the competition between mechanophore activity and non-selective chain scission due to uneven force distribution along the polymer chains under, *e.g.*, ultrasonication experiments.[7]

Summary and Outlook

Through this critical analysis of selected works that emphasize the methods for force exertion and the tactics for stress sensing in polymers, it can be deduced that establishing the challenging relationship between macroscopic force application and molecular-scale mechanophore activation in polymer mechanochemistry may be better achieved *via* a more detailed study of their in-between connection, *i.e.* the polymer chains themselves, as these not only bear the mechanophores but (should) transfer load to them as well.[72]

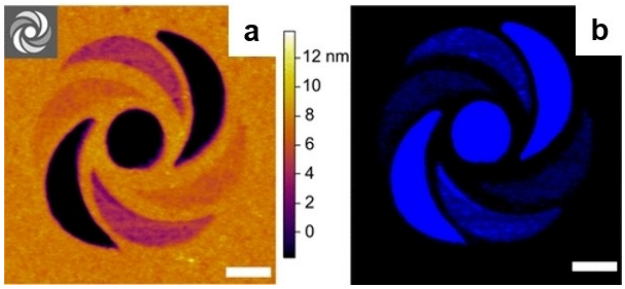

Figure 6. AFM topographic image (left) and fluorescence microscopy image (right) of a complex design pattern with intricate geometry replicated under a force range of 50–900 nN on a PGMA polymer brush immobilized by maleimide-anthracene mechanophores on a Si wafer. Scale bar: 1 μm. Adapted with permission from reference [12]. Copyright 2019 American Chemical Society.

Mechanophores are purposefully anchored at specific sites of polymer chains to selectively experience some form of disruption upon force application, and avert scission taking place at an, otherwise, random point of the polymer backbone. In particular, stress sensing mechanophores allow the collection of more quantitative information with regard to the methods reported to exert force on mechanophore-integrated polymer systems. Their selection is evidently based upon diverse criteria among which one can particularly discern the state of matter, the level of targeted force application, and the type of deformation induced on the bulk material. These, in turn, might dictate the mechanophores' local placement along the polymeric chain,[73] their number, and predetermine events, such as the force distribution within the polymeric structure, the number of activated mechanophores, or the effect of the activation of one mechanophore on a neighboring one. For that, multi-mechanophore polymers have also been recently introduced to potentially resolve some experimental drawbacks,[74] although fairly low crosslink densities have been potently reported to yield sufficient results so far.[36,37]

Other issues that need to be addressed relate to the clarification of any possible alterations of the structure upon the introduction of the labile bond-bearing units, in that the polymer senses stress at a specific, targeted region, which would have possibly been different for a mechanophore-free polymer. It is also highly likely that some mechanophores are placed near or at already compromised sites of the polymeric material and trigger a cascade of failure phenomena. The multiple chain length scales, however, being present in a polymeric material, and triggering random chain scission events of chemical crosslinks,[37,75] or the slim chances that all mechanophores are oriented in a direction that is favorable for a particular mechanical testing method,[76] render the pinpointing of targeted mechanophore activation a complex task. Further, as not all configurations lead to bond breakage and subsequent chain scission, the effect of the different stimuli needs to be deciphered and its experimental limitations thoroughly investigated to lead to a targeted mechanophore design and synthesis in order to manipulate different responses and serve the particular application. Mechanophore-assisted studies on the reversibility of elastomeric polymers, for instance, may well assist an in depth investigation through the establishment of connections between the loading history and the quantification of mechanophore activation, given that the deformation of a chain does not correspond to the macroscopic deformation of the material.[43] Additionally, the exploitation of mechanophores that lies on the direct visualization of the fracture crack patterns of materials[19,37,49] may well improve their structural integrity and further exemplify their structure-properties relationships.

On the endeavor of understanding the underlying mechanophore activation mechanisms and force transduction pathways in polymer materials *via* the coupling of mechanical and chemical phenomena, we are inevitably led to a categorization of approaches and strategies, which only remains constructive as long as extrapolation of behaviors and responses does not lead to erroneous estimations. However, experiments so far suggest that individual systems yield individual results which, one would argue that, presently constitutes the primary challenge of polymer mechanochemistry.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgements

R. G. is grateful for support by a Freigeist-Fellowship of the Volkswagen Foundation and acknowledges financial support from the European Commission (EUSMI, 731019).

Keywords: fluorescence · mechanical properties · mechanochemistry · mechanophores · polymer chemistry

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Manuscript received: December 17, 2019
Revised manuscript received: January 17, 2020
Accepted manuscript online: January 20, 2020