

A perspective on the force-induced heterolytic bond cleavage in triarylmethane mechanophores

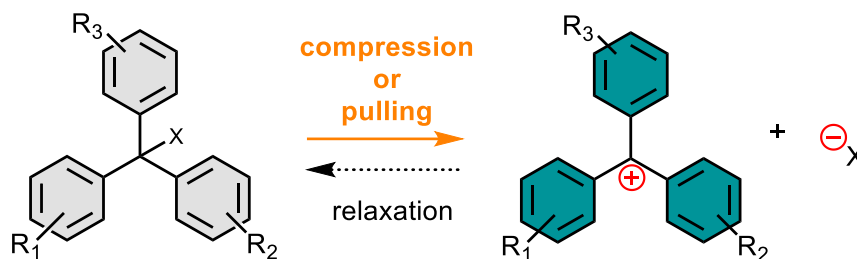
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Received:
Accepted:
Published online:
DOI:

Abstract Triarylmethane derivatives and their corresponding trityl carbocations are among the oldest chemical species synthesized and studied by chemists. The carbocationic platforms are particularly interesting due to their stability, high extinction coefficient, and tunable absorption of light in the visible spectrum, which can be achieved through structural modifications. These stable cations are traditionally obtained through heterolytic cleavage of judiciously designed, parent triarylmethanes by exposure to acids or UV light ($\lambda < 300$ nm), and methods based on electrochemistry or radiolysis. Our group has recently discovered that trityl carbocations can be generated also via mechanical stimulation of solid polymer materials featuring triarylmethane units as covalent crosslinks. In this Synpacts contribution, we expand on our previous finding by discussing some intriguing research questions that we aim to tackle in the immediate future.

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- 3 The potential reversibility of triarylmethane mechanophores
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Key words scissile mechanophore, heterolytic bond cleavage, triarylmethane, carbocation, mechanochromism, reversible mechanophore, visible absorption.

1. Introduction

Mechanophores can be defined as chemical species that provide physico-chemical responses as consequence of force-induced transformations.^{1–5} The term was coined less than two decades ago,⁶ and it quickly established itself due to the general scientific interest raised by the rise of polymer mechanochemistry.^{7–12} Although the definition of mechanophore previously offered is rather general, the most common practical scenario involving mechanophores consists in small molecules containing so-called *weak* chemical bonds – linkages that are mechanically labile – embedded in polymeric architectures (Figure 1). Applying a sufficiently high mechanical force to the polymer triggers the rupture of the small molecule's weak bonds,^{13–16} which can be

either covalent or supramolecular in nature. In this Synpacts contribution, we focus on systems comprising weak *covalent* bonds, *i.e.*, covalent mechanophores.

The force-triggered scission of the covalent bond can alter the chemical connectivity of the system with two possible outcomes. *Non-scissile* mechanophores retain a 1:1 stoichiometry between reagents and products, whereas *scissile* mechanophores cleave to produce two unbound species (Figure 1, left). Early examples of non-scissile and scissile motifs are spiropyrans¹⁷ and azo moieties,¹⁸ respectively. Non-scissile and scissile processes can occur reversibly or irreversibly, which further differentiates mechanophores into reversible and irreversible. Covalent mechanophores are generally irreversible, although reversible designs consisting of spiro-motifs such as spiropyrans,^{17,19} spirooxazines,²⁰ and naphthopyrans,²¹ rhodamines,^{22,23} and diarylbibenzofuranones^{24–26} and difluorenylsuccinonitriles²⁷ have been reported.

Besides the scissile/non-scissile nomenclature, mechanophores can also be differentiated by the operating bond cleavage mechanism, which affects the chemical nature of the species generated by the force-triggered process. Motifs that undergo the concerted cleavage of two or more weak bonds and afford neutral species are referred to as *concerted*.^{28,29} Mechanophores creating radicals are subjected to *homolytic* cleavage, whereas the term *heterolytic* is conventionally invoked when charged species are generated.^{1,30} All these descriptions are compatible with both scissile and non-scissile pathways. This Synpacts contribution focuses on heterolytic cleavage, hence the scissile/non-scissile distinction will be further elaborated for reactions that fall under the heterolytic category. Non-scissile heterolytic mechanisms produce zwitterions, *i.e.*, species in which both positive and negative charges co-exist. Scissile heterolytic processes generate unbound ion pairs, instead. Since the properties and chemical stabilities of zwitterions and ion pairs are significantly different, the use of separate terms appears appropriate. Thus, we will use

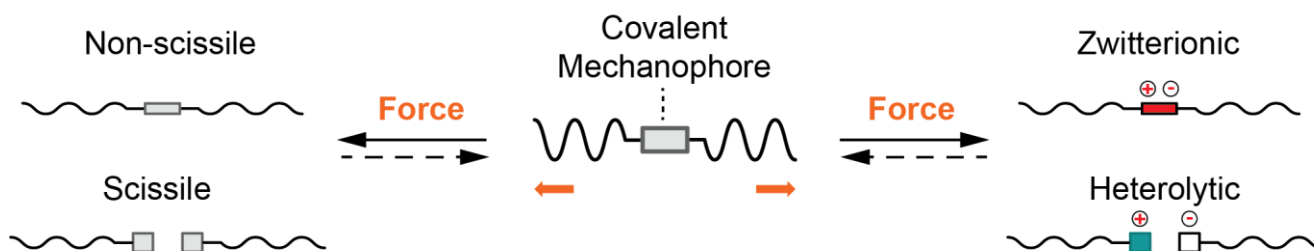


Figure 1. Left: general outcome of force-triggered chemical reactions involving covalent mechanophores, leading to non-scissile (top) and scissile events (bottom). Right: general case of heterolytic bond cleavage relevant in this Synpacts contribution, with the proposed nomenclature of zwitterionic (non-scissile heterolytic cleavage; top), and heterolytic (scissile heterolytic cleavage; bottom) mechanophores.

the terms *zwitterionic* and *heterolytic* mechanophores (Figure 1, right). This distinction is not marginal, since it should play a role on the stability of the mechanically generated species, as well as the overall reversibility of the mechanophore. The proximity relationship between the opposite charges should offer a qualitative explanation to both aspects. The vicinity of the opposite charges implies that zwitterions should not rely heavily on the medium for stabilization, especially in solid state. Moreover, the close proximity provides an enormous entropic advantage to favor recombination (and hence reversibility). The concept seems to be supported by the number of zwitterionic designs that have shown mechano-reversibility in apolar, solid-state materials, such as the previously mentioned spiro- and rhodamine derivatives.^{17,19–23} In stark contrast, heterolytic mechanophores generally require polar media to stabilize the ion pairs,^{28,29} and have been mostly reported as consequence of *irreversible* processes in polar solutions.^{28,29,31–39}

The scissile homolytic diarylbibenzofuranones^{24–26} and difluorenylsuccinonitriles²⁷ might appear as an exception in the discussion on the reversibility of covalent mechanophores. These motifs are reversible because they afford relatively stable radicals that display a high tolerance towards oxygen.^{24–26} In an effort to conceive a design with similar properties to diarylbibenzofuranones in terms of stability, yet with complementary characteristics (*i.e.*, heterolytic in nature), we embarked on the research question whether triarylmethanes⁴⁰ could serve as heterolytic mechanophores. Such question built on the notion that triarylmethane derivatives equipped with appropriate leaving groups “X” (**Tr**, Figure 2a, X = OH, CN, ...) undergo heterolytic dissociation of the C-X bond (Figure 2, highlighted in orange) upon application of a proper “stimulus”.^{40,41} The stimulated process transforms the neutral and colorless **Tr** into an ion pair comprising a brightly colored and relatively stable carbocation, and an anion (**Tr**⁺ and X⁻, respectively, Figure 2a).^{40,41} The bright colors of the **Tr**⁺ species have been exploited since the second part of the XIX century in the form of triarylmethane dyes, albeit initially without knowledge on the exact chemical structure.⁴⁰ Norris,⁴² and Kehrman and Wentzel⁴³ proposed the chemical structure of **Tr**⁺ generated with high concentrations of sulfuric acid (H₂SO₄) at the very beginning of the XX century. Ever since, chemists have found other creative methods to obtain **Tr**⁺ species by exposing *solutions* of small **Tr** derivatives to UV light ($\lambda < 300$ nm),^{44–47} ionizing radiation,⁴⁸ or electrical current.⁴⁹ Building on this wealth of previous literature, we hypothesized that the appropriate functionalization of **Tr** derivatives with polymer chains on at least two distal positions could pave the way to

heterolytic mechanophores (Figure 2b).⁵⁰ Such approach would allow to generate **Tr**⁺ species in *solid state* materials reliably, since the other chemical methods explored thus far have resulted in negligible extents of activation in this particular state of matter. In this Synpacts contribution, we will expand on our recent finding,⁵⁰ and discuss intriguing research questions associated to the **Tr** mechanophores that we aim to investigate in the immediate future, including their potential mechano-reversibility. The discussion will be focused on solid-state systems, in line with our previous work.⁵⁰

2. The development of our first triarylmethane mechanophore

At first, the potential mechanoresponsiveness of triarylmethanes was confirmed computationally through the constrained geometry simulate external force (CoGEF) method^{30,51} on virtual compound **Tr-A** (Figure 2c).⁵⁰ The pulling event was simulated in a polar environment, as previous literature suggested this method to be better suited for heterolytic bond cleavages.³⁰ Importantly, the CoGEF calculations indicated that introducing hydrogen-bond donors in the medium significantly decreased the virtual force necessary for bond scission, suggesting the importance of introducing moieties capable of furnishing this non-covalent interaction in the polymer matrix. The interplay between the properties of the medium and the chemical structure of the **Tr** mechanophore should be relevant for many aspects, starting from the mechanochemical activation of the **Tr** motif, as previously discussed.

The computational results were subsequently confirmed experimentally by converting **Tr-A** into compounds **Tr-1**, “transforming” the methyl groups of **Tr-A** into styrenyl handles, and synthesizing control **Tr-2**, with only one styrenyl group.⁵⁰ The styrenyl double bonds allowed to covalently incorporate **Tr-1** and **Tr-2** into poly(acrylates) as crosslinks and pendants, respectively. The studied **Tr** designs featured electron donating morpholine groups as aromatic substituents, which provided structures that closely resembled malachite green (which features two dimethylamino substituents, instead). As such, the resulting **Tr**⁺ deriving from **Tr-1** and **Tr-2** were expected to possess similar pK_{R+} (*i.e.*, chemical stability) and optical properties (blue-green color) to the malachite green **Tr**⁺. Indeed, applying excessive mechanical forces to glassy poly(*N,N*-dimethyl acrylamide) (compression) or elastic poly(methyl acrylate-*co*-2-hydroxyethyl acrylate) (tensile deformation) networks crosslinked with **Tr-1** motifs turned the originally colorless materials into blue-green, *i.e.*, mechanochromism (Figure 2d).⁵⁰ Materials comprising **Tr-2** as pendant group did

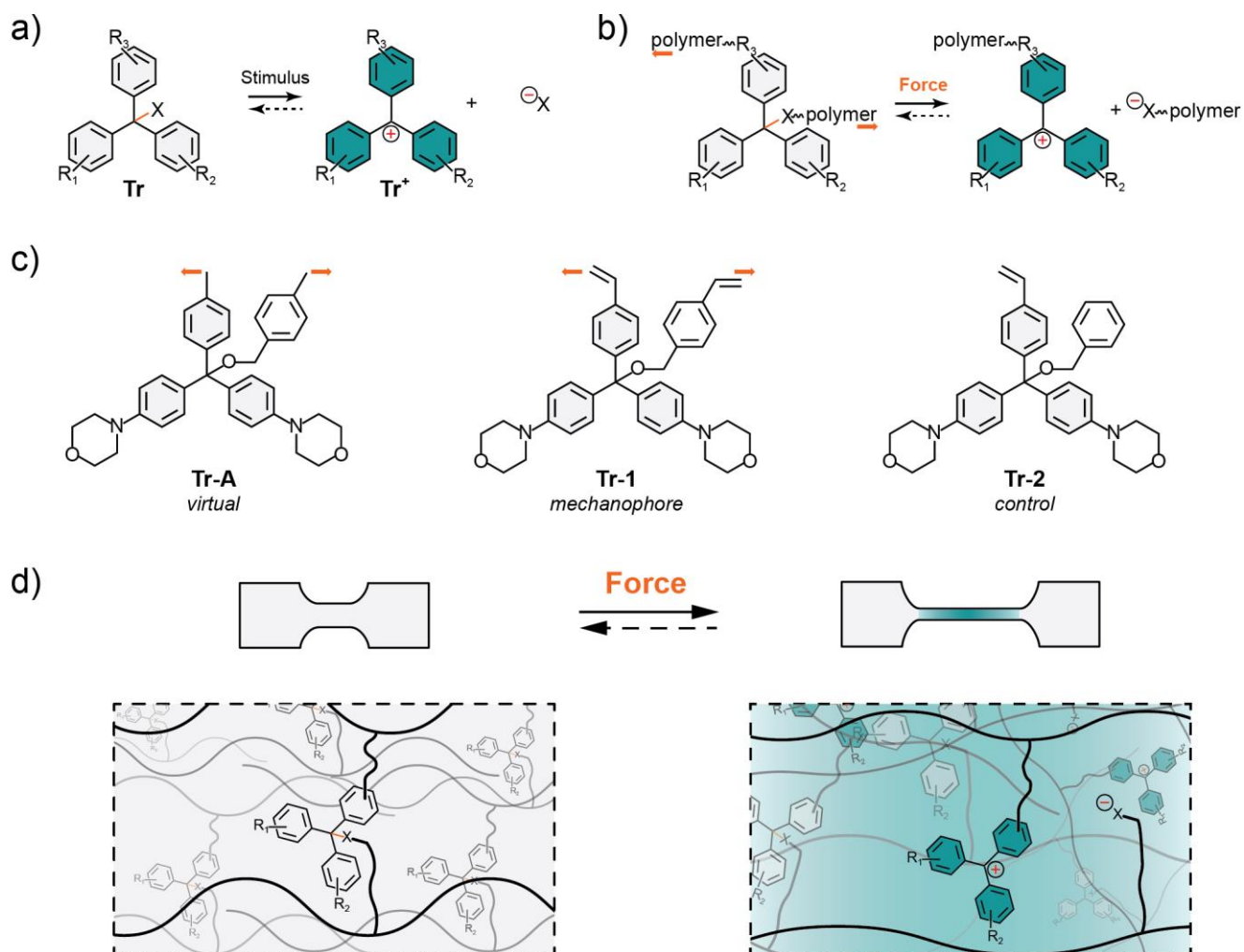


Figure 2. (a) Stimulus-induced heterolytic dissociation of small molecule triarylmethane derivatives (**Tr**) into triarylmethane cation (**Tr⁺**) and anionic counterpart (X^-). (b) Heterolytic dissociation of triarylmethane derivatives induced by mechanical force. (c) Chemical structure of virtual compound **Tr-A**, small molecule mechanophore **Tr-1**, and control compound **Tr-2** investigated in ref 49. (d) Schematic representation of dog bone specimens containing polymer networks featuring mechanoresponsive **Tr** crosslinks. The initially colorless materials produce a strong chromic response upon mechanical deformation, which is associated to the generation of **Tr⁺**.

not show any mechanochromic behavior, and this highlights the importance of applying at least two opposite force vectors on the weak bond (Figure 2c).⁵⁰ Quantitative evidence of the mechanochemical activation of the **Tr** crosslinks was obtained by combining mechanical experiments with *in situ* transmittance measurements. The mechanochemical activation of the **Tr** crosslinks is visible by naked eye (absorption in the visible), but determining the extent of mechanochemical activation in solid state materials is challenging, similarly to other solid-state mechanoresponsive systems. Nevertheless, empirical evidence⁵⁰ allowed to draw two reasonable conclusions:

- 1) The mechanical stimulation activates only a fraction of the **Tr** crosslinks.
- 2) The comparison between the chromic response of mechanically activated and UV light-irradiated polymer networks comprising **Tr** crosslinks by the unassisted eye supports that mechanochemistry is by far the more efficient activation method in solid state samples.

Another important observation is that glassy materials retained the blue-green color for days after mechanical activation.⁵⁰ In

contrast, the color of stretched elastic polymer networks disappeared over time, but could be re-instated by further mechanical activation. This suggested a certain repeatability of the mechanochemistry of **Tr** mechanophores, at least with elastic polymer networks. The cause of such repeatability is currently under investigation in our laboratory, but we hypothesize that it derives either from the activation of previously inactivated **Tr** motifs, or from the dynamic dissociation and recombination of **Tr⁺** and X^- into **Tr** (Figure 2b). In both cases, the significance of polymer chain relaxation and mobility are taken into consideration, because the glassy, stiff polymer matrix showed limited color reversibility. This aspect is further discussed in the following section, in which we will use “repeatability” to indicate systems with macroscopic mechanochromism, and “reversible” to describe systems that recreate the same chemical connectivity after mechanical stimulation. While reversibility implies repeatability, the relationship does not hold for the opposite.

3. The potential reversibility of triarylmethane mechanophores

In the context of polymer mechanochemistry, the characteristic of reversibility has traditionally been assigned to supramolecular

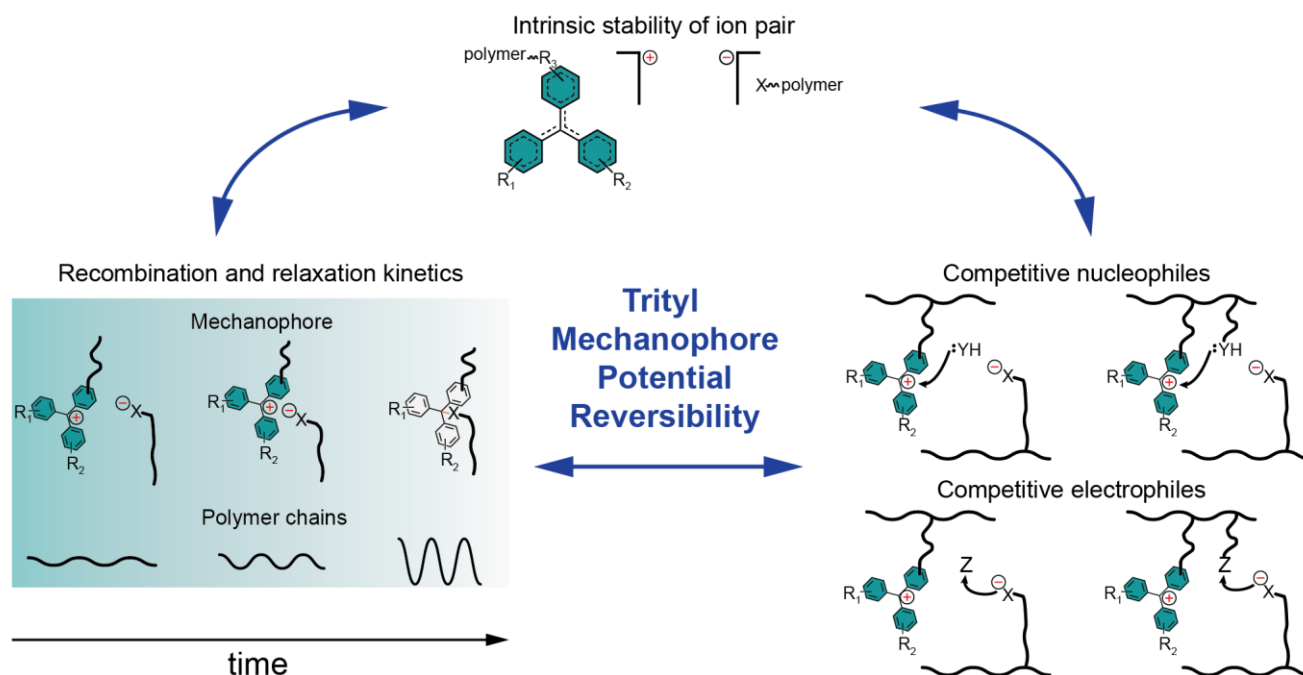


Figure 3. Elements contributing to the potential reversibility or repeatability of the mechanical activation of the **Tr** mechanophores. In a clock-wise order from the top: the intrinsic stability of the ion pairs, the presence of competitive nucleophiles (Y) or electrophiles (Z) that can lead to parallel reactions, and the interplay between the $\text{Tr}^+ - \text{X}^-$ recombination kinetics and the relaxation kinetics of the elastic polymer chains.

mechanophores.^{52,53} However, as previously discussed, a few covalent systems have been shown to be reversible. Diarylbibenzofuranones^{24–26} and difluorenylsuccinonitriles²⁷ are relevant conceptual examples to compare with **Tr**, since they are both scissile designs. The recombination process is not entropically favored with these motifs, thus the thermodynamic and kinetic stability of the mechanically activated species is paramount to avoid their decomposition or the incursion of parallel reactions involving them. When considering **Tr** mechanophores, conceiving designs that dissociate into intrinsically stable ion pairs is a key element to favor mechano-reversibility (Figure 3). In the homolytic systems mentioned above, the mechanical scission produces two identical fragments,^{24–27} which contrasts the situation in **Tr**-based systems. Thus, careful consideration of mesomeric/inductive effects on both Tr^+ and X^- is warranted. Literature data on the pK_{R^+} of specific Tr^+ (or similar),^{54,55} kinetic data on nucleophilic attack on Tr^+ species by H_2O and other nucleophiles,^{56,57} and nucleophilicity/ pK_{a} values of the anionic fragments^{58,59} (X^- , Figure 3, top) provide useful insights to design potentially promising **Tr** mechanophores. However, most of these values are only available for solutions, and do not necessarily allow accurate predictions of the stability of such species in solid polymers, where the matrix is expected to play a role.

The polymer matrix might contain species leading to chemistries that compete with the $\text{Tr}^+ - \text{X}^-$ recombination. Nucleophiles (generally indicated with the letter Y in Figure 3), either adventitiously present (*e.g.*, H_2O) or purposely placed in the polymer matrix, can attack on the mechanically generated Tr^+

(Figure 3). From the macroscopic point of view, both nucleophilic attacks shown in Figure 3 result in the disappearance of the color deriving from Tr^+ , since they afford a neutral **Tr** in which the original C-X linkage has been replaced with a new C-Y bond. However, the two nucleophilic attacks possess an intrinsic difference. The reaction of Tr^+ with the adventitious nucleophile leads to a non-mechanoresponsive **Tr**-derivative (conceptually similar to **Tr-2**), and thus to a permanent loss of mechano-responsiveness. The attack of the Y species purposely placed in the polymer matrix reshuffles the chemical connectivity of the matrix. If the newly established C-Y bond is of comparable energy to the initial C-X linkage and falls along a favorable mechanochemical pathway, the system might retain its mechano-responsive character. The mechanical activation would thus not be reversible from the microscopic point of view, as the nature of the involved chemical species would change, yet it would be repeatable.

The repeatability of the mechanical activation of **Tr** mechanophores is also susceptible to electrophiles Z within the polymer matrix (Figure 3). These species can react with X^- , and their presence can be adventitious or on purpose, similar to the nucleophiles previously discussed. If the reaction between X^- and Z has more favorable kinetics than the recombination between Tr^+ and X^- , the polymer material should retain the color of the carbocation – at least as a first approximation. However, the reaction involving X^- and Z should produce anionic species (charge preservation) that might combine with Tr^+ , quenching the chromic response, and potentially precluding the repeatable mechanochromism.

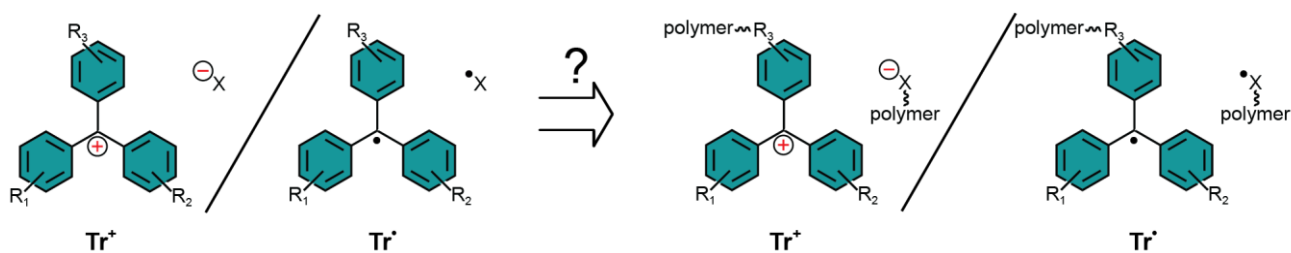


Figure 4. Small molecule triarylmethane carbocations (Tr^+) and radicals (Tr^\bullet) (left), and the associated question whether the mechanochemistry approach can provide the same species via force-induced heterolytic and homolytic bond cleavage, respectively, driven by rational design.

Finally, the mechanical properties of the polymer matrix comprising the Tr mechanophores are also expected to play a role on the reversibility/repeatability of the mechanical activation. In our previous study,⁵⁰ glassy materials displayed a persistent color associated to the carbocation obtained from the Tr-1 crosslinks, whereas the same colors disappeared over time with elastic polymer chains, showing a clear influence of chain mobility. Following this evidence, we expect the relaxation kinetics of elastic polymer chains to be an important parameter. The action of the mechanical force applied on the material stretches/bends the chains and simultaneously pulls aside Tr^+ and X^- (Figure 3). The relaxation of the polymer chains should enhance the proximity between Tr^+ and X^- , and ultimately favor their recombination (Figure 3). This means that the optical response associated to the intermolecular recombination should be a convenient tool to get insights into the relaxation of solid-state materials with molecular accuracy. However, it should be noted that the Tr^+ and X^- reactive functionalities originating from a Tr mechanophore might diffuse away upon chain relaxation, which will prevent them from finding each other. This situation is expected to occur especially in loosely crosslinked polymer networks, *i.e.*, with a high number of repeating units between crosslinks. Nevertheless, the recombination process with other reactive functionalities deriving from other Tr mechanophores should be statistically possible (if allowed by the chemical boundary conditions previously discussed).

4. A general molecular platform for force-induced, scissile, homolytic and heterolytic bond cleavage?

Triarylmethane small molecules have been shown to generate also stable radical species.^{49,60} Substituents effects should direct the heterolytic vs homolytic dissociation dichotomy due to better stabilization of either the radical or ionic species, although the medium should also play a role. Both Tr^+ and triarylmethane radicals (Tr^\bullet , Figure 4) display highly tunable absorption in the visible spectrum, a characteristic that has been applied extensively for dyeing and sensing applications.⁴⁰ The usefulness of Tr^+ and Tr^\bullet derivatives is underlined by the number of other applications exploiting them, of which we select here photo-switchable basicity (from heterolytic dissociation),⁶¹ organocatalysis (from heterolytic dissociation),⁶² and imaging (mostly from homolytic cleavage).⁶³ Having recently shown that Tr^+ species can also be produced via force-triggered reactions, one of the immediate challenges will consist in determining whether this wealth of knowledge and applications can be translated to solid state materials using a mechanochemistry approach. For example, it will be intriguing to understand if Tr designs can be used as a general platform for both scissile homolytic and heterolytic mechanophores through simple

structural variations (Figure 4). Further, it would be even more fascinating to prove if the same platforms can be pushed beyond the stress/strain sensing application recently demonstrated.⁵⁰

5. Conclusion

Triarylmethane carbocations have a special position in the history of organic chemistry. Thus far, these cationic species have been generated from judiciously designed triarylmethane compounds that undergo heterolytic cleavage triggered by acids, light, or ionizing radiations. We have recently developed a new approach for the generation of such carbocations, which relies on the use of mechanical force, effectively introducing triarylmethane designs into the realm of polymer mechanochemistry. In this Synpacts contribution we have expanded on our previous findings and critically discussed some of the challenges we plan to embark on in the immediate future. Defining their potentially repeatable/reversible mechanochemical activation, unraveling the influence of the polymer matrix, and understanding whether the triarylmethane platform could be used as a universal molecular skeleton for force-triggered heterolytic/homolytic bond cleavage are few of such questions we will try to answer.

Funding Information

The authors are thankful to the Adolphe Merkle Foundation and the Swiss National Science Foundation (SNSF) (20020_172619) for financial support.

Acknowledgment

The authors are grateful to Prof. Christoph Weder for his kind support.

Conflict of Interest

The authors declare no conflict of interest.

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Biosketch

José Augusto Berrocal studied Chemistry at University of Rome “Sapienza” (Italy), where he obtained his Ph.D. in Chemistry (2014), working on the quantification of the efficiency of intramolecular reactions (physical organic chemistry) under the supervision of Prof. Luigi Mandolini and Prof. Stefano Di Stefano. After PhD, he joined the group of Prof. E. W. (“Bert”) Meijer at the Eindhoven University of Technology (the Netherlands) as a postdoc, where he spent most of his time on supramolecular chemistry and materials (2014-2017). He then enrolled in the group of 2016 Chemistry Nobel Laureate Prof. Ben L. Feringa at the University of Groningen (the Netherlands) for a second postdoc, focusing on light-driven molecular motors and machines (2017-2019). José started as a Research Group Leader at the Adolphe Merkle Institute (AMI) of the University of Fribourg in September 2019. His research team combines organic and polymer chemistry to create stimuli-responsive materials, with a particular focus on mechano-, light-, and chemo-responsive systems.